The efficiency of sulfur modifier to neutralize toxic gases in sulfur-asphalt concrete technology

Huu Tuan Le, Sergey Inozemtcev, Evgeniy Korolev and Anna Grishina

Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, Russia

E-mail: huutuan1511@gmail.com

Abstract. Studies of the advantages of sulfur-asphalt concrete with toxic gas emission neutralizers show that the use of neutralizers reduces the amount of emission of these gases and improves the environmental problem of the use of sulfur-asphalt concrete. Zinc oxide and zinc oxide are not effective in neutralizing hydrogen sulfide and sulfur dioxide. Reducing the emission of toxic gases using dolomite and diatomite is due to the ability of carbonates to neutralize sulfur dioxide through chemical reactions, as well as absorb gases into the porous structure of grains. Other considered neutralization reactions and side processes according to the calculations mainly occur. The processes of interaction of neutralizers with toxic gases and secondary processes can proceed according to various chemical reactions, however, chemical reactions with the release of more energy occur predominantly. This is confirmed by experimental studies. As a result of theoretical and experimental studies, a list of effective toxic gas neutralizers has been established, the emission of which occurs when bitumen interacts with a sulfur modifier.

1. Introduction

The volume of cargo transportation is increasing in the current conditions of economic development. A long service life of roads without significant operating costs must be ensured in conditions of increased traffic intensity and loads for the development of various sectors of the economy. The use of modifiers, including those based on sulfur, as a component of the asphalt mix, is a promising direction for increasing the durability and transport and operational performance of the pavement. Sulfur increases the strength of asphalt concrete and significantly improves the adhesion of the binder to the surface of the mineral aggregate [4 ... 7]. Increased indicators of physical and mechanical properties (strength, shear resistance) and operational properties (rutting resistance, resistance to climatic factors) can improve the quality of the pavement.

The release of toxic gases (hydrogen sulfide and sulfur dioxide), when mixing bitumen and sulfur during the production of the sulfur-asphalt mix, is a significant limitation of the use of sulfur.

Therefore, the development of technology for the use of sulfur-based modifiers, in which the problem of the formation of toxic gases due to their neutralization or reduction of their emission is an urgent task.
2. Materials and Methods

Samples of bitumen binder were made using bitumen of oil road BND 60/90 produced by Moscow Oil Refinery LLC, which meets the requirements of state standard 22245-90 "Road bitumen. Specifications for determining the emission of toxic gases".

Crystalline sulfur that meets the requirements of state standard 127.1-93 "Technical sulfur. Technical conditions" were used as part of a bitumen binder.

Manganese (IV) oxide, zinc (II) oxide, copper (II) oxide, zinc, as well as dolomite powder and diatomite powder were used as toxic gas neutralizers [12 ... 15].

Manganese (IV) oxide complies with the requirements of state standard 4470-79 "Reagents. Manganese oxide. Specifications", zinc oxide – state standard 10262-73 "Reagents. Zinc oxide. Specifications", copper oxide – state standard 16539-79 "Reagents. Copper (II) oxide. Specifications", zinc – state standard 12601-76 "Zinc powder. Technical conditions".

Mineral powder from dolomite rock corresponded to the grade MP-1 in accordance with state standard 52129-2003 "Mineral powder for asphalt concrete and organic-mineral mixtures. Technical conditions". The chemical composition of dolomite powder is presented in table 1.

### Table 1. The chemical composition of dolomite powder

| Material | SiO₂ | Al₂O₃ | Fe₂O₃ | CaCO₃+MgCO₃ |
|----------|------|-------|-------|-------------|
| Dolomite | 7.64 | 0.34  | 1.12  | 90.9        |

The chemical composition of diatomite powder is presented in table 2.

### Table 2. The chemical composition of diatomite powder

| Material  | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO     | MgO  | SO₃ | LOI |
|-----------|------|-------|-------|---------|------|-----|-----|
| Diatomite | 82.30| 5.19  | 2.32  | 0.29    | 0.76 | 0.21| 8.93|

Sulfur-containing astringent with a sulfur content of 10 %, 20 % and 30 % by weight was used to determine the emission of toxic gases. The compositions of sulfur-bitumen binder without the use of toxic gas emission neutralizers were taken as the original. The effect of using neutralizers was evaluated on samples with the addition of 10 % neutralizers based on the mass of sulfur in the binder.

The preparation of a sulfur-bitumen binder and the study of the emission of toxic gases were carried out with constant stirring and a temperature of 140±1 °C.

The concentration of toxic gases was determined from the moment the components of the sulfur modifier (sulfur + neutralizer) were added to bitumen for 1 hour with a frequency of 1 measurement per minute using the developed device (figure 1). The ANKAD 7664 Micro-06 gas analyzer was used for determination with an upper limit of concentration measurement – 20 mg/m³. The scheme of operation of the device for determining the concentration of toxic gases includes the processes shown in Figure 2.
Figure 1. A device for measuring the concentration of toxic gases in a volume: 1 - a vessel with a volume of 5 liters; 2 - gas analyzer; 3 - thermometer; 4 - a bowl for samples; 5 - electric stove with a magnetic stirrer; 6 - compressor

Figure 2. The operation scheme of the installation: 1 - air supply using a compressor; 2 - temperature control of the sample; 3 - mixing of the sample; 4 - toxic gas emission; 5 - circulation and mixing of toxic gases with the air in a vessel; 6 - sampling for analysis

The theoretical assessment of the possibility of chemical reactions was carried out using the isobaric-isothermal potential (Gibbs free energy $\Delta G$), the calculation of which was carried out in accordance with the formulas [16]:

$$\Delta H_{T_2} = \Delta H_{T_1} + \frac{T_2}{T_1} \Delta C_p dT$$  \hspace{1cm} (1)

$$\Delta S_{T_2} = \Delta S_{T_1} + \frac{T_2}{T_1} (\Delta C_p/T) dT$$  \hspace{1cm} (2)

$$\Delta G_{T} = \Delta H_{T} - T \Delta S_{T}$$  \hspace{1cm} (3)

where $\Delta H$ is the change in enthalpy, kJ/mol; $\Delta S$ is the change in entropy, J/(mol·K); $\Delta C_p$ is the change in heat capacity, J/(mol·K); $\Delta G$ is isobaric-isothermal potential, kJ/mol; $T$ is the temperature, K.

3. Results and discussion

Sulfur dioxide and hydrogen sulfide are formed as a result of chemical processes of the interaction of bitumen and sulfur in the conditions of constant air circulation during the preparation of the sulfur-asphalt-concrete mixture. The cyclical character of this process is noted, that is, the formation of toxic gases stops only when one or more components are completely consumed. The use of neutralizing agents in the sulfur modifier, which are able to interact with hydrogen sulfide and sulfur dioxide with the formation of compounds that are slightly or insoluble in water, is the most effective way to solve the problem of the formation of toxic gases [13 ... 16]. Such substances are powdered zinc, manganese oxide, copper oxide, zinc oxide, calcium carbonate (one of the components of dolomite powder). Diatomite does not chemically interact with these gases but is capable of sorbing them due to the presence of an extensive pore structure. A study [17] showed that the addition of finely dispersed quartz to sulfur melt leads to their chemical interaction with the formation of $\text{SiS}_x$, which are water-soluble compounds (with decomposition). The results of the study of the effect of various emission neutralizers on the concentration of toxic gases are presented in table 3.
Table 3. Sulfur dioxide and hydrogen sulfide emission parameters

| Neutralizer         | Sulfur content, % | Sulfur dioxide emission parameters | Hydrogen sulfide emission parameters |
|---------------------|-------------------|-----------------------------------|--------------------------------------|
|                     |                   | Maximum concentration, mg/m³      | Time to reach maximum concentration, min | Average emission rate, mg/(m³·min) |
|                     |                   | SO₂ | H₂S | SO₂ | H₂S | SO₂ | H₂S |
| Zinc                | 10                | 6.5 | 3.7 | 30  | 58  | 0.217 | 0.064 |
|                     | 20                | 11.1| 6.5 | 32  | 60  | 0.347 | 0.108 |
|                     | 30                | 14.1| 7.9 | 35  | 59  | 0.403 | 0.134 |
| Zinc                | 10                | 5.6 | 3.5 | 28  | 60  | 0.200 | 0.058 |
|                     | 20                | 9.3 | 5.9 | 32  | 60  | 0.291 | 0.098 |
|                     | 30                | 12.2| 7.2 | 31  | 59  | 0.394 | 0.122 |
| Manganese (IV) oxide| 10                | 1.8 | 0.8 | 59  | 51  | 0.031 | 0.016 |
|                     | 20                | 1.9 | 1.0 | 58  | 57  | 0.033 | 0.018 |
|                     | 30                | 2.4 | 1.2 | 59  | 59  | 0.041 | 0.020 |
| Copper (II) oxide   | 10                | 1.8 | 1.0 | 50  | 58  | 0.036 | 0.017 |
|                     | 20                | 2.7 | 1.5 | 47  | 57  | 0.057 | 0.026 |
|                     | 30                | 3.5 | 2.0 | 43  | 59  | 0.081 | 0.034 |
| Zinc (II) oxide     | 10                | 6.5 | 4.3 | 36  | 60  | 0.181 | 0.072 |
|                     | 20                | 10.3| 7.0 | 43  | 60  | 0.240 | 0.117 |
|                     | 30                | 14.1| 8.3 | 34  | 60  | 0.415 | 0.138 |
| Dolomite            | 10                | 2.1 | 1.0 | 31  | 51  | 0.068 | 0.020 |
|                     | 20                | 3.3 | 2.0 | 34  | 59  | 0.097 | 0.034 |
|                     | 30                | 4.4 | 2.8 | 40  | 57  | 0.110 | 0.049 |
| Diatomite           | 10                | 2.2 | 1.7 | 26  | 58  | 0.085 | 0.029 |
|                     | 20                | 3.7 | 2.2 | 31  | 58  | 0.119 | 0.038 |
|                     | 30                | 5.0 | 3.1 | 34  | 58  | 0.147 | 0.053 |

The results obtained allow us to classify neutralizers according to their effectiveness. Zinc (II) oxide and zinc are the most ineffective neutralizers. Zinc (II) oxide reduces the emission of SO₂ by 10% and negatively affects the emission of H₂S. Zinc reduces the emission of toxic gases by 5...20%. Manganese oxide reduces the emission of SO₂ and H₂S gases by 5.8 and 6.5 times, respectively; copper oxide reduces the emission of SO₂ and H₂S gases by 4.1 and 4.3 times, respectively; diatomite powder reduces the emission of toxic gases to 3.0 times, and dolomite powder reduces the emission of SO₂ and H₂S gases to 3.4 and 3.7 times, respectively. It should be noted that the sulfur concentration in the sulfur-bitumen binder does not affect the effectiveness of toxic gas emission neutralizers. To establish the reasons for the different effectiveness of emission control agents, it is necessary to consider the processes of the formation of toxic gases (table 4).
Table 4. Thermodynamic calculation of chemical processes of the formation of toxic gases

| #  | Chemical reaction | Sulfur form | $\Delta H$, kJ/mol | $\Delta S$, J/(mol·K) | Coeff. equations $C_p = f(T)$, J/(mol·K) | $\Delta G$ at a temperature (°C/K), kJ/mol |
|----|------------------|-------------|---------------------|----------------------|------------------------------------------|------------------------------------------|
| 1  | $S + H_2 \rightarrow H_2S$ | $\alpha$-S | -20.9 | -21.5 | $\Delta \alpha$, $\Delta \beta$, $\Delta \gamma$ | 25 | 50 | 75 | 125 | 160 | 220 |
|    |                  | $\beta$-S | -20.6 | -20.6 | -33.5 | -34.5 | -36.5 | -41.1 | -41.1 | -41.1 | -41.1 |
|    |                  | gas       | -120.2 | -171.3 | 20.6 | 34.6 | 56.6 | 56.6 | 56.6 | 56.6 | 56.6 |
| 2  | $S + O_2 \rightarrow SO_2$ | $\alpha$-S | -297.3 | -8.9 | -3.9 | -310.2 | 301.5 | 301.9 | 301.9 | 301.9 | 301.9 |
|    |                  | $\beta$-S | -296.9 | -7.9 | -3.9 | -300.2 | 300.4 | 300.7 | 300.7 | 300.7 | 300.7 |
|    |                  | gas       | -396.5 | -158.7 | -20.6 | 34.6 | 56.6 | 56.6 | 56.6 | 56.6 | 56.6 |
| 3  | $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$ | $\alpha$-S | -1036.2 | -3.8 | -3.4 | -990.6 | 986.8 | -983 | -975.3 | 969.8 | 969.6 |
|    |                  | $\beta$-S | -144.4 | -184.4 | -71.5 | -65.3 | -54.9 | 54.9 | 54.9 | 54.9 | 54.9 |
| 4  | $2H_2S + SO_2 \rightarrow 3S + 2H_2O$ | $\alpha$-S | -441.6 | 17.1 | -372.7 | -366.8 | -356.8 | -356.8 | -356.8 |
|    |                  | $\beta$-S | -442.4 | 17.2 | -390.2 | -385.8 | 381.5 | 381.5 | 381.5 | 381.5 |
|    |                  | gas       | -243.2 | 152.6 | -489.3 | -513.9 | -558.1 | -558.1 | -558.1 |
| 5  | $2H_2S + O_2 \rightarrow 2S + 2H_2O$ | $\alpha$-S | -144.4 | 26 | -17.2 | -246.2 | 285.9 | 356.9 | 356.9 | 356.9 | 356.9 |
|    |                  | $\beta$-S | -145.5 | 23.1 | -90.0 | -85.4 | -80.8 | -80.8 | -80.8 | -80.8 |
|    |                  | gas       | 153.3 | 475.3 | -246.2 | 285.9 | 356.9 | 356.9 | 356.9 | 356.9 |
| 6  | $3S + 2H_2O \rightarrow SO_2 + 2H_2S$ | $\alpha$-S | 184.4 | -26 | 71.4 | 65.3 | 54.9 | 54.9 | 54.9 | 54.9 |
|    |                  | $\beta$-S | 186.3 | -23.1 | 90.0 | 85.4 | 80.8 | 80.8 | 80.8 | 80.8 |
|    |                  | gas       | -153.3 | -475.3 | -489.3 | -513.9 | -558.1 | -558.1 | -558.1 |

Based on the data obtained, the following conclusions can be drawn: the formation of $SO_2$ during the oxidation of sulfur is more energetically favorable than the formation of $H_2S$. The resulting $H_2S$ is oxidized predominantly with the formation of sulfur oxide and water. The formation of sulfur oxide occurs both due to the direct oxidation of sulfur and the oxidation of hydrogen sulfide. Water is also a reaction product, which promotes the formation of hydrogen sulfide [15]. The results obtained are consistent with the experimental data presented in table 3; the maximum concentration of sulfur oxide in the samples is 1.7...1.8 times higher than hydrogen sulfide, and the average emission rate of sulfur oxide is 3.0...3.4 times higher than hydrogen sulfide.

Also, chemical reactions of the interaction of neutralizers with the components of a sulfur-bitumen binder can potentially occur. The calculation results of the thermodynamic potentials for these chemical reactions are presented in tables 5...8.

Table 5. Thermodynamic calculation of chemical processes in the presence of zinc and zinc oxide (II)

| #  | Chemical reaction | Sulfur form | $\Delta H$, kJ/mol | $\Delta S$, J/(mol·K) | Coeff. equations $C_p = f(T)$, J/(mol·K) | $\Delta G$ at a temperature (°C/K), kJ/mol |
|----|------------------|-------------|---------------------|----------------------|------------------------------------------|------------------------------------------|
|    |                  | $\alpha$-S | -205.6 | 3.2 | $\Delta \alpha$, $\Delta \beta$, $\Delta \gamma$ | 298 | 323 | 348 | 398 | 433 | 493 |
|    |                  | $\beta$-S | -205.2 | 4.2 | -200.4 | -200.0 | -199.6 | -199.6 | -199.6 | -199.6 | -199.6 |
|    |                  | gas       | -304.8 | -146.5 | -140.6 | -124.7 | -97 | -97 | -97 | -97 | -97 |
| 2  | $Zn + 2S + O_2 \rightarrow ZnS + SO_2$ | $\alpha$-S | -502.8 | -5.7 | -5.0 | -499.8 | -499.2 | 499.2 | 499.2 | 499.2 | 499.2 |
|    |                  | $\beta$-S | -502.1 | -3.7 | -500.6 | -500.0 | -500.3 | -500.3 | -500.3 | -500.3 | -500.3 |
|    |                  | gas       | -701.3 | -305.2 | -383.6 | -352.7 | -297.8 | -297.8 | -297.8 | -297.8 | -297.8 |
\[ \text{ZnS} + 2\text{H}_2\text{S} + 2\text{SO}_2 \rightarrow \text{ZnO} + \text{H}_2 + \text{Zn} + \text{H}_2 \]

\[ \text{2Cu} + \text{O}_2 \rightarrow 2\text{CuO} + 3\text{O}_2 \]

\[ 2\text{CuO} + \text{O}_2 \rightarrow 2\text{CuO}_2 \]

\[ 3\text{S} + 2\text{ZnO} \rightarrow 2\text{ZnS} + \text{SO}_2 \]

\[ \text{ZnS} + 2\text{H}_2\text{O} \rightarrow \alpha-\text{S}_8 \]

\[ \beta-\text{S}_8 \]

\[ \text{gas} \]

\[ -356.5 \quad 181.5 \quad -26.8 \quad 16.9 \quad -17.1 \quad -410.6 \quad -415.1 \quad -419.5 \quad -428.8 \quad -434.6 \quad -444.2 \]

\[ -854.5 \quad -1744.4 \quad -780.5 \quad -44.1 \quad 78.3 \quad -137.4 \quad -66.7 \quad 59.2 \]

\[ -385.9 \quad -211.7 \quad 30.6 \quad -17.7 \quad -10.5 \quad -314.8 \quad -307.6 \quad -295.3 \]

\[ -399.3 \quad -212.4 \quad 29.7 \quad -17.7 \quad -10.5 \quad -336.0 \quad -320.7 \quad -315.5 \]

\[ -299.7 \quad 178.8 \quad 180.4 \quad -5.5 \quad -29.6 \quad -373.2 \quad -381.2 \quad -396.0 \]

\[ -184.6 \quad -59.1 \quad 24.7 \quad -16.9 \quad -4.3 \quad -166.9 \quad -165.5 \quad -164.0 \]

\[ -184.6 \quad -59.1 \quad 24.7 \quad -16.9 \quad -4.3 \quad -166.9 \quad -165.5 \quad -164.0 \]

\[ -78.3 \quad -2.8 \quad 0.9 \quad -4.5 \quad 4.6 \quad -77.4 \quad -77.3 \quad -77.2 \quad -77.1 \quad -77.0 \]

\[ -604.5 \quad -228.2 \quad 33.9 \quad -22.5 \quad -15.4 \quad -536.4 \quad -530.7 \quad -525.1 \quad -513.8 \quad -506 \quad -492.6 \]

\[ -398.9 \quad -211.7 \quad 30.6 \quad -17.7 \quad -10.5 \quad -314.8 \quad -307.6 \quad -295.3 \]

\[ -399.3 \quad -212.4 \quad 29.7 \quad -17.7 \quad -10.5 \quad -336.0 \quad -320.7 \quad -315.5 \]

\[ -299.7 \quad 178.8 \quad 180.4 \quad -5.5 \quad -29.6 \quad -373.2 \quad -381.2 \quad -396.0 \]

\[ -184.6 \quad -59.1 \quad 24.7 \quad -16.9 \quad -4.3 \quad -166.9 \quad -165.5 \quad -164.0 \]

\[ -78.3 \quad -2.8 \quad 0.9 \quad -4.5 \quad 4.6 \quad -77.4 \quad -77.3 \quad -77.2 \quad -77.1 \quad -77.0 \]

\[ -604.5 \quad -228.2 \quad 33.9 \quad -22.5 \quad -15.4 \quad -536.4 \quad -530.7 \quad -525.1 \quad -513.8 \quad -506 \quad -492.6 \]

\[ -398.9 \quad -211.7 \quad 30.6 \quad -17.7 \quad -10.5 \quad -314.8 \quad -307.6 \quad -295.3 \]

\[ -399.3 \quad -212.4 \quad 29.7 \quad -17.7 \quad -10.5 \quad -336.0 \quad -320.7 \quad -315.5 \]

\[ -299.7 \quad 178.8 \quad 180.4 \quad -5.5 \quad -29.6 \quad -373.2 \quad -381.2 \quad -396.0 \]

\[ -184.6 \quad -59.1 \quad 24.7 \quad -16.9 \quad -4.3 \quad -166.9 \quad -165.5 \quad -164.0 \]

\[ -78.3 \quad -2.8 \quad 0.9 \quad -4.5 \quad 4.6 \quad -77.4 \quad -77.3 \quad -77.2 \quad -77.1 \quad -77.0 \]

\[ -604.5 \quad -228.2 \quad 33.9 \quad -22.5 \quad -15.4 \quad -536.4 \quad -530.7 \quad -525.1 \quad -513.8 \quad -506 \quad -492.6 \]

\[ \alpha-\text{S}_8 \]

\[ \beta-\text{S}_8 \]

\[ \text{gas} \]

\[ \Delta H \quad \Delta S \quad \Delta G \]
of manufacture of sulfur and sulfur dioxide have been considered. Therefore, several schemes for neutralizing hydrogen sulfide proceed according to various chemical reactions; however, chemical reactions that are accompanied by the formation of more energy occur predominantly. Also, the chemical interaction of diatomaceous powder with these gases is theoretically impossible. The processes of interaction of neutralizers with toxic gases and secondary processes can occur. The processes of neutralizing hydrogen sulfide using dolomite powder are presented in a wide temperature range, that is, the processes of neutralization of toxic gases, as well as the processes of neutralization of elemental sulfur.

Based on the data obtained, the following conclusions can be drawn: neutralizers can interact with toxic gases and elemental sulfur. Therefore, in the manufacture of a sulfur modifier with a toxic gas, it is necessary to combine the components using additional additives, as suggested in [15]. It is necessary to carry out the rapid mixing of sulfur and neutralizers in order to avoid the removal of interaction products from their surface during the production process. Also, SO2 is not formed during the short-term and low-temperature production of the sulfur modifier. In addition, toxic gases can be trapped in the pores of the sulfur modifier.

An analysis of the data in Tables 5-8 shows that the value ∆G < 0 is typical for most of the reactions presented in a wide temperature range, that is, the processes of neutralization of toxic gases, as well as secondary processes can occur. The processes of neutralizing hydrogen sulfide using dolomite powder are an exception. Also, the chemical interaction of diatomaceous powder with these gases is theoretically impossible. The processes of interaction of neutralizers with toxic gases and secondary processes can proceed according to various chemical reactions; however, chemical reactions that are accompanied by the release of more energy occur predominantly. Therefore, several schemes for neutralizing hydrogen sulfide and sulfur dioxide have been considered.

The most likely chemical reactions occurring in the presence of zinc and zinc oxide at the temperature of manufacture of sulfur-bitumen binder (140 °C) have the following thermal effects:

\[
\begin{align*}
3Zn + SO_2 & \rightarrow ZnS + 2ZnO + 602.9 \text{ kJ/mol} \\
2Zn + SO_2 & \rightarrow 2ZnO + S(\text{oxygen}) + 397.1 \text{ kJ/mol} \\
2Zn + SO_2 & \rightarrow 2ZnO + S(\text{gaseous}) + 281.9 \text{ kJ/mol}
\end{align*}
\]
Zn + H₂S → ZnS + H₂ + 182.8 kJ/mol
ZnO + H₂S → ZnS + H₂O + 77.9 kJ/mol
2ZnS + 3O₂ → 2ZnO + 2SO₂ + 880.9 kJ/mol

An analysis of the reactions shows that among the chemical reactions of the interaction of zinc with sulfur dioxide, the reaction leading to the formation of sulfide and zinc oxide has the greatest thermal effect. And among the reactions of zinc or zinc oxide with hydrogen sulfide, the reaction leading to the formation of zinc sulfide and hydrogen has the greatest thermal effect. In this case, hydrogen as a reaction product can increase the volume of toxic gases formed (table 4, reaction 1). This is indicated by the experimental data of Table 3: the amount of hydrogen sulfide formed in the presence of zinc and zinc oxide is comparable or exceeds its emission to the ordinary composition. Chemical reactions taking place in the presence of manganese dioxide have the following of thermal effects:

MnO₂ + 2H₂S → MnS + S₀ + 2H₂O + 133.4 kJ/mol
MnO₂ + 2H₂S → MnS + S₈ + 2H₂O + 18.3 kJ/mol
MnO₂ + SO₂ → MnSO₄ + 242.9 kJ/mol

The formation of an additional amount of toxic gases does not occur when using manganese dioxide to neutralize toxic gases (table 4, reaction 6). It ensures a high efficiency of manganese dioxide to neutralize toxic gases.

Chemical reactions taking place in the presence of copper oxide have the following of thermal effects:

CuO + H₂S → CuS + H₂O + 112.1 kJ/mol
3CuO + H₂S → 3Cu + H₂O + SO₂ + 34.2 kJ/mol
2CuO + 2SO₂ + O₂ → 2CuSO₄ + 623.6 kJ/mol
2CuS + 3O₂ → 2CuO + 2SO₂ + 812.6 kJ/mol

In the interaction of copper oxide with hydrogen sulfide, the reaction occurs primarily, which is accompanied by the formation of copper sulfide and water. Copper sulfide is oxidized and forms sulfur dioxide, but the reaction products are able to interact with each other and re-enter the neutralization cycle. It explains the greater efficiency of CuO compared to Zn and ZnO.

4. Conclusion
It has been experimentally established that the emission of toxic gases (H₂S and SO₂) from a sulfur-bitumen binder can be reduced by using chemical compounds (neutralizers), which form low- and water-insoluble chemical reaction products. Copper oxide and manganese oxide are the most effective neutralizers, the use of diatomaceous powder and dolomite powder is also effective. Zinc powder has low neutralization efficiency, and the use of zinc oxide increases the emission of toxic gases. The kinetics of the emission of hydrogen sulfide and sulfur dioxide from a sulfur-bitumen binder shows that the formation of sulfur dioxide is the dominant process. This is consistent with thermodynamic calculations of the isobaric-isothermal potential of chemical reactions: the formation of SO₂ during the oxidation of sulfur is energetically advantageous than the formation of H₂S. In the manufacture of a sulfur modifier, it is necessary to reduce the mixing time of the sulfur melt and the toxic gas emission neutralizers, since the neutralizers are capable of chemically interacting with sulfur.

The thermodynamic calculation of the isobaric-isothermal potential of chemical reactions shows that a decrease in the emission of toxic gases in the presence of dolomite and diatomite is caused by the ability of carbonates to neutralize sulfur dioxide chemically, as well as due to physical absorption of gases. It was found that some neutralizers (zinc (II) oxide) can contribute to chemical reactions that increase the emission of toxic gases.
Thus, it is necessary to use a sulfur modifier containing emission neutralizers - copper oxide, manganese dioxide, dolomite and/or diatomite powders to solve the problem of work safety both at the stage of manufacturing sulfur-asphalt concrete and in the manufacture of pavement.

References

[1] Vasil'ev Yu E, Ivachev A V and Bratishchev I S 2014 Vestnik yevraziyskoy nauki 5 (24) 20.
[2] Doshlov O I and Kalapov I A 2015 Vestnik IGTU 11 (106) 107-111.
[3] Turayev F T, Beknazarov K S and Dzhalilov A T 2019 Universum: tekhnicheskiye nauki 2 (59), 65-69.
[4] Gladkikh V, Korolev E, Husid D and Sukhachev I 2016 MATEC Web of Conferences IPICSE-2016 86 04024.
[5] Yang R, Ozer H, Ouyang Y, Alarfaj A, Islam K, Khan M I, Khan K M and Shalabi F I 2019 Airfield and Highway Pavements 183-192.
[6] Gladkikh V, Korolev E and Smirnov V. 2019 E3S Web of Conferences 91 07014.
[7] Inozemtsev S and Korolev E 2019. IOP Conference Series: Materials Science and Engineering. 661 (1). 012136.
[8] Vasiliev Yu E 2012 Methodological fundamentals of automation of processes of industrial production of sulfur-asphalt concrete mixtures with optimization of the components of the mineral part according to particle size distribution Moscow 40 p.
[9] Andronov S Yu, Vasiliev Yu E, Timokhin D K, Repin A M, Repina O V and Talalay V V 2016 Bulletin of Eurasian Science 3 (34) p 107.
[10] Gladkikh V A, Korolev E V and Smirnov V A 2017 IOP Conf. Ser.: Earth and Env. Sc. 90 (1) 012079.
[11] David Yeoh, Koh Heng Boon and Norwati Jamaluddin 2015 J. Tech. Sc. & Eng. 77 (32) 179–188.
[12] Majid Jamshed Chughtai, Helen Jayne Davies, Richard Walter May and David Strickland 2013 A method providing for a low release of H$_2$S during the preparation of sulfur-extended asphalt (Pat. 2585540 United States Publ. 05/01/2013.
[13] Pat. 3,960,585 United States Reducing H$_2$S-emission from hot cast sulfur-asphalt mixtures. " Publ. 06/01/1976
[14] Gladkikh V A and Korolev E V 2014 Internet Herald VolgGASU 2 (33) 3.
[15] Gladkikh V A and Korolev E V 2014 Adv. Mat. Research 1040 387-392.
[16] Medvedev V A, Alekseev V I and Bergman G A 1978 Thermal constants of substances VINITI USSR Academy of Sciences Moscow 536.
[17] Korolev E V, Bazhenov Yu M and Albakasov A I 2010 Radiation-protective and chemically resistant sulfur building materials Penza-Orenburg. 364 p.

Acknowledgments

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (Project: Theoretical and experimental design of new composite materials to ensure safety during the operation of buildings and structures under conditions of technogenic and biogenic threats #FSWG-2020-0007).