Insight into the water–rock interaction process and purification mechanism of mine water in underground reservoir of Daliuta coal mine in China

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Abstract
The water quality of mine water is obviously improved after being stored in underground reservoir, but the process of water–rock interaction and the purification mechanism of mine water quality are not clear. In this study, the water samples and rock samples collected in the underground reservoir of Daliuta coal mine were taken as the research object. Based on the analysis of the hydrochemical characteristics of the reservoir water samples and the characterization of the rock samples, combined with PHREEQC analysis, the mechanism of water quality purification of mine water was discussed. The results showed that the rocks in the underground reservoir had layered silicate structure and flaky kaolinite structure, with some irregular edges and microcracks, and higher specific surface area and total pore volume. These characteristics made the rocks have a certain adsorption and removal capacity for heavy metal ions and other pollutants in the mine water. The water–rock interaction, such as the dissolution of albite and halite, the precipitation of gypsum and kaolinite, and the cation exchange, resulted in the increase of the concentration of Na+ and the decrease of the concentration of Ca2+, Mg2+, and TDS in the outlet water, and the hydrochemical type changed from SO42−-Cl−/Ca2+ type to SO42−-Cl−/Na+ type. Moreover, this study shows that PHREEQC analysis can be used to analyze the water–rock interaction of coal mine underground reservoir and can obtain more detailed information; therefore, it may have the potential ability to help assess the migration and transformation of pollutants during the storage process of mine water in underground reservoirs.

Keywords Coal mine underground reservoir · Mine water · Rock characteristics · Water–rock interaction · Water purification · PHREEQC

Introduction
The severe shortage of water has seriously hindered the development of the energy industry in many coal-producing areas (Chen et al. 2016; Rathi et al. 2017), especially in the Shendong Mining Area (Ma et al. 2013), located in the arid and semi-arid areas of northwest China but with rich coal reserves (Chen 2016). The protection and rational utilization of water resources have become an important scientific and technological problem to be solved by coal green mining in arid areas of Northwest China (Zhang et al. 2011). In view of the above problems, Gu (2015) proposed and successfully developed the coal mine underground reservoir technology using the cavity between the broken rock bodies in the mined space area formed after coal mining (Shi 2021). The technology solved both the mine water disaster problem and realized the efficient recycling of the mine water resources (Gu et al. 2016), providing more than 95% of the water used (Chen et al. 2016), which largely solved the production and domestic water problem in the mining area. During the operation of the underground reservoir in the coal mine, the collapsed rocks in the reservoir have a purification effect on the mine water (Gu et al. 2021), and scholars have also studied...
the purification effect of the rocks in the mined space area on the suspended matter, chemical oxygen demand (COD) (Fang 2020), dissolved organic matter (DOM) (Han et al. 2020b; Yu et al. 2018), heavy metals (Jiang et al. 2020; Shao 2009), and so on. However, the purification mechanism of mine water in the process of water–rock interaction between mine water and rock in reservoir storage stage is not clear.

The water–rock interaction in the study area is closely related to the actual situation of the site (Jannesar Malakooti et al. 2015), so researchers usually use the field investigation sampling (Ibrahim et al. 2019) and indoor simulation experimental data (Goren et al. 2011; Phan et al. 2018), combined with the ion ratio method (Jia et al. 2020) or hydrogeochemical simulation software to accurately describe the physical and chemical relationship between the water phase composition and the regional environmental background, thus exploring the evolution and migration laws between the water and the rock in the stratum (Kumar et al. 2020; Li et al. 2018). In addition, many scholars found that clay minerals in rocks can effectively adsorb heavy metals and other pollutants in water (Green-Ruiz 2005; Gu et al. 2018; Yuan et al. 2013) and characterize rock properties by mineral analysis methods such as SEM, XRD, and XRF (Chander et al. 2020; Ibrahim et al. 2019). Therefore, the study of rock properties and mineral composition is very necessary to analyze the water–rock interaction and the mechanism of mine water purification in the underground reservoir.

At present, some scholars (Han et al. 2020a) have analyzed the hydrochemical characteristics and formation mechanism of underground reservoir by testing the in-situ inflow and outflow water sample data of underground reservoir, combining multivariate statistical method, hydrochemical analysis method, and ion ratio method. Some scholars (Fang et al. 2020) have studied the mechanism of water–rock interaction and the source of ions in the underground reservoir from the change law of main ions (Zhang et al. 2019) and the characteristics of rock changes (Pearce et al. 2018; Zhang et al. 2020) through static simulation test of water–rock interaction. The influence of water–rock interaction on the binding characteristics of dissolved organic matter and heavy metals in mine water during the process of mine water flowing in goaf was also studied (Zhang et al. 2021). It can be seen that some achievements have been made in the study of water–rock interaction in underground reservoir of coal mine, but there is no study of water–rock interaction in reservoir combined with hydrogeochemical simulation.

Reverse geochemical simulation (Dai and Samper 2006; Embile et al. 2019) is to determine the water–rock reaction in the system based on the observed hydrochemical data, that is, to interpret the observed hydrochemical data. The purpose is to find out the complex reaction between groundwater and different minerals and gases and quantify it under reasonable conditions (Hidalgo and Cruz-Sanjulián, 2001). With the rapid development of computer technology, many hydrogeochemical simulation software appeared (Salcedo Sánchez et al. 2017). Among them, PHREEQC has the most powerful simulation ability among the similar software (Sprocati et al. 2019). It has a huge database of groundwater balance model and ion exchange model (Steding et al. 2020), which can simulate the chemical reaction and migration process of sewage and clean water in the environment, and is widely used in the world (Mahani et al. 2016). In addition, scholars (Chandrasekhar et al. 2018; Korrani et al. 2015) have also conducted a lot of simulation studies on groundwater hydrochemical evolution and water–rock interaction in artificial recharge process by using PHREEQC (Sharma and Mohanty 2018), and the water–rock interaction analysis software has been relatively mature (Shabani and Zivar 2020). Therefore, PHREEQC simulation was used in this study to analyze the water–rock interaction in underground reservoir of coal mine.

In this study, Daliuta coal mine underground reservoir inlet and outlet water and roof caving rock samples were taken as the research object. Based on the analysis of mineral chemical composition, surface morphology, specific surface area and pore structure of roof caving rock samples and suspended solids in mine water in the study area, as well as the test and analysis of in situ water samples. The variation rule and reason of main pollutants inflow and outflow of water were analyzed. The water–rock interaction was analyzed by using ion ratio method and combined with the reverse geochemical simulation analysis, which was carried out with PHREEQC software. The process of water–rock interaction and the mechanism of mine water purification in coal mine underground reservoir were revealed. It provided theoretical support and reference for the future application of PHREEQC software to simulate the process of water–rock interaction in coal mine underground reservoir and the efficient utilization of reservoir water.

**Study area**

The minefield area of Daliuta Coal Mine is 189.9 km², which is located in the northwest of Shenmu County, Yulin City, Shaanxi Province. The geographical coordinates are 39°13′53″N–39°21′32″N and 110°12′23″E–110°22′54″E. The mining area (Chen 2016) is a hilly, forest, grassland to desert, Gannan grassland transition zone, belongs to the desert grass beach area, close to the semi-desert nature, and the natural vegetation is very few.

The average annual precipitation in Daliuta Mine (Wang et al. 2018) is 194.7–531.6 mm, which is the indirect water source in the mining area. On the surface of the mine, there are two great gullies, the Wu Lan Mulun River and the Niuchuan River, and some small water bodies, but the water...
quantity is limited and easy to be released, which does not affect the safety of mine production. The aquifer water contains bulk layer water, bedrock fissure water, and caustic rock water. Due to the influence of mining failure in the mining area, the aquifer is rich in water and the overall recharge water is relatively limited. The data show that the unit water inflow of the Quaternary loose aquifer and Yan’an formation bedrock aquifer is $0.0026 \sim 0.6789$ L/(s·m) and $0.00014 \sim 0.083$ L/(s·m), respectively, which belong to the medium category. The old empty water is due to the goaf formed after the mining of the upper horizontal coal seam, collapse crack, and other filling channels accept the recharge of atmospheric precipitation, surface water, and groundwater, resulting in water accumulation in the low-lying area of the goaf, which is the main source of water filling in the mine. According to the principle of high or low, the hydrogeological type of Daliuta well is divided into medium type.

The coal seam of Daliuta coal mine (Chen et al. 2016) is shallowness, mainly $2^{-2}$ coal seam and $5^{-2}$ coal seam. The buried depth of $2^{-2}$ coal seam in mining area is $30.6 \sim 133.3$ m, the recoverable area is $73.1$ km$^2$, the average coal seam thickness is $4.37$ m, and at present, $2^{-2}$ coal seam has been mined. At present, $2^{-2}$ coal seam has been mined and divided into 5 disc areas; among them, Sipan District (goaf of 22,400–22,405 working face), Lao Liupan District (goaf of 22,601–22,607 working face), and Xin Liupan District (goaf of 22,608–22,616 working face) have built underground reservoirs of Nos. 1, 2, and 3, respectively. The water storage situation of underground reservoir in Daliuta Coal Mine is detailed in Table 1 (Song et al. 2020).

The buried depth of $5^{-2}$ coal seam in the second level is $162.9 \sim 280.0$ m, and the main mining area of Daliuta Mine is $5^{-2}$ coal Sanpan area. The goaf formed after mining of $5^{-2}$ coal seam has built two water recycling chambers, and the No. 4 underground reservoir is under construction. There are three kinds of water sources in underground reservoirs, including the water content of each underground water-bearing rock group, the entering goaf along the fissure zone formed by coal mining, and underground production sewage injected into goaf by drainage pipe (Song et al. 2020).

### Materials and methods

#### Sample collection

On the basis of the field conditions of Daliuta coal mine in the study area, the site water samples of the coal mine underground reservoir located in the $2^{-2}$ coal seam were collected at the No. 1 reservoir 400 outlet (S4) and 406 outlet (S5), No. 2 reservoir recharge facilities (S2) and outlet (S6), and No. 3 reservoir inlet (S3) and outlet (S7). The mine water samples (S1) and the fissure water samples (S8) were collected in the water recycling chamber and the side waterway of coal mining face in the $5^{-2}$ coal seam, respectively. The sampling scheme design and technology were strictly carried out in accordance with the industry standard “Technical guidance for Water quality sampling” (HJ 494–2009) and “Technical Design of Water quality sampling Scheme” (HJ 495–2009) implementation.

Since it was impossible to collect the rock samples from three coal mine underground reservoirs in $2^{-2}$ coal seam, this study collected roof caving rock samples from $5^{-2}$ coal seam mining face with similar characteristics for analyzing the characteristics of element composition, mineral composition, surface morphology, and specific surface area/pore structure of rock in reservoir.

#### Test methods of rock sample analysis

The collected rock samples and filtered suspended matter in mine water were ground to the particle size that could pass through 200 mesh sieve. Shimadzu (XRF-1800) Japanese Neo-Confucianism (ZSX Primus II) X-ray fluorescence spectrometer was used for qualitative and semi-quantitative analysis of elements. Using a SmartLab SE type X-ray

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**Table 1** Water storage and usage information of underground reservoir

| Underground reservoir | No. 1         | No. 2         | No. 3         |
|-----------------------|---------------|---------------|---------------|
| Average reservoir depth (m) | 7.9           | 5.8           | 8.3           |
| Area of goaf (km$^2$)     | 3.81          | 1.82          | 2.23          |
| Dynamic water ($\times 10^4$ m$^3$) | 165           | 89            | 153.8         |
| Static water ($\times 10^4$ m$^3$) | 171.2         | 103.5         | 27.99         |
| Maximum water storage capacity ($\times 10^4$ m$^3$) | 617.3 ($h=10$ m) | 339.2 ($h=16$ m) | 633.5 ($h=14$ m) |
| Sewage recharge (m$^3$/day)   | 9.78$\times 10^3$ |               |               |
| Underground water reuse (m$^3$/h) | 330           |               |               |
| Surface water consumption (m$^3$/day) | 4.5$\times 10^3$ |               |               |
| Total water storage ($\times 10^4$ m$^3$) | 710.5         |               |               |
d) X-ray diffractometer (XRD) (Cu target, Kα radiation, step size of 0.02°, power of 40 kV, 150 mA, continuous scanning) produced by Rigaku Corporation of Japan for mineral composition analysis, test conditions: 2θ angle range was 5–80° and scanning speed was 4°/min. According to the standard analysis method, the measured XRD data were used to determine the composition of the minerals contained in rock samples and suspended matter in mine water using the Jade 6.0 (MDI, Livermore, CA, USA) software in conjunction with the material standard powder diffraction data (PDF 2004) provided by the International Centre for Diffraction Data (ICDD). The surface morphology of the samples was observed by scanning electron microscopy (Phenom Desktop SEM) produced by Phenom-World companies in the Netherlands. The ASAP 2020 M Rapid Specific Surface/Pore Analyzer (BET) was used to analyze the specific surface area, total pore volume, and average pore size of the samples. The measuring range of the specific surface area of the instrument is 0.005 m²/g to infinity, the measuring range of pore size distribution is 0.35 to 500 nm, and the minimum detection limit of pore volume analysis is 0.0001 cm³/g (using H–K or DA analysis method).

**Test methods of water sample analysis**

Referring to the method of “groundwater quality inspection method” (DZ/T 0064–1993), the physical indexes such as chroma and visible matter of water sample were observed and recorded in the field. The pH value and electrical conductivity (EC) of water sample were measured immediately using handheld analyzing kits after the field collection. Some of the water samples were filtered through a 0.45-μm membrane filter and loaded into a polyethylene container. The collected samples were kept on ice in the dark and transported to laboratory as soon as possible for further analysis. The indexes of the samples were kept on ice in the dark and transported to laboratory as soon as possible for further analysis. The indexes of the samples was observed by scanning electron microscopy (Phenom Desktop SEM) produced by Phenom-World companies in the Netherlands. The ASAP 2020 M Rapid Specific Surface/Pore Analyzer (BET) was used to analyze the specific surface area, total pore volume, and average pore size of the samples. The measuring range of the specific surface area of the instrument is 0.005 m²/g to infinity, the measuring range of pore size distribution is 0.35 to 500 nm, and the minimum detection limit of pore volume analysis is 0.0001 cm³/g (using H–K or DA analysis method).

**Table 2** Test and analysis methods of various indexes in water samples

| Detection indexes | Test methods and instrument parameters |
|-------------------|----------------------------------------|
| SS and TDS        | Gravimetric method                      |
| Turbidity         | Turbidimeter                            |
| COD               | Rapid digestion spectrophotometry       |
| TOC               | Total organic carbon analyzer (TOC-LCPH CN200, Shimadzu, Japan) |
| UV254             | 752 UV–Vis spectrophotometer            |
| CO3²⁻ and HCO3⁻   | Double mixed indicator titration        |
| Cl⁻ and SO4²⁻     | Ion chromatograph (IC), and the chromatographic conditions: leaching solution concentration (sodium carbonate 0.0018 mol/L-sodium bicarbonate 0.0017 mol/L), 23 μL injection volume, the flow rate of leaching solution was 1.0 ± 2.0 mL/min, regenerated liquid was determined according to the flow rate of leaching solution |
| K⁺, Na⁺, Ca²⁺, Mg²⁺, THM, and DHM | PerkinElmer NexION 300D inductively coupled plasma mass spectrometry (ICP-MS) (USA) |

Total heavy metal (THM) concentration refers to the concentration of heavy metal ions filtered by 0.45-μm membrane filter after acidification and digestion in mine water. The concentration of dissolved heavy metal (DHM) refers to the concentration of heavy metal ions in mine water filtered directly by 0.45 μm membrane filter without acidification and digestion. The concentration of heavy metal ions in suspended matter (SHM) was the total heavy metal concentration (THM) minus the dissolved heavy metal concentration (DHM). Each water quality index in the water sample was tested continuously for three or more times under the same test conditions (Zhang et al. 2019). The ion charge balance of the measured data for eight sets of conventional ions needed to be within ±5% to be valid (Ibrahim et al. 2019). The average value of the measured data was calculated for subsequent analysis.

**PHREEQC-based reverse hydrogeochemical simulation**

In order to analyze the type of water–rock interaction occurring in coal mine underground reservoirs, the reverse geochemical simulation of water–rock interaction in coal mine underground reservoirs with different paths was conducted using the INVERSE-MODELING module of PHREEQC software. The principle of reverse geochemical simulations was based on the mass conservation model (Shabani and Zivar 2020), namely the composition and content of chemicals in final water downstream of the same path. Through a series of water–rock interaction such as precipitation, dissolution, ion exchange, mixing and evaporation occurring during the water flow, which reach equilibrium with the substances in the upstream initial water, and infer the possible geochemical action in the path. In this study, we selected each reservoir inlet water sample as the initial water and outlet water sample as the final water. That
is, the reverse simulation operation of coal mine underground reservoir is in four paths: path I (S1→S4), path II (S1→S5), path III (S2→S6), and path IV (S3→S7).

The reliability of hydrogeochemical simulation results mainly depended on the selection of the possible mineral phase and the determination of constraint variables (Dai and Samper 2006). According to the XRF, XRD, and SEM test results of the roof rock samples, the water chemical composition of the water samples and the storage conditions of the water in the underground reservoir, quartz, calcite, dolomite, gypsum, halite, albite, orthoclase, kaolinite, illite, chlorite, CO₂, and NaX-CaX₂ cation exchange were selected as the possible mineral phases in the model. Some “possible mineral phase” and its reaction equations are shown in Table 3 (Shabani and Zivar 2020; Zhang et al. 2020). We selected the K, Ca, Na, Mg, Cl, C, S, and Si eight elements and pH value as the constraint variables in the model.

### Results and discussion

#### Characterization of suspended matter and roof rock sample

#### Chemical and mineral composition analysis

By using the XRF, the spectral semi-quantitative mineral element composition analysis results of suspended matter in mine water and roof rock sample are detailed in Table 4. The main elements of suspended matter in mine water was C, its oxide CO₂ ratio was 91.63%, followed by SiO₂, Al₂O₃ and CaO, and contained a small amount of other elements. The proportion of SiO₂ and Al₂O₃ content in roof rock samples was 78.7%, followed by K, Na, Ca, Mg, C, S, Cl, and a small amount of other elements such as Fe, Mn, and Ti. It showed that the main mineral composition in the roof rock sample was meta-aluminate or silicate (Fang et al. 2020).

|  | CO₂ | Na₂O | MgO | Al₂O₃ | SiO₂ | P₂O₅ | SO₃ | Cl | K₂O | CaO |
|---|---|---|---|---|---|---|---|---|---|---|
| Roof rock | 8.6352 | 1.0352 | 1.2241 | 19.1005 | 59.614 | 0.2059 | 0.0597 | 0.0138 | 3.5551 | 0.4485 |
| Suspended matter | 91.6334 | 0.1213 | 0.1224 | 1.8917 | 2.9136 | 0.0222 | 0.2086 | 0.2347 | 0.1193 | 1.9888 |
| Composition | TiO₂ | CdO | Cr₂O₃ | MnO | Fe₂O₃ | CO₂ | NiO | CuO | ZnO | Ga₂O₃ |
| Roof rock | 0.8929 | — | 0.0131 | 0.0383 | 5.0591 | 0.0022 | 0.0057 | 0.0049 | 0.0261 | 0.0028 |
| Suspended matter | 0.0499 | 0.007 | 0.0019 | 0.018 | 0.6198 | — | 0.0005 | 0.0005 | 0.0166 | — |
| Composition | As₂O₃ | Rb₂O | SrO | Y₂O₃ | ZrO₂ | Nb₂O₅ | Br | |
| Roof rock | — | 0.0125 | 0.0167 | 0.003 | 0.0282 | 0.0027 | — |
| Suspended matter | 0.0007 | 0.0014 | 0.0104 | — | — | — | 0.0174 |
analysis showed that the Mg elements in the roof rock samples were mainly from chlorite, some of which may also come from dolomite or other minerals; K elements were mainly from orthoclase, illite, and mica minerals; Na elements were mainly from albite, and some may also come from mica minerals; and Ca elements were mainly from calcite, dolomite, and other impurity minerals. Some studies have shown that minerals containing K, Na, Ca, Mg, S, and other elements may participate in water–rock interaction and affect the concentration of ions in water (Chander et al. 2020; Tao et al. 2007). The XRD analysis results showed that the mineral composition and content of suspended matter and roof rock sample were basically consistent with the results of XRF element analysis.

The collected rock samples and suspended matter in mine water were observed by scanning electron microscope, and the surface morphology scanning results are as shown in Fig. 2. The layered silicate structure and flake kaolinite structure can be clearly seen on the rock sample surface of coal seam roof, and there were thin and strip shapes with irregular size and shape, as well as some irregular micro-cracks (as shown in Fig. 2a). When rocks interact with mine water, these edges and cracks may adsorb some ions in mine water (Pearce et al. 2018). The particles of roof rocks in underground reservoir of coal mine were arranged closely and the particle gradation was good. According to the engineering practice and the analysis results of water sample data on the spot, the roof rocks had a good filtration effect on mine water (Chen 2016; Chen et al. 2016). Figure 2b of suspended matter in mine water showed that there were a large number of other substances adsorbed on graphite surface, and the carbon molecules in pulverized coal had organic reducibility, which can make suspended matter in mine water adsorbed COD and other soluble substances (Jiang et al. 2020; Zhang et al. 2021).

The specific surface area of rock minerals can characterize the adsorption properties of substances, and the specific surface area and pore structure of collected rock samples and suspended matter in mine water are listed in Table 5. The specific surface area of roof rock samples was 7.7323–9.7297 m²/g, the average value was 8.6548 m²/g; the suspended matter was 9.103–11.9089 m²/g, and the average value was 10.1065 m²/g. The mean of total pore volume of roof rock samples was 0.02687 cm³/g, and the suspended matter was 0.03842 cm³/g. It can be seen that the specific surface area and total pore volume of roof rock
samples were lower than those of suspended matter in mine water. The higher specific surface area and total pore volume were more favorable for the adsorption and removal of ions or pollutants in mine water. The adsorption capacity of suspended matter in mine water was higher than that in roof rock samples (Zhang et al. 2020). XRF analysis and surface morphology analysis of suspended matter in mine water showed that other substances were attached to the surface of suspended matter, which indicated that the settlement of suspended matter had a certain purification effect on other pollutants in mine water. The measured pore size of roof rock samples was $8.6108 \pm 13.732$ nm, the average was $11.8978$ nm; the suspended matter was $9.6024 \pm 16.808$ nm, and the average was $14.5454$ nm. The pore size of suspended matter in mine water was larger than that of roof rock sample, which indicated that the pore distribution in suspended matter was more dense. The samples were classified according to the pore size classification standard proposed by the International Federation of Pure and Applied Chemistry (IUPAC). It can be seen that the field rock samples and mine water suspensions belong to mesoporous materials ($2 \sim 50$ nm) (Zhang et al. 2020).

**Hydrochemical characteristics analysis of water samples**

The physiochemical characteristics of the inlet and outlet water are summarized in Table 6. The water samples from underground reservoir in this area were slightly alkaline, and EC was $1627 \sim 1937 \mu s/cm$, characterized the concentration of soluble salt in the solution, belong to fresh water ($TDS < 1000 \text{ mg/L}$) (Zhang et al. 2021). The average value of inlet TDS concentration of underground reservoir was $937 \text{ mg/L}$, and the average value of effluent was $866 \text{ mg/L}$. The average value of influent of SS concentration was $1231 \text{ mg/L}$, the average turbidity of effluent was $98.5 \text{ NTU}$. The average value of inlet COD was $51.87$, and the average value of effluent was $30.17$. TOC and $UV_{254}$ can be used to characterize the DOM fractions (Han et al. 2020b; Zheng et al. 2015). The mean TOC and $UV_{254}$ concentrations of influent water samples were $0.163 \text{ mg/L}$ and $14.69/\text{ cm}$; effluent concentrations were $0.021 \text{ mg/L}$ and $10.54/\text{ cm}$ respectively. It can be seen that the pollutant concentration of TDS, suspended material and COD, and dissolved organic matter from the reservoir water decreased.

— means no detection.

The concentration of Fe and Mn in each sample and the percentage of its existence are shown in Fig. 3, and the concentration of other heavy metal ions was less than $0.01 \text{ mg/L}$, such as copper, zinc, and chromium. The average concentration of Fe-DHM in the influent was $0.053 \text{ mg/L}$, the average concentration of Fe-SHM was $9.79 \text{ mg/L}$, and
the proportion of Fe-DHM and Fe-SHM was 0.51% and 99.49%, respectively. The average concentration of Fe-DHM in effluent was 0.315 mg/L, the average concentration of Fe-SHM was 0.75 mg/L, and the proportion was 29.25% and 70.75%, respectively. The average concentrations of Mn-DHM and Mn-SHM in the inlet water of the reservoir were 0.107 mg/L and 0.577 mg/L, with a percentage of 14.71% and 85.29%, respectively. The average concentrations of Mn-DHM and Mn-SHM in reservoir effluent were 0.032 mg/L and 0.142 mg/L, with a percentage of 18.86% and 81.14%, respectively. The concentration of Fe-DHM and Mn-DHM in the effluent of the reservoir was higher than that in the influent (Han et al. 2020a). The analysis may be that the iron and manganese ions adsorbed on the suspended matter were desorbed into the water phase or the minerals containing Fe and Mn in the underground reservoir of the coal mine dissolved (Jiang et al. 2020).

Referring to the “Standard for groundwater quality” (GB/T14848-2017), although the water quality of inlet and outlet in coal mine groundwater reservoir generally conforms to the quality standard for class V groundwater, the outlet water quality was significantly improved compared with the inlet water quality. The overall failure to improve the effluent quality was due to the significant reduction of suspended solids (i.e. turbidity) in mine water, but it still belonged to the V class standard. The reservoir water sample analysis showed that the roof collapse rock in the underground reservoir in the coal mine had a certain purification effect on the mine water, and the effluent water quality was significantly improved (Chen et al. 2016; Gu et al. 2016). According to the analysis of the rock properties and mineral composition, the clay minerals such as kaolinite, illite, and chlorite in the rocks can absorb and remove the COD (Yu et al. 2018), DOM (Zhang et al. 2021), and heavy metals (Gu et al. 2018) pollutants in the mine water. The concentration of pollutants in water samples (S1) collected in water circulation chamber of 5−2 coal seam was higher than that of influent (S2 and S3) of underground reservoir in 2−2 coal seam. The collected S1 water sample was kept static for a period of time, and most of the suspended objects in the water sample were settled to the bottom of the container. Combined with the characteristic analysis results of suspended matter in mine water, it was shown that the sedimentation of suspended matter occurs in the water circulation chamber of 5−2 coal seam, which made the suspended matter in mine water be removed to a certain extent, and the adsorption of suspended matter surface also reduced the dissolved pollutants in mine water (Chen 2016; Gu et al. 2021). Therefore, in order to improve the pollutant purification effect and service life of the coal mine underground reservoir, the pollutants deposited at the bottom of the 5−2 coal bed water circulation chamber shall be removed.
in time. The pollutant indexes of fracturing water sample (S8) in underground reservoir were lower than that of inlet and outlet water samples of the reservoir. The reservoir effluent water samples were close to S8 water quality, indicating that the mixed effect of upper fissure water and mine water improved the effluent water quality of the reservoir (Chen et al. 2016).

**Analysis of the variation of hydrochemical types and major ions of water samples**

To intuitively compare the size differences between the ion concentrations of water samples collected in each field, the Schoeller diagram (Al-Barakah et al. 2017) was drawn with 3 groups of main cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$) and anions ($Cl^−$, $SO_4^{2−}$ and $HCO_3^{−} + CO_3^{2−}$) as the transverse coordinates, with the mole concentration and the ion valence product value (meq/L or meq/kg) as longitudinal coordinates, as shown in Fig. 4. Field water samples mainly contained $Na^+$, $Ca^{2+}$, $SO_4^{2−}$, and $Cl^−$ and less content of $Mg^{2+}$ and $HCO_3^{−}$. The $Na^+$ and $Cl^−$ content in the effluent of the reservoir increased and the $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2−}$ content decreased compared with the concentration of each ion in the influent of the reservoir. The concentration of each ion in the fissure water was similar to that in the reservoir effluent, which indicated that the mixture of mine water and fissure water occurs in the underground reservoir of coal mine (Chen et al. 2016). The interaction between water and rock may occurred between the influent and rock of the reservoir, which made the ion concentration of the effluent change (Al-Barakah et al. 2017; Zhang et al. 2019).

A tri-linear diagram of the Piper by the percentage of the molar concentration of each major anion and the valence product of ionization (Shan et al. 2019; Sun and Gui 2012), as shown in Fig. 5. According to the difference of the distribution area from the sample point to the diamond map, the hydrochemical type of the water sample can be directly reflected. Piper diagram results showed that the main hydrochemical types of mine water in the field were the $SO_4^{2−}-Cl^-/Ca^{2+}$, and the hydrochemical types of reservoir effluent mainly included $SO_4^{2−}-Cl^-/Na^+$ and $SO_4^{2−}-Cl^-/Ca^{2+}$. The main hydrochemical types of inlet and outlet water were 36-A type ($SO_4^{2−}-Cl^-/Ca^{2+}$) and 42-A type ($SO_4^{2−}-Cl^-/Na^+$) according Schukalev classification method (Eang et al. 2018), which was consistent with the results of Piper three-line graph analysis (Zhang et al. 2019). This transition from the main ion concentration and hydrochemical types indicated that mine water interacts with rocks during storage and migration of underground reservoirs in coal mines (Han et al. 2020a).

In order to determine the main water–rock interactions occurring and the source of ions in the effluent of underground reservoir in coal mine. Three scatter diagrams were plotted (Fig. 6) by ion ratio method (Eang et al. 2018). The main sources of $Na^+$ during water–rock interaction can be analyzed by the ion ratio method of $Na^+$ and $Cl^−$, as shown in Fig. 6a. Three reservoir inlet water samples ($Cl^−$, $Na^+$) scatter are all below on the line of $y = x$ (Bozau et al. 2017). The molar concentration ratio of $Na^+$ and $Cl^−$ of S2 and S3 water samples were greater than that of 1; then, the $Na^+$ content was higher than that of $Cl^−$, and the $Na^+$ and $Cl^−$ concentration ratio of the effluent water sample of No. 1 reservoir was larger than that of the influent water sample. The results showed that the cation exchange reaction and $Na^+$ dissolution occurred in the coal mine underground reservoir (Ettazarini 2005). Moreover, $Na^+$ mainly came from the dissolution of silicate minerals like sodium feldspar, which was consistent with the mineral composition analysis results of rocks (Zhang et al. 2020).

As shown in Fig. 6b, the inlet water samples ($Ca^{2+} + Mg^{2+}$) vs. ($SO_4^{2−} + HCO_3^{−}$) scatter were distributed along the line $y = x$ (Ettazarini 2005), while all outlet water all points were above the ratio line. It can be seen that the water–rock interaction makes the concentration of ($Ca^{2+} + Mg^{2+}$) in the reservoir effluent water sample deficient compared with that of ($SO_4^{2−} + HCO_3^{−}$). One of the reasons for the $Na^+$ excess and ($Ca^{2+} + Mg^{2+}$) deficiency may be a cation exchange reaction, thus causing the release of Na in the rock and reducing the concentrations of $Ca^{2+}$ and $Mg^{2+}$ in the water. The farther the ($Na^+−Cl^−$) vs. ($Ca^{2+} + Mg^{2+}−SO_4^{2−}−HCO_3^{−}$) plot distance of the line of $y = x$ indicating strong cation exchange (Zhang et al. 2019). Figure 6c shows that each water sample point in the influent was farther away from the $y = x$ line than the sample point in the effluent. The results showed that the cation exchange reaction occurred in coal mine underground reservoir (Ettazarini 2005), which made the $Na^+$ in the rock was replaced by $Ca^{2+}$ and $Mg^{2+}$ in the water, and the cation exchange ability of the effluent water samples weakens (Zhang et al. 2019).
**Reverse hydrogeochemical simulation results of water–rock interaction in coal mine underground reservoir**

The water–rock mass balance reaction model of coal mine underground reservoir under different paths is shown in Fig. 7. Positive value indicated that the mineral phase was dissolved, and the ions or elements entered into the mixed water; the negative value indicated that the mineral phase settled in the mixed water, and the ions leaved the mixed water; and “zero” meant that no reaction had occurred (Jannesar Malakooti et al. 2015; Salcedo Sánchez et al. 2017). The simulation results of path I (Fig. 7a) showed that orthoclase, albite, halite, and dolomite dissolved 0.039 mmol/L, 0.17 mmol/L, 1.7 mmol/L, and 0.53 mmol/L, respectively, while gypsum, kaolinite, quartz, and calcite precipitated 0.46 mmol/L, 0.10 mmol/L, 0.41 mmol/L, and 1.2 mmol/L, respectively; illite did not take part in the reaction. Path II (Fig. 7b) simulation results showed that halite and albite dissolved 1.6 mmol/L and 0.18 mmol/L, respectively; quartz, calcite, gypsum, and kaolinite precipitated 0.35 mmol/L, 0.15 mmol/L, 0.48 mmol/L, and 0.089 mmol/L respectively; and illite, orthoclase, and dolomite did not participate in the reaction. Path III (Fig. 7c) simulation results showed that halite and albite dissolved 0.28 mmol/L and 0.11 mmol/L, respectively; quartz, calcite, dolomite, gypsum, and kaolinite precipitated 0.21 mmol/L, 0.085 mmol/L, 0.0049 mmol/L, 0.80 mmol/L, and 0.053 mmol/L respectively; and cation exchange occurred (NaX: 2.83; CaX₂: –1.42). Orthoclase and illite did not participate in the reaction. Path IV (Fig. 7d) simulation results showed that calcite, halite, and albite dissolved 0.49 mmol/L, 0.34 mmol/L, and 1.15 mmol/L, respectively, and carbon dioxide gas dissolved 0.48 mmol/L; quartz, dolomite, gypsum, and kaolinite precipitated 2.3 mmol/L, 0.57 mmol/L, 0.15 mmol/L, and 0.58 mmol/L, respectively, and cation exchange occurred (NaX: 1.94; CaX₂: –0.97). Orthoclase and illite did not take part in the reaction.

According to the above analysis results, the dissolution of albite and halite, the precipitation of gypsum and the replacement of Na⁺ in rock by Ca²⁺ in the water mainly occurred in the underground reservoir of coal mine (Shabani and Zivar 2020), resulting in the increased of Na⁺ and Cl⁻ concentration and the decreased of Ca²⁺ and SO₄²⁻ concentration in the outlet water, and the hydrochemical type changes from type SO₄²⁻/Ca²⁺ to type SO₄²⁻/Cl⁻/Na⁺ (Kumar et al. 2017).
Little or no dissolution of orthoclase and illite resulted in little change of $K^+$ concentration in the effluent water. The dissolution or precipitation behavior of calcite and dolomite in rocks with different paths was inconsistent (Steding et al. 2020), which was mainly related to ionic strength in water, content in rocks, and environmental conditions (Salcedo 2020).
Sánchez et al. 2017). At the same time, the dissolution of carbon dioxide and the precipitation of quartz and kaolinite may occur in the reservoir. The simulation results of PHREEQC software were consistent with the analysis results of rock mineral composition and ion ratio, and more detailed information of water-rock interaction was obtained, which indicated that the hydrogeochemical reverse simulation software can be effectively used to analyze the water-rock interaction in underground reservoir of coal mine.

Conclusions

This study implied that the main mineral composition of roof caving rock samples in underground reservoir was met-aluminate or silicate. The layered silicate structure and flaky kaolinite structure can be clearly visible on the surface of the rock, with some irregular edges and microcracks, and the collapsed rock had a higher specific surface area and total pore volume. These characteristics made the collapse rocks in the reservoir have a certain adsorption and removal capacity for suspended solids, COD, DOM, heavy metal ions, and other pollutants in the mine water and have a certain purification effect on the mine water. In addition, the high content of graphite in the suspended solids in the mine water can absorb other dissolved pollutants in the water, and the mixing effect of overlying fissure water and mine water in the reservoir also made the water quality of the reservoir effluent water improved significantly. The water-rock interaction between the collapsed rock and the mine water, such as the dissolution of albite and halite, the precipitation of gypsum, quartz and kaolinite, and the cation exchange reaction, resulted in the concentration of Ca\(^{2+}\), Mg\(^{2+}\), and TDS in the reservoir outlet water, and the hydrochemical type changed from SO\(_4^{2-}\)-Cl\(^{-}/Ca^{2+}\) type to SO\(_4^{2-}\)-Cl\(^{-}/Na^{+}\) type. The simulation results of PHREEQC software were consistent with the analysis results of rock mineral composition and ion ratio method, and more detailed information of water-rock interaction can be obtained. It can be seen that the research method adopted in this paper can be effectively used to analyze the water-rock interaction and mine water purification mechanism in underground reservoirs of coal mine, but the relevant research on underground reservoirs under different environmental conditions still needs to be supplemented and improved.

Author contribution BJ and JG were involved in sample testing, data analysis, and manuscript writing in this study, and they were major contributors in writing the manuscript. KD tested and analyzed the characteristics of the reservoir water samples. XD tested and analyzed the characterization of the rock samples. KZ was involved in data analysis and manuscript writing. All authors read and approved the final manuscript.

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Availability of data and materials All data generated or analysed during this study are included in this published article.

Declarations

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Consent for publication Not applicable.

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