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Analysis of Influencing Factors and Genetic Types of H_2S Anomaly in Northern Binchang Mining Area of Huanglong Jurassic Coalfield, Ordos Basin, China

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Abstract: The H_2S anomalies occurred during the construction and trial production of the Ya Dian coal mine in the northern part of the Binchang mining area in the southern margin of Ordos Basin. During excavation, the maximum is about 140 ppm, and H_2S overrun often occurs in fully mechanized working-face of the first mining area. Distribution characteristics of sulfur content in No. 1 and No. 4 coal seams in the study area are mostly ferric sulfate, the pH value of groundwater is alkaline, the geothermal temperature is between 30 and 40 degrees, and the degree of coal metamorphism belongs to non-sticky coal-long flame coal in low rank. No. 1 and No. 4 coal in the western part of the mining area form high sulfur areas around the mining area. After analyzing the factors causing the H_2S anomaly, such as the sealing effect of the compact surrounding rock on the roof and floor of the coal seam, the fractured zone runs through the Luohe Formation rock strata, causing the water leaching or water gushing and the low degree of metamorphism, which weakly adsorbs H_2S. Measures such as monitoring, ventilation of roadways, blocking by grouting, strengthening drainage and alkaline spraying were taken to effectively prevent and control H_2S anomalies and ensure workers' health and mine safety. Ground temperature of 30 ~ 40°C is the optimum temperature for the reproduction of sulfate reducing bacteria (SRB). The coexistence of sulfate and coal provides material conditions for BSR. Natural gas C2-C8 and unsaturated hydrocarbons in gas residues of No. 1 and No. 4 coal seams provide energy and material basis for H_2S production by sulfate reduction. Weak alkaline groundwater with pH 7.7 ~ 8.3 provides living environment for SRB. The water quality belongs to $SO_4Cl^-K^+Na$ type, Salinity of the water is 4.826 ~ 5.277g/l, SO_4^{2-} content is 2 088.87 ~ 2 292.82 mg/l (greater than 1 500 mg/l), Water is rich in SO_4^{2-}, so under the condition of hydrocarbon-rich, BSR is easy to occur and hydrogen sulfide is formed. Combined with other conditions, the H_2S gas in the mine is determined to be BSR origin.

Keywords: Huanglong Jurassic Coalfield, Influencing Factors of H_2S Anomaly, Genesis Type, Binchang Mining Area, Ya Dian Coal Mine

1. Introduction

The abnormal H_2S area in coal mine gas refers to the area where the volume fraction of H_2S in coal mine exceeds 6.6×10^{-6} stipulated in the "Coal Mine Safety Regulations" (The 2022 Edition) [1]. H_2S is one of the most common toxic gases in underground coal mines. The lower limit of the volume fraction of H_2S smell is $(0.2 \sim 0.3) \times 10^{-6}$, there is a distinct smell of rotten eggs. When H_2S volume fraction is $(2 \sim 3) \times10^{-5}$, there is strong odor; when the volume fraction $(1 \sim 1.5) \times10^{-4}$, it will cause olfactory paralysis; when the volume fraction 1.0×10^{-3}, a few seconds can make people lose consciousness. and even death [2, 3]. H_2S has strong chemical activity and is easy to corrode metal iron equipment, So as to shorten the service life of downhole equipment and bring potential safety hazards [4, 5]. In order to ensure safe production, a hydrogen sulfide source classification evaluation system has been constructed, dividing the working face into four areas with low, medium, high, and ultra-high hydrogen sulfide hazards. H_2S has strong chemical activity, which greatly reduces the operating cycle and lifespan of underground equipment due to its corrosion to metal and iron equipment, reduces safety assurance, and becomes a safety hazard. The average removal rate of hydrogen sulfide by modified alkaline solution is 90.3%, And there is no phenomenon of hydrogen sulfide exceeding the limit and secondary escape, and the treatment effect is significant [6]. The efficiency of spraying absorption liquid hydrogen sulfide gas concentration at the coal cutting point of the shearer drum has decreased by 84.4% and 86.7%, respectively, achieving good treatment effect [7]. The "three pressure belt" segmented water injection process technology is used to pre inject hydrogen sulfide absorption liquid into the excavation working face and the high-pressure injection of hydrogen sulfide absorption liquid from the cutting head is used for treatment measures [8]. In Inner Mongolia, Xinjiang, Shanxi and Shaanxi provinces, there are some problems of H_2S overrun in some mines (>6.6×10^{-6}). Due to the lack of reliable management technology, some mining areas are forced to be closed, resulting in serious waste of resources [9-12].

At present, H_2S abnormal overrun management mainly adopts the following measures: strengthening monitoring and controlling, pre pumping, discharging lime, increasing air volume [12-15], enhancing personal protection [8], chemical injection of coal in the liquid [16], and reducing the speed of cutting coal [17], and so on. Except for conventional methods, at the same time, some experimental simulation and on-site process improvements have been taken by scholars, which have better H_2S treatment effect. Surfactant was added to reduce the surface tension of the absorbent solution, increase the permeation radius and improve the removal efficiency of hydrogen sulfide adsorbed in coal. Hufu [18] (2014) established an H_2S absorption simulation experiment system to simulate the actual situation of H_2S in coal mine. The experiment shows that the order of influencing factors of H_2S absorption efficiency are: wind speed > concentration of absorbent solution > concentration of H_2S > spray flow rate. In order to solve the problems in the process of injecting H_2S absorbent liquid into coal seam and the process of adding absorbent liquid, the research shows that the suitable conditions for injecting water into coal seam are 6 MPa, 0.3% mass fraction of wetting agent and 1.0% mass fraction of absorbent liquid [19]. Under these conditions, the absorption efficiency of H_2S in driver's place and support sidewalk is 65.1% and 71.4% respectively, the absorption efficiency of H_2S in the caving area can reach 56.3% during the caving period. Song Yucheng et al. [20] (2014) adopted water jet cutting and reaming technology to form the overall communication between cracks in the boreholes. The pulsed dynamic pressure injection of alkali water sorbent, with the advancing of the working face, injected two times the alkali water sorbent, which absorbed the H_2S efficiency internal coal body. Liu Kui [21] (2016) adopted the monitoring and analysis method of hydrogen sulfide, spraying absorbent liquid absorption at the cutting place of shearer drum, and a new technology of hydrogen sulfide treatment combined with intercepting and capturing absorbent liquid spraying under the air flow of shearer. The test and analysis showed that the reduction efficiency of hydrogen sulfide gas concentration at the driver's place and under the air flow of shearer reached 84.4% and 86.7%, respectively, and achieved good control effect.

According to the causes of H_2S, domestic and overseas scholars think that can be divided into 3 categories: microbial sulfate reduction (BSR), sulfate thermochemical reduction (TSR) and magmatic origin (TDS) [10, 11, 22, 23]. The abnormal contents of H_2S, CO_2, CO, N_2 and heavy hydrocarbon in mine gas have increasingly prominent influence on coal production and safety. Based on the abnormal accumulation of the above components in coal mine gas, the causes are analyzed, it is considered that abnormal thermochemistry, surface water infiltration, roof capping, coal rank and coal rock types are the main factors causing the abnormal composition of H_2S and CO_2 [24].

Binchang Mining Area of Huanglong Jurassic Coalfield has made rapid development in recent ten years. With the development of mining area, H_2S abnormal overrun occurred frequently, and H_2S abnormal emission occurred during the construction of Ya Dian coal mine in the northern part of the mining area [12]. Meanwhile, there were abnormal H_2S gas in Xiagou, Tingnan and Hu Jiahe Coal Mines in the South and central part of the mining area [13-15]. This paper studies the abnormal concentration of H_2S gas in the first set of working face of No. 1 and No. 4 coal seams and No. 4 coal seam exposed in the main air return roadway and belt roadway of the first mining area, which seriously affects the safety of production and the health of workers. According to the sulfur content and distribution characteristics of No. 1 and No. 4 coal seams, the influencing factors of H_2S gas anomaly are analyzed, and the origin of H_2S in low-rank coal mines is discussed based on the current research results. In view of the abnormal areas, scientific control measures have been taken to effectively control the abnormal outflow of H_2S, which ensures the safety of mine production and the health and safety of workers.

2. General Situation

The Ya Dian coal mine is located in the Bin county of Shaanxi province, and its production design capacity is 4 Mt/a. The mining area is 19 km long in E-W, 4.2 km wide in N-S, 53.05 km^2 in area, and 6.37×10^8t in geological reserves. The mine belongs to a low gas mine. No. 1 and No. 4 coal seams can be mined. The coal seams are stable in occurrence and simple in structure. The thickness of No. 1 coal seam is 0.20 ~ 3.60 m, with an average of 2.21 m, which belongs to most of the stable coal seams. The thickness of No. 4 coal seam is 0.15 ~ 20.87 m, with an average of 12.07 m, which belongs to mostly stable and stable coal seams. The thickness of No. 4 coal seam varies little along the strike, but greatly along the trend. Overall, the thickness from north to south is from thick to thin to pinch out, occupying four classifications of extra-thick, thick, medium-thick and thin coal seams, with extra-thick coal seams as the main one, and the thickest section of coal seam is located in No. 10-1 borehole. No. 4

coal belongs to non-sticky coal, medium-high volatile matter, high calorific value, low sulfur, low ash and low phosphorus. Which is a good power fuel, industrial gasification and low temperature dry distillation coal.

Ya Dian coal mine is located on the north wing of the Qilipu-Xipo slope anticline, which is a monoclinic structure tending to the N-W. The dip angle of the northern wing is 3 ~ 5 degrees, the southern wing dip is 2 ~ 3 degrees, the north dip is gentle and the South dip is steep, no faults and magmatic rocks are found, and the structure is simple (Figure 1). The stratas in the Binchang mining area are from the bottom up to the upper, such as the upper Triassic Hujiahe Formation (T_3h); the lower Jurassic Fuxian Formation (J_1f), and the middle Jurassic Formations as the Yan'an Formation (J_2y), the Zhiluo Formation (J_2z), and the Anding group (J_2a) et al., and the lower Cretaceous Formations as Yijun Formation (K_1y), the Luohe Formation (K_1l), and the Huachi Formation (k_1h), and the Neogene Xiao Zhang Gou Formation (N_2x), the Quaternary middle lower Pleistocene (Q_{1+2}), the upper Pleistocene Formation (Q_3m), Holocene alluvial horizon (Q_4). The Jurassic middle Yan'an Formation is the main coal bearing strata with a nearly horizontal occurrence.

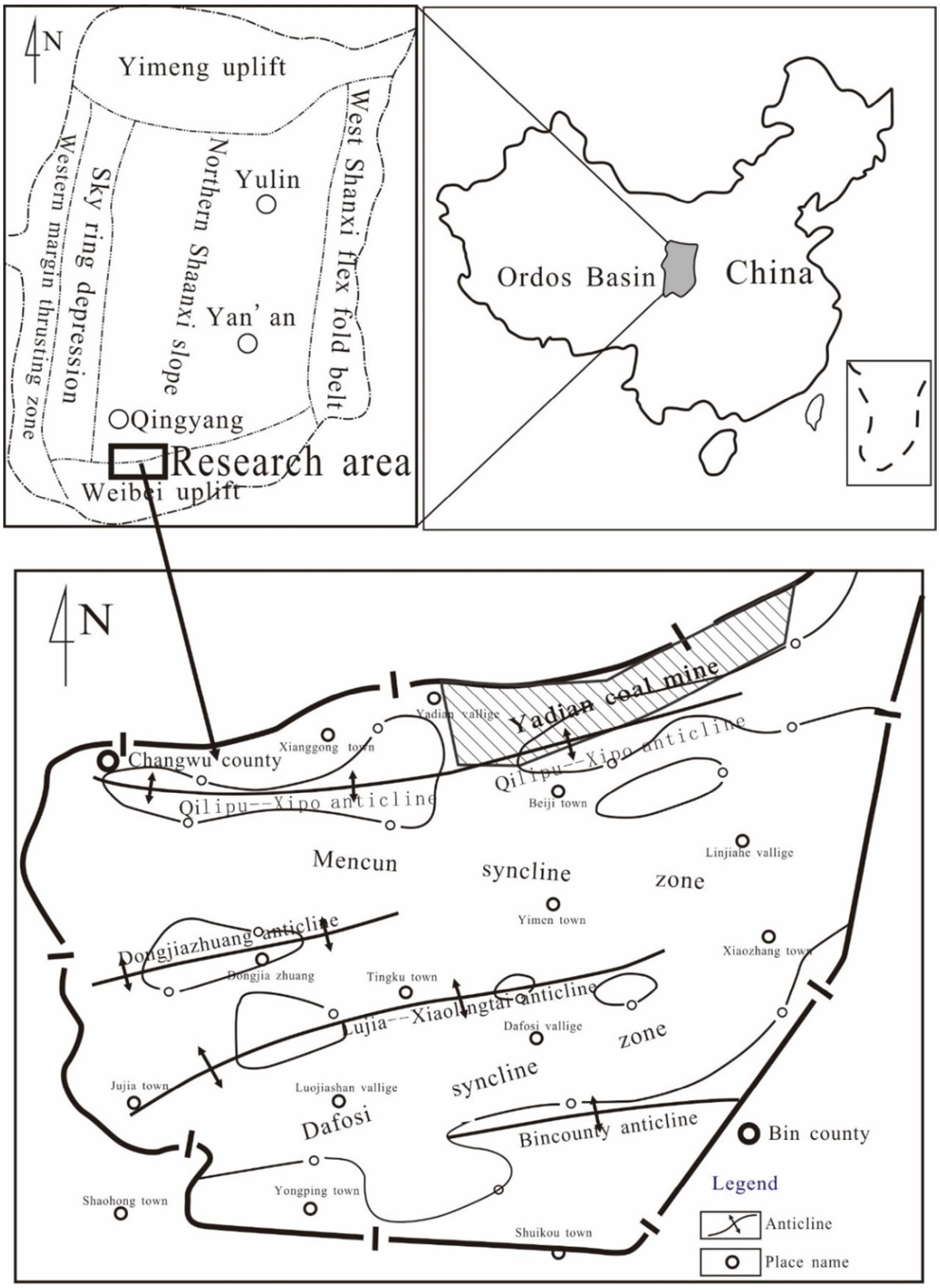

Figure 1. Structural Outline and Minefield Location Diagram of Binchang Mining Area.

Ya Dian coal mine adopts single horizontal development of vertical shaft and central parallel ventilation mode. The first mining area is located in the western part of the minefield. The No. 1 and No. 4 coal seams development roadways are arranged jointly, and the belt is centralized and shared downhill, the track and the return downhill are arranged independently, which are located about 50 m west of the 3-3' exploration line. The underground yard elevation of No. 1 coal return air roadway is +388m, which is located in the underlying Hujiahe Formation of No. 4 coal seam (+ 402 m). It drives in the direction west-northward of 21 degrees, upslope with 3‰ degree. After passing through the floor of No. 4 coal seam, the No. 1 coal seam is exposed to the north, and then the tunneling work is along the roof of No. 1 coal seam.

3. Analysis of Maceral Characteristics and Metamorphic Degree of No. 4 Coal Seam

3.1. Macroscopic Characteristics

Four samples of No. 4 coal seam (M1-M4) were taken in the development roadway of the mining area. The No. 4 coal seam was black, brown-brown black, pitch luster, heterogeneous and shell-like fracture. Strip, homogeneous, lenticular and linear structures, layered and massive structures. No. 4 coal burns with long flame and thick smoke. According to the test results of apparent density of samples, the apparent density is 1.38t/m^3. The main coal rock type is dim briquette, followed by semi-dark briquette, both of which accounted for 95.4% of the total coal seam. The gloss was bright in the upper part and dark in the middle and lower part. The bright coal belt (Sample M1) was about 1 cm in width, calcite veins (Samples M2 and M4) were produced by hydrothermal process (Figure 2).

Figure 2. *Typical photographs of coal samples in the study area.*

3.2. Industrial Analysis

Two typical coal samples were selected for industrial analysis and test of maximum oil-immersed reflectance ($R_{o, max}$) of vitrinite. The results show that (Table 1) the No. 4 coal seam belongs to long flame coal-gas coal, $R_{o, Max}$ is 0.63%-0.70%, and the average value is 0.67%. It belongs to bituminous coal of I-II metamorphic stage, i.e. non-sticky coal or long flame coal; dry base ash (A_d) ranges from 5.07% to 8.96%, and the average value is 7.02%. It belongs to ultra-low ash coal; Dry-based fixed carbon (FC_d) ranges from 63.09% to 69.56%, with an average value of 66.325%, belonging to medium-fixed carbon coal; Air-based moisture content (M_{ad}) ranges from 2.14% to 2.64%, with an average value of 2.39%, belonging to ultra-low total moisture coal; and dry ashless volatile content (V_{daf}) ranges from 26.73% to 30.71%, with an average value of 28.72%, belonging to medium-high volatile coal.

Table 1. *Basic Information Table for Industrial Analysis of Experimental Samples.*

Sample numbers	Industrial/%					$R_{o, max}$
	M_{ad}	A_d	V_{daf}	Characteristic of char residue (1-8)	FC_d	
M2	2.64	8.96	30.71	3	63.09	0.70
M3	2.14	5.07	26.73	2	69.56	0.63

3.3. Maceral Characteristics

Two typical coal samples from No. 4 coal seam were selected for macerals test. The organic content was 96.53% and 97.73% respectively. Among them, vitrinite content is 60.0%, 80.11%, inertinite content is 35.20%, 17.61%, exinite content is 1.33%, 0.0%, inorganic component content distribution is 2.27%, 3.47%. Among them, M2 inorganic component is mainly clay mineral, sulfide and carbonate are secondary, M4 inorganic component is mainly carbonate, sulfide is secondary, which may be related to hydrothermal intrusion (Figure 2).

Table 2. *Statistical Results of Macerals in No. 4 Coal Seam.*

Samples	Total measuring points	Vitrinite Numbers	Inertinite Numbers	Exinite Numbers	Inorganic Numbers	Vitrinite Content (%)	Inertinite Content (%)	Exinite Content (%)	Inorganic Content (%)
M2	375	225	132	5	13	60.00	35.20	1.33	3.47
M4	352	282	62	0	8	80.11	17.61	0.00	2.27

4. Sulfur Content and Distribution Characteristics of Raw Coal

According to GB/T 15224.2-2004 standard, the change of total sulfur in raw coal of No. 1 coal seam ranges from 0.24% to 3.75%. The average value of total sulfur is 1.80%. Mainly medium and high sulphur coal (60%), which is mainly distributed in the western part of the mining area, followed by medium sulphur coal (23%) and the average total sulphur of floating coal is 0.60%. The total sulfur content of raw coal in No. 4 coal seam varies from 0.25% to 1.72%, with an average of 0.72%. Low sulphur coal (55%) is dominant, and most of the mining areas are distributed, followed by ultra-low sulphur coal (24%) and medium sulphur coal (19%). Medium sulphur coal is in the edge of the exploration area and other local isolated points. The average total sulphur of floating coal is 0.38%. On the whole, the sulfur content of No. 1 coal is higher than that of No. 4 coal, and the high sulfur area of No. 1 coal accounts for a large proportion. In the first mining area, the coal-bearing section is in the range of medium and high sulfur, and the sulfur content of cleaned commercial coal is about 1.2%.

5. H_2S Anomaly Characteristics and Control Measures

Generally speaking, the absorption methods of H_2S gas are mainly divided into physical method, chemical method and biological method. In recent years, the method of removing hydrogen sulfide from air is changing to liquid absorption desulfurization. Absorption of liquids is a commonly used method, because it covers a small area, simple equipment, easy operation and low operating cost [25]. Chemical absorption method is based on the principle that acid gas has high solubility in alkaline solution, theoretically speaking, alkali absorption method is a very feasible method to control H_2S in underground coal mines.

5.1. H_2S Anomaly Characteristics of Coal Development and Uncovering Period

(1) During the period of mine development, the length of coal seam exposed in the seam No. 4 is about 42 m, H_2S gas is abnormal. The smell of rotten eggs is particularly obvious in the roadway return air. The concentration of H_2S is about 6 ~ 10 ppm, which is greater than the safety requirement of 6.6 ppm, and affects safe production. After 7 months, the smell of rotten eggs still exists, the monitoring concentration is reduced to about 1 ~ 3 ppm, and the CH_4 has not been detected in the return air flow. After uncovering No. 1 coal seam, the roadway drives along the roof of the coal seam. The coal thickness was about 1.8 ~ 2.3 m. The H_2S and CH_4 gas were not detected.

(2) Track roadway of No. 4 coal seam has been excavated from the underlying rock layer of No. 4 coal seam floor to the north direction. Construction by blasting, No. 1 intersection forword 24 m, a north-dipping normal fault with a fault distance of about 2 m was encountered. The top of the roadway exposes the No. 4 coal about 0.8 m. The thick of No. 4 coal seam in this area is about 3.8 m, exposing the length to about 20 m. During this period, the return air flow in the roadway has obvious H_2S odorous egg flavor, and there is a surge of water in the blast hole, the concentration of H_2S was about 16 ~ 30 ppm, and the H_2S concentration gradually decreased with the decrease of water flow. Then the tunnel shotcrete was carried out according to the engineering requirements, the concentration of H_2S decreased, but the smell of the rotten eggs could still be smelled in the nearby area.

(3) When the mine belt concentrating roadway exposes No. 4 coal seam in the southern part of the mining area and tunnels along the roof of the coal seam near No. 3-6 borehole, H_2S gushes out along the seam cracks and leaching water. The amount of H_2S gushes from the tunneling end is over 140 ppm, and the amount of H_2S gushes from the machine tail is as high as 60 ppm. Each time it lasts about 30 minutes, and the H_2S concentration decreases gradually around 100 m. When tunneling along the coal seam in the north of the mining area (north of borehole 3-2), H_2S appeared abnormal in the heading head, the concentration of H_2S in the newly exposed area was as high as 100 ppm, and it was lasted about 20 minutes after spraying lime water and lime.

5.2. H_2S Abnormaly Characteristics During Trial Production and Mining

During the trial production period, No. 1 coal seam was mined by strike-long-wall comprehensive mining method, and No. 4 coal seam was mined by strike-long-wall comprehensive caving method. During the mining period, the ZC1101 working face as the No. 1 coal seam trial mining face, and the H_2S was tested on the upper corner with a slight smell of rotten eggs, and no abnormalities were found. No. 4 coal seam has a pungent smell of rotten eggs on the upper corner and return air flow of the ZF1403 working face. The H_2S concentration is as high as 20 ppm, and the H_2S of the water flowing out of the upper corner is as high as 40 ppm. It seriously affects the safety of production and the health of workers. Measures such as sprinkling lime in the upper corner plugging section, on the roadway floor, at the point of water injection, and so on. These measures can control the H_2S anomalies in the air flow and the water inrush.

5.3. Control Measures

The H_2S monitoring and control system is installed in the laneway. The gas inspectors use the portable H_2S detector to detect the working face, the end of the roadway, the floor of the roadway and the seeper area. If the H_2S exceeds the limit, it is necessary to evacuate people in time. Real-time monitoring of important parts and areas where H_2S gas may burst, alternating construction, safety monitoring and monitoring, and grouping excavation are adopted.

Fully consider the gas content, wind speed, H_2S emission and other factors, comprehensive consideration of the selection of fans. When H_2S gas gushes out, the local fan with high power should be selected, and the distance between the end of the barrel and the working face should not exceed 5 m, so as to ensure the effective dilution and removal of H_2S gas and prevent the accumulation and concentration of H_2S from exceeding the limit.

Tunnel shotcrete can effectively block the overflow of H_2S in rock and coal seam through the cracks and crevices of coal body under mining disturbance, which can block the overflow passage of H_2S to a certain extent. For individual holes with excessive H_2S overflow, cement slurry can be used to block them completely, thus effectively reducing the H_2S concentration in the roadway. In the abnormal area of H_2S in the return air roadway, the mine adopts the measures of follow-up excavation and spraying, especially for the crack development or fractured area of coal and rock strata, adopting thick shotcrete or multiple circulation shotcrete to ensure the maximum limit of the rapid outflow of H_2S and ensure the safety of production.

Because the density of H_2S is larger than that of air and is easy to dissolve in water, the Yan'an Formation of No. 4 coal seam is weak aquifer. Both anchor cables and bolts are sprinkled with water, H_2S in coal and rock mass gushes out with sprinkled water. Meanwhile, dissolved H_2S in water also enters the airflow of roadway with the change of temperature and pressure conditions. Therefore, in the H_2S abnormal area, special personnel should be arranged to inspect the drainage system to keep the roadway draining in time, not long-term water accumulation, so as to prevent the potential danger caused by gas dissolving in water.

Because H_2S is easy to react with lime and alkali water, the use of lime or alkali water is an important method to reduce the concentration of H_2S, spray lime is easier to operate in construction site. In the roadway floor and the working face with H_2S, evenly sprayed with lime of no less than 2 cm, especially in the water accumulation area, the lime is directly spray, and stirring to make the reaction more fully.

In summary, H_2S in mine construction and trial production is seriously exceeding the limit, resulting in great potential safety hazards. Through monitoring and control, tunnel ventilation, shotcrete plugging, strengthening drainage and spraying alkaline treatment, the H_2S concentration quickly dropped to a safe range, which ensured safe production and personnel safety. But for 7 months, there was still a slight smell of rotten eggs in the roadway, indicating that there was still a very small amount of H_2S emission in the coal, which is related to the pore structure and H_2S adsorption and desorption in the coal seam. Sexuality is relevant and needs to be further explored.

6. Analysis of Abnormal Factors of H_2S

Xishan coalfield in Urumqi is one of the earliest discovered H_2S anomalies in coal seam gas in China. Based on the results of coalfield geological exploration and mine development, the factors affecting the H_2S content in the coal seam in situ are analyzed, and the cause of H_2S anomaly is discussed. The results show that the measured H_2S content is negatively correlated with the depth of coal seam, total gas content, CH_4, CO_2, N_2 content, moisture content (M_{ad}) and ash yield (A_d) in the exploration range of coalfield (buried depth is less than 600 m). and positively correlation between total sulfur content ($S_{t,\,d}$) and volatile matter yield (V_{daf}) [26].

6.1. Sealing of Surrounding Rock

Mudstone, sandy mudstone and siltstone are the main roof lithology of No. 1 and No. 4 coal seams in the mining area, while mudstone or carbonaceous mudstone are the main floor lithology. The thickness of roof mudstone in No. 1 coal seam is 1.76 m, and the floor mudstone is 2.33 m, the roof mudstone in No. 4 coal seam is 2.32 m, and the floor mudstone is 3.41 m. The mudstone stratum of coal seam roof and floor has low porosity and poor permeability, which is characterized by gas barrier. Therefore, gas accumulation is formed in the area with large thickness of roof mudstone and poor permeability, which also plays a certain role in sealing H_2S, resulting in H_2S anomaly.

6.2. Chemical Action of Groundwater

H_2S is a water-soluble gas, which forms hydro-sulfuric acid after dissolving water. Its solubility in water is about 2.7 times that of CO_2 and 93 times that of CH_4, and its chemical activity is very strong. It is easy to react with heavy metal ions in formation water and consume them [10]. In the study area, the thickness of No. 1 coal seam is 0.20 ~ 3.60 m, the average thickness is 2.21 m, the thickness of main seam No. 4 coal seam is 0.0 ~ 20.87 m, the average thickness is 12.07 m, and the change thickness is larger. In the thick coal seam area, the direct water filling aquifer is composed of sandstone fractured groundwater and straight rock group sandstone fractured groundwater. In the thin coal seam area, the direct water filling aquifer is a group of sandstone fractured groundwater, which has poor recharge conditions and poor water availability. In the mine development stage, the fracture influence scope is small, and it cannot lead to the groundwater with large water content. The direct filling water is the fissure water of Yan'an Formation, which has poor recharge and fluidity. Therefore, it does not have the ability to dissolve and consume the H_2S, resulting in the H_2S being released from the pore into the roadway and affecting production when the coal seam is initially exposed. The distance between No. 1 coal seam and No. 4 coal seam is generally about 40 m, and No. 1 coal is locally recoverable, and its water conducting fracture zone is contained in the water conducting fracture zone of No. 4 coal seam. Therefore, in the mining process of No. 1 and No. 4 coal seams, some sections of sandstone fissure water (medium water-rich) of Luohe Formation is brought into the mine through water-conducting fissures, which has a greater impact on water-soluble H_2S, and will affect a larger range of H_2S into the goaf and roadway. During the mining period of the trial mining face in the first mining area, the total water inflow of the mine is up to 1 000 m^3/h, and a large amount of H_2S gas can be dissolved in the water inflow. Therefore, attention should be paid to the prevention and control of hydrogen sulfide and groundwater, and corresponding safety measures should be taken in advance.

6.3. Coal Metamorphism

Mercury adsorption test and isothermal adsorption test under equilibrium water were carried out. The results showed that the adsorption isotherm of coal to H_2S accords with the Langmuir adsorption model. The isothermal adsorption process shows 3 stages: rapid rise, slow rise and adsorption equilibrium. The larger the percentage of small pores (transition pores and micro-pores), and the higher the degree of coal metamorphism and the greater the pressure of the coal, which are more favorable to absorb coal's H_2S. The reservoir pressure of No. 4 coal seam ranges from 0.28 MPa to 9.22 MPa, with an average of 5.59 MPa [27]. The amount of coal adsorbing H_2S increases with the increase of coal rank, which is an important factor affecting the amount of coal adsorbing H_2S. Through the isothermal adsorption experiments of different coal ranks, the amount of coal adsorbing H_2S is anthracite > lean coal > gas coal [28].

Table 3. *Microcontent and Reflectivity of Coal and Rock Measurements of Geological Exploration.*

Seams	Boreholes	Organic macerals (%)				Inorganic macerals (%)			Romax (%)
		Vitrinite +Semi vitrinite	Semi fusinite +Fusinite	Liptinite	Total organic matter	Clay soil	Carbonates	Sulfide	
4	2-2	25.8	68.9	1.0	96.7	1.2	0.3	1.9	0.698
4	3-3	15.6	73.1	1.7	90.4	0.5	9.1	0	0.650
1	8-5	26.1	64.1	1.5	91.7	0.2	5.0	3.1	0.643

The content of organic components in No. 4 coal seam was 90.4% and 96.7% respectively. Among them, vitrinite + hemivitrinite content is 15.6%, 25.8%, Semi fusinite + fusinite content is 68.9%, 73.1%, stable component is 1.0, 1.7%. The maximum reflectance of vitrinite of No. 4 coal seam are 0.650-0.698%, and that of No. 1 coal seam is 0.643%. It belongs to bituminous coal of I-II metamorphic stage, i.e. non-caking coal-long flame coal category (Table 1and Table 3).

The results of macerals test in the study area show that No. 4 coal is non-caking coal in low metamorphic stage (Table 3). It shows that the low metamorphism of No. 4 coal seam is not conducive to the adsorption of H_2S. At the same time, this stage is a relatively slow adsorption period. The pore surface of coal matrix has been covered by a large number of H_2S. H_2S molecules compete with each other for the remaining area, which makes the adsorption capacity increase slowly with the increase of pressure.

7. Analysis of Genesis Types

According to the existing research evidences and the distribution characteristics of H_2S bearing mines in the world [29, 30], BSR, TSR, TDS and magmatic activities are the main genetic types of H_2S, and BSR and TSR are the main types [30-32], and the main causes of H_2S anomalies are the spontaneous combustion of coal seams, BSR, TDS, TSR mixed causes, and the migration of groundwater [26]. The genetic types of hydrogen sulfide in coal mines can also be synthetically identified according to coal-forming environment, thermal evolution history of coal and rock, carbon and sulfur isotope compositions and gas compositions [33].

The current research results and genetic mechanism, it is concluded that TSR action must have high temperature, sufficient hydrocarbon organic matter and developed sulfate, and sulfate is reduced to H_2S under thermochemical action; BSR action means that microbial sulfate reducing bacteria use various organic matter or hydrocarbons to reduce sulfate, and then sulfate is reduced to H_2S, this method is also known as microbial sulfate reduction. The most obvious sign of magmatic origin H_2S gas is magma intrusion and H_2S gas $\delta^{34}S$ value close to the meteoric iron value, and is obviously different from other sulfide isotopic values [34]. BSR action requires three basic conditions: organic matter, sulfate and sulfate reducing bacteria [35, 36]. There are three methods to identify BSR: isotope method, gene method and extinction dilution method [37].

7.1. Geothermal Characteristics

By means of approximate steady-state temperature measurement, it is determined that the temperature of the isothermal zone in the study area is 18.5°C and the depth is about 160 m. According to the temperature measurement data of 18 boreholes, the maximum geothermal gradient is 2.58°C/100 m, the minimum is 1.52°C/100 m, and the average geothermal gradient is less than 3°C/100 m. However, the geothermal gradient of 10 boreholes in coal measures is more than 3°C/100 m, and there exists geothermal gradient anomaly (Figure 3).

Because the coal seam is deeply buried in this area, the lowest temperature at the bottom of the hole is 27.9°C, the highest temperature is 34.4°C, and the bottom temperature of 11 boreholes is higher than 31°C and lower than 37°C. Therefore, the exploration area is the first-class high temperature area north of the 1-1, 7-1, 14-1 boreholes connection and west of the 1-1'exploration line (Figure 4).

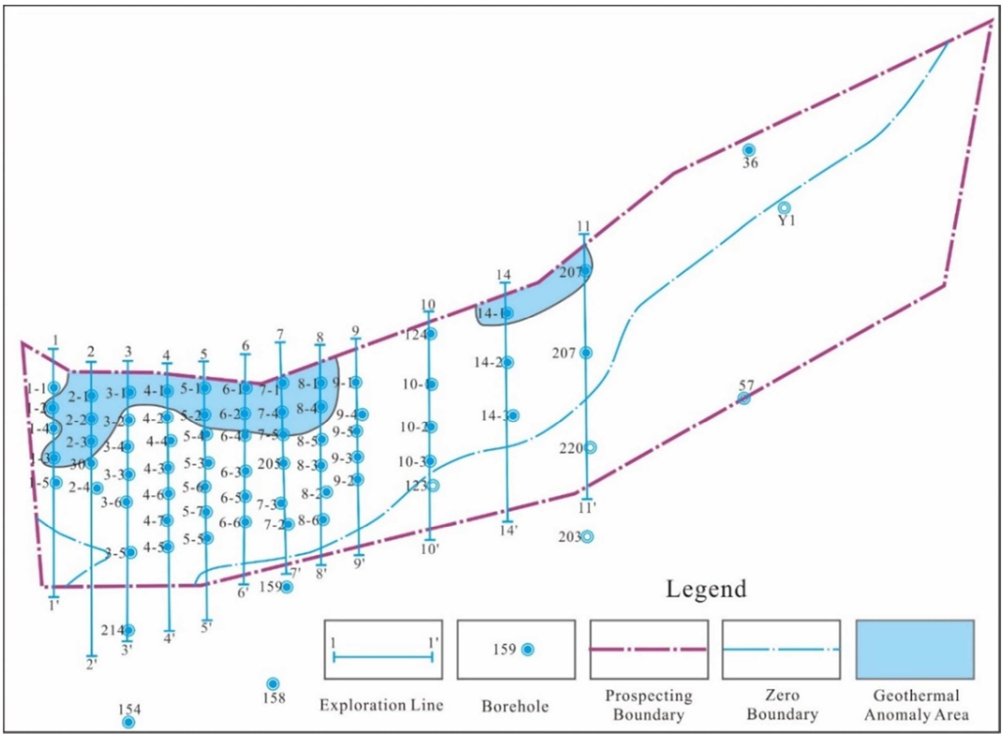

Figure 3. *Distribution Map of Geothermal Gradient Anomalies in the Study Area.*

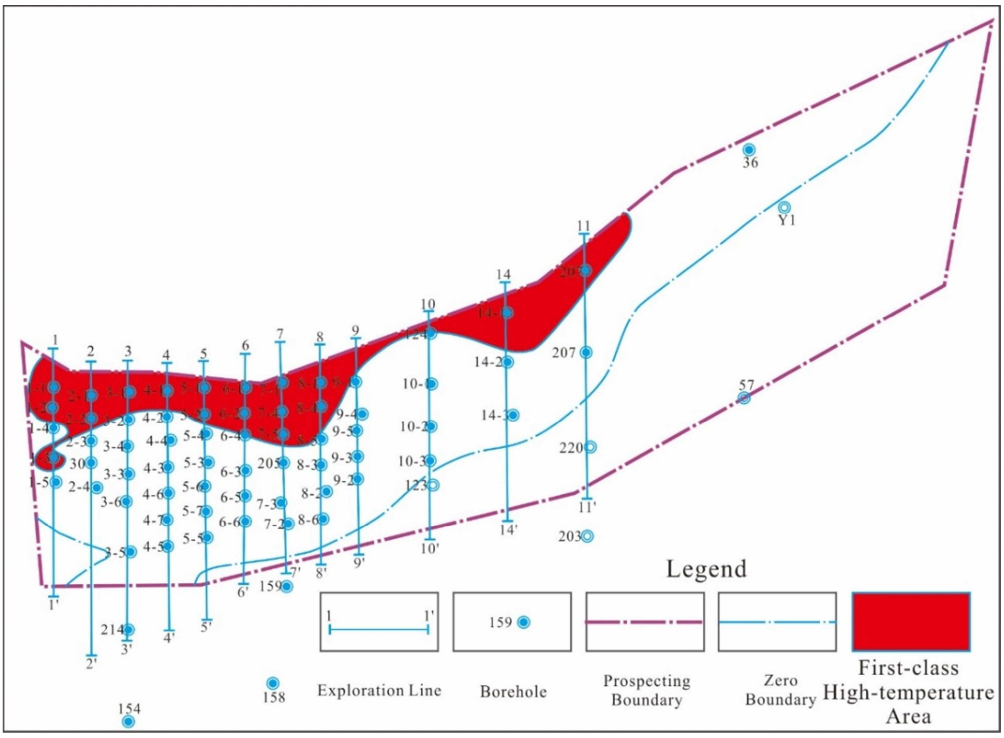

Figure 4. *Distribution Map of First Class High Temperature Zone.*

7.2. Sulfate Characteristics

The sulfur monitoring results of exploration results in the study area show that the main sulfur in No. 1 and No. 4 coal seams is iron sulfide ($S_{p,d}$), followed by organic sulfur ($S_{o,d}$), and a small amount of sulfate sulfur ($S_{s,d}$). A small amount of sulfate was reduced to H_2S by reducing bacteria under anaerobic conditions (Table 4).

Table 4. *Table of sulphur determination results in coal seam.*

Seams	$S_{s,d}$ (%)	$S_{p,d}$ (%)	$S_{o,d}$ (%)
1	0.02~0.27 0.09 (14)	0.07~3.20 1.18 (14)	0.14~0.91 0.43 (14)
4	0.01~0.11 0.05 (59)	0.07~1.29 0.45 (59)	0.13~0.51 0.23 (59)

7.3. Judgment of Survival Conditions of Sulfate Reducing Bacteria (SRB)

According to the research, sulfate reducing bacteria (SRB) are a kind of anaerobic bacteria with different morphology, different nutritional types, and can use sulfate as electron acceptor to dissimilate organic substances, which have strong viability. The results of the British Geological Survey and the Department of Energy's Deep Stratum Microbiology Program show that microorganisms can grow at temperatures above 125°C, pH values of 1-11, aerobic or anoxic conditions. Bacteria are viable within a single cell, almost everywhere; in addition, microorganisms can live and remain dormant under harsh conditions. Many microbiologists believe that the dormancy period of bacteria can last for thousands of years. Once the environment is suitable, bacteria can quickly recover from dormancy. Analysis of formation water taken from many oil layers shows that the presence of short chain fatty acids such as acetate, propionate and butyric acid can be consumed by certain bacteria, thereby providing energy [38]. The possibility of activity of sulfate reducing bacteria in coal seam is discussed from the aspects of survival temperature, pH range and metabolic conditions.

(1) SRB can survive at -5 ~ 75°C and adapt to the new temperature environment quickly. Certain bacteria can grow below -50°C, and spore-bearing bacteria can tolerate high temperatures of 80°C. In neutral medium, SRB grows most actively at 37°C, while SRB grows slowly when the temperature rises to 50°C; it cannot survive at temperatures below -15°C or above 100°C; and thermotolerant bacteria (tSRB, bacteria active at 55 ~ 75°C or higher) always seem to exist in high temperature and deep stratum environment [39]. At present, there is no final conclusion about the temperature environment that SRB can adapt to exit. An important condition for SRB to generate hydrogen sulfide gas in coal seam is that the temperature of coal seam is suitable for the survival of SRB. Sulfate-reducing bacteria (SRB) are suitable for survival and reproduction in the anaerobic reduction environment below 60 ~ 80°C. The optimum temperature is 20 ~ 40°C [10, 31, 40]. The coal mine in the southeast margin of the Zungarian basin is low rank coal. The formation temperature is less than 40°C, which is suitable for the growth and reproduction of sulfate reducing bacteria. SRB has been growing vigorously [33]. The No. 4 coal seam of Ya Dian coal mine in the bin Chang mining area is located in the lower part of the lower Jurassic lower Yan'an Formation. The coal measures of Yan'an Formation are deposited in inland environment of fluvial-marsh facies and the vitrinite reflectance is 0.650 ~ 0.698%. During the burial process, the temperature of the layer is not greater than 150°C [34].

The results of geological exploration in the study area show that the main sulfur in seams 1 and 4 is iron sulfide ($S_{p,d}$). The lowest temperature is 27.9°C, the highest temperature is 34.4°C, and the bottom temperature of 11 boreholes is higher than 31°C, but lower than 37°C. Thereby, it is judged that the study area has the geothermal and material conditions for the survival of sulfate reducing bacteria (SRB).

(2) The optimum pH value for SRB growth ranged from 6.5 to 7.5. In this range, the amount of SRB bacteria changed little. When the pH value was greater than 7.5, the bacterial population gradually decreased; when the pH value was equal to 9.0, a small amount of SRB still survived; when the pH value was greater than 9.5, SRB could not survive. When the pH value is less than 6.5, the bacterial count decreases gradually, and when the pH value is equal to 3.0, a very small amount of SRB still survives. If conditions permit, SRB can recover from dormancy and multiply in large numbers [37]. Along the direction of runoff, the mineralization degree of groundwater increases gradually, and the pH value increases gradually. The water body is rich in SO_4^{2-}, under the condition of hydrocarbon enrichment, BSR plays a role in the formation of hydrogen sulfide [33]. The study on the variation characteristics of groundwater quality in the Cretaceous of Binchang mining area shows that the total hardness is not high due to the high content of $HCO_3^-$and the low content of Ca^{2+}/Mg^+ in the mining area, resulting in the low total hardness. The pH value generally ranges from 7.7 to 8.3, which belongs to weak alkaline water [41]. Pan Xufang et al. [42] (2009) concluded that by reducing sulfate concentration and increasing pH value, hydrogen sulfide gas can be prevented from precipitating, indicating that sulfate concentration and pH value have an important influence on BSR.

The fracture pore aquifer of Lower Cretaceous Luohe Formation sandstone is the main water-filled aquifer affecting coal seam mining in the study area. It is distributed in the whole area, and its lithology is mainly purple red, dark purple-red medium and coarse sandstone with a thickness of 200 ~ 300 m. According to the data of drilling and pumping in exploration area, the water quality belongs to HCO_3-Ca·Mg, $HCO_3 \cdot SO_4^-$Na·Ca, SO_4^-Na and $SO_4 \cdot Cl^-$Na, with total hardness of 54.46 ~ 63.82 Deutschland degrees, no corrosive CO_2, weak alkaline pH and no corrosive to iron. The water quality belongs to $SO_4 \cdot Cl^-$K+Na type water. Its salinity ranges from 4.826 to 5.277 g/l and SO_4^{2-} content ranges from 2088.87 to 2292.82 mg/l (greater than 1500 mg/l), which is moderately corrosive to concrete and steel structures. According to these conditions, sulfate reducing bacteria (SRB) have the pH conditions for survival.

In coal seams, sulfate reducing bacteria use coal-forming organic matter, mainly unsaturated hydrocarbons as energy and material sources, to reduce sulfate. Previous scholars believe that SRB can only indirectly utilize organic acids, which are metabolites of hydrocarbons by aerobic microorganisms. However, recent experiments have found that SRB can directly utilize crude oil as its carbon source and energy source [43], which indicates that BSR can be achieved under the coexistence of coal and sulfur. No. 1 and No. 4 coal seams in the study area are symbiotic with sulfides, and have the condition of BSR.

Table 5. *Measurements of Coal Seam Gas Content in Research Area.*

Seams		No. 1 Coal Seam			No. 4 Coal seam		
	N_2	90.60%			91.52%		
Natural Gas	CH_4	8.87%			6.94%		
Composition	CO_2	0.50%			1.51%		
	C2-C8	0.03%			0.03%		
Moisture	M_{ad}	0.76%			0.57%		
Ash	A_{ad}	38.59%			21.13%		
Volatiles	V_{daf}	43.25%			34.15%		
Samples Weight	G	231.2g			288.5g		
Combustible Weight	GO	140.22g			225.90g		
Degassing Gas Volume Before Crushing (ml/g)		CH_4=0.16	CO_2=0.01	C2-C8=0.00	CH_4=0.11	CO_2=0.02	C2-C8=0.00
Degassing Gas Volume After Crushing (ml/g)		CH_4=0.11	CO_2=0.01	C2-C8=0.01	CH_4=0.14	CO_2=0.01	C2-C8=0.00
Gas Residual of Coal (ml/g)		CH_4=0.27	CO_2=0.02	C2-C8=0.01	CH_4=0.25	CO_2=0.03	C2-C8=0.00

The identification of gas parameters in the study area (Table 5) shows that the content of C2-C8 unsaturated hydrocarbons in natural gas of No. 1 coal and No. 4 coal are both 0.03%. There are also 0.01% C2-C8 unsaturated hydrocarbons in the degassed gas volume and gas residue of No. 1 coal after pulverization, which possess the condition of sulfate reducing bacteria (SRB) using coal-forming organic matter to form hydrogen sulfide.

Therefore, according to the geothermal characteristics, groundwater quality type, alkaline pH value increase, sulfate reducing bacteria (SRB) better conditions, unsaturated hydrocarbon occurrence and other comprehensive conditions, combined with exploration results, no magma intrusion has been found in the mining area, so it does not belong to the results of TSR and magma genesis type. Therefore, according to sedimentary environment and temperature, the H_2S gas in the mine is preliminarily judged as BSR causes.

8. Conclusions and Recommendations

a. The vitrinite reflectance test in the study area shows that No. 1 and No. 4 coal seams belong to bituminous coal of metamorphic stage I-II, i.e. non-sticking coal to long-flame coal. Distribution maps of total sulfur content of No. 1 and No. 4 coal seams show that high sulfur areas are formed in the west of No. 1 coal seam and around the mining area of No. 4 coal seam, and H_2S anomaly should be paid great attention to in this area.

b. The factors affecting the H_2S anomaly in the study area are the sealing effect of roof and floor compact wall rocks; during the mining period of No. 1 and No. 4 coal seams, two coal seams are penetrated by local fractured zones and water-rich rocks of Luohe Formation, resulting in a large amount of H_2S coming out with water leaching or gushing; the low degree of coal metamorphism results in a weak adsorption of H_2S and a small amount of adsorption, mostly in free state.

c. In the light of anomal H_2S area, measures such as monitoring, ventilation, blocking by grouting, strengthening drainage and spraying alkalinity are taken to prevent and control the concentration exceeding limit caused by H_2S anomaly, which ensures the health and safety of workers and the safe production of mines.

d. The optimum temperature for large-scale reproduce of sulfate-reducing bacteria (SRB) in the study area is 30 ~ 40°C. The coexistence of sulfate and coal provides material conditions for BSR. The existence of unsaturated hydrocarbons in natural gas C2-C8 and gas residues provides energy and material basis for H_2S production by sulfate reduction. Weak alkaline groundwater provides living environment for SRB. Combining with other conditions, H_2S gas in the mine can be judged is the origin of BSR.

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