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Original Research

Hydrogeochemical Characteristics of Limestone Water in Taiyuan Formation of Hengyuan Coal Mine and Its Response to High Pressure Grouting Project

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Abstract

Years mining activities have changed the distribution characteristics of groundwater hydrochemical field, which may lead to the deterioration of groundwater quality and the occurrence of mine water inrush disasters. The study of groundwater hydrogeochemical evolution can provide a theoretical basis for the prevention of mine water inrush disaster and the rational utilization and protection of groundwater. Using the Piper trigram, Person correlation analysis matrix, Gibbs diagram, ion proportion coefficient diagram, and mineral saturation index to study the hydrogeochemical evolution mechanism of Taiyuan Formation limestone water before grouting (2010) and after grouting (2020) in this study. The results show that the concentrations of anion and cation in the limestone water of Taiyuan Formation have the same change trend before and after grouting in the study area, the anion concentration changes to $SO_4^{2-}>HCO_3^->Cl^-$, the cation concentration changes to $Na^++K^+>Ca^{2+}>Mg^{2+}$. The correlation coefficient between most ions of limestone water after grouting is reduced. The hydrogeochemical type is gradually transformed from Na^++K^+-SO_4^{2-} type to Mg^{2+}-SO_4^{2-} type and Ca^{2+}-SO_4^{2-} type. Rock weathering and cation exchange are the main factors affecting the hydrogeochemical characteristics of limestone water. The higher concentration of SO_4^{2-} is related to the dissolution of gypsum and the oxidation of pyrite.

Keywords: hydrogeochemical characteristics, Huaibei coalfield, Taiyuan Formation limestone water, formation mechanism, grouting effect

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Introduction

The hydrogeological conditions of coal mines in China are complex, and the threat of karst water disaster is serious [1-2]. With the in-depth exploitation of coal resources, the ground temperature and water pressure rise significantly, the threat of karst water disaster increases, and mine water inrush accidents occur occasionally [3]. Huaibei coalfield is located in the north of Huaibei plain, China, a concealed coalfield covered by thick loose layer of Cenozoic. The coal-bearing strata include Taiyuan Formation of Carboniferous system, Shanxi Formation of Permian system, Lower Shihezi Formation and Upper Shihezi Formation [4]. The limestone of the Taiyuan Formation of Carboniferous system comprises of 12 layers of thin limestone, with a total thickness of 50-81 m. The first layer limestone and second layer limestone in the upper part are relatively light (1.5-3.5 m), with poor water yield and easy to drain; The average thickness of the third layer limestone is 8.09m, with developed karst, strong water yield, and high water-pressure. Hengyuan coal mine, located in the north of Huaibei coalfield, the sixth coal seam is the main minable coal seam, and the thickness of the water-resisting layer of the coal seam floor (the distance between the coal seam and the limestone roof) is 50-60 m. Affected by the stratum structure, the local area is less than 20 m, which is very prone to water inrush accidents.

The water inrush from the coal seam floor depends on two critical factors: the water pressure acting on the floor waterproof layer and the thickness of the floor waterproof layer. Drainage depressurization has been rarely used because of the uncertainty of safety factors, high drainage cost and severe damage to the balance of groundwater resources. In recent years, to reduce the threat of limestone water in Taiyuan Formation (limestone water for short), Hengyuan coal mine has adopted surface directional drilling and high-pressure grouting technology (Fig. 1). The drilling adopts the method of segmented drilling that the first straight hole section passes through the topsoil to the bedrock layer, the second inclined hole section is directionally drilled to the top of the first layer of limestone, and the third straight layer section is drilled along the third limestone aquifer. The cracks and water affluent abnormal areas of the third layer of limestone are exposed, and the third layer of limestone ("target layer") in Taiyuan Formation is reinforced by regional high-pressure grouting [5]. This method not only increases the thickness of the floor water resisting layer, but also effectively blocks the third layer of limestone karst fissures and vertical water guide channels [6-7]. From the effect of regional governance, this method increases the effective thickness of the water-resisting layer of the coal seam floor by about 20 m, directly cuts off the hydraulic connection between limestone water and mining activities, and provides a guarantee for the safe mining of coal.

In the process of grouting to strengthen the third layer of floor limestone, the water discharged from the cement slurry will change the distribution characteristics of the Groundwater Hydrogeochemical field in a certain period. The limestone water of Taiyuan formation is the main water filling source for mining the lower formation coal in Huaibei coalfield, as well as the domestic water for the residents in the mining area and the industrial water for the surrounding power plants. However, the influence of mining activities on the hydrogeochemical characteristics of limestone water in Taiyuan formation is rarely reported. Hengyuan coal mine began to carry out high-pressure grouting in 2014 to strengthen the third layer of limestone in Taiyuan Formation limestone. Based on the conventional hydrogeochemical test results of the limestone water samples before grouting (2010) and after grouting (2020), this paper studies the differences of the limestone water chemical characteristics and evolution law under the influence of high-pressure grouting engineering by using Piper trigram, correlation analysis and ion proportion coefficient and mineral saturation index, it provides a scientific basis for the utilization and protection of deep groundwater resources in the mining area.

Materials and Methods

Study Area

Hengyuan coal mine is located in Huaibei City in north of Anhui province, China (Fig. 2), with east longitude of 116º37′30“-116º41′15”, and north latitude of 33º54′30“-33º58′00”. The working face in the study area crosses the Wenzhuang syncline, which is high at both ends and low in the middle, the structural fissures of the floor rock stratum in the syncline axis area are developed, with rich water content and strong water conductivity. Especially in mining areas II 62 and II 63, the water pressure borne by the floor of the sixth coal is 5.30 MPa, and the maximum water inrush coefficient is 0.12 MPa/m, far exceeding the critical value of 0.06MPa/m in the structural area, which poses a severe threat to the mining of the sixth coal in Hengyuan coal mine.

Sample Collection and Processing

Hydrogeochemical characteristics record the information of groundwater recharge sources, migration, and circulation to a certain extent [8-9]. To explore the hydrogeochemical evolution mechanism of the limestone water before and after grouting, 62 limestone water samples were collected from January to September 2010 (before grouting) and January to December 2020 (after grouting), including 37 samples in 2010 and 25 samples in 2020. All samples were taken from the third layer of limestone water in the limestone of Taiyuan Formation of Hengyuan coal

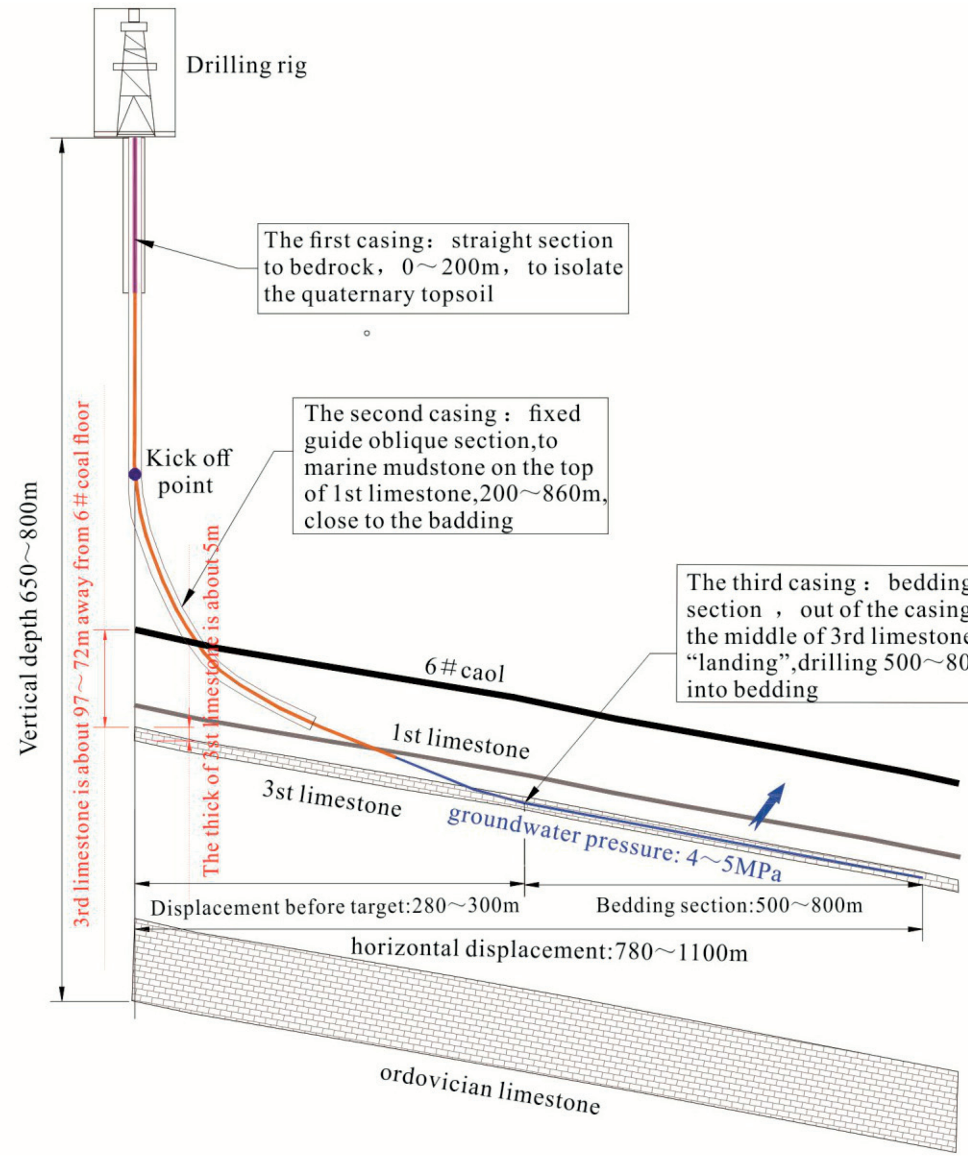

Fig. 1. Profile of surface directional drilling.

mine. The sampling points were the water outlet during the Hengyuan coal mine production process.

Before sampling, 2.5 L sampling barrel was washed with deionized water three times and cleaned the sampling barrel with the collected water sample three times during sampling. After the samples were collected, the portable instrument Ohaus (Shanghai, China) was used to test the pH, TDS and other indicators of the water samples on site. The collected samples passed through 0.45μm filter membrane, added ultra-pure nitric acid to acidify to pH<2, so that the metal ions were in free state. After sealed and stored, it was sent to the laboratory of the national coal mine water disaster prevention engineering technology research center of Suzhou University within 8 h, and stored in a 4ºC refrigerator for further testing. The contents of conventional ions Na^++K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} in water samples were tested by ion chromatograph (ICS-600-900), and the contents of CO_3^{2-} and HCO_3^- were determined by acid-base titration. Through calculation, the error of cation anion balance is within the standard limit of 5%, which shows that the test data is reliable.

Results and Discussion

Hydrogeochemical Characteristics

Conventional components such as Na^++K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, HCO_3^- account for more than 90% of the inorganic content in groundwater. Therefore, the conventional components of groundwater determine the hydrogeochemical type. In this study, the pH, TDS, Na^++K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, HCO_3^- of the limestone water in Hengyuan coal mine are statistically analyzed. The data are shown in Table 1.

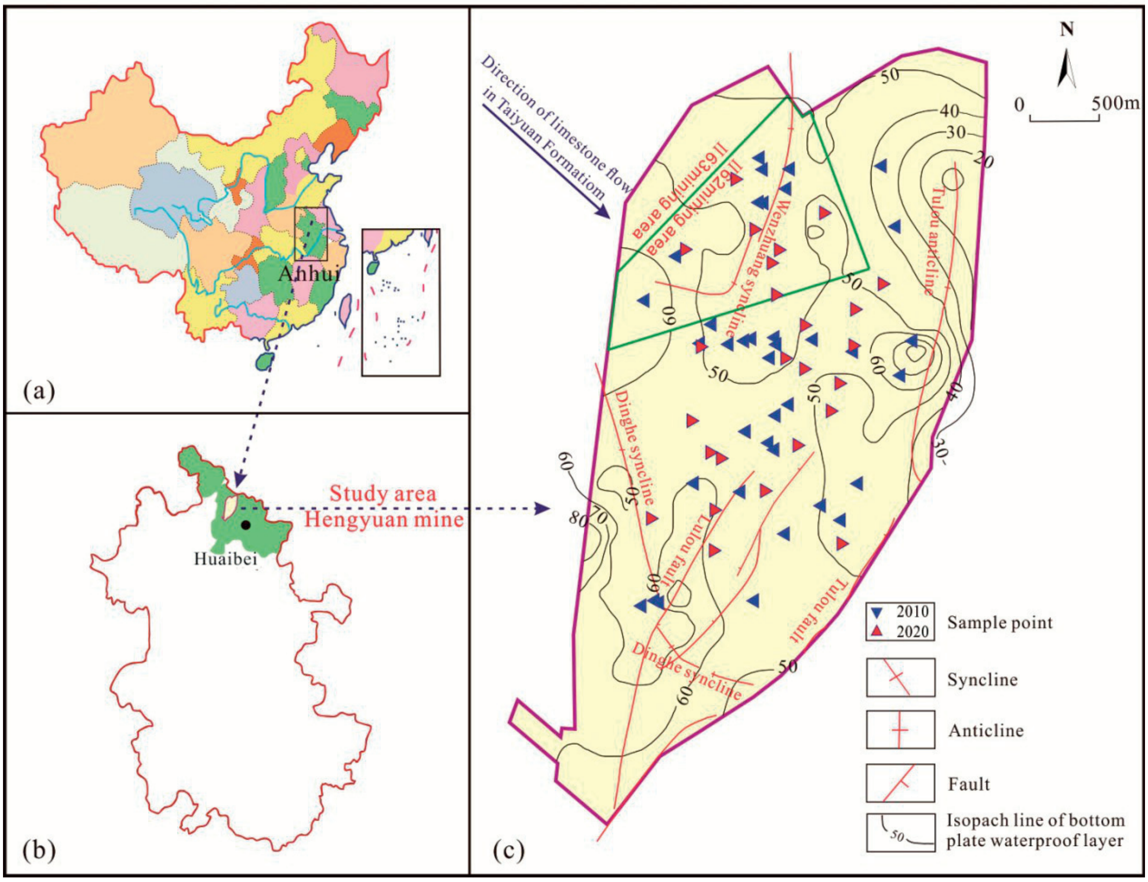

Fig. 2. Regional geographic location and distribution of sampling points. a) China; b) Geographical location of the study area; c) Structural map of the study area and the location of sampling sites.

It can be seen from Table 1 that in 2010 (before grouting) and 2020 (after grouting), the variation range of pH value of the limestone water in the study area is 7.3-8.62 and 7.68-7.9 respectively, with average values of 7.89 and 7.83 respectively, which are weakly alkaline. The variation range of pH value of the limestone water in 2020 is lower than that in 2010, and the coefficient of variation C.V is 4.35% lower than that in 2010. According to the WHO drinking water quality standard (2011), the over standard rate of pH value is also reduced from 2.7% in 2010 to 0, indicating the pH value of the limestone water tends to be stable in 2020. In addition to pH, TDS, Na^++K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- and HCO_3^- in the limestone water in 2010 and 2020 have large coefficients of variation, indicating that the limestone water is greatly affected by coal mining disturbance in 2010 and high-pressure grouting disturbance in 2020. In 2010 before grouting and 2020 after grouting, the concentrations of anion and cation in the limestone water have the same change trend, the anion concentration from high to low is SO_4^{2-}>HCO_3^->Cl^-, the main anion is SO_4^{2-}, the cation concentration changes to Na^++K^+>Ca^{2+}>Mg^{2+}, and the main cation is Na^++K^+. Except for SO_4^{2-}, the water quality exceeding standard rate of the limestone water in 2020 is lower than that in 2010.

Hydrogeochemical Type

Piper trigram can intuitively see the relative content of each component ion, which will not be affected by human factors [10-11]. Therefore, it is often used to study the general chemical characteristics and evolution law of groundwater [12].

It can be seen from the lower left triangle of Piper trigram shown in Fig. 3 that in 2010 (before grouting), the content of alkali metal ions Na^++K^+ is greater than that of alkaline earth metal ions Ca^{2+} and Mg^{2+}, and the cation Na^++K^+ is dominant. In 2020 (after grouting), the water sample points gradually move to the direction of increasing the content of Ca^{2+} and Mg^{2+}, but the content of Na^++K^+ is still greater than that of Ca^{2+} and Mg^{2+}. In the lower right triangle of Fig. 3, whether in 2010 (before grouting) or 2020 (after grouting), most water samples of the limestone water fall on the side of SO_4^{2-}, the content of strong acid ion SO_4^{2-} is greater than that of weak acid ion HCO_3^-, and the anion SO_4^{2-} is dominant. In 2010, the hydrogeochemical type of the limestone water in the study area is Na^++K^+-SO_4^{2-} type, accounting for 97.3%. In 2020, the hydrogeochemical type of the limestone water in the study area is relatively complex, with Mg^{2+}-SO_4^{2-} type accounting for 52%, Ca^{2+}-SO_4^{2-} and Na^++K^+-SO_4^{2-} types accounting

Table 1. Content statistics of conventional components of the limestone water.

Year	Parameters	pH	TDS	Na^++K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
2010 (n = 37) (Before grouting)	Min	7.3	1158.97	139.33	24.78	0.43	74	62.08	155.87
	Max	8.62	4275.03	1200.19	338.56	177.27	386.78	2131.43	991.86
	Mean	7.89	2411.68	530.3	160.85	45.88	151.12	1167.63	342.51
	C.V(%)	4.89	31.32	51.2	41.27	90.22	33.14	36.66	50.52
	Over standard (%)	2.70	100	54.05	—	—	2.7	91.89	—
2020 (n = 25) (After grouting)	Min	7.68	1934.78	68.49	48.41	78.49	40.25	1169.75	166.69
	Max	7.9	5443.74	1114.88	429	364.76	154.6	3496.71	524.22
	Mean	7.83	2914.58	336.08	229.2	217.83	104.56	1756.45	270.47
	C.V(%)	0.54	29.23	82.49	45.8	32.58	31.32	34.43	28.29
	Over standard (%)	0	100	24	—	—	0	100	—

Note: n is the number of samples, pH is dimensionless, and other indicators are mg/L; The standard value is in accordance with the drinking water quality guidelines (Fourth Edition) of the World Health Organization, and the „-" index has no standard limit.

for 24% respectively. The content of Na^++K^+ decreased and the content of Ca^{2+} and Mg^{2+} increased. Under the treatment of high-pressure grouting, the influence of cement slurry precipitated water on the ion content of the limestone water is mainly reflected in Na^++K^+, Ca^{2+} and Mg^{2+}.

Correlation of Hydrogeochemical Components

There is a certain connection between chemical components in groundwater, and the correlation of chemical components is usually used to indicate the degree of connection between them [13-14]. Pearson correlation analysis matrix is a statistical method to describe the correlation between two or more variables, representing the relationship between various indicators. Therefore, it is often widely used in hydrogeochemical research [15].

In 2010 before grouting (Fig. 4a), TDS in the limestone water has strong positive correlation with Na^++K^+, Cl^-, SO_4^{2-} and HCO_3^-; Na^++K^+ has strong positive correlation with TDS, Cl^-, SO_4^{2-} and HCO_3^-;

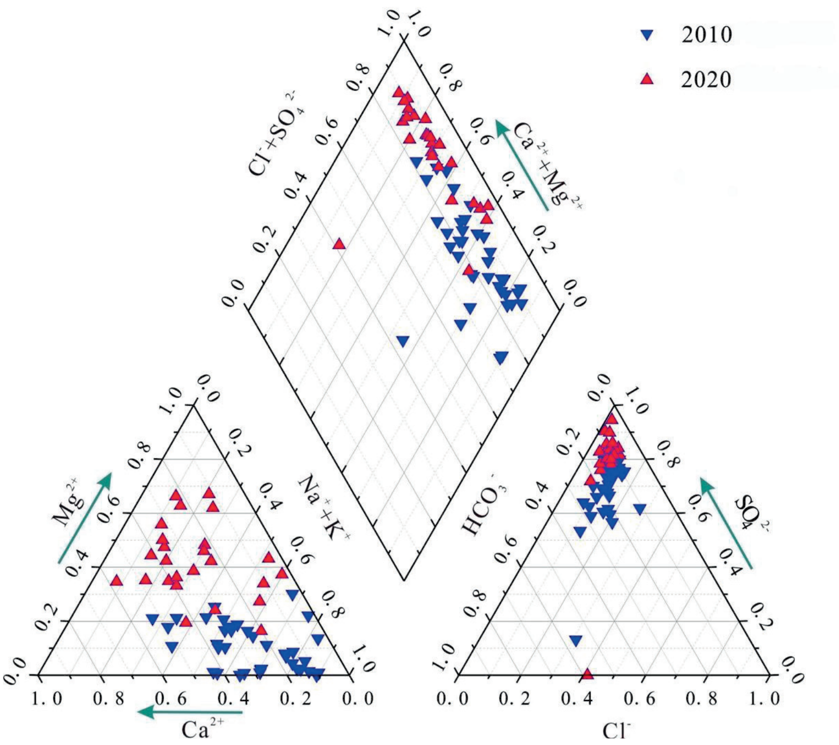

Fig. 3. Hydrogeochemical types of the limestone water before and after grouting.

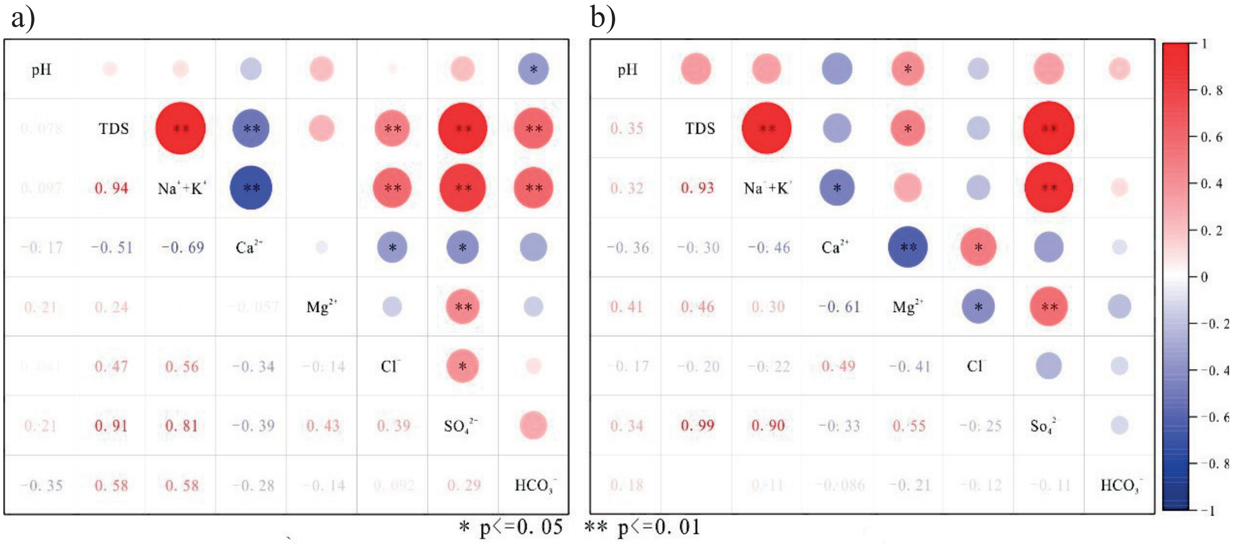

Fig. 4. Correlation coefficients of main chemical components of the limestone water before a) and after b) grouting.

SO_4^{2-} has strong positive correlation with TDS, Na^++K^+, Mg^{2+}; Ca^{2+} has strong negative correlation with TDS and Na^++K^+. In 2020 after grouting (Fig. 4b), TDS has strong positive correlation with Na^++K^+, SO_4^{2-}; SO_4^{2-} has strong positive correlation with TDS, Na^++K^+, Mg^{2+}; Ca^{2+} has strong negative correlation with Mg^{2+}.

As shown in Fig. 4, TDS has a strong positive correlation with Na^++K^+ and SO_4^{2-} in 2010 (before grouting) and 2020 (after grouting), which shows that the level of TDS depends on the content of main ions in the limestone water. Compared with 2010, in 2020, the correlation coefficient between most ions in the limestone water decreased, and the correlation parameters of medium and above ions decreased, only Ca^{2+} has increased significantly with Mg^{2+}, TDS, Na^++K^+, Mg^{2+}, Cl^-. It is speculated that the mixing of water from grouting slurry breaks the balance between ions in the limestone water, and the abnormal correlation coefficient of Ca^{2+} may be related to the fact that the main component of cement used for grouting is calcium oxide.

Hydrogeochemical Process

Evolution Mechanism of Hydrogeochemical Components

Gibbs diagram divides the evolution mechanism of Hydrogeochemical Composition of groundwater into rock weathering dominated, evaporation dominated and rainfall dominated [16]. As can be seen from Fig. 5a), the TDS of the limestone water in 2010 (before grouting) and 2020 (after grouting) are distributed between 1000~6000 mg/L. In 2010, the range of $Na^+/(Na^+ + Ca^{2+})$ is 0.3-0.99, and most sample points are between 0.5 - 0.85, indicating that the content of Na^+ in the limestone water is higher than that of Ca^{2+}. In 2020, $Na^+/(Na^+ + Ca^{2+})$ is distributed in the range of 0.1-0.95, and most water samples fall between 0.35-0.65, the content of Na^+ in the limestone water is basically the same as that of Ca^{2+}. As can be seen from Fig. 5b), in 2010 before grouting, $Cl^-/(Cl^- + HCO_3^-)$ ranged from 0.18 to 0.723, and most water samples are concentrated between 0.3 and 0.5. In 2020 after grouting, $Cl^-/(Cl^- + HCO_3^-)$ ranged from 0.2 to 0.6, and most water samples are concentrated between 0.3 and 0.5, that is, the Cl^- content in the limestone water in the study area is higher than that of HCO_3^- in 2010 and 2020.

As shown in Fig. 5, most water sample points are concentrated in the rock weathering control area. Therefore, it can be considered that rock weathering is the main factor affecting the hydrogeochemical characteristics of the limestone water in the study area. Some water sample points fall outside the solid line, indicating other functions controlling groundwater's chemical composition, such as cation exchange. No water sample points fall in the precipitation area, meaning that there is no direct hydraulic connection between the limestone water and atmospheric precipitation in the study area.

Evolution Form of Hydrogeochemical Components

The common forms of water-rock interaction include silicate weathering, evaporation salt dissolution and carbonate dissolution. Generally, the main types of water-rock interaction can be determined by the ratio of Na^++K^+, Ca^{2+}, Mg^{2+} and HCO_3^- [17].

As can be seen from Fig. 6, in 2010 (before grouting) and 2020 (after grouting), most water samples fall in the silicate weathering area and the area between silicate weathering and evaporite dissolution, which shows that the ion content in the limestone water is dominated by silicate weathering dissolution and affected by evaporite karst dissolution, and the effect of silicate weathering in 2020 is more significant than

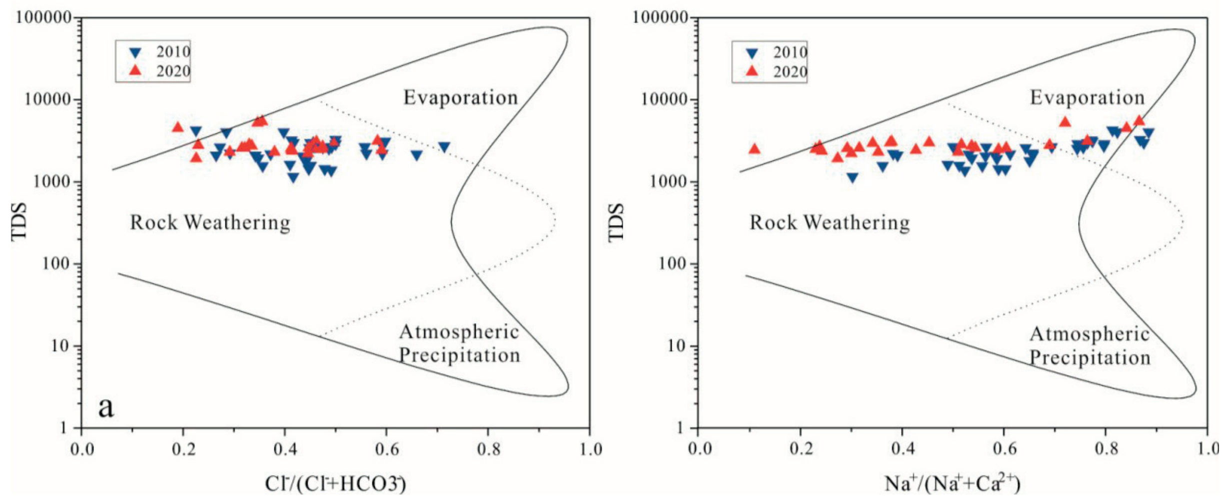

Fig. 5. Gibbs diagram of the limestone water before and after grouting.

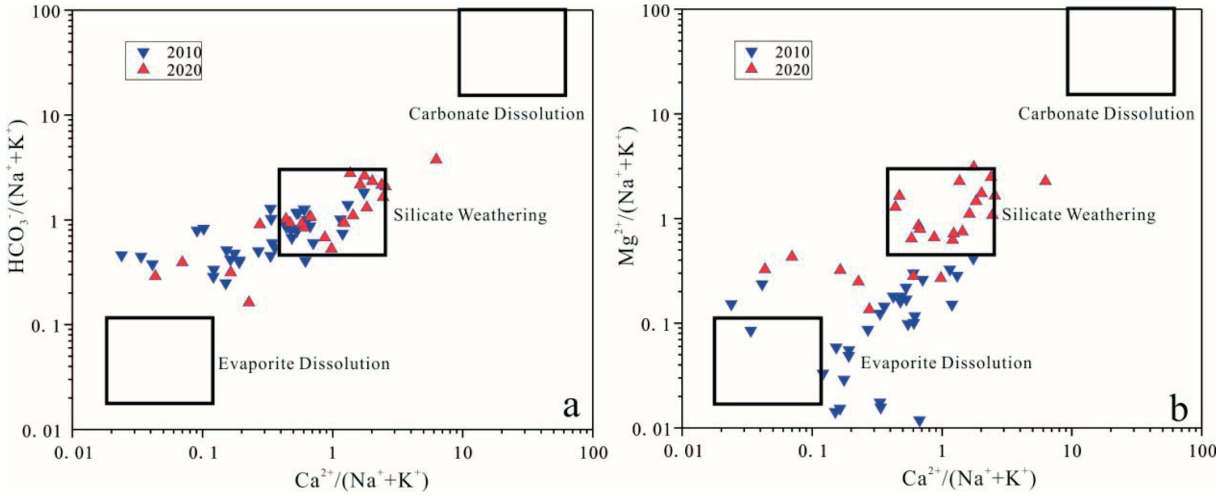

Fig. 6. Proportion diagram of the limestone water ions before and after grouting.

that in 2010. It is speculated that due to the influence of grouting, the runoff speed of the limestone water is accelerated, the retention time is shortened, the influence of evaporite dissolution is weakened, and the corresponding silicate leading role is enhanced.

Cation Exchange Degree

The influencing factors of groundwater hydrogeochemical composition depend not only on the chemical composition of surrounding rock, but also on the degree of ion exchange [18-19]. The ratio of ($Mg^{2+}+Ca^{2+}-SO_4^{2-}-HCO_3^-$) to ($Na^++K^+-Cl^-$) can be used to judge whether cation exchange occurs [20-21]. If the ratio is close to -1, it indicates that cation exchange occurs [22]. It can be seen from Fig. 7 that the ratio of ($Mg^{2+}+Ca^{2+}-SO_4^{2-}-HCO_3^-$) to ($Na^++K^+$ $-Cl^-$) of the limestone water in 2010 (before grouting) and 2020 (after grouting) is close to -1, indicating that the cation exchange effect of the limestone water in the study area is obvious.

Many factors control the hydrogeochemical characteristics of groundwater. In addition to groundwater recharge and water-rock interaction, the retention time of groundwater in an aquifer is also critical, the degree of ion exchange depends on the length of retention time [23]. The limestone of Taiyuan Formation in Hengyuan coal mine contains thin coal seams. The marine clay of the roof and floor of the coal seam is rich in Ca^{2+} and Mg^{2+}, which are easy to dissolve, migrate, and transform. The limestone water has sufficient leaching and ion exchange with surrounding rock, and a large amount of Ca^{2+} (Mg^{2+}) is fully replaced by Na^+ in surrounding rock. $Na^+_{\text{rock}}+Ca^{2+}(Mg^{2+})_{\text{groundwater}} \rightarrow Na^+_{\text{groundwater}}+Ca^{2+}(Mg^{2+})_{\text{rock}}$. Therefore, the content of Na^+ in the limestone water is high [24]. The content of Na^++K^+ in 2020 (after grouting) is lower than that in 2010 (before grouting), which indicates that grouting treatment has effectively blocked the groundwater diversion channel, improved the water circulation of the limestone water, shortened the residence time, and weakened the leaching and

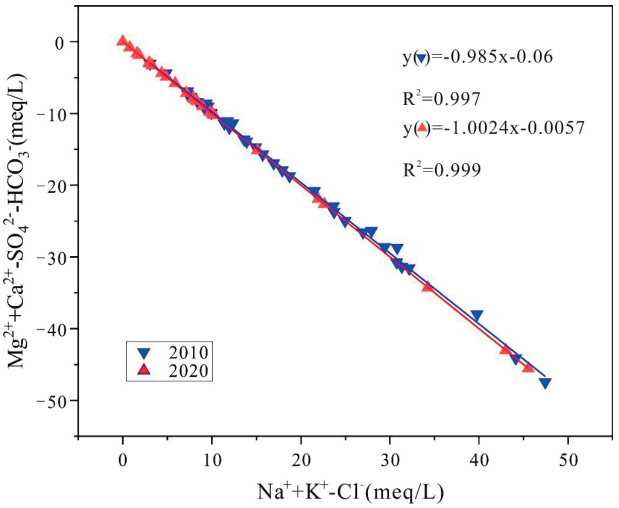

Fig. 7. Cation exchange degree of the limestone water before and after grouting.

ion exchange with the surrounding rock. However, the content of calcium and magnesium in the cement is high, which increases the content of Ca^{2+} and Mg^{2+} in the limestone water, which is conducive to the positive reaction direction of cation exchange. Therefore, under the influence of the increase of Ca^{2+} and Mg^{2+} content and the reduction of residence time, the degree of cation exchange in limestone water is slightly enhanced after grouting in 2020, but the enhancement effect is not obvious.

Source of Hydrogeochemical Components

The proportion of main ions produced by weathering and leaching of rocks is fixed. Therefore, the formation and dominant factors of groundwater hydrogeochemical components can be revealed through the combination and proportion of different ions in groundwater [25]. In 2010 and 2020, the water sample points of the limestone water fall above the isoline γ (Cl^-+ SO_4^{2-}) / γ (HCO_3^-) = 2 (Fig. 8a), indicating that the ions in the limestone water mainly come from the dissolution of silicate, such as gypsum and feldspar. The dissolution of rock salt releases the same amount of Na^+ and Cl^-, and the ion concentration in groundwater under natural conditions γ (Na^++K^+) / γ (Cl^-) is about 1:1, it is commonly used γ (Na^++K^+) / γ (Cl^-) to explain the dissolution of rock salt in groundwater [26]. It can be seen from Fig. 8b) that the water sample points of the limestone water in 2010 all fall above the isoline γ (Na^++K^+) / γ (Cl^-) = 1, which indicates that rock salt dissolution is not the only source of Na^+, such as feldspar dissolution and cation exchange also affect γ (Na^++K^+) / γ (Cl^-) ratio [27]. In 2020, some water sample points fall below the isoline γ (Na^++K^+) / γ (Cl^-) = 1, the proportion of Cl^- content increases, which may be related to the weathering and dissolution of chlorinated minerals, but it does not rule out the possibility of artificial pollution of groundwater. As shown in Fig. 8c), most water sample points are distributed above the isoline γ (HCO_3^-) / γ (Ca^{2+}+Mg^{2+}) = 1, which indicates that carbonate dissolution is not the only source of HCO_3^-. For example, the dissolution of silicate minerals and feldspar dissolution will also release a certain amount of Na^+, K^+, HCO_3^-.

When the ratio of γ (Ca^{2+}+Mg^{2+}) / γ (HCO_3^-+SO_4^{2-}) is far less than 1, the ionic components in groundwater mainly come from sulfate dissolution; When the ratio of γ (Ca^{2+}+Mg^{2+}) / γ (HCO_3^-+SO_4^{2-}) is greater than 1, the ionic components in groundwater mainly come from carbonate dissolution. When it is close to 1, the ionic components in groundwater are affected by both carbonate dissolution and sulfate dissolution [28]. In 2010, the ratio of γ (Ca^{2+}+Mg^{2+}) / γ (HCO_3^-+SO_4^{2-}) of most water sample points is less than 1 (Fig. 8d), indicating that the ionic components in the limestone water are mainly affected by sulfate dissolution. Compared with 2010, the ratio of γ (Ca^{2+}+Mg^{2+}) / γ (HCO_3^-+SO_4^{2-}) is close to 1 in 2020, indicating that the ionic components in the limestone water are affected by both sulfate dissolution and carbonate dissolution. The ratio γ (Ca^{2+}+Mg^{2+}+HCO_3^-) / γ (SO_4^{2-}+Cl^-+Na^+) of ion concentration is close to 1 in groundwater (Fig. 8e), indicating that SO_4^{2-} mainly comes from gypsum dissolution. In 2010 and 2020, all water sample points of the limestone water fall below the isoline γ (Ca^{2+}) / γ (SO_4^{2-}) = 1 (Fig. 8f), which shows that SO_4^{2-} comes not only from the dissolution of gypsum, but also other sources. The limestone of Taiyuan Formation contains thin coal seams, rich in sulfide minerals dominated by pyrite. Combined with Fig. 8e) and Fig. 8f), it can be seen that the concentration of SO_4^{2-} in the limestone water is high, indicating that in addition to the dissolution of gypsum, some may come from the oxidation of pyrite and the dissolution of other sulfate minerals [29].

According to the above analysis, Na^+, K^+ and Cl^- in the limestone water in the study area mainly come from the dissolution of rock salt and some feldspar, and Ca^{2+} and Mg^{2+} mainly come from the dissolution of gypsum and dolomite. The high concentration of SO_4^{2-} in the limestone water is related to the dissolution of gypsum and pyrite oxidation.

Mineral Dissolution Balance

Saturation index (SI) is often used to characterize minerals' hydrogeochemical state and reaction process relative to groundwater [30]. When SI>0, a mineral is in a supersaturated state and precipitates from groundwater. When SI = 0, the dissolution or precipitation form of the mineral in groundwater is in dynamic equilibrium. When SI<0, the mineral is in unsaturated condition and dissolved in groundwater [31]. Therefore, PHREEQC software is used to evaluate the saturation index of the main minerals in the study area.

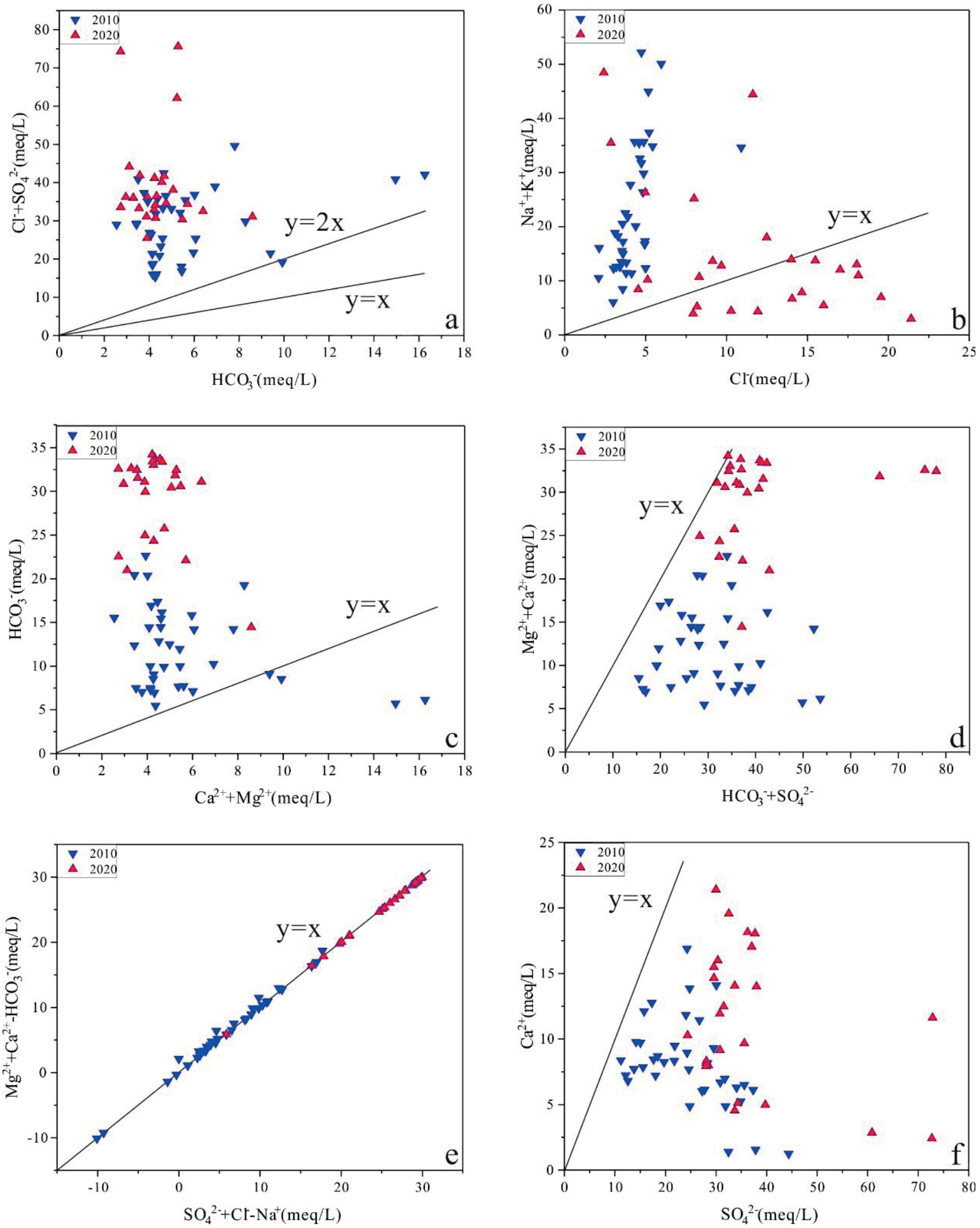

Fig. 8. Proportion diagram of ion combination in the limestone water before and after grouting.

The result shows that in 2010 (before grouting) and 2020 (after grouting), calcite and dolomite are in a supersaturation state (Fig. 9a,b), gypsum and rock salt are always in dissolution state (Fig. 9c,d), and the dissolution / precipitation state of minerals in each water sample point is the same. In 2010 and 2020, the calcite and dolomite saturation index at most water sample points is more significant than 0.5 (Fig. 9(a,b)), indicating that the saturation degree of these two minerals in the limestone water is always high. The saturation index of rock salt is less than -5 (Fig. 9d), indicating that groundwater has strong solubility in rock salt, and that rock salt dissolution is the primary source of cation Na^++K^+ in the limestone water [32]. The saturation index of gypsum in all water sample points is less than 0 (Fig. 9c), indicating that gypsum is in a dissolved state in the limestone water. The geological exploration results show that pyrite

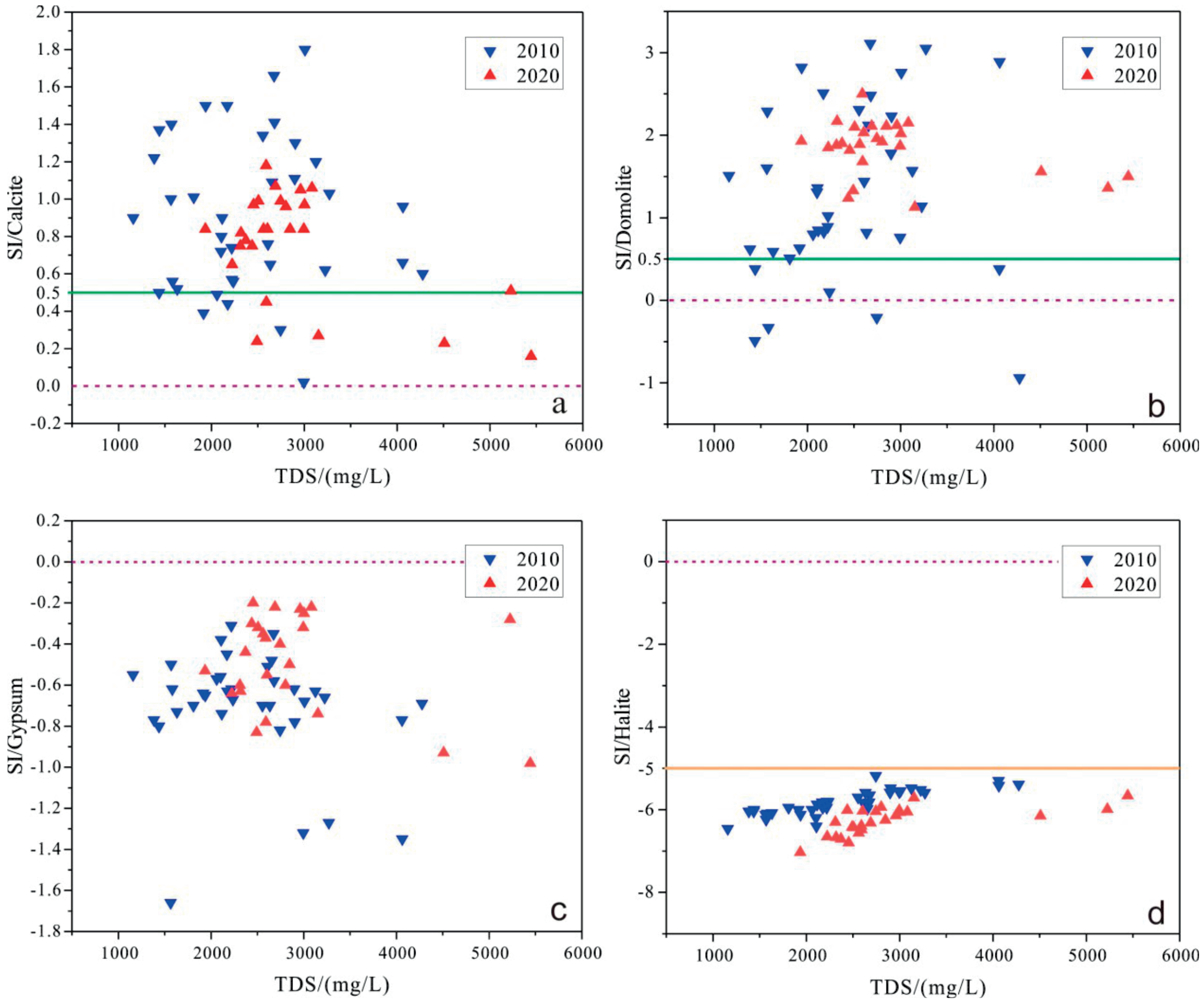

Fig. 9. Mineral saturation index before and after grouting.

is rich in thin coal seams. It is demonstrated again that the high SO_4^{2-} in the limestone water is related to the dissolution of gypsum and the oxidation of pyrite.

Conclusions

This study analyzed the conventional hydrochemistry of the limestone water before grouting in 2010, and after grouting in 2020 in Hengyuan coal mine, the main conclusions are as follows:

(1) In 2010 (before grouting) and 2020 (after grouting), the concentrations of anions and cations in the limestone water have the same change trend. The anion concentration from high to low is $SO_4^{2-}>HCO_3^->Cl^-$, the main anion is SO_4^{2-}, the cation concentration changes to $Na^++K^+>Ca^{2+}>Mg^{2+}$, and the main cation is Na^++K^+. The hydrogeochemical type is gradually transformed from Na^++K^+-SO_4^{2-} type to Mg^{2+}-SO_4^{2-} type and Ca^{2+}-SO_4^{2-} type. Except for SO_4^{2-}, the over standard rate of the limestone water in 2020 after grouting is lower than in 2010 before grouting.

(2) Compared with 2010 before grouting, in 2020, due to the mixing of grouting water, the balance between ions is broken in the limestone water, the correlation between most ions is weakened, and the relevant parameters of medium and above ions are reduced.

(3) Rock weathering and cation exchange are the main factors affecting the hydrogeochemical characteristics of the limestone water in the study area. Na^+, K^+ and Cl^- in the limestone water mainly come from the dissolution of rock salt, Ca^{2+} and Mg^{2+} mainly come from the dissolution of gypsum and dolomite, and the higher concentration of SO_4^{2-} is related to the dissolution of gypsum and the oxidation of pyrite.

(4) PHREEQC simulation shows that limestone water is affected by grouting in 2020, the mineral saturation index of gypsum, calcite, dolomite and rock salt is lower than that in 2010, and the leaching effect of minerals is weakened. Calcite and dolomite are in supersaturated state, while gypsum, rock salt and other soluble salts have been in dissolved.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. GUI H.R., SONG X.M., LIN M.L. Water-inrush mechanism research mining above karst confined aquifer and applications in North China coalmines. Arabian Journal of Geosciences, **10** (7), 180, **2017**.
2. GUI H.R., LIN M.L. Types of water hazards in China coalmines and regional characteristics. Natural Hazards, **84** (2), 1501, **2016**.
3. HUANG X.J., WANG G.C., LIANG X.Y., CUI L.F., MA L., XU Q.Y. Hydrochemical and stable isotope (δD and δ18O) characteristics of groundwater and hydrogeochemical processes in the Ningtiaota coalfield, Northwest China. Mine Water Environment, **37** (1), 119, **2017**.
4. JU Q.D., LIU Y., HU Y.B., WANG Y.Q., LIU Q.M., WANG Z.T. Hydrogeochemical evolution and control mechanism of underground multiaquifer system in coal mine area. Geofluids, **2020**, 1, **2020**.
5. GUO Y., WEI J.C., GUI H.R., ZHANG Z., HU M.C., FANG P., LI G.P., GAO C., WANG X. Hydrogeochemistry of water in coal measures during grouting treatment of Taoyuan mine, China. Ground Water, **59** (2), 256, **2020**.
6. LI Q.X. Drilling technology of directional drilled borehole for advance grouting reinforcement of seam floor. Coal Science and Technology, **42** (1), 138, **2014**.
7. GUO Y., GUI H.R., WEI J.C., NI J.M., CHENG R.F., PANG Y.C., ZHANG Z., HONG H., HU M.C., CUI Y.L., LIANG Z., LI J., CHEN J.Y., LI C. Mechanism of water rock interaction in coal measure sandstone aquifer disturbed by grouting engineering: A case study of Taoyuan Coal Mine. Coal Geology & Exploration, **49** (1), 232, **2021**.
8. SEFIE A., ARIS A.Z., RAMLI M.F., NARANY T.S., SHAMSUDDIN M.K.N., SAADUDIN S.B., ZALI M.A. Hydrogeochemistry and groundwater quality assessment of the multilayered aquifer in Lower Kelantan Basin, Kelantan, Malaysia. Environmental Earth Sciences, **77** (10), 397, **2018**.
9. LIU J., WANG H., JIN D.W., XU F., ZHAO C.H. Hydrochemical characteristics and evolution processes of karst groundwater in Carboniferous Taiyuan formation in the Pingdingshan coalfield. Environmental Earth Sciences, **79** (6), 151, **2020**.
10. JIANG B. Research on advanced regional governance technology for thin layer high-pressure limestone water hazard in coal floor. China Energy and Environmental Protection, **41** (7), 63, **2019**.
11. ZHANG T., HE J., LI J.J., CAO Y.T., GONG L., LIU J.W., BIAN C., CAI Y.M. Major ionic features and possible controls in the groundwater in the Hamatong River Basin. Environmental Science, **39** (11), 4981, **2018**.
12. LIU J., JIN D.W., WANG T.T., GAO M., YANG J., WANG Q.M. Hydrogeochemical processes and quality assessment of shallow groundwater in Chenqi coalfield, Inner Mongolia, China. Environmental Earth Sciences, **78** (12), 347, **2019**.
13. ZHOU J.X., DING Y.J., ZENG G.X., WU J.K., QIN J. Major ion chemistry of surface water in the upper reach of Shule River Basin and the possible controls. Environmental Science, **35** (9), 3315-, **2014**.
14. WANG L.H., DONG Y.H., XU Z.F., QIAO X.J. Hydrochemical and isotopic characteristics of groundwater in the northeastern Tennger Desert, northern China. Hydrogeology Journal, **25** (8), 2363, **2017**.
15. YU D., ZHOU J.L., WEI X., CHEN J.S., ZHANG J., AIKELAMU A. Analysis of chemical characteristics and evolution of phreatic water in Western Kashgar Prefecture, Xinjiang. Environmental Chemistry, **40** (8), 1, **2021**.
16. LI P.Y., WU J.H., QIAN H. Assessment of groundwater quality for irrigation purposes and identification of hydrogeochemical evolution mechanisms in Pengyang County, China. Environmental Earth Sciences, **69** (7), 2211, **2012**.
17. WU C., WU X., QIAN C., ZHU G. Hydrogeochemistry and groundwater quality assessment of highfluoride levels in the Yanchi endorheic region, Northwest China. Applied Geochemistry, **98**, 404, **2018**.
18. GAN Y.Q., ZHAO K., DENG Y.M., LIANG X., MA T., WANG Y.X. Groundwater flow and hydrogeochemical evolution in the Jianghan Plain, central China. Hydrogeology Journal, **26** (5), 1609, **2018**.
19. LI P.Y., WU J.H., TIAN R., HE S., HE X.D., XUE C.Y., ZHANG K. Geochemistry, hydraulic connectivity and quality appraisal of multilayered groundwater in the Hongdunzi coal mine, Northwest China. Mine Water and the Environment, **37** (2), 222, **2018**.
20. LI P.Y., WU J.H., QIAN H., LYU X.S., LIU H.W. Origin and assessment of groundwater pollution and associated health risk: a case study in an industrial park, northwest China. Environmental Geochemistry and Health, **36** (4), 693, **2014**.
21. LI P.Y., TIAN R., LIU R. Solute geochemistry and multivariate analysis of water quality in the Guohua phosphorite mine, Guizhou Province, China. Exposure and Health, **11** (2), 81, **2018**.
22. GUAN L.S., GUI H.R., ZHAO H.H., WANG M.C., YU H., FANG H.X. Nitrogen source analysis and health risk assessment in goaf water of Kouquangou mining area, Datong, China. Fresenius Environmental Bulletin, **29** (12), 10346, **2020**.
23. XIAO J., JIN Z.D., WANG J., ZHANG F. Hydrochemical characteristics, controlling factors and solute sources of groundwater within the Tarim River Basin in the extreme arid region, NW Tibetan Plateau. Quaternary International, **380**, 237, **2015**.
24. GAO H.Y., YAO D.X., XU P.Y. Analysis on water sources of watery zone in No. II6117 coal mining face in Liuqiao No. 2 mine. Coal Science and Technology, **40** (5), 100, **2012**.
25. XING.L.N., GUO H.M., ZHAN Y.H., Groundwater hydrochemical characteristics and processes along flow paths in the North China Plain. Journal of Asian Earth Sciences, **70-71**, 250, **2013**.
26. ROGELIO L.R., ERNESTO P.Z., THOMAS H., JURGEN M. Investigation of the geochemical evolution

of groundwater under agricultural land: A case study in northeastern Mexico. Journal of Hydrology, **521**, 410, **2015**.

27. ZHU G., WU X., GE J.P., LIU F., ZHAO W.G., WU C. Influence of mining activities on groundwater hydrochemistry and heavy metal migration using a self-organizing map (SOM). Journal of Cleaner Production, **257**,120664, **2020**.
28. LI Z.H., WANG G.C., WANG X.S., WAN L., SHI Z.M., WANKE H., UUGULU S., UAHENGO C.I. Groundwater quality and associated hydrogeochemical processes in Northwest Namibia. Journal of Geochemical Exploration, **186**, 202, **2018**.
29. WANG M.C., GUI H.R., HU R.J., ZHAO H.H., LI J., YU H., FANG H.X. Hydrogeochemical characteristics and water quality evaluation of carboniferous Taiyuan formation limestone water in Sulin mining area in Northern Anhui, China. International Journal of Environmental Research and Public Health, **16** (14), 2512, **2019**.
30. HUANG H., CHEN Z.H., WANG T., ZHANG L., ZHOU G.M., SUN B.T., WANG Y. Characteristics and processes of hydrogeochemical evolution induced by long-term mining activities in karst aquifers, southwestern China. Environmental Science and Pollution Research, **26** (29), 30055, **2019**.
31. ZHANG X.B., LI X., GAO X.B. Hydrochemistry and coal mining activity induced karst water quality degradation in the Niangziguan karst water system, China. Environmental Science and Pollution Research, **23** (7), 6286, **2015**.
32. SINGH C.K., KUMAR A., SHASHTRI S., KUMAR A., KUMAR P., MALLICK J. Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India. Journal of Geochemical Exploration, **175**, 59, **2017**.