Study on the hydro-chemistry process after mixing between water and rocks
Xiuyan Jing, Hongbin Yang and Na Wang

ABSTRACT

The chemical evolution of groundwater has received close attention from hydro-geologists. Northwest China largely consists of arid and semi-arid regions, where surface water and groundwater frequently exchange with each other, and where the mixing and water-rock interactions significantly affect the direction of water quality evolution. Based on experimental simulation, this paper investigates the interactions among the Yellow River water, groundwater and rocks in Yinchuan. The study found that when groundwater is mixed with the Yellow River water, the Yellow River water has a certain dilution effect on the hydro-chemical composition of groundwater; however, this effect is not simply diluted by proportion for no reaction between irons, but a portion of calcium, sulfur, and carbonate form precipitates. After mixing of the Yellow River water, groundwater and rocks, the pH increased, and the carbon dioxide system reached equilibrium again. In addition, \( CO_3^{2-} \) was produced. While \( Na^+ \) increase was mainly due to dissolution, \( SO_4^{2-} \) decrease was because of precipitation. The precipitation or dissolution of \( Ca^{2+}, Mg^{2+}, \) and \( CO_3^{2-} \) mainly depended on the mixing ratio between groundwater and river water, which suggested the reversible behavior of the dissolution-precipitation of carbonate minerals.

Key words | hydro-geochemistry, mixing, water-rock interaction

INTRODUCTION

The knowledge of spatial-temporal distribution and formation of the groundwater quality along with the factors influencing the quality is the key to understanding the circulation, evolution, and ecological effects of groundwater. At present, the research on the forming mechanism of hydro-geochemistry has basically focused on several aspects, including provenance, hydro-geochemical action, migration theory, and numerical simulation. Many studies have indicated that the chemical characteristics are a significant attribute to the regime of the groundwater. Especially, the features of hydro-chemical composition often reveal intense zoning by the hydro-geological units from mountainous to flatlands (Shen & Wang 2002; Shen et al. 2012).

From recharge through runoff to the discharge area, in hydro-geological reservoir structures, various sections differ to varying degrees in terms of water-bearing stratum rocks, water abundance, infiltration rate, cyclic alternation, and hydro-geochemical environment. Consequently, the same region may present different hydro-chemical characteristics. Several studies (Frappé et al. 1984; Hem 1989; Cao & Hu 1994; Shen & Wang 2002; Cao et al. 2009; Shen et al. 2012) have investigated the water–rock interactions of water-bearing strata, and found that the chemical formation process of groundwater includes lixiviation, alternate adsorption of cations, decarbonization, desulfation, evaporation and concentration, and mixing. The existence of these processes has been confirmed using comprehensive techniques, such as water-rock test (Dang & Hou 1995; Wu et al. 1996; Négrel et al. 2010; He et al. 2011; Lassaad 2011), isotope geochemistry method.
(Petelet et al. 2007; Négrel et al. 2010), thermodynamic method (Schofield & Jankowski 2004; Karro et al. 2004; Jalali 2005; Wang et al. 2007; Tyagi et al. 2009), and hydro-geochemical survey (Li et al. 2000; Litaor et al. 2010; Monjerezi et al. 2011). For example, Carlyle et al. (2004) adopted an indoor test to measure cation exchange capacity and selection coefficient, while Yang et al. (2011) investigated the existence of evaporation through isotope and ion ratios. Various water–rock interactions play a vital role in the evolution of the hydro-chemical components of groundwater, in addition to providing horizontal or vertical zonation characteristics. Anbeek (1993) introduced geochemistry and microbial action to classify water-bearing strata into high-iron belt and low-iron belt along water flow paths. Lou & Jin (2006) divided five types of hydro-chemical profile units, which are mainly mudstone and clay, in the Songliao Basin China, in the vertical direction from shallow to deep strata as follows: (1) atmospheric water downward infiltration and dilution belt, (2) near-surface evaporation and concentration belt, (3) mudstone compaction drainage and dilution belt (C1-filter pressing and concentration belt (C2), (4) clay mineral dehydration and dilution belt, and (5) percolation and concentration belt.

In general, the thermodynamic equilibrium theory is employed to explain water–rock interactions; however, hydro-chemical components are generally not in equilibrium in the natural environment. For example, in the natural system, the behaviors of minerals with a relatively low solubility, such as calcite, gypsum, halite, and fluorite, are generally reversible, and can easily reach an equilibrium within a short period of time. In contrast, for the majority of other minerals such as plagioclase, biotite, and silicate rock that have a significant influence on natural hydro-chemistry, it is very difficult for them to reach an equilibrium in the natural system (Glynn & Plummer 2005). This suggests that many geochemical processes are complicated nonlinear kinetic processes.

The Yinchuan Plain is a typical semi-arid and arid region in northwestern China, which experiences intense irrigation activities and an extreme blend of irrigation water and groundwater. Eighty percent of groundwater in the region comes from surface water, due to which the formation and zonation of groundwater in this region is critical (Zhang & Zhang 2010; Jing et al. 2014). The aims of this paper were to: (1) investigate the possible physical and chemical processes in various mixing processes, through simulating the interactions among groundwater, irrigation water, and water-bearing rocks via indoor test and (2) provide the theoretical basis for explaining the chemical formation of groundwater in this region.

MATERIALS AND METHODS

Sample collection and analysis

Sample collection

Samples were collected from the Yellow River and civil wells during August 2015. The groundwater samples were collected from an alluvial-proluvial plain of the recharge area, which has limited irrigation activities, while the river samples were taken from the Yellow River. Samples of groundwater were from civil wells with depths from about 3 to 5 m. The samples of groundwater were preserved in polyethylene bottles. The rock samples were collected from groundwater-bearing strata, 20 m away from the wells, through excavating the profile dominated by fine silt at a depth of 1.2–2 m. The rock samples were placed indoors for air drying, and ground and evenly blended for use later. Surface water samples were taken from the middle of the Yellow River.

Test analysis methods

In the mixing simulation test, analysis was conducted mainly on the hydro-chemical components of river water and groundwater, the mineral characteristics of rocks, and the soluble salts. The water sample analysis was carried out in accordance with the standard DZ/T 0064-1993, where ions like Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), SO\(_4\)\(^{2-}\), HCO\(_3\)\(^-\), and Cl\(^-\) were analyzed by the instrument ICP-AES (iCAP6300) at room temperature of 25 °C and humidity of 35%. Similarly, the soluble salts were analyzed for ions such as K\(^+\), Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4\)\(^{2-}\), Cl\(^-\), and HCO\(_3\)\(^-\) in accordance with the standard GB/T 1121-2006 using the ICP-AES (iCAP6300) at room temperature of...
25 °C and humidity of 35%. The X-ray diffraction semi-quantitative phase analysis was conducted by the powder X-ray diffractometer (D/MAX-2600) at a humidity of 40% and a temperature of 20 °C to investigate the mineral characteristics of rocks.

Test methods

Mixing between the Yellow River water and groundwater

The Yellow River water and groundwater were mixed by ratios of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, respectively, to prepare nine samples, each with a volume of 600 mL. The samples were placed in nine 650 mL polyethylene bottles, and blended. After 24 h, the samples were analyzed for eight hydro-chemical components; namely, pH, K⁺, Na⁺, Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻, and HCO₃⁻. The tested concentrations were compared against theoretically calculated concentrations to investigate the possible physical and chemical processes.

Mixing among the Yellow River water, groundwater, and rocks

The Yellow River water and groundwater were mixed at respective ratios of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 to prepare nine samples, each with a volume of 500 mL. Rock samples were added to the mixtures at a mass ratio of 5:1, and stirred. After 15 days, the concentrations of the same eight hydro-chemical components in the mixture samples were determined and compared with the theoretical values to identify any possible physical and chemical actions/processes.

Change in the interactions between the Yellow River water and rocks with time

The Yellow River water and rock mixtures at a mass ratio of 5:1 were prepared by mixing 600 mL of water sample with 100 g of rock sample. Nine parallel mixtures were prepared and stirred, and the samples were withdrawn in a sequence of 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d, 9 d, and 22 d. The samples were tested for the eight hydro-chemical components to monitor any change in the interactions between the Yellow River water and rocks with time.

Change in the interactions among the Yellow River water, groundwater, and rocks with time

The Yellow River water and groundwater were mixed at a ratio of 8:2, and followed by the addition of rocks at a mass ratio of 5:1 (total volume of water sample, 600 mL; total mass of air-dried rock sample, 100 g) to prepare nine parallel samples. The samples were withdrawn in a sequence of 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d, 9 d, and 22 d, to test the eight hydro-chemical components. The change in the interactions among the Yellow River water, groundwater, and rocks with time was continuously observed.

Data analysis

(1) Hydro-chemical types: The hydro-chemical types of groundwater were classified based on the main anion (or cation) exceeding 25% of total charge for cation (or anion) (Shen 1986).

(2) Theoretical calculation of concentration: The theoretically calculated concentration of a component in mixed water samples was calculated as follows:

$$C = \frac{V_1 \cdot C_1 + V_2 \cdot C_2}{V}$$

where $V_1$ = the volumes of Yellow River water, $V_2$ = the volumes of groundwater, $V$ = the volumes of mixing between the Yellow River water and groundwater, while $C_1$, $C_2$, and $C$ represent the theoretically calculated concentrations of the components in the Yellow River water, groundwater, and water mixture, respectively. When $C_{\text{measured}} \approx C$, there is no chemical interaction between the Yellow River water and groundwater, whereas $C_{\text{measured}} < C$ suggests that the components have been reduced from the mixture. After the addition of rock samples into the mixed water samples, $C_{\text{measured}} > C$ suggests that the components have entered into the mixture via rocks due to dissolution, while $C_{\text{measured}} < C$ suggests that the components have been reduced from the mixture due to rock adsorption or precipitation.
RESULTS

Chemical characteristics of groundwater, the Yellow River water, and rocks

The chemical characteristics of groundwater, the Yellow River water, and rocks are presented in Tables 1 and 2.

Physical and chemical characteristics of groundwater

The groundwater is colorless, odorless, and transparent (Table 1). It is also neutral, hard, and brackish as suggested by its pH, hardness, and total dissolved solids (TDS) being 7.71, 320 mg/L, and 1,835 g/L, respectively. The groundwater is Na–HCO₃·SO₄, in which the cation and anion concentration follows the order of Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ and HCO₃⁻ > SO₄²⁻ > Cl⁻ as per the respective geological and climatic conditions. The piedmont alluvial plain is characterized by a flat terrain, relatively shallow burial depth of groundwater (less than 3 m), dry climate, high evaporation (six times that of rainfall), frequent salt leaching on the earth's surface, and intense evaporation effect. A combined effect of these characteristics provides favorable environmental conditions for the enrichment of ions in groundwater and forms Na–HCO₃·SO₄ water type with a relatively high content of Na⁺ and medium-salinity water.

Chemical characteristics of the Yellow River water

The Yellow River water is neutral, hard, and brackish, and is Na · Ca · Mg–HCO₃, as shown in Table 1. Additionally, the ion content decreases in the following order: Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ and HCO₃⁻ > SO₄²⁻ > Cl⁻. Among the cations, Ca²⁺, Mg²⁺, and Na⁺ have relatively close concentrations, while HCO₃⁻ has a relatively higher concentration than those of Cl⁻ and SO₄²⁻. The main recharge source of the Yellow River is the atmospheric rainfall (Zhang & Zhang 2010). The flow of the river from upstream to downstream constantly dissolves riverbed rocks, resulting in the enrichment of various ions and giving rise to the formation of Na · Ca · Mg–HCO₃ water type with a relatively high-salinity water.

Mineral characteristics of rocks

The mineral facies of rock samples mainly consist of primarily aluminosilicates followed by carbonates (Table 2). Illite is rich in K, Na, Mg, and Fe, whereas chlorite is rich in Fe and Mg. Plagioclase is rich in Ca and Na and potassium feldspar is rich in K. During the weathering process, these rocks are dissolved, and converted into HCO₃⁻, Na⁺, Ca²⁺, Mg²⁺, and K⁺ in groundwater. As indicated by the analysis of soluble salts (Table 2), the order of anion and cation content; that is, HCO₃⁻ > SO₄²⁻ > Cl⁻ > CO₃²⁻ and

### Table 1 | Hydro-chemical constituent of groundwater and the Yellow River

<table>
<thead>
<tr>
<th>Location</th>
<th>pH</th>
<th>Ca²⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>K⁺ (mg/L)</th>
<th>Na⁺ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>TDS (g/L)</th>
<th>Hardness</th>
<th>Water type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>7.7</td>
<td>81.7</td>
<td>28</td>
<td>2.3</td>
<td>408</td>
<td>689</td>
<td>197</td>
<td>430</td>
<td>1,835</td>
<td>320</td>
<td>HCO₃·SO₄·Na</td>
</tr>
<tr>
<td>Yellow River</td>
<td>7.2</td>
<td>66.7</td>
<td>32</td>
<td>3.3</td>
<td>92</td>
<td>608</td>
<td>146</td>
<td>176</td>
<td>1,124</td>
<td>301</td>
<td>HCO₃·Na·Ca·Mg</td>
</tr>
</tbody>
</table>

### Table 2 | The rock mineral identification and the components of soluble salt

<table>
<thead>
<tr>
<th>Item</th>
<th>Rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral (%)</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>61</td>
</tr>
<tr>
<td>The components of soluble salt (mg · kg⁻¹)</td>
<td>Ca²⁺</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
</tr>
</tbody>
</table>
K⁺ > Mg²⁺ > Na⁺ > Ca²⁺, in the soluble salt components suggests that the components of rocks are consistent with soluble salt components.

**Mixing and water–rock interactions**

**Mixing between the Yellow River water and groundwater**

Table 3 presents the ion concentrations during the mixing between the Yellow River water and groundwater. The theoretical concentrations of Mg²⁺, K⁺, Na⁺, and Cl⁻ were approximately equal to their measured values, suggesting that these ions did not engage in any chemical reactions after the mixing. In contrast, the measured concentrations of SO₄²⁻ and Ca²⁺ were lower than their theoretical values, indicating that their concentrations were reduced in the mixture. As for HCO₃⁻, the measured concentrations were greater than the theoretical values for ratios of 1:9–3:7, and lower than the theoretical concentrations for ratios of 4:6–9:1. Thus, the concentration of HCO₃⁻ increased in the former scenario, while it decreased during the latter.

**Interactions among the Yellow River water, groundwater, and rocks**

The results of the interactions among the Yellow River water, groundwater, and rocks are shown in Table 4. The measured value of Cl⁻ was approximately equal to its theoretical concentration, suggesting that Cl⁻ components did not engage in any chemical interaction. The theoretical concentrations for K⁺, Na⁺, and CO₃²⁻ were lower than their measured values, indicating that their components had entered the mixture via rocks during dissolution. Similarly, the theoretical concentrations of SO₄²⁻ and HCO₃⁻ were higher than their measured values, suggesting that their components were reduced from the mixture due to rock adsorption or precipitation. The relationship between the theoretical and measured concentration of Ca²⁺ and Mg²⁺ varied depending on the differences in the mixing ratio of the Yellow River water and groundwater: When the ratio was 1:9–5:5, Ca²⁺ was adsorbed or precipitated, resulting in the reduction in concentration in the mixture, while

### Table 3 | Interaction results between river and groundwater under different ratios

<table>
<thead>
<tr>
<th>River:groundwater</th>
<th>Theoretical values – measured values/(mg · L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>1:9</td>
<td>5.3</td>
</tr>
<tr>
<td>2:8</td>
<td>1.0</td>
</tr>
<tr>
<td>3:7</td>
<td>1.1</td>
</tr>
<tr>
<td>4:6</td>
<td>1.4</td>
</tr>
<tr>
<td>5:5</td>
<td>1.2</td>
</tr>
<tr>
<td>6:4</td>
<td>1.1</td>
</tr>
<tr>
<td>7:3</td>
<td>1.1</td>
</tr>
<tr>
<td>8:2</td>
<td>1.7</td>
</tr>
<tr>
<td>9:1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 4 | Interaction results among river, groundwater and rock under different ratios

<table>
<thead>
<tr>
<th>River:groundwater</th>
<th>Theoretical values – measured values/(mg · L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>1:9</td>
<td>12.4</td>
</tr>
<tr>
<td>2:8</td>
<td>2.7</td>
</tr>
<tr>
<td>3:7</td>
<td>2</td>
</tr>
<tr>
<td>4:6</td>
<td>5.9</td>
</tr>
<tr>
<td>5:5</td>
<td>−1.4</td>
</tr>
<tr>
<td>6:4</td>
<td>−0.6</td>
</tr>
<tr>
<td>7:3</td>
<td>−8.1</td>
</tr>
<tr>
<td>8:2</td>
<td>−6.7</td>
</tr>
<tr>
<td>9:1</td>
<td>−7.5</td>
</tr>
</tbody>
</table>
Mg$^{2+}$ dissolved leading to increased concentration in the mixture. When the ratio was 5:5–9:1, Mg$^{2+}$ concentration had reduced in the mixture due to adsorption or precipitation, whereas Ca$^{2+}$ concentration in the mixture had increased because of the dissolution. Additionally, mixing among the Yellow River water, groundwater, and water-bearing rocks also resulted in the release of CO$_3^{2-}$.

**DISCUSSION**

**Interactions between the Yellow River water and groundwater**

The mixing of the Yellow River water and groundwater did not have any influence on Mg$^{2+}$, K$^+$, Na$^+$, or Cl$^-$, as shown in Table 3. This can be attributed to their tendency to react relatively weakly with other ions and inability to easily form colloid or precipitation, despite their easy migration and enrichment. However, the concentrations of other ions had changed according to the mixing ratio. As evident from Figures 1–4, declining trends for Na$^+$, SO$_4^{2-}$, HCO$_3^-$, pH, and TDS were observed with an increasing proportion of the Yellow River water. This probably means that the Yellow River water has lower contents of Na$^+$, SO$_4^{2-}$, HCO$_3^-$ and a lower pH in comparison to groundwater, resulting in declining trends with increasing Yellow River water proportion. The results further suggest that the Yellow River water has a dilution effect in groundwater, as confirmed by the gradual decline of TDS (Figure 2).

However, it is worth noting that the decline of ion contents and the change of hydro-chemical components can also be due to the interactions among various elements in addition to the mixing effect. According to the analysis of
the hydro-chemical characteristics, \( \text{HCO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{Na}^+ \), and \( \text{Ca}^{2+} \) are the main contents of groundwater and the Yellow River water, of which \( \text{HCO}_3^- \) and \( \text{SO}_4^{2-} \), in particular \( \text{HCO}_3^- \), exhibit significant changes after the mixing. This is mainly because \( \text{HCO}_3^- \) is relatively active and its equilibrium in water is controlled by the \( \text{CO}_2 \) in the air, the \( \text{pH} \), and the precipitation generated by other ions. When mixing the Yellow River water and groundwater at a ratio of 1:9–3:7, \( \text{HCO}_3^- \) presented a declining trend slowly with the increase in the mixing ratio, with the \( \text{pH} \) value basically being above 7.5 (Figure 1). This suggests that the \( \text{CO}_2 \) in the air is soluble in water, and the \( \text{CO}_2 \) system reaches equilibrium again and generates new \( \text{HCO}_3^- \), as evident from the increase in \( \text{HCO}_3^- \) after mixing. When mixing the Yellow River water and groundwater at a ratio of 4:6–9:1, \( \text{HCO}_3^- \) was gradually reduced with the increase in the proportion of the Yellow River water. This can be because \( \text{HCO}_3^- \) seized relative dominance, reacting with \( \text{Ca}^{2+} \), \( \text{Fe}^{3+} \) and other cations to generate calcium carbonate, ferric hydroxide, and so forth, along with \( \text{CO}_2 \) gas, with the \( \text{pH} \) value gradually declining to 7.3.

**Interactions among the Yellow River water, groundwater, and water-bearing rocks**

Figures 5 and 6 show the changes of \( \text{pH} \) and TDS after mixing the Yellow River water, groundwater, and rocks at a certain ratio. The \( \text{pH} \) value of the mixture was higher than those of groundwater and the Yellow River water, and it gradually became stable between 8.2 and 8.4 with increasing Yellow River water proportion. This suggests that alkaline substances had been released by water-bearing rocks, resulting in the rise of \( \text{pH} \) value; in addition, with stirring the water is agitated and \( \text{CO}_2 \) is released from the mixed water, causing a change and increase of \( \text{pH} \) in the stirred water. The TDS gradually declined with increasing Yellow River water proportion. The TDS value in the mixture of ratio 3:7 was lower than that of the Yellow River water, suggesting that the total content of hydro-chemical components declined after mixing and that gas production, precipitation, or adsorption occurred.

A positive value represents the decrement in hydro-chemical components due to mixing, while a negative value represents the increment. The influence of the mixing ratio on the chemical components of anionic water is given in Figure 7.
With the increase in the proportion of the Yellow River water, the decrement in $\text{HCO}_3^-$ gradually increased. Additionally, the most significant content change among all the ions before and after mixing was for $\text{HCO}_3^-$, leading to the decline of TDS. The $\text{CO}_3^{2-}$ was not detected before the addition of rocks; however, it was detected in a range between 1.44 and 5.75 mg/L after adding rocks. This suggests that the addition of rocks had changed the neutral pH value condition of the mixture system, resulting in the pH moving to the alkaline region. Consequently, this led to the presence of $\text{CO}_3^{2-}$ in the mixture. Additionally, the $\text{CO}_2$ equilibrium system moved towards the equilibrium direction of $\text{CO}_3^{2-}$, suggesting that the reduction of $\text{CO}_3^{2-}$ was mainly due to the precipitation of carbonates. With the increase in the proportion of the Yellow River water, the decrement of $\text{SO}_4^{2-}$ gradually declined, and ranged between 19 and 55 mg/L. This can be attributed to the fact that the content of $\text{SO}_4^{2-}$ in groundwater was far higher than that in the Yellow River water (Table 1); hence, it declined with the increase in the proportion of the Yellow River water. Another possible reason could be the precipitation of sulfate that occurred during mixing.

The influence of the mixing ratio on the chemical components of cations in water can be seen in Figure 8. The most significant change in increment was observed for $\text{Na}^+$. The increment gradually increased with the increase in the mixing ratio, ranging between 6 and 30 mg/L. In contrast, the release of $\text{K}^+$ did not cause any significant change; that is, it varied only between 0.6 and 4 mg/L. Since $\text{Na}^+$ and $\text{K}^+$ are soluble salts with a high solubility, the increased change in $\text{Na}^+$ can be due to the dissolution of sodium salts and potassium after the addition of rocks.

The changes in $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ were related to the mixing ratio. When the mixing ratio ranged between 1:9 and 5:5, $\text{Ca}^{2+}$ was reduced due to mixing by an amount of 5–12 mg/L, whereas $\text{Mg}^{2+}$ increased by an amount of 0.08–1.84 mg/L. In contrast, $\text{Ca}^{2+}$ content increased, while $\text{Mg}^{2+}$ decreased, when the mixing ratio ranged between 5:5 and 9:1. These changes can be related to the components of the original water and the components of rocks. The $\text{Ca}^{2+}$ content of groundwater was higher than that of the Yellow River water, while the $\text{Mg}^{2+}$ content of the former was lower than that of the latter. In rocks, the content of $\text{Mg}^{2+}$ was higher than that of $\text{Ca}^{2+}$. Consequently, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ exhibited alternate precipitation and dissolution with the mixing ratio.

### Change trend of water–rock interactions with time

The change trend of water–rock interactions with time is presented in Figures 9–12. As shown by Figure 9, their pH
values presented a rising trend relatively consistently over the time. In particular, after mixing the Yellow River water, groundwater, and rocks, the pH of the mixture and its change amplitude were large, suggesting that the components in the mixture were significantly affected by the components in rocks. Consequently, the mixture moved from neutral towards the slightly alkaline direction. As evident from Figure 10, TDS was gradually reduced with time, suggesting that precipitation or the escape of gas occurred during the water–rock interactions.

In the case of cations and anions, Na\(^+\) showed a rising trend, while neither Mg\(^{2+}\) nor Ca\(^{2+}\) experienced any obvious change (Figure 11). Similarly, both SO\(_4^{2-}\) and HCO\(_3^-\) showed a declining trend, while Cl\(^-\) did not experience any change (Figure 12). An increase in sodium salts can be attributed to dissolution during the water–rock interaction process, while the reduction in sulfates can be because of precipitation. Similarly, carbonates were reduced because of the precipitation or the escape of gas. There was no change observed in Ca\(^{2+}\), Mg\(^{2+}\), or Cl\(^-\), suggesting that the released sodium salts or precipitated sulfates and carbonates were not limited to the precipitation of calcium sulfate, calcium carbonate, or magnesium carbonate; instead, the release or precipitation of other salts could also have played a role. This highlights the complexity of water–rock interactions.

It is important to note that the water–rock interactions presented relatively consistent trends regardless of whether it was the mixing between the Yellow River water and rocks or the mixing among the Yellow River water, groundwater, and rocks. This can be mainly due to the relatively high proportion of the Yellow River water in the mixture, suggesting that the water–rock interactions of this region mainly depend on the main components of the Yellow River water and rocks.

**CONCLUSIONS AND SUGGESTIONS**

In arid regions, the mixing between surface water and groundwater is very common. Various physical and chemical processes during mixing determine the direction of water quality evolution in these regions. Based on the indoor simulation test on the water–rock interactions in Yinchuan, the study concludes the following:

- After the mixing of the Yellow River water and groundwater, the Yellow River water had a dilution effect on groundwater. The contents of major ions were reduced with the increase in the proportion of the Yellow River water; however, the decrements were not the result of a simple mixing and dilution. Ca\(^{2+}\) and SO\(_4^{2-}\) mainly experienced precipitation; HCO\(_3^-\) produced changes with the ratio of the mixing. When mixing the Yellow River water and groundwater at a ratio of 1:9–3:7, CO\(_2\) dissolved in water, and resulted in the increase of HCO\(_3^-\). However, in the mixture of a ratio of 4:6–9:1, HCO\(_3^-\) was reduced due to precipitation.
- In the mixture of the Yellow River water, groundwater, and rocks, the pH reached 8.4 from neutral pH. The CO\(_2\) system reached the equilibrium again, and produced
CO\(_2^−\). Further, K\(^+\), Na\(^+\), and CO\(_3^{2−}\) increased in the mixture due to dissolution and lixiviation of rocks. However, the amount of SO\(_4^{2−}\) and HCO\(_3^−\) reduced in the mixture because of precipitation. The amount of Ca\(^{2+}\) and Mg\(^{2+}\) varied depending on the mixing ratio between the Yellow River water and groundwater. For example, when mixing the Yellow River water and groundwater at a ratio of 1:9–5:5, Ca\(^{2+}\) content decreased due to adsorption or precipitation, while the Mg\(^{2+}\) amount increased as a result of dissolution. However, for a ratio of 5:5–9:1, Mg\(^{2+}\) content decreased due to adsorption or precipitation, whereas Ca\(^{2+}\) content increased because of dissolution. This suggests a reversible behavior of the dissolution-precipitation of carbonate minerals.

- Whether it was the mixing between the Yellow River water and rocks or the mixing among the Yellow River water, groundwater and rocks, the water-rock interactions presented relatively consistent trends with time, suggesting that the water-rock interactions of this region mainly depend on the main components of the Yellow River water and rocks.

**ACKNOWLEDGEMENTS**

This work was supported by the National Natural Science Foundation of China (41472220) and (51708447).

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First received 20 July 2018; accepted in revised form 6 August 2018. Available online 25 September 2018