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Review Article

# Towards green asphalt materials with lower emission of volatile organic compounds: A review on the release characteristics and its emission reduction additives

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## HIGHLIGHTS

- Asphalt VOCs release law can be explained by qualitative and quantitative methods.
- Newly developed VOCs reduction additives for asphalt materials were concluded.
- Field emission reduction strategies and future developments were forwarded.

## ARTICLE INFO

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## ABSTRACT

Recently, researchers in the road field are focusing on the development of green asphalt materials with lower emission of volatile organic compounds (VOCs). The characterization methodology of asphalt VOCs and the influencing factors on VOCs release have always been the basic issue of asphalt VOCs emission reduction research. Researchers have proposed a variety of asphalt VOCs characterization methodologies, which also have mutually irreplaceable characteristics. Asphalt VOCs volatilization is affected by many factors. In this study, asphalt VOCs characterization methodologies were summarized, including their advantages, disadvantages, characteristics and applicable requirements. Subsequently, the influencing factors of VOCs release, such as asphalt types and environment conditions, are summarized to provide theoretical support for the emission reduction research. The classification and mechanism of newly-development asphalt VOCs emission reduction materials are reviewed. The reduction efficiencies are also compared to select better materials and put forward the improvement objective of new materials and new processes. In addition, the prospects about development of VOCs release mechanism of asphalt materials during the full life cycle and feasibility research of high-efficiency composite emission reduction materials in the future were put forward.

## 1. Introduction

Asphalt binder is the basic raw material of road construction. With the development of the transportation industry, asphalt material causes serious pollution to the environment (Boczkaj et al., 2014; Huang, 2018; Zhang et al., 2022). More and more researchers have conducted in-depth research on green road construction from several aspects under the concept of environmental protection. Science Citation Index database from Web of Science was adopted to plot the develop trend of scientific annual citations on green bituminous materials, with advanced search equation of (TI= (bitumen or asphalt or pavement) and TI= (VOC or fume or emission or volatile organic compounds or PAH or polycyclic aromatic hydrocarbon)), as Fig. 1 shows. Fig. 1 concludes the annual citation times on publications in the research field of environmental

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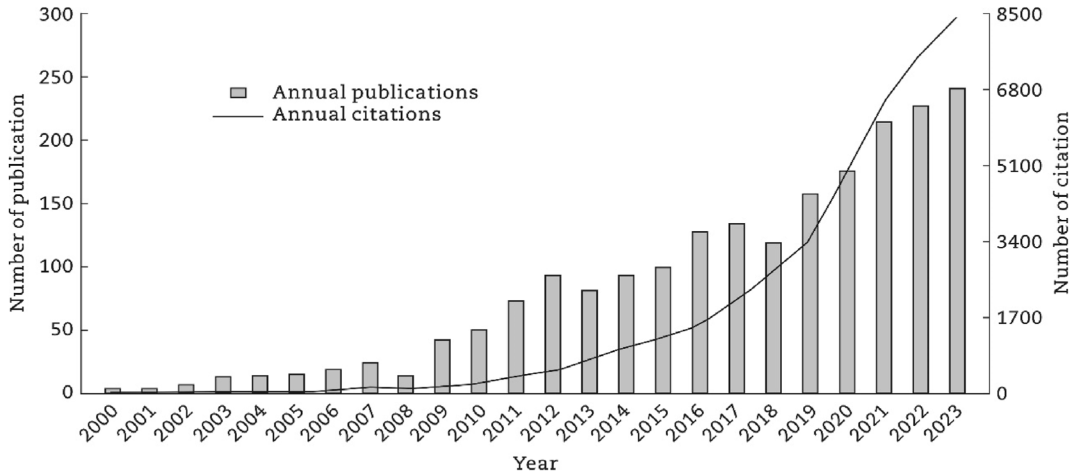



**Fig. 1.** Trend of annual publications and citations on green bituminous materials.

concern of bituminous materials in the past 24 years. Obviously, an increasing trend of annual citations can be observed, illustrating that research on green bituminous materials is attracting more and more attentions.

The detailed chemical composition in bituminous material varies due to its original source of crude oil, the manufacture method and process. Generally, fumes from bituminous binder are a mixture of many components.

Asphalt fume can be divided into gas, vapour and aerosol according to their states, as shown in Fig. 2 (Asphalt-Institute, 2015). Gas mainly includes some light components with small weight (Cui, 2015). Due to the low boiling point, gas is gaseous state at the construction temperature with strong diffusion capacity. Vapor is a kind of mixture of gas evaporated by heating near the heat source (Ruehl et al., 2006). Some gaseous molecules will liquefy into a fog to form vapour. Aerosol include condensed vapour and liquid bitumen droplets, which is due to the distance from the heat source with the low temperature (Ruehl et al., 2007). Some large molecules will liquefy into liquid to form a liquid particle dispersion system in the gaseous medium. Gas molecules and bitumen droplets are typically a minor proportion of the emissions from hot asphalt binder. Besides, particulate matters include aerosol matter from the asphalt binder and inorganic material such as dust, rock fines, filler etc. Total particulate matter (TPM) are often used to define the volatilization during asphalt mixing. They include macromolecular organic substances and solid particles formed by the settlement of other impurities (Trumbore, 1999).

As asphalt binder is a complex organic mixture, asphalt materials will release alkanes, hydrocarbon derivatives with oxygen, benzene series, organosulfur and organonitrogen compound and more toxic component like polycyclic aromatic hydrocarbons (PAHs) when heated (Cavallari et al., 2012b; Rogge et al., 2013; Trumbore et al., 2005). Long-term exposure to organic compounds may affect the skin and respiratory system, and may even increase the risk of cancer (Ravindra et al., 2008; Wang et al., 2023). In order to reduce the harm of organic compound to the environment and human, different countries and regions have formulated different asphalt VOCs standard. According to AP-42 compilation of air pollutant emission factors published by the U.S. Environmental Protection Agency in 1995, the hydrocarbon emissions from tank and trucks with petroleum products can be estimated (Cheremisinoff, 2016). In the U.S., National Institute for Occupational Safety and Health (NIOSH) limited the asphalt emission no more than 5 mg/m$^3$ within 15 min, and defined 16 kinds of PAH that are extremely harmful to human body as carcinogenic components (Possebon et al., 2019). In Europe, VOC emission reduction were conducted based on VOC Solvents Emissions Directive (Liebscher, 2000). China's Ministry of Environmental Protection has also issued many norms and standards to limit asphalt VOC, including GB 16297-2019 which limits the comprehensive emission of air pollutants (Ministry of Ecology and Environment of the People's Republic of China, 2019). In 2004, Canada planned to limit VOC emission for commercial products. In June 2006, Health Effects of Occupational Exposure to Emissions from Asphalt and Bitumen Symposium was held in Dresden, Germany. It is a continuous issue and challenge for asphalt industry and pavement engineering.

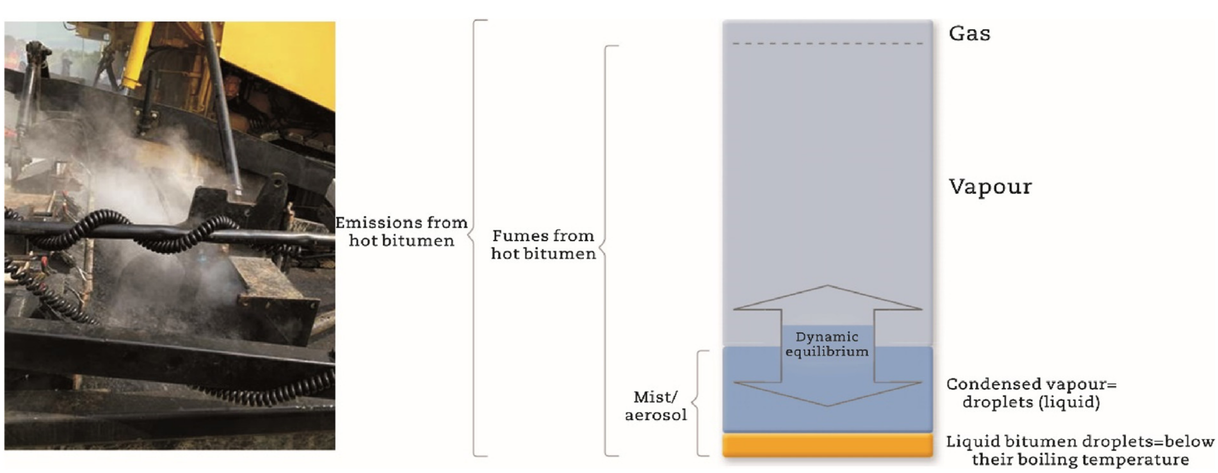



**Fig. 2.** Definition of asphalt emissions (Asphalt-Institute, 2015).

It is therefore obvious that technologies that result in reductions in asphalt fume exposure are important to the asphalt industry. There are many techniques to reduce VOCs from bituminous. NIOSH determined that the VOCs from the hot mix asphalt and roof asphalt were different due to their different components, production processes and heating temperatures (Butler et al., 2000). Gasthauer et al. (2008) also reported that reducing the mixing temperature and oxygen content can significantly decrease the VOCs amount.

In view of the complex composition characteristics of asphalt VOCs, scholars have carried out a lot of research on the release mechanism and emission reduction methods of asphalt VOCs (Huang, 2018; Cong et al., 2023). Due to the restrictions of the open environment of asphalt construction, asphalt VOCs are so difficult to be collected that be disposed as industrial waste gas. Some researchers proposed to add inhibitory materials as modified asphalt binder to reduce VOCs emission (Xiao et al., 2010b). At present, asphalt additives materials on VOCs reduction can be divided into three categories according to their emission reduction forms: inhibitors, warm mix additives and flame retardants. Although their emission reduction mechanisms are different, they all have emission reduction effects on asphalt VOCs.

The characterization methodologies of asphalt VOCs were reviewed in this research to correspond to the different detection requirements for asphalt VOCs qualitative and quantitative research. The research status of asphalt VOC emission reduction materials is summarized according to the volatile characteristics of asphalt VOCs. Many methods can be used to reduce the VOCs from asphalt materials, which includes temperature control, application methods and modification in asphalt binder. The emission reduction mechanism and efficiency are compared to guide the future development trend and improvement direction of emission reduction materials.

## 2. Analytical methods

Asphalt binder is a complex mixture of hydrocarbons with different molecular weights. This means the asphalt VOCs is as complicated as asphalt binder. Therefore, many technologies have been adopted to characterize the VOC features from asphalt materials. With chemical analysis methodologies developed, many new and productive methods were then adopted in the research on asphalt VOC. Table 1 lists the reviewed methods used for characterize the asphalt VOC. According to the detection purpose, these analysis methods can be divided into three broad categories, including qualitative and quantitative, semi-qualitative, quantitative. Quantitative analysis includes gravimetric analysis (GA), photoionization detection (PID), flame ionization detector (FID), ultraviolet-visible (UV-Vis). Semi-qualitative analysis includes mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR). Qualitative and quantitative analysis includes gas chromatography-mass spectrometry (GC-MS), pyrolysis-gas chromatography-mass spectrometry (PY-GC-MS), thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS), headspace-gas chromatography-mass spectrometry (HS-GC-MS).

Different detection methods were selected according to the different research purposes. PID, FID, UV-Vis and FTIR can respond differently to VOCs with different concentrations. PD and FID are quick quantitative methods for total asphalt VOCs. They can be used for instantaneous and rapid detection on construction sites without giving the detail component information of VOCs. UV-Vis can compare roughly VOCs amount based on different absorbance of solvent containing VOCs. FTIR is used to the accurate analysis of VOCs components with specific functional groups, but it is not suitable for full component analysis and accurate quantitative analysis. Therefore, GC-MS is the most widely used characterization method for asphalt VOCs, which can achieve qualitative and quantitative analysis with high-precision. The front-end equipment, such as PY, TD, HS, is also combined with GC-MS to achieve qualitative and quantitative analysis of asphalt VOCs according to different asphalt heating process and research requirement.

## 3. Release characteristic on asphalt VOCs

Based on different detection methods, VOC composition information is also different. According to the data summary from different researchers, asphalt VOCs can be divided into four categories: hydrocarbons, hydrocarbon derivatives with oxygen, aromatic compounds, organosulfur and organonitrogen compound (Cavallari et al., 2012b; Chang, 2020; Kitto et al., 1997; Tang et al., 2022; Yang et al., 2022). The release amount and mechanisms of VOCs from asphalt materials will not only be affected by both materials-specific factors, but also affected by conditioning-specific factors. The materials-specific factors include mixture composition, composition of asphalt binder and aggregate properties. And the conditioning-specific factors include the air temperature and wind speed.

### 3.1. Raw materials

Asphalt materials from different crude oil sources and produced with different processes will differ in the composition, fume and VOCs.

Zanetti et al. (2016) investigated the influence of asphalt type, concentration and mixture gradation on the VOCs characteristics. Results showed significant differences of VOCs between different mixtures. Asphalt binders with very similar percent contents of saturate, aromatic, resin and asphaltene will consequently result in the same overall emission spectrum. Stroup-Gardiner and Lange (2007) has studied the association between composition and VOCs variation. Emulsified asphalt, which is widely used for cold applied asphalt pavement, has much lower VOCs emissions, by comparing to asphalt binder. Warm mix technologies are another currently employed ways to decrease the asphalt fumes.

Chang (2020) investigated the VOCs from five different asphalt binders (including 2 types of 70#, 2 types of 90# and 1 type of SBS modified asphalt). There were 91, 79, 64, 72 and 71 kinds of asphalt VOCs detected, respectively, which were divided into common components, unique components and ultramicro components. It was found that asphalt 70A contained more cyclic compounds, while SBS modified asphalt released more sulfide due to the addition of sulfur stabilizer. Their common components contain 29 kinds of VOCs, indicating that asphalt VOCs have some similarities as Fig. 3.

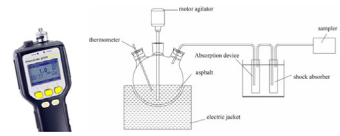
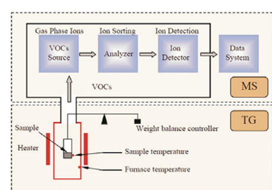
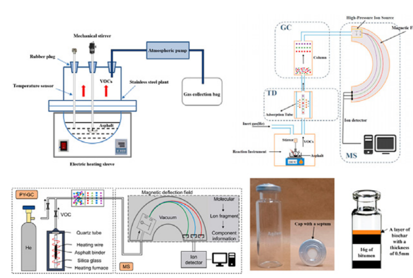
Xiao et al. (2020) summarized 80 kinds of asphalt VOCs from different researches and proposed the concept of asphalt VOCs fingerprint components. 12 kinds of substances in asphalt VOCs with high frequency and large volatilization are selected as fingerprint components. The fingerprint component database was established for the quantitative calculation of asphalt VOC. Liu et al. (2023) compared the VOC composition and content between crumb rubber modified bitumen (CRMB) and base asphalt binder and confirmed that the type of asphalt is the main influencing factor on asphalt VOCs. He also selected 23 kinds of VOCs molecules as the fingerprint components of CRMB, which have 10 overlapping components with the fingerprint components selected by Xiao et al. (2020) and benzene series and PAHs were mainly added.

Asphalt pavement is a compacted mix of aggregate and asphalt binder. Hence the nature of aggregate is the second important factor that will influence the VOCs characteristics during asphalt production. The mineral content, porosity, moisture content, aggregate size and relative hardness might affect the interaction between asphalt and aggregate, and thereby affect the asphalt VOCs. Some previous research by the authors showed both the aggregate surface area and asphalt binder film thickness had a profound effect on the laboratory-produced VOCs (Lange and Stroup-Gardiner, 2005). Therefore, adjusting the mix ratio and construction technology is also feasible to reduce asphalt VOC emissions.

### 3.2. Environmental conditions

VOCs from asphalt binder can be significantly affected by variable field factors and environmental conditions (Zanetti et al., 2016). Since the environmental conditions change significantly, the VOCs produced

**Table 1**
The classification and feature of asphalt VOCs analysis methods

| Purpose | Feature | Analysis methods | Combination | Advantage | Detection diagram | Reference |
|---|---|---|---|---|---|---|
| Quantitative analysis | VOCs concentration is different at different construction sites. Quantitative method is used to preliminatively estimate the total amount of asphalt VOCs to explore VOCs exposure coefficient. | GA | TGA | 1. Refer to specification GB 31570-2015<br>2. VOC emission adsorbed into benzene solution and dried to constant weight in a drying oven at 80 °C and weighed |  | Guo et al. (2021); Wang et al. (2021); Zhang (2014a) |
| | | PID | – | 1. Ionize organic molecules are captured by detector for total VOCs amount<br>2. Portable, real-time monitoring | | Autelitano et al. (2017) |
| | | FID | GC-FID | The concentration and amount of total VOC are calculated by the number of ions separated by hydrogen ion flame | | Boczkaj et al. (2014); Sutter et al. (2016) |
| | | UV-Vis | – | The total VOC amount was calculated by quantitatively absorbance of the solvent containing VOCs | | Chen et al. (2020); Cui et al. (2015b); Zhang (2014a) |
| Semi-qualitative analysis | Semi-qualitative analysis mainly relies on the functional group or mass-charge ratio (*m*/*z*) analysis of substances by high-precision detection to infer the possible substances of VOCs. | MS | TG-MS | 1. Integration of generation-detection<br>2. Infer VOCs by the *m*/*z* of ion fragments |  | Cui (2015); Cui et al. (2015a) |
| | | FTIR | TG-FTIR | 1. Integration of generation-detection<br>2. Infer VOCs by detected functional groups<br>3. The integrated peak area of characteristic peak represents the total amount of this kind of VOCs | | Xu et al. (2014); Xu and Huang (2010) |
| Qualitative and quantitative analysis | GC system can effectively separate different components and greatly improve the qualitative accuracy. The combination of PY, TD or HS are adopted to further realize different VOCs detection requirements | GC-MS | – | 1. Chromatographic separation<br>2. High detection and qualitative accuracy |  | Lee et al. (2004); Wang et al. (2001); Zhang et al. (2021a) |
| | | | PY-GC-MS | 1. Rapid heating mode with small dosage (0.3 mg)<br>2. Vacuum, reduce oxygen interference on VOCs<br>3. Simulate the volatilization of asphalt binder that are not in contact with air during heating | | Chang et al. (2023a); Li et al. (2017); Shu et al. (2019); Zhou et al. (2020) |
| | | | HS-GC-MS | 1. Generation-collection-detection integrated equipment with 5 g sample<br>2. Higher accuracy of quantitative analysis | | Autelitano et al. (2017); Boczkaj et al. (2014); Lange and Stroup-Gardiner (2007) |
| | | | TD-GC-MS | 1. Low detection limit and high accuracy<br>2. Good detection of small gaseous molecules<br>3. Can connect with the generation platform | | Chang (2020); Chang et al. (2023c); Chen et al. (2022b) |

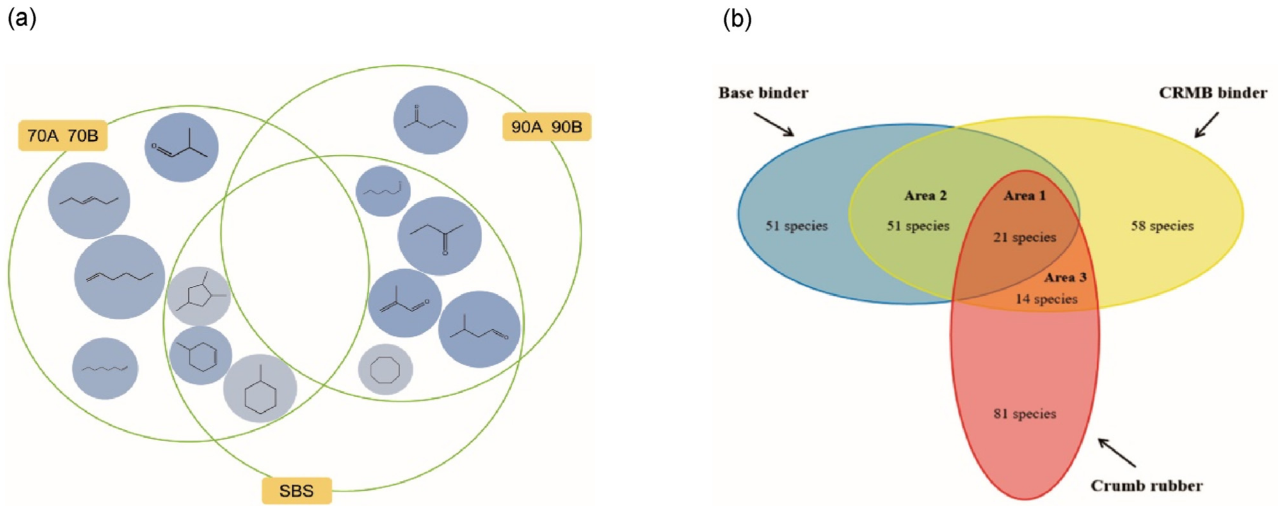



**Fig. 3.** Similarities and differences of VOCs from different asphalt binder. (a) From Chang (2020). (b) From Liu et al. (2023).

with standard laboratory test were found to be different from those collected from asphalt production field.

Temperature is an important determinant of asphalt fumes. Asphalt VOCs have two release characteristics with temperature change. Firstly, Li et al. (2021) considered that under the conditions of the same heating time and asphalt weight, VOCs release amount gradually increases with the increase of temperature, as shown in Fig. 4(a). The chromatogram showed that with temperature increasing, the number and peak areas of peaks gradually increased, indicating that asphalt VOC owned more complex composition and larger content. Chang (2020) proposed that the VOCs amount of base asphalt showed a binomial increase with temperature increase between 50 °C and 160 °C and the temperature difference of 60 °C could lead to a three-fold difference in VOCs content, as shown in Fig. 4(b). The release law of asphalt emission between 170 °C and 230 °C were explored by Bolliet et al. (2015), as Fig. 4(e). It was proposed that there are two trends, one is a linear increase, the other is a more dramatic increase, greatly affected by the flux oil used in the feedstock. He proposed that flux oil would promote PAC emission at temperatures above 200 °C, dependent on its quality and dosage. Nilsson et al. (2018) compared the VOCs from base bitumen and rubber bitumen at different temperatures and found that PAHs emission of the two asphalt binders at 160 °C was 1.8 times and 1.5 times that at 140 °C, respectively, as shown in Fig. 4(c).

Secondly, Peng and Li (2010) put forward that the higher the temperature, the longer the time required for asphalt to reach the volatile stability stage, as Fig. 4(d). When the temperature is below 165 °C, the asphalt VOC has reached a stable release state after heating for 150 min, while the volatilization rate of 150 min is still rising at higher temperature.

Chen et al. (2022a) carried out real-time VOCs detection on the whole process of asphalt VOCs release, with the release diagrams as shown in Fig. 5. The shapes of the three temperature release lines did not change, confirming that the increase of heating temperature did not affect the behavior of asphalt VOCs release, but affected the volatilization rate and total amount.

Reduction of the temperatures at which asphalt is handled reduces asphalt fumes. Cavallari et al. (2012a) have shown that reducing application temperature of hot mix asphalt from 149 °C to 127 °C reduced asphalt fumes by 42%–82%. They also studied the relationships between temperature and emission concentration with 20 paving asphalts and 5 roofing asphalts (Cavallari et al., 2012a). Research results presented a log-linear relationship for both paving asphalt and roofing asphalt, indicating that the concentration of polycyclic aromatic compounds increased exponentially with temperature.

Therefore, the increase of temperature will lead to the rapid increase of asphalt VOCs types and amount. That is because at higher temperature, VOCs attain greater internal energy and lower thermal stability, resulting in more light components volatilized. In addition, high temperature meets the activation energy required for more reactions, thus promoting the positive progress of various chemical reactions, resulting in more complex VOCs components and greater volatilization.

In addition to temperature, collection location also affects the content and composition of VOC in actual construction. The construction process is outdoors, and the detection of VOC will be affected by environmental conditions such as wind speed. Stroup-Gardiner and Lange (2007) compared the difference of VOC between collected in field construction and simulated heating in laboratory, finding that field VOC concentrations were much lower than that predicted in laboratory simulation, about 25%–50%. Because it is much easier to concentrate VOC under highly controlled laboratory conditions than in the field condition. Wang et al. (2020b) investigated and analyzed the VOC levels of five construction sites, finding that the asphalt storage tank emitted the largest amount, nearly 0.11 mg/L, about 3 times and 27 times of the assessed amount of asphalt plant and paving yard, respectively. The data confirmed that laboratory technicians were exposed to two to four times the VOC concentrations (4.08 μg/L) of field workers. It is necessary to effectively reduce VOCs emissions at asphalt tanks and the exposure factor of laboratory technicians.

Therefore, the difference of VOC detection data between collection location is not the root cause of the difference in asphalt VOC amount, but only affects the VOC concentration in a certain area at a certain time. It is not the main influencing factor of asphalt VOC, but should be used as an indicator to guide safe emission and reduce the harm to human health. Therefore, it is considered that asphalt types and heating temperature have the greatest influence on asphalt VOC. The influencing factors on asphalt VOC determine the research direction of asphalt emission reduction materials, therefore, improving asphalt binder, reducing heating temperature or changing construction procedures are of great significance to realize the development of green pavement.

## 4. Asphalt VOC reduction technology

Composition of asphalt binder is so complex that it can be considered as an emission source in the full life cycle, especially when it is at the high construction temperature. According to road construction procedures, the generation of asphalt VOCs can be divided into two stages: short-term high temperature heating and long-term low temperature service. The high temperature stage includes the heating and paving stages, usually with the temperature higher than 130 °C. Chang (2020) has confirmed that the VOCs in 160 °C include more toxic components, such as thiophene, disulfide, benzene series, etc. It means asphalt VOCs are more

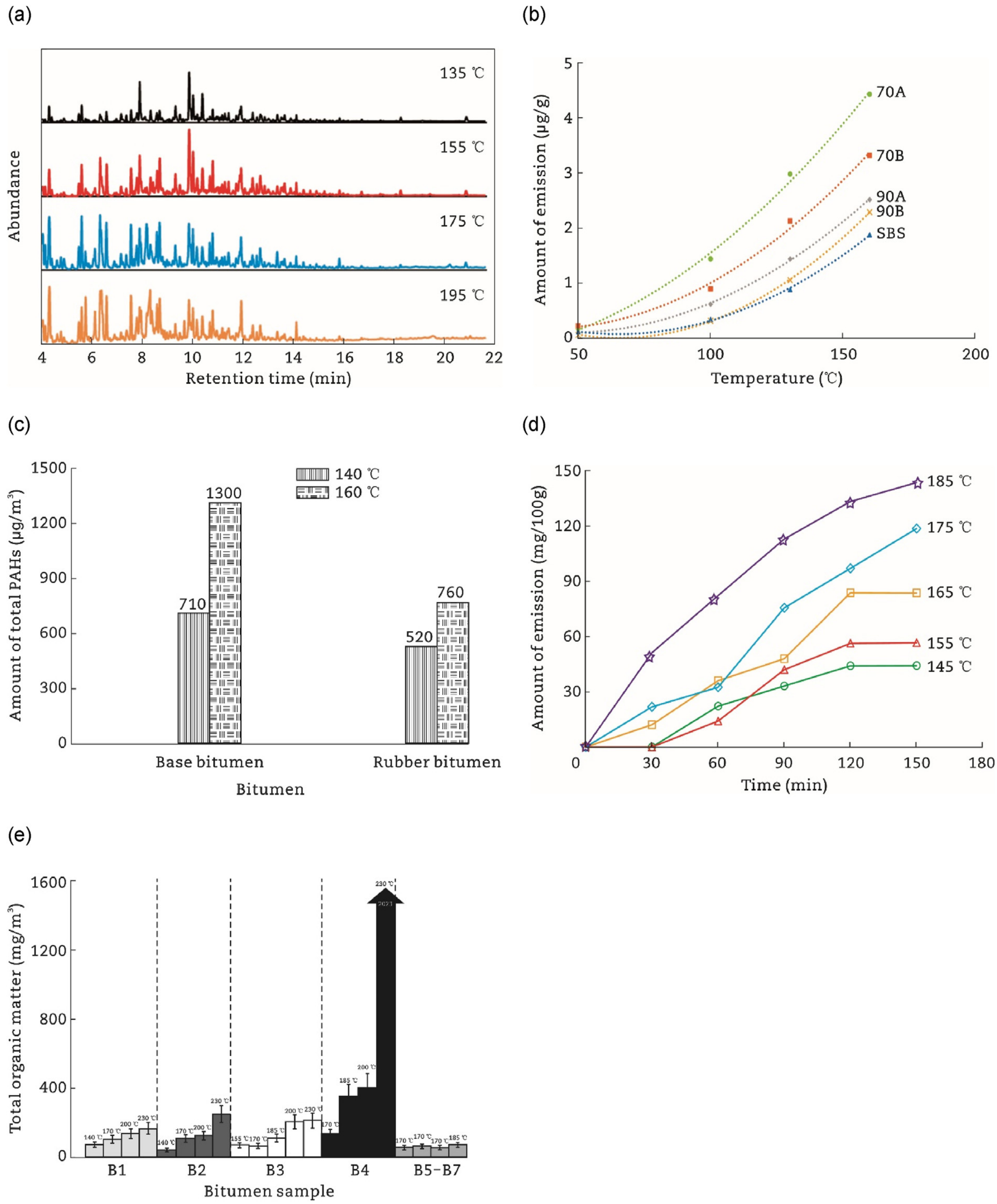



**Fig. 4.** Release characteristics of asphalt VOCs with temperature (Bolliet et al., 2015; Chang et al., 2023b). (a) From Li et al. (2021). (b) From Chang (2020). (c) From Nilsson et al. (2018). (d) From Peng and Li (2010). (e) From Bolliet et al. (2015).

harmful to the environment and construction workers under high temperature conditions. Low temperature stage refers to the long-term service stage after pavement completion, usually with the temperature lower than 70 °C. The volatilization rate is relatively slow, but there will still be a small amount of volatilization (Chang et al., 2023a).

In order to achieve green road construction, asphalt reduction materials have undergone a series of innovations about additives and technologies, as shown in Fig. 6. The traditional emission reduction method is based on the VOCs emission standards of various countries in the ambient air, usually using mechanical methods to collect VOCs for reprocessing, including electric capture method, condensation method and adsorption method. With the improvement of social demand, emission reduction technology is gradually upgraded to innovative reduction method. Some researchers exploit modified asphalt with low emission VOCs to achieve active emission reduction.

The innovative reduction technology can be divided into three categories based on their using stages and reduction methods, including inhibitory modifier, warm mix additives and flame retardant. The Inhibitory modifier

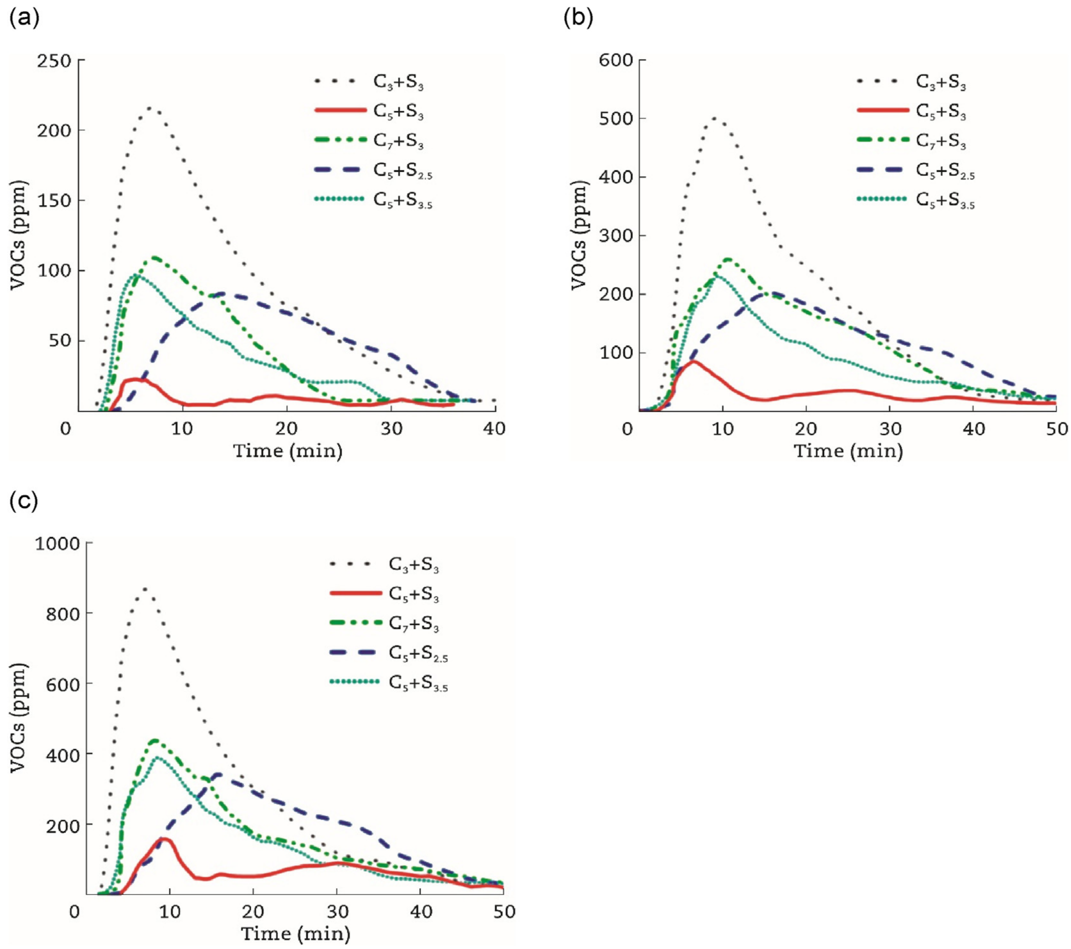



**Fig. 5.** Temperature effect on the release behavior of VOCs amount (Chen et al., 2022a). (a) 135 °C. (b) 155 °C. (c) 175 °C.

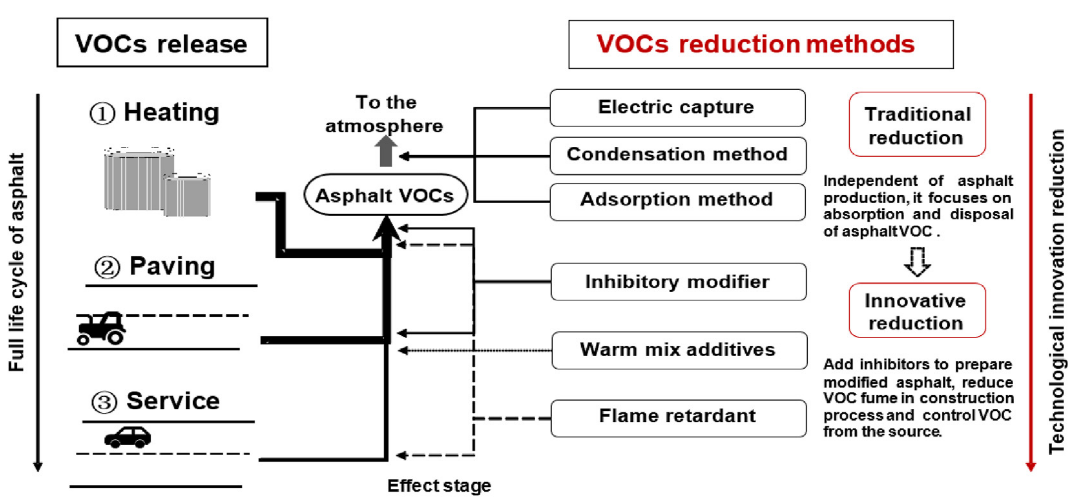



**Fig. 6.** Development of asphalt VOCs emission reduction technologies.

is usually as additives to add into asphalt binder to directly reduce the volatilization of VOCs. The action mechanism includes physical adsorption, chemical inhibition and catalysis. Warm mix additives usually play an indirect role in VOCs reduction by reducing the construction temperature.

Flame retardant can block heat conduction and reduce ambient oxygen content to prevent light components escaping and asphalt burning. The flame-retardant mechanism is complex due to high action temperature and chemical reactions between multi-component composites.

### *4.1. Mechanical methods to remove VOCs*

In 1999, mechanical methods were proposed to control asphalt VOCs below the emission standard. The most effective and direct way is to install an absorption device at the discharge outlet of the production site. Fiber filter was extensively used to control asphalt fumes in the construction fields (Lee et al., 2004; Trumbore, 1999). The control efficiency of fiber filter for both VOCs and particulate emissions was first studied by

Trumbore. Table 2 summaries the estimated results. The particulate collection with filter exceeded 90%. However, the VOCs removal varied widely with an average removal near zero, indicating that the investigated fiber bed filters had no removal efficiency on VOCs.

Lee et al. (2004) used an air pollution control device, including a cyclone and bag filter which installed on the top of batch mixer, to remove particulate matters. They found that the removal efficiencies of the installed air pollution control device on total PAHs and total benzo-[a] pyrene were 22.1% and 93.7%, respectively. But it should be noticed that such device successfully reduced VOCs because cyclone and bag filter were used as adsorption materials during asphalt mixing. The adsorption efficiency of cyclone and bag filter will then degrade according to mixing time, till lose its VOCs adsorption efficiency when they reached the maximum adsorption capacity of VOCs. Furthermore, fiber filter is not capable for CO and $H_2S$ emissions (Trumbore, 1999).

However, these methods can only control the VOCs emission flowing into the atmosphere. But pavement sites in construction is not closed, the way of collection to reprocess will no longer be applicable to reduce asphalt VOCs fundamentally. To develop environmentally friendly pavement, more researchers design new materials and new processes with low emission.

### 4.2. Reduction additive

Since 2010, the research on asphalt VOCs inhibitors has developed rapidly, types of reduction additive gradually from 5 to more than 10, as shown in Fig. 7. Porous and layered materials have been applied to asphalt VOCs reduction early because of their large specific surface area and excellent adsorption properties. With the development of nanomaterials and their preparation technology, new reduction additives based on nano effects have received widespread attention and been gradually designed and prepared.

According to the reaction type of inhibitor in asphalt VOCs reduction, the reduction mechanism can be divided into physical adsorption and chemical inhibition.

(1) Physical adsorption, such as activated carbon, always have a porous structure and supply an extremely high surface energy to capture nonpolar or low polarity molecules to reduce its own surface energy (Chaala et al., 1996). In the field of industrial and civil engineering, physical adsorption is widely used in the adsorption of various harmful gases, with strong adsorption capacity, weak shape-selection, simple adsorption mechanism.
   - Abundant pores, rough surface, the van der Waals Force.
   - Cross-linked structure by polymer heated expanding.
   - Diffusion path with high density and short range provided by nano effect.

(2) Chemical inhibition, reduce the asphalt VOCs emission by chemical decomposition of inhibitors, or promoting the chemical reaction between asphalt molecules. It also includes anti-aging agents, which can protect the asphalt binder from UV light due to the inorganic shield effect (Pang et al., 2014). Furthermore, with the structure of metal layer sheets and negative ions, these kinds of material can chemically absorb UV light (Chai et al., 2009; Cui et al., 2014b; Wu et al., 2012).
   - Inhibitor cracking for cooling or generating flame-retardant gas.
   - React with specific functional groups to imprison some VOCs.
   - Act as a catalyst for the interaction between organic molecules.

**Table 2**
Effectiveness of fiber filters for emission control from asphalt tanks (Trumbore, 1999).

| Plant | Equipment | Pollutant | Reduction efficiency (%) |
|---|---|---|---|
| Asphalt | Tank 1 | VOCs | −35.7 |
| | | | 5.7 |
| | | | 43.4 |
| | Tank 2 | VOCs | 5.3 |
| | Tank 1 | Total particulate | 95.7 |
| | Tank 2 | Total particulate | 90.7 |
| Roofing | Coater | VOCs | 0.0 |

Asphalt VOCs reduction additive can be divided into six categories according to the emission reduction mechanism, as shown in Fig. 8, including porous materials, layered materials, electrostatic effect inhibitor, polymer, chemical inhibitor and composite inhibitor. The first three VOCs reduction materials mainly depends on physical adsorption. The polymer and chemical inhibitor can cause structural and chemical property changes of asphalt binder to prevent VOCs escaping. The composite inhibitor combines VOC inhibition mechanism of these five asphalt inhibitors to improve VOCs reduction effect.

#### 4.2.1. Porous material

The reduction research on VOCs from asphalt binder referred on the method of VOCs reduction in atmosphere by using porous materials. Porous materials generally have abundant pore structure and large specific surface area, which can provide effective physical space for the adhesion of light components. Initially, porous materials have irregular pores with different pore sizes and complex shapes, which can absorb various VOCs molecules. With the developed demand for VOCs adsorption, researchers began to design and prepare materials with regular pore structure to achieve selective adsorption of VOCs molecules with specific functional groups. Based on the rapid development of nanomaterials, their large specific surface area and surface effect also promote the continuous upgrading of porous materials used in asphalt emission reduction.

*4.2.1.1. Irregular pore structures.* In the early stage of asphalt VOCs emission reduction research, activated carbon attracted the attention of many researchers because of its excellent pore structure and high adsorption capacity (Wei et al., 2021). Activated carbon (AC) is amorphous structure with many irregulars and variform pore structures, that can provide a theoretical adsorption on various VOC molecules. During the activation process, the surface of activated carbon is not completely carbonized and carries other elements in the form of organic functional groups, such as carboxyl groups, hydroxyl groups, phenols, etc. These organic functional groups can form chemical bonds with adsorbed substances and have excellent potential adsorption effects (Peng and Li, 2010). The current researches on activated carbon and biochar in the ecological design of asphalt materials can be summarized in Table 3.

In 2010, Xiao et al. (2010a) measured the release amount of asphalt VOCs by gravimetric method and took the lead in exploring the reduction efficiency of AC on asphalt VOCs. The result showed that capillary adsorption was the main reduction effect when AC dosage was small. With AC dosage increasing, the oxygen-containing compounds or complexes on the surface of AC would catalyze new reaction to generate VOCs, resulting in a weakening trend on emission reduction. Zhang (2011) also confirmed this finding and considered that the adsorption capacity of AC was affected by two mutually restrictive factors, the pore capacity of adsorbed volume material and the surface catalytic reaction, and there was an optimum dosage on emission reduction. Zhang (2014a) analyzed the optimum dosage of AC is 3%–6%, which reached the same conclusion from (Xiao et al., 2010a). When AC dosage is 5%, the emission reduction efficiency on asphalt VOCs is the best, which can reach 33.5%.

Both Xiao et al. (2010a) and Zhang (2011) found that the catalytic activity of AC would also promote side reactions. There was a strong smell of penicillin during experiment, which had a negative impact on the subsequent research. At the same time, Huang (2013) also verified this finding by comparing the VOCs reduction efficiency of various flame retardant, non-polar organic substance and physical adsorption inhibitor. It was confirmed that although the adsorption effect of non-polar organic

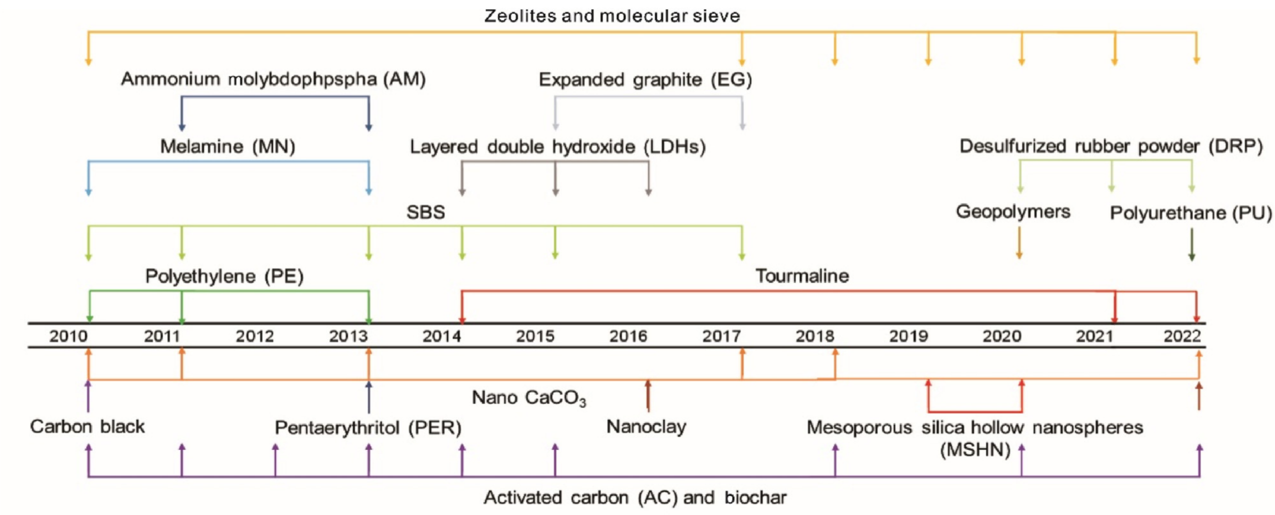



**Fig. 7.** Development history of reduction additive on asphalt VOCs.

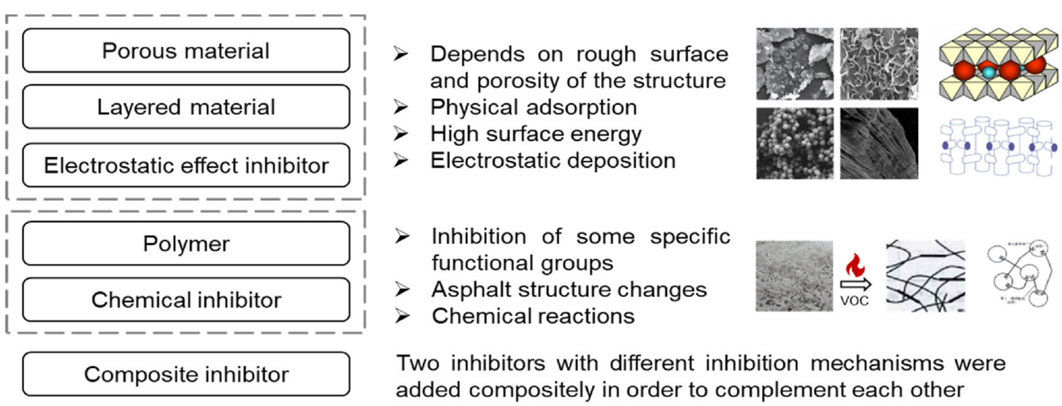



**Fig. 8.** The classification and characteristics of reduction additive.

AC on asphalt VOCs could reach 20%, there would be a lot of irritating odors to result in secondary environmental pollution when added into asphalt binder. Therefore, the catalytic action of AC and the chemical interaction between functional groups need to be further studied and verified.

Long et al. (2018) explored adsorption mechanism between AC structural characteristic and reduction effect on single VOC molecule by GC-MS. The results showed that the used AC with a specific surface area of 540 $m^2/g$ and pore volume of 0.4278 $cm^3/g$ could reduce emission of small molecule substances by more than 60%, PAHs and macromolecules by 35%–50%. It reflects the bidirectional selection between asphalt VOCs and AC.

The emission reduction efficiency of inhibitor is determined by two factors: inhibitor type and dosage. The reduction efficiency of AC with different dosages is shown in Fig. 9. The data showed that there were some differences in asphalt VOCs reduction effect of the four kinds of AC, mainly due to the different types of AC. The reduction efficiency of AC on small molecules is more than 40%, while reduction efficiency on PAHs and macromolecular substances (such as naphthalene and pentadecane) can also reach more than 20%, indicating that AC has excellent emission reduction effect of various molecules. Zhang (2014a) pointed out that the softening point and ductility of AC modified asphalt were lower than that of based asphalt when the addition dosage is less than 5%. It shows that the addition of AC will reduce the high and low temperature performance of asphalt, and lead asphalt to be brittle. The index is still within the standard range, which does not affect its road performance. However, when the AC addition dosage is more than 5%, it is necessary to balance the road performance and low emission. More experiment on the pavement performance of activated carbon modified asphalt should be carried out in the future to verify the feasibility of its extensive application.

Biochar can be obtained from biomass pyrolysis products, such as microalgae, feces and waste wood. It has large surface area and porosity and have microbial activity to increase the probability of VOC adhesion. Some biochar with nitrogen-containing functional groups on the surface is considered to have potential adsorption capacity to selectively adsorb certain types of VOCs. Zhou et al. (2020) studied the emission reduction characteristic of three kinds of biochar on the total VOCs and 18 kinds of VOCs molecules. The results showed that the reduction efficiency of long-chain alkane was relatively good, while the reduction efficiency of aromatic substances was greatly affected by the type of biochar. So biochar was considered that can achieve effective reduction on most VOCs but more toxic VOCs. The experiment also analyzed the inhibition mechanism of biochar from the view of adsorption heat and concluded that the inhibition process of pig manure-based biochar (PB) with small adsorption heat was mainly physical adsorption, while the inhibition process of straw-based biochar (SB) and waste wood-based biochar (WB) was mainly chemical inhibition.

Metal incorporation can usually change the active site of the material. Mousavi et al. (2023) carried out metal loading on biochar and obtained excellent VOC emission reduction efficiency. The Fe-rich biochar and low-iron biochar, with rich nitrogen, are produced various blends of microalgae CM and SM by hydrothermal co-liquefaction. The four

**Table 3**
Classification and asphalt VOCs reduction characteristics of irregular porous materials.

| Irregular porous materials | VOCs reduction characteristic | Reduction efficiency (efficiency @ dosage) | Reference |
|---|---|---|---|
| Activated carbon (AC) | • Low packing density (0.38–0.65 g/cm$^3$)<br>• Large specific surface area (>1000 m$^2$/g)<br>• Mesoporous microporous coexistence, monolayer and capillary adsorption<br>• Active complex on the surface | 27.8% @ 3%<br>30.3% @ 4%<br>33.5% @ 5%<br>30.8% @ 6% | Zhang (2014a) |
| | | 21.6% @ 2%<br>18.9% @ 3% | Huang (2013) |
| | | PAHs:<br>38.4% @ 3%<br>14.1% @ 4%<br>46.0% @ 5%<br>Alkanes:<br>36.7% @ 3%<br>42.7% @ 4%<br>47.6% @ 5%<br>Total:<br>38.2% @ 3%<br>17.9% @ 4%<br>46.2% @ 5% | Long et al. (2018) |
| | | 41.6% @ 1%<br>33.0% @ 3% | Qian and Wang (2012); Xiao et al. (2010a); Zhang (2011) |
| | | 24.5% @ 1%<br>19.6% @ 5% | Peng and Li (2010) |
| | | 33.9% @ 3%<br>38.4% @ 4%<br>42.0% @ 5%<br>39.3% @ 6% | Cui et al. (2015b) |
| | | Alkanes: 81.0% @ 6%<br>PAHs: 75.4% @ 6%<br>Total: 76.2% @ 6% | Zhang et al. (2021a) |
| | | 26.9% @ 3%<br>30.7% @ 4%<br>32.6% @ 5% | Xiao et al. (2017) |
| Carbon black | • Amorphous carbon<br>• Light, loose and extremely fine | −4.8% @ 4% | Xiao et al. (2010b) |
| Biochar | • PB-no voids, amorphous carbon<br>• WB-porous, amorphous carbon<br>• SB-dense, perfect crystals<br>• Adsorption order: saturates-aromatics-resin-asphaltene | SB: 59.8%<br>WB: 96.4%<br>PB: 47.6%<br>Great reduction efficiency on alkanes, PAHs and sulfide | Zhou et al. (2020) |
| Fe-biochar | • Abundant N sites to form C–N–Fe bonds<br>• –N–Fe coordination promote the degradation of dibenzothiophene | Fe-rich biochar: 76%<br>Low-Fe biochar: 59%<br>Great reduction efficiency on alkanes and PAHs | Mousavi et al. (2023) |

N-functional groups (amide, amine, pyrrole, and pyridine) can adsorb three O-containing compounds (benzoic acid, benzofuran, and hexanal) and three S-containing compounds (dibenzothiophene, 3-pentylthiophene, and hexanethiol). When loaded with iron, the abundant N sites could be coordinated with Fe form C–N–Fe bonds. Simulation showed that the adsorption energy was 8–10 times higher than that of the original biochar, and the adsorption was enhanced. At the same time, the presence of Fe can enhance the catalytic performance of biochar to promote the degradation of dibenzothiophene. Low-Fe biochar has stronger alkanes adsorption, while Fe-rich biochar has better emission reduction on non-polar aromatics.

The reduction efficiency of biochar on total VOC, hydrocarbon and aromatic compounds is shown in Fig. 10. Among them, the two kinds of microalgal biochar loaded with Fe have a good emission reduction effect on aromatic compounds. Waste wood-based biochar has the highest VOC emission reduction efficiency, reaching 96%. This is because the surface area of WB is as high as 412 nm$^2$, indicating that the surface area of the porous material plays an important role in VOCs adsorption. By comprehensive comparison with the data in Table 3 and it is found that the VOCs reduction efficiency of biochar is slightly higher than that of AC, which is because biochar has the decomposition effect of microorganisms and improves the surface activity, thus improving the adsorption capacity.

*4.2.1.2. Regular pore structure.* Although irregular porous materials can widely absorb various VOCs, the adsorption mechanism is difficult to accurately define duo to its irregular pores. Therefore, some research proposed to add regular porous materials into asphalt binder and explored the reduction efficiency and mechanism. Zeolite is a new kind of synthetic material with rich pore structure and excellent high temperature stability that it has gradually become a common adsorbent for industrial VOCs emission reduction. Zeolite can also realize the positive design of pore size, shape and acid-base functional group by adjusting the preparation process. In the field of pavement emission reduction, classification and asphalt VOCs reduction characteristics of regular porous materials are shown in Table 4.

(1) Microporous zeolite

According to physical adsorption theory, when the adsorption pore size is close to the molecular dynamic diameter of VOCs, the adsorption efficiency is higher. Too large pore size will lead to the re-desorption of the adsorbed gas, while too small pore size will lead to the ineffective adsorption of molecules unable to enter the pore. Most of the asphalt VOCs molecules are in the micropore size, so theoretically microporous zeolite has good physical adsorption property. The asphalt reduction efficiency of 3 kinds of zeolite was detected by Chang (2020) as 16.0%, 11.1% and 42.9% of asphalt VOCs, respectively. The study proposed that zeolite with large granularity can inhibit VOCs types, but the total inhibition efficiency is not high, while zeolite with small granularity can reduce cycloalkanes VOCs. Chen et al. (2022b) prepared zeolite ceramics by 13X zeolite powder and attapulgite clay. This zeolite ceramics had mainly micropores with pore size 0.88 nm and had good physical adsorption property. This study considered that zeolite used as fine aggregate with 50% dosage could attain 45% emission reduction efficiency. Zhang et al. (2021a) also confirmed that the specific surface area and pore volume of emission reduction materials are important, but the number of micropores has a greater impact on the emission reduction effect. When the proportion of micropores is large, the adsorption effect of asphalt VOC is better.

(2) Mesoporous zeolite

Compared with microporous zeolite ZSM-5, mesoporous zeolite has better emission reduction potential due the more diversified pore structure, which can achieve physical adsorption and the chemical action of functional groups at the same time. Xiao et al. (2019) designed zeolite with a 1:2 aluminum-calcium ratio. It can not only adsorb asphalt VOCs by pore structure, but also reduce the viscosity of asphalt binder by crystal water evaporating. The data confirm that the optimal emission reduction efficiency is achieved when the dosage is 5%.

Zeolite with $Ca(OH)_2$ as raw material designed by Zhang et al. (2021c) and Sharma and Lee (2017b) verified the emission reduction mechanism of physical and chemical adsorption coexistence. Sharma and

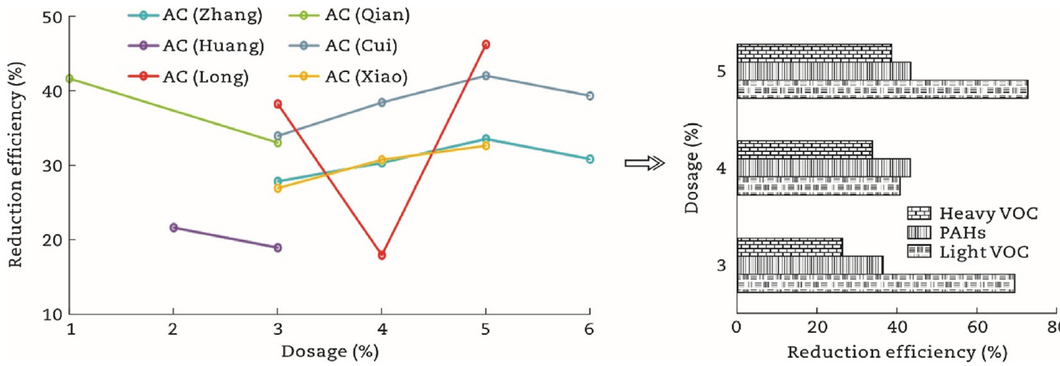



**Fig. 9.** Dosage and asphalt VOCs reduction efficiency of activated carbon (Cui et al., 2015b; Huang, 2013; Long et al., 2018; Qian and Wang, 2012; Xiao et al., 2017; Zhang, 2014a).

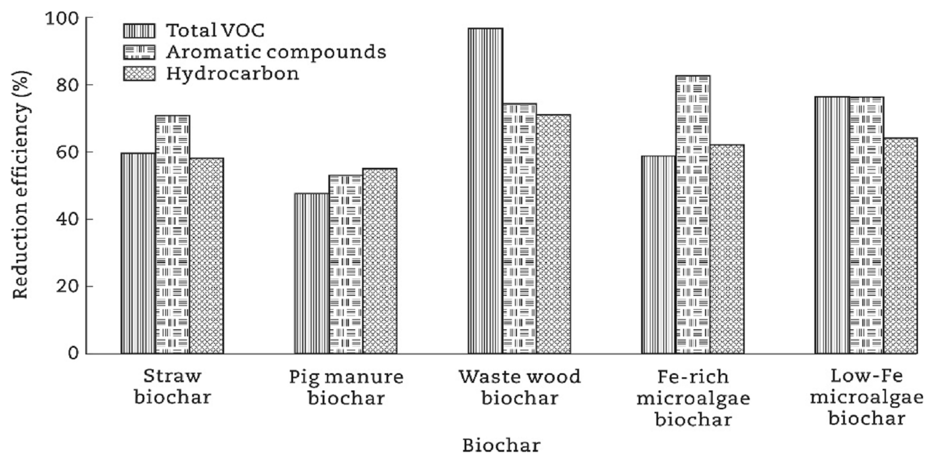



**Fig. 10.** Asphalt VOCs reduction efficiency of different biochars (Mousavi et al., 2023; Zhou et al., 2020).

Lee conducted research on its dosage and selectivity of VOCs emission reduction. At 180 °C, the reduction efficiency of zeolite with 2%–6% dosage is about 61%–98%, aldehydes for 52%–92%. Zhang (2020) and Wu et al. (2022) prepared mesoporous zeolite using solid waste to achieve effective inhibition of hydrocarbon VOCs. The results showed that with the increase of the dosage, the reduction efficiency of solid waste-based zeolite on aromatic compounds increased first and then decreased, and the optimal efficiency was as high as 60%.

Besides zeolite, metal–organic framework (MOF), geopolymer and spent fluid catalytic cracking catalyst (SFCCC) are also porous materials with zeolite-like crystal structure, which are also used in asphalt VOCs reduction research. MIL-101(Cr) belongs to MOF material, which has not only regular pore structure, but also metal active sites, and has good catalytic sieving ability. Yang et al. (2020) incorporated MIL-101(Cr) into SBS modified asphalt and found that it could achieve over 50% VOC emission reduction efficiency, mainly due to its large specific surface area 2860 $m^2/g$ and SBS swelling for adsorption of light components.

Geopolymer is a potential replacement for cement to achieve low-carbon emissions (Zhang et al., 2021b). Geopolymer has porous structure with catalytic, separation and purification functions. It is an amorphous three-dimensional network gel composed of $SiO_4$ and $AlO_4$. Yang (2020) tried to prepare polymers warm mixing agent by using NaOH and water glass as activators. The detailed reduction efficiency on three types of VOCs (small molecules, PAHs, and others) was shown as Table 5. In general, 6% geopolymer can significantly reduce the volatilization of small molecules. It had the best emission reduction efficiency on naphthalene in PAHs, and the emission reduction efficiency did not change significantly with temperature. At 135 °C, water released by geopolymer can reach 11.47%, which can effectively reduce the mixing temperature. Therefore, geopolymer is usually used for warm mixing of asphalt binder (Tang et al., 2018).

SFCCC mainly consists of zeolite crystals, alumina oxide and quartz. The rough surface of SFCCC may adsorb VOC molecules to its surface, and with the van der Waals force and pore blocking effect, VOC molecules diffuse to the internal pore structure of SFCCC and be fixed. Xue et al. (2020) confirmed that the addition of SFCCC reduced the number of asphalt VOCs types, especially PAHs, such as naphthalene, anthracene, phenanthrene and their derivatives. The proportion of alkanes in VOCs increased, while the proportion of more toxic molecules such as PAHs decreased significantly. It can be considered that SFCCC catalytic effect reduced the toxicity of asphalt VOCs.

(3) Prospect of catalytic effect

Chen et al. (2016) tested structure of zeolite by dynamic adsorption experiment and found that the catalytic performance of zeolite can promote the conversion and adsorption of asphalt VOCs. Therefore, combined with the rich pore structure of zeolite, zeolite pore modification can be carried out to achieve the selective reduction of VOC molecules with specific functional groups. It will be a very feasible design and development direction of zeolite in the field of asphalt VOCs reduction. Kamal et al. (2016) summarized the research progress and mechanism of zeolite on VOCs in catalytic system, and provided ideas for realizing specific types of VOCs emission reduction.

The reduction efficiency of regular porous materials on asphalt VOCs is summarized as shown in Fig. 11. Zeolite type and pore size have a great influence on the inhibition effect. The reduction efficiencies of all zeolites

**Table 4**
Classification and asphalt VOCs reduction characteristics of regular porous materials

| Regular porous material | VOCs reduction characteristic | Reduction efficiency (efficiency @ dosage) | Reference |
|---|---|---|---|
| ZSM-5 zeolite | • Three dimensional cross channels<br>• Micropore, the pore size is 0.55–0.90 nm<br>• Strong thermal stability, large specific surface area | 2–11 types of VOCs↓<br>A: 16.0%<br>B: 11.1%<br>C: 42.9% | Chang (2020) |
| Zeolite ceramsite (13X zeolite) | • Main structures are Si–O tetrahedrons and Al–O tetrahedrons<br>• Contains traces of iron, magnesium, and calcium oxides<br>• pore volume 0.38 $cm^3$/g, surface ratio 709.34 $m^2$/g<br>• Dosage 50% as fine aggregate | Alkanes: 4.9% @ 5%<br>43.9% @ 50%<br>Aromatic compounds:<br>13.3% @ 5%<br>54.1% @ 50%<br>Total: 8.7% @ 5%<br>45.1% @ 50% | Chen et al. (2022b) |
| 4A zeolite | • Pore volume 0.39 $cm^3$/g, specific surface area 513.77 $m^2$/g<br>• Obviously granular, flat surface | Alkanes: 78.6% @ 6%<br>PAHs: 87.5% @ 6%<br>Total: 78.4% @ 6% | Zhang et al. (2021a) |
| Solid wastes-based zeolite | • Irregular octahedral structure<br>• Distinct granular shape with smooth surface<br>• Mesoporous materials<br>• High temperature stability<br>• Pore volume 0.0702 $cm^3$/g, specific surface area 685 $m^2$/g | 45.7% @ 2%<br>60.0% @ 5%<br>45.9% @ 7%<br>Alkanes:<br>41.0% @ 2%<br>71.3% @ 5%<br>55.2% @ 7% | Zhang (2020)<br><br>Wu et al. (2022) |
| $Ca(OH)_2$-based zeolite | • Rough surface, flower clusters<br>• Part amorphous<br>• Water evaporate to reduces asphalt viscosity | 35.0% @ 5%<br><br>74.3% @ 2%<br>80.5% @ 4%<br>83.1% @ 6% | Xiao et al. (2019);<br>Sharma and Lee (2017a, b) |
| MIL-101(Cr) | • Specific surface area 2860 $m^2$/g, pore volume 1.34 $cm^3$/g<br>• MIL-101(Cr) causes SBS to sufficiently expand<br>• High decomposition temperature | 48.1% @ 0.02%<br>59.3% @ 0.05%<br>57.4% @ 0.08% | Yang et al. (2020) |
| Geopolymers | • Slit mesoporous structure of parallel plates<br>• Pore diameter 11.09 nm, pore volume 0.135 $cm^3$/g, specific surface area 47.658 $m^2$/g | – | Yang (2020) |
| SFCCC | • Zeolite crystals, alumina oxide and quartz<br>• Pore diameter 5.37 nm, pore volume 0.145 $cm^3$/g, specific surface area 107.8 $m^2$/g | Aliphatic hydrocarbons ↑<br>hydrocarbon derivatives ↓<br>PAHs ↓ | Xue et al. (2020) |

Note: A represents Si/Al 300, B represents Si/Al 600, C represents Si/Al 1200.

are greater than 30%. Zeolite ceramite prepared by Chen et al. (2022b) has the best inhibition effect, as high as 87%. It can be inferred that adding inhibitory modifier to asphalt binder as fine aggregate may have better reduction efficiency than as modifier. Solid waste-based zeolite has better emission reduction effect on alkanes, but has no obvious influence on aromatic compounds, considered has the potential of selective reduction. Each incorporation of inhibitor will break the balance of the asphalt. Some of them may cause to the deterioration of high temperature performance. But the performance indicator is still within the standard range, so these inhibitor addition does not reduce emissions at the expense of road performance. After long-term standing, the added reduction material may sink or float in the asphalt due to its own density. Researchers should pay more attention to how to improve the storage stability of modified asphalt binders.

*4.2.1.3. Nano-porous material.* VOCs emission reduction of nano-materials mainly depends on the large specific surface area and surface electrostatic effect of nano-structures (Guillet-Nicolas et al., 2020). The common nano-porous materials on VOCs reduction are shown in Table 6. Zhang (2011) confirmed that nano-calcium carbonate has a strong adsorption on light components due to its electrostatic effect. The electrostatic effect makes the adsorption capacity of light components stronger than the ability to break free, reducing the desorption of light components. Ma (2004) considered that nanoparticles have the large specific surface area and strong activity, so VOCs molecules have a greater contact probability with them to form stable groups and be fixed on the surface and inside of nanoparticles. Besides, Sun et al. (2017) believed that nano-calcium carbonate can improve the thermal stability and anti-aging performance of asphalt binder, and promote the development of asphalt performance in the direction of road durability.

The mesoporous silica hollow nanospheres (MSHSs) with nano-structure were applied by Shu et al. (2019) in the study of VOCs adsorption. MSHSs has the characteristics of large specific surface area, abundant porosity and strong adsorption capacity. There is strong intermolecular interaction between MSHSs and hydrocarbon derivatives through surface hydrogen bonding, so MSHSs has the best reduction efficiency on hydrocarbon derivatives. Some studies have shown that reduction efficiency of hydrocarbon derivatives was enhanced with temperature increasing (Wu et al., 2020). Zhang et al. (2021a) compared the VOC emission reduction effect of three porous materials, activated carbon, 4A zeolite and nano $CaCO_3$ on waste rubber modified asphalt. It was found that nano $CaCO_3$ had the best effect on VOC in asphalt, because nano $CaCO_3$ had the largest micropore volume and the highest proportion of micropores, which could realize VOCs effective adsorption without desorption.

*4.2.1.4. Mechanism and effect comparison of porous materials.* Comparison of reduction efficiency on asphalt VOCs by porous material are shown as Fig. 12. The reduction mechanism of porous materials such as activated carbon and zeolite mainly depends on physical adsorption by pore structure. The reduction efficiency of activated carbon is about 20%–50%, while that of zeolite is generally more than 40%. It can be considered that zeolite, as a heat-stable material, has higher emission reduction value when incorporated into asphalt. In addition, compared with microporous zeolite (Micro-PZ), mesoporous zeolite (Meso-PZ) has more complex pore structure and better designability. Specific zeolite materials can be designed and developed by combining the dual functions of catalysis and adsorption. The emission reduction effect of different nano-materials (Nano-PM) is different due to the large difference in structural properties synthesis. Although nanomaterials are currently popular materials, and its VOCs reduction performance still need more improvement.

*4.2.2. Layered material*

Porous materials can adsorb VOCs through pore structure, while layered materials can also reduce VOCs escape by using their interlayer interactions.

*4.2.2.1. Common layered material.* At present, the layered materials used to inhibit asphalt VOCs include expanded graphite (EG) and layered double hydroxides (LDHs), the reduction characteristic can be summarized as Table 7. Loose porous expanded graphite can be preparate by graphite after a series of treatments. The SEM images of EG before and

**Table 5**
Reduction efficiency of geopolymer on various VOC molecules (Tang et al., 2018).

| VOCs type | VOCs component | Reduction characteristic | Reduction efficiency (%) |
|---|---|---|---|
| Light components | $H_2O/H_2S/CO_2/NO_2/SO_2$ | • Inhibitory effect on small molecules<br>• The release of small molecules except water decreases with increasing temperature | 70–90<br>60<br>60–75<br>80–90<br>40–55 |
| PAHs | $C_{10}H_8/C_{12}H_{10}/C_{13}H_{10}/C_{14}H_{10}/C_{16}H_{10}$ | • For PAHs, especially naphthalene<br>• With the increase of temperature, the release of naphthalene showed an obvious decreasing trend<br>• The other four PAHs did not change significantly with temperature | 50–60<br>25–30<br>20–30<br>25<br>30–40 |
| Others | $C_7H_7Cl/C_{15}H_{12}/C_{15}H_{32}$ | • Inhibit alkanes and halogenated hydrocarbons<br>• With the increase of temperature, the release of pentadecane firstly increased and then decreased | 20<br>25–45<br>30 |

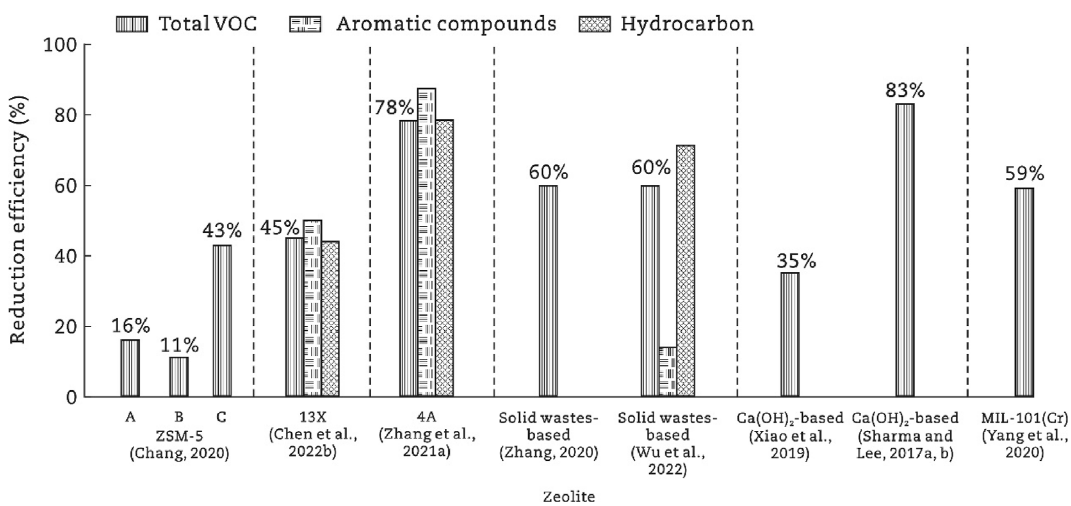



**Fig. 11.** Asphalt VOCs reduction efficiency of different zeolites (Chang, 2020; Chen et al., 2022b; Sharma and Lee, 2017b; Wu et al., 2022; Xiao et al., 2019; Yang et al., 2020; Zhang, 2020; Zhang et al., 2021a).

after adding to asphalt confirmed that the structure of EG changes greatly when it is heated in asphalt binder (Huang et al., 2015). The graphite layer became folded and curled, and the interlayer structure is intercalated or stripped by asphalt components, thus adsorbing the light components and PAHs. Sun et al. (2017) also confirmed this conclusion. After EG with shape of loose porous added into asphalt binder, its layers spread out and specific surface area increased, which was conducive to the adsorption of highly toxic PAHs. The research results of Huang et al. (2015) and Ma (2004) mutually verified and gave three emission reduction characteristics of EG. Firstly, the inclusion amount of EG is generally small, ranging from 0.25% to 2.50%. Because the layer spreading of EG will greatly increase the specific surface area, and the amount required to reach the adsorption limit is small. Secondly, the adsorption effect of EG is great, higher than 60%. Thirdly, the dosage has little impact on the emission reduction effect, and has the best reduction efficiency when the dosage is 1.5%. So adjusting the EG dosage may not effectively improve emission reduction efficiency. It is also pointed out in the study that although EG has excellent VOCs inhibition effect, its incorporation into asphalt binder will lead to a sharp decrease in asphalt ductility. More research on enhancing asphalt compatibility should be carried out for its wide application as an asphalt modifier (Zhang, 2014b).

In addition, Cui et al. (2015a) proposed that layered double hydroxide (LDHs) has a special Mg-Al double-layer structure, which can realize the physical adsorption of VOCs by relying on its interlayer van der Waals force to reduce asphalt VOCs. TG-MS was used to characterize its VOCs reduction abilities. 20 types of molecules with the mass charge ratio varying from 18 to 278 were studied. Firstly, LDHs have the potential to reduce asphalt VOCs. The reduction effect varies on different molecules. Significant on smaller molecules. LDHs affect the volatile speed of more carcinogenic volatile components such as naphthalene. Four percent of LDHs is an optimum additive to achieve the best emission reduction efficiency of VOCs, which is 40%–60% reduction. Results illustrated that environmental temperature has significant influence only on the volatile characteristics of smaller molecules in the pure bituminous binder, and marginal for volatile speed of bigger molecules and LDHs modified asphalt binder, as Fig. 13.

Fig. 14 shows that the dosage of layered material has a large difference in VOCs reduction efficiency. Zhang (2014a) also verified the VOCs inhibition effect under different LDHs dosages. The study showed that the VOCs reduction efficiency of LDHs was lower than 10%, and with the increase of LDHs content, the inhibition efficiency showed a trend of first increasing and then decreasing with the best dosage of 4%, which was consistent with Cui's conclusion (Cui et al., 2015b). Although the emission reduction effect of LDHs is poor on asphalt VOCs, some researchers have confirmed that some LDH materials also reduce carbon dioxide ($CO_2$) emissions. Bhowmik et al. (2021) prepared calcium aluminum nitrate layered double hydroxide (Ca-Al-$NO_3$ LDH) nanocomposites. $CO_2$ was converted to carbonic acid ($H_2CO_3$) by proton transfer of LDH hydroxyl (OH) group. The 6% dosage had the best $CO_2$ emission reduction efficiency.

*4.2.2.2. Nanoclay.* Adding nanoclay to the asphalt binder can form the intercalation structure to block the diffusion of oxygen. It is considered to have flame retardant properties, which is used for asphalt flame retardant

**Table 6**
Classification and asphalt VOCs reduction characteristics of nano porous materials.

| Nano porous material | VOCs reduction characteristic | Reduction efficiency (efficiency @ dosage) | Reference |
|---|---|---|---|
| Nano $CaCO_3$ | • Large specific surface area (>40 $m^2/g$) and strong adsorption capacity<br>• Quantum size effect, surface effect<br>• Good compatibility with asphalt | 4.8% @ 3.0%<br>5.7% @ 4.0%<br>7.4% @ 6.0% | Qian and Wang (2012); Yang et al. (2013); Zhang (2011) |
| | | 4.8% @ 4.0%<br>7.0% @ 4.5%<br>8.4% @ 5.0%<br>9.2% @ 5.5%<br>9.3% @ 6.0% | Sun et al. (2017) |
| | | Alkanes: 91.9% @ 6.0%<br>PAHs: 87.6% @ 6.0%<br>Total: 89.9% @ 6.0% | Zhang et al. (2021a) |
| MSHSs | • Large specific surface area and load capacity<br>• Strong intermolecular forces with hydrocarbon derivatives<br>• Surface hydroxyl group forms hydrogen bonds with the carboxyl group substance | 7.6% @ 0.5%<br>28.0% @ 1.0%<br>38.2% @ 2.0% | Shu et al. (2019); Wu et al. (2020) |

**Table 7**
Classification and asphalt VOCs reduction characteristics of common layered materials.

| Layered material | VOCs reduction characteristic | Reduction efficiency (efficiency @dosage) | Reference |
|---|---|---|---|
| Expanded graphite (EG) | • Large specific surface area, high surface activity and non-polarity<br>• Trace polar groups on the surface to adsorb polar molecules<br>• A loose porous worm-like, interlayer structure that can be intercalated or stripped by asphalt components<br>• Strong temperature stability (−204°C–1650 °C)<br>• Thermal expansion to interdict heat source | 61.1% @ 0.50%<br>60.6% @ 1.00%<br>61.6% @ 1.50%<br>61.2% @ 2.00%<br>61.4% @ 2.50% | Sun et al. (2017) |
| | | 69.1% @ 0.25%<br>67.5% @ 0.50%<br>62.0% @ 0.75%<br>64.5% @ 1.00%<br>67.4% @ 1.25%<br>69.8% @ 1.50% | Huang (2013); Huang et al. (2014, 2015) |
| Layered double hydroxides (LDHs) | • Mg-Al double layer structure<br>• The van der Waals force action | Reduce 4 kinds of light molecules | Cui et al. (2015a, 2016) |
| | | 6.7% @ 3.00%<br>9.8% @ 4.00%<br>8.5% @ 5.00% | Zhang (2014a) |
| | | 4.4% @ 3.00%<br>7.1% @ 4.00%<br>6.2% @ 5.00% | Cui et al. (2015b) |

and improve the anti-aging properties of asphalt. The dynamic shear rheometer (DSR) test found that with the nanoclay adding, performance grade and the ability to resist permanent deformation was improved (Ezzat et al., 2016).

Organo-montmorillonite nanoclay, which has unique one-dimensional layered nanostructures and cation exchange properties, was added into asphalt and the VOCs reduction behavior was studied by

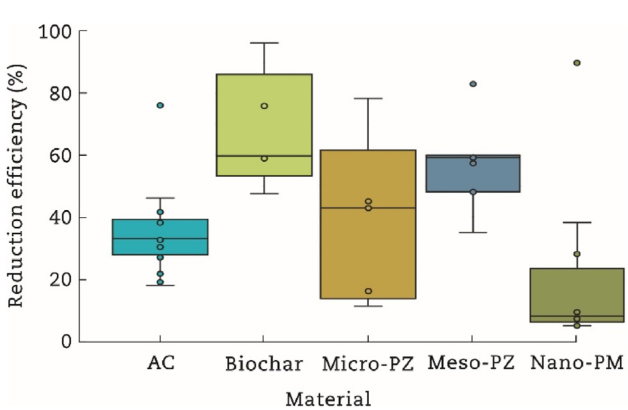



**Fig. 12.** Comparison of reduction efficiency on asphalt VOCs by porous materials.

Li et al. (2017). They claimed that the light components in asphalt binder can be intercalated by the interlayer space of nanoclay, resulting in less VOCs. The decrease of chromatographic peak area of major VOCs when two types of organic montmorillonite nanoclay showed that most types of asphalt VOCs have been reduced when nanoclay was used, with most changes of peak areas have negative values. The emission reduction efficiency of two kinds of nanoclays was compared as Fig. 15. The nanoclay-A achieved more than half VOCs reduction. The reason was that nanoclay-A had octadecyl trimethyl ammonium surfactants, while nanoclay-B had benzyl dimethyl hexadecyl ammonium surfactants. The former surfactants had better compatibility with the light components of asphalt binder.

Liu et al. (2023) subsequently investigated the VOCs emission of rubber modified asphalt and the emission reduction efficiency of another organic montmorillonite nanoclay. The quantitative calculation method of asphalt VOCs was improved by using fingerprint components. The data showed that the addition of rubber resulted in the increase of emission amount about two times, but the volatilization of two small molecules was reduced, possibly because rubber could absorb the two light components. Nanoclay with distearylammonium chloride as the surfactant can achieve 30.6% VOCs reduction efficiency, which was attributed to its intercalation structure. However, the adhesion between asphalt and aggregate will be reduced when nanoclay is incorporated into asphalt. Researchers should also consider feasibility of applications for practical engineering to balance emission reduction and road performance.

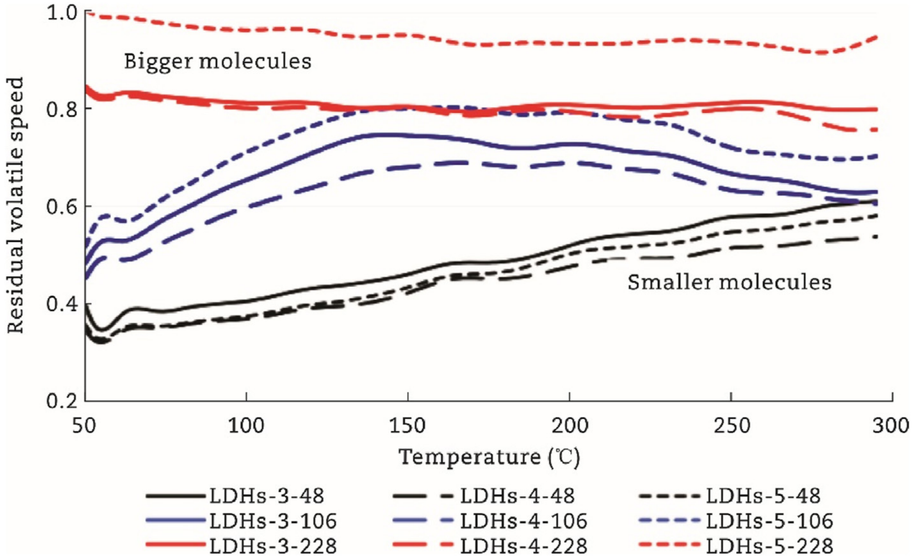



**Fig. 13.** Emission reduction trend on different molecules by LDHs at different temperatures (Cui et al., 2016).

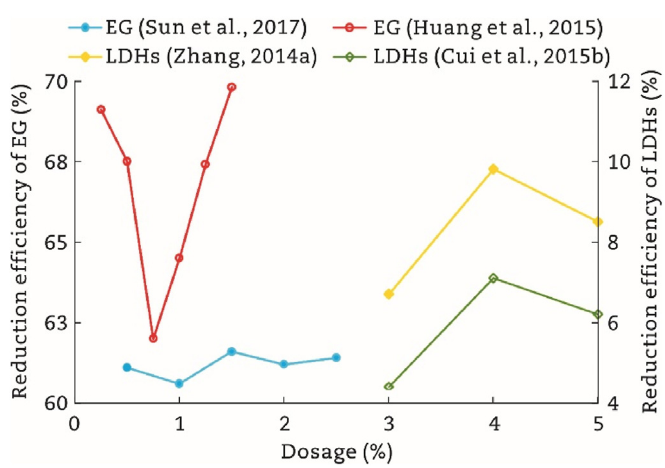



**Fig. 14.** Emission reduction efficiency of layered materials with different dosage (Cui et al., 2015a; Huang et al., 2015; Sun et al., 2017; Zhang, 2014a).

*4.2.2.3. Mechanism and effect comparison of layered materials.* Layered materials adsorb VOCs molecules mainly through interlayer spreading. Due to the difference in surface polarity and surface energy, different layers also have different adsorption amounts for different VOCs molecules, shown as Fig. 16. The data in the box diagram showed EG has generally higher reduction efficiency (about 60%), while LDHs has lower reduction efficiency (less than 10%). The main function of LDHs incorporated into asphalt is not to reduce VOC, but to protect the asphalt from UV light due to the inorganic shield effect. It is a layered material that integrates UV aging resistance and VOC reduction. Nanoclay has different surfactant on its surface, so the VOC emission reduction effect of nanoclay is quite different. The future study for VOC emission reduction of nanoclay can focus on the mechanism of VOC inhibition by its surface-active groups.

*4.2.3. Electrostatic effect inhibitor*

Tourmaline comprises widespread borosilicate minerals in nature, containing with $SiO_2$, $B_2O_3$, $Al_2O_3$, $Fe_2O_3$, MgO, CaO and other substances (Ding et al., 2017). Its basic unit is trigonal ring of silicon-oxygen tetrahedron $(SiO_4)_6$ (Setkova et al., 2011). Tourmaline has thermoelectric and piezoelectric properties due to its spontaneous polarization of the

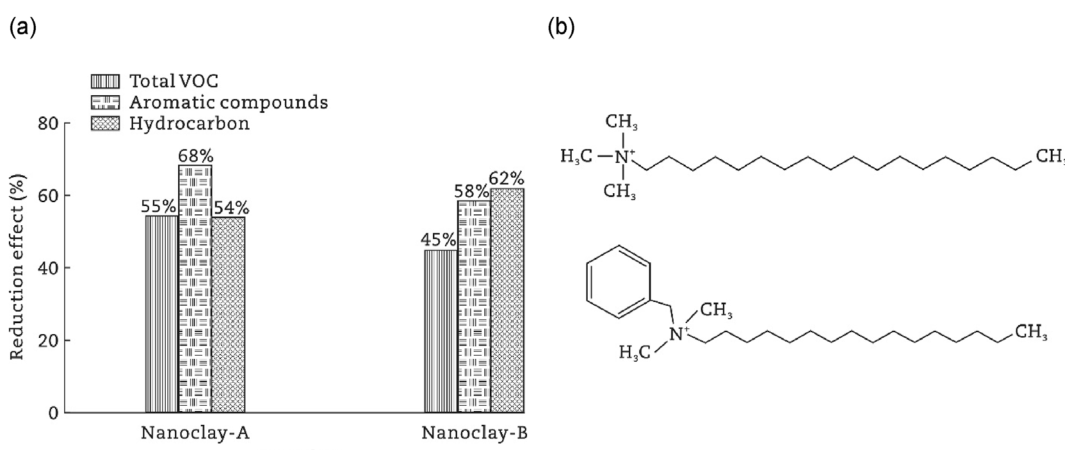



**Fig. 15.** Information of nanoclay. (a) Emission reduction efficiency of different nanoclay. (b) Structures of octadecyl trimethyl ammonium cation and benzyl dimethyl hexadecyl ammonium cation.

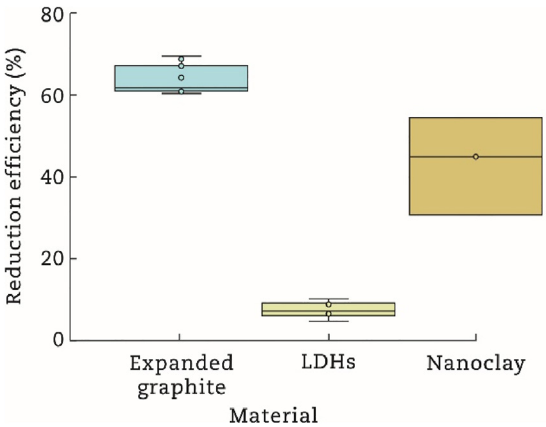



**Fig. 16.** Comparison of reduction efficiency on asphalt VOCs by layered materials.

surface electrostatic field, which can achieve high temperature emission reduction. It is widely used in air and water purification (Li et al., 2015; Wang et al., 2020a), environmental protection and textile industries (Wang and Dong, 2007).

*4.2.3.1. Classification and VOCs reduction mechanism of electrostatic effect inhibitor.* With the diversification of emission reduction methods, VOCs reduction materials are not limited to pore and interlayer adsorption. Gradually, researchers developed thermoelectric and piezoelectric materials for asphalt modification. At first, adding tourmaline into asphalt binder was aim to enhance its pavement performance. Later studies confirmed that when pressure or temperature changes, positively charged particles can be deposited together with released free electrons to reduce asphalt VOCs. Its emission reduction characteristics are summarized as Table 8.

Wang et al. (2014) proposed that the emission reduction of tourmaline depended on the highly active electrostatic field and piezoelectric effect formed at high temperature. Continuous mechanical agitation during mixing made the internal stress of tourmaline constantly change, resulting in a strong piezoelectric effect. Many negative ions were released and adsorbed with positively charged particles on the surrounding surface. Negative ions can also disperse some organic molecules to achieve multi-level emission reduction. SEM showed that tourmaline can be uniformly dispersed and there is no obvious agglomeration phenomenon after mixing with asphalt, which confirms that the compatibility of tourmaline and asphalt is good, and its incorporation will not have a great impact on the road performance.

In order to enhance the emission reduction effect of tourmaline, some researchers tried to mix the composite agent and tourmaline into asphalt binder (Zhang et al., 2021d). Graphene is an excellent reinforcement material to improve tourmaline performance. It promoted the redistribution of positive and negative charges around the tourmaline cell. The change of the whole dipole moment of tourmaline crystal was intensified, resulting in an increase in the intensity of surface electrostatic field. In addition, due to the layered structure, graphene had large specific surface area, providing more adsorption sites, thereby improving the purification effect of the air.

**Table 8**
Asphalt VOCs reduction characteristics of tourmaline-based materials.

| VOCs reduction characteristic | Reduction efficiency (efficiency @ dosage) | Remark | Reference |
| --- | --- | --- | --- |
| • Temperature field promotes surface electrostatic field<br>• Piezoelectricity and thermoelectricity<br>• Releases negative ions to absorbs positive particles<br>• Disperse VOC molecules | Tourmaline:<br>12.5% @ 14%<br>44.1% @ 17%<br>66.6% @ 20%<br>Tourmaline anion:<br>18.8% @ 14%<br>48.6% @ 17%<br>65.9% @ 20% | Differences of VOCs reduction between the two tourmalines | Wang et al. (2014) |
| | Tourmaline: 69.3% @ 10%<br>Graphene A/tourmaline<br>0.5% GA/T: 76.2% @ 10%<br>1.0% GA/T: 79.4% @ 10%<br>1.5% GA/T: 82.4% @ 10% | Complex tourmaline | Qiao et al. (2021) |
| | Tourmaline: 36.1% @ 10%<br>Graphene B/tourmaline<br>0.5% GB/T: 37.8% @ 10%<br>1.0% GB/T: 41.4% @ 10%<br>1.5% GB/T: 44.9% @ 10% | | Guo et al. (2021) |
| | Tourmaline:<br>13.50% @ 14%<br>44.80% @ 17%<br>66.20% @ 20%<br>Graphene/tourmaline:<br>19.60% @ 14%<br>49.90% @ 17%<br>67.10% @ 20% | Graphene/tourmaline can replace part of mineral powder | Chen et al. (2020) |
| | Tourmaline:<br>45.0% @ 5%<br>55.7% @ 10%<br>64.3% @ 15%<br>65.6% @ 20%<br>71.8% @ 25% | Four-step surface active treatment to improve the compatibility with asphalt binder | Zhang et al. (2021d) |
| | Graphene oxide/KH 550 tourmaline<br>Tourmaline: 35.1% @ 10%<br>0.5% GO/KT: 37.8% @ 10%<br>1.0% GO/KT: 39.2% @ 10%<br>1.5% GO/KT: 41.1% @ 10% | Two surfactants | Wang et al. (2021, 2022) |

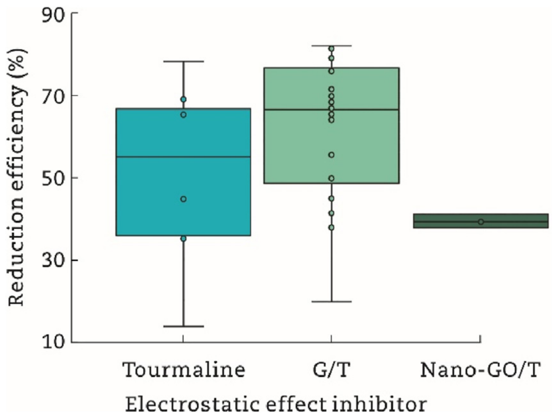



**Fig. 17.** Comparison of reduction efficiency on asphalt VOCs by electrostatic effect inhibitors.

The tourmaline prepared by Qiao et al. (2021) had reduction efficiency exceeds 80%. Its composite agent is a special two-dimensional material graphene with a density much lower than tourmaline. Guo et al. (2021) confirmed that graphene/tourmaline composites can not only improve the VOCs reduction efficiency, but also enhance the temperature sensitivity, high temperature resistance, aging resistance and rheological properties of asphalt binder. The emission reduction effect of composite graphene/tourmaline material is better than that of pure tourmaline material. The inhibition effect of VOCs is gradually enhanced with the increase of composite agent content. Compared with pure tourmaline, two composite agents were confirmed that can improve the reduction efficiency by about 13% and 8%, respectively. Wang et al. (2020a) demonstrated that graphene could enhance the emission reduction effect of tourmaline by mechanism. The research considered that graphene could improve the infrared radiation and negative ion release performance of tourmaline and reduce the band gap of tourmaline.

To solve the surface polarization effect of tourmaline for better stratigraphic stacking, some researchers focus on surface modification of tourmaline. Zhang et al. (2021d) proposed a surfactant (SCA KH-550) to modify its surface. Considering VOC emission reduction, distribution uniformity and road performance, the optimal dosage of tourmaline powder was determined to be 15%. Wang et al. (2021) proposed graphene oxide/KH 550 tourmaline (GO/KT) composites to alleviate asphalt VOCs emission. The results showed that 3-aminopropyl triethoxysilane is superior than hexadecyl trimethyl ammonium bromide in surface modification of tourmaline.

*4.2.3.2. VOCs reduction effect comparison of electrostatic effect inhibitor.* The VOCs reduction effect of tourmaline and its composite modifiers is summarized as Fig. 17. The emission reduction efficiency of pure tourmaline varies greatly with the source and dosage of tourmaline. As shown in Table 8, with the dosage increasing, VOCs reduction efficiency shows a gradual growth trend. When layered material graphene is combined with it, the emission reduction efficiency is generally improved, up to 80%. The composite emission reduction efficiency of GO/KT is about 40%, lower than another research, that is because the emission reduction efficiency of this pure tourmaline is low.

**Table 9**
Classification and asphalt VOCs reduction characteristics of polymer.

| Polymer | VOCs reduction characteristic | Reduction efficiency (efficiency @ dosage) | Reference |
|---|---|---|---|
| SBS | • Swell to form 3D network structure<br>• Coated small molecule polymerization, increase molecular cohesion<br>• Bind with light molecules<br>• Good compatibility, improve the thermal stability of asphalt | 8.0% @ 1.0%<br>19.2% @ 3.0%<br>21.2% @ 4.0%<br>14.6% @ 3.0%<br>17.1% @ 4.0% | Qian and Wang (2012); Xiao et al. (2010a);<br>Zhang (2011)<br>Zhang (2014a) |
| | | 11.3% @ 4.0%<br>17.5% @ 4.5%<br>21.3% @ 5.0%<br>24.5% @ 5.5%<br>26.1% @ 6.0% | Sun et al. (2017) |
| | | 22.1% @ 3.0%<br>26.5% @ 4.0%<br>23.9% @ 5.0% | Cui et al. (2015b) |
| | | Proportion of 5 kinds of PAH decreased, especially naphthalene | Lei et al. (2018) |
| Polyethylene (PE) | • Swelling with heat | 4.0% @ 1%<br>6.5% @ 3%<br>10.2% @ 1%<br>14.1% @ 5% | Qian and Wang (2012);<br>Zhang (2011)<br>Peng and Li (2010) |
| Polyurethane (PU) | • The crosslinking networks may be generated through polymerization<br>• Isocyanate modification can promote VOC to higher molecular weight and aromatic ring numbers | 145 °C: 63.1%<br>170 °C: 48.5% | Li et al. (2022b) |
| Polypropylene and ethylene vinyl acetate copolymer | • EVA can form a steady state surface layer | 260 °C:<br>64.6% @ 0.32%<br>61.5% @ 0.48%<br>288 °C:<br>70.7% @ 0.32%<br>68.3% @ 0.48% | Franzen and Trumbore (2000) |
| Desulfurized rubber powder (DRP) | • Expands to a network structure<br>• Crosslinking reaction with light components | $SO_2$: 40.0%<br>$NO_2$: 54.8%<br>$NO_x$: 57.3% | Li et al. (2022a) |
| $C_9$ petroleum resin | • Low content<br>• High temperature melting vaporization | 53.1% @ 0.5% | Huang (2013) |
| Gumarlon resin | • Suppression effect is not stable | 11% @ 2% | |
| Phthalocyanine blue | • Reacts with PAHs | 18.9% @ 1%<br>26.2% @ 2% | |

The emission reduction of asphalt VOC by tourmaline is all above 30%, which can be considered to achieve effective emission reduction. At the same time, tourmaline also has good purification effect on automobile exhaust, especially on $NO_x$, with the highest purification rate up to 93.1% (Wang et al., 2017). Tourmaline is a very good additive material for green asphalt pavement. How to better improve its surface compatibility with asphalt and enhance emission reduction efficiency will be the focus of future research direction.

#### 4.2.4. Polymer

From the performance of asphalt binder, the incorporation of additive will inevitably break the colloidal balance state existing in the asphalt binder before, resulting in significantly reducing its road performance and shortening its service life. In order to reduce the impact of inhibitors on compatibility of asphalt, some researchers proposed to add polymer with adhesive effect to asphalt binder. According to the Fick's Second Law, polymer can crosslink and increase the viscosity of asphalt to prevent the volatilization of small molecular substances. It achieves the dual requirements of high emission reduction efficiency and good road performance (Yuan et al., 2005).

*4.2.4.1. Classification and VOCs reduction mechanism of polymer.* Common polymer materials and their reduction characteristics on asphalt VOCs are shown as Table 9. Polymer substances, such as styrene butadiene styrene (SBS), are widely used in modifying base asphalt binder to improve the material behaviors for pavement construction and roofing purposes. SBS has the characteristics of thermal expansion crosslinking.

Possebon et al. (2019) showed that compared with base asphalt, SBS modified asphalt generally had a lower total emission of volatile organic compounds, which preliminarily confirmed SBS has VOCs emission reduction effect. Xiao et al. (2010a) investigated the VOCs emission reduction effect of SBS modified asphalt through gravimetric analysis of the fiber filter. The results showed that dosage 4% SBS can promote 21.2% asphalt VOCs reduction. The study also proposed two adsorption mechanisms of SBS. (1) SBS can swell with small molecules to form large molecules, which increases molecular cohesion and reduces the escape of VOCs. (2) After swelling equilibrium, the dispersed phase is physically cross-linked with the aggregated phase to form a network structure to adsorb part of VOCs. The double adsorption mechanism of SBS on emission suppression was also confirmed by Zhang (2014a). Qian and Wang (2012) studied on the influence of SBS dosage on emission reduction efficiency. The result found that 3% SBS additive can achieve 19.2% emission reduction, and the emission reduction efficiency is gradually enhanced with the increase of the dosage. Lei et al. (2018) proposed that SBS modifier can inhibit PAHs release amount. SBS modifier can not only adsorb some aromatic components, but also swell in the asphalt binder to form 3D network structure to limit VOCs release.

Theoretically, polyurethane (PU) and polyethylene (PE), which also have the cross-linking effect, also have the potential to reduce emissions. But the inhibition effect of PE has been proved to be inferior to the polymer SBS, in which polyurethane was confirmed that can achieve 4.0%–6.5% VOCs reduction, especially light components (Zhang, 2011).

Based on PU, Li et al. (2022b) developed a new additive, which is a mixture of polyfunctional aromatic isocyanate based on monomeric and oligomeric methylene diphenyl diisocyanate. On the one hand, isocyanate, with –NCO functional groups, can react with some VOCs bearing different reactive functional groups, such as hydroxyl, amino, imino, anhydride, and carboxyl acid to produce the carbamate/urea/amide linkages. On the other hand, there is a three-dimensional covalent crosslinking network developed between the asphaltene aggregations by chemical linkages of isocyanate, which can enwrap VOCs to the "cage". Then, 12 fingerprint

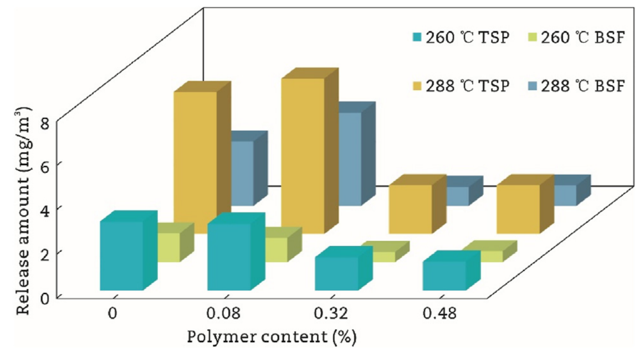



**Fig. 19.** Relationship between polymer content and fuming amount.

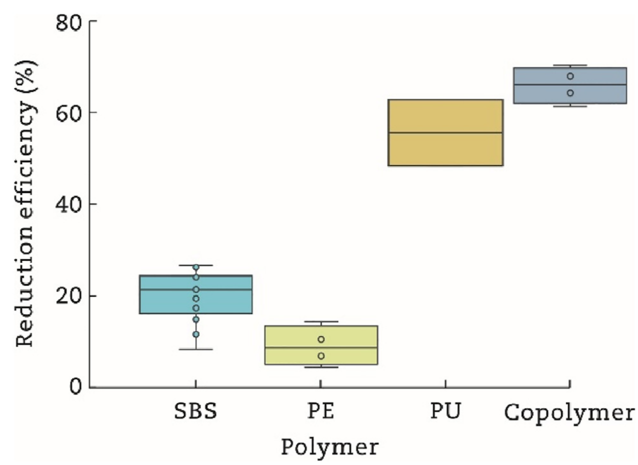



**Fig. 20.** Comparison of reduction efficiency on asphalt VOCs by polymer.

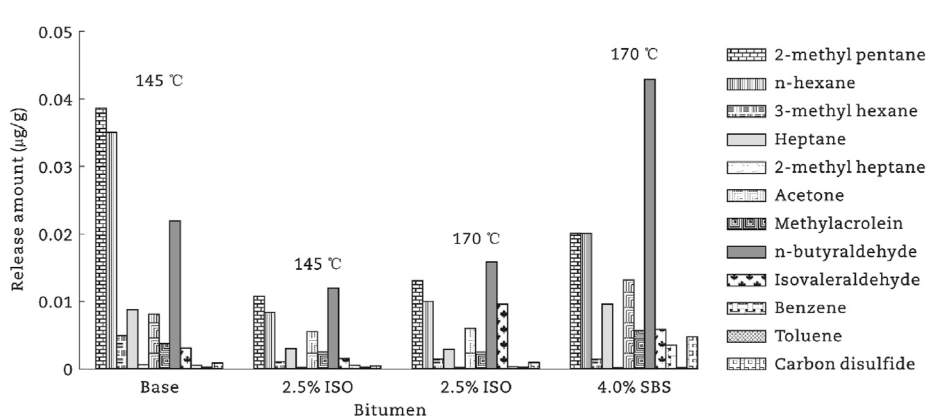



**Fig. 18.** Release amounts of fingerprint components from asphalt binder at 145 °C and 170 °C (Li et al., 2022b).

**Table 10**
Classification and asphalt VOCs reduction characteristics of chemical inhibitor.

| Chemical inhibitor | VOCs reduction characteristic | Reduction efficiency (efficiency @ dosage) | Reference |
|---|---|---|---|
| Melamine (MN) | • Decomposes into $N_2$, $CO_2$ and $H_2O$<br>• Non-combustion gases reduce the ambient oxygen concentration<br>• Absorb a lot of heat and reduce the temperature | 23.5% @ 1%<br>45.1% @ 3%<br>27.5% @ 2%<br>30.0% @ 3%<br>25.0% @ 4%<br>18.3% @ 1%<br>24.0% @ 5% | Qian and Wang (2012); Xiao et al. (2010a); Zhang (2011)<br>Huang (2013)<br><br><br><br>Peng and Li (2010) |
| Ammonium phosphomolybdate (AM) | • Oxidized to viscous oxic acid<br>• Accelerated surface carbonization<br>• Isolation of external oxygen | −15.0% @ 1%<br>23.3% @ 3% | Zhang (2011) |
| Pentaerythritol (PER) | • As a stabilizer<br>• Easy to segregate, affect the road performance | 5.3% @ 2%<br>7.9% @ 3%<br>8.2% @ 4% | Huang (2013) |

components were proposed for quantitative calculation of total VOCs release amount, compared as Fig. 18. The amount reduction of aldehyde and aromatic compounds are obvious. The emission reduction efficiency is 63.1% and 48.5%, respectively at 145 °C and 170 °C.

Franzen and Trumbore (2000) used polymer additives to reduce the asphalt fumes in roofing asphalt, which is polypropylene and ethylene vinyl acetate copolymer. The polymer reduces VOCs emission by floating on the surface of the asphalt to act as a barrier for VOCs release. He found that blend 1% of polymers will form a steady state surface layer that acting a steady-state barrier to reduce the release of fumes from asphalt. Furthermore, they investigated asphalt fumes, including total suspended particulate (TSP) and benzene soluble fraction (BSF), from field pilot plant. Fig. 19 concluded the relationship between polymer content and fuming amount. This research achieved significant reduction of VOCs more than 50%, comparing polymer content of 0.48 to 0 or 0.08 and regardless of temperatures. The reduction mechanism of this additive is not like other inhibitors. So if the floating film disturbed, they are not consistently working on VOCs emission reduction.

Desulfurized rubber powder (DRP) was reported by Li et al. (2022a) as a cheap and clean modifier to reduce inorganic fume emission of asphalt. DRP with stable chemical bonding can increase swelling to absorb the light components, while the unstable polysulfide bond in DRP fragmented and react with light molecules to form a much more stable structure. DRP also can improve the system stability and achieve the $SO_2$, $NO_2$ and $NO_x$ emission reduction of 40.0%, 54.8%, and 57.3%. It's a pity that this study only focused on inorganic fume emissions, including, but not asphalt VOCs emissions.

*4.2.4.2. VOCs reduction effect comparison of polymer.* Emission reduction effect of various polymer on asphalt VOCs are shown in Fig. 20. The VOCs reduction efficiency of polymer is highly correlated with the type of polymer, among which the emission reduction efficiency of SBS and PE are low, ranging from 4% to 22%. The emission reduction efficiency of SBS is enhanced with the increase of its dosage, and the reduction effect tends to be stable when the dosage is 4%. PU and copolymer have a high reduction effect, more than 50%, which can be further studied in the future.

### 4.2.5. Chemical inhibitor

Chemical inhibitor usually achieves VOCs emission reduction by two ways. The one is the inhibitor can reduce the temperature by decomposition reaction. Another one is that an isolation layer can be created by chemical reaction to prevent VOCs molecules to escape. The emission reduction situation is shown in Table 10. However, the chemical inhibition is greatly affected by the active site and the randomness of the reaction is strong. Under high temperature conditions, uncertain reactions happened frequently duo to complex components. Therefore, chemical inhibition is not often used in the study due to the uncontrollable reaction, and it is mostly combined with physical adsorption to achieve multiple emission reduction of asphalt VOCs.

Zhang (2011) focused on chemical inhibitors melamine (MN) and ammonium phosphomolybdate (AM) on asphalt VOCs reduction. Experiments have confirmed that after being heated, MN would decompose and release non-combustion gases such as $N_2$, $CO_2$ and $H_2O$ to reduce the ambient oxygen concentration and absorb heat. Huang (2013) explored

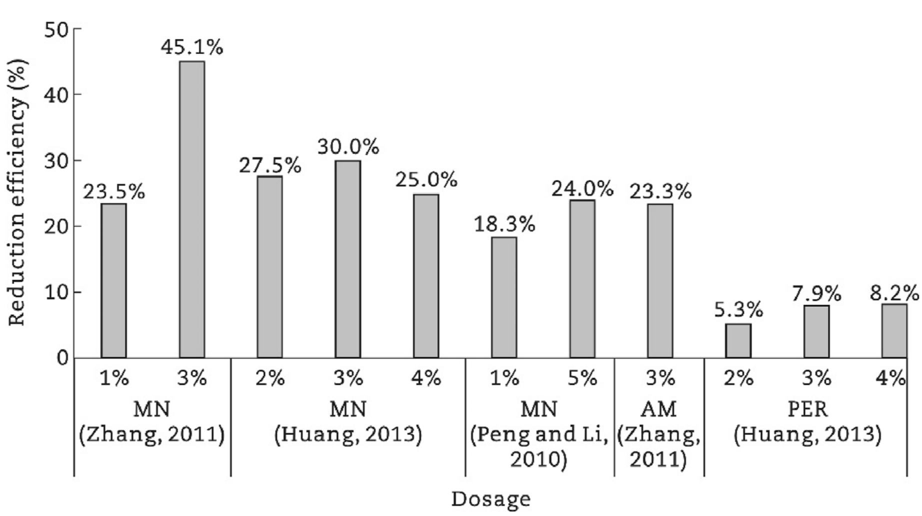



**Fig. 21.** Comparison of reduction efficiency on asphalt VOCs by chemical inhibitors (Huang, 2013; Peng and Li, 2010; Zhang, 2011).

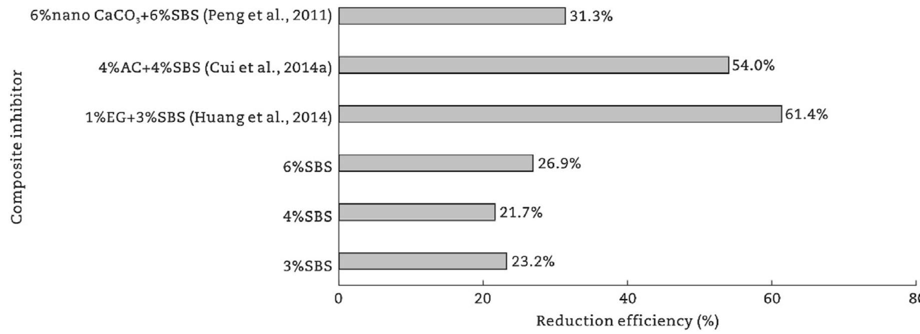



**Fig. 22.** The improvement of composite inhibitors on VOCs emission reduction (Cui et al., 2014a; Huang et al., 2014; Peng et al., 2011).

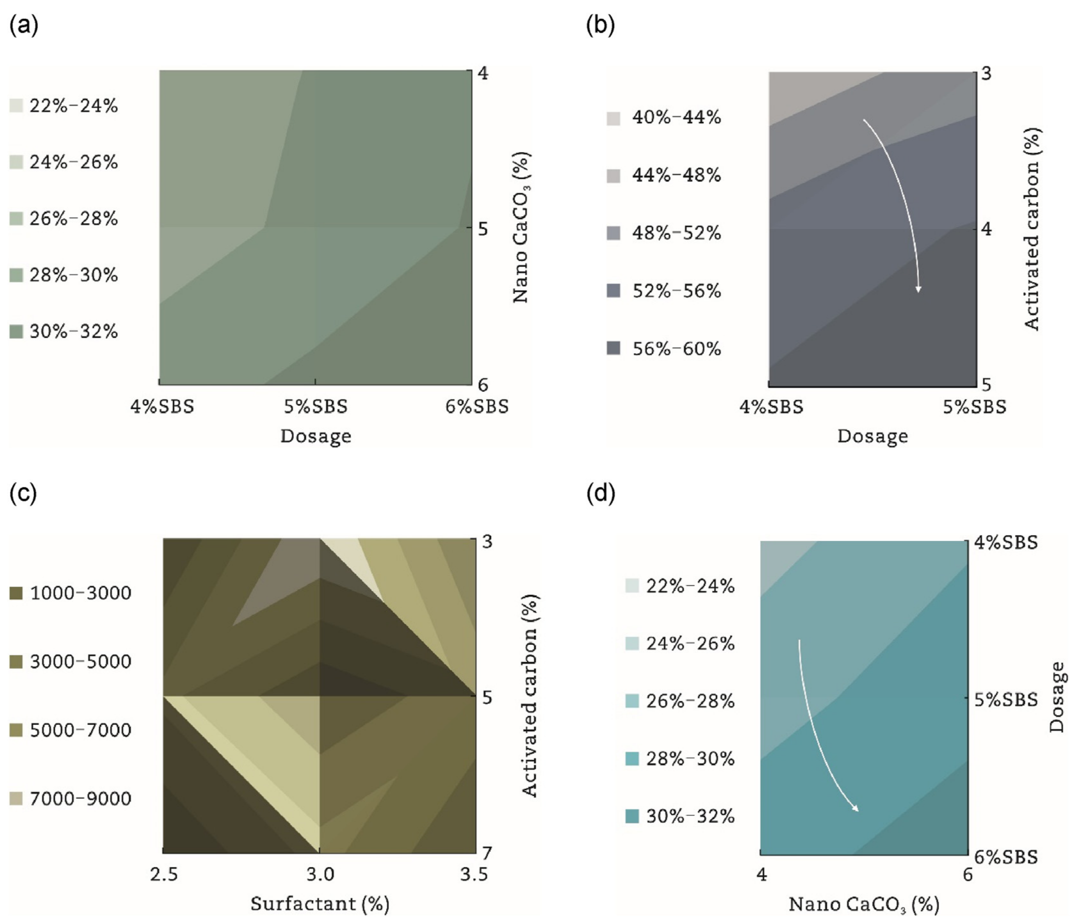



**Fig. 23.** Emission reduction trend on asphalt VOCs with different dosage. (a) From Zhang (2011). (b) From Xiao et al. (2017). (c) From Chen et al. (2022a). (d) From Peng et al. (2011).

the emission reduction effect under the dosage gradient and proposed that the emission reduction effect of MN is enhanced first and then weakened with the increase of the dosage. When the dosage is 3%, the emission reduction efficiency is up to 45.1%.

AM can also decompose and release light substances such as $H_2O$ and $NH_3$ at high temperatures. While absorbing heat and reducing oxygen content, phosphorus is oxidized to oxygen-containing acid attached to the asphalt surface. This process can accelerate dehydration and carbonization to isolate the asphalt binder from external oxygen. With the increase of the dosage, the inhibition effect is enhanced, when the dosage is 3%, the inhibition effect reaches 23.3% (Zhang, 2011).

Pentaerythritol (PER) was confirmed by Huang (2013) that have the ability of VOCs emission reduction, but the emission reduction efficiency was generally lower than 10%. At the same time, crystallization phenomenon was found in the experiment, indicating that the asphalt had serious segregation after mixing. It means that PER was not suitable for the emission reduction of asphalt because it would lead to the deterioration of road performance.

The emission reduction efficiency of the three chemical inhibitors is shown in Fig. 21. The VOCs reduction efficiency ranges from 20% to 50%, which is between zeolite materials and polymer materials. Although MN have good inhibition ability, but it was found that some white substances were collected on the filter cylinder after heating, which is speculated to be caused by the instability of MN. It means the additive may reduce the road performance of asphalt binder. Therefore, the chemical reaction mechanism of chemical inhibitors needs to be further explored before they are used for large-scale inhibition of asphalt VOCs, and they are not suitable for high temperature emission reduction

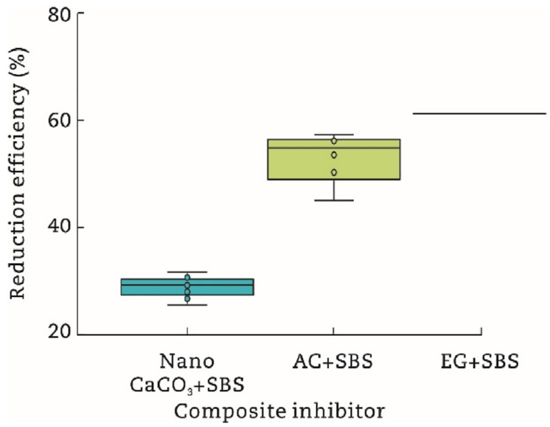



**Fig. 24.** Comparison of reduction efficiency on asphalt VOCs by composite inhibitor.

inhibitors of asphalt binder.

#### 4.2.6. Composite inhibitor

In view of the different emission reduction mechanisms of the above-mentioned different types of inhibitors on asphalt VOCs, some researchers try to add complex additives to achieve multi-layer emission reduction on asphalt VOCs.

The studies have proved that both SBS and AC have good VOCs emission reduction efficiency with different reduction mechanisms (Cui et al., 2014a). reported that 4% SBS and 4% AC can achieve 53.96% reduction of VOCs. Result shows that SBS + AC can significantly decrease the VOC emission speed with different decreasing influence, depending on VOCs type. The volatile speed of naphthalene and normal octane can be decreased by more than 70% and 20%, respectively.

The emission reduction effect of the two compound inhibitors is compared as Fig. 22. The emission reduction efficiency can be increased by 20% when the compound is added. The inhibitory effect of SBS alone was lower than that of the combined inhibitors with EG, AC and nano $CaCO_3$. Among them, the combined EG + SBS can improve the emission reduction efficiency to 60.8% (Huang et al., 2014). It was because the intercalation structure of EG and SBS swell to form a three-dimensional structure, which can promote each other on emission reduction. The incorporation of EG also improves road performance, larger needle penetration, higher softening point and better ductility, which means that it can have good plasticity and high temperature performance. Therefore, the inhibitor that combines multiple inhibition mechanisms has a broad prospect of VOCs emission reduction.

In order to explore the influence rule of inhibitor dosage, many researchers conducted the dosage experiments on reduction effect with data comparison shown as Fig. 23. The reduction efficiency of nano $CaCO_3$+SBS and AC + SBS composite inhibitors was positively correlated with their dosage. When adding a class of inhibitors alone in asphalt, the enhancement trend on VOCs emission reduction effect is slow, but when the two inhibitors are combined, the enhancement trend of VOCs emission reduction effect is obvious. It indicated that the two different types of inhibitors can complement each other, and even promote the overall inhibition efficiency threshold. It was found that the effect of AC and nano $CaCO_3$ on emission reduction is more obvious than that of SBS. It can be considered that the effect of porous material dosage on emission reduction efficiency is greater than that of polymer in composite inhibitors.

In addition to the above composite inhibitors, researcher clarified the VOCs emission reduction mechanism of LDHs on SBS modified asphalt through FTIR and fluorescence microscopy. LDHs was confirmed that can form denser coke by increasing the activation energy of SBS modified asphalt, thus significantly improving the flame-retardant property of asphalt binder.

The emission reduction efficiency of various composite inhibitors on asphalt VOC is shown as Fig. 24. AC + SBS and EG + SBS all have high VOCs emission reduction efficiency, while nano $CaCO_3$+SBS has poor effect. Many factors need to be considered to achieve higher emission reduction. When the emission reduction mechanisms of the two inhibitors are similar, the limit of inhibition may be the main factor that cause ineffective composite addition. When the emission reduction mechanisms of the inhibitors are quite different, the composite addition can complement each other, thus significantly improving the overall threshold of emission reduction efficiency.

### 4.3. Warm mixing additive

Warm mixing agent is an additive that reduce emissions by reducing the temperature. Its VOCs emission reduction effect is reflected in: compared with hot mixing asphalt, the mixing and rolling temperature of warm mixing asphalt mixture can be reduced by about 20 °C.

Previous studies have confirmed that the VOCs release of base asphalt presents a binomial increase with temperature increasing. When the temperature reaches 100 °C, the temperature difference of 60 °C can result in a three-fold difference in the VOCs volatile amount (Chang, 2020). The significance of warm mixing is usually to reduce the mixing temperature, thereby reducing the emission of pollutants, while reducing the energy consumption and carbon emissions.

In 1995, warm mixing agents began to appear in Europe that could inhibit the production of VOCs by reducing the asphalt construction temperature. Subsequently, according to its warm mixing mechanism, a warm mixing system based on organic additives, surfactants and foaming technology mainly and new warm mixing agents under other special conditions were gradually formed (Wang et al., 2012). Table 11 shows the classification and mechanism of warm mixing agents. Organic warm mix agents can reduce the viscosity of asphalt, including Sasobit, Asphaltan B, etc. Surfactants can change the adhesion between asphalt and aggregate, including Evotherm DAT/ET, Cecabase RT, etc. Foaming technologies involve the addition of a small amount of water into the asphalt binder, including the chemical foaming agent Aspha-min and the

**Table 11**
Classification and characteristics of warm mixing additives.

| Warm mixing additive | Mechanism, characteristics and effect | Type | Reference |
|---|---|---|---|
| Organic additive | • Melting point at about 100 °C<br>• Reduces asphalt viscosity | Sasobit, asphaltan B, fisher-tropsch, SLA | Cao et al. (2019); Wen et al. (2018); Zhao and Tu (2021) |
| Surfactant | • Change the adhesion<br>• Improve the ability of asphalt binder to coat aggregate particles | Evotherm-DAT/ET, cecabase RT, rediset WMX | Ji et al. (2020); Leng et al. (2018); Yang (2019) |
| Foaming technology | • Induct water<br>• Vaporizes and expands causing foaming | Chemical foaming agent: aspha-min, advera<br>Mechanical foaming: double-drum mechanical foaming technology | Yang (2020); Zhang et al. (2018) |
| New warm mixing agent | • For specific environment | Siligate<br>SEAM (brimstone) | Luo et al. (2021); Zhou et al. (2015) |

**Table 12**
Classification and characteristics of flame retardants.

| Flame retardant | Characteristic | Color | Function |
|---|---|---|---|
| Expanded graphite (EG) | Purity 95%–99%<br>Expansion rate >270 mL/g | Black | Creates an expansive layer to impedes oxygen supply and heat transfer at 160 °C. |
| $Al(OH)_3$ (ATH) | $Al_2O_3$ 64%<br>Firing loss 34.5% ± 0.5% | White | Decomposition starts at 240 °C to reduce the temperature.<br>$H_2O$ released at 320 °C dilutes the concentration of combustible volatiles and oxygen, while generating $Al_2O_3$ to cover the asphalt surface, preventing the carbonization layer from falling off caused by EG decomposition. |
| $Mg(OH)_2$ (MH) | Firing loss >28% | White | MH thermal decomposition absorbs heat at 330 °C.<br>Generated active magnesium oxide promoted the carbonization of the EG expansion layer at high temperature to form a superimposed thick barrier layer. |
| $Ca(OH)_2$ (HL) | Effective content >95% | Purple | The $CaCO_3$ layer generated by $CaO/CO_2$ covers the surface and prevents the release of VOCs.<br>The active CaO carbonizes at high temperature to form a carbonized layer. |
| Microencapsulated red phosphorus (MRP) | Effective P content >80% | Purple | MRP is decomposed by oxidation reaction to produce phosphorus oxide and phosphoric acid, which are flame retardant in coordination with MH. |

double-drum mechanical foaming technology. In order to meet various other special needs, some researchers have developed Siligate, which is suitable for road construction in low temperature area, and SEAM warm mixing agent, which can reduce sulfur concentration, and obtained good warm mixing effect.

Amidic-modified hydrocarbon wax and hydrocarbon paraffinic wax were used in 70/100 penetration neat asphalt binder, acting as reduction of production and paving temperatures and as asphalt fume suppressants (Autelitano et al., 2017). When the waxes were used, about 70%–80% reduction at 90 °C, 40%–45% reduction at 110 °C and 15%–30% reduction at 180 °C can be achieved. Higher VOC reduction can be detected when the asphalt binder was heated at temperatures below and close the waxes melting point, which is 110 °C.

Cao et al. (2019) and Leng et al. (2017) investigated the emission reduction effect of different types of warm mixing agents on asphalt VOCs based on the design of warm mixing asphalt mixture. This study established a life cycle evaluation framework combined with uncertainty analysis, and quantified the life cycle energy consumption of pavement construction using organic wax, surface active additives and zeolite warm mixing agents. Zeolite material as a reduction additive can directly adsorb asphalt VOCs molecules. Due to the existence of special structural water crystal water structure in some zeolite, it is also used by researchers as warm mixing foaming technology. Zhang et al. (2018) used traditional urban sludge ash as raw material to synthesize zeolite as a warm-mixed asphalt additive to achieve 25 °C temperature reduction in construction temperature, thus reducing energy consumption and pollutant emission. The use of sewage sludge ash SSA raw material to prepare zeolite not only realizes the effective utilization of sludge ash, but also promotes the emission reduction of asphalt VOCs, which has high environmental benefits.

Warm mixing agent has been widely used in asphalt construction as a relatively mature technology. The current research on warm mixing agent is more focused on how to improve the pavement performance of warm mixing asphalt mixture. However, since all kinds of warm mixing agents can reduce the mixing temperature by 10°C–40°C. Combined with the change law of asphalt VOCs emissions with temperature, it can be inferred that warm mixing agents can reduce asphalt VOCs emissions by about 50%–70%, which is generally better than the emission reduction effect of reduction additives.

In the future, warm mixing can develop through innovation in additives and technology to achieve greater reduction in mixing temperature. In addition, in view of zeolites used as both inhibitors and warm mixing agents, warm mixing additive can be combined with inhibitors in the future to break through technical barriers and achieve multiple improvements in the performance of asphalt materials.

### 4.4. Flame retardant

The purpose of flame retardants initially used in highway tunnels was to prevent the occurrence and spread of fire. Its flame retardancy process has the potential to reduce the pyrolysis speed and inhibit harmful flue gas emissions. At present, commonly used flame retardants and their effects are shown in Table 12. Aluminum-magnesium flame retardants can increase the thermal decomposition temperature of asphalt, and their pore structure can inhibit harmful gas emissions to achieve flame retardancy and environmental protection benefits.

Bonati et al. (2013) reported that flame retardants do not chemically interact with the binder, but exert a beneficial cooling action on the asphalt matrix thanks to the endothermic decomposition. They can be used as additive to significant decrease the mixing and compaction temperatures, resulting in less emission releases. When flame retardants were coupled with organic montmorillonite, the performance of protective layer was further enhanced due to mechanism of migration that drives the clay platelets to the top of burning sample and resulted in a dramatic decrease of heat and VOCs releases.

Xu et al. (2014), Xu and Huang (2010) and Xu et al. (2011) added magnesium hydroxide as flame retardant into asphalt binder and used TG-FTIR to characterize the release amount of volatile components. His result shown that the total amount of VOCs from magnesium hydroxide modified binder was obviously lower than that from pure asphalt binder.

The flame-retardant mechanism and the inhibition mechanism confirmed that both can promote the molecular transformation of asphalt VOCs through chemical action. The inert gas released after the heating covers the asphalt surface, reducing the oxygen concentration on the asphalt surface, blocking the heat transfer, and cutting off the conditions required for the generation of more VOCs. However, the action temperature of a single flame retardant is fixed, and the asphalt cannot be continuously flame retardant. So the composite flame retardant effectively solves this bottleneck. The flame retardant process can be summarized into three steps: carbonization blocks heat transfer, decomposition endothermic cooling, and inert gas atmosphere reduces oxygen concentration.

Xu et al. (2013) conducted an in-depth and systematic study on the flame retardant mechanism and application technology of asphalt flame retardants. The composite flame retardants (CFR) and nano-composite flame retardants (NCFR) used can form more compact and stable carbon slag on the asphalt surface, thus reducing the volatilization of asphalt VOCs. The flame retardant properties of the composite flame retardants were also confirmed by Yu et al. (2007). In this study, a ternary composite flame retardant SBS modified asphalt was prepared. With the addition of the ternary composite flame retardant, the oxygen index of the asphalt reached 27.5%, becoming a self-extinguishing material. Reduce the emission of light components of asphalt by crosslinking with SBS.

## 5. Conclusions and outlook

The asphalt VOCs analysis method, components composition and reduction technology with newly-developed additives were reviewed in this study. The following conclusions can be addressed.

(1) The characterization methods of asphalt VOCs develop from rapid quantitative analysis to accurate qualitative and quantitative analysis for a long time. Different detection methods were selected according to the different research purposes. Asphalt VOCs can be roughly divided into hydrocarbons, hydrocarbon derivatives with oxygen, aromatic compounds, organosulfur and organonitrogen compound. The composition of VOCs is mainly affected by the source of asphalt type and construction temperature. Therefore, improving asphalt itself and reducing the construction temperature is crucial for asphalt VOCs emission reduction.
(2) The current emission reduction methods of asphalt VOCs can be roughly divided into four categories, mechanical method, reduction additives, warm mixing additive and flame retardant. The mechanical method is generally used to capture VOCs at stationary sources such as terminals, storage tanks, and hot mix plants. They are not suitable for mobile sources to reduce emissions into the atmosphere. The last three emission reduction methods are innovative and can reduce VOCs generation at the source.
(3) Porous materials reduce asphalt VOCs by physical adsorption mainly, so its emission reduction effect depends on their pore structures, including specific surface area, pore volume and pore size. The inhibition efficiency of AC and zeolite materials are 20%–50% and greater than 40%, respectively. The incorporation of AC has been proved to lead to more by-products, so AC application for emission reduction should be studied in greater depth. Zeolite can add surface functional groups through pore modification to achieve selective adsorption. In addition, zeolite also has been proved to have catalytic properties, which can possibly provide better VOCs reduction efficiency. Layered materials, such as EG, LDHs and nanoclay, adsorb VOCs through interlayer interactions. In general, the reduction efficiencies of EG and LDHs are about 60% and less than 10%, respectively. The reduction efficiency of nanoclay depends on the active groups on its surface.
(4) Tourmaline is a typical electrostatic effect inhibitors for asphalt VOCs reduction, whose reduction efficiency is above 40%–80%. It can release negatively charged particles under the action of thermoelectricity to combine with positively charged VOCs particles to converge. At the same time, tourmaline can also purify automobile exhaust, especially on $NO_x$. To solve the surface polarization effect of tourmaline for better stratigraphic stacking, graphene has been used to modify tourmaline.
(5) The initial purpose of polymer used in asphalt modification is to improve the road performance with its good compatibility. Polymer can swell and form a network structure to adsorb asphalt VOC light components. The emission reduction efficiency is related to the type of polymer, PU and copolymer are higher than 50%, SBS and PE are lower than 30%. The VOCs reduction efficiencies of most chemical inhibitors are less than 30%. However, the experiment found that chemical inhibitors have poor storage stability, so they are rarely used in asphalt binder as reduction additives.
(6) Composite inhibitor combines the emission reduction mechanism of different emission reduction materials. They utilize the separate benefits of different additives to have a positive overall benefit in reducing VOCs. The composite addition of porous material AC, nano $CaCO_3$ and layered material EG with polymer SBS can increase the single reduction efficiency by 20%.
(7) Warm mixing additive and flame retardant are indirect methods to reduce VOCs. Warm mixing additive can generally reduce the asphalt mixture construction temperature of 10°C–40°C, resulting in the indirect emission reduction efficiency of 50%–70%. Flame retardants can decompose non-combustion gas when heated to prevent asphalt VOCs generation. They are proved that can achieve high temperature flame retardancy and low temperature emission suppression.

Overall, there is an innovation asphalt VOCs emission reduction system formed by inhibitors, warm mix additives and flame retardant. But the internal mechanism of a single VOCs molecule has not been fully clarified. In the future, more emission reduction at the molecular level should be carried out to attain reduction mechanism from a microscopic perspective. In addition, there are some side reactions and incompatibility problems in modified asphalt, which may eventually lead to the deterioration of asphalt road performance. So the subsequent research should balance the relationship between emission reduction and road performance, not achieve one at the expense of another. The proposed composite inhibitor may help to solve this problem, and composite emission reduction will become a new development direction in the future.

## Declaration of competing interest

Yue Xiao is a young academic editor of Journal of Road Engineering and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

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## Appendix Table 1A

| Abbreviation | Full name |
|---|---|
| AC | Activated carbon |
| $CaCO_3$ | Calcium carbonate |
| MSHSs | Mesoporous silica hollow nanospheres |
| EG | Expanded graphite |
| LDHs | Layered double hydroxide |
| PU | Polyurethane |
| PE | Polyethylene |
| DRP | Desulfurized rubber powder |
| MN | Melamine |
| AM | Ammonium phosphomolybdate |
| PER | Pentaerythritol |

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