GEOLOGICAL AND HYDRGEOLOGICAL CHARACTERISTICS OF ACID MINE DRAINAGE FROM AN ABANDONED COAL MINE: A CASE STUDY OF SHANDI COAL MINE IN NIANGZIGUAN SPRING CATCHMENT, SHANXI

Dissertation submitted to the University of the Western Cape in the fulfilment of the degree of Doctor of Philosophy

By

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April 2022

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DECLARATION

I declare that **GEOLOGICAL AND HYDROGELOGICAL CHARACTERISTICS OF ACID MINE DRAINAGE FROM AN ABANDONED COAL MINE: A CASE STUDY OF SHANDI COAL MINE IN NIANGZIGUAN SPRING CATCHMENT, SHANXI** is my own work, and that has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Full name: Zhaoliang Wang Date: April 2022

Signed... Zhaoliang Wang

ABSTRACT

Geological and hydrogeological characteristics of acid mine drainage from an abandoned coal mine: a case study of Shandi coal mine in Niangziguan spring catchment, Shanxi

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PhD Thesis

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Keywords: Acid mine drainage; abandoned coal mine; water pollution; groundwater; geological characteristics; hydrogeological characteristics; Niangziguan spring catchment; engineering measure

As Shanxi Province is rich in coal resources, the output of raw coal approximately accounts for one quarter of China's production. It is one of the most important energy and heavy chemical bases and plays a significant role in the sustainable development of the national economy and energy security. With the continuing exploitation of coal resources in Shanxi, water environmental problems such as the destruction of water resources and deterioration of water quality have become increasingly prominent. Especially with the closure of many depleted coal mines, water pollution caused by acid mine drainage (AMD) has become more and more serious, which aggravated the shortage of water resources and threatens the safety of local drinking water supply. Since 2008, more than 100 coal mines have been abandoned in the Yangquan coalfield of Shanxi, and the AMD has polluted the surface water and groundwater in the Niangziguan spring catchment. However, there are no successful examples of treatment for AMD in Shanxi. In 2005, Shandi coal mine in Yangquan coalfield was abandoned and the AMD pollution has not been controlled at present. Therefore, it is of great significance to review the research findings on AMD in

Shanxi, and it is necessary to carry out further research on the geological and hydrogeological characteristics of AMD from abandoned coal mine to control AMD pollution for in-situ treatment.

This thesis is focused to control AMD pollution in the Shandi coal mine and protect the water resources in the Niangziguan spring catchment, as well as to provide theoretical basis for water resource protection and AMD pollution treatment in abandoned coal mines in the nation and even in the world. By retrieving and analyzing about more than 90 domestic and international publications, the thesis critically reviews the AMD research results in Shanxi's abandoned coal mines from the perspectives of formation mechanism, migration and transformation, prediction, treatment and management. On the basis of field investigation and sample tests of water, coals and associated minerals, the thesis researched the geological and hydrogeological characteristics of the abandoned Shandi coal mine. Finally, a framework and the feasible engineering measures were put forward and applied for AMD treatment to control AMD pollution in abandoned coal mines. The main findings of the thesis are presented as follows.

1. Sulfur-containing minerals and groundwater replenishment are main sources for the formation of AMD, pyrite is the prerequisite, oxygen is the inducement, water is the carrier, Fe^{3+} and microorganisms are the catalysts; the water-refilling process of AMD in abandoned coal mines has its uniqueness: there are developed underground roadways and water conducting fissures; there is no successful case for the AMD treatment in Shanxi abandoned coal mines, and the treatment technology has not been applied in practice and engineering.
2. There are still some problems in the previous research of AMD in Shanxi abandoned coal mines: (1) the regional distribution characteristics of pyrite and its occurrence in coal-bearing strata in six major coalfields need to be further investigated and researched; (2) the developed underground roadways in abandoned coal mine is highly involved, and it is very difficult to generalize and analyze the AMD flow field; (3) the distribution and occurrence law of AMD gathering-water space in abandoned coal mines are very complicated and difficult to grasp and determine the water head and water accumulation coefficient in the goafs; (4) the research on the large leakage

channels, such as faults and collapse columns, is relatively lacking; (5) in the research of AMD migration and transformation, the participation of microorganisms and multi-gas components is not considered, and there is a lack of attention to the processes of water-refilling and gathering-water of AMD; (6) there is a lack of research on the influences of gas composition, pressure, water temperature and ion concentration of AMD on the hydrochemical balance; (7) no relevant investigations and studies have been carried out on the prediction about which mine would be prone to AMD outflow, when it would outflow and where it would outflow; (8) the AMD treatment method is in its infancy of laboratory theoretical research, and the artificial wetland and permeable reactive barrier (PRB) is still blank; and (9) the management policy (norms) and AMD pollution monitoring data are relatively lacking; AMD risk assessment and early warning mechanisms have not yet been established, and the research on risk identification and risk-index system is blank.

3. The way forward of the research on AMD in Shanxi abandoned coal mines should be further strengthened in the following aspects: (1) actively carry out the research on the regional distribution characteristics of pyrite in the six major coalfields and the occurrence law in coal-bearing strata; (2) improve the comprehensive detection method of AMD; (3) strengthen the research on the formation mechanism of AMD and construct a reasonable pollution risk assessment model for AMD; (4) analyze the influence of various gas composition, pressure, temperature and ion concentration on the hydrochemical balance; and (5) research on the management, treatment and early warning mechanism of AMD should be further strengthened.
4. Water quality characteristics of AMD: (1) AMD from abandoned Shandi coal mine presents the low characteristics of pH, DO, and Eh and high characteristics of sulfate ion, iron ion and toxicity; (2) the open environment has a more significant effect on the iron ion and sulfate ion compared with the closed environment; (3) From the upstream to the downstream of the Shandi River in the study area, the pH value rapidly decreases firstly and then increases gradually, while the change of HCO_3 and all metal elements (except Cd) is the opposite. (4) the Shandi River contributes greatly the heavy metal elements to the Wenhe River.

5. Geological characteristics: (1) coal seams are composed of organic and inorganic components, and the inorganic minerals are mainly clay minerals and quartz, followed by carbonates and sulfides; (2) due to a lot of carbonates and clay minerals in coal itself, the formation of AMD is not closely related to the coal quality; (3) the associated minerals (mainly including pyrite and clay) provide a large number of elements and play an essential role on the formation of AMD from Shandi coal mine; (4) the elements of AMD are multi-sources rather than one kind of sulfide minerals; and (5) the distribution and reserves of sulfide minerals are the main factors of the formation of AMD in abandoned coal mine.
6. Hydrogeological characteristics: (1) the goafs were connected by the developed roadways, the developed roadways were made up an organic whole by the seven pairs of inclined shafts, which provide good space for AMD; (2) for the recharge of AMD, Shandi River has become a rapid recharge by water-conducting fissures; (3) the water-flowing fissures and roadways have become the new important runoff channels for AMD; (4) the runoff of AMD was transformed to be complex, water-conducting fissures, roadways, open-pit, collapse columns and shafts caused the great changes of the groundwater flow field and its dynamic field; and (5) the discharge of AMD was uneven in time and space, the distribution of AMD has obvious zoning characteristics, controlling factors mainly include geological structure, outcrop of coal seam and the Shandi River.
7. Engineering measures were put forward as follows: (1) the abandoned shafts should be blocked; (2) the ground fissures should be rehabilitated; (3) the river leakage should be controlled; (4) different water quality of AMD in different zones should be treated separately; (5) the existing open-pit should be refilled; and (6) AMD should be classified by water quality for treatment.
8. The thesis would contribute towards the geological and hydrogeological characteristics of AMD from the Shandi coal mine, research results would provide important theoretical basis for water resources protection of Niangziguan spring and AMD pollution treatment in abandoned coal mines in the nation and even in the world.

ACKNOWLEDGE

This thesis would not have been possible without the assistance and support of many institutions and individuals. I would like to acknowledge my sincere thanks to the following,

- My supervisor Professor Yongxin Xu from the Department of Earth Sciences at University of the Western Cape for his creative and thoughtful coaching.
- This thesis was supported by the funding of the National Natural Science Foundation of China 41572221.
- The local organizations, Shanxi Rock Research Institute and Shanxi Yingruize Monitoring Co., Ltd. for their supports of sample testing.
- Taiyuan University of Technology and College of Water Resources Science and Engineering for their assistance during my PhD study.
- Professor Yongbo Zhang, and Dr. Qiang Zheng from Taiyuan University of Technology for helpful discussion, advice and support during my study and research.
- My fellow classmates namely Dr. Zhixiang Zhang, Dr. Heng Zhang, Mr. Haoyong Shen, Mr. Ming Lu and Ms. Jihong Qi from the University of the Western Cape for their assistance and cooperation.
- Mrs. Chantal Carnow and Mrs. Mandy Naidoo from the University of the Western Cape for all their hard work and care for assisting the author to complete the research.

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Chapter 1

Introduction

1.1 Background

Acid mine drainage (AMD) problems in abandoned coal mines have become a worldwide issue. For instance, in the Rio region of Spain, AMD has been a continuous pollution source of the Tinto River (Grande et al. 2003). AMD formed by a large number of abandoned coal mines in the USA has polluted the rivers with a total length of about 23,000 km (Cravotta et al. 2011; Gammons et al. 2010), causing serious environmental consequences (Veb et al. 2001). AMD in the closed pits of the mines located in the Witwatersrand Basin of South Africa has become an important issue of national concern (Netshitungulwana et al. 2013; McCarthy 2011; Oohieng et al. 2010; Geldenhuis and Bell 1998). The AMD problems of abandoned coal mines are widespread in other countries such as the Makum coal mine in India (Equeenuddin et al. 2010), the Gangreung coal mine in South Korea (Kim and Chon 2001), and the Douro coal mine in Portugal (Ribeiro et al. 2010), which have caused serious damages to the local water resources and water environment. In China, according to the statistics from the China Coal Industry Association, the number of coal mines has been reduced from more than 80,000 in the peak period to about 5,800 at the end of 2018 (Zhang et al. 2019a; Gao 2019). Unfortunately, the closed coal mines in China have caused a series of water environmental problems such as destruction of water resources and deterioration of water quality (Shang and Qi 2018; Wu et al. 2019). Therefore, it is very necessary to conduct research on AMD in abandoned coal mines globally.

Over the years, AMD research has received extensive attention from scholars both nationally and internationally. For example, Banks and Banks (2013) evaluated the environmental impact of AMD emissions from abandoned coal mines in the UK using relevant water quality data, and pointed out that AMD had already resulted in groundwater pollution and the pollution degree had become more serious as the water level continued to rise. Wood et al. (1999) analyzed the changing trend of water quality of 32 monitoring drainage points of the abandoned coal mine in the Midland Valley of Scotland and found that the surface water pollution was the most serious in the first few decades. Eccarius (1998) studied the chemical properties of groundwater around an abandoned open-pit coal mine in central Germany and found that about 5% of AMD seeped into the local aquifer, causing serious groundwater and surface water pollution (Lottermoser 2010). Nassery and Alijani (2014) researched the impact of AMD from abandoned coal mines in the Zirab area in northern Iran on spring water, and concluded that AMD promoted the dissolution of carbonate rocks, which was the main factor for the geochemical evolution of groundwater. In the GVS coal mines in India, AMD caused an increase in the TDS of the entire area (Brake et al. 2001), SO_4^{2-} reached up to 63,000 mg/l, and metals such as Pb, Zn, Cd, Cr, Ni, Be, and V also increased significantly (Fang et al. 2007). AMD outflowed from a large number of abandoned coal mines polluted surface rivers in the Stockett–Centerville area of the USA (Gammons et al. 2013). Grodner (2002) established a numerical model of groundwater flow in the Sigma coal mine in South Africa using MODFLOW, and predicted the water level rise of the AMD after the pit was closed. Gitari et al. (2008) treated the AMD of coal mine using fly ash, achieving the mine water treatment. Song et al. (2008) carried out a two-year in-situ source treatment of AMD from an abandoned coal mine in central Tennessee, USA by using remote sensing and biogeochemical technology, and achieved successful results, but this treatment method was very expensive and difficult to be popularized to other mines for the insufficient budget. Actually, the appropriate measures should be taken to treat different mines in their specific situations (Rezaie and Anderson 2020). In addition, many active preventative strategies should be considered to limit sulfide oxidation, such as physical barrier, bacterial inhibition and chemical passivation (Liu and Sun 2011; Sahoo et al. 2013).

However, the groundwater in Hongshan and Zhaili coal mines in Zibo, China was in cross strata pollution, which had directly resulted in the scrapping of hundreds of water supply wells and threatened the water quality of Xuzhou water supply source and the Grand Canal from Beijing to Hangzhou (Zhang et al. 2015; Wu and Zeng 2015; Lv et al. 2005). Due to the continuous discharge of AMD in recent decades in Guizhou, China, the Maoshitou Reservoir in the Xingren coalfield has been severely acidified (Cao et al. 2019;

Sun et al. 2013; Tang et al. 2009). Meanwhile, the pollutants in the Yudong River Basin mainly came from the discharge of AMD in abandoned coal mines (Liang et al. 2019; Duan et al. 2018); Jiang et al. (2007) tested the sulfur isotopes in coal seams of upstream coal mines, other mineral deposits and downstream surface water of Wujiang River, and concluded that the sulfate contents from the oxidation of sulfide in coal seams of upstream coal mines and other mineral deposits account for 0.27% and 20.5% of the Wujiang River, respectively. He et al. (2019) researched the typical AMD of a closed coal mine in Hunan, China, and confirmed that the continuous discharge of AMD into the river had caused geochemical and environmental biological changes in the aquatic system. Wang et al. (2018) selected a small watershed in Guizhou of China and studied the migration and transformation process of sulfate in AMD in karst areas by testing water and sediment samples, the results showed that the AMD was mainly discharged from the abandoned coal mines in Zhijin coalfield. Xu (2017) studied the three-phase reaction equilibrium of water-rock-gas under different conditions in closed coal mine using PHREEQC software, the results showed that if the pH decreased slightly, the solubility of CO_2 and the concentration of HCO_3^- and Ca^{2+} decreased gradually, which confirmed that the mineral dissolution of calcite was the most obvious due to the addition of sulfate. Zhang et al. (2011) treated AMD by using Na_2CO_3 modified fly ash, the research results provided technical support for the comprehensive utilization of AMD with high concentration of Fe and Mn. Sun (2014) studied the refilling mechanism of AMD water level in closed coal mines and verified that the factors mainly included the water storage rate, permeability coefficient and initial water inflow. By using PHREEQC software, Zhang (2004) predicted that the water refilling time is about 160 days after the closure of Zhangshuilou coal mine. According to the geological and hydrogeological conditions of the Daihe coal mine, Bi et al. (2018) calculated the storage of AMD in the goafs after mine closure by spatial and temporal distribution, and obtained the relational algebra expression between water level and time. Zhong et al. (2019) predicted that the water-refilling time is about 1950 days after the closure of Liuqiao coal mine using relational expression between the water level and time. Pan et al. (2017) compared the flow field maps of 1 year, 3 years and 10 years after mine closure in the Xuzhou mine area by using GMS software, and showed that the average rise of groundwater level was 1.14 m/a in the first year, 0.165 m/a from the second year to the third year, 0.27 m/a from the fourth year to the tenth year. Combined with the original goafs in the mine area, Zhou et al. (2011) analyzed the hydrodynamic characteristics and water exchange between different aquifers, and established the water balance equation. Liu and Sun (2011) classified the groundwater pollution caused by the closed coal mine, and put forward some effective technical measures and feasible prevention strategies. Sun et al. (2015) collected sediment samples for geochemical and microbial community analysis, and concluded that AMD from the upstream abandoned coal mines continuously polluted the Aha watershed in southwestern China. Wei et al. (2013) proposed that the combination of directed source control and terminal treatment technology was the hotspot and development trend of AMD research in China in the future. All these results can provide theoretical basis for regional and local AMD evaluation and management.

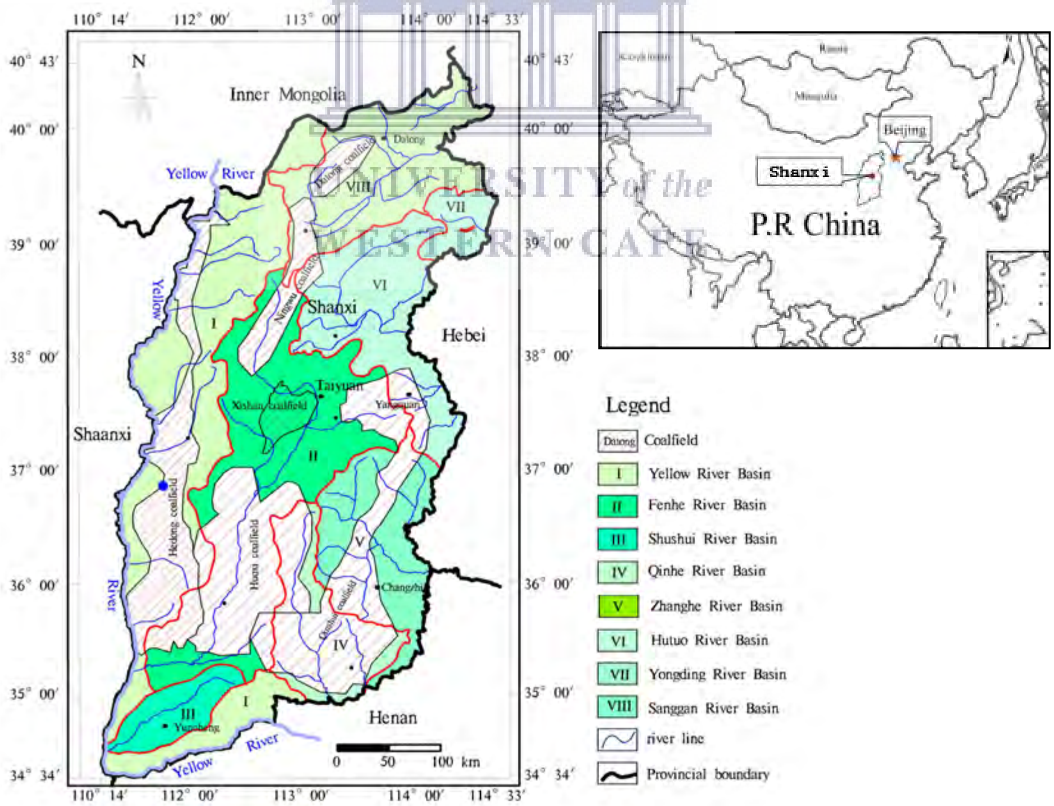


Figure 1-1 Six major coalfields in Shanxi Region

Shanxi Region, located in northern China, is rich in coal resources with six major coalfields, including Datong, Ningwu, Xishan, Hedong, Qinshui and Huoxi from the north to the south (Figure 1-1). The output of raw coal accounts for one quarter of China's production, so the Shanxi Region is an important energy and heavy chemical base in China, and it plays a significant role in the sustainable development of the economy, society, and energy security. There are eight large river basins in Shanxi. According to statistics, the coal mine areas in Shanxi is 61,050 km^2, accounting for 39.1% of the total area of the Shanxi region. Over the years, with the continuing exploitation of coal resources in Shanxi, water environmental problems such as destruction of water resources and deterioration of water quality have become increasingly prominent. Under the influence of national macro policy, a large number of coal mines in Shanxi were integrated by the government. In 2000, the number of coal mines in Shanxi exceeded 9,800. After the first and second round of integration and upgrading in 2005 and 2009, there were 1,078 coal mines with an annual production capacity of 1.46 billion tons by the end of 2015. There were 988 coal mines in Shanxi At the end of 2018 (Sun 2020). In accordance with the requirement of the Development and Reform Commission, Shanxi authority announced that 32 coal mines had been shut down in 2019-2020. Therefore, about 8,780 coal mines of different sizes were closed in the past two decades. With the closure of the coal mines, a series of environmental problems caused by AMD occurred and became more and more serious (Zhang et al. 2019b), which aggravated the shortage of water resources and threatened the safety of local drinking water supply in Shanxi.

Xu et al. (2007) found that Sitai coal mine, a mining history of more than 100 years in the Datong coalfield, had formed collapses and ground fissures after its disorder mining and a certain amount of acid mine water was produced. Meantime, Zhao et al. (2007) studied the migration characteristics of harmful elements by the principles and methods of hydrogeochemistry, mineralogy and geochemical simulation, the results showed that the migration of harmful elements in acid mine water was mainly controlled by pH, Fe-Al-Mn content and mineral composition of particulate matter, and the removal sequence of ions with the increase of pH is as follows: Th>Fe>Pb>Cr>Al>Cu>Be>U>Zn>AsCd>Mn>Co>Ni>Ba. Liang et al. (2017) considered that the outflow of AMD from old coal mines is the main reason for the accelerated pollution of Niangziguan spring in recent years in the Yangquan coalfield by the isotope analysis and the hydrochemical content (sulfate, salinity, total hardness and chloride) of spring water. Zhang et al. (2019b) reviewed the karst springs in Shanxi and pointed out that AMD had accumulated the whole underground water-bearing space with a series of physical, chemical and biological changes and intensified effect on karst water in Niangziguan spring catchment. Lei (2011) and Shen (2011) reported the redistribution of ground stress had made the faults in Ximing and Duerping coal mines become a transmitting fault due to mining, which resulted in the infiltration of surface water and other upper aquifers. Based on a large number of investigations, sampling and analysis of groundwater and coal mine wastewater in Taiyuan Xishan coalfield, Zhao et al. (2008) revealed that the water-rock interaction and the change of redox environment had led to the great increases of hardness, sulfate and concentration of many heavy metals. On the basis of the previous research results, irreversible changes have taken place in the water-bearing medium structure, hydrodynamic field, chemical field and microorganism in the closed coal mines of Shanxi such as Datong coalfield, Yangquan coalfield and Taiyuan Xishan coalfield.

The outflow of AMD has already affected the aquatic environment of downstream rivers in Shanxi. For example, a large amount of AMD have been stored in the small abandoned coal mines in Xishan coalfield (Qiao et al. 2010), and the AMD leaked into the underlying karst aquifer through cracks and faults in the coal seam floor, moreover, the AMD in Niujiakou coal mine threatened the karst water quality of Jinci spring (Li and Wang 2019).

According to field investigation, the Shandi coal mine, which is located in Yangquan, Shanxi and has a mining history of about 60 years with longwall method. The mine was closed in 2005, and the goaf was filled with AMD in 2009. Based on the monitoring data in 2013, the salinity, sulfate and pH value were 8,274 mg/L, 5,781 mg/L and 3.51 mg/L, respectively (Yang 2017); at the end of 2016, the pH value was 2~3, and the sulfate was 11,370~18,900 mg/L. AMD outflowed the surface and polluted the groundwater and surface water resources in the Shandi River Basin (Zhang et al. 2019; Li and Wang 2019). Some scholars (Wang 2015; Huo et al. 2015; Liang et al. 2017) pointed out that both the AMD leakage into the aquifer and AMD outflow to the surface were the causes of the pollution of karst groundwater and surface water in the Niangziguan spring catchment in Shanxi. These case studies opened up a good warning and model to the research of AMD in Shanxi and attracted more scholars to conduct research on AMD.

It can be seen that the AMD is very common in abandoned coal mines. Due to the redistribution of ground stress and the recovery of groundwater level, different distribution of coal seams and associated minerals, the geological conditions (including invisible goaf, faults, collapse columns, fissures, roadways, etc.) had changed their original states. In addition, the formation of AMD is controlled by the factors such as precipitation, surface water, and aquifers. So the hydrogeological condition of AMD became more and more complex. The closure of coal mines in Shanxi mainly occurred after 2000, and the research on the water environment and ecological problems that may be induced by AMD in abandoned coal mines is still in its infancy. As one of the main coal energy bases in China, Shanxi has a large number of abandoned coal mines with complex hydrogeological conditions. What's more, coal and water co-exist in Shanxi coal mines, which have close hydraulic connection with the 19 major karst springs of Shanxi. Once the AMD problem continues to worsen, it will seriously threaten the safety of drinking water in the 19 spring catchments (Figure 1-2). Therefore, it is necessary to carry out further research on the geological and hydrogeological characteristics of AMD in Shanxi abandoned coal mines.

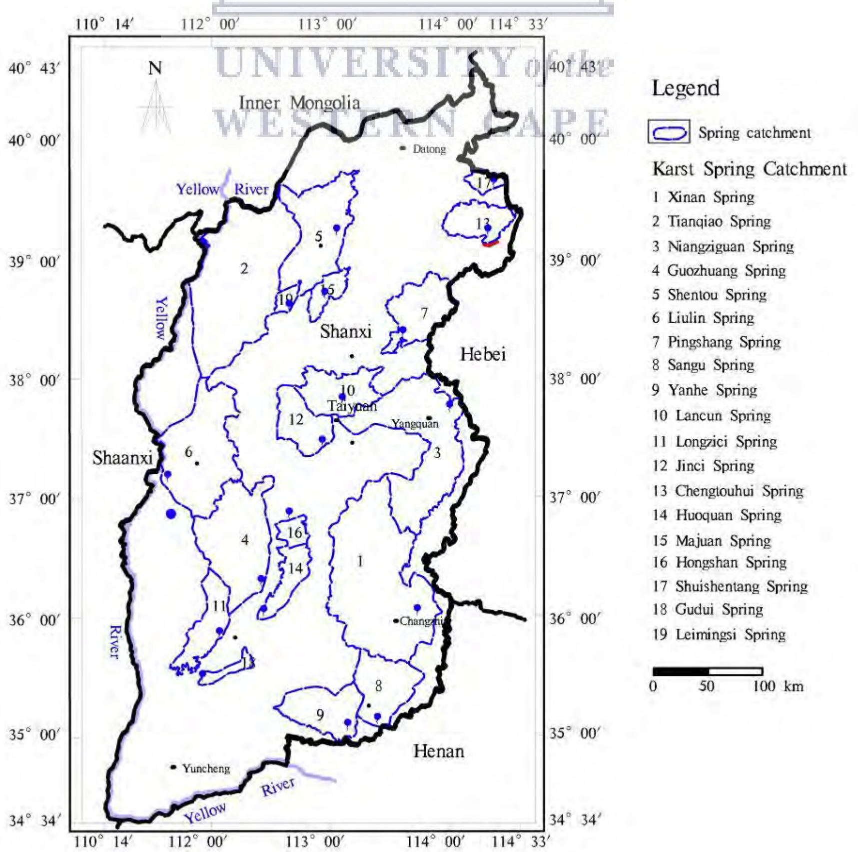


Figure 1-2 19 major karst springs in Shanxi Region

1.2 Research Objects

This thesis is focused to control AMD pollution in the Shandi coal mine and protect the water resources in the Niangziguan spring catchment, as well as to provide theoretical basis for water resource protection and AMD pollution treatment in abandoned coal mines in the nation and even in the world. By retrieving and analyzing the previous literature, the thesis critically reviews the AMD research results in Shanxi's abandoned coal mines from the perspectives of formation mechanism, migration and transformation, prediction, treatment and management. On the basis of field investigation and sample tests, the thesis researched the geological and hydrogeological characteristics of AMD from the abandoned Shandi coal mine. Finally, the feasible, affordable and self-sustaining engineering measures were put forward to control AMD pollution for local ecological environment. Hence, the research objects of the thesis are expected as follows,

1. Through the retrieval and analysis of about more than 90 national and international publications, the thesis aims to review the research findings on AMD from the perspectives of formation mechanism, migration and transformation, prediction, treatment and management, to analyze the problems and shortcomings in Shanxi abandoned coal mines, and to point out the way forward of the research on AMD in Shanxi.
2. On the basis of field investigation and sample tests, the thesis aims to analyze the water samples, coal seams and associated minerals in abandoned Shandi coal mine, and to research the geological and hydrogeological characteristics of AMD.
3. Based on the analysis of the geological and hydrogeological characteristics, the thesis aims to put forward the feasible, affordable and self-sustaining engineering measures to control the AMD pollution of local ecological environment.
4. The thesis would contribute towards the geological and hydrogeological characteristics of the Shandi coal mine, and the research results would provide important theoretical basis for water resource protection of Niangziguan spring and AMD treatment in abandoned coal mines in the nation and even in the world.

Chapter 2

Literature Review

The previous literature on AMD formation mechanism, migration and transformation, prediction, treatment and management in Shanxi abandoned coal mines are reviewed in the following sections.

2.1 coal and AMD in Shanxi

The major coal-bearing strata in Shanxi is dominated by the Taiyuan Formation of Upper Carboniferous (C_3t) and the Shanxi Formation of Lower Permian (P_1s) in Late Paleozoic, the coal reserves account for 98% of the region. The second coal-bearing strata in Shanxi is the Datong Formation of Middle Jurassic (J_2d) in Mesozoic and the coal-bearing construction of the Early Paleogene in Cenozoic.

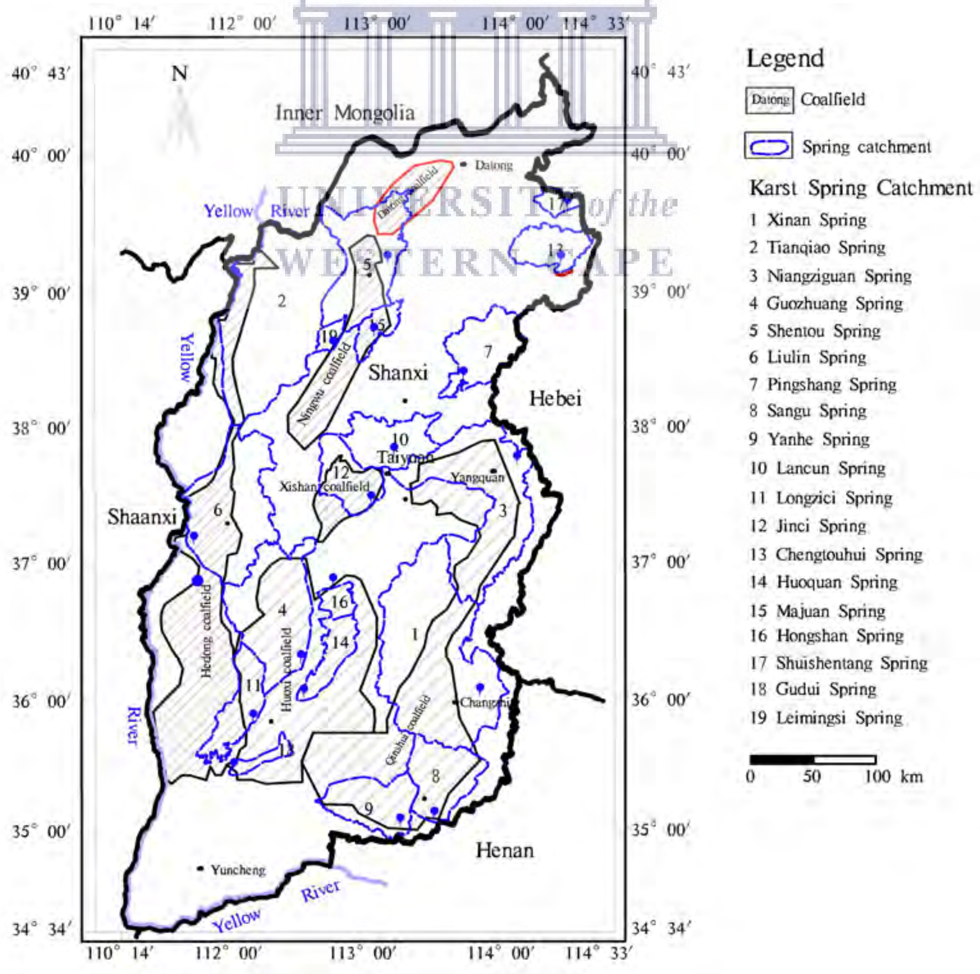


Figure 2-1 Location of 6 coalfields and 19 karst springs

Shanxi is the place with the most extensive karst distribution in northern China. There are 19 major karst springs (Figure 2-1) with stable flows and good water quality (Zhang et al. 2019b), which are convenient for centralized development and utilization, and has become one of the important water supply sources for Shanxi energy bases. According to statistics, there are 265 centralized drinking water sources in Shanxi. The groundwater supply in the 19 spring catchments accounts for more than 90% of the total water sources, of which approximately 83% is karst water. Over the years, researchers have conducted a certain degree of research on the relationship between AMD and water supply resources in Shanxi abandoned coal mines, and achieved many important results, which have good practical value and can lay the foundation for the research on AMD.

2.2 AMD formation mechanism

2.2.1 Source

Based on the existing research results of AMD in Shanxi abandoned coal mines, the pyrite associated with the coal seams is the main cause of AMD. When pyrite reacts with oxygen and water, the products are iron ion and sulfuric acid. The specific reaction equations are as follows:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (2\text{-}1)$$

$$12FeSO_4 + 6H_2O + 3O_2 \rightarrow 8Fe^{3+} + 12SO_4^{2-} + 4Fe(OH)_3 \quad (2\text{-}2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2\text{-}3)$$

It can be easily obtained from equations (2-1~2-3) that the oxidation of pyrite produces a large amount of H^+, and the O_2, H^+ and Fe^{3+} can directly or indirectly affect the oxidation rate. It is generally believed that the main oxidants for the oxidation of pyrite under aseptic conditions are O_2 and Fe^{3+} in aseptic environment (Moses et al. 1987; Nicholson et al.1988; Holmes and Crundwell 2000; Janzen et al. 2000; Long and Dixon 2004). The previous results showed that oxidation rate of pyrite increases with the increase of the Fe^{3+} and O_2 concentration in the lab test.

If the microorganisms on the surface of pyrite such as acidophilus thiobacillus ferrooxidans (Deng et al. 2013) are extremely active, the microorganisms obtain electrons firstly and combine with O_2, and the pyrite will be oxidized and leach a large amount of

Fe^{3+} simultaneously. The reaction equations are as follows:

$$4Fe^{2+} + O_2 + 4H^+ + A.f \rightarrow 4Fe^{3+} + 2H_2O \quad (2\text{-}4)$$

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S \quad (2\text{-}5)$$

The S generated by the above reactions is oxidized as the energy source of A.f:

$$2S + 3O_2 + 2H_2O + A.f \rightarrow 4H^+ + 2SO_4^{2-} \quad (2\text{-}6)$$

Under the action of microorganisms, the production rate of Fe^{3+} is $10^5 \sim 10^8$ times higher than that of aseptic environment (Kirby and Elderbrad 1998) and 1 million times (Singer and Stumm 1970). Meantime, Devasia and Natarajan (2010) showed that the extracellular polymers secreted by microorganisms contained a variety of functional groups which are easier to be adsorbed on mineral interface and interact with minerals.

Obviously, the oxidation mechanism of S_2^{2-} and Fe^{2+} are particularly important. Based on previous research results and the principle of redox, the reducibility of S_2^{2-} is greater than that of Fe^{2+}, that is, the S_2^{2-} preferentially oxidizes with O_2 in aseptic environment. The specific reaction equations are as follows:

$$S_2^{2-} + O_2 + OH^- \rightarrow S_2O_3^{2-} + H^+ \quad (2\text{-}7)$$

$$2S_2O_3^{2-} + 0.5O_2 + 2H^+ \rightarrow S_4O_6^{2-} + H_2O \quad (2\text{-}8)$$

$$S_2O_3^{2-} \rightarrow S + SO_3^{2-} \quad (2\text{-}9)$$

$$S + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (2\text{-}10)$$

$$SO_3^{2-} + 0.5O_2 \rightarrow SO_4^{2-} \quad (2\text{-}11)$$

The sulfur-containing intermediates (S_2^{2-}, S^0, $S_2O_3^{2-}$-, $S_4O_6^{2-}$, and SO_3^{2-}) had been detected when pyrite was oxidized in the lab (Mckibben and Barnes 1986; Moses et al. 1987). Because S_2^{2-}, S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$, and SO_3^{2-} have greater ability to obtain electrons than Fe^{2+} based on the molecular orbital theory and chemical bonding theory (Luther 1987), so the reaction rate of Fe^{2+} is basically negligible and basically exists in the form of Fe^{2+} in a closed environment with limited dissolved oxygen. Even if a large amount of dissolved oxygen exist, the reaction rate is quite slow. The excess Fe^{2+} reacts with the remaining O_2 after the reaction of equations:

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (2\text{-}12)$$

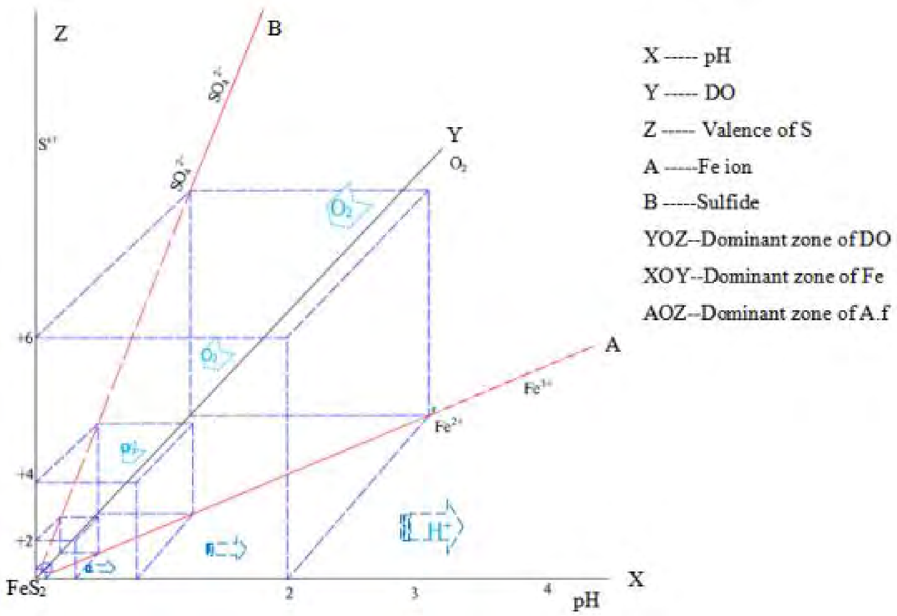


Figure 2-2 FeS₂ oxidation reaction

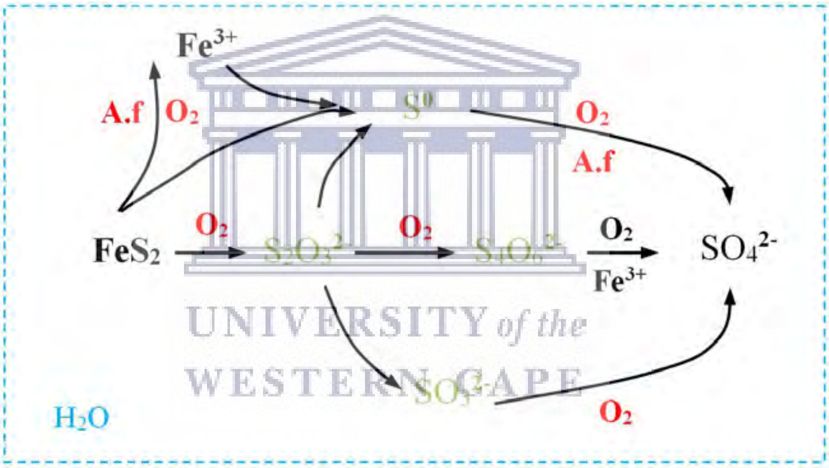


Figure 2-3 Intermediate reaction of FeS₂ oxidation

While the number of microorganisms is small, the activity is weak, and the two environments coexist. When the $S_4O_6^{2-}$ is produced, the Fe^{3+} can also participate in the oxidation reaction. The reaction formula is as follows:

$$S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 3Fe^{2+} + 4SO_4^{2-} + 9H^+ \quad (2\text{-}13)$$

Therefore, it comes to a simplified formation mechanism of AMD: pyrite is the prerequisite, oxygen is the inducement, water is the carrier, Fe^{3+} and microorganisms are the catalysts.

However, does the SO_4^{2-} content come entirely from the oxidation of pyrite? Is pyrite mainly from coal seams or the associated minerals? Is it mainly inorganic sulfur or organic sulfur? So there are still some puzzles waiting for further research. Li et al. (1998)

conducted a certain sampling analysis on the basis of the collected data. The results showed that the SO_4^{2-} from dissolution of natural gypsum ore in associated minerals accounts for about 30%, and the SO_4^{2-} from oxidation of pyrite accounts for about 60%~70%. The dissolution of natural gypsum ore and oxidation of sulfide were the main causes for the high concentration of SO_4^{2-}. Zhao et al. (2008) confirmed that the organic sulfur in coal seams can also generate acid after oxidation, which aggravates the decrease of pH value to a certain extent; when the organic sulfur content is >5%~7%, the pH value is 6~5.5; when the organic sulfur content is >7%~9%, the pH value is 5.5~3.5; when the organic sulfur content is >9%~11%, the pH value is 3; when the organic sulfur content is >12%, the pH value is below 2.5. According to the qualitative analysis (Liu et al. 2017; Zhang et al. 2007), AMD in abandoned coal mines in Shanxi is also generated by a series of oxidation reactions involving the pyrite mixed in coal seams.

It can be seen from the above results that the research on the formation of AMD is mainly concentrated in internationally and domestically, but there are still few studies in the Shanxi abandoned coal mines, so there is a big gap between Shanxi and domestic as well as international, such as inconsistent descriptions of the reaction process and insufficient consideration of influencing factors which limits the theoretical development of AMD's formation mechanism. For example, Liu (2007) pointed out that the No. 2, 3, and 5 coal seams of the Datong coalfield contain very low pyrite with the form of limonite, and confirmed that there is no AMD in many coal mines, the solubility of dissolved oxygen is basically maintained at 8~10 mg/L at a standard atmospheric pressure, which can demonstrate that the AMD are more likely to be formed where the pyrite is rich and dissolved oxygen is enough. The result is very helpful in determining the discharge location of AMD in an abandoned coal mine. In addition, all the complex recharges from precipitation, surface water, the overlying aquifers, coal-fissure water of adjacent mines, and underlying karst water may inundate the goafs, so it is difficult to determine that which goafs are flooded, how long the goafs will be re-inundated, whether the water in the adjacent mines and aquifers are neutral or acidic, what does the water-rock-coal interaction do. These also bring great difficulties to the research on AMD in an abandoned coal mine. The mine water may be acidic or neutral depending on the content of pyrite (Tiwary 2001) and dissolution depletion (Lambert et al. 2004) in the coal seam, but no similar researches have been done in Shanxi.

2.2.2 Water refilling process

As the water hazards in Shanxi coal mines are more prominent, scholars have focused on the water filling process of the conduction of the overlying aquifers and the underlying karst aquifer by the water conducting fissure, fault and collapse column, and many results have been achieved. For example, Zhang et al. (2011; 2015) systematically studied the development and evolution of the water conducting fissure, and explored the law of water filling of overlying aquifers caused by different mining thickness and buried depth. By numerical simulation methods, Kang (2012) researched the water conducting fissure of Nancha coal mine in Ningwu coalfield, and concluded that the main water refilling channels are the water conducting fissures, faults, collapse columns and poorly sealed boreholes. It reveals that the water filling process of the goafs is a dynamic process with diversity. In recent years, as the mining depth of Shanxi coal mines has changed from shallow to deep, the research on the limestone aquifers underlaying the coal seams as the main water sources has also received more and more attention. For example, Li (2018) summarized the factors affecting the water richness of limestone aquifers in the Fengfeng Formation of Ordovician in Shanxi six major coalfields, and believed that it was the main aquifer for water inrush from the coal floor of the lower formation, and pointed out the faults and collapse columns in each coal mine can be used as water filling channels for groundwater circulation. It can be seen that the content of previous researches has developed from the height of the water conducting fissure to the relationship between rock mechanical properties and water conducting channels.

In order to meet safe production, groundwater in the overlying aquifers is discharged in the form of mine water by pumping in Shanxi coal mines, which is a discharge process during the mining period. On the contrary, after the coal mine is closed, initial hydrogeological condition has been changed due to the goaf, fissure and roadway into a flow field dominated by pipeline flow. However, the water refilling process in abandoned coal mine is ignored. Up to now, the research on water refilling process has never been reported in Shanxi.

According to field investigations, the water refilling process of AMD in Shanxi abandoned coal mines has its uniqueness: the developed roadway systems left behind by underground mining are highly involved. These roadways not only run through the water refilling channels of different mining levels vertically, but also connect the water refilling space of different mining areas at a mining level, forming the strongest runoff corridor for mine water. After the coal mines were completely abandoned, the shafts and roadways were not effectively blocked, the goafs were not filled, and the runoff of groundwater had an essential change: at the same mining level, the water refilling space of different mining areas was connected in series, which accelerated the refilling process of groundwater; at different mining levels, the water refilling channels run through the upper and lower mining levels, so that the groundwater seeps into the lower level from the upper level. This kind of water refilling corridor breaks through the limits of water conducting channels such as water-conducting fissure, fault, collapse column, etc. The groundwater flow field and dynamic field have been changed, essentially and irreversibly. In fact, the research on water refilling process under the impact of water-conducting fissure, fault, collapse column, etc. in Shanxi abandoned coal mine has not been reported., but it will have a great theoretical guiding significance for the management of abandoned coal mines.

2.2.3 Water gathering space

Theoretically, when there is no recharge in the goaf or the discharge amount from the goaf is greater than the amount of refilling, there will be no water/AMD in the goaf; when the amount of refilling is greater than the discharge amount from the goaf, the goaf will be partially or fully refilled with water/AMD. It can be seen that not all the goafs can be refilled with water, and only the goaf with refilling water can be called AMD water gathering spaces.

So far, all the goafs formed by coal mining in Shanxi are about 20,000 km^2, equivalent to one eighth of Shanxi's land area (156,700 km^2). The goafs with refilling water (AMD) are prone to cause inrush accident during coal mining. Some scholars conducted research on the water gathering spaces in the goafs of Shanxi abandoned coal mines. Based on the collected data from 42 water gathering spaces of 28 coal mines in Qinshui coalfield, Xiong and Wang (2005) put forward the important term of water accumulation coefficient (the ratio of water volume Vz in goaf to coal volume Vp is called water accumulation coefficient C, that is, C=Vz/Vp) by laboratory research and theoretical analysis. Di (2007) discussed the storage and distribution law of AMD in the goaf of Datong-Ningwu coalfield, and believed that geological structure is the dominant factor controlling the distribution of AMD. Zhu (2014) confirmed that the partial sections of goaf can gradually gather water because it is located at a low level in the inclined direction of the coal seam. Wen and Zhang (2017) detected the water gathering space in a Shanxi large coal mine by using transient electromagnetic and direct current methods, and delineated the water gathering space of the goaf of No. 3 coal seam. Xu (2019) found out the location and scope of the goaf and the water gathering space of the coal mine using transient electromagnetic prospecting method. The above research results provide a reliable basis for the flood prevention, and also point out the direction and methods for the investigation and research of the water gathering space of AMD. However, these research results are without considering the water ecological environment problems caused by AMD in abandoned coal mines. In fact, geological structure is the dominant factor that controls the distribution of water gathering space of AMD (Pope et al. 2010).

In Shanxi Region, abandoned coal mines should be paid more attention and the research on water gathering space of AMD and geological structure need to be further strengthened.

2.3 Migration and evolution

Most of Shanxi abandoned coal mines were closed after 2000, and the water environment problems caused by AMD gradually emerged. At present, there are few research on the hydrochemical evolution of AMD in abandoned coal mines during the migration process. Regarding the research on the migration law of AMD in groundwater, some theories and opinions have been only put forward in individual coal mine. For example, Zhao et al. (2007) studied chemical composition and phase composition of AMD and its precipitates of Malan coal mine in Xishan coalfield by means of icP-MS, ION chromatography (IC) and X-ray diffraction (XRD), and the Pb, Th, U, Be, Zn, Ni, Co, Cd, Cu, As, Cr, V and Ba in typical AMD. The results showed that 1) the migration of harmful elements in AMD is mainly controlled by pH, Fe-Al-Mn content and mineral composition of water particles; 2) the contents of Fe, Al and Mn decreased rapidly with the increase of pH value, and controlled the migration behavior of Pb, Th, U, Be, Zn, Ni, Co and Cu; 3) V can not be removed with the increase of pH value, but more V will be dissolved in water; and 4) the removal sequence of ions with the increase of pH value is as follows: Th>Fe>Pb>Cr>Al>Cu> Be>U>Zn>As>Cd>Mn>Co>Ni>Ba. Zhao et al. (2012) used a soil column leaching experiment method to adsorb sulfate in AMD, the results showed that under the condition of a certain volume of loess, the processing capacity is in the order of Malan loess＞Lishi loess＞paleosol. Sun et al. (2012) tested the AMD, sediment, and rare earth element (REE) in two different coal mines in Shanxi, and revealed that: 1) the REE in acid mine water mainly came from the acid leaching of surrounding rock and pyrite; 2) pH value was the most important factor affecting REE content and distribution pattern in AMD; 3) with the increase of pH value of AMD, Mn hydroxide precipitation had the greatest influence on REE content; and 4) iron-bearing sediment preferentially adsorbed heavy and rare earth element.

It can be seen that the hydrochemical evolution of AMD in the migration process is concentrated in the migration and evolution laws of pH value and metal elements, which points out the direction for subsequent research. However, it can also be seen that the previous research methods are relatively simple. Strictly speaking, the Malan and Sitai coal mines are still mining the lower coal seams and pumping the mine water, which is different from the completely abandoned coal mines. Compared with the abandoned Shandi coal mine in 2005, the concentration of metals in AMD is still lower, indicating that the characteristics of hydrochemistry in the mining period and the abandoned period are quite different. Especially, the sulfate concentration in different stages is more than 10,000 mg/L, and it must has a greater impact on the hydrochemical equilibrium. Although the previous results have a certain of reference, it is difficult to fully promote the research on all abandoned coal mines in Shanxi.

The migration and evolution of AMD is a comprehensive process of active participation of multi-minerals (coal, pyrite, clay, etc.) and multi-gas components (CO_2, O_2, CH_4, etc.)

under the synergistic action of oxidation-reduction, dissolution-precipitation, adsorption-desorption, ion exchange, complexation and microbial action. Adsorption experiments and PHREEQC software are difficult to achieve this comprehensive process. For example, many minerals in the surrounding stratum have a buffering effect on AMD. Pyrite is the prerequisite of AMD, and the pyrite reserves determine the acid production capacity. If the acid production capacity exceeds the neutralization and digestion of alkaline minerals, the pH value will be lower and the mine water turn into the AMD. Meanwhile, the solubility will increase with the oxidation and dissolution of associated minerals; if the oxidation and dissolution of associated minerals achieve equilibrium with precipitation, adsorption and complexation, the solubility of AMD keeps a maximum value and will control the strength and activity of all ions in AMD.

The chemical reaction equations of common minerals in coal seams of Shanxi abandoned coal mines are as follows:

1) Main oxidation-reduction reactions:

It is the same as the former equations 2-1, 2-2, and 2-3.

2) Main dissolution reactions:

It can be described as the equations 2-14, 2-15, and 2-16.

$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ (2-14)

$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O$ (2-15)

$K_mNa_nCa_oMg_pFe_qAI_rSiO(OH)_2 + (0.5r+4s-12)H_2O + (22-4s-3r)H^+ \rightarrow mK^+ + nNa^+ + oCa^{2+} + pMg^{2+} + qFe^{3+} + 0.5r(AI_2O_3 \cdot 2SiO_2 \cdot 2H_2O) + (s-r)H_4SiO_4$ (2-16)

3) Main precipitation reactions:

It can be described as the equations 2-17 and 2-18.

$Na_{0.7}Ca_{0.3}AI_{1.3}Si_{2.7}O_8 + 1.3H^+ + 1.3H_2O \rightarrow 0.3Ca^{2+} + 0.7Na^+ + 1.3AI(OH)_3 + 2.7SiO_2$ (2-17)

$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$ (2-18)

4) Main ion exchange reactions:

It can be described as the equations 2-19 and 2-20.

$KAI_2(AISi_3O_{10})(OH)_2 + H^+ + 1.5H_2O \rightarrow K^+ + 1.5AI_2Si_2O_5(OH)_4$ (2-19)

$K(Mg,Fe)_3AISi_3O_{10}(OH)_2 + 7H^+ \rightarrow K^+ + 3(Mg^{2+},Fe^{2+}) + AI(OH)_3 + 2SiO_2 + 3H_2O$ (2-20)

5) Main microorganism reactions:

It is the same as the former equations 2-4 and 2-6.

6) Main adsorption-desorption reactions:

It can be described as the equations 2-21 and 2-22.

$$M^{+} + 3Fe^{3+} + 2HSO_4^{-} + 6H_2O \rightarrow MFe_3(SO_4)_2(OH)_6 + 8H^{+} \quad (2\text{-}21)$$

$$8Fe^{3+} + xSO_4^{2-} + (16\text{-}2x)H_2O \rightarrow Fe_8O_8(OH)_{8-2x}(SO_4)_x + (24\text{-}2x)H^{+} \quad (2\text{-}22)$$

7) Main complexation reaction:

It can be described as the equation 2-23.

$$Fe^{3+} + SiO(OH)_8^{-} \rightarrow FeSiO(OH)_8^{2+} \quad (2\text{-}23)$$

If there are insufficient acid-consuming minerals in the goaf, AMD will be formed. However, the main lithology of Shanxi coal-bearing strata are limestone, sandstone, mudstone and shale; among them, K2-K4 limestones have a good neutralization effect on acid, and sandstone, mudstone and shale are rich in clay minerals (kaolinite, montmorillonite, hydromica) with a good adsorption effect on metal ions. It can be seen that many factors control the evolution of hydrochemistry and the release of heavy metals. However, no studies have been reported on the environmental effects and release mechanism of heavy metals in Shanxi abandoned coal mines.

When the AMD in the goaf outflows to the surface water, it will enter into an open environment from a relatively closed environment, and the old hydrochemical balance is broken. Its water quality migration and evolution is accompanied by the reactions such as oxidation-reduction, dissolution-precipitation, adsorption-desorption, ion exchange, complexation and microorganisms, etc., and there are multiple minerals and gas components involved. The current researches mainly focus on the investigation of water quality in the polluted areas after the coal mines were closed, and there is a lack of targeted research on the migration and transformation of AMD in specific closed coal mines. A lot of work should be done to study the migration and transformation of AMD in Shanxi abandoned coal mines, and it is necessary to further strengthen the study of the respective effects of these factors and the coupling effects among multiple factors.

2.4 Prediction

In terms of time cycle, AMD will be discharged through different channels after the completion of water refilling in water gathering space of the goaf in Shanxi. Zhang et al. (2019b) pointed out that AMD leaked into the underlying karst aquifer; Li and Wang (2019) believed that the outflow of AMD polluted surface water; some scholars believed that AMD was discharged simultaneously to groundwater and surface water (Wang 2015; Huo et al. 2015; Liang et al. 2017). In fact, the water environment problems in Niangziguan spring (Yang 2017) and Jinci spring (Li and Wang 2019) caused by AMD are unavoidable problems in water sources protection. At present, a large number of valuable research results have been accumulated for the prediction of water inrush in the goaf of Shanxi. For example, Xiong et al. (2005) analyzed the hydrogeological conditions and possible causes of water inrush of the Qinshui coalfield, and proposed the concept of water accumulation coefficient, and determined the water gathering space in the goaf. Di (2007) predicted the water accumulation in the goaf of Tongxin coal mine using the water accumulation coefficient; Kang (2012) analyzed the water gathering space in the Nancha coal mine of Ningwu coalfield using comprehensive method. Wen and Zhang (2019) accurately determined the range of gathering water by using the combination of transient electromagnetic exploration method and direct current method, and predicted the amount of gathering water in the goaf. These theoretical methods and practical experience research provide a reliable theoretical basis for Shanxi AMD prediction.

It is important to emphasize that prediction of AMD in abandoned coal mines is different from the mining coal mines, the prediction should focus on the process of water refilling, change of AMD storage (groundwater level) and outflow of AMD. Based on associated prediction, the impact of AMD on the environment can be evaluated at any time to provide environmental load capacity for the scientific prevention strategies and treatment measures.

To sum up, the above researches can only solve the water inrush and gathering problems in AMD, but there are still many weaknesses in the research on the prediction of change of AMD storage (groundwater level) and outflow of AMD. For abandoned coal mines, the scholars prefer to solve these problems with prediction result of AMD as follows: when the AMD will outflow, where it will outflow and how long it will last. As mentioned above, the Shandi coal mine was abandoned in 2005, and the goaf was refilled with AMD in 2009

(Yang 2017). At present, scholars have not reported any researches on AMD's prediction in Shanxi abandoned coal mines.

From a regional perspective, the AMD environmental problems in Shanxi are mainly concentrated in Datong mining area (Xu et al. 2007; Zhao et al. 2007), Yangquan mining area (Liang et al. 2017; Zhang et al. 2019c), and Taiyuan Xishan mining area (Lei 2011; Shen 2011; Zhao et al. 2008). A further study is needed to explain that why the outflow of AMD occurred firstly in these coal mining areas. From a single coal mine, the AMD will outflow through different channels, and the spatial distribution of discharge points should have their own particularity. Up to now, a total of about 8,780 coal mines of various sizes in Shanxi have been abandoned, so it is more necessary to conduct research on the prediction of the AMD, including water refilling process, change of AMD storage (groundwater level) and outflow of mine water/AMD. These studies can gain precious time for AMD prevention and provide precise spatial instructions for AMD prevention and control areas (points).

2.5 Treatment

AMD pollution is a global problem and has received more attention from global scholars. For many years, in order to desire for the highest profit, coal mining always trends to never engage in environment protection, and Shanxi governance has no corresponding plan for the treatment of the closed mines.

At the same time, due to the constraint of economy and technology in Shanxi, the AMD treatment is mostly concentrated in the centralized treatment of mine water during coal mining. Most coal mines treated the AMD by using lime and limestone neutralization as well as sedimentation methods in the form of sewage treatment stations. Recently, the reverse osmosis membrane has been added with the upgrading of the standard. At present, scholars have studied the AMD treatment in Shanxi abandoned coal mines by different methods. For example, Yin (2007) and Liu (2008) remedied AMD using the desulfurization vibrio in the sludge of sewage purification plant as the bacterial strain. The test showed that the maximum removal rate of sulfate in AMD was 64.75%, and the maximum removal rate of sulfate was 81.9%. Yang et al. (2008) simulated the bioremediation of AMD in natural drainage pool using an open reactor in laboratory, and explored the feasibility of the bioremediation under the condition of enough required carbon sources. Zhao et al. (2012) used a method of column leaching experiment to adsorb sulfate in AMD, the results showed that the sequence of the adsorption capacity is in the order of Malan loess ＞ Lishi loess ＞ paleosol. Zhou et al. (2014) used sodium hydroxide (NaOH) to treat AMD, and gained better results. Taking four groups of sandy soils (screened from Malan loess) as an adsorption material for AMD, Wu et al. (2018) studied the removal efficiency of sulfate ion in AMD by different particle sizes of less than 0.075 mm, 0.075-0.500 mm, 0.500-2.000 mm and 2.000-5.000 mm, the result showed that the removal efficiency was up to 62.36% for the group of less than 0.075 mm. By using Malan loess, iron slag and carbon steel slag as adsorbent, Zheng et al. (2019; 2020) tested the effect of solid-liquid ratio, contact time, initial concentration, temperature and pH on sulfate adsorption in AMD, and the result indicated that acid condition was favorable for sulfate adsorption. Wan and Li (2004) introduced the corncob as a new carbon source for Sulfate Reducing Bacteria (SRB) to verify the feasibility of biological treatment for AMD and the possibility of resource utilization of wastewater from sulfate mines. Lu et al. (2018) studied the modified red mud for AMD adsorption and obtained a good effect. Wang et al. (2005) and Zhang (2007) proposed the method of treating AMD using "loess-wetland-plant-microbial ecosystem", this is because that the loess is an alkaline weathering crust with rich void, clay mineral, organic matter and microbial, it can provide conditions for neutralization reaction, adsorption, ion exchange and biochemical reaction. Soil is the substrate and carrier of wetland, it has strong retention and accumulation capacity of metals by inorganic and organic components in itself. Duckweed has a high enrichment coefficient of heavy metals, especially Zn, it can greatly reduce Fe and Zn in AMD, and the removal efficiency of Mn can reach 100%, the Reed can purify Pb, Mn and Cr with removal efficiency of 80.18%, 94.54% and 100%, respectively. They both enriched Al, Fe, Ba, Cr, Co, B, Cu, Mo, V and Zn, the reduction of sulfide produced by sulfuric acid reducing bacteria in AMD, the heavy metals will generate sulfide precipitation and be effectively purified. So "loess-wetland-plant-microbial ecosystem" has its feasibility and advantages. These researches have a significant guiding role in dealing with AMD problems in Shanxi abandoned mines, but they are basically at the stage of laboratory experiment and theoretical research.

Due to the variety of metals and high concentrations in AMD, it increases the difficulty of large-scale treatment for AMD. The above-mentioned treatments mainly focus on neutralization, permeable membrane filtration, adsorption, microbial method, etc. Although these methods have their applicability in some certain scenarios, their successful results are not applied to treat AMD in the abandoned mines. At present, the permeable membrane filtration method has the advantages of non-waste generation, fast separation rate, and high selectivity. However, it has several problems of polarization, scaling and corrosion. In consideration of lower energy consumption and simpler operation, the adsorption method is popularly used to treat AMD, but it only achieves the transfer of pollutants and will result in the secondary pollution. Microbial method has the advantages of low cost, strong applicability, great potential, and non-secondary pollution, but it will take a long time to domesticate the particular microorganisms with economic organic carbon source.

It can be seen from the above researches that most of researchers studied the removal of pollutants in AMD by a single method and AMD treatments were limited by the technology and the fund in Shanxi. There is no successful case for the AMD treatment in Shanxi abandoned coal mines. The groundwater pollution caused by AMD in Shanxi abandoned coal mines has not received enough attention. Therefore, AMD has become a serious pollution source to the surrounding environment and forms a potential threat to the safety of the downstream drinking water. The research on the comprehensive treatment of AMD in Shanxi abandoned coal mines is of great significance to prevent the water pollution and water safety of drinking. Therefore, exploring an affordable, efficient, environmental treatment technology for AMD will become a hotspot in Shanxi.

2.6 Management

Based on the investigation and data verification, when the Shanxi abandoned coal mines were closed, the main measures were both shaft closure and roadway blockage, but both of measures can not prevent the formation and discharge of AMD. At present, due to the lack of monitoring data of AMD in abandoned coal mines, the damage to groundwater can not be effectively estimated. Up to now, Shanxi government has not promulgated the special policies and regulations for AMD management, and lacked the technical chart for AMD risk management and AMD risk early warning mechanism of abandoned coal mines.

It can be seen that the situation of AMD management in Shanxi abandoned coal mines is still severe, and policies and regulations for AMD management are still lacking. It is urgent to strengthen research on the risk assessment, early warning mechanism and management of abandoned coal mines. The results can provide technical support for the formulation of relevant policies and regulations, so it is of great significance for the standardization of AMD management and the sustainable development of the ecological environment as well as the safety of drinking water in Shanxi.

2.7 Problems and difficulties

With the continuous increase of abandoned coal mines in Shanxi, environmental problems such as the destruction of water resources and the deterioration of water quality caused by AMD pollution are becoming an urgent topic for research. Scholars have accumulated rich experience in Shanxi coal mines for the research on water inrush, mining under pressure, decompression drainage and water resources evaluation and management, and achieved a series of important research results. However, the existing theories, technologies and methods are mainly suitable for newly-built and active mines, there are still many doubts and difficulties to be solved in the research of AMD from abandoned coal mines in Shanxi, which mainly include the following contents.

2.7.1 Distribution of AMD

Pyrite is a common mineral widely distributed in coal-bearing strata, but there is no detailed study on the distribution of pyrite in Shanxi. The content of pyrite in No. 2, 3, 5 coal seams of Datong coalfield is reported that it is very low and not easy to form AMD (Liu 2007), so it is very partial that the pyrite in the coal-bearing strata can cause AMD without its content and mineral reserve. Therefore, the occurrence law and spatial distribution of pyrite in Shanxi coal-bearing strata are worthy of further study, especially in abandoned coal mines.

Among the six major coalfields in Shanxi, only the specific positions in Datong, Ningwu, Xishan and Qinshui coalfields emerge AMD problems. Their common characteristics of spatial distribution of AMD zone are that the outcrops of coal seams are exposed and the coalfield always is cut by the nearby river (Figure 2-4), which carries a large amount of dissolved oxygen and organic matter for the oxidation of sulfide minerals, so the surface water plays an irreplaceable role as a carrier of oxygen and organic matter. Due to the complex recharge of AMD, including precipitation, surface water, overlying aquifers, underlying karst water and fissure water of adjacent mines, all these may enter into the goaf, and their different types and rates of water circulation also bring great difficulties to the AMD research. AMD has a close hydraulic connection with surface water and groundwater, but there is few research on the hydraulic connection between them. The hydraulic connection of AMD with surface water and groundwater is of great guiding significance for determining the regional distribution of AMD, so further investigation and research are needed.

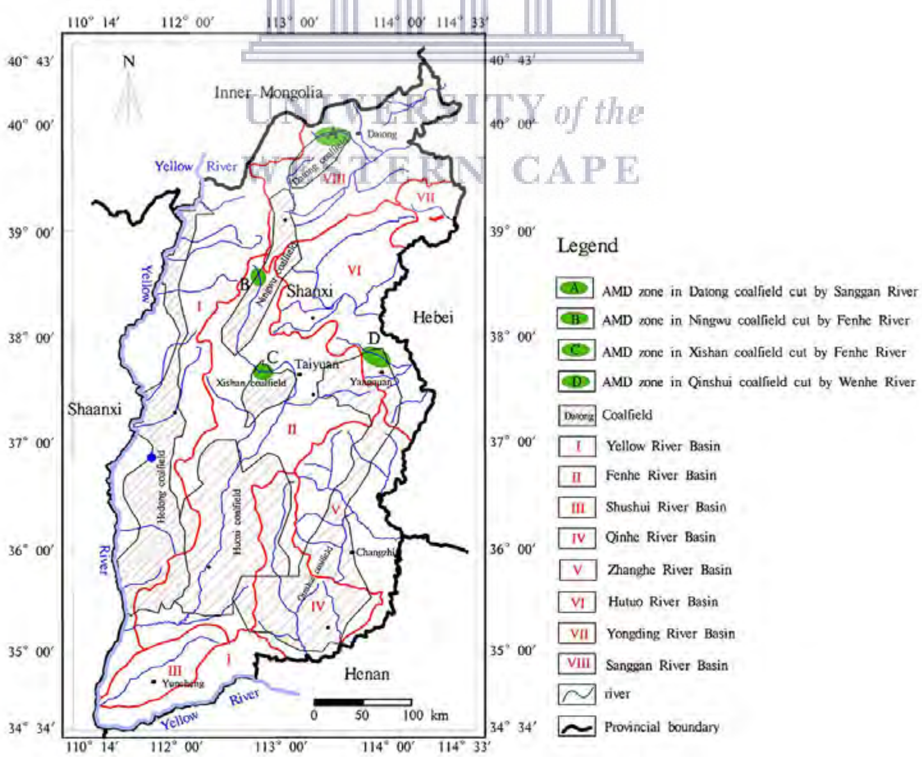


Figure 2-4 Specific AMD zones in four coalfields cut by three rivers

2.7.2 High participation in roadway system

As a runoff gallery, the groundwater in the underground roadway presents a significant state of the pipeline flow. Because the underground roadway extends to all directions, so this special pipeline fluid of groundwater in abandoned coal mines is different from the fissure flow in the aquifers. In terms of groundwater simulation in mining areas, the current main focus is to simulate the fissure flow, the pipeline fluid in the underground roadway system has been rarely reported. In fact, there is a multi-layer and multi-channel flow formed by the overlapping of the fissure flow in the water conducting fissure and the pipeline flow in the abandoned underground roadways. The relationship between the recharge and discharge of groundwater is directly or indirectly determined by the geology, underground roadway and water conducting fissure. As a result, this kind of multi-layer and multi-channel flow makes it difficult for generalization, analysis and prediction due to its randomicity, fuzziness and uncertainty. So the research results on the multi-layer and multi-channel flow are rarely reported for abandoned coal mines in Shanxi. Therefore, it is necessary to study the dynamic evolution of groundwater flow under the action of underground roadway in Shanxi abandoned coal mines (Figure 2-5).

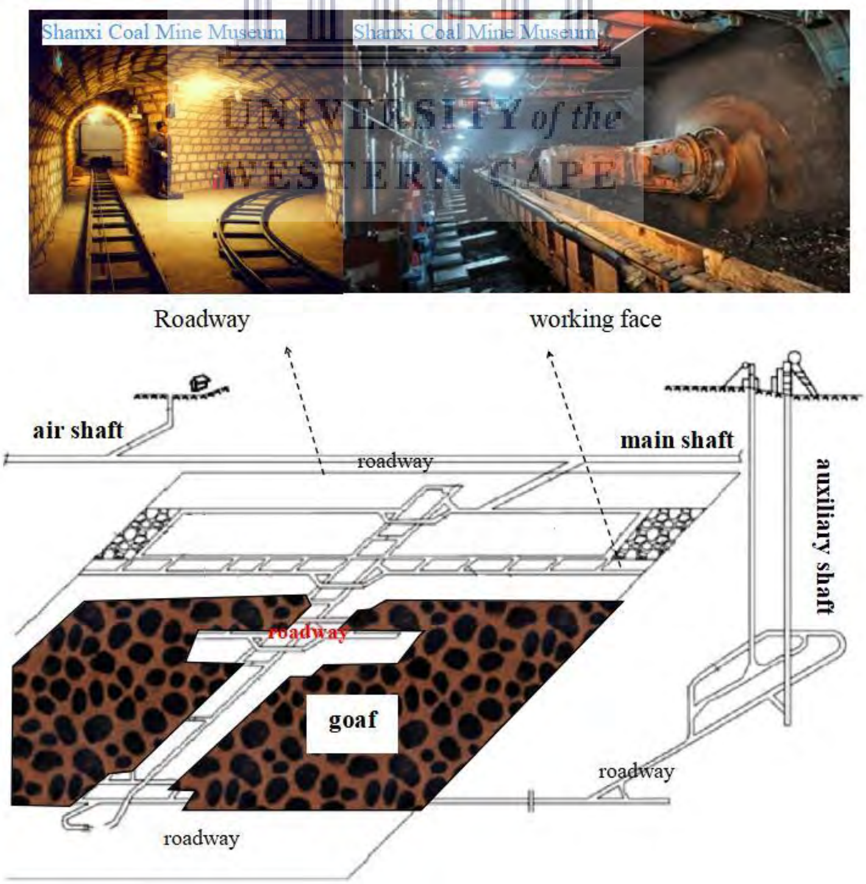


Figure 2-5 Underground roadway system

2.7.3 Effective water gathering space

It is of great significance to carry out the research on the detection of water gathering space. Due to the hidden characteristics of gathering water in the goaf, its spatial distribution (boundary and shape) and occurrence law are very complicated, so relationship between the water storage and spatial distribution presents its non-linear variation with time, and the parameters such as groundwater head and water accumulation coefficient are difficult to be determined and bring great trouble to the detection work of AMD.

In addition, the detection result of a single coal mine or a certain goaf is limited by its hydrogeological condition, and can be not applied to other mines. Therefore, it is necessary to carry out research on effective water gathering space of AMD. Theoretically speaking, the goafs will be easier to form effective water gathering space at the working face of the lower formation, the two wings of the middle and lower anticlines, the syncline axis and the lower plate of the positive fault. Geological structure is the dominant factor of controlling the distribution of effective water gathering space in the goaf. Besides, there are other important impact factors, such as the depths of mining and the hydrogeological properties (Figure 2-6). Hence, study on the inner relation between impact factors and effective water gathering space is further needed including geological structure, the depths of mining, the hydrogeological properties etc.

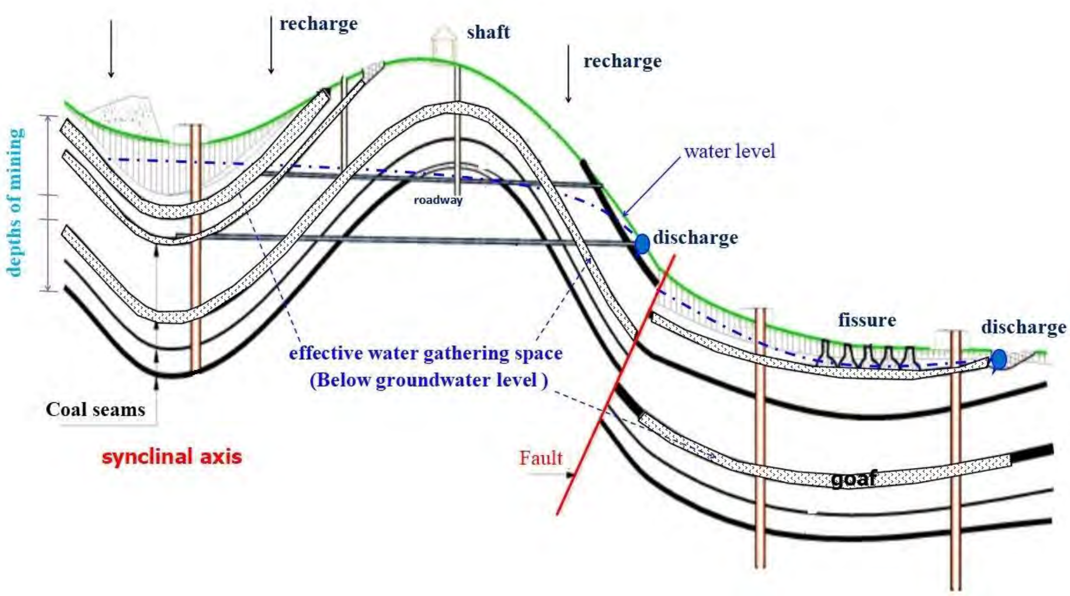


Figure 2-6 Refilling and discharge of AMD in abandoned coal mine

2.7.4 Discharge channel

The closure of Shanxi coal mines mainly occurred after 2000. According to field survey, most of the closed coal mines are in the water refilling and water gathering stage. The previous literature only qualitatively reported that AMD had recharged into the local coal-bearing aquifers and directly outflowed to the surface water after coal mines were closed, but the researchers did not further discuss how to recharge and discharge.

As the typical Carboniferous-Permian coal-accumulating area in northern China, Shanxi coal seams have close hydraulic connections with the underlying Ordovician karst aquifers. Once AMD in abandoned coal mines is generated, there are only three discharge channels: outflow to the surface water; recharge to coal-bearing aquifer; leak into underlying karst aquifer. So the leakage into the underlying karst aquifer is one of the main channels of AMD discharge, and its discharge capacity depends on the fault and collapse column (Figure 2-7) between the water gathering space and the karst aquifer.

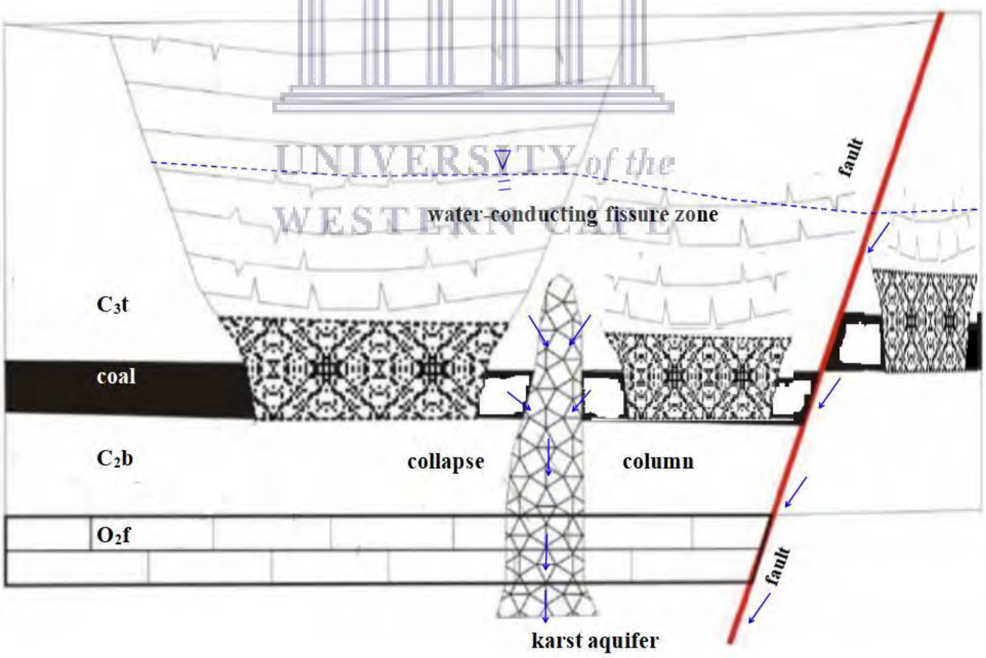


Figure 2-7 The fault and collapse column

However, there are few studies on the AMD leakage through these leakage channels, such as faults and collapse columns. For example, the faults in Dahangou coal mine in Ningwu coalfield directly connect the coal-bearing aquifer with the Ordovician aquifers. There are about 450 and 400 collapse columns found in Qinshui and Xishan coalfields, respectively, which can directly become the leakage channels of AMD, and have great influences on the water quality of the underlying karst aquifers. Due to the control of other factors such as geological structure, refilling material, cementation and water pressure, the research on discharge channel in Shanxi abandoned coal mines is more complicated. Therefore, from the perspective of protecting Shanxi's karst water resources and drinking water safety, it is necessary to carry out research on the discharge channel of AMD in abandoned coal mines, especially the faults and collapse columns.

2.7.5 Water quality migration and evolution

At present, research on the migration law and hydrochemical balance of AMD in Shanxi abandoned coal mines is basically theoretical. For example, Zhao et al. (2007) studied the chemical composition and phase composition of AMD and sediments in Malan coal mine in Taiyuan. Sun et al. (2012) determined the content of rare earth elements in AMD, sediments and coal samples in two different mining areas in Shanxi. The previous research did not consider the participation of microorganisms, gas components, etc. Due to irreversible changes in the water-bearing medium and groundwater channel in abandoned coal mines, the hydrogeological conditions have become more complex. Considering that it is more difficult to collect water and rock samples from abandoned coal mines, the research is suffering more challenges. In fact, hydrochemistry research on the migration and evolution of AMD during water refilling and water gathering has rarely attracted scholars' attention in Shanxi. Therefore, it is necessary to further carry out research on the migration and evolution of AMD.

2.7.6 Hydrochemistry equilibrium

After AMD overflows to the surface water from a relatively closed environment into an open environment, the hydrochemical equilibrium is broken and tends to a new chemical equilibrium. For example, the AMD from an abandoned coal mine in Yangquan coal mining area has polluted the Shandi River Basin (Figure 2-8). According to the test results, the AMD near Shandi coal mine is highly acidic with pH value at 2~3, and contains high sulfate with 11,370 mg/L, which exceeds the class III of "China Groundwater Quality Standard" (GB/T14848-2017) by 45 times, and heavy metals such as Fe, Mn, Zn, Cd exceed the standard by 1100, 510, 10, and 50 times, respectively.

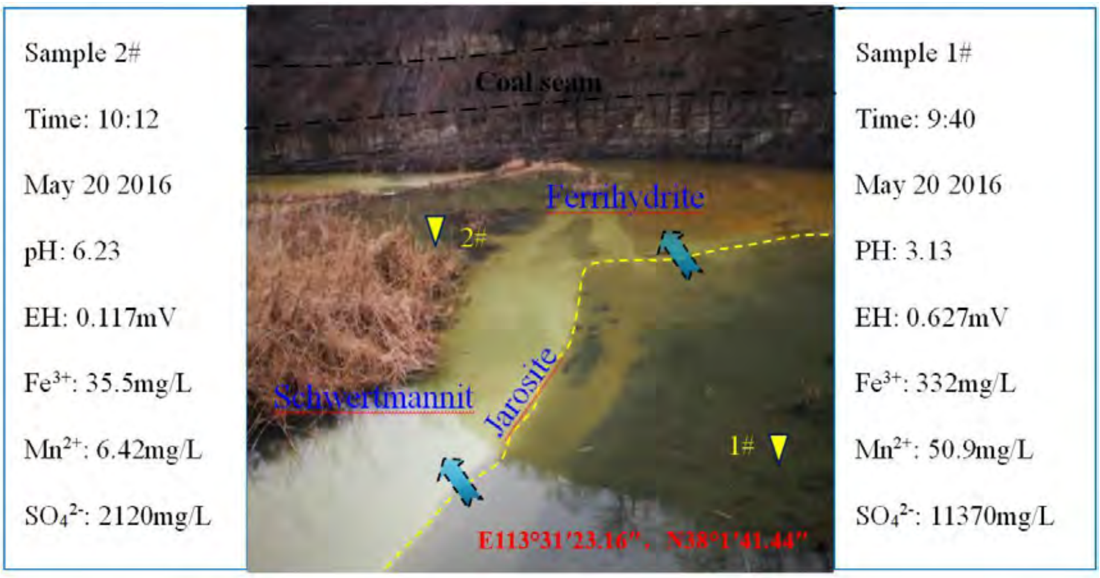


Figure 2-8 AMD in Shandi Village, Yangquan, Shanxi

It can be seen from Figure 2-8 that the secondary minerals were produced in the river. Once the AMD outflow into the surface water, the Jarosite (K, Na, $H_3O[Fe_3(OH)_6(SO_4)_2]$), Schwertmannite ($Fe_8O_8(OH)_6(SO_4)$) and Ferrihydrite ($Fe(OH)_3$) can be clearly identified in the sediment of the river bed. In an open environment, the EH will lower rapidly with plenty of oxygen, at the same time, the massive heavy metals (Fe, Mn) and SO_4^{2-} are reduced by surface adsorption and co-precipitation process of these secondary minerals as the following equations:

$$3Fe^{3+} + 2SO_4^{2-} + (K^+,Na^+,NH_4^+,H_3O^+) + 6H_2O \rightarrow (K,Na,NH_4,H_3O)Fe_3(SO_4)_2(OH)_6(s) + 6H^+ \quad (2\text{-}24)$$

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(OH)_6(SO_4)(s) + 22H^+ \quad (2\text{-}25)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \quad (2\text{-}26)$$

$$HCO_3^- + H^+ \rightarrow CO_2(g) + H_2O \quad (2\text{-}27)$$

In the end, a large quantity of generated H^+ is consumed by the neutralization of HCO_3^- and the pH goes up. These data indicated that through physical and chemical reactions such as oxidation, deposition and adsorption, AMD is in a new chemical equilibrium state and destroys the water ecological environment of the downstream rivers.

Moreover, the pressure and temperature of various gases and ion concentration of AMD have an impact on the hydrochemical equilibrium. At present, there is no report on the research of AMD hydrochemical equilibrium in Shanxi abandoned coal mines. Therefore, it is necessary to strengthen the research on hydrochemical equilibrium of AMD under the outflow state.

2.7.7 Outflow prediction of AMD

After coal mines have been closed for decades or even hundreds of years, AMD pollution to the regional water environment still exists. According to statistics, as the main coal production area in China, Shanxi has at least 8,780 closed coal mines, so it is very necessary to predict the change of AMD storage (groundwater level) and outflow of AMD to solve the following issues, such as when the AMD would outflow, where it would outflow and how long it would last.

In order to facilitate the description of the prediction of outflow of AMD, the abandoned coal mine is regarded as a trapezoidal reservoir, the outflow of AMD can be equivalent to a releasing/discharge process in exceeding maximum reservoir capacity. Based on the previous research on water accumulation coefficient and the principle of water balance, the thesis establishes a dynamic prediction model as the following equation 2-28.

$$V(t,h) = C(t,h)A(t,h)\frac{dh}{dt} = Q(t) - q(t) - L(t,h) \quad (2\text{-}28)$$

Where, V(t,h) is storage volume, m^3/d; C(t,h) is water accumulation coefficient; C(t,h)=V(t,h)z/V(t,h)p; A(t,h) is water gathering spaces, m^2; Q(t) is recharge volume, m^3/d; L(t,h) is leakage volume, m^3/d; q(t) is discharge volume, m^3/d; h is groundwater level, m.

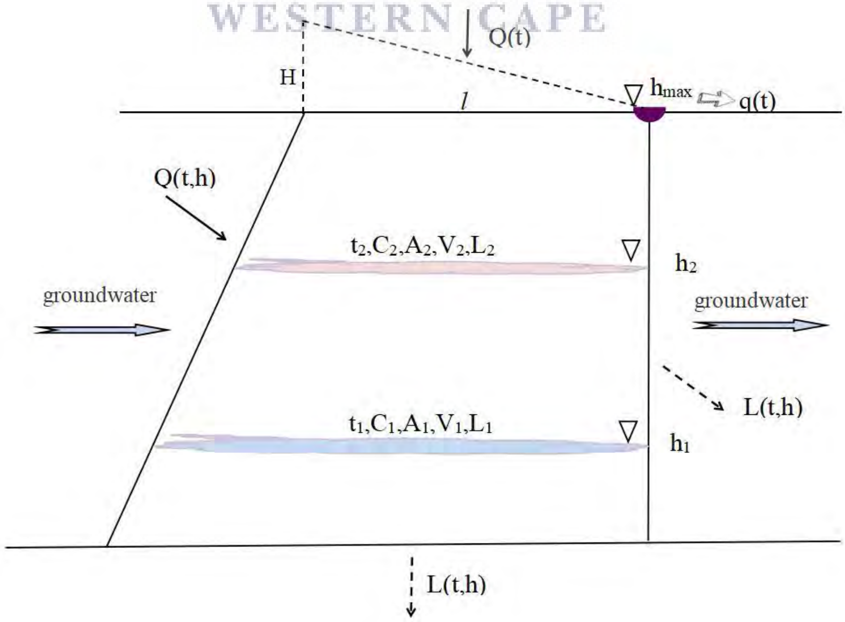


Figure 2-9 Dynamic prediction model of AMD discharge

It can see that in Figure 2-9, when $h < h_{max}$ and $Q(t) > L(t,h)$, the q(t) can be predicted as 0 and it is a water refilling process in water gathering space; when $h = h_{max}$ and $Q(t) > L(t)$, q(t)=Q(t)-L(t) can be obtained, and so it forms a discharge process.

At this time, L(t) is approximately equal to a constant. According to the hydraulics theory, it is assumed that outflow of AMD at the end of spillway follows the pipeline flow equation, so the water inrush depends on the spillway diameter and the hydraulic gradient. The discharge volume can be calculated by the following equation 2-29:

$$q(t)=\frac{\pi d^4 r}{128\mu}\frac{H(t)-h_{\max}}{l} \tag{2-29}$$

If it is assumed that h_{max}=0, so a new equation on how long outflow of AMD will last can be obtained:

$$\Delta T=\frac{Q(t)}{q(t)}=\frac{128\mu l}{\pi d^4 r}\frac{Q(t)}{q(t)} \tag{2-30}$$

Where, Q(t) is recharge volume, m^3/d; l is the distance between H and h_{max}, m; q(t) is discharge volume, m^3/d; H is relative height of groundwater level, m; d is equivalent spillway diameter.

The AMD outflow is affected by many factors, such as water recharge, water gathering space, and discharge capacity. At the same time, the AMD quantity changes over time. However, the current research cannot fully and truly reappear the water level dynamics of AMD in abandoned coal mines. In addition, the spatial location of the discharge point is controlled by many factors such as geological structure, underground roadway system, coal outcrop and shaft. The concealment of the goaf increases the difficulty of research. At present, there is a lack of research on the correlation between the outflow of AMD and impact factors in Shanxi abandoned coal mines, and no relevant investigation and research have been carried out on the time and location of the AMD outflow. Therefore, it is necessary to carry out research on the outflow prediction of AMD in Shanxi abandoned coal mines.

2.7.8 Treatment

Due to the constraints of economy and technology, the treatment method for AMD in Shanxi abandoned coal mines is relatively simple. For example, Yin et al. (2007), Zhao et al. (2007) and Liu (2008) used desulfurization bacteria in natural loess and desulfurization vibrio bacteria in sewage purification plant sludge to remove sulfate. In addition, the neutralization precipitation method (Zhou et al. 2014), sandy soil (Wu et al. 2018), Malan loess, ferrous slag and carbon steel slag (Zheng et al. 2019; Zheng et al 2020), corn cob and SRB method (Wan and Li 2004), red mud (Lu et al. 2018), "Loess-Wetland-Plant-Microbial Ecosystem" (Wang et al. 2005; Zhang 2007) have been used to treat AMD in Shanxi abandoned coal mines. However, all of these methods are in the laboratory and theoretical stages, and there is still not a successful case for the AMD treatment in Shanxi abandoned coal mines. Therefore, it is necessary to explore an efficient, inexpensive, environmental treatment technology for AMD treatment, such as artificial wetland and PRB restoration technology. These technologies are widely used internationally, while national applications are more concentrated in the AMD treatment for metal mines, and the AMD treatment in Shanxi abandoned coal mines is relatively lacking. Therefore, it is necessary to adopt a comprehensive method and apply it in practice to treat AMD in Shanxi abandoned coal mines.

2.7.9 Management

Currently, Shanxi lacks management policies and regulations for abandoned coal mines. Coupled with the lack of monitoring data of AMD pollution, the harm of AMD cannot be estimated. The measures such as shaft closure and roadway blockage are difficult to completely avoid the recharge of AMD and groundwater channel, and helpless to prevent the discharge of AMD from destroying the regional water environment.

Moreover, Shanxi has not promulgated the policies and regulations for AMD management of abandoned coal mines, and has not constructed the AMD risk assessment model and early warning mechanism for abandoned coal mines. For 8780 Shanxi abandoned coal mines, the utilization rate of AMD is extremely low. Therefore, it is urgent to strengthen the research on the management, risk assessment and early warning mechanism of AMD in Shanxi abandoned coal mines.

2.8 Way forward

For the sake of avoiding further deterioration of water resources and water environment in Shanxi caused by AMD, the researchers and Shanxi government should carry out further research from the following aspects.

(1) The regional distribution of pyrite and the occurrence law in coal-bearing strata in six major coalfields of Shanxi should be actively carried out; the hydraulic connections among surface water, groundwater, geological structure, water-conducting fissure and the formation, migration and evolution of AMD should be further researched.

(2) The researchers should improve the comprehensive detection method of the hydrogeological condition, water channel, water gathering space and underground roadway system of abandoned coal mines, and pay more attention on the formation, migration and prediction of AMD and the related environmental issues. The groundwater model under combined action of underground roadway system, geological structure and primary fissures needs to be established.

(3) The formation mechanism of AMD in abandoned coal mines needs to be studied, and it is necessary to consider the influence of microorganism, gas component and other factors. To effectively predict and prevent the generation of AMD, the sulphate and the harmful elements should be clarified. Furthermore, the risk assessment of AMD pollution needs to be constructed to provide effective support for scientific plan and decision-making.

(4) It is necessary to predict mine water/AMD and solve the following issues such as when the AMD would outflow, where it would outflow and how long it would last. Research on the correlation between AMD outflow and impact factors should be strengthened, and relevant investigation and prediction should be carried out to solve the above three issues. More attention should be paid to the effects of gas composition, pressure, temperature and ion concentration of AMD on the hydrochemical equilibrium.

(5) It is necessary to actively carry out research on the application of comprehensive treatment method such as the artificial wetland and PRB in abandoned coal mines, and explore an efficient, affordable, environmental technology for the AMD.

(6) Technical guidelines should be issued to guide coal mine closure and supervision as soon as possible. A network system for monitoring the AMD groundwater in abandoned coal mines should be established to provide effective information for AMD risk identification. Research on management, risk assessment and early warning mechanism for the AMD in abandoned coal mines should be strengthened.

(7) To alleviate the shortage of water resources in Shanxi and ensure the safety of drinking water, in-depth study of the hydraulic connection between the AMD in abandoned mines and karst springs should be strengthened, which is helpful to the sustainable development of coal, water resources and ecological environment.

2.9 Summary

This chapter introduced an overview of AMD in abandoned coal mines in Shanxi, China. It is concluded that that sulfur minerals and refilled water are main sources for the formation of AMD, pyrite is the prerequisite, oxygen in the refilled water is the inducement, water is the carrier, Fe^{3+} and microorganisms are the catalyst. The underground roadway system and geological structure are the dominant factors that control the water gathering space of AMD. The AMD from abandoned coal mines has worsened the severe water ecological environment. It has aggravated the current situation of water shortage in Shanxi, and brought the problem of ecological environment and the crisis of drinking water safety, so it is necessary to conduct further research on AMD in abandoned coal mines.

There are still some problems in the previous research of AMD in Shanxi abandoned coal mines: (1) the regional distribution of pyrite and its occurrence law in coal-bearing strata in six major coalfields need to be further investigated and researched; (2) the developed underground roadway system of abandoned coal mines is very difficult to be generalized to analyze the AMD flow field; (3) water gathering space in abandoned coal mines are very complicated and it is difficult to grasp and determine the water head and water accumulation coefficient in the goaf; (4) the research on the leakage channel, such as fault and collapse column, is relatively lacking; (5) in the research of AMD migration and evolution, the participation of microorganism and multi-gas components is not considered, and there is less attention to the water refilling and water gathering process of AMD; (6) there is a lack of research on the influence of gas composition, pressure, water temperature and ion concentration of AMD on the hydrochemical balance; (7) no relevant investigations and studies are carried out on when the AMD would outflow, where it would outflow and how long it would last; (8) in Shanxi, the AMD treatment methods are basically at the infancy stage of laboratory theoretical research, and the artificial wetland and PRB are still blank; and (9) the management policies/regulations and AMD pollution monitoring data are relatively lacking. AMD risk assessment and early warning mechanisms have not yet been established, and the research on risk identification and index systems is blank.

Chapter 3

Shandi coal mine and Niangziguan spring catchment

3.1 Shandi coal mine

3.1.1 Mining history

Shandi coal mine is located between 113°29′39″~113°32′45″E and 37°57′52″~ 38°01′52″N in the southwest of Shandi Village, Yangquan city, Shanxi, China (Figure 3-1). It is a part of the Qinshui coalfield and its main coal-bearing strata are the Upper Taiyuan Formation of Carboniferous (C_3t) and the Lower Shanxi Formation (P_1s) of carboniferous system. 8#~9# coal seams can be mined in partial region, 12# coal seam is in most region, 15# coal seam is in the whole region.

The surrounding mines are in production. The Yuejin coal mine and Guzhuang coal mine are both mining the 12# coal seam in the west and the south of Shandi coal mine.

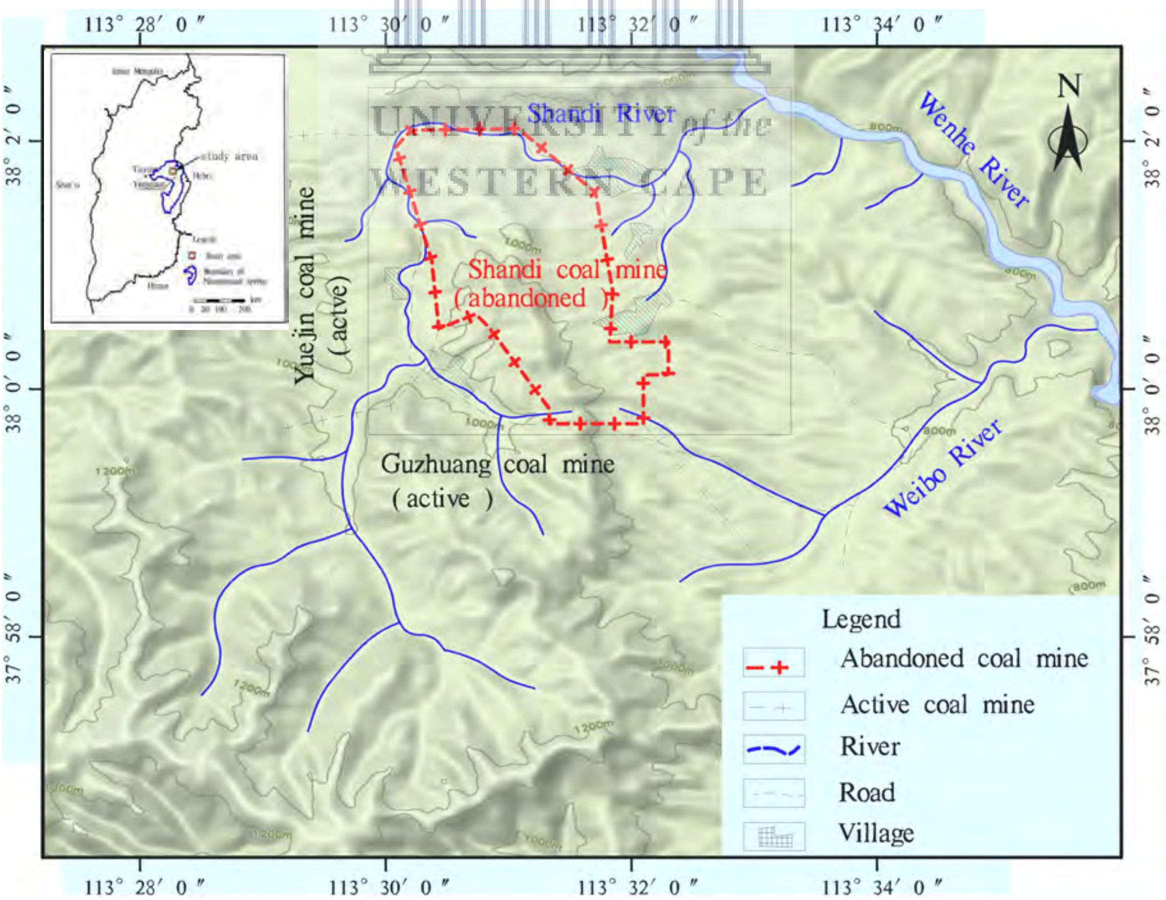


Figure 3-1 Location map of the study area

The Shandi coal mine has experienced a mining history of about 60 years, which can be roughly divided into 8 stages:

(1) In 1963~1965, it was first constructed and officially put into operation of mining 8#, 9# and 12# by a pair of inclined shafts and two pairs of inclined shafts for 15# coal seam.

(2) In 1969~1970, a new pair of inclined shafts was built for 9# coal seam and put into production.

(3) In 1974~1976, a new pair of inclined shafts was independently built for 12# coal seam and put into production.

(4) In 1993~1994, another two pairs of inclined shafts, both of which are independent mining systems, were built for the production of 12# and 15# coal seams.

(5) In 2001, all inclined shafts for the 8# and 9# coal seams were closed.

(6) In 2005, all inclined shafts for the 12# and 15# coal seams were closed.

(7) In 2008, open pit was used for mining the rest of the 8#~15# coal seams in the north of Shandi coal mine.

(8) By 2009, the coal seams had been mined out, and the Shandi coal mine was abandoned.

At the same time, AMD pollution was found in/near the Shandi River (Figure 3-2).

Open pit Discharge zone Shandi River

Figure 3-2 AMD pollution in/near the Shandi River

3.1.2 Landform and geomorphology

The Shandi coal mine is a middle and low mountain landform. After long time of weathering and erosion, the topography is very complex with many gullies. The overall terrain is lower from the west (1120.76 m asl) to the east (826.80 m asl) with a relative difference of 293.96 m asl.

3.1.3 River

The Shandi River is a largest tributary to the Wenhe River in the Haihe River Basin. There is no surface water in the dry season, but the vertical and horizontal gullies are developed. It flows from north to south and turns east at the northeast of the Shandi coal mine (Figure 3-3), with a flow of about 0.4 L/s in the rainy season, a length of 16.5 km and a basin area of about 27 km^2. The Wenhe River originates in the southwest of Fangshan Mountain with a length of 39 km and a watershed area of 388 km^2, its maximum flow is 450 L/s in wet year, and the normal flow is 1-10 L/s. Salinity is 0.3-1 g/L. The main pollution of Wenhe River is the outflow of Mining waste water and AMD from Shandi River Basin.

3.1.4 Climate

The Shandi coal mine has a semi-arid continental monsoon climate, and it is characterized by drought and wind, concentrated precipitation, strong evaporation and four distinct seasons. The mean annual rainfall is 590 mm, and 74-98 percent of the annual rainfall is concentrated from June to September. However, the mean annual evapotranspiration (1319 mm) is 2.24 times than the mean annual rainfall. The average wind speed over the years is 4-17 m/s, and the maximum wind speed is 28 m/s. The frost period is from November of the year to March of the next year. The maximum depth of frozen soil is 0.68 m (1968). The annual average frost-free period is 184 days.

3.1.5 Geology

The regional coal-bearing strata are the Upper Taiyuan Formation of Carboniferous and the Lower Shanxi Formation of Permian. According to the exposure of the surface, drilling holes and underground roadways, the strata from old to new are: the Middle Fengfeng Formation of Ordovician (O_2f), the Middle Benxi Formation (C_2b) and the Upper Taiyuan Formation of Carboniferous (C_3t), the Lower Shanxi Formation (P_1s) and the Lower Shihezi Formation of Permian (P_1x), and the Quaternary (Q). Geological distribution and geological structure are shown in Figure 3-3 and Figure 3-4.

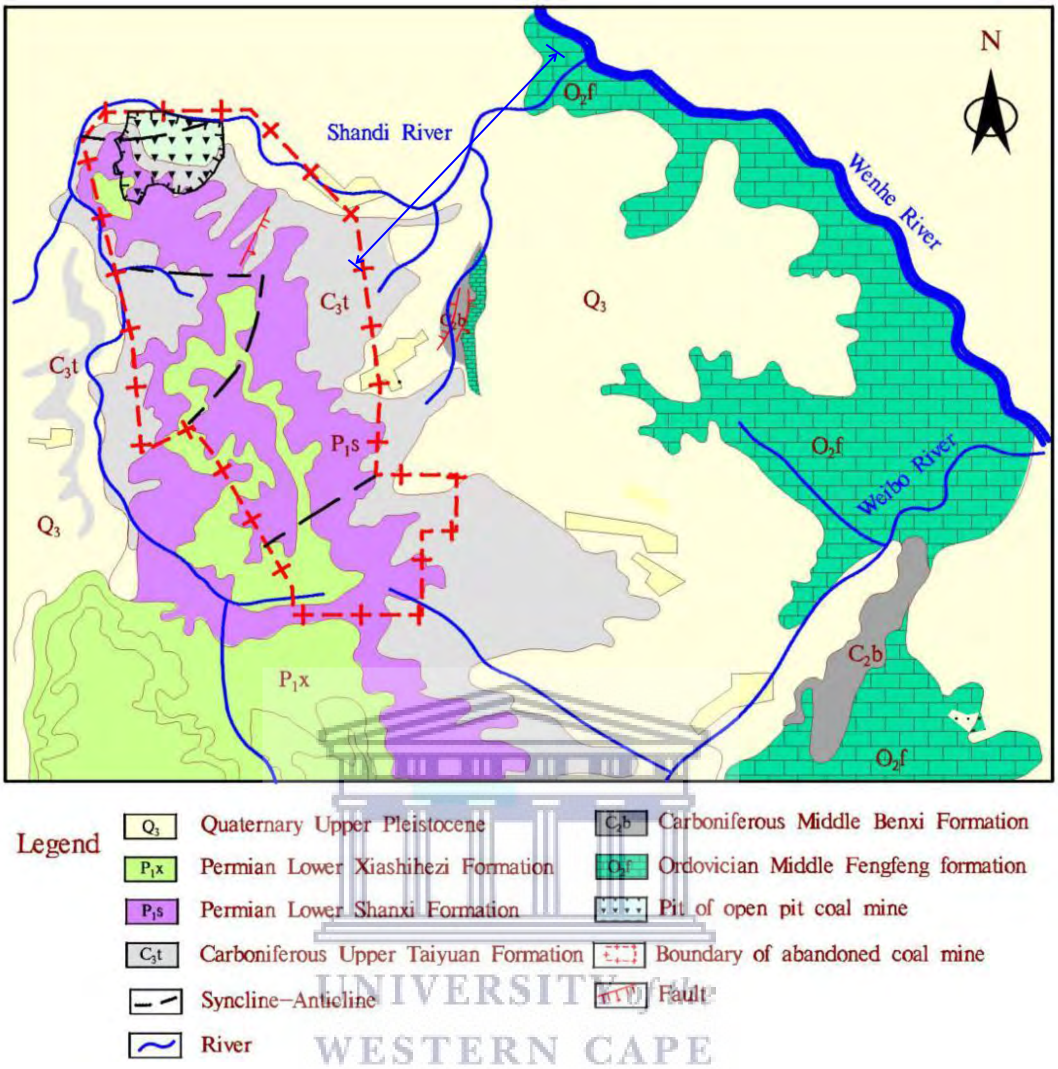


Figure 3-3 Geological map of the study area

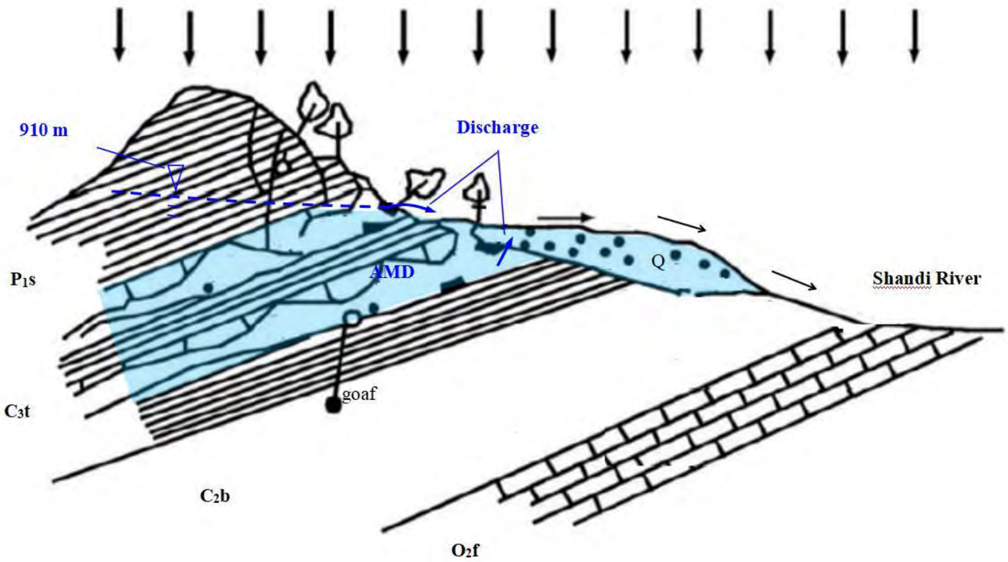


Figure 3-4 Geological section of the study area

1) Middle Fengfeng Formation of Ordovician (O_2f)

It is the base of coal strata, and the lithology is gray-yellow micritic dolomite, marlitic dolomite, dolomitic limestone, argillaceous limestone, blue-gray medium-thick porphyritic limestone and bioclastic limestone. The limestone is hard and brittle, and its top is often stained with light red due to ferri iron, and the thickness is more than 100m.

2) Middle Benxi Formation (C_2b)

Parallel unconformity contact with the underlying strata. Lithology is composed of gray-black sandy mudstone, mudstone, gray-white sandstone, gray aluminum clay and 2-3 layers of dark-gray limestone. It can be roughly divided into two parts, the lower part is mainly aluminum rock, the upper part is mainly sand and mudstone, and the average thickness of the formation is 32.00 m.

3) Upper Taiyuan Formation of Carboniferous (C_3t)

It is one of the main coal-bearing strata and continuously deposited on Benxi Formation. The lower part is composed of gray black sandy mudstone, mudstone, gray sandstone, 3-4 layers of dark gray limestone and 6-9 layers of coal seam. No. 8, 8, 9, 12 and 15 coal seams in this group are recoverable. The Benxi Formation is separated by a layer of light gray fine sandstone (K1) at the bottom of the formation. The thickness of the formation is 74.78-160.63 m, with an average thickness of 135.78 m.

4) Lower Shanxi Formation (P_1s)

It is one of the main coal-bearing strata and continuously deposited on Upper Taiyuan Formation of Carboniferous (C_3t). The bottom is bounded by a layer of medium-fine grained sandstone (K7) and Taiyuan Formation. The lithology is mainly composed of gray-black sandy mudstone, mudstone, gray-white fine sandstone and 4-6 layers of coal seams, all of which can be not mined out. K8 sandstone at its top is the marker layer with the lower formation. The thickness of the formation is 12.34-67.50 m with an average of 63.90 m.

5) Lower Shihezi Formation of Permian (P_1x)

It is continuously deposited on the Lower Shanxi Formation (P_1s) with a thickness of 145.21-176.60 m and an average of 161.00 m. According to lithology and characteristics, it can be divided into three parts:

The lower part (P_1x^1) is composed of gray-black sandy mudstone, sandy mudstone and green sandstone. The bottom is a layer of gray-white sandstone (K8) with a thickness of 6.12-8.29 m and an average of 7.11 m. The lower part is mostly sandy mudstone, which contains 1-2 layers of oolitic clay with siderite nodules, 2-3 layers of coal lines. The thickness of this section is 51.77-68.14 m, with an average of 59.00 m.

The middle part (P_1x^2) is composed of gray-black sandy mudstone and yellow-green sandstone. The bottom is a layer of gray-white sandstone (K9) with argillaceous cementation and easy weathering with an average of 9.60 m. The thickness of this section is 57.64-69.28 m, with an average of 63.00 m.

The upper part (P_1x^3) is composed of 1-2 layers of gray-white medium-coarse-grained sandstone, 2-4 layers of yellow-green sandy mudstone and a layer of yellow-red aluminum clay. The top layer is a yellow-red bauxite mudstone (K10) with a thickness of 5.10-8.30 m and an average of 6.30 m. The thickness of this part is 34.06-43.78 m with an average of 39.00 m.

6) Quaternary (Q)

The Middle and Upper Pleistocene Quaternary (Q_{2+3}) is widespread in the coalfield. The lithology is composed of light yellow sand and clay. The bottom is sand and gravel containing calcareous nodules with a thickness of 0-30 m in angular unconformity contact with the underlying strata.

Quaternary Holocene (Q_4) is mainly distributed in the valley and composed of sand, gravel and other alluvial sediment with a thickness of 0-5.00 m.

3.1.6 Hydrogeology

According to the data collected from Shandi coal mine, the various aquifers are fully developed from the bottom to the top. There are: ①limestone karst fissure aquifer in the Middle Ordovician; ②clastic rock fissure aquifer in the Upper Carboniferous Taiyuan Formation; ③sandstone fissure aquifer in the Lower Permian; and ④pore aquifer in the Quaternary. The main aquifers are shown in Figure 3-5.

The followings are the descriptions of the aquifers of the Shandi coal mine.

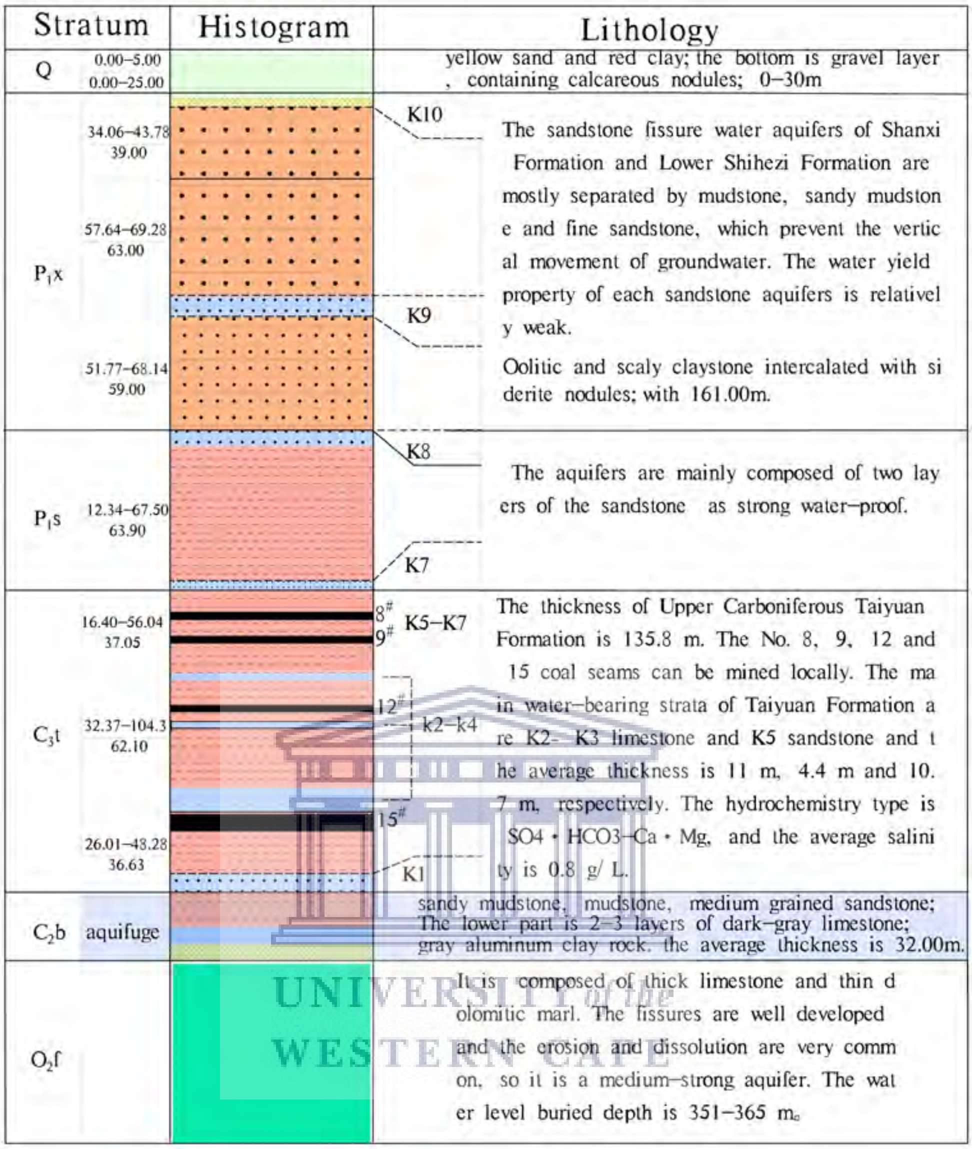


Figure 3-5 Comprehensive column chart of the aquifers

1) Limestone karst fissure aquifer in the Middle Ordovician

It is deeply buried and composed of thick limestone and thin dolomitic marl. The fissures are well developed and the erosion and dissolution are very common, so it is a medium-strong aquifer. The water inflow per unit in the pumping test is 0.5-2.5 L/s·m, and the hydraulic conductivity is 0.9-2.4 m/d. The water level buried depth is 351-365 m, and the hydrochemistry type is $SO_4 \cdot HCO_3$-Ca·Mg, and the salinity is 1.0 g/ L.

The Ordovician aquifer is affected by human mining activities in study area. The Fengfeng Formation is lower than the regional groundwater level, so the Ordovician aquifer get a lot of leaking recharges of mine water/AMD from the overlying aquifers and surface rivers. Its water yield property of the aquifer is uneven, and there are great changes in both vertical and horizontal direction. The Upper and Lower Majiagou Formations are the main aquifers in the middle and lower part of the Upper Majiagou Formation and the middle and upper part of the Lower Majiagou Formation.

2) Clastic rock fissure aquifer in the Upper Carboniferous Taiyuan Formation

The thickness of Upper Carboniferous Taiyuan Formation is 135.8 m. The No. 8, 9, 12 and 15 coal seams can be mined locally. The main water-bearing strata of Taiyuan Formation are K2~ K3 limestone and K5 sandstone and the average thickness is 11 m, 4.4 m and 10.7 m, respectively. The hydrochemistry type is $SO_4 \cdot HCO_3$-Ca·Mg, and the average salinity is 0.8 g/ L.

The average thickness of gray K2 limestone is 11 m and there is a certain head pressure. The water inflow rate is 0.44 L/s, the unit water inflow is 0.032 L/s·m, and the hydraulic conductivity is 0.661 m/d. K3 limestone has an average thickness of 4.4 m, and K4 limestone has an average thickness of 4.5 m with the unit water inflow rate of 0.0005-0.08 L/s·m and the hydraulic conductivity of 0.012-0.047 m/d. The water yield property of the K3 and K4 aquifers are weak and less than K2 limestone. K5 sandstone belongs to a weak fissure aquifer and the unit water inflow of pumping test is 0.00081 L/s·m, and the hydraulic conductivity is 0.03-1.5 m/d.

3) Sandstone fissure aquifer in the lower Permian

The aquifers are mainly composed of two layers of the sandstone such as K7 of the Shanxi Formation and K8 of the Shihezi Formation. The thickness of each layer is mostly 3-12 m, deposited alternately with sandy-mudstone and mudstone as strong water-proof. Without the faults, collapse columns and other geological structures, there is generally no hydraulic connection between adjacent aquifers. The water yield property of the aquifer is restricted by the buried depth, and fissure.

The measured unit water gushing was 0.05 L/s·m, and hydraulic conductivity was 0.16 m/d in 2010. Influenced by gully cutting, sandstone aquifers receive meteoric precipitation and their hydrochemistry type was HCO_3-Na·Mg, and the average salinity was 0.6 g/L.

The sandstone fissure water aquifers of Shanxi Formation and Lower Shihezi Formation are mostly separated by mudstone, sandy mudstone and fine sandstone, which prevent the vertical movement of groundwater. The water yield property of each sandstone aquifers is relatively weak.

4) Pore aquifer in the Quaternary

The aquifer is mainly distributed in hilly area and gully zone of modern riverbed, it is composed of sand cobble layer, sand and gravel layer, sand and calcareous nodule layer. Precipitation and river leakage are the main recharge sources. The aquifer is laterally replenished by fissure water in local areas.

This area is an erosional uplift area, and the quaternary strata are thin. The middle Pleistocene strata are mainly distributed on both sides of the modern valley, and the thickness varies greatly with, 0-50 m, and only perched water exists in partial sand and gravel lenses. The upper Pleistocene strata are generally weak and permeable, distributed sporadically on gentle slopes and hilltops in the region. The Holocene strata are mainly distributed in the valley bottom and terraces on both sides. The lithology is mainly sand and gravel with the thickness of 10-15 m, so it is the main rich aquifer in this formation.

According to the pumping test data in 2000, the water inflow rate was 2.40-2.09 L/s, and the unit water inflow rate was 2.895-2.09 L/s·m. The average hydraulic conductivity was 68.95 m/d. Affected by the season, the amount of water varies greatly, increasing in rainy season and decreasing in dry season. Its hydrochemistry type is HCO_3-Na, and the average salinity was 0.6 g/L.

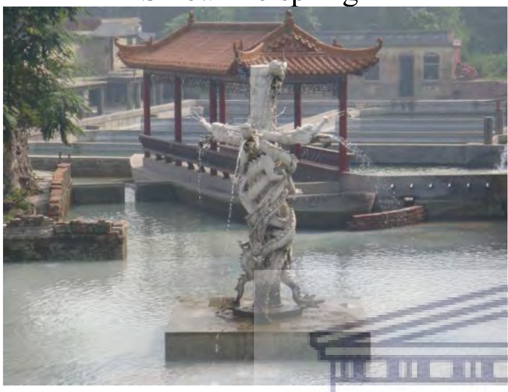
3.2 Niangziguan spring catchment

3.2.1 Niangziguan spring clusters

The Niangziguan spring clusters distributed on the floodplain and terrace from Chengjia village to Weizeguan village and consists of 11 main springs (Podi spring, Chengjia spring, Shibanmo spring, Gun spring and Wulong spring, Chengxi spring, Hebeicun spring, Qiaodun spring, Forbidden area spring, Shuiliandong spring and Weizeguan spring) (Figure 3-6) with an outcrop elevation of 360-392 m asl.

Shibanmo spring

Gun spring



Wulong spring

Chengxi spring

Figure 3-6 Niangziguan spring clusters

According to the report of Niangziguan spring water resource evaluation by the Institute of Karst Geology, Chinese Academy of Geological Sciences, the average annual flow of the Niangziguan spring clusters is 10.95 m^3/s (1956-2000), which is the first major spring of the 19 karst springs in Shanxi Region. The hydrochemical types of spring water are generally $SO_4 \cdot HCO_3$-$Ca \cdot Mg$ and $SO_4 \cdot HCO_3$-Ca type with total dissolved solids (TDS) of 600-700 mg/L, total hardness (TH) of 450-480 mg/L. Since the 21st Century, the average flow of spring water was 6.66 m^3/s.

3.2.2 Hydrogeological subsystem

The Niangziguan spring catchment is an independent hydrogeological system, which takes Niangziguan spring as the discharge area and gathers the groundwater of the whole karst water system. Its recharge is mainly from direct infiltration of meteoric precipitation and river leakage in exposed and semi-exposed limestone areas. According to the storage and migration characteristics of karst groundwater, the Niangziguan spring catchment is divided into four hydrodynamic areas: recharge-runoff area, confluence area, discharge area and stagnation area (Figure 3-7).The hydrogeological section of Niangziguan spring catchment is shown in Figure 3-8.

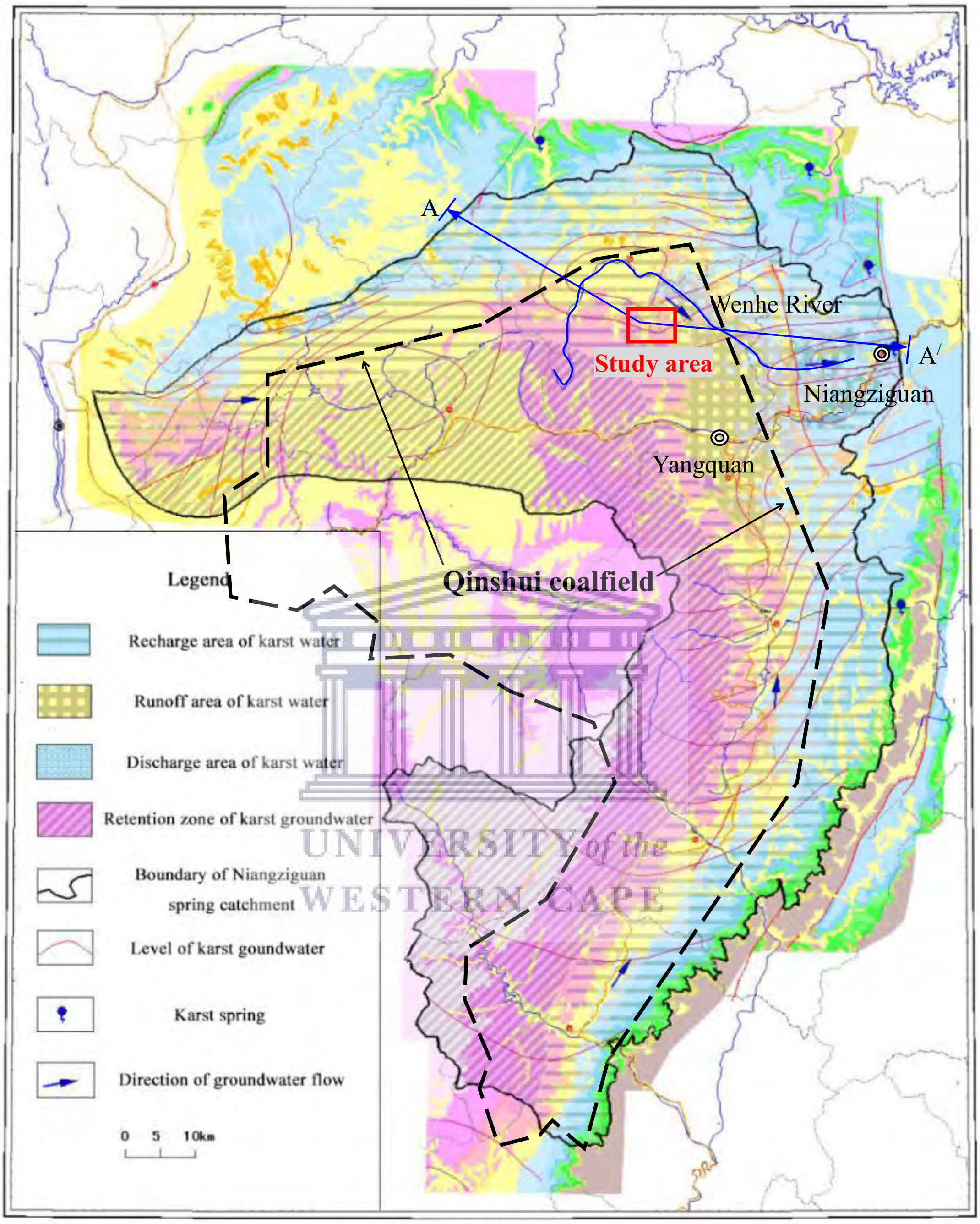


Figure 3-7 Hydrogeological subsystem of Niangziguan spring catchment

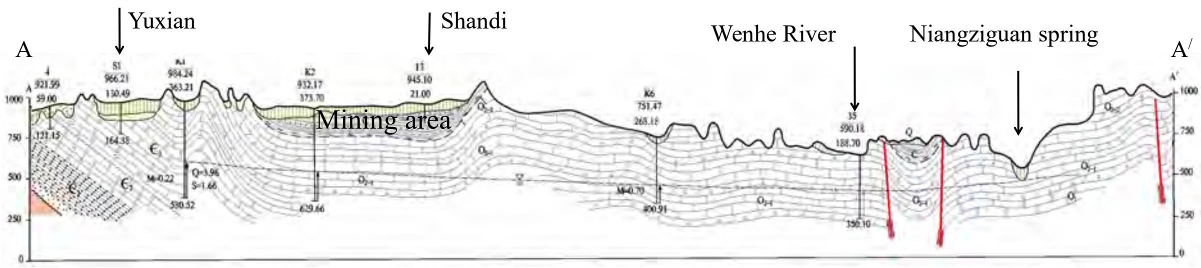


Figure 3-8 Hydrogeological section

3.2.3 Water resources and coal mining

Karst water in the Niangziguan spring catchment is the main water source for local industry and urban life. According to the official report of Niangziguan spring water resources evaluation by the Institute of Karst Geology, Chinese Academy of Geological Sciences, the natural recharge resources of karst groundwater is 3.605×10^8 m^3/a (11.43 m^3/s) and the exploitable resources is 8.73 m^3/s. At present, karst groundwater is used in two ways: water diversion project and pumping well. In fact, the designed total lifting water capacity is 1.64×10^8 m^3/a and there are 129 pumping wells for about 0.4066×10^8 m^3/a in the spring catchment.

Coal mining has always been an important industry in the Niangziguan spring catchment. The distribution area of coal is about 4,748 km^2. After decades of large-scale mining, a large number of goafs had been formed in Niangziguan spring catchment. Due to the influence of tunneling, blasting vibration and mining, there are three deformation zones in the upper strata of the goaf, namely caving zone (I), fissure zone (II) and bending zone (III) (Figure 3-9), which have the greatest impact on the water resources in different overlying aquifers of the Carboniferous, Permian and Triassic systems. So coal mining has been most important factor leading to a series of severe water environment problems, such as the attenuation of spring flow, the continuous decline of regional karst groundwater level and the continuous deterioration of water quality. Since the 1960s, the spring flow has been in a trend of decrease except for certain fluctuation due to the influence of rainfall. From 1956 to 2000, the average spring flow was 10.95 m^3/s.

From 1982 to 2004, the karst groundwater level has declined about 20m in Yangquan region, and the area trapped by the karst groundwater level of 410m expanded nearly 300km^2 in discharge zone. Since the 21st Century, the average spring flow decreased to 6.66 m^3/s, which was only 60.8% of that before the 20th century. In 2019, the measured flow is 7.19 m^3/s and the annual runoff is 226,744 m^3, but Chengjia spring, Shiqiao spring, shuiliandong spring dried up (Yang 2020). The dynamic changes of runoff in Niangziguan spring flow during 1956-2019 are shown in the Figure 3-10.

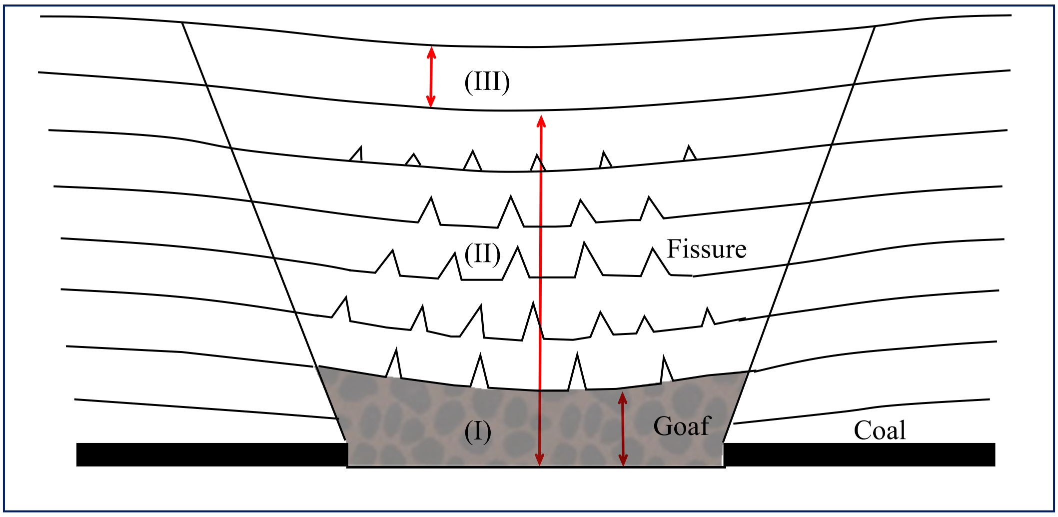


Figure 3-9 Three deformation zones in overlying strata

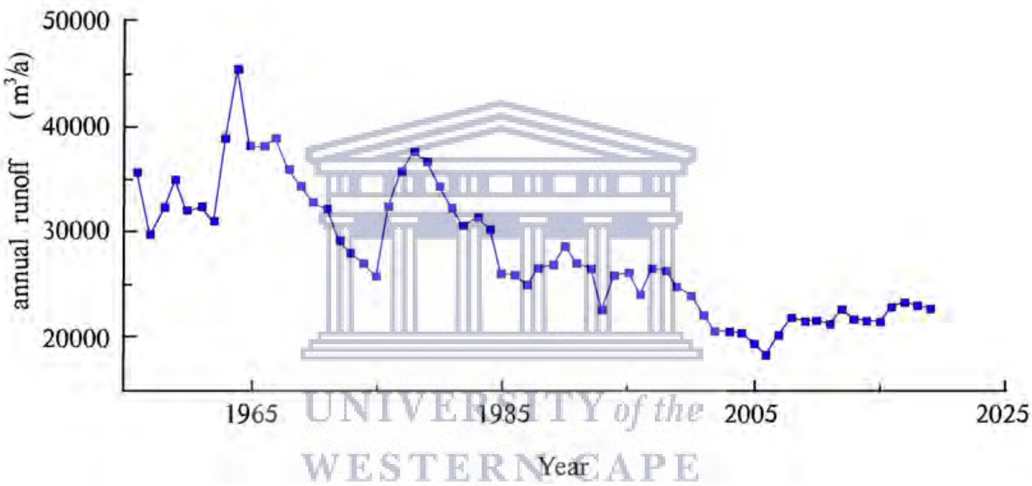


Figure 3-10 The attenuation of Niangziguan spring flow (Yang 2020)

Li et al. (2002) conducted a hydrochemical-isotope analysis of Niangziguan spring clusters and pointed out that the TDS content of each spring showed an increasing trend. According to the measured result from June to December in 2014, the average flow of AMD from the abandoned Shandi coal mine is 8134.7 m^3/d and pH is 2.67-5.26, TDS is 6171 mg/L, SO_4^{2-} is 4419 mg/L, causing AMD pollution to the karst water. AMD is the main reason for the accelerated pollution of Niangziguan spring in recent years (Liang et al. 2017). According to official statistics, the water quality analysis of 177 samples in Niangziguan spring catchment showed that the salinity and total hardness increased by 8.84 mg/L and 7.49 mg/L each year, respectively.

The AMD issues from Shandi coal mine in the Niangziguan spring catchment have received widespread attention from the domestic scholars, but the geological and hydrogeological characteristics of AMD have not been specifically reported.

Chapter 4

Geological and hydrogeological characteristics of AMD from abandoned coal mine

In this chapter, taking the abandoned Shandi coal mine as an example, the study analyzed the water samples, coals and associated minerals, and researched the geological and hydrogeological characteristics of AMD from abandoned Shandi coal mine.

4.1 Sample and test

The study carried the field survey in October 2019, and sampled the AMD points, open-pit water, and surface water. The water sample collection were conducted in accordance with the relevant water sample requirements. There are a total of 12 water samples, including one open-pit water (No.3), three AMD points (No.4, 5, and 6), and eight surface water samples (No.1, 2, 7, 8, 9, 10, 11, and 12). Their distributions are shown in Figure 4-1.

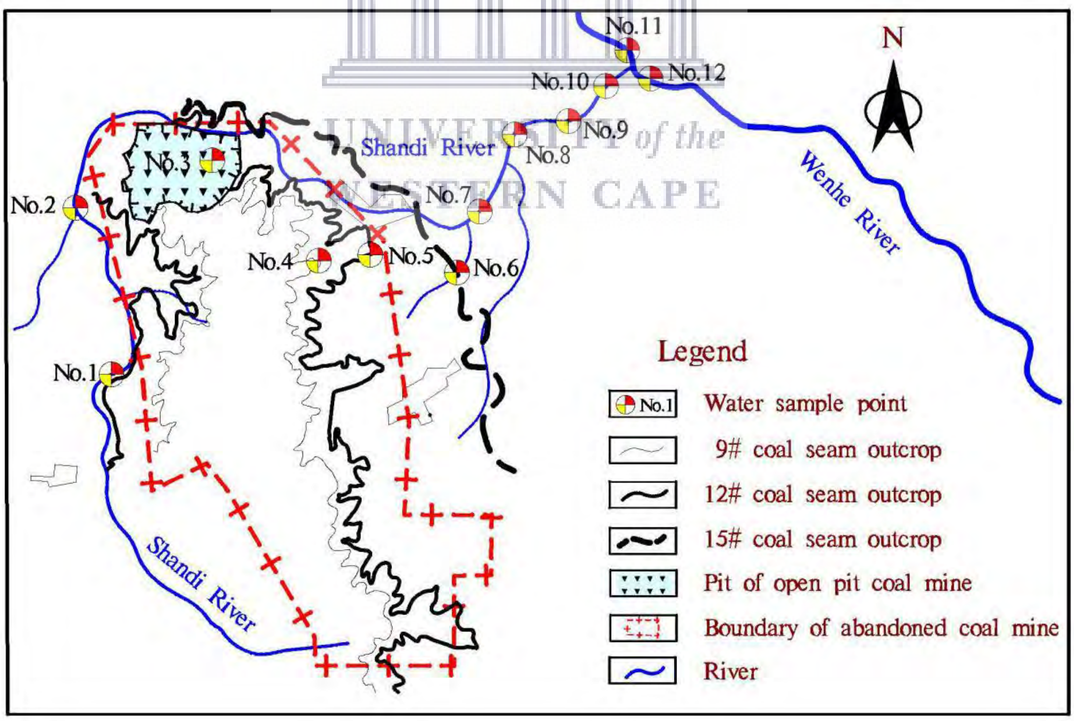


Figure 4-1 Distribution map of water sample points

Using portable water quality parameter instrument (Multi 3430), variable parameters such as pH, dissolved oxygen (DO), redox potential (Eh) and temperature (T) were measured on site. In laboratory, the cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) were tested by flame atomic absorption spectrophotometer (ICE3500), the anions (SO_4^{2-}, HCO_3^-, Cl^-, CO_3^{2-}, and F^-) were measured by ion chromatograph (ICS-1100), the Fe and Mn were tested by flame atomic absorption spectrophotometer (ICE3500), and the trace elements (Cu, Pb, Zn, Cr, Cd, As) were measured by ICP-MS. All chemical tests were completed in the laboratory of Shanxi Yingruize Monitoring Co., Ltd.

In October 2019, five samples of each coal seams of 8#, 9#, 12# and 15# were selected in the study area for coal quality analysis and five samples of associated minerals were selected for its composition. The analysis of coals and associated minerals were done at the Testing Center of Shanxi Rock Research Institute.

4.2 Analysis method

4.2.1 Standard index method

The Standard index method is used to determine the water quality of AMD by comparing the monitoring value of single index with the corresponding quality standard. This method has a clear concept and a simple calculation and can intuitively show the pollution degree of AMD. It is the most widely used method in water quality evaluation at present (Li et al., 2012); Luo et al., 2016). The model expression is as follows:

$$P_i = \frac{C_i}{C_{oi}} \tag{4-1}$$

$$P_{pH} = \frac{7.0 - pH_{ci}}{7.0 - pH_{coi}} \quad pH_{ci} \le 7.0$$
$$P_{pH} = \frac{pH_{ci} - 7.0}{pH_{coi} - 7.0} \quad pH_{ci} \ge 7.0 \tag{4-2}$$

Where, P_i is single factor pollution index; C_i is measured concentration, mg/L; C_{Oi} is standard concentration, mg/L; P_{pH} is pH pollution index; pH_{Ci} is measured pH value; pH_{COi} is standard pH value.

When Pi≤1, water quality meets the standard. When Pi＞1, water quality exceeds the corresponding quality standard and will cause harm to human health.

4.2.2 Correlation analysis

Correlation analysis can reflect the close degree of interrelation among elements related to each other through correlation Coefficient. If the two sample elements are x_i and y_i, respectively, then the correlation coefficient between them (Xu 2016) is:

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}\sqrt{\sum_{i=1}^{n}(y_i - \bar{y})^2}} \quad (4\text{-}3)$$

Where, $\bar{x}$ and $\bar{y}$ are the average values, the correlation coefficients r_{xy} are between -1 and 1. $r_{xy} > 0$ means positive correlation and $r_{xy} > 0$ means negative correlation. If the absolute value of r_{xy} is closer to 1, it shows a closer relationship between the two elements.

4.2.3 Water-conducting fissure zone

At present, the most common method for calculation of water-conducting fissure zone is the empirical formula method (Qian et al. 1996; Li 2007; Shi et al. 2012). It is the premise of studying the influence of coal mining on groundwater and accurately predicting water-conducting fissure zone in coal mine. It mainly includes the formula shown in the guidelines of "exploration specification of hydrogeology and engineering geology in mining area" (Equation 4-4), "exploration specification of coal pressing mining under buildings, water body, railway and pillar retention of main shaft and roadway" (Equation 4-5) and "Manual of Coal Mine Water Prevention and Control" (Equation 4-6). Therefore, different formulas are used to calculate the height of water-conducting fissure zone and the maximum of calculation value is adopted as a final result.

$$H_{li} = \frac{100M}{3.3n + 3.8} + 5.1 \quad (4\text{-}4)$$

$$H_{li} = \frac{100\sum M}{1.6\sum M + 3.6} + 5.6 \quad (4\text{-}5)$$

$$H_{li} = \frac{100M}{0.26M + 6.88} + 11.49 \quad (4\text{-}6)$$

Where, H_{li} is the maximum height of water-conducting fissure zone, m; M is the cumulative coal thickness, m; n is the number of layer of coal seam.

4.3 Results and discussion

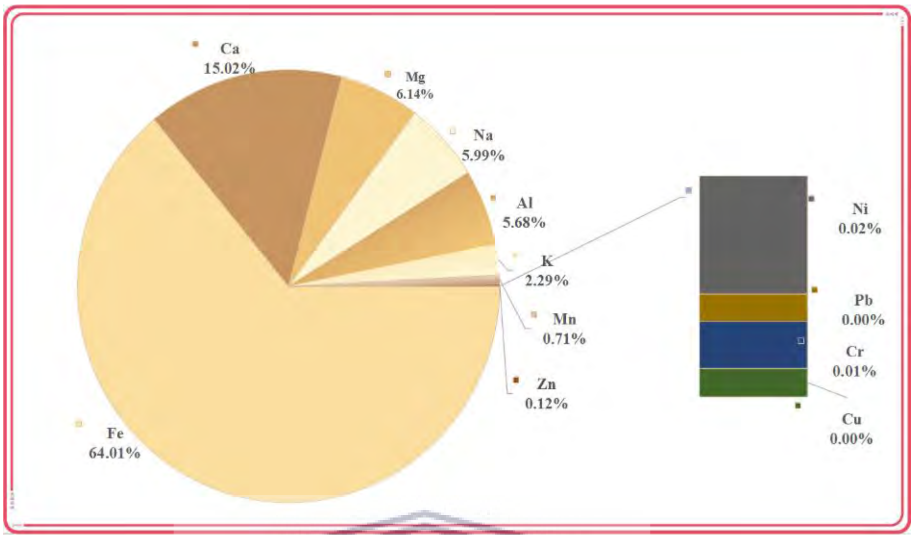
4.3.1 Water Characteristics of AMD

Table 4-1 shows the main chemical components of the AMD samples collected in the study area. The standard index method was used to calculate the pollution degree of the corresponding pollutants compared with China's drinking water standard.

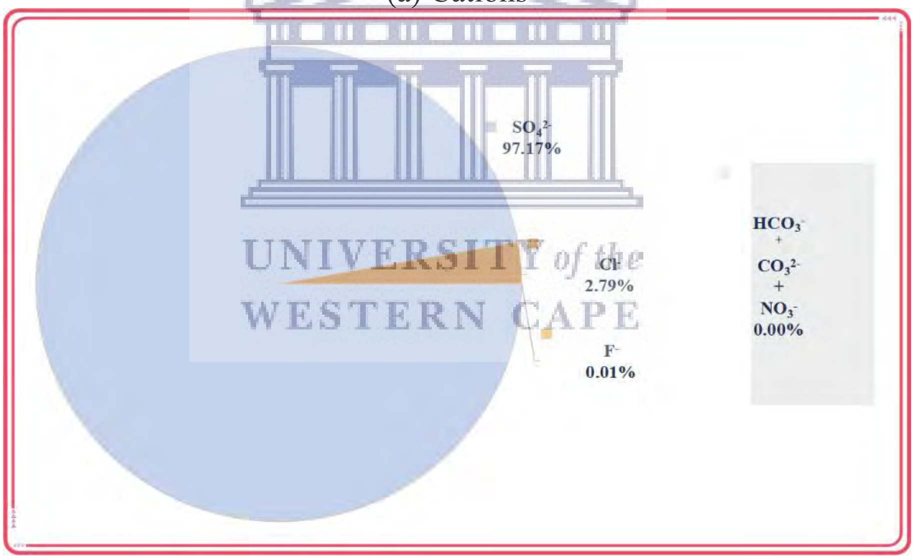
Table 4-1 The main chemical components of the AMD

No.	Point	pH	Do	Eh(V)	K	Na	Ca	Mg	SO_4	HCO_3	Cl	CO_3
3	pit	2.33	0.4	-0.623	164.7	472.3	1012.6	438.6	9085	/	310.3	/
4	8+9#	2.81	0.3	-0.627	187.5	446.7	1135.4	467.5	10371	/	324.4	/
5	12#	2.23	0.2	-0.630	176.8	442.8	1122.7	448.3	11124	/	332.7	/
6	15#	2.75	0.2	-0.632	156.9	436.5	1336.5	586.7	12110	/	316.8	/
Average		2.53	0.3	-0.628	171.5	449.6	1126.8	460.3	11172	/	321.1	/
drinking standard		6.5-8.5	--	--	--	200	--	--	250	/	250	/
Pi		9.54				2.36			48.4		1.33	
No.	**Point**	**F**	**Fe**	**Mn**	**Al**	**Cu**	**Zn**	**Ni**	**Pb**	**As ($\times10^{-3}$)**	**Cd**	**Cr**
3	pit	1.012	4521.3	50.57	418.7	0.308	8.754	1.224	0.285	1.52	0.005	0.514
4	8+9#	0.978	5320.4	50.93	426.5	0.313	9.373	1.256	0.296	1.59	0.003	0.506
5	12#	0.977	5552.8	52.66	428.8	0.315	9.421	1.324	0.308	1.54	0.003	0.528
6	15#	1.033	6023.6	57.53	430.5	0.315	9.422	1.355	0.309	1.55	0.004	0.525
Average		1.000	4800.8	52.91	426.1	0.313	9.243	1.290	0.300	1.55	0.004	0.518
drinking standard		1.000	0.3	0.1	0.2	1.0	1.0	0.02	0.01	0.01	0.005	0.05
Pi		1.03	20079	575	2153	--	9.42	67.75	30.90	--	--	10.56

It can be seen from Table 4-1 that and Figure 4-2: (1) the pH of the four samples is in lower state (pH=2.23-2.81) and the water shows very strong acidic, with HCO_3^- and CO_3^{2-} hardly being detected; (2) based on the statistics data of cations and anions, the average of sulfate ion accounts for 97.17% of the total anions and Fe accounts for 64.01% of the total cations; compared with China's drinking water quality calculated by standard index method, the average values of sulfate, Fe, Mn, and Al are 48.4 times, 20,079 times, 575 times, and 2,153 times, respectively. Besides, the heavy metals (including Ni, Pb, Cr, and Zn) are 67.75 times, 30.90 times, 10.56 times and 9.42 times, which has become a threat for the safety of drinking water by high toxicity; (3) for the water quality of AMD (No.4, 5, and 6 from different coal seams), sulfur content is getting a little higher with the increasing depth of the coal seam, but open pit water (No.3) has several different. For example, the concentrations of Fe ion and sulfate ion decrease less than 15% and 12%, respectively. It shows that the open environment of open-pit mining is different from the closed environment of well mining. In the open environment, the concentration of Fe ion and sulfate ion is relatively lower than coal seams due to the neutralization and adsorption of Quaternary loess, Permian sandstone and mudstone.



(a) Cations



(b) Anions

Figure 4-2 Statistics of Cations and Anions

Why the concentrations of Fe ion and sulfate ion are relatively lower in an open-pit environment? Through the field survey, one reason is that there are smaller amount of sulfide minerals themselves at the bottom of the dump under the groundwater level where the Quaternary loess and Permian mudstone have better absorptive effects; while the coal strata rich in sulfide minerals and other metal minerals mainly are accumulated in the middle and upper part of the dump above the groundwater level. The other reason is that the open-pit can get abundant recharge from the Shandi River, and the water quality is diluted to a certain extent.

4.3.2 Water Characteristics of the polluted Shandi River

According to location relationship and water quality characteristics, the study area can be divided into four areas: the AMD upstream area, the AMD storage area, the AMD affected area, the Wenhe River upstream area, and the Wenhe River downstream area.

Table 4-2 Quality characteristics of polluted Shandi River (Unit: mg/L, except pH and Eh)

No.	pH	Do	Eh(V)	K	Na	Ca	Mg	SO_4	HCO_3	Cl	CO_3
1	8.05	6.6	-0.175	74.6	116.7	682.5	255.6	994	136	45.4	6
2	8.13	5.9	-0.146	157.4	114.5	685.6	260.5	1033	144	56.9	12
7	3.52	4.6	-0.307	84.5	337.3	987.5	284.2	5714	/	197.5	/
8	4.55	5.3	-0.214	84.6	275.5	863.8	290.7	3081	/	176.3	/
9	4.74	6.5	-0.213	34.5	281.3	577.6	294.6	2184	/	175.7	/
10	5.02	6.6	-0.208	31.8	295.6	486.4	192.7	1450	32.4	176.8	/
11	8.05	8.1	-0.152	12.5	173.7	275.8	163.7	508	58.5	38.2	6
12	6.85	6.8	-0.185	21.6	217.8	394.5	156.2	887	88.4	122.7	6
No.	F	Fe	Mn	Al	Cu	Zn	Ni	Pb	Cd	As($\times10^{-3}$)	Cr
1	1.093	25.6	1.38	0.12	0.006	0.002	0	0.002	0.002	0	0
2	0.899	36.3	1.56	0.28	0.007	0.004	0	0.003	0.003	0	0
7	0.94	3105.6	21.53	156.7	0.174	4.583	0.558	0.092	0.003	4.12	0.248
8	0.957	1084.8	10.47	66.4	0.058	2.769	0.232	0.023	0.003	5.57	0.136
9	0.889	771.7	7.29	62.6	0.037	2.339	0.104	0.017	0.004	6.61	0.098
10	0.712	355.4	4.78	46.9	0.015	2.286	0.055	0.011	0.003	6.60	0.062
11	1.132	22.5	0.36	0.22	0.007	0.008	0.006	0.002	0.002	0	0
12	0.96	137.8	1.47	16.7	0.011	1.127	0.034	0.006	0.002	2.43	0.024

It can be seen from Table 4-2 and Figure 4-3: (1) No.1 and No.2 samples are located in the AMD upstream area of Shandi coal mine, HCO_3^- and CO_3^{2-} can both be detected, the water quality is slightly alkaline. But the concentration of Ca, Mg, SO_4, Fe, Mn, and Al still exceeds the regional background value, the investigation confirmed that the Shandi River has been polluted in a certain extent by mine waste drainage from upstream coal mines (the active Guzhuang coal mine and Yuejin coal mine). The concentration of F, Cu, Zn, Ni, Pb, Cd, As, and Cr is low or not detected, indicating that these metal elements are mostly adsorbed, complexed or precipitated in the surface water. (2) The No.11 sample is located in the Wenhe River upstream area, and the heavy metals show the same characteristics as the No.1 and No.2, but the pollution degree is the lowest. (3) Compared No.12 with No.10, the contribution rate of the heavy metals from Shandi River to Wenhe River is extremely large: Ni, As, Cr contributes 100% to Wenhe River, and the contribution rates of Fe, Mn and Pb are 62%, 61%, 67%, respectively, and the contribution rate of Al and Zn is more than 99%. Once these AMD is discharged into the Wenhe River and Niangziguan spring, it will seriously pollute the surface water and the karst groundwater of the spring catchment.

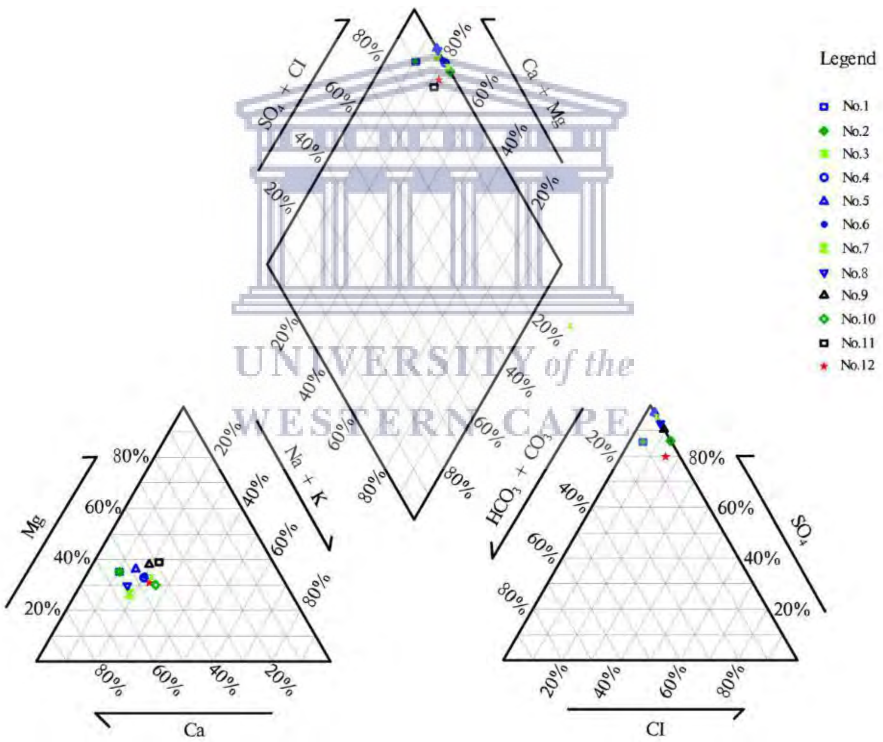


Figure 4-3 Piper Diagram of the water quality

Through the comparative analysis of AMD quality and upstream surface water (Figure 4-4), AMD shows the obvious characteristics of low pH (2.23~2.81), low DO (0.2~0.4 mg/L) and low Eh (-0.623V~-0.632V), meanwhile, it also contains a great deal of sulfate and Fe, resulting in a high toxic waste for water ecological circulation. Thus, it is concluded that AMD has the low characteristics of pH, DO and Eh and the high characteristics of sulfate, Fe and toxicity.

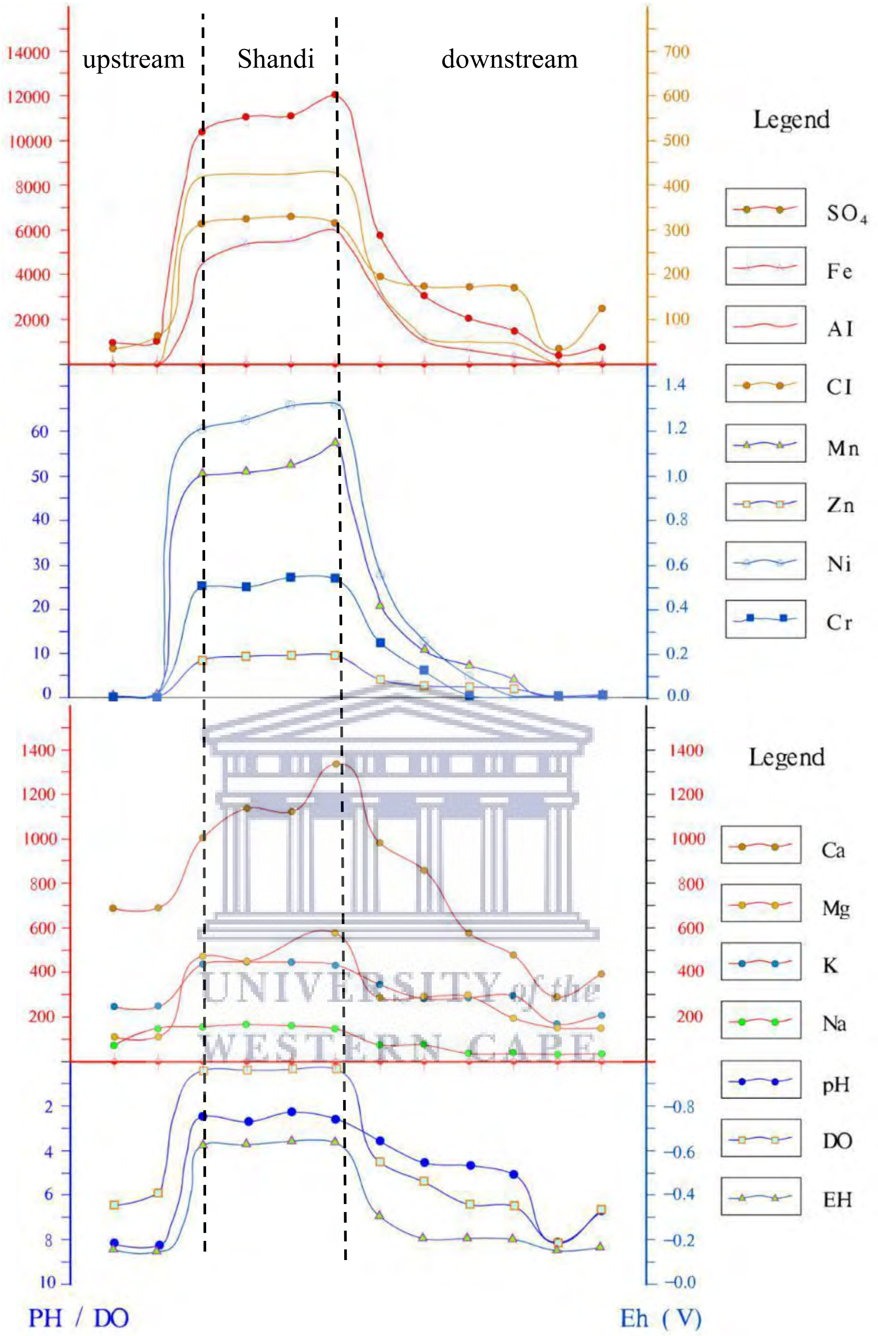


Figure 4-4 Trend diagrams of major ion changes

On the other hand, all the elements (excluding HCO_3, CO_3, F and Cd) tend to rise rapidly, the reason lies in the oxidation, dissolution and ion exchange in the coal-bearing strata and mined-out goaf, which also is consistent with the previous review.

Shandi River had been aggravated the pollution as a result of the outflow of AMD storage near the river from the abandoned Shandi coal mine. For the samples from upstream to downstream, as the only three elements such as F, Cr and As always keep very stable even within AMD pollution. With strong oxidation environment of continuous exchange of dissolved oxygen in the air, the concentration of SO_4^{2-} decrease quickly at the beginning, it has the same attenuation trend as heavy metals after AMD discharged along the Shandi River.

In order to further describe the relationship between these elements, their correlation coefficients of 20 water quality indexes in AMD are obtained and shown in Table 4-3. It can be seen from Table 4-3 that the indexes in AMD have different correlation degrees.

As the main anion, SO_4^{2-} is significant positive correlated with Fe, Mn, Al, Cu, Zn, Ni, Pb and Cr, positive correlation coefficients are greater than 0.98; positive correlation coefficients of Na, Ca and Mg are greater than 0.91, correlation coefficients of K and Cd are less than 0.80. Based on the difference of correlation coefficient, it is suggested that SO_4^{2-} is mainly from the oxidation of sulphide metallic minerals including pyrite and associated minerals, the next source of SO_4^{2-} is homologous with Ca and Mg from dissolution of carbonate and sulfate minerals and a small amount comes from ion exchange. In the study area, sulphide metallic minerals are dominant factor of AMD pollution.

As the main cation, Fe is closely correlated with SO_4^{2-}, the correlation coefficient is positive greater than 0.99 in all the samples along the Shandi River. The attenuation of Fe is closely related to the precipitation of SO_4^{2-} with the increasing of Do, pH and Eh. At the same time, SO_4^{2-} is significant positive correlated with Mn, Al, Cu, Zn, Ni, Pb and Cr, so heavy metals in water is positively related to the SO_4^{2-} and has negative correlation with Do, pH and Eh. For example, the concentration of Fe and SO_4^{2-} has a strict negative correlation with the value of pH, the smaller the pH, the larger amount of Fe and SO_4^{2-} are dissolved in AMD. With the increase of Do and Eh in Shandi River, Fe and SO_4^{2-} will form $Fe(OH)_3$ and other secondary minerals adsorbed at the bottom of the river bed. Their attenuation can reflect a purified tendency of surface water.

Table 4-3 The correlation coefficient

	pH	Do	Eh	K	Na	Ca	Mg	SO_4	Fe	Mn	Al	Cu	Zn	Ni	Pb	Cd	Cr
pH	1	0.8483	0.8565	-0.5765	-0.9740	-0.7994	-0.7806	-0.8756	-0.8805	-0.8688	-0.8725	-0.8771	-0.9260	-0.8660	-0.8321	-0.6861	-0.9045
Do		1	0.9822	-0.8766	-0.8844	-0.9133	-0.9387	-0.9778	-0.9694	-0.9857	-0.9838	-0.9782	-0.9727	-0.9843	-0.9825	-0.5990	-0.9818
Eh			1	-0.7928	-0.9177	-0.8523	-0.9170	-0.9802	-0.9765	-0.9947	-0.9986	-0.9864	-0.9855	-0.9936	-0.9974	-0.5818	-0.9907
K				1	0.5915	0.8501	0.8299	0.7994	0.7830	0.8042	0.7968	0.8004	0.7567	0.8046	0.8126	0.4780	0.7866
Na					1	0.7634	0.7978	0.9077	0.9135	0.9173	0.9273	0.9197	0.9617	0.9149	0.8964	0.6675	0.9427
Ca						1	0.9325	0.9171	0.9089	0.8893	0.8631	0.8894	0.8721	0.8861	0.8574	0.5465	0.8850
Mg							1	0.9440	0.9276	0.9392	0.9209	0.9108	0.9072	0.9249	0.9213	0.6441	0.9198
SO_4								1	0.9978	0.9934	0.9855	0.9887	0.9845	0.9932	0.9832	0.5600	0.9894
Fe									1	0.9899	0.9829	0.9920	0.9839	0.9919	0.9796	0.5490	0.9886
Mn										1	0.9972	0.9926	0.9883	0.9985	0.9951	0.5982	0.9955
Al											1	0.9913	0.9907	0.9963	0.9965	0.5974	0.9956
Cu												1	0.9850	0.9963	0.9873	0.5777	0.9949
Zn													1	0.9873	0.9782	0.6090	0.9953
Ni														1	0.9953	0.5692	0.9959
Pb															1	0.5573	0.9873
Cd																1	0.6147
Cr																	1

4.3.3 Geological Characteristics

(1) C*haracteristics of* coal quality

For Shandi coal mine, the coal formations are the Upper Taiyuan Formation of Carboniferous (C_3t) and the Lower Shanxi Formation of Permian (P_1s). Geological distribution and geological structure are shown in the previous Figures 3-3~3-4. The average thickness of the Upper Taiyuan Formation is 135.78 m, the total thickness of coal seams is 12.64 m, and the mineable coefficient is 9.31%. The average thickness of Shanxi Formation (P_1s) is 63.90 m and the coal seams are not mineable (Figure 4-5). The mineable coal seams and coal quality in the study area are shown in Table 4-4.

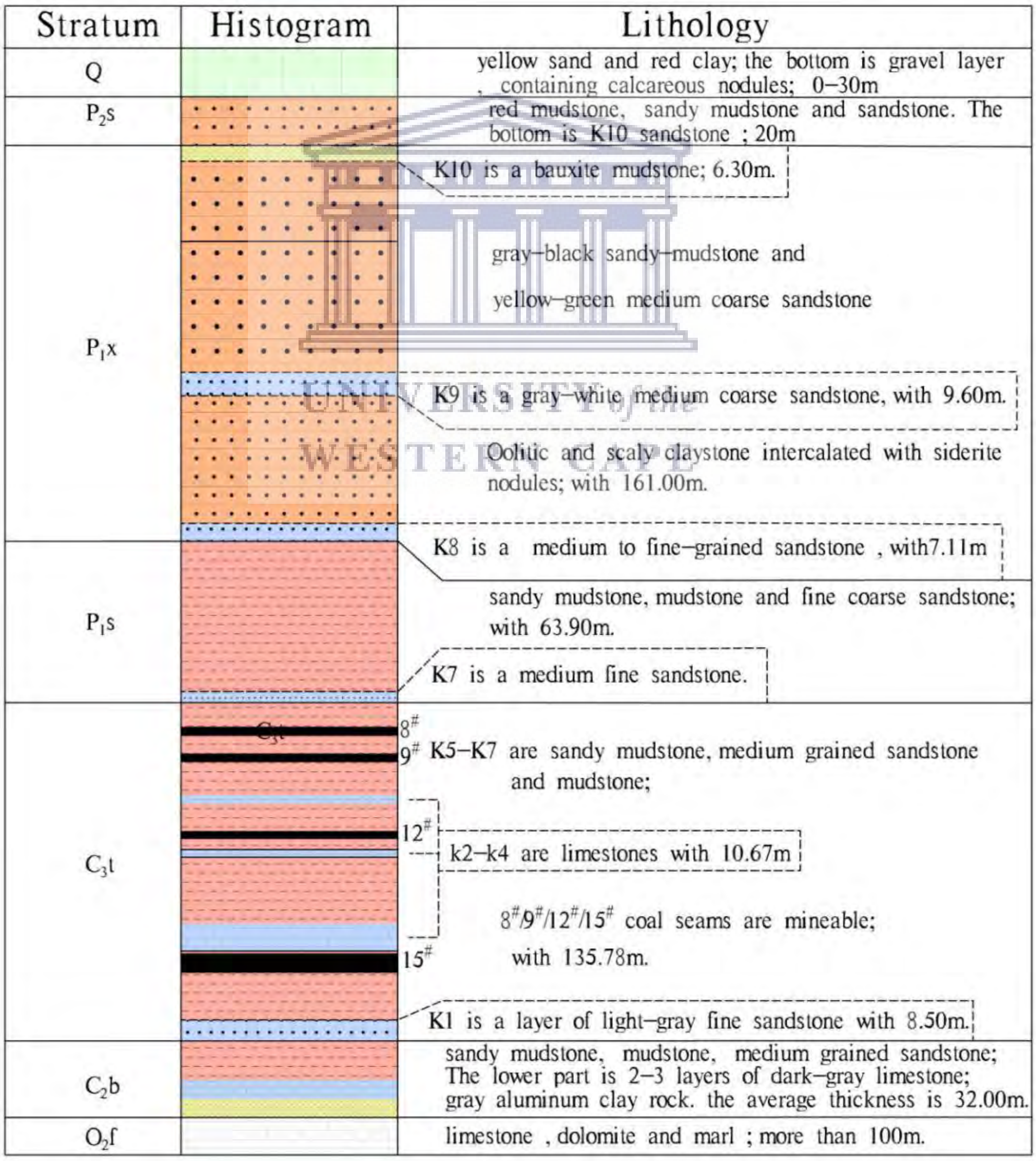


Figure 4-5 Geological column-map of the Shandi coal mine

Table 4-4 Coal seams and coal quality in the study area

Coal seam	Thickness	Organic constituent (%)			Inorganic component (%)				$S_{t.d}$ (%)
		vitrinite	inertinite	exinite	clay	quartz	sulphide	carbonate	
8#	2.36	75.18	19.48	0	1.97	2.82	0.03	0.52	0.65
9#	1.67	78.20	12.72	0	3.65	5.23	0.08	0.12	0.91
12#	1.53	74.04	20.16	0	1.88	2.64	0.12	1.16	1.34
15#	7.08	71.64	23.03	0	1.75	2.42	0.14	1.02	1.47

Five samples are collected in each coal seam and tested in lab. It can be seen from Table 4-4, the result shows that each coal seam in the study area is composed of organic and inorganic components, and the inorganic minerals are mainly clay minerals and quartz, followed by carbonates and sulfides. The carbonate content of the coal in itself is from 0.52% to 1.02% with a neutralizing effect, the clay content is 1.75% to 3.65% with a buffering effect, and the inorganic sulfur content is the lowest from 0.03% to 0.14%. In addition, the inorganic sulfur content and total sulfur content ($S_{t.d}$) is getting higher from 0.03% to 0.14% and 0.65% to 1.47% with the increasing depth of the coal seam.

As we know, the formation of AMD is a comprehensive process of oxidation-reduction, dissolution-precipitation, adsorption-desorption and microbial action with the active participation of sulfide mineral, oxygen and water. However, according to the analysis of coal quality from 8#-12# coal seams, the sulfide in coal itself is lower than the clay, quartz and carbonate in the inorganic component. If sulfide minerals in coal can be fully oxidized, but the content is so low that there is no possibility to form AMD under the condition of neutralization and adsorption from carbonate and clay. Based on the above analysis, it is inferred that the formation of AMD is not closely related to sulfide mineral in coal itself but other sulphide minerals elsewhere in abandoned coal mine.

(2) *Characteristics of* associated minerals

In order to find out the origin of other sulphide minerals, the study also carried out field investigation on coal strata and analysis of the composition of the main minerals in abandoned Shandi coal mine. In all, the main minerals were found, such as Shanxi-style iron ore, pyrite, limestone, sandstone and clay.

Shanxi-style iron ore: it is located at the bottom of the Middle Benxi Formation of Carboniferous (C_2b), and main composed of the pyrite, hematite and limonite. The ore bodies are distributed in a nest shape, generally 0-3.09 m, and present brownish red after weathering. The pyrite depth in Qianniu Town of Yangquan is generally 0-60 m.

Pyrite: it is distributed in the bottom of 8# coal seam, the roof of 12# coal seam and bottom of 15# coal seam, and they all occur in irregular lentils and nests (Figure 4-6).

Limestone: the Middle Benxi Formation of Carboniferous (C_2b) and the Upper Taiyuan Formation of Carboniferous (C_3t) also contain several layers of medium-thick layered limestone. There are about 3-6 layers and the thickness is generally 2-3 m per layer, the thickest is the Taiyuan Formation K2 (four-section stone) limestone, 8-12 m.

Sandstone: distributed in the formations of the Lower Shanxi Formation (P_1s) and the Lower Shihezi Formation (P_1x), and mainly composed of the quartz and feldspar sandstone, containing the silicon, calcium, clay and iron oxide. The roof and floor of sandstone are attached with the Manganese iron ore (Figure 4-7), which is generally oolitic in the stratum, extending more than ten meters. The ore layer contains many impurities. If its surface is brownish black, the clay will be contained.

Clay: mainly occurs in the formations of the Lower Shanxi Formation (P_1s), the Upper Taiyuan Formation (C_3t) and the Middle Benxi Formation (C_2b). There is a good quality in bottom of Benxi Formation and it belongs to the hard-clay (hydrouminite kaolinite bauxite); the clay in Shanxi Formation and Taiyuan Formation (Figure 4-8) are exposed around the Shandi village in Qianniu Town with light gray, and generally belongs to the semi-soft clay (Quartz-bearing kaolinite claystone). "Mudstone" is also called the claystone. Its main component is clay minerals (including the kaolinite, hydromica and montmorillonite), followed by the quartz, muscovite and a small amount of the Feldspar.

The result shows that besides abundant coals, there are considerable reserves of associated minerals such as iron ore and clay. The Shanxi-style iron ore is located at the bottom of the Middle Benxi Formation of Carboniferous and the mining of 15# coal seam doesn't have an impact on its natural environment generally.

The pyrite and clay were tested and the components are shown in Table 4-5~4-6.

Figure 4-6 Mineral survey of the pyrite

Figure 4-7 Mineral survey of Manganese iron ore

Figure 4-8 Mineral survey of the clay

Table 4-5 Mineral components of the pyrite

Al_2O_3 (%)	12.22～30.02	B (%)	0.003～0.005
SiO_2 (%)	8.24～45.0	Cr (%)	0.001～0.02
Fe_2O_3 (%)	2.65～33.07	V (%)	0.005～0.03
TiO_2 (%)	0.8～1.4	Be (%)	0.001～0.002
CaO (%)	0.75～10.06	Ni (%)	0.005～0.03
MgO (%)	0.29～2.08	As (%)	＜0.001
SO_3 (%)	1.10～34.75	Pb (%)	＜0.001
Zn (%)	0.005～0.03	Co (%)	＜0.001

Table 4-6 Mineral compositions of the clay

Designation	Rock	SO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	CaO %	MgO %	K_2O+Na_2O %	S %	Other components
Hard clay	Hydroumininite kaolinite bauxite	40～49	33～44	0.90～1.5	2～2.48	0.36～0.67	0.20～0.30	0.02～1.42	0.01～0.03	Aluminite is 10%, iron ore, dolomite, lignite, and organic matter.
Semi-soft clay	uartz-bearing kaolinite claystone	46～53	32～36	0.90～1.5	1.8～2.50	0.22～0.39	0.20～0.57	0.02～1.20	0.10～0.73	Quartz is 10%, hematite, dolmica, etc.

However, the limestone and sandstone both belong to weak alkaline rocks and do not produce AMD at all, so it can be determined that the associated minerals (mainly including pyrite and clay) can provide a large amount of essential elements and play an indispensable role on the formation of AMD from Shandi coal mine in the study area.

Based on mineral survey and testing data of the pyrite and clay in Table 4-5~4-6, the followings are obtained:

(1) In the study area, three layers of relatively stable pyrite are located at the bottom of the 8# coal seam, the roof of the 12# coal seam, the bottom of the 15# coal seam respectively in the study area. It can be seen once the oxygen and water enter into the goaf, a part of the pyrite will be oxidized in the goaf and on the way to the goaf.

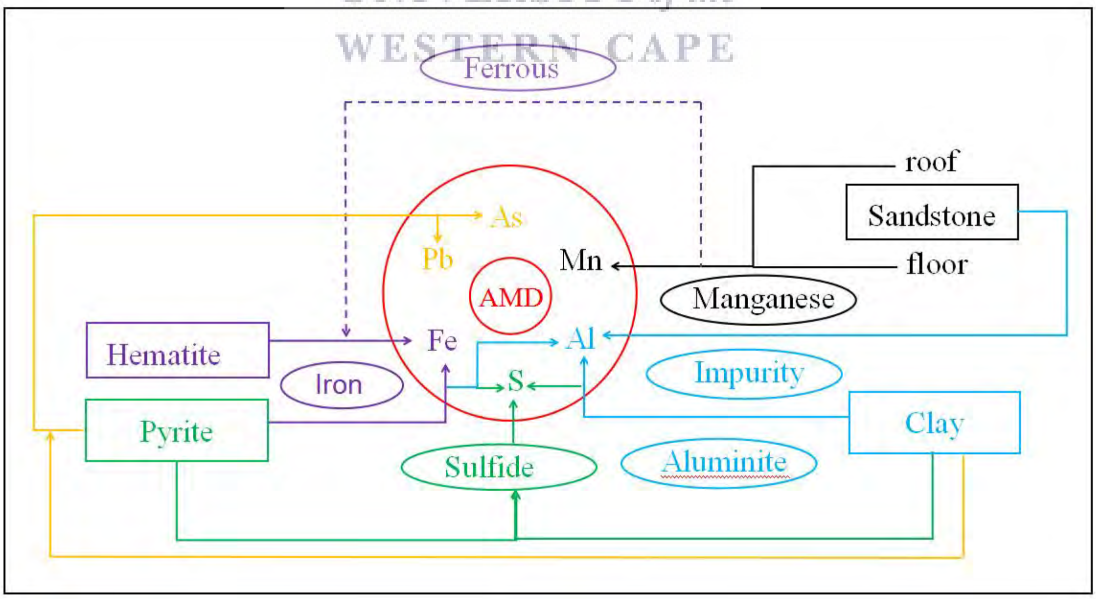


Figure 4-9 The sources of characteristic elements from associated minerals

(2) The Fe and S contents are very high in the composition of pyrite, but As and Pb contents are very low, and Al and Mn contents are not detected at all in testing. Combined with other associated minerals, the vast majority of Fe and S are mainly from the

manganese, pyrite, and other ore bodies by oxidation-reduction reactions, and a little part may be derived from the sandstone and clay by the dissolution and neutralization. For the source of Al in AMD, it should come from clay and impurities from sandstone, and the main source of Mn should be manganese iron ore on the roof and floor of sandstone. So the elements of AMD are multi-sources rather than one kind of sulfide minerals (such as pyrite) (Figure 4-9).

(3) Based on contrastive analysis of coal quality and pyrite, the sulfide in coal itself is much smaller than sulfide minerals in surrounding rocks. Therefore, the distribution and reserves of sulfide minerals are the main factors that determine the formation of AMD in consideration of the oxygen and water in abandoned coal mine.

In summary, it is no doubt that the AMD in abandoned coal mine is caused by oxidation of sulfide minerals, but the distribution and reserves of sulfide minerals are the main factors to determine the formation of AMD. The associated minerals also provide a large amount of essential elements, so the elements of AMD are multi-sources rather than one kind of sulfide minerals.

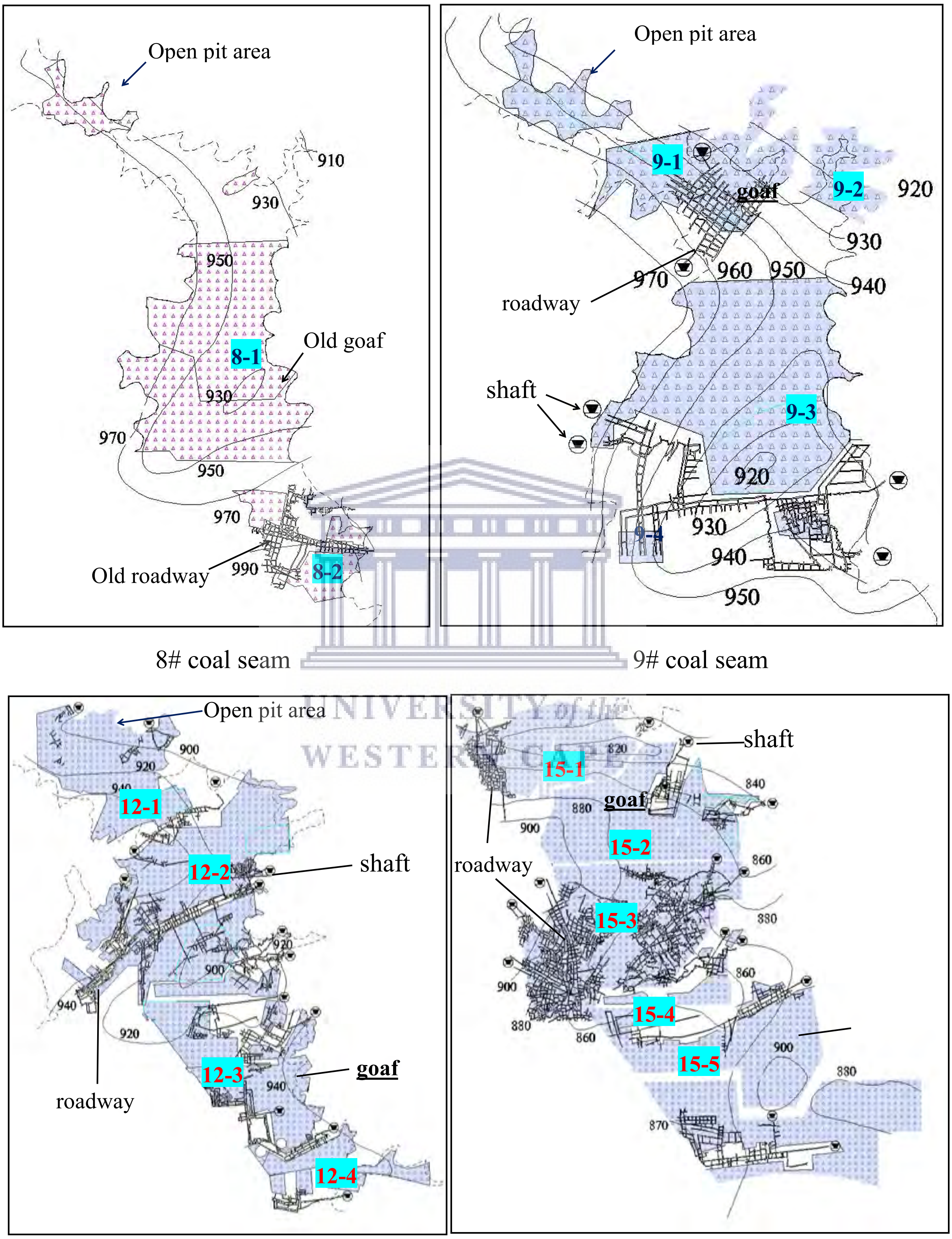
4.3.4 Hydrogeological Characteristics

(1) Goaf and roadway

Based on mining history of Shandi coal mine, the coal mining activities had destroyed the original geological structure and left large areas of goaf under the ground. A total of seven pairs of inclined shafts and attached developed roadways were abandoned in Shandi coal mine after 2005 (Figure 4-10). According to statistics, the total area of the goafs is about 19.9054 km^2 (Table 4-7).

Table4-7 Statistical data of goaf area (excluding open pit)

Coal	Serial number	Area (km^2)	Coal	Serial number	Area (km^2)
8	8 -1	1.2156	12	12-3	1.5320
	8 -2	0.2679		12-4	1.1440
9	9-1	0.4158	15	15-1	1.1032
	9-2	0.7810		15-2	1.0875
	9-3	0.4920		15-3	1.7795
	9-4	1.7920		15-4	2.2330
12	12-1	0.3028		15-5	1.6478
	12-2	0.6433		15-6	1.4680
total	19.9054				



8# coal seam　　9# coal seam

12# coal seam　　15# coal seam

Figure 4-10　Distribution of the goafs, shafts and roadways in Shandi coal mine

It can be seen from Figure 4-10 that the original geological structures have be transformed into a new characteristics in the abandoned Shandi coal mine: 1) the goafs and roadways have bigger cracks and corridors; 2) the intricate goafs had been connected into an organized consortium by the developed roadways left in each coal seam and show a good horizontal connectivity; and 3) the roadways were been made up an organic whole from top to bottom by the seven pairs of inclined shafts (including main shafts, vertical shafts and auxiliary shafts, etc.) in the study area and show a good vertical connectivity.

(2) Water-conducting fissure zone

In this study, water-conducting fissure in Shandi coal mine is calculated by the former empirical formulas. The height of the water conducting fissure caused by coal mining and the results are shown in Table 4-8.

Table 4-8 The result of the height of the water conducting fissure

Mining thickness (m)					Height of the water conducting fissure (m)			
8#	2.36				42.98①			
9#	4.03	1.67			62.32②	34.32		
12#	5.56	3.20	1.53		78.27③	52.98	32.51	
15#	12.64	11.81	8.61	7.08	135.82④	130.18	105.91	104.82

①,②, ③, ④ are shown in Figure 4-11.

For the coal seams in the study area, the following results can be obtained: 1) the buried depth of 8# coal seam is 0-199 m, and the calculated height is 42.98 m. In the northern area, the surface has been connected; 2) similarly, the buried depth of 9# coal seam is 0-209 m, and the height is 62.32 m. The northern and central areas have been connected to surface water; 3) the buried depth of 12# coal seam is 2-249 m, and the northern and central areas is less than 78.27 m. The water-conducting fissure zone can reach up to the surface; and 4) the buried depth of 15# coal seam is 0-301 m. Most of the coal buried depth in the northern area is less than 135.82 m, the water-conducting fissures run through the surface directly and increased the precipitation in the rainy season. To sum up, water-conducting fissures had destroyed five overlying aquifers, including the K7 sandstone aquifer of the Shanxi Formation, the K5 sandstone aquifer of the Taiyuan Formation and K2, K3, K4 limestone aquifers (Figures 4-11~4-12).

It should be emphasized that water-conducting fissures had extended to the bottom of

Shandi River. The Shandi River has become a major recharge through the water-conducting fissures caused by mining 12# and 15# coal seams in Figure 4-13 and strength the hydraulic connection with the five overlying aquifers. Most of the precipitation will seep into the underground through fissures both in the fissure covered zone and water conducting fissure zone.

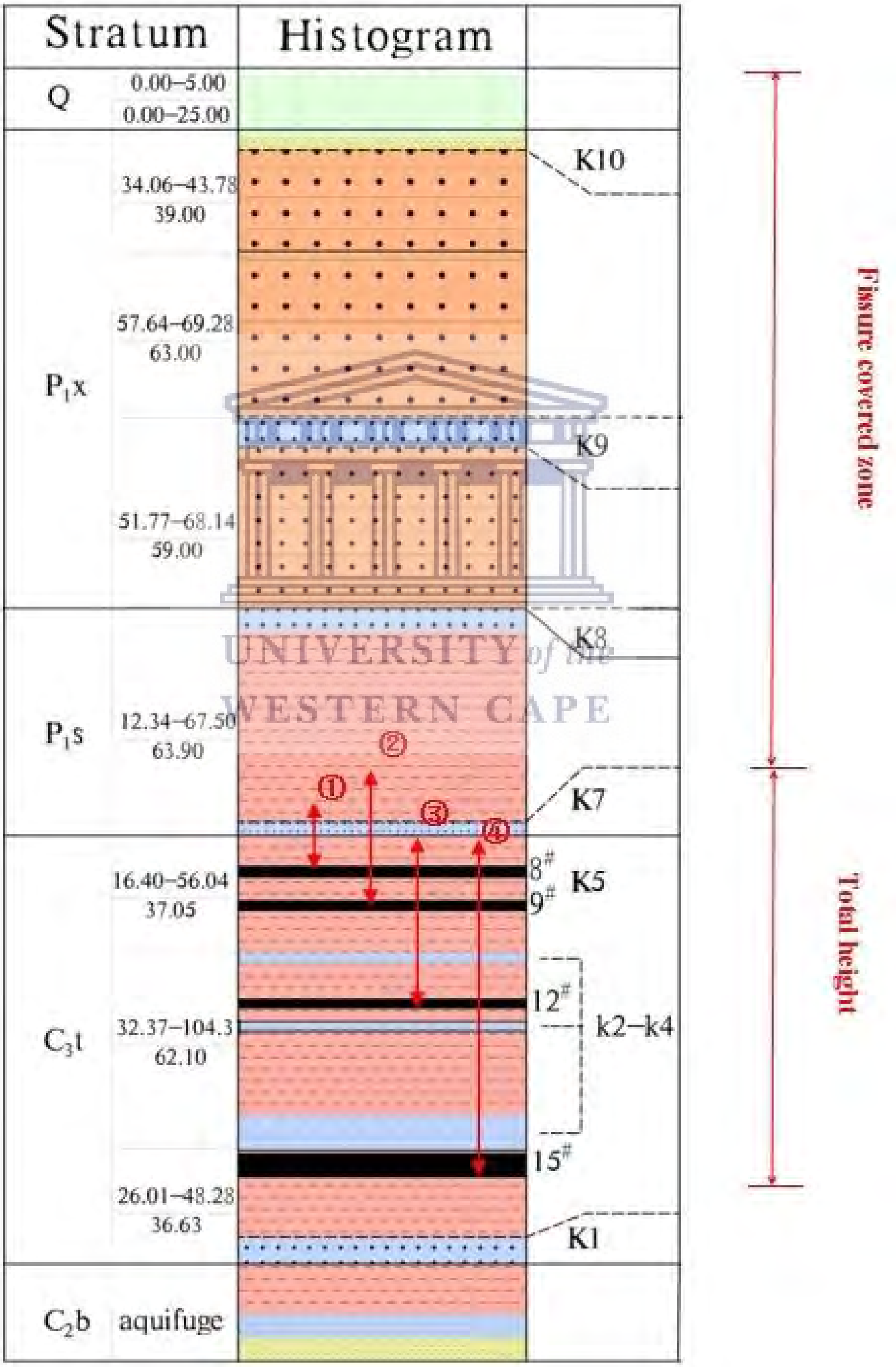


Figure 4-11 Height of the water conducting fissure

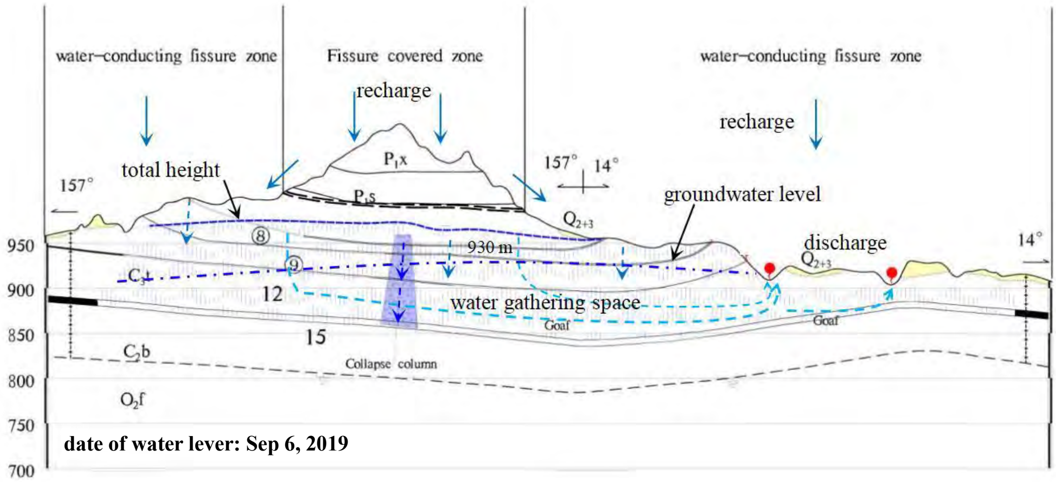


Figure 4-12 The profile of water conducting fissure in Shandi coal mine

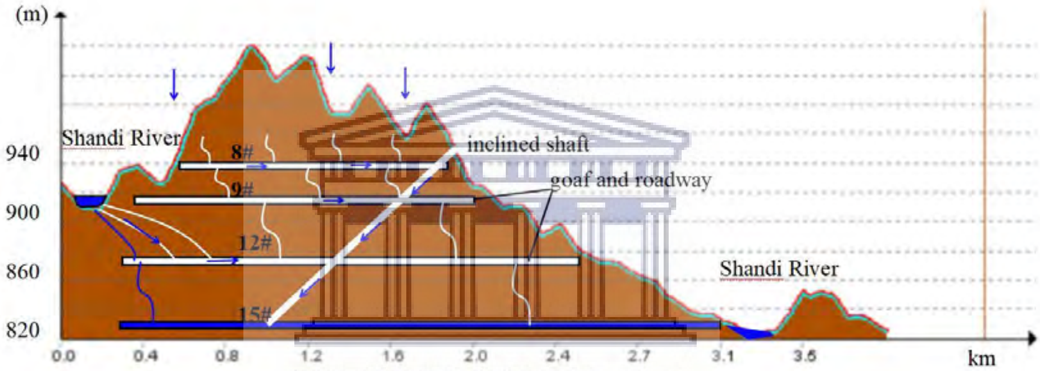


Figure 4-13 The refilling process of groundwater

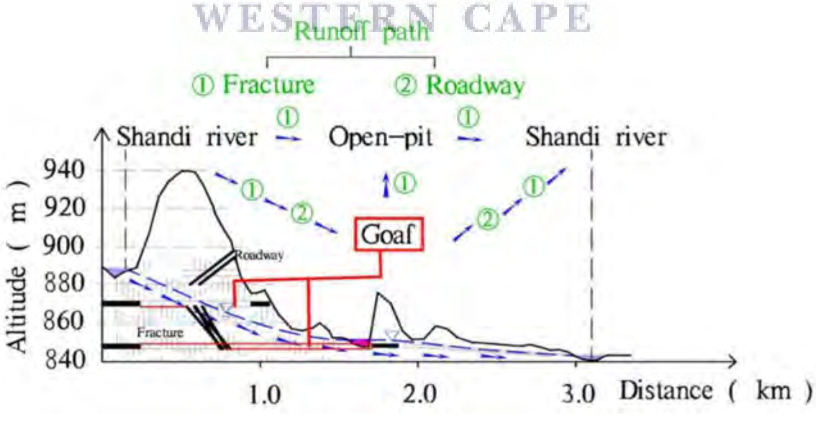


Figure 4-14 The runoff of AMD in open pit near Shandi River

(3) Hydrogeological Characteristics

There is no doubt that the groundwater level will rise after the coal mine is closed, the groundwater refills into the goaf mainly through water-conducting fissure and roadway rather than original fissure. Until now, Shandi coal mine has been abandoned for about 12 years, its hydrogeological conditions had irreversible changes.

1) The recharge of AMD increases

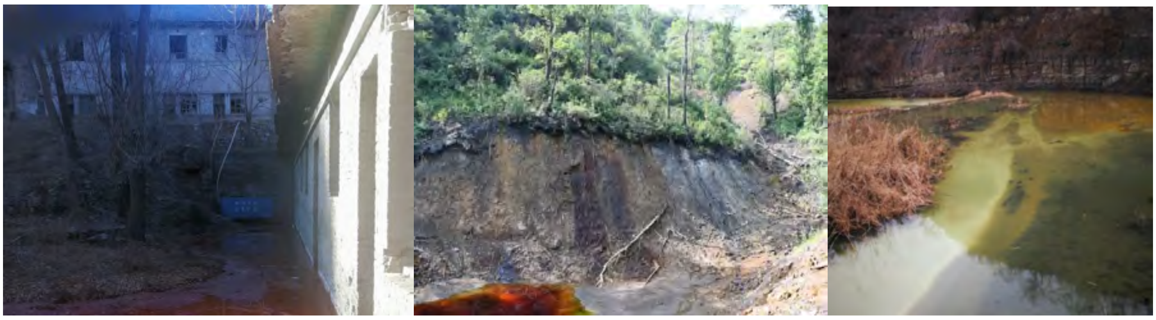
After Shandi coal mine was abandoned: ①water-conducting fissures will run through 5 overlying aquifers in the fissure covered zone (Figure 4-11); ②the fissures reach up to the surface in water conducting fissure zone and cause that a large amount of surface water is converted into groundwater and the infiltration from atmospheric precipitation increases (Figure 4-12); ③Shandi River become a rapid recharge of AMD by water-conducting fissures instead of the original weak leakage, the amount of recharge will increase in a limited time, especially during the rainy season (Figure 4-13); and ④in the north of Shandi coal mine, open pit indirectly get the recharge of atmospheric precipitation and Shandi River at a faster speed (Figure 4-14).

2) The runoff of AMD was transformed to be complex

①Water-conducting fissures broke the confining beds among five overlying aquifers (Figure 4-11) and their flow is converted into vertical instead of the original laminar flow towards the goaf, so water-conducting fissures have become a new important runoff of AMD; ②Coal mining had disturbed the collapse columns, therefore, total 11 collapsed columns had caused hydraulic channels between the upper and lower goafs and increased the uncertainty of the runoff. For example, collapsed column (Figure 4-12) can directly connect the goaf located in the 8#-15# coal seems, speeding up the runoff of groundwater/AMD from the top to the bottom; ③The developed roadways connected the intricate goafs and were connected by the seven pairs of inclined shafts, causing the great changes of the groundwater flow field and its dynamic field, so the goafs and roadways had become bigger and faster corridors for the runoff of AMD than water-conducting fissures (Figure 4-13); and ④The open-pit area is located below the erosion base level of the Shandi River, surface so the water directly entered into the open pit instead of the original pores and fissures (Figure 4-14).

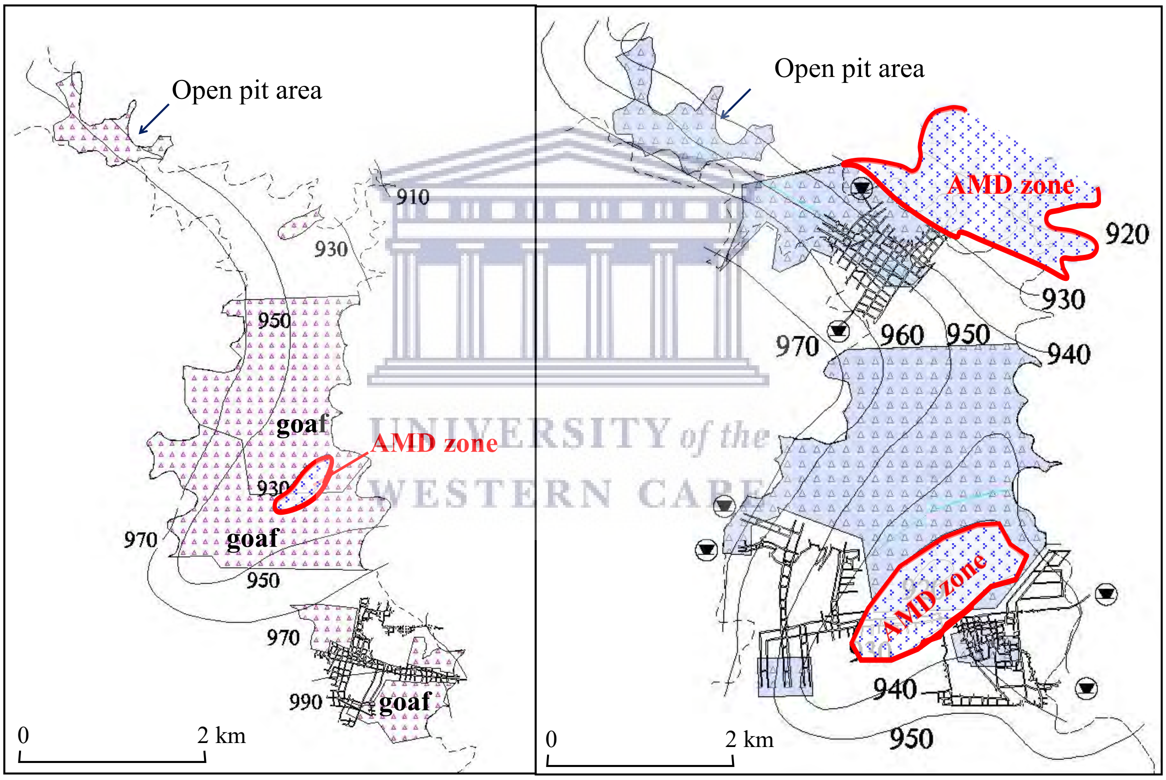
3) The discharge of AMD was uneven in time and space

According to field survey, the discharge of AMD in Shandi coal mine mainly occurred in the lowest outcrop of coal seam and lowest shaft. AMD flows outside the shaft in the form of spring and along outcrop of coal seam in a banding distribution. When there was a heavy rainfall, the roadways got fastest recharge and groundwater level rose rapidly, so a part of AMD would be discharged rapidly through the shaft at the lowest altitude (Figure 4-15).



The lowest shaft (910m) **Outcrop of 9# coal (870m)** **Outcrop of 12# coal (830m)**

Figure 4-15 Main discharge point of AMD

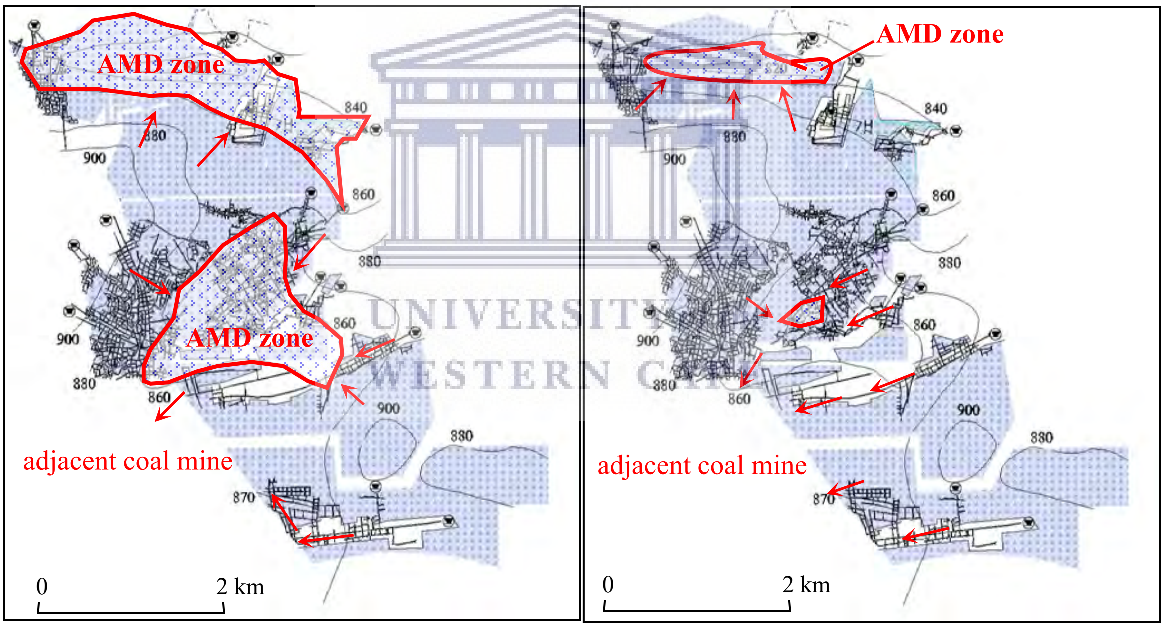


8# coal seam **9# coal seam**

Figure 4-16 Distribution prediction of AMD at groundwater level 930 m in Shandi coal mine

According to the distribution of AMD in the goafs of 8# and 9# coal seams and their floor elevations (Figure 4-16), It can be seen that AMD has refilled the goafs of 12# and 15# coal seams and is mainly stored in the roadways, caving zones and water-conducting fissure zones in a stable retention state. By calculation of groundwater head in the goaf 12# and 15# coal seam, the head of AMD rose about 110 m from the west (930 m) to the east (820 m) in the northeast of Shandi coal mine and herein AMD will outflow along outcrop of coal seam in a dynamic discharge state. Due to lack of oxygen at this depth, AMD always is stored in a relative closed environment, In addition of the Pyrite at the roof of 12# coal seam, so the water appears to be more acidic than that of 8# and 9# coal seams.

Based on the distribution of AMD and floor elevation of 15# coal seam (Figure 4-17), it can be inferred that distribution of AMD storage continues to expand with the groundwater level rising, and presents the same zoning characteristics as 8# and 9# coal seams. In the south of Shandi coal mine, AMD storage is in a stable retention state or discharges to adjacent active mines without protective coal pillars; in the northeast of Shandi coal mine, AMD storage is in a dynamic discharge state along outcrops of 8#, 9#, 12# and 15# coal seams or through the roadways and shafts during the heavy rain.



at groundwater level 860 m **at groundwater level 830 m**

Figure 4-17 Distribution prediction of AMD at 830 m and 860 m in the goaf of 15 coal seam

There are two obvious zones for AMD storage, defined as detention zone and discharge zone (Figure 4-18~4-19). As a representative of geological structure, the syncline and anticline in the study area play a crucial role in the distribution of AMD. The detention zone is mainly distributed in the axis of the syncline and the lowest position in the goafs and roadways; the discharge zone is mainly along the outcrops of coal seams and the Shandi River (including open-pit).

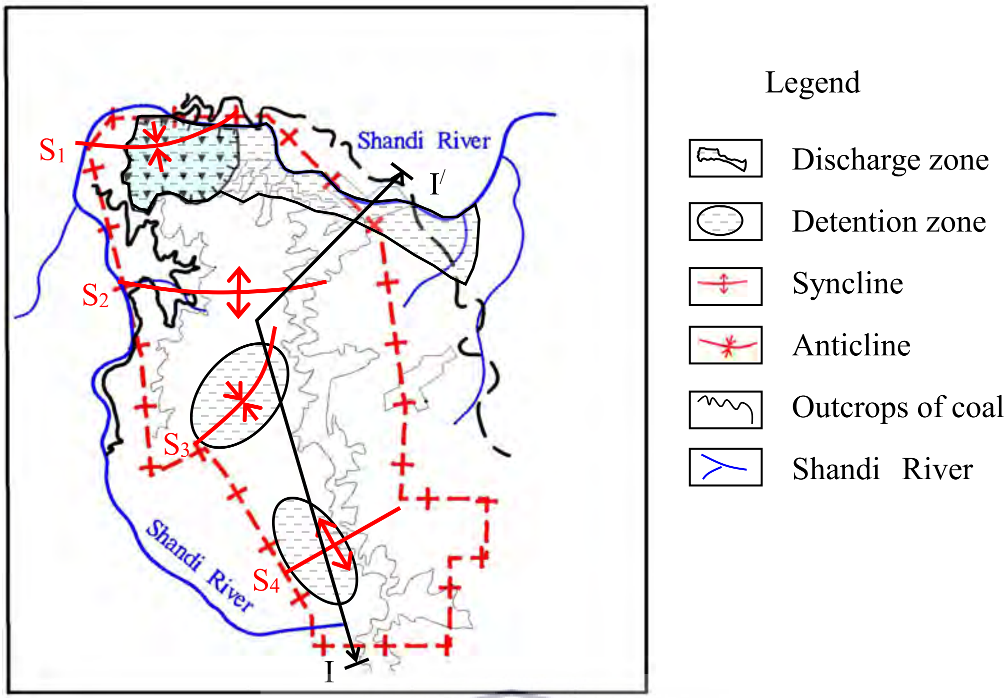


Figure 4-18 Storage zone of AMD of Shandi coal mine

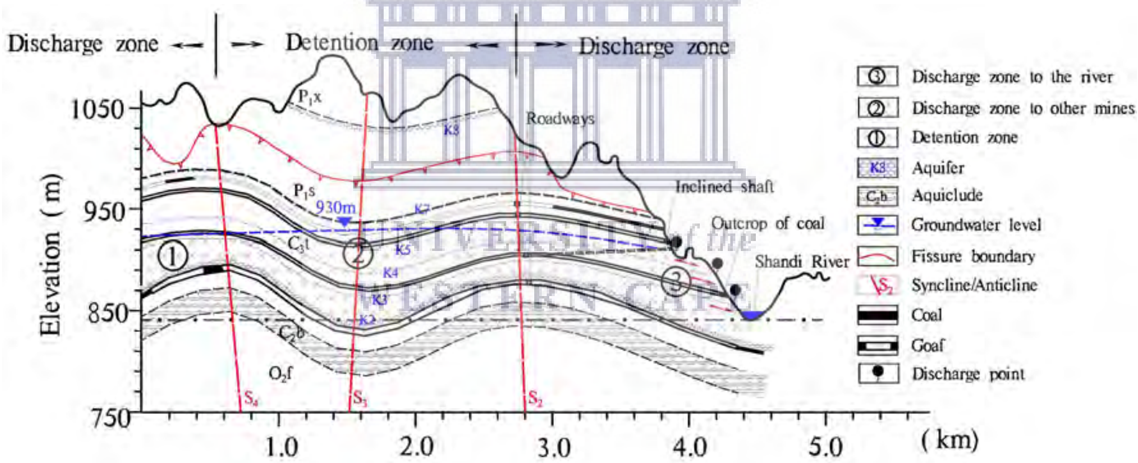


Figure 4-19 I-I/ cross-section of Shandi coal mine

4.4 Summary

Water quality characteristics of AMD: (1) AMD from abandoned Shandi coal mine presents the obvious characteristics of low pH, low DO, low Eh, high SO_4, high Fe and high toxicity; (2) the open environment has a more significant effect on the ion of Fe and sulfate compared with closed environment; (3) the concentration of SO_4^{2-} and heavy metals decrease quickly at the beginning after AMD discharged along the Shandi River; and (4) the Shandi River contributes greatly the heavy metal elements to the Wenhe River.

Geological characteristics: (1) coal seams are composed of organic and inorganic components, and the inorganic minerals are mainly clay minerals and quartz, followed by carbonates and sulfides; (2) due to a lot of the carbonate and the clay in coal itself, the formation of AMD is not closely related to the coal quality; (3) the associated minerals (mainly including pyrite and clay) provide a large amount of elements and play an essential role on the formation of AMD from Shandi coal mine; (4) the elements of AMD are multi-sources rather than one kind of sulfide minerals; and (5) the distribution and reserves of sulfide minerals are the main factors of the formation of AMD in abandoned coal mine.

Hydrogeological characteristics: (1) the goafs had been connected by the developed roadways, the developed roadways were made up an organic whole by the seven pairs of inclined shafts, they provided good space for AMD; (2) For the recharge of AMD, Shandi River has become a rapid recharge by water-conducting fissures; (3) the water-flowing fissures and roadways have become a new important runoff channels for AMD; (4) the runoff of AMD was transformed to be complex, water-conducting fissures, roadways, open-pit, collapse columns and shafts caused the great changes of the groundwater flow field and dynamic field; and (5) the discharge of AMD was uneven in time and space, the distribution of AMD has obvious zoning characteristics, the controlling factors mainly include geological structure, outcrop of coal seam and the Shandi River.

Chapter 5

Engineering measures for AMD pollution

AMD has been defined as a delayed and continuous geochemical disaster, so the AMD treatment is a long-term process and will require the huge amount of budget. In view of the cost of time and money, the ideal solution is to explore a reliable, affordable and self-sustaining system for AMD treatment.

In this chapter, based on the analysis of the geological and hydrogeological characteristics, a framework (Figure 5-1) is put forward and applied for AMD treatment in the abandoned coal mines.

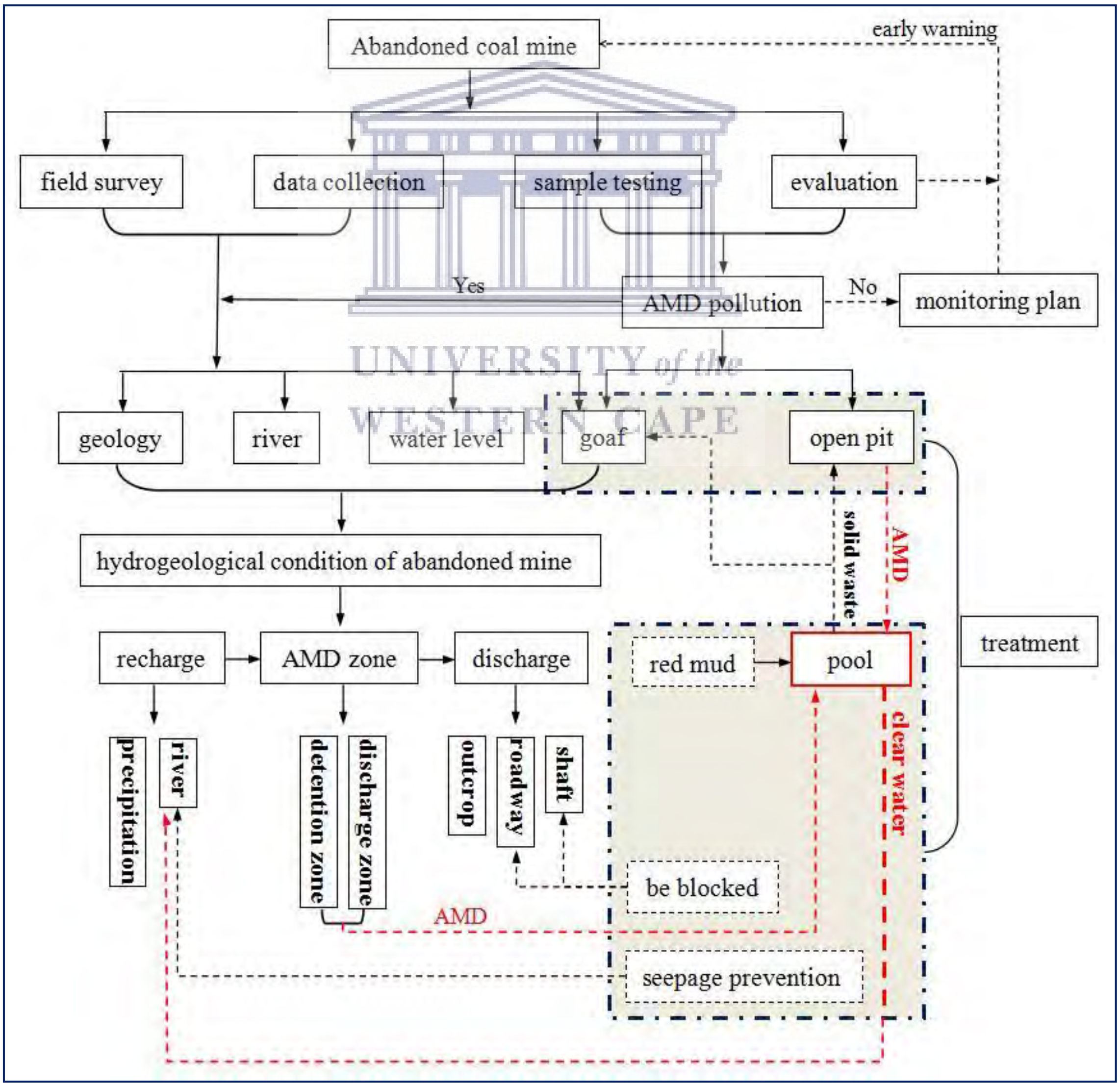


Figure 5-1 AMD treatment chart of abandoned coal mine

5.1 Objective

Since 2009, AMD has polluted the Shandi River for 12 years, but it has not been controlled. Therefore, it is urgent to take a few feasible measures to promote the treatment of AMD in study area. If AMD can't be eradicated, the objectives will become clearer in work: 1) in terms of quantity, keep the total generation amount of AMD as minimum as possible; 2) in terms of quality, reduce the pollution degree of AMD as low as possible; and 3) strive for the harmlessness and recycle of AMD in abandoned coal mines.

For the Shandi coal mine, there is an open pit in the northern. While AMD is treated, it needs to be refilled with large amounts of solid materials. For Shanxi Region, the output of alumina (20.82 Mt/a) accounts for about one third of the national total capacity, the large amounts of alkaline red mud not only occupy precious land resources, but also pollute groundwater. And because of this, so it is the best choice of treating AMD and red mud simultaneously.

5.2 Engineering Measures

(1) The abandoned shafts should be blocked

Due to the mining history of Shandi coal mine in study area for about 60 years, many shafts had been abandoned in the ground including the main shaft, auxiliary shaft and air shaft. Above all, these shafts have a direct hydraulic connection with underground roadways and a large amount of oxygen for the oxidation of pyrite will be transported into the goafs by the roadways in a certain area. So scientific shaft closure can prevent a part of the oxygen into the goafs and underground roadways. Thus, the abandoned shafts should be blocked (Figure 5-2).

(2) The ground fissures should be rehabilitated

The ground fissures around the subsidence area became the most dominant infiltration pathway of atmospheric precipitation. For large ground fissures, the three-step treatment method of "solid material filling--soil covering--vegetation planting" is adopted to block the infiltration pathway. Meanwhile, the rock and soil body on the slope side is strengthened by grouting anchorage and other methods. If the rehabilitated effect is better, it can not only reduce the volume of the atmospheric precipitation, but also help to improve the fertility of the soil and increase the consumption of the oxygen by the microbial metabolism in the vadose zone. Therefore, the ground fissures should be rehabilitated.

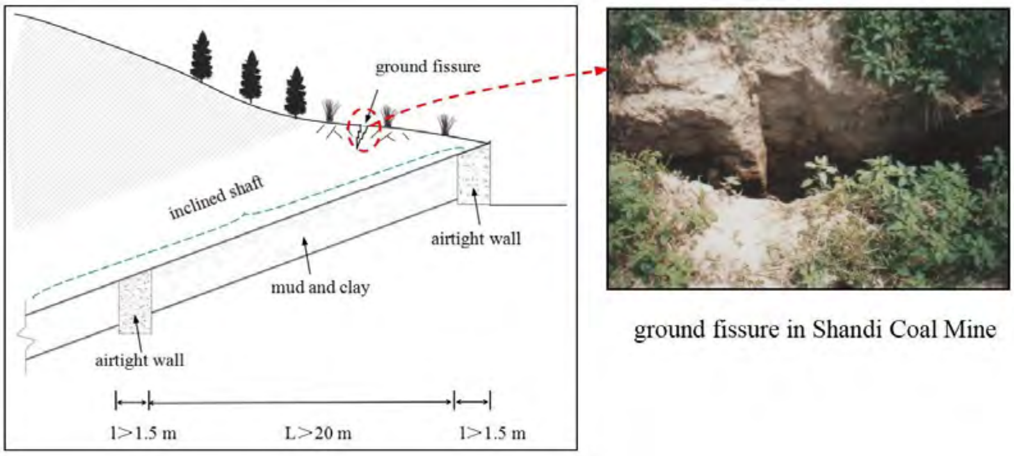


Figure 5-2 The parameter of inclined shaft for Shandi coal mine

(3) River leakage should be controlled

In the study area, the Shandi River (Figure 5-3) has become a rapid recharge of AMD, especially near the open pit in the north of the Shandi coal mine. AMD gets a large-volume and long-time recharge from surface water through water-conducting fissures under the riverbed and open pit. If the leakage project for Shandi River is not implemented, the AMD always get recharge from the Shandi River and can not be completely resolved. Thus, river leakage should be controlled.

Figure 5-3 Overflow weir of Shandi River

(4) Different zones should be treated separately

According to the difference of retention zone and discharge zone, different measures are adopted, for example, drainage tube shall be laid in the discharge zone and the siphons are often used in the retention zone. They can accelerate the discharge of AMD and decrease groundwater level for reducing the storage of AMD. On the other hand, the time of the redox reaction will be shortened (Figure 5-4). Thus, existing open pit should be refilled.

(5) Existing open pit should be refilled

First of all, while it is refilled, the cobble layer and drainage tube will be laid at the bottom of the open pit with coarse limestone and gravel filter. So AMD can be automatically drained to the neutralized pool. After the cobble layer is finished, the treated red mud (pH=6.5-8.5) can be used as a solid material to refill the open pit. The red mud overburden greatly reduces the infiltration of atmospheric precipitation into the open pit (Figure 5-4). As a result, Both AMD and red mud are comprehensively utilized at the same time.Thus, existing open pit should be refilled.

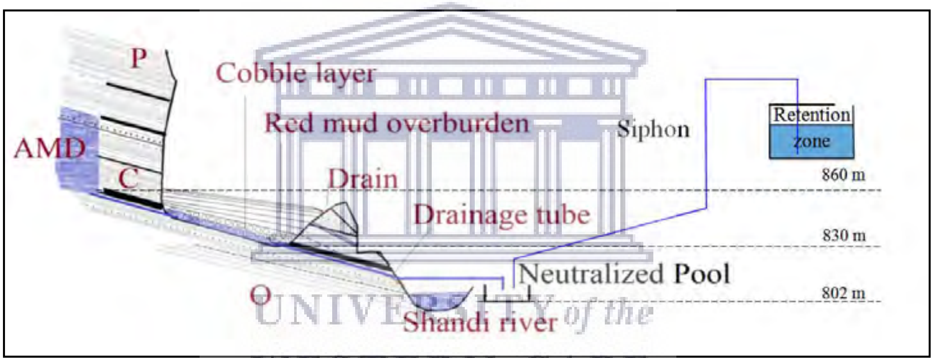


Figure 5-4 Refilled open pit and pool

(6) AMD should be classified by water quality for treatment

Different water qualities of AMD were treated with the red mud (pH=12.2-13.5) in seven-days pilot-scale experiment near the Shandi River. When pH＜6.5, the red mud was stored in neutralized pool and fully blended with AMD until the pH is adjusted to 6.5-8.5. In this process, the ratio of red mud to AMD is approximately18.4-32.7 kg/m^3 and the ratio of loess to AMD is approximately6.8-9.3 kg/m^3, in such a ratio, most pollutants would be adsorbed. Therefore, AMD should be classified by water quality for treatment.

The treated mixtures would be compressed for pre-dehydration with the compressor, and finally sent to the open pit for solidification, which avoids secondary pollution from treated mixtures. If the pH has been adjusted to 6.5-8.5, AMD will be drained into the Shandi River, and water quality is slowly improved by the self-purification of surface water. The pilot test has achieved good results (Figure 5-5).

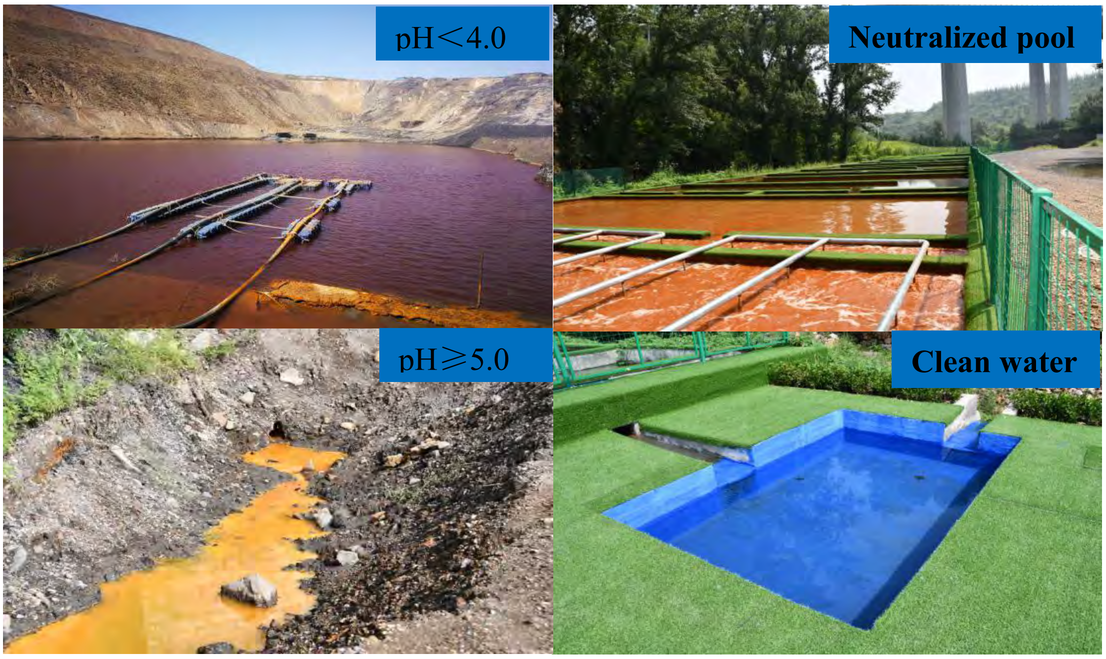


Figure 5-5 Experimental base of Shandi River

5.3 Summary

Engineering measures should be implemented as follows: (1) the abandoned shafts should be blocked; (2) the ground fissures should be rehabilitated; (3) river leakage should be controlled; (4) different water quality of AMD in different zones should be treated separately; (5) existing open-pit should be refilled; and (6) AMD should be classified by water quality for treatment.

Chapter 6

Summary and Recommendation

6.1 Summary

Through the retrieval and analysis of about more than 90 domestic and international publications, this thesis critically reviews the AMD research results in Shanxi's abandoned coal mines from the perspectives of formation mechanism, migration and transformation, prediction, treatment and management. On the basis of field investigation and sample tests of water samples, coals and associated minerals, the thesis researched the geological and hydrogeological characteristics of the abandoned Shandi coal mine. Finally, a framework and measures are put forward and applied for AMD treatment in abandoned coal mines. The main results of the thesis are presented as follows.

Formation and treatment of AMD

It is concluded that that sulfur minerals and refilled water are main sources for the formation of AMD, pyrite is the prerequisite, oxygen in the refilled water is the inducement, water is the carrier, Fe^{3+} and microorganisms are the catalyst. The underground roadway system and geological structure are the dominant factors that control the water gathering space of AMD. The AMD from abandoned coal mines has worsened the severe water ecological environment. It has aggravated the current situation of water shortage in Shanxi, and brought the problem of ecological environment and the crisis of drinking water safety, so it is necessary to conduct further research on AMD in abandoned coal mines.

Problems in the study of AMD in Shanxi abandoned coal mines

There are still some problems in the previous research of AMD in Shanxi abandoned coal mines: (1) the regional distribution of pyrite and its occurrence law in coal-bearing strata in six major coalfields need to be further investigated and researched; (2) the developed underground roadway system of abandoned coal mines is very difficult to be generalized to analyze the AMD flow field; (3) water gathering space in abandoned coal mines are very complicated and it is difficult to grasp and determine the water head and water accumulation coefficient in the goaf; (4) the research on the leakage channel, such as fault and collapse column, is relatively lacking; (5) in the research of AMD migration and evolution, the participation of microorganism and multi-gas components is not considered, and there is less attention to the water refilling and water gathering process of AMD; (6) there is a lack of research on the influence of gas composition, pressure, water temperature and ion concentration of AMD on the hydrochemical balance; (7) no relevant investigations and studies are carried out on when the AMD will outflow, where it will outflow and how long it will last; (8) in Shanxi, the AMD treatment methods are basically at the infancy stage of laboratory theoretical research, and the artificial wetland and PRB is still blank; and (9) the management policies/regulations and AMD pollution monitoring data are relatively lacking. AMD risk assessment and early warning mechanisms have not yet been established, and the research on risk identification and index systems is blank.

Water quality characteristics of AMD

(1) AMD from abandoned Shandi coal mine presents the obvious characteristics of low pH, low DO, low Eh, high SO_4, high Fe and high toxicity; (2) the open environment has a more significant effect on the ion of Fe and sulfate compared with closed environment; (3) the concentration of SO_4^{2-} and heavy metals decrease quickly at the beginning after AMD discharged along the Shandi River; and (4) the Shandi River contributes greatly the heavy metal elements to the Wenhe River.

Geological characteristics

(1) coal seams are composed of organic and inorganic components, and the inorganic minerals are mainly clay minerals and quartz, followed by carbonates and sulfides; (2) due to a lot of the carbonate and the clay in coal itself, the formation of AMD is not closely related to the coal quality; (3) the associated minerals (mainly including Pyrite and Clay) provide a large amount of elements and play an essential role on the formation of AMD from Shandi coal mine; (4) the elements of AMD are multi-sources rather than one kind of

sulfide minerals; and (5) the distribution and reserves of sulfide minerals are the main factors of the formation of AMD in abandoned coal mine.

Hydrogeological characteristics

(1) the goafs had been connected by the developed roadways, the developed roadways were made up an organic whole by the seven pairs of inclined shafts, they provide good space for AMD; (2) for the recharge of AMD, Shandi River has become a rapid recharge by water-conducting fissures; (3) the water-flowing fissures and roadways have become the new important runoff channels for AMD; (4) the runoff of AMD was transformed to be complex, water-conducting fissures, roadways, open-pit, collapse columns and shafts caused the great changes of the groundwater flow field and its dynamic field; and (5) the discharge of AMD was uneven in time and space, the distribution of AMD has obvious zoning characteristics, the controlling factors mainly include geological structure, outcrop of coal seam and the Shandi River.

Engineering measures

(1) the abandoned shafts should be blocked; (2) the ground fissures should be rehabilitated; (3) river leakage should be controlled; (4) different water quality of AMD in different zones should be treated separately; (5) existing open-pit should be refilled; and (6) AMD should be classified by water quality for treatment.

Comments on the case study of Shandi coal mine

The thesis will contribute towards the geological and hydrogeological characteristics of AMD from Shandi coal mine, research results will provide important theoretical basis for water resources protection of Niangziguan spring and AMD pollution treatment in abandoned coal mines in the nation and even in the world.

6.2 Recommendation

Based on this study, some recommendations for future research are presented in the following aspects:

(1) The regional distribution of pyrite and the occurrence law in coal-bearing strata in six major coalfields of Shanxi should be actively carried out; the hydraulic connections among surface water, groundwater, geological structure, water-conducting fissure and the formation, migration and evolution of AMD should be further researched.

(2) The researchers should improve the comprehensive detection method of the hydrogeological condition, water channel, water gathering space and underground roadway system of abandoned coal mines, and pay more attention on the formation, migration and prediction of AMD and the related environmental issues. The groundwater model under combined action of underground roadway system, geological structure and primary fissures needs to be established, and the groundwater flow that are highly involved in underground roadway system should be actively researched.

(3) The formation mechanism of AMD in abandoned coal mines needs to be studied, and it is necessary to consider the influence of microorganism, gas component and other factors. To effectively predict and prevent the generation of AMD, the sulphate and the harmful elements should be clarified. Furthermore, the risk assessment of AMD pollution needs to be constructed to provide effective support for scientific plan and decision-making.

(4) It is necessary to predict mine water/AMD and solve the following issues such as when the AMD would outflow, where it would outflow and how long it would last. Research on the correlation between AMD outflow and impact factors should be strengthened, and relevant investigation and prediction should be carried out to solve the above three issues. More attention should be paid to the effects of gas composition, pressure, temperature and ion concentration of AMD on the hydrochemical equilibrium in the process of the conversion of the environment.

(5) It is necessary to actively carry out research on the application of comprehensive treatment method such as artificial wetland and PRB in the active treatment of AMD in

abandoned coal mines, and explore an efficient, affordable, environmental technology for the AMD.

(6) Technical guidelines should be issued to guide coal mine closure and supervision as soon as possible. A network system for monitoring the AMD groundwater in abandoned coal mines should be established to provide effective information for AMD risk identification. Research on management, risk assessment and early warning mechanisms for the AMD in abandoned coal mines should be strengthened.

(7) To alleviate the shortage of water resources in Shanxi and ensure the safety of drinking water, in-depth study of the hydraulic connection between the AMD in abandoned mines and karst springs should be strengthened, which will realize the sustainable development of coal, water resources and ecological environment.

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***Appendix A** Publication*

water MDPI

Review

Review: Acid Mine Drainage (AMD) in Abandoned Coal Mines of Shanxi, China

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Abstract: Excessive exploitation and massive coal mine closures have brought about extensive goafs in Shanxi where 8780 coal mines have been abandoned in the last 20 years. Acid mine drainage (AMD) poses severe environmental impact and has become a prominent problem in Shanxi abandoned coal mine areas, which has aggravated the shortage of water resources and threatened the safety of the local drinking water supply. The purpose of this review is to protect the precious water resources and maintain sustainable use in Shanxi coal mines and downstream. By retrieving and analyzing about 90 domestic and international publications, a critical review of the AMD research results in Shanxi abandoned coal mines is conducted from the perspective of the formation mechanism, migration and transformation, prediction, treatment and management. The results shows that pyrite is the prerequisite for the formation of AMD, oxygen is the inducement, water is the carrier, and Fe^{3+} and microorganisms are the catalyst. The roadway system and geological structure are the dominant control factors. Finally, current difficulties and future research are pointed out. It is necessary to further strengthen the systematic research on the geological and hydrogeological conditions of abandoned coal mines, and explore an efficient, cheap, environmental technology, and construct the pollution risk assessment model for the AMD treatment. This study provides a scientific basis for the comprehensive treatment and management of AMD in abandoned coal mines in Shanxi.

Keywords: acid mine drainage; abandoned coal mine; water pollution; groundwater; Shanxi province

Citation: Wang, Z.; Xu, Y.; Zhang, Z.; Zhang, Y. Review: Acid Mine Drainage (AMD) in Abandoned Coal Mines of Shanxi, China. *Water* **2021**, *13*, 8. https://dx.doi.org/10.3390/w13010008

Received: 24 November 2020
Accepted: 19 December 2020
Published: 23 December 2020

1. Introduction

Nowadays, acid mine drainage (AMD) problems in abandoned coal mines have become a worldwide environmental concern. For example, in the Rio region of Spain, AMD has been a continuous pollution source of the Tinto River [1]. AMD formed by a large number of abandoned coal mines in the USA and all of the world has polluted rivers with a total length of about 23,000 km [2,3], causing serious environmental consequences [4–7]. AMD in the closed pits of the Witwatersrand mine in South Africa has become an important issue of national concern [8–10]. The AMD problems of abandoned coal mines are widespread in other countries such as the Makum coal mine in India [11], the Gangreung coal mine in South Korea [12], and the Douro coal mine in Portugal [13], which have caused serious damage to the local water resources and the water environment. In China, according to statistics from the China Coal Industry Association, the number of coal mines has been reduced from more than 80,000 in the peak period to about 5800 at the end of 2018 [14,15]. Unfortunately, the closed coal mines in China have caused a series of water environmental problems such as destruction of water resources and deterioration of water quality [16,17]. Therefore, it is necessary to conduct research on AMD in abandoned coal mines globally.

Over the years, AMD research on the impact, formation, migration, prediction and treatment has received extensive attention from scholars both nationally and internationally.

For example, Banks and Banks [18] evaluated the environmental impact of AMD emissions from abandoned coal mines in the UK using relevant water quality data, and pointed out that AMD had already resulted in groundwater pollution and the pollution degree had become more serious as the water level continued to rise. Wood et al. [19] found that the surface water pollution was the most serious in the first few decades by 32 monitoring drainage points of the abandoned coal mine in the Midland Valley of Scotland. Studies have shown that the groundwater in Hongshan and Zhaili coal mines in Zibo, Shandong, China, was in cross strata pollution, resulting in the scrapping of hundreds of water supply wells, which directly threatening the water quality of Xuzhou's water supply source and the Grand Canal from Beijing to Hangzhou [20–22]. In the Green Valley coal mines (GVS) in Indiana, AMD caused an increase in the Total dissolved solids (TDS)of the entire area [23], SO_4^{2-} reached up to 63,000 mg/L, and metals such as Pb, Zn, Cd, Cr, Ni, Be, and V also increased significantly [24]. AMD outflowed from a large number of abandoned coal mines in the Stockett–Centerville area of the USA's polluted surface rivers [25]. AMD has had an irreversible impact on the environment. Plenty of studies have showed that AMD is produced as a result of the oxidation of pyrite with water and oxygen [26,27]. For the migration, Nassery and Alijani [28] confirmed that AMD from abandoned coal mines in the Zirab area in northern Iran promoted the dissolution of carbonate rocks, which was the main factor for the geochemical evolution of groundwater. Jiang et al. [29] studied and concluded that the oxidation of sulfide in coal-measure strata and the oxidation of sulfide in mineral deposits respectively input 0.27% and 20.5% SO_4^{2-} by the sulfur isotopes in the Wujiang River Basin. He et al. [30] confirmed that the continuous discharge of AMD from a closed coal mine in Hunan, China, into rivers has caused biological migration in the water system. Sun et al. [31] collected sediment samples for geochemical and microbial community analysis, and concluded that AMD generated from the upstream abandoned coal mines in southwestern China [32]. Wang et al. [33] selected small watersheds where AMD was relatively concentrated in the Zhijin abandoned coal mine area in Guizhou and studied the migration and transformation process of sulfate in AMD in karst areas. For prediction, Grodner [34] established a numerical model of groundwater flow in the Sigma coal mine in South Africa using MODFLOW (USGS, Reston, VA, USA), and predicted the water level rise of the AMD after the pit was closed. Bernd E [35] studied the chemical properties of groundwater around an abandoned open-pit coal mine in central Germany. Xu [36] studied the chemical reaction in the water flow path of closed coal mines and revealed the law of hydro-geochemical conversion using PHREEQC software (USGS, Reston, VA, USA). Many scholars have selected typical abandoned coal mines to predict the spatiotemporal process of the water level rebound [37–41]. A lot of efforts have been made to treat AMD. Sun [42] studied the rise mechanism of AMD water level in closed coal mines and proposed effective measures to protect water resources. Gitari et al. [43] treated the AMD of a coal mine using fly ash, achieving the goal of waste treatment. Song et al. [44] carried out a two-year in situ source treatment of AMD from an abandoned coal mine in central Tennessee, USA by using remote sensing and biogeochemical technology, and achieved successful results at a high cost. It can be seen that the treatment solution is only suitable for specific project situations [45]. Zhang et al. [46] treated AMD by using Na_2CO_3-modified fly ash, the research results provide technical support for the comprehensive utilization of AMD. Liu and Sun [47] clarified the groundwater pollution problem caused by a closed coal mine, and put forward some effective technical means and feasible prevention methods. Wei et al. [48] proposed that the development trend of the combination of directed source control and terminal treatment technology was a hotspot of AMD research in China in the future. All these results can provide theoretical basis for regional and local AMD evaluation and management.

Located in northern China, Shanxi Province is rich in coal resources, with six major coalfields including Datong, Ningwu, Xishan, Hedong, Qinshui and Huoxi from north to south (Figure 1). The output of raw coal accounts for 1/4 of the whole country. It is an important energy and heavy chemical base in China, and plays a significant role in the sustainable development of the economy and society and energy security. There are 8 large river basins in Shanxi. According to statistics, the coal mine areas in Shanxi are 61,050 km^2, accounting for 39.1% of the total area of the region. Over the years, with the continuing exploitation of coal resources in Shanxi, water environmental problems such as destruction of water resources and deterioration of water quality have become increasingly prominent. In recent years in particular, with the closure of 8780 coal mines, water pollution caused by AMD has become increasingly serious [49], which has aggravated the shortage of water resources and threatened the safety of the local drinking water supply in Shanxi.

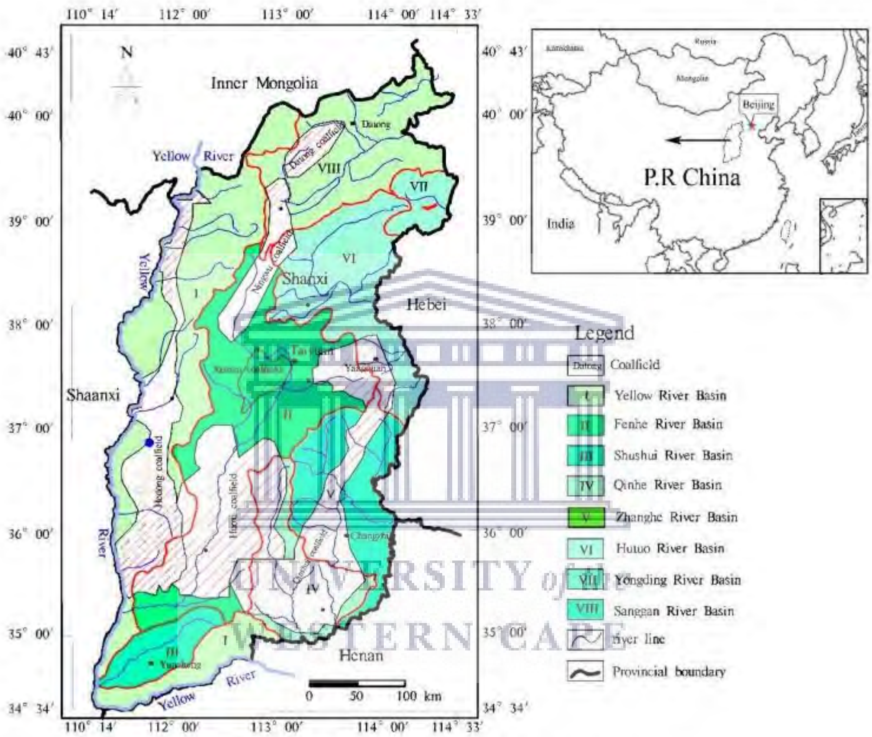

Figure 1. Six major coal fields in Shanxi.

On the basis of the previous investigations in the closed coal mines of Shanxi such as Datong coalfield [50,51], Yangquan coalfield [52,53], Taiyuan Xishan coalfield [54–56], etc., irreversible changes have taken place in the water-bearing medium structure, hydrodynamic field, chemical field and microorganism. The outflow of AMD has already affected the aquatic environment of downstream rivers. For example, a large amount of AMD have been stored in the small abandoned coal mines in Xishan coalfield [57]. These AMD leaked into the underlying karst aquifer through cracks and faults in the coal seam floor, moreover, the AMD in Niujiakou coal mine threatened the karst water quality of Jinci Spring [58]. Most unfortunately, a large amount of karst groundwater were dewatered in many pressurized coal mines [59], which further exacerbated the shortage of karst groundwater in the Jinci spring catchment.

According to a recent field investigation, the coal mine of Shandi Village in Yangquan, Shanxi, was closed in 2005, and the goaf was filled with AMD in 2009. Based on the monitoring data in 2013, the salinity, TDS, sulfate, and pH were 8274 mg/L, 4870 mg/L, 5781 mg/L, and 3.51, respectively [60]; at the end of 2016, the pH was 2–3, and the sulfate was 11,370–18,900 mg/L. AMD outflowed the surface and polluted the groundwater and surface water resources in the Shandi River Basin [58,61]. Some investigators [52,62,63] pointed out that the leakage and outflow of AMD was the cause of the pollution in the Niangziguan Spring catchment in Shanxi. This case study was a warning and attracted more scholars to research the AMD from abandoned coal mines in Shanxi.

It can be seen that the mechanism of AMD formation in abandoned coal mines is very complex, which is closely related to hydrogeological conditions such as precipitation, surface water, aquifers and so on. The closure of coal mines in Shanxi mainly occurred after 2000, and research on the water environment and ecological problems that may be induced by AMD in abandoned coal mines is still in its infancy. As one of the main coal energy bases in China, Shanxi has a large number of abandoned coal mines with a wide distribution and complex hydrogeological conditions. Furthermore, coal and water co-exist in Shanxi coal mines, which have close hydraulic connections with the 19 major karst springs in Shanxi. If the AMD problem continues to worsen, it will seriously threaten the safety of drinking water in the 19 spring catchments. Therefore, it is necessary to carry out further research on AMD in abandoned coal mines in Shanxi.

The purpose of this review is to protect the precious water resources and maintain sustainable utilization in Shanxi coal mines and downstream. By retrieving and analyzing about 90 national and international publications, a critical review of AMD research results in Shanxi abandoned coal mines was conducted from the perspective of the formation mechanism, migration and transformation, prediction, treatment and management. The current difficulties and future researches are pointed out. It is necessary to further strengthen the systematic research on the geological and hydrogeological conditions of abandoned coal mines, actively explore an efficient, cheap and environmental treatment technology, and formulate AMD risk assessment and early warning mechanism for abandoned coal mines. This review cements a scientific basis for the comprehensive treatment and management of AMD in abandoned coal mines in Shanxi.

2. Overview of Acid Mine Drainage (AMD) Studies in Shanxi

The major coal-bearing strata in Shanxi is dominated by the Taiyuan Formation of Upper Carboniferous and the Shanxi Formation of Lower Permian in Late Paleozoic, the coal reserves account for 98% of the region. The second coal-bearing strata in Shanxi is the Datong Formation of Middle Jurassic in Mesozoic and the coal-bearing construction of the Early Paleogene in Cenozoic.

Shanxi is the place with the most extensive karst distribution in northern China. There are 19 major karst springs (Figure 2) with stable flows and good water quality [49], which are convenient for centralized development and utilization, and they have become one of the important water supply sources for Shanxi energy bases. According to statistics, there are 265 centralized drinking water sources in Shanxi. The groundwater supply accounts for more than 90% of total water sources, of which approximately 83% is karst water. Over the years, researchers have conducted a certain degree of research on the relationship between AMD and water supply resources in abandoned coal mines in Shanxi, and achieved many important results, which have good practical value and can lay the foundation for research on AMD.

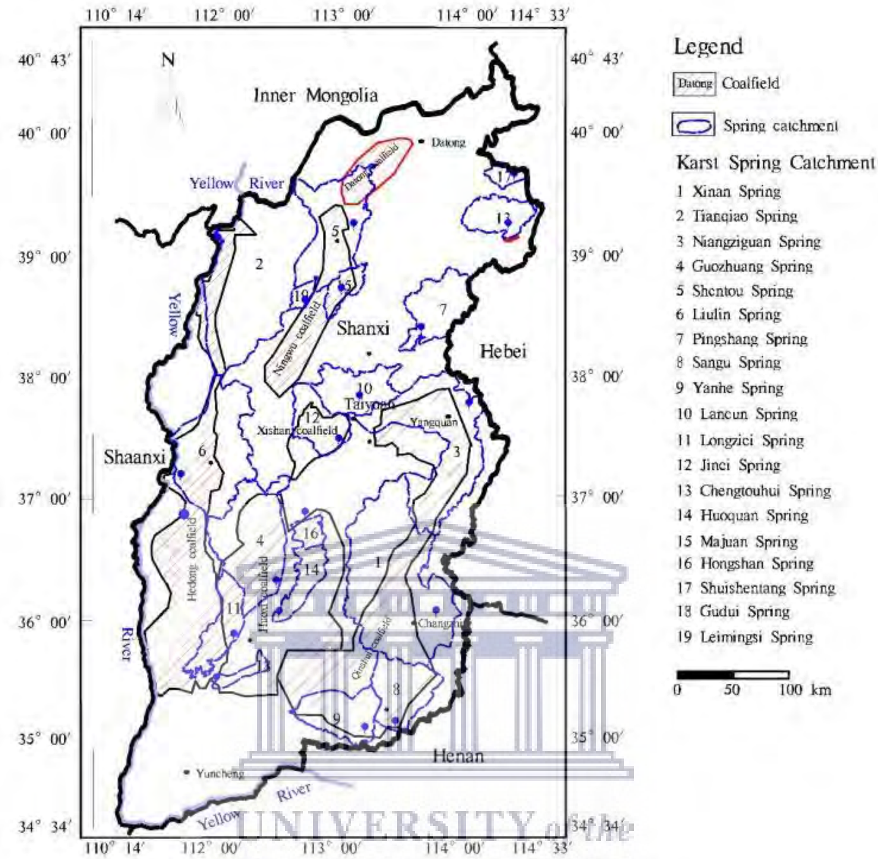

Figure 2. The 19 major karst springs in Shanxi.

2.1. The Formation Mechanism of AMD

2.1.1. Source

Based on the research results of AMD in abandoned coal mines in Shanxi, the exposed pyrite in the coal seams is the main cause. When pyrite reacts with oxygen and water, the products are Fe ions and sulfuric acid. The specific reaction equations are as follows:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4\,SO_4{}^{2-} + 4H^+ \tag{1}$$

$$12FeSO_4 + 6H_2O + 3O_2 \rightarrow 8Fe^{3+} + 12\,SO_4{}^{2-} + 4Fe(OH)_3 \tag{2}$$

Li et al. [64] conducted a certain sampling analysis on the basis of the collected data. The results showed that the $SO_4{}^{2-}$ from gypsum accounts for about 30%, and the $SO_4{}^{2-}$ from oxidation of pyrite accounts for about 60–70%. The dissolution of gypsum and oxidation of sulfide in aquifers were the main causes for the high concentration of $SO_4{}^{2-}$. Zhao et al. [56] confirmed that the organic sulfur in coal can also generate acid after its oxidation, which aggravates the decrease of pH to a certain extent; when the sulfur content is >5–7%, the pH is 6–5.5; when the sulfur content is >7–9%, the pH is 5.5–3.5; when the sulfur content is >9–11%, the pH is 3; when the sulfur content is >12%, the pH is below 2.5. According to qualitative analysis by scholars [65], AMD in abandoned coal mines in Shanxi is also generated by a series of oxidation reactions involving the pyrite mixed in coal seams, oxygen and water.

The above results show that there are still few studies on the formation of AMD in Shanxi abandoned coal mines, and there is a big gap between Shanxi and domestic as well as international cases, such as inconsistent descriptions of the reaction process and insufficient consideration of influencing factors (especially microorganisms such as *Acidophilus thiobacillus ferrooxidans*, A.f) which limits the theoretical development of AMD's formation mechanism.

The authors of this article believe that S_2^{2-} and Fe^{2+} exist simultaneously on the surface of pyrite in the FeS_2+H_2O+O_2 system in Shanxi abandoned coal mines (Figure 3). According to the principle of redox, the reducibility of S_2^{2-} is greater than that of Fe^{2+}, that is, the S_2^{2-} in water first oxidizes with O_2. The specific reaction equations are as follows:

$$S_2^{2-} + O_2 + OH^- \rightarrow S_2O_3^{2-} + H^+ \quad (3)$$

$$2S_2O_3^{2-} + 0.5O_2 + 2H^+ \rightarrow S_4O_6^{2-} + H_2O \quad (4)$$

$$S_2O_3^{2-} \rightarrow S + SO_3^{2-} \quad (5)$$

$$S + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (6)$$

$$SO_3^{2-} + 0.5O_2 \rightarrow SO_4^{2-} \quad (7)$$

Since S_2^{2-}, S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$, and SO_3^{2-} have a greater ability to obtain electrons than Fe^{2+}, in a closed environment with limited dissolved oxygen, the reaction rate is basically negligible, and iron basically exists in the form of Fe^{2+}. Even if a large amount of dissolved oxygen exists, the reaction rate is quite slow. The excess Fe^{2+} reacts with the remaining O_2 after the reaction of Equations (3)–(7):

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (8)$$

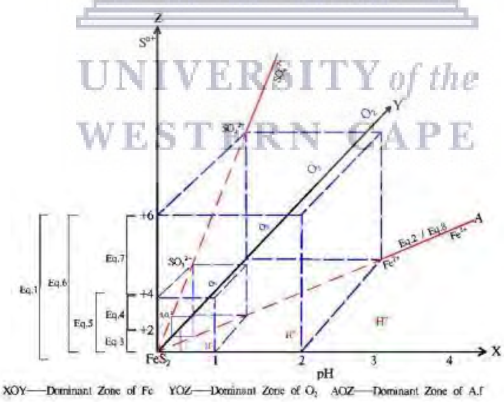

Figure 3. FeS_2+H_2O+O_2 reaction diagram in abandoned coal mines of Shanxi.

If microorganisms on the surface of pyrite such as *Acidophilus thiobacillus ferrooxidans* [66] are extremely active, the microorganisms obtain electrons firstly and combine with O_2, pyrite will be oxidized and leach a large amount of Fe^{3+} simultaneously. The reaction equations are as follows:

$$4Fe^{2+} + O_2 + 4H^+ + A.f \rightarrow 4Fe^{3+} + 2H_2O \quad (9)$$

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3\,FeSO_4 + 2S \quad (10)$$

The S generated by the above reactions is oxidized as the energy source of A.f:

$$2S + 3O_2 + 2H_2O + A.f \rightarrow 4\,H^+ + 2SO_4^{2-} \quad (11)$$

Under the action of microorganisms, the production rate (Equation (9)/Equation (8)) of Fe^{3+} is 105–108 times higher than that of sterile environment [67]; while the number of microorganisms is small, the activity is weak, and the two environments co-exist. When the $S_4O_6^{2-}$ is produced, the Fe^{3+} can also participate in the oxidation reaction. The reaction formula is as follows:

$$S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 3Fe^{2+} + 4SO_4^{2-} + 9H^+ \quad (12)$$

Therefore, we come to a simplified mechanism of AMD formation in abandoned coal mines, that is, pyrite is the prerequisite, oxygen is the inducement, water is the carrier, Fe^{3+} and microorganisms are the catalysts.

At a 25 °C (1atm), the solubility of dissolved oxygen is basically maintained at 8–10 mg/L, and the distribution of underground microorganisms is not artificially controlled. Hence, it can be inferred that the AMD, where the pyrite is rich, the coal is buried to a shallow extent and mine water circulates faster, is more likely to be formed. This is very helpful in determining the location of abandoned coal mine which is prone to the outflow of AMD. It must be pointed out that the No. 2, 3, and 5 coal seams of the Datong coalfield contain very low pyrite with the form of limonite, although buried to a shallow extent [68]. Therefore, the mine water may be acidic or neutral, depending on the content of pyrite in the coal seams [69] and dissolution depletion [70]. In addition, the complex sources of water that forms AMD, including precipitation, surface water, the overlying loose pore water, coal-bearing fissure water of adjacent mines, and underlying karst water, may all enter into the goaf. These different types and rates of water circulation also bring create difficulty in research on AMD.

2.1.2. Water Filling Process

As the water hazards in Shanxi coal mines are more prominent, scholars have focused on the water-filling process of the conduction of the overlying pore and fractured aquifer and the underlying karst aquifer by the factors such as the height of the water-conducting fissure zone, floor water inrush, water-conducting fault, and collapse column, and many results have been achieved. For example, researchers [71,72] systematically studied the development and evolution of the water-conducting fissure zone, and explored in depth the law of water filling of overlying aquifers caused by different mining thicknesses and buried depth. By means of hydrogeological and numerical simulation methods, Kang [73] researched the water-conducting fissure zone of Nancha coal mine in Ningwu coalfield, and concluded that the main water-filling channels are the water-conducting fissure zone formed by roof collapse, the water-conducting fissure zone, faults, collapse columns and poorly sealed boreholes. It reveals that the water accumulation of the goaf is a dynamic process with diversity.

In recent years, as the mining depth of Shanxi coal mines has changed from shallow to deep, research on the limestone aquifer beneath the coal seams as the main water source has also received increasing attention. For example, Li [74] summarized the factors affecting the water richness of limestone aquifers in the Lower Fengfeng Formation in Shanxi six major coalfields, and believed that it was the main aquifer for water inrush from the coal seam floor of the lower group of coal, and pointed out the faults and collapse columns in each coal mine can be used as water diversion channels for groundwater convergence, which accelerates the water-filling process. It showed that the content of previous researches has developed from the height of the water-conducting fissure zone to the relationship between rock mechanical properties and water-conducting channels, which has an important guiding role in the study of the water filling process in Shanxi abandoned coal mines.

However, the above study of water filling process is for the needs of coal mine safety production, and it is a pumping process for groundwater. On the contrary, water accumulation in the phase of abandonment of coal mines is an incremental process, which is a dynamic process of water filling-water accumulation-outflow.

According to our field investigation, the water filling process of AMD in the Shanxi abandoned coal mines has its own uniqueness: the developed roadway systems are highly involved. The developed roadway systems are left behind by underground mining, they not only run through the water filling channels of different mining levels vertically, but also connect the water accumulation space of different mining areas at a mining level, forming the strongest runoff corridor for AMD. After the coal mines were completely abandoned, the shaft and roadway were not effectively blocked, the goaf was not filled, and the runoff mode of groundwater had an essential change: at the same mining level, the water accumulation space of different mining areas was connected in series, which accelerated the accumulation of groundwater; at different mining levels, the water filling channel run through the upper and lower mining levels, so that the accumulated water from the upper level enters into the lower level. This kind of water-filled corridor breaks through the limits of water-conducting channels such as water-conducting fissure zone, floor water inrush, fault water-conducting, collapse column, etc. The groundwater flow field and dynamic field have undergone tremendous changes, but these have not been concerned by researchers. In fact, although the research on the impact of the roadway systems on AMD in Shanxi abandoned coal mines has not been reported so far, it has a great theoretical guiding significance for the water-filling process of AMD.

2.1.3. Water Gathering Space

Theoretically, when there is no water source in the goaf or the amount of water discharged from the goaf is greater than the amount of water filled, there will be no water in the goaf; when the amount of water filled in the goaf is greater than the amount of water discharged from the goaf, the goaf will be partially or fully filled with water. It can be seen that not all of the goaf can be accumulated with water, and only the goaf with accumulated water can be called AMD water-gathering spaces.

Up to now, the goaf areas formed by coal mining in Shanxi are about 20,000 km^2, equivalent to 1/8 of Shanxi's land area (156,700 km^2). The goaf with accumulated water is prone to cause water inrush accidents during coal mining, which has attracted much attention by scholars.

Some scholars conducted research on the water accumulation problem in the goaf of Shanxi abandoned coal mines, which provide a scientific basis for the safe production. Based on the collected data from 42 water accumulation areas of 28 coal mines in Qinshui coalfield, Xiong and Wang [75] put forward the important term of the water accumulation coefficient by laboratory research and theoretical analysis. Di [76] discussed the storage and distribution law of water accumulation in the goaf of Datong-Ningwu coalfield, and believed that the geological structure is the dominant factor controlling the distribution of AMD. Zhu [77] confirmed that the partial sections of the goaf can gradually accumulate water because it is located at a low level in the inclined direction of the coal seam, and there is no roadway to drain mine water. Wen and Zhang [78] detected water accumulation in a Shanxi large coal mine by using transient electromagnetic and direct current methods, and delineated the water accumulation area of the goaf of No. 3 coal seam. Xu [79] found out the location and scope of the goaf and the water-filled area of the coal mine using a transient electromagnetic prospecting method.

The above research results provide a reliable basis for the flood prevention, and also point out the direction and methods for the research of the water-gathering space of AMD. However, the purpose of these research results is to ensure safe production, without considering the water ecological environment problems caused by AMD in abandoned coal mines. In fact, the geological structure is the dominant factor that controls the distribution of AMD [80]. The focus of our attention is the goaf which can gather AMD in abandoned coal mines. Therefore, research on water-gathering spaces of AMD and geological structure still needs to be further strengthened.

2.2. Migration and Transformation

Most of Shanxi's abandoned coal mines were closed after 2000, and the water environment problems caused by AMD gradually emerged. At present, there is little research on the hydrochemical evolution of AMD in abandoned coal mines during the migration process. Regarding the research on the migration law of AMD pollutants in groundwater, some theories and opinions have been put forward only in individual coal mines. For example, Zhao et al. [51] studied the chemical composition, phase composition and migration characteristics of harmful elements of AMD of the Malan coal mine in Xishan coalfield using adsorption experiments and PHREEQC software [81–83], and pointed out that the migration of harmful elements in AMD is mainly controlled by pH, Fe-Al-Mn content and mineral composition of water particles. By using the same methods, Sun et al. [84] determined the AMD, sediments, and content of rare earth elements in coal samples in two different coal mines in Shanxi, and revealed the contribution of pH, hydroxide (Fe-Al-Mn), sediments and complexation, etc. in controlling the distribution pattern of rare earth elements in AMD.

It can be seen that the hydrochemical evolution of AMD is concentrated in the migration and transformation laws of pH and metal elements, which points out a direction for researchers. However, previous research methods were relatively simple. Strictly speaking, the Malan and Sitai coal mines are still mining the lower coal seam, which is different from the completely abandoned coal mines. Compared with the coal mine of Shandi Village, the concentration of metal ions in AMD at sampling points of the former two coal mines is lower, indicating that the characteristics of hydrochemistry in the mining period and the abandoned period are quite different. In particular, the difference of the sulfate concentration in different stages is 10,000 mg/L, which has a greater impact on the hydrochemical equilibrium. Although the previous results have certain reference significance, it is difficult to fully promote research on all abandoned coal mines in Shanxi.

In our opinion the migration and transformation of AMD is a comprehensive process of active participation of multi-mineral and multi-gas components under the synergistic action of oxidation-reduction, dissolution-precipitation, adsorption-desorption, ion exchange, complexation and microbial action. Adsorption experiments and PHREEQC software make it difficult to achieve this comprehensive process. For example, many minerals in the surrounding rock have a buffering effect on AMD. Pyrite is the prerequisite of AMD, and the pyrite reserves determine the acid production capacity. When the acid production capacity exceeds the neutralization and digestion of alkaline minerals, the pH will be increasingly low; when the dissolved heavy metals exceed the adsorption of viscous minerals, the metal ions will become higher and higher.

The chemical reaction equations of common minerals in coal seams of Shanxi abandoned coal mines are as follows:

Calcite: $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$

Dolomite: $CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O$

Muscovite: $KAI_2(AISi_3O_{10})(OH)_2 + H^+ + 1.5H_2O \rightarrow K^+ + 1.5AI_2Si_2O_5(OH)_4$

Biotite: $K(Mg,Fe)_3AISi_3O_{10}(OH)_2 + 7H^+ \rightarrow K^+ + 3(Mg^{2+},Fe^{2+}) + AI(OH)_3 + 2SiO_2 + 3H_2O$

Plagioclase: $Na_{0.7}Ca_{0.3}AI_{1.3}Si_{2.7}O_8 + 1.3H^+ + 1.3H_2O \rightarrow 0.3Ca^{2+} + 0.7Na^+ + 1.3AI(OH)_3 + 2.7SiO_2$

Illite: $K_mNa_nCa_oMg_pFe_qAI_rSiO(OH)_2 + (0.5r + 4s\text{-}12)H2O + (22\text{-}4s\text{-}3r)H^+ \rightarrow mK^+ + nNa^+ + oCa^{2+} + pMg^{2+} + qFe^{3+} + 0.5r(AI_2O_3 \cdot 2SiO_2 \cdot 2H_2O) + (s\text{-}r)H_4SiO_4$

If there are insufficient acid-consuming minerals in the goaf, AMD will be formed. However, the main lithology of Shanxi coal-bearing strata are limestone, sandstone, mudstone and shale; among them, K_2–K_4 limestones have a good neutralization effect on acid, and sandstone, mudstone and shale are rich in clay minerals (kaolinite, montmorillonite, hydromica) with a good adsorption effect on metal ions. It can be seen that many factors control the evolution of AMD's hydrochemistry and the release of heavy metals. However, no studies have been reported on the environmental effects and release mechanism of heavy metals in Shanxi abandoned coal mines.

When the AMD in the goaf outflows to the surface water, it enters into an open environment from a relatively closed environment, and the hydrochemical balance is broken. Its water quality migration and transformation is accompanied by reactions such as oxidation–reduction, dissolution–precipitation, adsorption–desorption, and ion exchange, complexation, microorganisms, etc., and there are multiple minerals and gas components involved. The current research mainly focuses on the investigation of water quality in the polluted areas after the coal mines were closed, and there is a lack of targeted research on the migration and transformation of AMD in specific closed coal mines. A lot of work should be done to study the migration and transformation of AMD in Shanxi abandoned coal mines, and it is necessary to further strengthen the study of the respective effects of these factors and the coupling effects among multiple factors.

2.3. Prediction

In terms of time cycle, AMD will be discharged through different channels after the completion of a water filling and water gathering process of the goaf in Shanxi. Zhang et al. [49] pointed out that AMD leaked into the underlying karst aquifer; Li and Wang [58] believed that the outflow of AMD polluted surface water; some scholars believed that AMD was discharged simultaneously to groundwater and surface water [52,62,63]. In fact, the water environment problems in Niangziguan Spring [60] and Jinci Spring [58] caused by AMD are unavoidable problems in water source protection. At present, a large number of valuable research results have been accumulated for the prediction of water accumulation in the goaf of Shanxi. For example, Xiong et al. [75] analyzed the hydrogeological conditions and possible causes of water inrush of the Qinshui coalfield, and proposed a concept of water accumulation coefficient, and determined the water accumulation in the goaf. Di [76] predicted the water accumulation in the goaf of Tongxin coal mine using the water accumulation coefficient; Kang [73] analyzed the water accumulation in the Nancha coal mine of Ningwu coalfield using a comprehensive method. Wen [85] accurately determined the range of water accumulation using the combination of a transient electromagnetic exploration method and direct current method, and predicted the amount of water accumulation in the goaf. These theoretical methods and practical experience from research provide a reliable theoretical basis for Shanxi AMD prediction.

To sum up, the above research can solve the water accumulation problem in AMD, but there are still some shortcomings in the research on the proportion of the AMD outflow, how long it can outflow, and where it can outflow in Shanxi abandoned coal mines. As mentioned above, the coal mine of Shandi Village was closed in 2005, and the goaf was filled with AMD in 2009 [60]. At present, scholars have not reported any researches on AMD's prediction in Shanxi abandoned coal mines. From a regional perspective, the AMD environmental problems in Shanxi are mainly concentrated in Datong mining area [50,51], Yangquan mining area [52,53], and Taiyuan Xishan mining area [55,56]. A further study is firstly needed as to why these coal-mining areas became AMD discharge sites. From a single coal mine, AMD is discharged through different channels, and the spatial distribution of discharge points must have their own particularity. Due to the existence of many abandoned coal mines in Shanxi, it is more necessary to conduct research on the proportion of the AMD outflow, how long it can outflow, and where it can outflow. These studies can gain precious time for AMD prevention and provide precise spatial instructions for AMD prevention and control areas (points).

2.4. Treatment

AMD's pollution is a global problem and has received extensive attention from scholars globally. For many years, as a result of the lure of high profit, environmental protection was generally neglected in coal mining, and the governance has no corresponding plan for the treatment of the closed pit.

At the same time, due to the constraint of economy and technology in Shanxi, the AMD treatment is mostly concentrated in the centralized treatment of mine water during coal mining. Most coal mines treated the AMD by using lime and limestone neutralization as well as sedimentation methods in the form of sewage treatment stations. Recently, the reverse osmosis membrane has been added with the upgrading of the standard. At present, scholars have studied the AMD treatment in Shanxi abandoned coal mines by different methods. For example, Yin [86] and Liu [87] remedied AMD using the bacterial strain from loess and sludge of sewage. The tests showed that the maximum removal rate of sulfate in AMD was 81.9% and 64.75%, respectively. Yang et al. [88] simulated the bioremediation of AMD in natural drainage mines using an open reactor in laboratory, and explored the feasibility of using natural drainage mines with the appropriate amounts of microorganisms and required carbon sources to remedy AMD. Zhao et al. [89] used a soil column leaching experiment to adsorb sulfate radicals in AMD, and the results showed that under the condition of a certain volume of loess, the processing capacity is Malan loess > Lishi loess > paleosol. Zhou et al. [90] used NaOH neutralization method to treat AMD, and gained better results. Taking sand as a repair material for AMD, Wu et al. [91] studied the removal efficiency of sulfate ions in AMD by different particles, and the results showed that the removal efficiency was up to 62.36% for less than 0.075 mm. By using Malan loess, iron slag and carbon steel slag as adsorbent, the effect of solid-liquid ratio, contact time, initial concentration, temperature and pH on sulfate adsorption in AMD were studied [92,93], and the results indicated that acid conditions were favorable for sulfate adsorption. Wan and Li [94] introduced a new carbon source corncob for Sulfate Reducing Bacteria (SRB) to treat AMD, discussed the resource utilization of wastewater from sulfate mines, and verified the feasibility of biological treatment. Lu et al. [95] studied the effect of modified red mud on AMD adsorption. Wang et al. [96] and Zhang [97] proposed the method of treating AMD using "loess-wetland-plant-microbial ecosystem", and discussed its feasibility and advantages. These research works have a significant guiding role in dealing with AMD problems in Shanxi abandoned mines, but they are basically at the state of laboratory experiments and theoretical research.

Due to the variety and high concentration of metals in AMD, large-scale treatment is very difficult. The aforementioned treatment research focuses on neutralization, permeable membrane filtration, adsorption, microbial method, etc. Although the mentioned methods have their applicability in certain scenarios, they have limitations in Shanxi abandoned mines. At present, the permeable membrane filtration method has the advantages of no waste generation, fast separation speed, and high selectivity. However, it faces several problems of polarization, scaling and corrosion. As a treatment process with low energy consumption and simple operation, the adsorption method only realizes the transfer of pollutants and also has the secondary pollution. A microbial method has the advantages of low cost, strong applicability, great potential, and no secondary pollution, but it takes a long time for domestication and lacks an economic organic carbon source.

The above research showed that technical limitations were exposed in AMD's treatment of Shanxi. Most scientific researchers studied the removal of pollutants in AMD by a single method. There is not a successful case for the AMD treatment in Shanxi abandoned coal mines, and the treatment technology has not been applied in practice and engineering.

The treatment of groundwater pollution caused by AMD in Shanxi abandoned coal mines has not received enough attention. Therefore, AMD has caused serious water pollution to the surrounding environment and a potential threat to the safety of the downstream drinking water. The research on the comprehensive treatment of AMD in Shanxi abandoned coal mines is of great significance to prevent water environmental effects and drinking water safety issues that are induced by AMD. Thus, exploring a cheap, efficient, environmental treatment technology for AMD will become a hotspot.

2.5. Management

Through investigation and data verification, we found that the main measures were shaft plugging and tunnel filling when the coal mines in Shanxi were closed, but these measures cannot prevent the formation and discharge of AMD. Due to the lack of AMD monitoring data in Shanxi abandoned coal mines, the damage to groundwater cannot be measured. Up to now, exclusive specifications and regulations have not been promulgated for AMD management, a technical chart has been absent for AMD risk management, and an AMD risk early warning mechanism has not been formulated for abandoned coal mines.

It can be seen that the situation of AMD management in Shanxi abandoned coal mines is still severe, and policies and regulations for AMD management are still lacking. It is urgent to strengthen research on the risk assessment, early warning mechanism and management process of AMD in Shanxi abandoned coal mines, and provide technical support for the formulation of relevant policies and regulations. It is of great significance for standardizing AMD management and ensuring the water ecological environment as well as drinking water safety in abandoned coal mines.

3. Problems and Difficulties

With the continuous increase in the number of Shanxi abandoned coal mines, environmental problems such as the destruction of water resources and the deterioration of water quality caused by AMD are becoming an urgent topic for research. Scholars have accumulated rich experiences in Shanxi coal mines in the study of water inrush mechanisms, exploration of hydrogeological conditions, mining under pressure, decompression drainage, grouting for water blocking and curtain closure, and water resources evaluation and management, and achieved a series of important research results. Since the existing theories, technologies and methods are mainly for newly-built and producing mines, there are still many doubts and difficulties in the research of AMD in Shanxi abandoned coal mines that need to be solved and overcome, which are mainly reflected in the following aspects.

3.1. Distribution of AMD

Pyrite is a common widely distributed mineral in coal-bearing strata, but there is no detailed study on the occurrence of pyrite in Shanxi. The content of pyrite in the No. 2, 3, 5 coal seams of Datong coalfield is very low [68], and AMD is not easy to form. It can be seen that simply saying that the pyrite in the coal-bearing strata in Shanxi can cause AMD problems seems to be insufficient. Therefore, the occurrence law and spatial distribution characteristics of pyrite in Shanxi coal-bearing strata are worthy of further study.

Among the six major coalfields in Shanxi, only the Datong coalfield, Qinshui coalfield, and Xishan coalfield emerge AMD problems. Their common point is that the coal seams are exposed and the mining areas were cut by rivers, so it can be seen that the surface water plays an irreplaceable role as a carrier of oxygen. Due to the complex sources of AMD, including precipitation, surface water, overlying loose pore water, coal-bearing fissure water of adjacent mines, and underlying karst water, they may all enter into the goaf, and their different types and rates of water circulation also bring great difficulty to the AMD research. AMD has close hydraulic connection with surface water and groundwater, but there is little research on the hydraulic connection between them. The hydraulic connection of AMD with surface water and groundwater is of great guiding significance for determining the regional distribution of AMD, and further investigation and research are needed.

3.2. High Participation in Roadway System

As a runoff gallery, the groundwater fluid in the roadway system presents a significant state of the conduit flow, and the roadway system extends to all directions. Its special state determines that the groundwater fluid of abandoned coal mines is different from the fissure flow in aquifers. In terms of groundwater simulation in mining areas, the current focus is to simulate the seepage field of fractured media. In fact, a multi-layer and multi-channel flow is formed in the abandoned coal mine by the overlapping of the fissure flow in the water-conducting fissure zone and the conduit flow in the abandoned roadway. The relationship between the input and output of the system is directly or indirectly determined by the geology, roadway and fissure. However, these factors appear to be random and uncertain, and this kind of runoff corridor breaks through the theory and model of groundwater seepage, making it difficult for generalization, analysis and prediction, so the research results are rarely reported in Shanxi. Therefore, it is necessary to study the dynamic evolution of groundwater flow field with high participation of roadway system in Shanxi abandoned coal mines.

3.3. Effective Water Gathering Space

It is of great significance to carry out research on the detection of AMD's water-gathering space. Due to the hidden characteristics of water accumulation in the goaf, its spatial distribution pattern (boundary, shape of water accumulation) and occurrence law are very complicated; the water volume presents non-linearities and time variation, and the parameters such as water head and coefficient of water accumulation are difficult to determine. These factors cause great problems for the detection of AMD.

In addition, the detection results of a single coal mine or a certain goaf are limited by hydrogeological conditions, so it is difficultly to apply in other goaf. Therefore, it is necessary to carry out research on AMD's effective water gathering space. Theoretically speaking, the goaf will easily form a water-gathering space at the working face of the lower coal level, the two wings of the middle and lower anticlines, the syncline axis and the lower plate of the positive fault. Geological structure is the dominant factor that controls the distribution of water accumulation in the goaf. Hence, study on the inner relation between geological structure and AMD's effective water gathering space is further needed.

3.4. Discharge Channels

According to field survey, most of the closed coal mines are in the water-filling and water-gathering stages. The previous literatures only qualitatively reported that AMD had recharged into the local coal-bearing aquifers and directly outflowed to the surface water after coal mines were closed. However, the researchers did not further discuss how to recharge and discharge.

As typical Carboniferous-Permian coal-accumulating area in northern China, Shanxi coal seams have close hydraulic connections with the underlying Ordovician karst aquifers. Once AMD in abandoned coal mines is generated, there are only three discharge ways: outflow to the surface water; recharge to coal-bearing aquifers; leak into underlying karst aquifers. So the leakage into the underlying karst aquifers is one of the main ways of AMD discharge. This discharge capacity depends on the leakage channels between the water gathering space and the karst aquifers.

However, there are few studies on the AMD leakage through these leakage channels, such as faults and collapse columns. For example, the faults in Dahangou coal mine in Ningwu coalfield directly connect the coal-bearing aquifer with the Ordovician aquifers. There are about 450 and 400 collapse columns found in Qinshui and Xishan coalfields, respectively, which can directly form the leakage channels of AMD, and have great impact on the water quality of the underlying karst aquifers. Due to the control of other factors such as geological structure, filling material, cementation and water pressure, the research on AMD discharge channels in Shanxi abandoned coal mines is more complicated. Therefore, from the perspective of protecting Shanxi's karst water resources and drinking water safety, it is necessary to carry out research on the discharge channels of AMD in abandoned coal mines, especially the impact of AMD on Shanxi's karst water resources through faults and/or collapse columns.

3.5. Water Quality Migration and Transformation

At present, research on the migration law and hydrochemical balance of AMD in Shanxi abandoned coal mines is basically theoretical. For example, Zhao et al. [51] studied the chemical composition and phase composition of AMD and its sediments in Malan coal mine in Taiyuan. Sun et al. [84] determined the content of rare earth elements in AMD, sediments and coal samples in two different mining areas in Shanxi. The previous research has not considered the participation of microorganisms, gas components, etc. Due to irreversible changes in the water-bearing medium and pollution channels of the groundwater system in Shanxi abandoned coal mines, the hydrogeological conditions have become more complex. Considering that it is more difficult to collect water and rock samples from abandoned coal mines, the research objectively faces more challenges. In fact, hydrochemistry research on the migration and transformation of AMD during water filling and water gathering has rarely attracted scholars' attention in Shanxi. Therefore, it is essential to carry out further research on the migration and transformation of AMD.

3.6. Hydrochemistry Equilibrium

After AMD overflows to the surface water, a new chemical equilibrium is formed. For example, the AMD from an abandoned coal mine in Yangquan coal mining area has polluted the Shandihe River Basin. According to the test results, the AMD in the basin is highly acidic with pH = 2–3, and contains the highest sulfate with 11,370 mg/L, which exceeds the class III of "China Groundwater Quality Standard" (GB/T14848-2017) by 45 times, and heavy metals such as Fe, Mn, Zn, Cd exceed the standard by 1100, 510, 10, and 50 times, respectively. These data indicated that through physical and chemical reactions such as oxidation, deposition, adsorption and microbial degradation, AMD is in a new chemical equilibrium state and destroys the water ecological environment of the downstream rivers (Figure 4).

Figure 4. Acid mine drainage (AMD) in Shandi Village, Yangquan, Shanxi.

Moreover, the pressure and temperature of various gases and ion concentration of AMD have impacts on the hydrochemical equilibrium. It is a regret that there is no report on the research of AMD hydrochemical equilibrium in Shanxi abandoned coal mines. Therefore, research on the hydrochemical equilibrium of AMD under the outflow state should be strengthened.

3.7. Outflow Prediction of AMD

After coal mines have been closed for decades or even hundreds of years, AMD's pollution to the regional water environment still exists. Due to numerous abandoned coal mines in Shanxi, it is necessary to find out which closed coal mine will be prone to AMD outflow, how long the AMD will continue to outflow, and where the AMD will outflow. The AMD outflow is affected by many factors, such as water source, water gathering space, and discharge capacity. At the same time, the AMD quantity changes over time. However, the current research cannot fully and truly reproduce the water level dynamics of AMD in abandoned coal mines. In addition, the spatial location of the discharge point is controlled by many factors such as geological structure, roadway system, coal outcrop and wellbore. Their stronger concealment increases the difficulty of research. At present, there is a lack of research on the correlation between the outflow of AMD and influencing factors in Shanxi abandoned coal mines, and no relevant researches have been carried out on the time and location of the AMD outflow. Therefore, research on the AMD outflow prediction in Shanxi abandoned coal mines should be carried out.

3.8. Treatment

Due to the constraints of economy and technology, the treatment method for AMD in Shanxi abandoned coal mines has to be relatively simple. For example, Yin et al. [86], Zhao et al. [51] and Liu [87] used desulfurization bacteria in natural loess and desulfurization vibrio bacteria in a sewage purification plant sludge to remove sulfate. Moreover, the neutralization precipitation method [90], sandy soil [91], Malan loess, ferrous slag and carbon steel slag [92,93], corn cob and SRB method [94], red mud [95], "Loess Wetland Plant Microbial Ecosystem" [96,97] have been used to treat AMD in Shanxi abandoned coal mines. However, all of these methods are undertaken in the laboratory and theoretical research stages, and there are still no successful cases for the AMD treatment project in Shanxi abandoned coal mines. Therefore, it is necessary to explore an efficient, inexpensive, environmental treatment technology for AMD, such as artificial wetland and Permeable Reactive Barriers (PRB) restoration technology. These technologies are widely used internationally, while national applications are more concentrated in the AMD treatment for metal mines, and the AMD treatment in Shanxi abandoned coal mines is relatively lacking. Thus, it is necessary for Shanxi to adopt a comprehensive method to treat AMD in abandoned coal mines and actively apply to the engineering practice of treating AMD.

3.9. Management

Currently, management policies and regulations for abandoned coal mines in Shanxi is still lacking. Coupled with the shortage of historic monitoring data of AMD pollution, the harm of AMD cannot be measured. The measures such as shaft closure and roadway blockage make it difficult to completely avoid AMD's water sources and water channels, and prevent the formation and discharge of AMD from destroying the regional water environment.

Moreover, Shanxi has not promulgated the standards and regulations for AMD management of abandoned coal mines, and has not constructed the AMD risk assessment model and early warning mechanism for abandoned coal mines. Among massive Shanxi closed coal mines, the utilization rate of AMD is extremely low. Therefore, it is urgent to strengthen research on the management, risk assessment and early warning mechanism of AMD in Shanxi abandoned coal mines.

4. Future Research

For the sake of avoiding further deterioration of water resources and water environment caused by AMD in Shanxi, researchers and government administrators should carry out further research on the following aspects.

(1) The regional distribution characteristics of pyrite and the occurrence law in coal-bearing strata in six major coalfields of Shanxi should be actively carried out, and the

hydraulic connections among surface water, groundwater, geological structure, water-conducting fissure zone and the formation, migration and transformation of AMD should be characterized.

(2) The researchers should improve the comprehensive detection methods of the hydrogeological conditions, water channels, water gathering spaces and roadway systems of abandoned coal mines, and promote research on the formation, migration and prediction of AMD and related environmental issues. The groundwater seepage theories and models that involve the roadway system, geological structure and primary fissures need to be explored, and the groundwater flow dynamics that are highly involved in the roadway system should be actively researched.

(3) The formation mechanism of AMD in abandoned coal mines needs to be studied, and the main modes of groundwater resources pollution caused by AMD should be summarized. It is necessary to fully consider the influence of microorganisms, gas components and other factors on the migration law of AMD in groundwater and the hydrochemical balance of abandoned coal mines. To effectively predict and prevent the generation of AMD, the oxidation of coal-based sulphate and the release of harmful elements should be clarified. Furthermore, a risk assessment model of AMD pollution needs to be constructed to provide effective support for scientific planning and decision-making.

(4) It is necessary to further identify the three issues of which coal mine will be prone to AMD outflow, how long it will continue to outflow, and where it will outflow. Research on the correlation between AMD outflow from abandoned coal mines and influencing factors should be strengthened, and relevant investigations and predictions should be carried out on these three issues of AMD. More attention should be paid to the effects of gas composition, pressure, temperature and ion concentration of AMD on the hydrochemical equilibrium during the conversion of the environment.

(5) It is necessary to actively carry out research on the application of comprehensive treatment technologies such as artificial wetlands and PRB in the active treatment of AMD in abandoned coal mines, and explore an efficient, cheap, environmental technology for AMD.

(6) With regard to management, technical guidelines for the closure of coal mines should be issued to guide coal mine closure and supervision as soon as possible. A network system for monitoring the AMD groundwater in abandoned coal mines should be established to provide effective information for AMD risk identification. Research on management, risk assessment and early warning mechanisms for the AMD in abandoned coal mines should be strengthened.

(7) To alleviate the shortage of water resources in Shanxi and ensure the safety of drinking water, the in-depth study of the hydraulic connection between the AMD in abandoned mines and karst springs should be strengthened, which will help us to achieve the sustainable development of coal, water resources, and the ecological environment.

5. Conclusions and Recommendations

This review gives an overview of AMD in abandoned coal mines in Shanxi, China. It critically reviews the research results of AMD from the five aspects of formation, migration, prediction, treatment and management. The relevance between the uniqueness of hydrogeological conditions of abandoned coal mines and drinking water safety were further analyzed, and governance ideas and management measures were proposed.

The review showed that sulfur-containing minerals and groundwater replenishment are the main sources of the mechanism of AMD formation, pyrite is the prerequisite, oxygen is the inducement, water is the carrier, and Fe^{3+} and microorganisms are the catalyst. The roadway system and geological structure are the dominant factors that control the water-gathering space of AMD. The problem of abandoned coal mines has worsened the current water ecology and water environment. It has aggravated the current situation of water shortages in Shanxi, and caused ecological and environmental problems and a drinking water safety crisis, so it is necessary to conduct further research on AMD.

The main problems in the previous research of AMD in Shanxi abandoned coal mines are: (1) The detailed investigations have never been carried out on the regional distribution characteristics of pyrite and its occurrence in coal-bearing strata in six major coalfields; hydraulic connection between AMD and surface water as well as groundwater is not emphasized. (2) Roadway systems in abandoned coal mines are often overlooked in the aspect of generalization and analyzation of AMD flow field. (3) The distribution and occurrence laws of AMD water-gathering spaces in abandoned coal mines are difficult to grasp; the water head and water accumulation coefficient in the goaf are difficult to detect as they vary in time. (4) The research on water channels between the water-gathering space and the karst aquifer such as faults and collapse columns is relatively lacking. (5) The participation of microorganisms and multi-gas components are not considered in the research of AMD migration and transformation; there is a lack of attention to the water filling and water accumulation process of AMD; and it is difficult to collect underground water samples and rock samples from abandoned coal mines. (6) The influence of gas composition, pressure, temperature and AMD ion concentration on hydrochemical equilibrium is not studied from reduction to oxidation when AMD flows out. (7) No relevant investigations have been carried out to address three issues of comparative concern: which mine will be prone to AMD outflow, how long it will continue to outflow, and where it will outflow. (8) The AMD treatments in Shanxi abandoned coal mines are basically at the stage of laboratory theoretical research; research on the restoration technology of artificial wetland and PRB is still not adequated. (9) The management policy (norms) and AMD historic monitoring data for Shanxi abandoned coal mines are relatively lacking; the research on risk identification and index systems is basically absent for risk assessment and early warning mechanisms.

The research on AMD in Shanxi abandoned coal mines should be further strengthened in the following aspects: (1) actively carry out the research on the regional distribution characteristics of pyrite in the six coalfields and its occurrence in coal-bearing strata. (2) It is necessary to improve the comprehensive detection method of AMD, explore the groundwater theory and model of abandoned coal mines involving roadway systems and primary fissures; the study of the internal relationship between geological structure and AMD gathering space through faults and/or collapse columns should be strengthened to determine the influence on karst water resources. (3) It is necessary to further strengthen research on the mechanism of AMD formation, migration and hydrochemical equilibrium under the influence of microbial action, gas composition, pressure, temperature and ion concentration, and construct a reasonable pollution risk assessment model for AMD. (4) There is an urgent need to research the following three issues: which mine will be prone to AMD outflow, how long it will continue to outflow and where it will outflow. (5) Research on artificial wetlands and PRB in the AMD treatment should be further strengthened. (6) It is necessary to advise the government to promulgate specific policy for AMD risk assessment and early warning mechanisms as soon as possible.

There are 19 major karst springs in Shanxi. Under the influence of climate change and human activities, the quantity and quality of karst water resources in these springs have been changed seriously. Some springs such as Jinci spring, Lancun spring and Gudui spring ceased to flow for many years. However, for most spring catchments, karst water resources are symbiotic with coal mines. If the AMD from abandoned coal mines continues to deteriorate, the shortage of Shanxi karst water resources will be further aggravated and will threaten the karst water ecosystem and drinking water safety. To avoid the deterioration of karst water resources in Shanxi, more attention must be attracted to focus on AMD by water resource management departments and coal-mining enterprises.

Author Contributions: Z.W., Z.Z.: Methodology, Formal analysis, Investigation, Writing—original draft, Writing—review & editing. Y.X.: Writing—review and editing, Supervision. Y.Z.: Investigation, Supervision, Project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Fund Projects of China, grant number 41572221.

Acknowledgments: The author would be like to acknowledge the National Natural Science Foun.

Conflicts of Interest: The authors declare no conflict of interest.

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