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## Origin of hydrogen sulfide in coal seams in China<sup>☆</sup>

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### ABSTRACT

In recent years, coal mines in China have seen accidents caused by sudden release of hydrogen sulfide (H<sub>2</sub>S), with higher severity. Based on recent local and overseas research on the origin of hydrogen sulfide and the comparative analysis of isotopes, the paper presents three formation models of hydrogen sulfide: bacterial sulfate reduction (BSR), thermo-chemical sulfate reduction (TSR) and igneous activity, as well as the characteristics for identification. This paper analyzes and categorizes the formation models of some hydrogen sulfide in coal seams in China. Some suggestions were put forward for future research of H<sub>2</sub>S in coal mines in China.

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### 1. Introduction

In coal mining, unusual release and disastrous accidents aroused by the H<sub>2</sub>S abnormal gathering frequently occur in coal mines in China as well as abroad. Accidents of this type have been reported in succession in North America, Russia, France and Australia. Abnormal release has happened in Collinsville, Oaky Creek and Southern Colliery of Bowen Coal Field, Australia (Philips et al., 1990; Smith et al., 1982; Smith and Philips, 1990).

China has experienced very severe situation. So far, it has been sudden release of H<sub>2</sub>S from more than 30 coal mines in such provinces as Henan, Hunan, Inner Mongolia, Shandong, and Shanxi, accompanied by accidents. Since 2004, over 10 casualty accidents caused by H<sub>2</sub>S poisoning have occurred. For exam-

ple, on August 10th, 2004, H<sub>2</sub>S poisoning accidents happened to a colliery in Tuokexun town, Baicheng County, Akesu district, Xinjiang Province, causing 3 deaths. On May 9, 2009, a H<sub>2</sub>S poisoning accident happened in Xinxing Coal Mine, Shexingshan town, Shuangfeng County and 2 people died. Worse still, in 2010, 2 serious poisoning accidents which were brought by the sudden release of H<sub>2</sub>S happened. On July 16th, 6 persons were suffocated to death in the H<sub>2</sub>S poisoning accidents in Luanshigou Colliery, Xuanan County, Dazhou City, Sichuan Province; on March 7th, a H<sub>2</sub>S poisoning accident happened in the tunneling surface, +550 Northwest transport gateway in Guang'an Colliery of Siyuan Mining Group, in which 3 people died, Guizhou Province, a large number of hydrogen sulfide emissions during the drilling in Xin'tian Colliery of Yonggui Energy. When the fully mechanized mining roof caving work face, panel 45<sup>#</sup> steep-inclined coal seam (65°) at +645 m elevation in Xinjiang Tie-changgou Coal Mine, was advanced to 1250–1130 m, sudden rise of harmful gases in the south half of the work face, tail laneway and return laneway occurred, which leads to concentrate H<sub>2</sub>S far exceeding the limit: 0.132% in the south tail laneway, 0.01–0.08% in the return laneway. In Suhetu and Wuhushan Coal Mine of Wuda coal field in Inner Mongolia, when #9 and #10 coal seams were mined, H<sub>2</sub>S content in the advancing blasthole was as high as 540 ppm, 500 ppm in the return air flow when blasting, and 210 ppm in fully mechanized mining face. Such situation also exists in Xin'an Coal Mine in Henan Province and Jixi Gui'min Coal Mine in Tongchuan City, Shanxi Province. Though no injuries or deaths occurred, yet many people fainted and the collieries were forced to shut down because of the great threat to the occupational health and safety of the workers in the collieries. Apart from the above, quite a number of unexpected H<sub>2</sub>S releases

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**Table 1**  
List of H<sub>2</sub>S accidents in coal mines in China.

No.	Provinces	Number of mines	Disaster situation
1	Shanxi	6	Coming from roof water, low sulfur coal seam
2	Xinjiang	3	In weak coal of high sulfur coal seam, 5 casualties
3	Inner mongolia	4	H <sub>2</sub> S is more than 100 ppm in 23 working faces
4	Gansu	5	H <sub>2</sub> S is 50 ppm in return air
5	Sichuan	4	7 casualties
6	Henan	6	H <sub>2</sub> S abnormal release, 17 casualties
7	Shandong	3	The concentration is 400 ppm in abnormal area
8	Guizhou	3	Five casualties
9	Shanxi	1	H <sub>2</sub> S is more than 80 ppm in working faces

occurred in some coal mines, e.g., Xinjiang, Sichuan, Ningxia, to name a few. Some mines are shown in Table 1.

## 2. Current studies on the origin of H<sub>2</sub>S

Fu et al. (2006) carried out a research on the geographical backgrounds, gas composition and density, and sulfur isotopes in the district with abnormal H<sub>2</sub>S in Bayi Colliery in Zaozhuang, Shandong Province, China. It is suggested that the thermal effect of diabase dykes in late Yanshan Period caused thermochemical decomposition and thermochemical reduction in organic sulfur and sulfate rock in surrounding strata, and thus producing H<sub>2</sub>S.

Compared with H<sub>2</sub>S in oil and gas fields, one of the notable characteristics of that in coal seams is the comparatively low density (Ma et al., 2008). According to Jinxing Dai (1985), H<sub>2</sub>S in coal seams should be categorized as light nitrogen sulfide (0.5–2.0%) and slight nitrogen sulfide (0–0.5%). Bayi Colliery and Xin'an Colliery in China are sight nitrogen sulfide; while Cuizhuang Colliery in Weishan, China, belongs to light nitrogen sulfide. The research on formation models of H<sub>2</sub>S in coal mines is far less extensive than that in oil and gas fields. However, achievements on the origin of light nitrogen sulfide and slight nitrogen sulfide can function as a reference for that in coal mines. Scholars at home and abroad carried out their research from the perspective of temperature, sulfate source, sulfur isotope characteristics and rock strata order of BSR and TSR (Orr, 1974; Machel, 2001; Cody et al., 1999; Cross et al., 2004; Krouse et al., 1988; Desrocher et al., 2004; Worden et al., 1995; Worden and Smalley, 1996; Manzano et al., 1997). Chinese scholars have studied the formation models of H<sub>2</sub>S of oil and gas fields in Sichuan Basin (Dai et al., 2002; Duan et al., 2005; Hao et al., 2008), Tarim Basin (Hou et al., 2005), Songliao Basin (Luo et al., 2005), Ordos Basin (Manzano et al., 1997), Bohai Bay Basin (Machel et al., 1995), etc. Most of the scholars presently believe the H<sub>2</sub>S in oil and gas reserves mainly stems from three sources: (i) Bacterial sulfate reduction (BSR); (ii) Thermal decomposition of sulfides (TDS); (iii) Thermochemical sulfate reduction (TSR).

Due to the bacterial poison of H<sub>2</sub>S and the content of sulfide compounds in rocks, H<sub>2</sub>S concentration formed from BSR and TDS generally does not exceed 3–5%. Therefore, it is now generally believed that the origin of high H<sub>2</sub>S content (H<sub>2</sub>S content >5%) in natural gas is TSR. For H<sub>2</sub>S of different origins, because of differences in sulfur isotope kinetic fractionation and fractionation mechanism, the sulfur isotope compositions in H<sub>2</sub>S significantly vary. Among them, sulfur isotope fractionation due to BSR is the largest (formed from sulfate reducing bacteria metabolism under low temperature), about 20–25‰ lower than sulfate sulfur isotope. On the contrary, the fractionation due to TSR is lower. With TSR extent increasing, the sulfur isotope in H<sub>2</sub>S products gradually closes to the value of the sulfur isotope in sulfide. That in some reaction products

generally is 5–15‰ lower than in sulfide, mostly about 10‰. Compared with the H<sub>2</sub>S due to TSR, H<sub>2</sub>S formation process is relatively slow. Because <sup>32</sup>S bond breaks more easily than <sup>34</sup>S, there are more chances to choose <sup>32</sup>S, and fractionation is more evident. As a result, H<sub>2</sub>S differs significantly from the sulfur isotope in corresponding sulfide, generally being about 15‰. Hence, the origin of H<sub>2</sub>S can be identified by the sulfur isotope and content in sulfide.

The researches show that TSR contributes to the H<sub>2</sub>S in oil and gas fields. It is demonstrated by domestic and overseas researches that the basic conditions for TSR of H<sub>2</sub>S are hydrocarbon organic, sulfate rock and suitable temperature, among which temperature acts as the driving force and one of the keys to control the TSR process and H<sub>2</sub>S origin. And 120 °C is the minimum (Orr, 1974; Machel, 2001). Sulfur isotope in H<sub>2</sub>S is measured as well, and δ<sup>34</sup>S is generally over +10.0‰, with high concentration in one oil and gas field (Orr, 1974; Machel, 2001). The above researches offer reference for determining the TSR of H<sub>2</sub>S in coal seams and differentiating from BSR (Machel, 2001; Desrocher et al., 2004).

## 3. Formation models of H<sub>2</sub>S in coal seams

H<sub>2</sub>S comes into being from the biochemical degradation in the early phase of peat accumulation, bacterial sulfate reduction in peat accumulation, thermochemical decomposition in diagenesis phase and TSR. In addition, igneous activity brings H<sub>2</sub>S. However, according to the current research contribution and the distribution of H<sub>2</sub>S coal mines in China, BSR, TSR and igneous activity constitute the major formation models of H<sub>2</sub>S in coal mines.

### 3.1. BSR

The sulfate-reducing bacteria absorbs sulfate without the participation of oxygen, obtains energy from the oxidation of organic compound and discharges H<sub>2</sub>S produced by the reduction of sulfate, which metabolic process is defined as bacterial sulfate reduction (BSR) (Orr, 1974; Machel et al., 1995; Machel, 2001; Ma et al., 2008; Ni and Hong, 1999). Sulfate reduction bacteria deoxidizes sulfate using coal-forming organic matter, mainly unsaturated hydrocarbon, as the source of energy and material. Oxidized by the sulfate-reducing bacteria, the electrons of these organic matters are transferred to the sulfate which is absorbed to cell membranes. Sulfate accepts the electrons; and sulfate is then reduced to H<sub>2</sub>S and discharged. The occurrence of BSR requires three basic conditions: organic matter, sulfate and sulfate-reducing bacteria (Machel et al., 1995; Machel, 2001). Organic matters and sulfate widely exist in such sedimentary circumstances as marine facies, littoral facies and marine-terrestrial facies. However, sulfate-reducing bacteria will be able to reproduce in oxygen-free environments with the temperature below 60–80 °C, in which the most suitable is 20–40 °C (Orr, 1974; Ma et al., 2008). If the earth temperature gradient is 3 °C/100 m, BSR mainly takes effects in the coal seams buried shallower than 2500 m, which is more common in the peatification and diagenesis phase of coal.

In the medium and high sulfur coal seams in China, BSR is common. Two primary evidences support the fact. First, pyrites are widely discovered in Southern Permian Longtan Formation and Changxing Formation, Northern Permo-carboniferous Taiyuan Formation and Shanxi Formation and high sulfur coal seams, which occupies 67% of sulfur on average. Most organic sulfur is above 1.0% in proportion (Luo et al., 2005), which exceed that (0.8%) in coal-forming plants. H<sub>2</sub>S plays an important part as the intermediate product and basic condition in the production of pyrites and parts of organic sulfur (Ma et al., 2008; Philips et al., 1990), which offers direct proof for H<sub>2</sub>S through BSR when there is high content of organic sulfur and pyrites. Second, sulfur isotope is usually light. In high and

medium sulfur coal seams (total sulfur >1.0%) of China and other countries in the world, the isotope value of sulfur of organic sulfur, dispersive pyrites, block pyrite varies greatly, with a negative mean, with characteristic BSR fractionation (Bernier, 1984; Seal, 2006).

The sulfur in coal seams mainly has two sources. One is organic sulfur, which is produced when the sulfate is assimilated and reduced by coal-forming plants, whose content is usually below 0.8%; The other is the pyrites and organic sulfur produced through BSR (Bernier, 1984; Casagrande et al., 1979). The total sulfur content in high sulfur coal seams is over 10% at highest. If the H<sub>2</sub>S produced is totally transformed into pyrites and organic sulfur, then one ton of coal will produce 64.27 m<sup>3</sup> of H<sub>2</sub>S. Only a small part (<10%) of H<sub>2</sub>S produced through BSR can be used to generate pyrites (Chambers and Trudinger, 1979; Bernier, 1984). It can be roughly estimated that the highest output of H<sub>2</sub>S is 449.87 m<sup>3</sup>/t, which is basically equal to that of methane produced by anthracite. BSR takes effect under strictly anaerobic condition, within deep buried coal seams, which is beneficial to the storing and gathering of H<sub>2</sub>S. However, the number high sulfur coal seams of China whose H<sub>2</sub>S release exceeds the national coal mine regulated 6.6 ppm is small. That means the restoration of H<sub>2</sub>S in high sulfur coal seams requires much more than that of methane.

### 3.2. TSR

Sulfate electronation refers to the process that sulfate is restored H<sub>2</sub>S under the influence of thermochemistry. The essence is that sulfate interacts and affects with organics or HC on the condition of high temperature, and restore sulfate back into H<sub>2</sub>S and CO<sub>2</sub> (Cai et al., 2005; Cody et al., 1999; Cai et al., 2001). In the process, sulfate is restored and organics (HC) is oxygenized. A good deal of domestic and overseas researches confirm that TSR is the major form of producing high hydrogen sulfide gas and hydrogen sulfide gas (Cai et al., 2009; Chambers and Trudinger, 1979). At the same time, some low hydrogen sulfide gas and slight hydrogen sulfide gas are also proved to be formed under the influence of TSR (Desrocher et al., 2004; Fu et al., 2006; Krouse et al., 1988). It is generally acknowledged that high temperature, abundant HC organics and grown sulfate are the general conditions of forming natural gas containing H<sub>2</sub>S (Cheng et al., 2009). Nearly no high H<sub>2</sub>S gas fields through TSR currently discovered were produced under the temperature below 100 °C (except Zhaolanzhuang in North China). Hence, TSR occurrence needs high temperature condition. Goldhaber and Orr (1995), based on the experimental data for fluid inclusions, inferred that TSR reaction needs the lowest temperature of 100–140 °C. Rooney (1995) and Claypool and Mancini (1989), from the research on Smackover formation, discovered that TSR occurrence temperature is 160–180 °C. Worden and Smalley (1996) believed only when the temperature in the reservoir is higher than 140 °C, will sulfur-bearing gases be observed. Machel (1987), based on the fluid inclusions data of oolite dolomite in Devonian system Nisku formation in the west of Canada, and by combining heat maturity data and the organic geochemical data in basin gases, inferred that TSR occurred in the temperature range of 125–145 °C. Machel (2001) proposed that TSR mainly occurred in the temperature of 120 °C. Though the process of TSR is complex, on the condition of extraordinarily enrichment of H<sub>2</sub>S, the genetic type can be recognized all the same combining petrology, stratigraphic geology, isotope fractionation characteristics and fluid inclusion and temperature determination by means of apatite fission.

At present, the study of cause of formation from H<sub>2</sub>S is still a blind point, but as far as the temperature and sulfur isotope character are concerned, and sulfate meets the requirements, H<sub>2</sub>S from TSR factor is possible. There are a good deal of coal field in our country that has become peranthracite and dry-burning coal. The reflectivity of coal vitrinite is  $R_{\max} > 1.5$ . On the basis of roughly

correspondence of temperature and vitrinite reflectivity, the temperature of thermal evolution is over 120 °C (Seal, 2006) and reaches the temperature condition of TSR. For example, in the Permian-carboniferous coal seams of Xiqinshui Basin (Taiyuan Formation and Shanxi Formation), the highest temperature can be 268 °C and it is usually above 150 °C (Smith and Philips, 1990; Shen et al., 1997). Permian coal seams (Longtan Formation and Changxing Formation) in southern China it is also provided with the temperature condition of TSR. It is just the mines of this coal rank where H<sub>2</sub>S toxication fatal accidents and abruption gush take place.

Both BSR and TSR produce the fractionation of sulfur isotope. The  $\delta^{34}\text{S}$  of H<sub>2</sub>S from the former is heavily loosened and usually negative, the smallest being  $-50.0\text{‰}$ . The latter fairly approaches the sulfur isotope in sulfate and is mostly above  $+10.0\text{‰}$  (Dai et al., 2002; Giveina and Miller, 1985). Presently the measurement data of H<sub>2</sub>S gas isotope of coal rake is rare (Bernier, 1984; Berresheim and Jaeschke, 1983) and the determination of sulfur isotope is focused on organic sulphur and iron pyrite (Rye, 2005). Since the sulphur isotope of iron pyrite approaches H<sub>2</sub>S (Seal, 2006), the sulfur isotope of iron pyrite can be essentially regarded as the sulphur isotope of H<sub>2</sub>S and be analyzed. The data of sulfur isotope of organic sulfur and pyrite in the medium and high coal seams is negative overall. But the range ability is huge (Orr, 1974; Rye, 2005) and the reason may be synthetic action of different factors. For example, the data of organic sulfur and pyrite in the high coal seams of Longtan Formation of the later Permian in Guizhou, China is respectively  $-30.30\text{‰} \sim +62.69\text{‰}$  and  $-13.43\text{‰} \sim +10.87\text{‰}$ . And that of the iron pyrite is between  $-9.18\text{‰} \sim -30.30\text{‰}$  and  $+9.45\text{‰} \sim +38.40\text{‰}$  (Orr, 1974). These data of isotope illustrate that vauculian spring group coal rake may experience the double forming process of BSR and TSR.

### 3.3. Igneous activity

H<sub>2</sub>S from igneous activity mainly refers to the one that volatilizes from underground igneous activity and then comes to the rock stratum. H<sub>2</sub>S caused by coal seams pyrolysis due to igneous activity roasting or TSR is not included.

The abundance of sulfur element in inner earth is higher than it is on the crust. Igneous activity from the mantle contains volatile components such as sulfur dioxide and H<sub>2</sub>S. In the process of surface migration, the temperature of igneous activity gradually decreases, causing degassing process. Volatile gas departs from igneous activity, producing steam, carbondioxide, sulfur dioxide and H<sub>2</sub>S. The quantity of H<sub>2</sub>S, which is less than the others (Wang et al., 2006), is dependent on the components of igneous activity, gas migration conditions and so on. According to the statistics by observing volcanic eruption, the percentage of sulfur dioxide is up to 10–15%, while H<sub>2</sub>S only occupies 6.0–7.0% of sulfur dioxide (Worden and Smalley, 1996; Worden et al., 1995). Gas departed from igneous activity will condense when the temperature decreases, and the proportion of H<sub>2</sub>S will increase to some extent. The proportion of carbondioxide, however, is higher than sulfur dioxide and H<sub>2</sub>S, and a large part of H<sub>2</sub>S will be soluble in water, so the proportion of H<sub>2</sub>S will be no more than 3.0–3.5%; on average it is less than 1%. Furthermore, after it comes to the coal seams and combines with other gas, the real proportion of H<sub>2</sub>S in the coal seams is even lower. According to the statistics, the average  $\delta^{34}\text{S}$  proportion of H<sub>2</sub>S caused by degassing process is close to aerosiderite, changing from  $-5\text{‰}$  to  $+5\text{‰}$  (Smith and Philips 1990).

## 4. Identification of H<sub>2</sub>S in coal seams

The exact identification of the formation models of H<sub>2</sub>S is the foundation of finding out the distribution of H<sub>2</sub>S, predicting the

release amount and taking corresponding measures. The formation models of H<sub>2</sub>S can be identified based on their different characteristics, if the thermal evolution, sedimentary environment, igneous activity, sulfate sources and sulfur isotope is commanded in the first place.

#### 4.1. Identification of BSR

The primary identification mark for BSR is the coal forming environment, thermal evolution and sulfur isotope. Marine facies, littoral facies and transgression in the coalification phase are thought as the material bases of BSR, as well as thermal history, as the condition, sulfur isotope is the main manifestation of sulfur isotope through BSR. When the sedimentary environment satisfies the condition of sulfate (this sedimentary environment can accept the supply of the sulfate from the sea) and the temperature is below 120 °C, BSR can be identified. When the value of sulfur isotope, especially the  $\delta^{34}\text{S}$  of the pyrites tend to be negative, BSR can be basically determined.

No. 9 and No. 10 coal seams in Wuda Colliery, Inner Mongolia, are below the Taiyuan Formation, and they are both high sulfur coal seams, among which the percentage of the sulfate in coal N.9 is 1.56–6.69%, with the mean of 3.46%. The sedimentary environment of coal seams is mainly littoral facies, with  $R_{o,max} = 0.81$ –1.22% (Dai et al., 2002). The two coal seams are the major extracting seams, whose H<sub>2</sub>S content is high. 50% of the working surfaces have H<sub>2</sub>S release in large amount during the extracting process (Wang et al., 2008). According to the vitrinite reflectance anisotropy, the maximum temperature in the burial process is below 120 °C (Smith et al., 1982). The sedimentary environment and temperature define that it is BSR. Besides, the  $\delta^{34}\text{S}$  distribution of pyrites in No. 9 coal seam is  $-18.7\text{‰} \sim +1.1\text{‰}$  (Casagrande et al., 1979), which further proves that H<sub>2</sub>S from No. 9 and No. 10 coal seams in Wuda Colliery results from BSR.

#### 4.2. Identification of TSR

The study of coal rake H<sub>2</sub>S gas TSR factor is vacant at home and abroad, but the abundant research of oil gas, esp. H<sub>2</sub>S natural gas can be taken as example. According to the study of oil gas field, there are three outstanding features of this type: firstly, coal rock stratum should be full of sulfate (gypsum); secondly, the hiding temperature of coal rake should be over 120 °C in the process of alteration and the  $R_{o,max}$  is roughly above 1.2% for the coal Permian period in our country; thirdly, the  $\delta^{34}\text{S}$  of iron pyrite is positive value, being usually above +10‰. In fact, the coal rake equipped with the condition of TSR is usually also equipped with the condition of BSR and the production of the both approach to each other, therefore, in the places where the coal rake H<sub>2</sub>S is rich it is very difficult to make a distinction between BST factor and TSR factor. The medium to high sulphur-containing coal rake of Permo-carboniferous period in south and north China possesses this feature, and it is necessary to study the preservation condition, stratum sequence feature and petrology feature of coal rake gas and make overall judgements on the basis of measuring various sulfur compounds, carbon and oxygen isotope in the coal seams. According to the study of natural gas (Desrocher et al., 2004; Luo et al., 2005), the  $\delta^{34}\text{S}$  data of TSR factor H<sub>2</sub>S distribute gathering and approaches that of sulphur (within 10‰). The  $\delta^{34}\text{S}$  data may become an important feature of judging coal rake TSR factor type.

Presently, no adequate evidences prove coal seams and coal shafts are formed due to TSR. However, according to the distribution of organic sulfur and sulfide, stratum sequence features and  $\delta^{34}\text{S}$  feature in Permian coal seams in South China, it is assumed that the two H<sub>2</sub>S poisoning accidents in Sichuan and H<sub>2</sub>S abnormal

emission in Xiqu Coal Mine in Shanxi in 2010 were related to H<sub>2</sub>S due to TSR origin.

#### 4.3. Identification of igneous activity

The most prominent characteristics of the formation of igneous activity are that the concentration and contents of H<sub>2</sub>S in the coal seams has no direct relation with sulphur content and its existing form. H<sub>2</sub>S that causes the formation of igneous activity has two obvious marks: one is that igneous activity intrusion is obvious; the other is that the average  $\delta^{34}\text{S}$  proportion of H<sub>2</sub>S is close to aeroderite, changes from  $-5\text{‰}$  to  $+5\text{‰}$ , which is quite different from the isotopic ratios of other sulfides. It is easy to judge the formation modes of igneous activity under the condition of low sulfur coal seams and obvious igneous activity intrusion. It will be easier to draw the conclusion if the percentage of  $\delta^{34}\text{S}$  of sulfides can be provided.

Bayi Coal Mine in Zaozhuang, Shandong Province is a good example to illustrate the formation of igneous activity. The igneous activity rocks are advanced intrusions of Yanshan magmatite, and their occurrence is mostly dike. The abnormal area of H<sub>2</sub>S lies in the west side of igneous activity rocks, No. 1 mining area in the west of Shanxi groups 3. The surface of coal seams is narrow, and becomes wider as the depth goes deeper. It is consistent with the change of the thickness of dike. The average proportion of sulfur in coal seams is 0.69%, and the concentration of H<sub>2</sub>S is 0.02% to 0.5%. Two  $\delta^{34}\text{S}$  of H<sub>2</sub>S is 1.24‰ and 1.67‰, and the  $\delta^{34}\text{S}$  of carbonate in Taiyuan group is 1.44‰. The  $\delta^{34}\text{S}$  of H<sub>2</sub>S in coal seams is identical with the characteristics of isotopic ratios formed by igneous activity, and is different from BSR and TSR. Therefore, H<sub>2</sub>S in Bayi Coal Mine belongs to the formation modes of igneous activity, other than thermochemical effect caused by thermal action. Judging from available materials, Cuizhuang Coal Mine in Shandong Province belongs to the formation modes of igneous activity (Brinkmann and Santos, 1974).

### 5. Problems and discussions

Theoretically, H<sub>2</sub>S will be generated from the degradation of the peat accumulation phase under oxygen-rich environment and thermochemical decomposition at a high temperature (over 100 °C) of the coalification phase. However, considering the current research, there is little possibility of existing H<sub>2</sub>S produced by the above two conditions. Moreover, how to identify the formation models of H<sub>2</sub>S is the basis of seeking the occurrence laws and enacting prevention measures.

#### 5.1. Discussions on thermochemical decomposition and pyrolysis

Coal-forming plants are changed into sulfur organic compounds through complicated assimilation and reduction, to which biochemical reactions happened close to the peat surface during the peat accumulation phase. Then, if oxygen is available, sulfur organic in plants will decay and decompose to produce H<sub>2</sub>S. H<sub>2</sub>S produced in the above is universal, yet it is released to the air through water. In line with the practical determination (Wu et al., 1997), the content of H<sub>2</sub>S in the lakes of the Amazon is as high as 1.5 g/m<sup>3</sup>, while that in peat during the accumulation phase is 0.0–130 g/t (0–0.1 m<sup>3</sup>/t), majority of which comes from BSR (Zhu et al., 2005). Therefore, H<sub>2</sub>S formed through biochemical decomposition has no practical effect on the occurrence and release of H<sub>2</sub>S in coal mines. At the moment, there should be no H<sub>2</sub>S from biochemical decomposition.

The contribution of H<sub>2</sub>S formed by biochemical decomposition still calls for further research (Zhu et al., 2006a, 2006b). Yet there should be no such H<sub>2</sub>S in coal seams. Yi Duan et al. (Zhang et al., 2005) calculated the productivity of H<sub>2</sub>S in the thermal simulation

of coal and peat; the density is 0–0.8%. Compared with the output rate from the BSR, this result can be ignored. H<sub>2</sub>S is seldom analyzed or mentioned in the analysis of coalbed gas and mash gas and the simulation experiments of the coalbed gas pyrolysis, either because of the low productivity during the pyrolysis process or the low density of H<sub>2</sub>S in coal seams (Clayton, 1998), which failed to attract attention.

### 5.2. Concentration in coal seams

H<sub>2</sub>S is more chemically active, soluble in water and readily oxidized to sulfate as well as pervasive in comparison with other common gases in the coal seams, such as methane, CO<sub>2</sub>, Nitrogen and heavy hydrogen. And this explains the scarcity of H<sub>2</sub>S in coal seams. On the contrary, H<sub>2</sub>S is similar to other gases, especially methane, in the preservation and transportation process since the amount of H<sub>2</sub>S will increase with the depth of the burial coal seams. In recent years, an increasing number of casualty accidents and shutdowns resulting from the sudden release of H<sub>2</sub>S have happened to coal mines in China, which is likely to be associated with H<sub>2</sub>S content and the increase in mining depth and mining amount.

Another problem worthy of attention is: the relationship between H<sub>2</sub>S content and concentration and the sulfur of other forms in coal seams. Coal seam H<sub>2</sub>S is the intermediate product generated from the organic and inorganic sulfur in coal seams. Through the complicated biochemical process in BSR and TSR, it is converted into metal sulfides mainly in the form of organic sulfur and pyrite (Philips et al., 1990). Theoretically, in the given generation amount, the more the conversion, the less the remaining H<sub>2</sub>S. In fact, a large amount of H<sub>2</sub>S was generated through BSR and TSR, while only a small part of it was converted into organic sulfur and pyrite (Rye, 2005; Shen, 1994). Moreover, the Fe<sup>2+</sup> is considerably abundant in coal seams, high content sulfur in coal seams is actually the mark by which a large quantity of H<sub>2</sub>S was generated in coal-forming process. Hence, the H<sub>2</sub>S content and concentration in coal seams should have a positive correlation with total sulfur content: the higher total sulfur content, the higher H<sub>2</sub>S content and concentration. Wuda coal field in Inner Mongolia is such an example (Wang et al., 2008).

## 6. Conclusions and prospects

The abnormal H<sub>2</sub>S gathering mainly results from BSR, TSR and igneous activity. Biochemical degradation and pyrolysis contribute little to H<sub>2</sub>S gathering, which can be ignored. The formation models of H<sub>2</sub>S in coal seams can be determined from the perspective of geological structure, sulfate source, thermal evolution, isotope property, petrology and so on. H<sub>2</sub>S increases with the depth of coal seams, which manifests a positive correlation with sulfur in coal seams.

H<sub>2</sub>S formation models and gathering are little trodden in the colliery safety and the development of coal seam gas. H<sub>2</sub>S will impose more threat on the safety and health of colliery workers and the negative effects on the coal mining and gas development will grow increasingly greater, thus:

- Extensive researches on the formation models, identification and gathering principles of H<sub>2</sub>S need to be carried out by beginning with the basic researches through multidisciplinary methods so as to lay foundation for predicting H<sub>2</sub>S distribution law and content, and to take appropriate preventive measures;
- More sophisticated testing technique is needed for H<sub>2</sub>S content within coal seams;
- The law of three-phase interaction between H<sub>2</sub>S, chemical additive and coal body needs to be further researched so as to improve H<sub>2</sub>S prevention and control technique.

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## References

- Berner, R.A., 1984. Sedimentary pyrite formation: an update. *Geochimica et Cosmochimica Acta* 48, 605–615.
- Berresheim, H., Jaeschke, W., 1983. The contribution of volcanoes to the global atmosphere sulfur budget. *Journal of Geophysical Research* 88 (C6), 3732–3740.
- Brinkmann, W.L.F., Santos, U.D.M., 1974. The emission of biogenic hydrogen sulfide from Amazonian floodplain lakes. *Tellus* 26 (1–2), 261–267.
- Clayton, J.L., 1998. Geochemistry of coalbed gas: a review. *International Journal of Coal Geology* 35 (1–4), 159–173.
- Claypool, G.E., Mancini, E.A., 1989. Geochemical relationships of petroleum in Mesozoic reservoirs to carbonate source rocks of Jurassic Smackover Formation, southwestern Alabama. *American Association of Petroleum Geologists Bulletin* 73, 904–924.
- Casagrande, D.J., Gronli, K., Sutton, N., 1979. The distribution of sulfur and organic matter in various fractions of peat: origins of sulfur in coal. *Geochimica et Cosmochimica Acta* 44 (1), 25–32.
- Cai, C.F., Hu, G.Y., He, H., 2005. Geochemical characteristics and origin of natural gas and thermochemical sulfate reduction in Ordovician carbonates in the Ordos Basin, China. *Journal of Petroleum Science and Engineering* 48, 209–226.
- Cody, J.D., Hutcheon, I.E., Krouse, H.R., 1999. Fluid flow, mixing and the origin of CO<sub>2</sub> and H<sub>2</sub>S by bacterial sulfate reduction in the Mannville Group, Southern Alberta, Canada. *Marine and Petroleum Geology* 16, 495–510.
- Cai, C.F., Hu, W.S., Worden, R.H., 2001. Thermochemical sulfate reduction in Cambro-Ordovician carbonates in Central Tarim. *Marine and Petroleum Geology* 18, 729–741.
- Cai, C.F., Li, K.K., Ma, A.L., 2009. Distinguishing the Cambrian source rock from the Upper Ordovician, evidence from sulfur isotopes and biomarkers in the Tarim basin. *Organic Geochemistry* 40, 755–768.
- Chambers, L.A., Trudinger, P.A., 1979. Microbiological fractionation of stable sulphur isotopes: a review and critique. *Geomicrobiology* 1 (3), 249–293.
- Cheng, Jin, Wang, Xinwen, Wang, Xiaoni, 2009. Characteristic of thermal history in shanxi qinshui basin. *Geoscience* 23 (6).
- Cross, M.M., Manning, D.A.C., Bottrell, S., Worden, R.H., 2004. Thermochemical sulphate reduction (TSR): experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. *Organic Geochemistry* 35, 393–404.
- Dai, Jinxing, 1985. Discussion on the distribution characteristics, classification and cause of formation: genesis of natural gas including hydrogen sulfide gas in China. *Aggradation Transaction* 3 (4), 109–120.
- Desrocher, S., Hutcheon, I., Kirste, D., Henderso, C.M., 2004. Constraints on the generation of H<sub>2</sub>S and CO<sub>2</sub> in the subsurface Triassic, Alberta Basin, Canada. *Chemical Geology* 204, 237–254.
- Dai, S.F., Ren, D.Y., Tang, Y.G., 2002. Distribution, isotopic variation and origin of sulfur in coals in the Wuda coalfield, Inner Mongolia, China. *International Journal of Coal Geology* 51, 237–250.
- Duan, Y., Wu, B.X., Zheng, C.Y., et al., 2005. Thermal simulation of the formation and evolution of coalbed gas. *Chinese Science Bulletin* 50 (Supp.), 40–44.
- Fu, Xuehai, Wang, Wenfeng, Yue, Jianhua, et al., 2006. Analysis on the abnormal reason of hydrogen sulfide gas in gas of zaozhuang bayi mine. *Coal Transaction* 31 (2), 206–210.
- Givena, P.H., Miller, R.N., 1985. Distribution of forms of sulfur in peats from saline environments in the Florida Everglades. *International Journal of Coal Geology* 5 (4), 397–409.
- Goldhaber, M.B., Orr, W.L., 1995. Kinetic controls on thermochemical sulfate reduction as a source of sedimentary H<sub>2</sub>S [A]. In: Vairavamurthy, M.A., Schoonen, M.A.A. (Eds.), *Geochemical Transformations of Sedimentary Sulfur* [C]. ACS Symposium Series, vol. 612. pp. 412–425.
- Hao, F., Guo, T.L., Zhu, Y.M., 2008. Evidence for multiple stages of oil cracking and thermochemical sulfate reduction in the Puguang gas field, Sichuan Basin, China. *American Association of Petroleum Geologists Bulletin* 92, 611–637.
- Hou, Lu, Hu, Jun, Tang, Jun, 2005. Distribution characteristics and cause of formation: cause of formation of hydrogen sulfide gas of carbonate rock giant gas field in China. *Oil Transaction* 26 (3), 26–32.
- Krouse, H.R., Viau, C.A., Eliuk, L.S., Ueda, A., Halas, S., 1988. Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature* 333, 415–419.
- Luo, Yunfei, Li, Wenhua, Jiang, Ying, et al., 2005. Research on distribution characteristics of coal in china. *Coal Conversion* 28 (3), 14–18.
- Machel, H.G., 1987. Saddle dolomite as a by-product of chemical compaction and thermochemical sulfate reduction. *Geology* 15, 936–940.
- Machel, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings—old and new insights. *Sedimentary Geology* 140, 143–175.

- Manzano, B.K., Fowler, M.G., Machel, H.G., 1997. The influence of thermochemical sulfate reduction on hydrocarbon composition in Nisku reservoirs, Brazeau river area, Alberta, Canada. *Organic Geochemistry* 27 (7/8), 507–521.
- Machel, H.G., Krouse, H.R., Sassen, R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry* 10, 373–389.
- Ma, Yuzhen, Tao, Mingxin, Zhang, Xinmin, et al., 2008. Hydrogen sulfide gas and sulfur dioxide in coalbed methane and natural gas and their perniciousness. *Geology Transaction* 82 (10), 1408–1415.
- Ni, Jianyu, Hong, Yetang, 1999. Community characteristics of sulphur isotope of late permianepoch coal in guizhou. *Geology Earth Science* 27 (2), 63–69.
- Orr, W.L., 1974. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation—study of big horn basin Palaeozoic oils. *American Association of Petroleum Geologists Bulletin* 50, 2295–2318.
- Philips, R., Smith, J.W., Byrnes, R., 1990. Hydrogen sulfide gas occurrence at Southern Colliery. Bowen Basin Symposium, 91–97.
- Rooney, M.A., 1995. Carbon isotopic ratios of light hydrocarbons as indicators of thermochemical sulfate reduction. In: Grimah, J.O. (ed.), *Organic Geochemistry: Applications to Energy, Climate and Human History*. San Sebastian, A. I. G. O. A., Donostia, pp. 523–525.
- Rye, R.O., 2005. A review of the stable-isotope geochemistry of sulfate minerals in selected igneous environments and related hydrothermal systems/isotope properties of sulfur compounds in hydrothermal processes. *Chemical Geology* 215 (1–4).
- Shen, Ping, 1994. A brief study on integrated control technique of hydrogen sulfide in wuda mining area. *Coal Safety*, 3.
- Seal, R.R., 2006. Sulfur isotope geochemistry of sulfide minerals. *Mineralogy and Geochemistry* 61 (1), 633–677.
- Smith, J.W., Gould, K.W., Rigby, D., 1982. The stable isotope geochemistry of Australian coals. *Organic Geochemistry* 3 (2).
- Smith, J.W., Philips, R., 1990. Isotopic study of coal associated hydrogen sulfide. In: Orr, W.L., White, C.M. (Eds.), *Geochemistry of Sulfur in Fossil Fuels*. American Chemical Society Symposium, Series No. 429, pp. 568–574 (Chapter 28).
- Shen, Ping, Xu, Yongchang, Wang, Jinjiang, et al., 1997. Hydrogen sulfide sulfur isotopic compositions and sedimentary geochemistry phase in natural gas. *Aggradation Transaction* 15 (2), 216–219.
- Wang, Liansheng, Liu, Li, Guo, Zhan qian, et al., 2006. Discussion on hydrogen sulfide cause of formation in associated gas in daqing oil field. *Natural Gas Geoscience* 17 (1), 51–54.
- Worden, R.H., Smalley, P.C., 1996. H<sub>2</sub>S-producing reactions in deep carbonate gas reservoirs, Khuff Formation, Abu Dhabi. *Chemical Geology* 133, 157–171.
- Worden, R.H., Smalley, P.C., Oxtoby, N.H., 1995. Gas souring by thermochemical sulfate reduction at 140 C. *American Association of Petroleum Geologists Bulletin* 79, 854–863.
- Wang, Hongyan, Wan, Tianfeng, Li, Jingming, et al., 2008. The control to high coal rank, Coalbed methane beneficiation from regional tectothermal event. *Earth Science Frontiers* 15 (5), 364–369.
- Wu, Chonglong, Yang, Qi, Liu, Gang, et al., 1997. Theory and method of thermokinetic analysis of coal metamorphism. *Coal Transaction* 22 (3), 225–229.
- Zhu, Guangyou, Zhang, Shuichang, Liang, Yingbo, et al., 2005. Isotopic evidence of cause of formation: origin of natural gas TSR full of hydrogen sulfide in feixianguan group ES area sichuan. *China Science (D volume)* 35 (11), 137–1046.
- Zhu, Guangyou, Zhang, Shuichang, Liang, Yingbo, et al., 2006a. Cause and evidence of hydrogen sulfide of weiyuan gas field in sichuan basin. *Science Bulletin* 51 (23), 2780–2788.
- Zhu, Guangyou, Zhang, Shuichang, Liang, Yingbo, et al., 2006b. Discussion on isotopic component and cause of formation: origin of hydrogen sulfide in sichuan basin. *Earth chemistry* 35 (4), 432–442.
- Zhang, S.C., Zhu, G.Y., Liang, Y.B., et al., 2005. Geochemical characteristics of the zhaolanzhuang sour gas accumulation and thermochemical sulfate reduction in the jixian sag of bohai bay basin. *Organic Geochemistry* 36, 1717–1730.