Research Article

Simulation Experiment of TSR Promotes Cracking of Coal Generation H₂S

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Thermochemical sulfate reduction (TSR) is one of the main contributors to the formation of hydrogen sulfide (H₂S) in coal seam strata. Four reaction systems (coal, coal+water, coal+water and MgSO₄, and coal+water and MgSO₄ and AlCl₃) were selected and simulated from 250°C to 600°C with eight temperature steps using a high-temperature and high-pressure reaction device, and the evolution characteristics of the gaseous products of hydrocarbons (methane, C₂-5) and nonhydrocarbon gases (CO₂, H₂, and H₂S) were studied. Thermal simulation experiments showed that the TSR led to the reduction of heavy hydrocarbons, and the presence of salts accelerated the evolution of hydrocarbons; SO₄²⁻, Al³⁺, and Mg²⁺ had a certain promoting effect on the TSR, which increased the total amount of alkane gas, H₂S, and CO₂ production. Improving the salinity of the reaction system can promote the occurrence of TSR, and water plays a key role in hydrocarbon generation evolution and the TSR.

1. Introduction

Abnormal emission and casualty accidents caused by the enrichment of hydrogen sulfide (H₂S) in coal mines occur frequently domestically and internationally. High-sulfur natural gas reservoirs (volume percentage of H₂S greater than 5%) are widely distributed around the world, and all are closely related to the distribution of sulfate reservoirs. Previous studies have shown that thermochemical sulfate reduction (TSR) is one of the main ways to form hydrogen sulfide in coal seam strata. Four reaction systems (coal, coal+water, coal+water and MgSO₄, and coal+water and MgSO₄ and AlCl₃) were selected and simulated from 250°C to 600°C with eight temperature steps using a high-temperature and high-pressure reaction device, and the evolution characteristics of the gaseous products of hydrocarbons (methane, C₂-5) and nonhydrocarbon gases (CO₂, H₂, and H₂S) were studied. Thermal simulation experiments showed that the TSR led to the reduction of heavy hydrocarbons, and the presence of salts accelerated the evolution of hydrocarbons; SO₄²⁻, Al³⁺, and Mg²⁺ had a certain promoting effect on the TSR, which increased the total amount of alkane gas, H₂S, and CO₂ production. Improving the salinity of the reaction system can promote the occurrence of TSR, and water plays a key role in hydrocarbon generation evolution and the TSR.

2. Samples and Experimental Methods

2.1. Experimental Samples. An anthracite fresh coal sample used in this experiment was selected from the no. 15 coal seam in a coal mine of Mountain Fenghuang, southern Qinshui Basin, Shanxi Province, China, where the H₂S is
abnormally enriched, and the parameters of the samples were measured. The industrial analysis, elemental analysis, and sulfur composition are shown in Table 1. After the coal sample was crushed, it was sieved out with the particle size of 80-150 μm in the constant temperature vacuum drying oven at 50°C to make a dry sample of 8000 g as the experimental coal sample, and the sieved sample was divided into 8 portions; each portion of 1000 g was stored in a dry bottle and injected with nitrogen and sealed for use.

\( M_{ad} \) is the air-dried moisture, \( A_d \) is the dry ash, \( V_{daf} \) is the dry ash-free volatile, \( S_{d,b} \) is the dry basis total sulfur, \( S_{d,ad} \) is the dry basis organic sulfur, and \( S_{p,ad} \) is the dry basis pyritic sulfur. The coal of sample no. 15 is mostly black and powdery, and a small part is massive. It is a semibright briquette with mirrored coal ribbon and silk carbon lens. It has a thin-medium strip structure and occasionally white calcite and dispersed, nodular, and film-shaped pyrite.

2.2. Experimental Method. The experimental device mainly consists of a reactor, control device, degassing device, loading device, and gas collection and analysis device. The system diagram is shown in Figure 1 [11]. The maximum temperature control of the system is 650°C, and the accuracy is ±1°C. The maximum pressure control is 25.0 MPa, and the accuracy is ±0.5 MPa. During the experiment, the quartz tube containing 1000 ± 0.1 g of the experimental samples was successively put into the kettle. After connecting all air circuits and temperature sensors of the equipment and detecting the air tightness of each air circuit, the vacuum degasses the entire system. After degassing, different media were injected into the quartz tube in the reactor from the loading device according to the experimental scheme. Into the quartz tube in the reaction kettle, 300 mL of an ion aqueous solution with a molar concentration of 1.0 mol/L of mineral aqueous solution containing additives was injected. The initial pressure in the kettle is set to 5.0 MPa, and the final pressure of the reaction system is between 12.0 and 20.0 MPa. The reaction is heated at a heating rate of 20°C/h, simulating gaseous products at 8 temperature points of 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, and 600°C, and these were analyzed. The heating time for each experiment stage was 24 hours. At the end of each experimental stage, the gaseous products in the reactor were collected using a special sampler for hydrogen sulfide and a Tedlar gas sample bag. Using a gas chromatograph, the gaseous products of hydrocarbon gases (methane, heavy hydrocarbons) and nonhydrocarbon gases (CO₂, H₂, and H₂S) were measured.

3. Experimental Results and Discussion

The coal sample used in this experiment can be regarded as a typical porous medium. Its fine particle size and its connected internal channels allow the gas to flow smoothly through its surface and inside, and it is also a place for heat transfer and physical and chemical reactions. The gaseous product test results of hydrocarbon gas (CH₄, C₂–₅) and nonhydrocarbon gas (CO₂, H₂, and H₂S) are shown in Table 2.

Coal is a complex polymer compound with condensed aromatic nuclei derived from lignin as the main body, condensed internal channels allow the gas to flow smoothly through its surface and inside, and it is also a place for heat transfer and physical and chemical reactions. The gaseous product test results of hydrocarbon gas (CH₄, C₂–₅) and nonhydrocarbon gas (CO₂, H₂, and H₂S) are shown in Table 2.

The yield of methane and total gas is higher, which is expressed as “coal+water and MgSO₄ and AlCl₃” > “coal+water and MgSO₄” > “coal+water” > “coal.” Comparison of the gas yield results showed that the presence of water and additives led to a significant increase in the total gas yield and methane gas yield, as shown in Figures 3 and 4.

Heavy hydrocarbons are dominated by C₃H₆, and their output increases first and then decreases as the temperature of the simulated experiment increases. Compared with the

| Table 1: Experimental sample parameter determination numerical value. |
|---------------------------------------------------------------|
| **Industrial analysis (%)**                                  |
| **Elemental analysis (%)**                                   |
| **Sulfur composition (%)**                                   |
| \( M_{ad} \) | \( A_d \) | \( V_{daf} \) | C | H | N | O | \( S_{d,ad} \) | \( S_{d,ab} \) | \( S_{p,ad} \) |
| 1.12 | 24.27 | 7.15 | 88.47 | 3.19 | 0.35 | 3.15 | 3.44 | 0.82 | 2.62 |
groups of “coal” and “coal+water,” the addition of MgSO4 makes the heavy hydrocarbon reach its maximum value at 400°C, which obviously reduces the temperature required to reach the peak of the heavy hydrocarbon yield and has a certain promotion effect on the formation of heavy hydrocarbon, as shown in Figure 5. Heavy hydrocarbons are mainly produced by the reaction of -OH attached to the C atom in the middle part of the aliphatic hydrocarbon chain in coal to form -COOH, and its formation can be described as follows [11]:

\[
R - C(OH)_{2} - CH_{2} - CH_{3} \rightarrow R - COOH + C_{2}H_{4} \tag{1}
\]

\[
R - CH_{3} - C(OH)_{2} - CH = CH_{2} \rightarrow R - CH_{2} - COOH + C_{2}H_{4} \tag{2}
\]

\[
R - CH_{2} - C(OH)_{2} - CH_{2} - CH_{2} - CH_{3} \rightarrow R - CH_{2} - COOH + C_{2}H_{4} \tag{3}
\]

The heavy hydrocarbon yield decreases rapidly with increasing thermal simulation temperature after 400/450°C. The comparison revealed that the decrease in heavy hydrocarbon content was intensified in the presence of water, indicating that water was involved in the TSR reaction process, while the presence of additives accelerated the reaction of heavy hydrocarbons with sulfur-containing compounds and played a certain role in promoting it. The equation can be described as follows [11]:

\[
C(\sum C_{n+1}H) + SO_{4}^{2-} \text{(Dissolved)} + H_{2}O \xrightarrow{Mg^{2+}/Al^{3+}} H_{2}S + CO_{2} + HCO_{3}^{-} \tag{4}
\]

The sources of H2 were mainly polycondensation between free radicals and aromatic structures and polycondensation dehydrogenation reaction of hydrogenated aromatic structures [17–19]. The generation of H2 in the first stage mainly includes hydrogen radicals mainly generated by the oxidation of hydrocarbons by minerals (sulfates) before 400°C, the cracking of long-chain aliphatic hydrocarbons to generate short-chain fatty radicals, and the secondary of light paraffins. Hydrogen radicals generated by cracking are combined with each other to generate hydrogen gas. At the second stage of 400–600°C, it is mainly formed by polycondensation between free radicals. They are the hydrogen radicals generated by the C-H bond breaking, cyclization, and aromatization of aliphatic hydrocarbons and the hydrogen radicals generated by the polycondensation reaction between aromatic rings and the reaction of C, CO, and H2O. After 350°C, the H2 yield drops significantly, and the H2 formed by the C-H bond breakage reacts with sulfur radicals to generate H2S. H2 is generated only when there is a slight surplus, thereby reducing the hydrogen production rate. After the temperature reaches 500°C, it may be due to the insufficient supply of sulfur radicals in the sample and the deep reaction in the coal, such as the reaction of carbon and water and the reaction of CO and water to form H2, which leads to an increase in the yield of H2. In particular in the experimental conditions of anhydrous and water-free and salt-free addition of hydrogen, the hydrogen production has always been higher under the conditions of water-free and salt-free addition. This indicates that under anhydrous conditions, hydrogen consumption is lower and TSR is more difficult to occur, and water plays a very important role in TSR occurrence, which is consistent with the involvement of water in the TSR reaction mentioned earlier. The variation characteristics of H2 production are shown in Figure 6, and its formation can be described as follows.

\[
CO + H_{2}O \rightarrow CO_{2} + H_{2} \tag{5}
\]

\[
C + 2H_{2}O \rightarrow CO_{2} + 2H_{2} \tag{6}
\]

\[
\text{CO}_{2} + \text{H}^{+} \rightarrow \text{CO}_{2} + H_{2} \tag{7}
\]

CO2 is the hallmark product of TSR [12, 20, 21]. The precipitation of CO2 between 250 and 350°C is mainly due to the
Table 2: Test results of gaseous products.

| Media type                                      | Temperature (°C) | CH₄ (mL/g) | C₂₋₅ (mL/g) | CO₂ (mL/g) | H₂ (mL/g) | H₂S (mL/g) |
|------------------------------------------------|------------------|------------|-------------|------------|-----------|------------|
| Coal                                           | 250              | 12.436     | 1.306       | 6.127      | 1.369     | 0.002      |
|                                                | 300              | 13.758     | 1.432       | 7.264      | 1.410     | 0.006      |
|                                                | 350              | 15.845     | 2.069       | 8.655      | 1.479     | 0.008      |
|                                                | 400              | 18.828     | 2.845       | 9.655      | 1.319     | 0.013      |
|                                                | 450              | 21.184     | 3.616       | 9.909      | 1.056     | 0.017      |
|                                                | 500              | 22.621     | 3.855       | 10.073     | 0.871     | 0.016      |
|                                                | 550              | 22.969     | 2.375       | 9.964      | 0.892     | 0.015      |
|                                                | 600              | 23.128     | 0.986       | 9.627      | 1.012     | 0.009      |
|                                                | 250              | 12.714     | 1.085       | 6.300      | 1.502     | 0.003      |
| Coal+deionized water                           | 300              | 14.941     | 1.416       | 8.182      | 1.519     | 0.008      |
|                                                | 350              | 17.168     | 2.305       | 10.045     | 1.561     | 0.019      |
|                                                | 400              | 20.625     | 3.077       | 10.545     | 1.641     | 0.035      |
|                                                | 450              | 25.282     | 3.582       | 9.609      | 1.716     | 0.067      |
|                                                | 500              | 27.247     | 2.537       | 9.991      | 1.748     | 0.072      |
|                                                | 550              | 26.984     | 1.333       | 10.573     | 1.605     | 0.047      |
|                                                | 600              | 26.387     | 0.393       | 10.095     | 1.487     | 0.023      |
|                                                | 250              | 13.288     | 1.143       | 6.380      | 1.430     | 0.019      |
|                                                | 300              | 15.276     | 1.519       | 7.871      | 1.677     | 0.019      |
|                                                | 350              | 17.722     | 2.645       | 10.468     | 1.704     | 0.062      |
|                                                | 400              | 20.245     | 4.096       | 10.068     | 1.017     | 0.123      |
| Coal+deionized water+MgSO₄                      | 450              | 27.157     | 2.984       | 9.151      | 0.530     | 0.165      |
|                                                | 500              | 29.068     | 1.869       | 10.018     | 0.406     | 0.149      |
|                                                | 550              | 29.456     | 1.016       | 10.287     | 0.419     | 0.102      |
|                                                | 600              | 29.600     | 0.085       | 10.393     | 0.569     | 0.061      |
|                                                | 250              | 13.765     | 1.109       | 6.585      | 1.372     | 0.004      |
|                                                | 300              | 16.377     | 1.654       | 7.922      | 1.528     | 0.029      |
|                                                | 350              | 19.066     | 3.281       | 9.467      | 1.597     | 0.099      |
|                                                | 400              | 23.293     | 4.734       | 9.167      | 0.774     | 0.215      |
| Coal+deionized water+MgSO₄+0.02 mol AlCl₃      | 450              | 30.099     | 3.811       | 8.806      | 0.417     | 0.276      |
|                                                | 500              | 31.845     | 2.214       | 10.243     | 0.343     | 0.298      |
|                                                | 550              | 32.132     | 0.842       | 10.815     | 0.364     | 0.230      |
|                                                | 600              | 32.213     | 0.061       | 10.875     | 0.606     | 0.158      |

Figure 2: Reaction pathways for the briquette pyrolysis.
Figure 3: Variation characteristics of total gas.

Figure 4: Variation characteristics of methane production.

Figure 5: Variation characteristics of heavy hydrocarbon.

Figure 6: Variation characteristics of H₂ production.

Figure 7: Variation characteristics of CO₂ production.

Figure 8: Variation characteristics of H₂S production.
decomposition of oxygen-containing carboxyl groups in coal by heat. After the temperature hits 350°C, most of the fatty bonds, oxygen-containing functional groups, and some aromatic weak bonds in coal are broken. Part of the broken carbonyl group is precipitated in the form of CO₂, and a part of it is combined with the oxygen atoms in the coal and precipitated in the form of CO₂. After the temperature reaches 450°C, the CO₂ precipitation gradually increases, indicating that deep TSR has occurred. From the four yield curves, it can be seen that the amount of CO₂ production is significantly increased with the participation of water compared with the “coal” group alone, while MgSO₄ and AlCl₃ have a certain driving effect on the TSR reaction. The variation characteristics of CO₂ production are shown in Figure 7.

Decomposition of carboxyl groups, ether bonds, and other oxygen-containing functional groups occurs [20]. The reaction occurs as follows:

\[ R - \text{COOH} \rightarrow \text{RH} + \text{CO}_2 \]  

\[ \text{Ar} - \text{COOH} + \text{HOOC} - \text{Ar} \rightarrow \text{Ar} - \text{O} - \text{Ar} + \text{H}_2\text{O} + \text{CO}_2 \]  

\[ R - \text{CH}_2\text{CH}_3 + \text{S} \rightarrow \text{R}-\text{CH}_2\text{CH}_2\text{SH} + \text{H}_2\text{S} \]  

Sulfur in coal includes organic sulfur and inorganic sulfur. Most of the organic sulfur in coal is part of the molecular structure of kerogen, mainly including mercaptans, sulfides, disulfides, thiophenes, sulfoxides, and sulfones, and most of them are mainly thiophene sulfur [22–24]. Sulfur in coal includes organic and inorganic sulfur, and organic sulfur in coal is mostly a component of the molecular structure of cheese root, mainly including mercaptans, sulfides, disulfides, thiophene, sulfoxide, and sulfone and mainly thiopehene sulfur [22–24]. Its shape is complex and diverse, and the thermal stability varies greatly. The precipitation, migration, and morphological distribution of sulfur during the TSR and pyrolysis process are affected by the pyrolysis environment and the kerogen structure and mineral species in coal. Inorganic sulfur usually exists in the form of sulfide, sulfate, and trace elemental sulfur, mainly pyrite [22, 25].

In the initial low-temperature stage, the TSR was low, and a small amount of H₂S may form by the bond breakage of unstable organic sulfur (such as thioether, thiol), hydrocarbon oxidation, and sulfate reduction. H₂S formed by hydrocarbon oxidation and sulfate reduction can in turn act as a catalyst to react with the dissolved form of sulfate to form S₀, so the production of H₂S was less. The possible reactions are as follows [8, 26, 27]:

\[ \text{HC} + \text{HSO}_4^- (\text{MgSO}_4) \overset{\text{Slow}}{\rightarrow} \begin{array}{c} \text{SO}_3 + \text{HC} \\ \text{S}_2\text{O}_3 \overset{\text{Rapid}}{\rightarrow} \text{SO}_3 + \text{S}_0 \\ \text{S}_0 + \text{HC} \overset{\text{Rapid}}{\rightarrow} \text{H}_2\text{S} + \text{Tar} \end{array} \]

(11)

During thermal evolution, the formed hydrocarbons can react with the generated H₂S to produce organic sulfides.

\[ \text{H}_2\text{S} + \text{HC} \rightarrow \begin{bmatrix} \text{R} - \text{SH} \\ \text{R} - \text{S} - \text{R} \end{bmatrix} \Delta \rightarrow \text{H}_2\text{S} + \text{R} - \text{S}^0 (\text{R} \text{ is alkyl}) \]

(12)

As the temperature rises, unstable organic sulfides can undergo reduction reactions with sulfates.

\[ \begin{bmatrix} \text{R} - \text{SH} \\ \text{R} - \text{S} - \text{R} \end{bmatrix} + \text{HSO}_4^- (\text{MgSO}_4) \rightarrow \begin{bmatrix} \text{SO}_3 + \text{HC} \\ \text{S}_2\text{O}_3 \overset{\text{Rapid}}{\rightarrow} \text{SO}_3 + \text{S}_0 \\ \text{S}_0 + \text{HC} \overset{\text{Rapid}}{\rightarrow} \text{H}_2\text{S} + \text{Tar} \end{bmatrix} \]

(13)

The presence and formation of S₀ in turn provide a way for saturated hydrocarbons to be converted into naphthenic acids, aromatic hydrocarbons, and other sulfides, which usually contain two major blocks [28]:

The first block is dehydrogenation (oxidation):

\[ \text{R-CH}_2\text{CH}_3 + \text{S} \rightarrow \text{R-CH=CH}_2 + \text{H}_2\text{S} \]

(14)

The second block is sulfide formation.

\[ \text{R} - \text{H} + \text{S} \rightarrow \text{R-Sh} \text{(Mercaptan)} \]

\[ 2\text{R} - \text{H} + 2\text{S} \rightarrow \text{R-S-R} + \text{H}_2\text{S} \text{(Sulfide)} \]

\[ \text{R-C}_x\text{H}_y + 2\text{S}^0 \rightarrow \text{R-S} + \text{H}_2\text{S} \text{(Cyclic sulfide)} \]

\[ \text{R-C}_x\text{H}_y + 4\text{S}^0 \rightarrow \text{R-S} + 3\text{H}_2\text{S} \text{(Thiophene heterocyclic compounds)} \]

(15)

R is the fatty group.

Thiophene only begins to decompose at 450°C. The alkyl-substituted phosgene loses its alkyl group around 500°C, and the thiophene begins to decompose at 550°C. The thiophene...
ring is stable, and decomposition begins only after at 800°C [29, 30]. The pyrolysis products of thiophene are usually some small-molecule compounds, such as sulfur, carbon, hydrogen sulfide, and acetylene. Under a hydrogen-rich atmosphere, these compounds react as follows [11, 31, 32]:

\[
\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{S}
\]

Thiophene compounds can be generated by the reaction of sulfur or H_2S with organic matter, or pyrite with organic molecules similar to ethylene, and salts such as bauxite and magnesium sulfate may promote the reaction.

\[
\text{C}_4\text{H}_8 \rightarrow \text{Al}_2\text{O}_3, \text{MgSO}_4 + \text{H}_2\text{S}
\]

The sulfur in this experimental sample is mainly organic sulfur. The peak of H_2S precipitation reaches its maximum at 450–500°C, which obviously belongs to the form of sulfide. Subsequently, hydrogen sulfide is mainly formed by pyrite and thiophene sulfur, and FeS_2 can be reduced to FeS and H_2S at about 500°C. Structures such as aliphatic hydrocarbons and hydrogenated aromatic hydrocarbons in coal generate internal hydrogen radicals with hydrogen supply capability during the thermochemical reduction reaction, which promotes the reduction and decomposition of pyrite. The comparison of the hydrogen sulfide gas yield shows that the maximum yield of H_2S in the "coal+water and MgSO_4" system is 2.5 times higher than the maximum yield of H_2S in the "coal+water" system and 8.5 times higher than the maximum yield of H_2S in the "coal" system. This shows that the addition of MgSO_4 intensifies the TSR reaction and promoted the production of H_2S gas. The variation characteristics of H_2S production are shown in Figure 8.

Water plays an important role as a solvent, reactant, and reaction carrier in aqueous thermal simulation reactions. The H element in the water is added to the coal sample under the synergistic effect of free radicals and ion effects, or ion exchange occurs with the minerals in the coal; it changes the environment of hydrothermal reaction to promote the cleavage of weak chemical bonds in the coal structure. In the process, it will also replace the oxygen-containing functional groups in the coal, so that the oxygen-containing functional groups decompose to form small-molecule gases and polar substances remaining in the water. It can also exchange with the hydrogen in coal and transfer in the coal structure. At the same time, the hydrogen and oxygen elements in the water may also be replaced by hydrogen atoms on the benzene ring under the synergistic effect of free radicals and ionic effects to form phenols.

4. Conclusion

The results of thermal simulation experiments showed that TSR promoted the cracking of coal, which led to an increase in the production of hydrogen sulfide and methane and a decrease in the production of heavy hydrocarbons. The presence of salts accelerates the evolution of hydrocarbon formation, and SO_4^{2-}, Al^{3+}, and Mg^{2+} contributed greatly to the TSR, resulting in an increase in the total amount of alkane gas and the production of H_2S and CO_2. Improving the salinity of the reaction system can promote the development of TSR.

In the thermal simulation system of coal, water is actually a hydrogen donor, providing some protonic hydrogen to stabilize the unstable intermediate material and accompanying the generation of H_2. In terms of gas production, the participation of water provides an additional source of hydrogen for the TSR reaction to produce gas, which accelerates the reaction and promotes gas production. Water media play an important role in the evolution of hydrocarbon generation.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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