



Quality Assessment and Hydrogeochemical Characteristics of Groundwater from Coal Bearing Aquifer in Sunan Coal Mine, Anhui Province, China

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ABSTRACT

Major ion concentrations were analysed for twenty eight groundwater samples collected from coal bearing aquifer in Sunan coal-mining area, Anhui Province, China. The conventional graphical and multivariate statistical approaches were used to discuss the geochemical characteristics, ions source and hydrogeochemical process of groundwater. Moreover, the applicability of groundwater is also evaluated based on a series of indexes. The results showed that the groundwater samples are mainly featured alkaline in nature, with the high value of TDS ranging from 860 to 5431 mg/L. The concentration of Cl⁻ is low comparing with the concentrations of SO₄²⁻ and HCO₃⁻; otherwise, the cations are mainly composed of Na⁺+K⁺ and Ca²⁺. Therefore, the hydrochemical types of groundwater samples are mainly divided into Na-HCO₃ and Na-SO₄ types. The dissolution of dolomite, evaporation and weathering of feldspar are the main hydro-geochemical processes, which contribute most ions to groundwater. The groundwater samples could not meet the demand of drinking water, comparing with the standard of WHO. Especially, all the groundwater samples are sealed for irrigation, with the higher values of RSC and SAR.

INTRODUCTION

Groundwater, being the most important freshwater storage, plays a key role at present. Especially in the North China Plains, the surface water storage problem becoming serious, and exploration of groundwater is the main water supply for agricultural, domestic and industrial use. The formation and evolution of groundwater is affected by such factors as physical, chemical and biological conditions. Moreover, the characters of surrounding rock could change the chemical composition and the quality of groundwater through water-rock interaction over a long period of time. Thus, the studies on the hydro-geochemistry and its geological significance of groundwater are necessary for understanding the geochemical characteristics of groundwater and its applicability.

Previous studies showed that hydro-geochemical research could contribute to the understanding of groundwater quality, ions source and its formation process (Kumar et al. 2009, Ramkumar et al. 2013). So many studies focused on the groundwater quality, hydro-geochemical process and anthropogenic influences on the groundwater system had been completed (Srinivas et al. 2014), for better exploitation and utilization of groundwater. In addition, deep groundwater in coal mine area could be a threat for the coal mining exploration safely. So, many investigations on major ions, rare earth elements, stably isotopes of deep

groundwater have been carried out in coal mine area. Taking for instance, studies about discriminate the source of inrush water to avoid the mining accident had been accomplished in northern Anhui Province, China (Chen et al. 2014). However, the studies about quality evaluation of deep groundwater are limited. Water quality evaluation is one of the most important aspects in deep groundwater analysis, what is always used as a basis to talk about utilizing groundwater.

The purpose of this study is to discuss the geochemical characteristics of deep groundwater collected from coal bearing aquifer in Sunan Coal mine, Anhui Province, China, which can form a basis to evaluate the quality of groundwater and reveal the influenced factors of the groundwater, using hydrochemical and multivariate statistical methods. The results would be used for making sustainable groundwater development schemes and understanding the applicability of deep groundwater.

MATERIALS AND METHODS

The Sunan coal-mining district, belonging to Huaibei mining area, was mainly constituted by five coal mines (Qidong coal, Qinan coal, Qianyingzi coal, Taoyuan coal and Longwangmiao coal), which is situated in north Anhui Province (Fig. 1). The region has a warm temperate monsoon climate with an annual temperature of 14.6°C. The average annual precipitation and evaporation in the area are 867.0

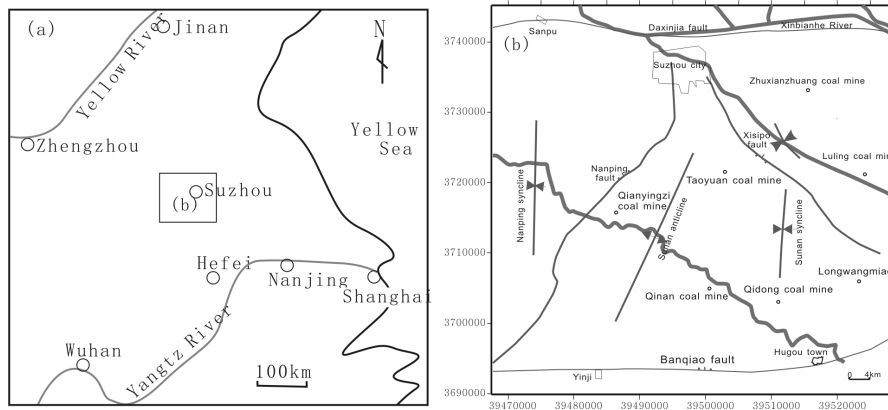


Fig. 1: Location of the study area.

and 832.4mm, respectively. Groundwater is the main water supply source for drinking, irrigation and industry, for the surface water is scarce. Carboniferous and Permian are the coal-bearing formations with thickness more than 1300m in Sunan coal-mining area. Previous studies showed that Quaternary aquifer, Coal bearing aquifer and Limestone aquifer are the main aquifers in the area (Gui & Chen 2007). The Quaternary aquifer is mainly constituted by yellow mudstone, sandstone and conglomerate, with a depth between 280-300m. The coal bearing aquifer is featured by mudstone, sandstone and coal bed, with a depth ranging from 300 and 700m. Limestone aquifers are mainly composed of limestone with clastic rocks, which belong to Taiyuan formation and Ordovician.

This study focused on the geochemical characteristics of groundwater from coal bearing aquifer in Sunan coal-mining district, Anhui Province. Twenty eight groundwater samples were analysed for major ions, which were collected from limestone aquifer in five coal mines. Water samples were collected via drainage holes in alleys, and then filtered through 0.45 mm pore-size membrane and collected into polyethylene bottles that had been cleaned using trace element clean procedures.

Major ion analysis was done in the analysis testing center of the Department of Coal Geology of Anhui province, China. K^+ and Na^+ was analysed by atomic absorption spectrometry, SO_4^{2-} and Cl^- by ion chromatography, Ca^{2+} and Mg^{2+} by EDTA titration, and alkalinity by acid-based titration. A Piper diagram was used and calculations done about the carbonate equilibrium, total dissolved solids (TDS) content, density, conductivity and hardness using Aqqa software, while statistical analysis of the sample data was carried out with SPSS software (version 19). Groundwater quality was assessed based on chemical comparison with drinking water standard from World Health Organization (WHO 1993) and

a series of indices like residual sodium carbonate (RSC), sodium adsorption ratio (SAR) and percent sodium (Easton 1950, USSL 1954).

RESULTS AND DISCUSSION

Descriptive statistics: The analytical results for groundwaters samples collected from the limestone aquifer are listed in Table 1. In general, the pH values of groundwater varied from 6.8 to 9.1, with an average value 7.9, which indicates that most of groundwater samples are alkaline in nature. The amount of total dissolved solids (TDS) of groundwater ranges from 860 to 5431 mg/L, with an average of 2119 mg/L. The anionic concentrations (Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-}) in the groundwater range from 144.4 to 407.4, 2.9 to 2837.6, 290.8 to 860.9 and 0 to 129.4 mg/L, with average values of 249.4, 688.1, 519.6 and 25.4 mg/L, respectively. The cationic concentrations (K^+Na^+ , Ca^{2+} and Mg^{2+}) range from 171.7 to 1718.0, 3.2 to 384.7 and 3.4 to 122.0 mg/L, with average values of 464.6, 134.9 and 56.2, respectively. The hydrochemical type of groundwater samples are mainly divided into $Na-HCO_3$ and $Na-SO_4$ types, with few samples be $Ca-SO_4$ type.

In order to obtain more information about the hydrochemical characters, the groundwater geochemical data were plotted on a Piper diagram (Fig. 2). Almost all the groundwater samples are characterized by low concentration of Cl^- , higher content of SO_4^{2-} and HCO_3^- , and the cations are constituted mainly by K^+Na^+ , with little Ca^{2+} and Mg^{2+} .

Quality evaluation: In order to further understand the applicability of the groundwater, the analytical results of groundwater samples were compared with the WHO standard (WHO 1993). The results showed that the average concentration of magnesium (56.2 mg/L), calcium (134.9 mg/L) and pH values could meet the demand of WHO, however,

Table 1: Composition of major ions in groundwater samples collected from coal bearing aquifer in Sunan coal mine (The values are in mg/L except pH).

| No. | K ⁺ +Na ⁺ | Ca ²⁺ | Mg ²⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | CO ₃ ²⁻ | pH | Water type | TDS |
|------|---------------------------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|-------------------------------|-----|----------------------|------|
| QYZ1 | 652.3 | 4.8 | 3.8 | 181.7 | 375.8 | 738.6 | 115.8 | 8.5 | HCO ₃ -Na | 1957 |
| QYZ2 | 582.5 | 3.2 | 3.4 | 282.2 | 4.5 | 817.1 | 129.4 | 8.9 | HCO ₃ -Na | 1693 |
| QYZ3 | 1178.0 | 24.5 | 4.8 | 199.3 | 1688.0 | 736.3 | 0.0 | 8.1 | SO ₄ -Na | 3831 |
| QYZ4 | 1718.0 | 26.1 | 11.5 | 149.9 | 2837.6 | 687.8 | 70.4 | 8.6 | SO ₄ -Na | 5431 |
| QYZ5 | 543.7 | 6.3 | 3.8 | 188.7 | 125.1 | 854.0 | 70.4 | 8.3 | HCO ₃ -Na | 1721 |
| QYZ6 | 471.8 | 5.5 | 3.8 | 146.4 | 21.4 | 860.9 | 72.7 | 8.7 | HCO ₃ -Na | 1509 |
| QYZ7 | 524.3 | 16.6 | 19.2 | 407.4 | 8.6 | 817.1 | 0.0 | 8.0 | HCO ₃ -Na | 1793 |
| QYZ8 | 949.9 | 102.1 | 87.4 | 287.5 | 1899.5 | 290.8 | 34.1 | 8.4 | SO ₄ -Na | 3617 |
| QD1 | 405.3 | 50.8 | 34.7 | 227.1 | 427.7 | 469.7 | 0.0 | 7.5 | SO ₄ -Na | 1615 |
| QD2 | 352.6 | 84.0 | 56.9 | 230.0 | 496.4 | 395.9 | 0.0 | 8.3 | SO ₄ -Na | 1615 |
| QD3 | 382.9 | 5.5 | 10.5 | 187.8 | 21.8 | 545.9 | 92.7 | 9.1 | HCO ₃ -Na | 1154 |
| QD4 | 939.8 | 21.4 | 16.8 | 230.2 | 1233.6 | 617.9 | 29.8 | 8.8 | SO ₄ -Na | 3059 |
| QN77 | 242.5 | 8.9 | 12.2 | 144.4 | 2.9 | 449.6 | 18.9 | 8.5 | HCO ₃ -Na | 860 |
| QN78 | 347.1 | 40.3 | 33.2 | 213.7 | 417.4 | 315.0 | 0.0 | 7.8 | SO ₄ -Na | 1366 |
| TY3 | 292.3 | 356.9 | 122.0 | 356.7 | 1118.7 | 439.8 | 0.0 | 7.4 | SO ₄ -Ca | 2686 |
| TY4 | 171.7 | 367.8 | 104.1 | 341.0 | 885.8 | 391.5 | 0.0 | 6.9 | SO ₄ -Ca | 2261 |
| TY5 | 266.2 | 384.7 | 118.9 | 339.3 | 118.0 | 369.3 | 0.0 | 6.8 | Cl-Ca | 1596 |
| TY6 | 273.5 | 373.7 | 108.7 | 327.1 | 1122.8 | 422.9 | 0.0 | 6.9 | SO ₄ -Ca | 2628 |
| TY7 | 263.0 | 350.1 | 119.4 | 324.4 | 1129.4 | 368.8 | 0.0 | 7.8 | SO ₄ -Ca | 2555 |
| TY8 | 270.6 | 358.6 | 117.4 | 330.5 | 1144.3 | 378.2 | 0.0 | 7.9 | SO ₄ -Ca | 2599 |
| TY9 | 246.2 | 335.0 | 114.1 | 312.2 | 1013.4 | 425.2 | 0.0 | 6.9 | SO ₄ -Ca | 2446 |
| QD5 | 384.0 | 48.3 | 50.8 | 221.4 | 395.6 | 506.3 | 15.1 | 8.4 | HCO ₃ -Na | 1606 |
| QD6 | 274.3 | 167.2 | 85.3 | 247.7 | 661.0 | 398.7 | 0.0 | 7.4 | SO ₄ -Na | 1834 |
| QD7 | 204.2 | 203.4 | 97.0 | 244.2 | 658.6 | 390.5 | 0.0 | 7.1 | SO ₄ -Ca | 1980 |
| QD8 | 205.6 | 201.2 | 102.1 | 249.4 | 662.7 | 398.7 | 0.0 | 7.4 | SO ₄ -Ca | 1819 |
| QD9 | 349.4 | 4.7 | 9.4 | 161.4 | 4.1 | 630.2 | 37.1 | 8.5 | HCO ₃ -Na | 1159 |
| QD10 | 307.2 | 24.4 | 21.4 | 202.7 | 129.7 | 430.1 | 26.1 | 8.4 | HCO ₃ -Na | 1116 |
| QD11 | 210.1 | 200.0 | 100.8 | 249.5 | 662.7 | 401.1 | 0.0 | 7.1 | SO ₄ -Ca | 1824 |

Table 2: Correlation matrix of major ions for coal bearing aquifer groundwater in Sunan coal mine.

| Parameter | Na ⁺ +K ⁺ | Ca ²⁺ | Mg ²⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | CO ₃ ²⁻ |
|---------------------------------|---------------------------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|-------------------------------|
| Na ⁺ +K ⁺ | 1.00 | | | | | | |
| Ca ²⁺ | -0.46 | 1.00 | | | | | |
| Mg ²⁺ | -0.49 | 0.94 | 1.00 | | | | |
| Cl ⁻ | -0.33 | 0.72 | 0.69 | 1.00 | | | |
| SO ₄ ²⁻ | 0.65 | 0.26 | 0.27 | 0.10 | 1.00 | | |
| HCO ₃ ⁻ | 0.47 | -0.61 | -0.75 | -0.32 | -0.19 | 1.00 | |
| CO ₃ ²⁻ | 0.39 | -0.56 | -0.64 | -0.46 | -0.17 | 0.66 | 1.00 |

the other parameters are all exceed the boundary value. Especially, almost all the TDS values of groundwater samples are higher than 1000 mg/L, what suggested that the groundwater is not suitable for drinking before processed.

The higher concentration of Na⁺ in groundwater could affect the crop growth, when used for irrigation. The irrigation usability of groundwater is usually evaluated by few index values, such as residual sodium carbonate (RSC) and sodium adsorption ratio (SAR) (USSL 1954), what could be calculated by the formula $RSC = HCO_3^- + CO_3^{2-} - Ca^{2+} - Mg^{2+}$ and $SAR = Na^+ / \sqrt{((Ca^{2+} + Mg^{2+})/2)}$ respectively. Previous study showed three degrees could be divided basing the

value RSC: perfect (<1.5), permissible (1.5-2.5) and unsuitable (>2.5) (USSL 1954). The calculated results showed that the groundwater samples collected from coal bearing aquifer in the area could not used for irrigation, for the average value of RSC 4.4. But, the spatial distribution of RSC in Sunan coal-mining area has differences. We can say that the groundwater samples collected from Qianyingzi coal mine are unsuitable for irrigation with the higher RSC value, otherwise, the other groundwater samples collected from coal mine are permissible, with the lower RSC value, especially in the Taoyuan coal mine.

Four groundwater types could be discriminated by SAR

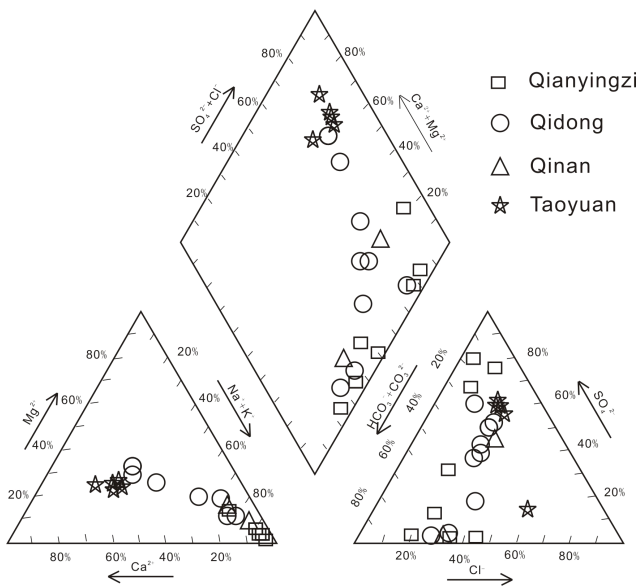


Fig. 2: Piper diagram of groundwater from coal bearing aquifer in Sunan coal mine

as follows: perfect (<10), good (10-18), sealed (18-26) and unsuitable (>26). And the calculated results about SAR also indicated that the groundwater samples are sealed for irrigation, with the average value 18.8. And the results could be supported by the previous analysis.

Multivariate statistical analysis: Previous studies showed multivariate statistical analysis was an efficient way to display complex relationships among many variables and their roles (Chen et al. 2013). In order to reveal the relation between the parameter, the multivariate methods of statistical analysis (PCA and CA) were obtained in the study, the results are present in Table 2 and Table 3.

It could be concluded that strong positive correlation between Mg^{2+} and Ca^{2+} was observed for the correlation matrix 0.94, what could suggest that dissolution of dolomite is existed in the hydro-geochemical process. The positive correlations also exist between Ca^{2+} - Cl^- , Na^+ + K^+ - SO_4^{2-} , and Mg^{2+} - Cl^- with the correlation matrix 0.72, 0.65 and 0.69. All this should indicate that weathering of feldspar also contributes cations to groundwater, and the weathering process was caused by sulphuric acid, for there is much sulphur dioxide present in coal bed.

The rotated PCA loadings are presented in Table 3, what could be usually used for obtaining the detailed statistical information, three principal components (PC) were emerged, with more than 89.9% of cumulative variance. The parameter of Cl^- , Ca^{2+} and Mg^{2+} are all have high value in PC1, with the value 0.74, 0.91 and 0.96, especially the values of Ca^{2+} and Mg^{2+} are very high, which revealed that the factor

is the dissolution of dolomite and evaporite dissolution. The aquifer rock could provide the Ca^{2+} and Mg^{2+} , which is composed of limestone and dolomite. Thus, the PC1 is the major factor for the ions form in groundwater samples. PC1 accounts for 55.84% of total variance, with the initial eigen value of 3.91. PC2 accounts for 23.01% of total variance, with the high loading for Na^+ + K^+ , and SO_4^{2-} . It suggested that the weathering process of feldspar by sulphuric acid is existed, and the influenced factor is explained by PC2. PC3 accounts 11.05% of variance, indicating the process of feldspar weathering by the carbonate acid as the HCO_3^- and CO_3^{2-} have high values.

In summary, the dissolution of dolomite, limestone and weathering of feldspar are the main hydrochemical processes, otherwise, the carbonate acid process also existed.

Ions source: Hydrogeochemistry of groundwater is always influenced by such factors like recharging and water-rock interaction, and the degree of interaction being controlled by the residence time within the aquifer (Gaillardet et al. 1999). Evaporite dissolution, carbonate dissolution and silicate weathering are three general processes contributing to the generation of solutes in groundwater. As can be seen from Fig. 3, the groundwater in the area is mainly controlled by silicate weathering and evaporite dissolution.

The dissolution of halite in groundwater releases equal concentrations of Na^+ and Cl^- into solution, and mechanisms by which salinity is acquired in groundwater systems can be identified using the Na-Cl relationship (Sami et al. 1992). Therefore, the ratio Na^+/Cl^- would be represented by a line with a value of Na^+/Cl^- close to one, if the Na^+ and Cl^- present came solely from halite dissolution. However, Fig. 3C presented the different characteristics, with the Na^+/Cl^- ratios of some samples higher than one. This could indicate an additional source of Na^+ , what could be thought as the weathering of silicate minerals, such as feldspar. This view would be supported by that groundwater aquifer is constituted by some silicate mineral(s). And the weathering process often along with increased HCO_3^- concentrations, what is presented in Fig. 3D.

The most probable source of Ca^{2+} and Mg^{2+} in groundwater can be determined using the equation $(Ca^{2+}+Mg^{2+})/HCO_3^-$, in which all of the chemical species are represented by their concentrations expressed in mg/L. The ratio would be about 0.5, if the Ca^{2+} and Mg^{2+} in the groundwater were derived only by the dissolution of carbonates in the aquifer or the weathering of pyroxene and amphibole (Meybeck et al. 1987). The ratios of almost all the groundwater samples are above 0.5 (Fig. 3E), what suggests that the balance between the concentrations of $Ca^{2+}+Mg^{2+}$ and HCO_3^- must have changed somehow. The strong positive

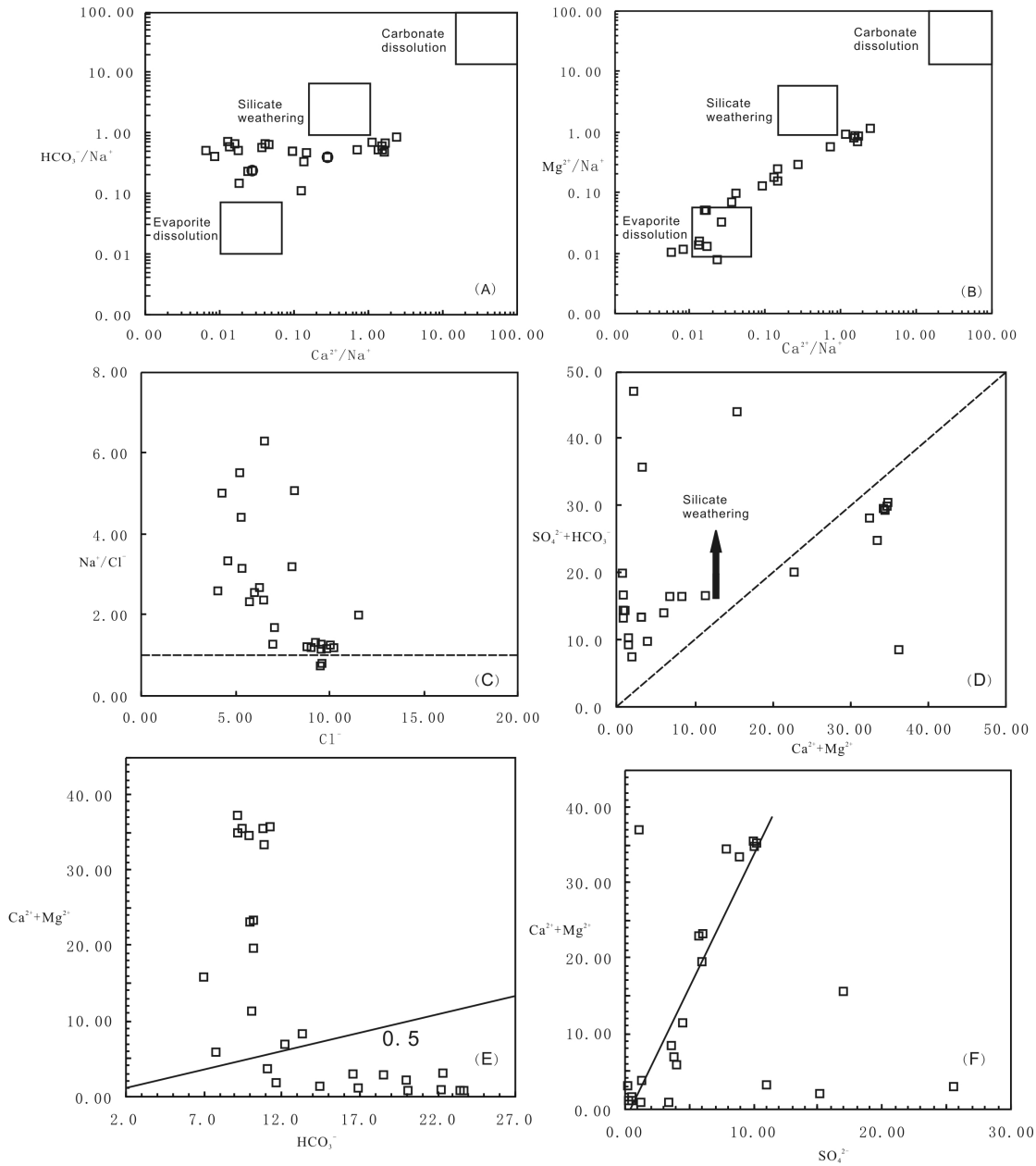


Fig.3: Plots of major ions of Limestone aquifer in Sunan mining area.

correlation between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and SO_4^{2-} shown in Fig. 3F, suggests that sulphate dissolution could be an important source of the extra $\text{Ca}^{2+} + \text{Mg}^{2+}$. On the other hand, the low $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ ratio seen in a few groundwater samples could be caused by $\text{Ca}^{2+} + \text{Mg}^{2+}$ depletion arising from cation exchange.

CONCLUSIONS

Twenty eight groundwater samples collected from coal bear-

ing aquifer in Sunan coal-mining area were tested, and the analytical results were analysed by conventional graphical and multivariate statistical approach.

1. The groundwater samples are mainly featured alkaline in nature, with the high value of TDS ranging from 860 to 5431 mg/L. Compared with the concentrations of SO_4^{2-} and HCO_3^- , the content of Cl is low for almost all groundwater samples, whereas the content of $\text{Na}^+ + \text{K}^+$ and Ca^{2+} are higher than Mg^{2+} . The hydrochemical type

Table 3: Variance explained and component matrixes for coal bearing groundwater in Sunan coal mine.

| Parameter | PC1 | PC2 | PC3 |
|---------------------------------|-------|-------|-------|
| Na ⁺ +K ⁺ | -0.58 | 0.79 | 0.05 |
| Ca ²⁺ | 0.91 | 0.11 | 0.23 |
| Mg ²⁺ | 0.96 | 0.11 | 0.06 |
| Cl ⁻ | 0.74 | 0.05 | 0.59 |
| SO ₄ ²⁻ | 0.16 | 0.98 | -0.07 |
| HCO ₃ ⁻ | -0.80 | -0.02 | 0.50 |
| CO ₃ ²⁻ | -0.77 | -0.06 | 0.34 |
| Initial eigen value | 3.91 | 1.61 | 0.77 |
| Percentage of variance | 55.84 | 23.01 | 11.05 |
| Cumulative % of variance | 55.84 | 78.85 | 89.90 |

of groundwater samples are mainly divided into to Na-HCO₃ and Na-SO₄ types, with few samples be Ca-SO₄ type.

2. The dissolution of dolomite, limestone and evaporite weathering of feldspar are the main hydro-geochemical processes, which contribute most cations to groundwater.
3. The groundwater samples could not meet the demand of drinking water, comparing with the standard of WHO. Especially, all the groundwater samples are sealed for irrigation, with the higher values of RSC and SAR.

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