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Article

Mixing Precipitation of $CaCO_3$ in Natural Waters

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Abstract: The mixing precipitation of $CaCO_3$ in natural waters was theoretically studied by the methods of chemical equilibrium calculation. Results show that mixing precipitation of $CaCO_3$ can be produced by mixing between two unsaturated water samples with respect to $CaCO_3$, two oversaturated water samples, an unsaturated water sample and an oversaturated water sample. Mixing precipitation can be classified into two major different types: mixing precipitation in a strict sense and mixing precipitation in a broad sense. Mixing precipitation in a strict sense refers to the mixing effect that makes the state of $CaCO_3$ change from dissolution into precipitation, or the increases in the precipitability of $CaCO_3$ in mixed water. Mixing precipitation in a broad sense refers to the mixing effect that reduces the solubility of $CaCO_3$ in mixed water. Mixing precipitation is controlled by simultaneous chemical equilibria. Generally, if the HCO_3^- concentration is higher in one solution and the Ca^{2+} concentration is higher in the other, mixing precipitation of $CaCO_3$ will occur when they are combined.

Keywords: $CaCO_3$; equilibrium model; mixing precipitation; natural water

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1. Introduction

Mixing of the waters has become a hot hydrogeological and hydrogeochemical topic since Buneyew discovered the phenomenon of mixing corrosion in 1932 [1–5]. In recent years, much work

has been done relating to mixing corrosion due to the occurrence of many geological hazards such as salt water intrusion in and around coastal areas, karstic corrosion and karstic aquifer pollution [6–9]. Mixing processes are difficult to understand and are much more complex and ambiguous. Bogli recognized the phenomenon and interpreted it with the solubility curve of $CaCO_3$ in CO_2 solution in 1961 [10]. Chen *et al.* carried out seven groups of static experiments in a closed CO_2-H_2O system to study the mixing corrosion effects and the mechanism for the development of littoral karst [11]. Ramos-Leal *et al.* studied the mixing processes in the aquifer of San Luis Potosi valley (Mexico) by using chlorides and fluorides as conservative elements, from which they quantified the contribution of each member to groundwater quality [12]. Zou *et al.* recognized that the intensive mixing corrosion effect occurred in the middle of the transition zone between sea water and fresh water through laboratory experiments [13]. Furthermore, Qian and Li conducted theoretical research on mixing corrosion and concluded that mixing corrosion can be made by mixing between two initially unsaturated water samples, between two oversaturated water samples and even between an oversaturated water sample and an unsaturated water sample [14].

However, most of the current literatures are about the mixing corrosion phenomenon theoretically and experimentally [11–17]. Actually, the mixing effect between different natural waters is very complex, and can produce not only mixing corrosion, but also mixing precipitation; also even a proportion-dependent mixing phenomenon can also be observed [18]. The mixing precipitation has long been ignored by scientists, but it is an important phenomenon in natural waters which can also cause serious environmental and geological disasters. In this study, the mixing precipitation of $CaCO_3$ in natural water systems was discussed theoretically.

2. Materials and Methods

2.1. Materials

Eight water samples were used in this study and were selected from a previous study which was conducted by Tong *et al.* [19]. The analytical results of the water samples are listed in Table 1.

Table 1. Analysis results of water samples, including pH value, temperature (t), chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and SI_c.

Sample No.	pH	t °C	Cl^- mg/L	SO_4^{2-} mg/L	CO_3^{2-} mg/L	HCO_3^- mg/L	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	SI_c
1	6.65	35.0	4.20	431.00	0	392.00	6.90	26.20	232.00	47.30	0.927
2	6.50	35.5	532.00	441.00	0	1870.00	980.00	98.00	33.20	6.58	0.313
3	6.80	58.0	37.60	39.90	0	1963.60	717.50	62.60	14.00	1.80	0.779
4	7.00	51.5	328.00	192.00	0	2230.00	970.00	73.00	50.60	22.90	3.723
5	7.00	27.0	2.90	327.00	0	359.00	6.10	19.70	204.00	36.20	1.599
6	7.25	25.0	3.40	279.00	0	306.00	4.40	13.70	164.00	27.90	2.073
7	6.71	35.0	4.20	431.00	0	393. 00	6.80	26.30	232.00	47.20	1.106
8	7.26	25.0	3.40	284.00	0	306.00	4.40	14.40	167.00	28.40	2.155

In Table 1, the first three samples are unsaturated with $CaCO_3$ and the last five samples are oversaturated with $CaCO_3$ at the temperature listed in the table. The SI_c is the saturation index with respect to $CaCO_3$ (calcite) which is calculated using Equation (1).

$$SI_c = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{sp}} \tag{1}$$

where, $\{Ca^{2+}\}$ and $\{CO_3^{2-}\}$ are respectively the activities of Ca^{2+} and CO_3^{2-} in the solution; and K_{SP} is the solubility product of calcite. Apparently, the solution is unsaturated with calcite when $SI_c < 1$; when $SI_c > 1$, the solution is oversaturated with calcite; and when $SI_c = 1$, the solution is in equilibrium with calcite.

2.2. Methods

In the mixing process, many factors are involved, among which the most important are the readjustment of equilibrium distribution of species, and changes of pH values and water compositions. Hence, during the calculation of the solubility (precipitability) of $CaCO_3$ in mixed water, these important factors should be considered and calculated simultaneously. For the calculation of equilibrium distribution of species, the methods proposed by Crerar, Qian and Arnórsson are adopted [20–22]. The equilibrium chemical model for the calculation involves 17 chemical reactions as shown in Table 2. This model has been successfully used and verified in studies conducted previously [14,18,23]. It contains 9 major components and 17 derived species.

Table 2. Chemical model for the speciation calculation (9 major components and 17 derived species).

Major components		**Derived species**		
No.	**Components**	**No.**	**Species**	**Chemical reactions**
1	Cl^-	1	$NaCl$	$Na^+ + Cl^- \leftrightharpoons NaCl$
2	SO_4^{2-}	2	KCl	$K^+ + Cl^- \leftrightharpoons KCl$
3	CO_3^{2-}	3	H_2SO_4	$2H^+ + SO_4^{2-} \leftrightharpoons H_2SO_4$
4	Na^+	4	HSO_4^-	$H^+ + SO_4^{2-} \leftrightharpoons HSO_4^-$
5	K^+	5	$NaSO_4^-$	$Na^+ + SO_4^{2-} \leftrightharpoons NaSO_4^-$
6	Ca^{2+}	6	KSO_4^-	$K^+ + SO_4^{2-} \leftrightharpoons KSO_4^-$
7	Mg^{2+}	7	$CaSO_4$	$Ca^{2+} + SO_4^{2-} \leftrightharpoons CaSO_4$
8	H^+	8	$MgSO_4$	$Mg^{2+} + SO_4^{2-} \leftrightharpoons MgSO_4$
9	OH^-	9	H_2CO_3	$2H^+ + CO_3^{2-} \leftrightharpoons H_2CO_3$
		10	HCO_3^-	$H^+ + CO_3^{2-} \leftrightharpoons HCO_3^-$
		11	$CaCO_3$	$Ca^{2+} + CO_3^{2-} \leftrightharpoons CaCO_3$
		12	$MgCO_3$	$Mg^{2+} + CO_3^{2-} \leftrightharpoons MgCO_3$
		13	$CaHCO_3^+$	$Ca^{2+} + H^+ + CO_3^{2-} \leftrightharpoons CaHCO_3^+$
		14	$MgHCO_3^+$	$Mg^{2+} + H^+ + CO_3^{2-} \leftrightharpoons MgHCO_3^+$
		15	$CaOH^+$	$Ca^{2+} + OH^- \leftrightharpoons CaOH^+$
		16	$MgOH^+$	$Mg^{2+} + OH^- \leftrightharpoons MgOH^+$
		17	H_2O	$H^+ + OH^- \leftrightharpoons H_2O$

For the calculation of pH values in which physicochemical process have caused pH changes, Plummer *et al.* introduced a charge neutrality equation into the mass action and mass balance

equations; the simultaneous equations were solved by the quadratic interpolation method [24]. In a previous study, we used the golden section method to solve the simultaneous equations and verified results using experimental data [25]. In this study the modified method was adopted.

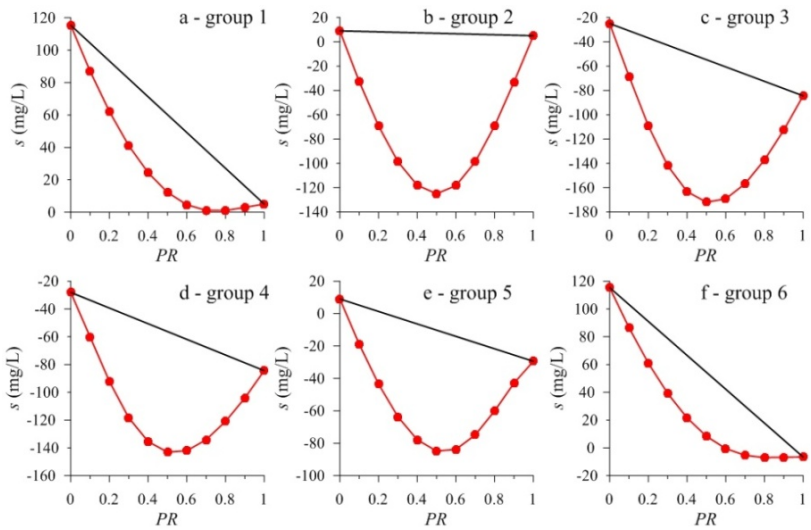
The method for calculating the solubility (precipitability) of $CaCO_3$ in natural waters has been introduced and successfully used by Qian *et al.* [23]. In the present study, the solubility (precipitability) of $CaCO_3$ for mixed water of given mixing ratios was calculated with this method, and the calculated result was designated as s_1. $s_1 > 0$ and $s_1 < 0$ indicate the occurrence of dissolution and precipitation in mixed water, respectively. To show mixing effects, the dissolution (precipitation) amount of $CaCO_3$ for the mixed water under no mixing precipitation assumption was also calculated and the result was designated as s_2. The method for the calculation of s_2 is as follows: First, the solubility (precipitability) of the two end member mixing waters is calculated by the above method separately; then the s_2 under a given mixing ratio is calculated by the linear mixed model. Based on this, let $\Delta s = s_1 - s_2$; obviously, Δs is a useful index for indicating the presence of mixing effects. When $\Delta s < 0$, it shows that mixing precipitation has occurred, and that, on the contrary, mixing corrosion has occurred.

3. Results and Discussion

3.1. Results

Six groups of mixed water were obtained by mixing the water samples from Table 1. Groups 1 to 6 are respectively obtained by mixing between water samples 1 and 2, samples 1 and 3, samples 4 and 5, samples 4 and 6, samples 3 and 8, and samples 2 and 7 at the ratios of 0:10 (0), 1:9 (0.1), 2:8 (0.2), 3:7 (0.3), 4:6 (0.4), 5:5 (0.5), 6:4 (0.6), 7:3 (0.7), 8:2 (0.8), 9:1 (0.9) and 10:0 (1.0). The s_2 and s_1 of these mixed waters were calculated with the aforementioned model and methods. The calculated results are shown in Figure 1.

Figure 1. Dissolution (Precipitation) of $CaCO_3$ for the six groups of mixed water. The *x*-axis *PR* is the mixing ratio, and the *y*-axis *s* is the dissolution amount of $CaCO_3$ in mixed waters ("+": dissolution, "−": precipitation). The red curve represents the calculated results considering mixing precipitation (s_1), and the black line is the results under no mixing precipitation assumption (s_2).



The six groups of mixed water can be categorized into three types, which are mixing between two initially unsaturated samples (groups 1 and 2), two oversaturated samples (groups 3 and 4), as well as an unsaturated sample and an oversaturated sample (groups 5 and 6), respectively.

Compared with s_2, which changes linearly with the mixing ratio (Figure 1), s_1 is observed as a downwards curve for all three types of mixed waters. It can be seen from Figure 1 that s_1 is less than s_2 for each group. Obviously, mixing effects occurred during the mixing process.

3.2. Discussion

3.2.1. Mixing Precipitation between Two Unsaturated Water Samples

Group 1 and group 2 are mixed with two unsaturated water samples. The calculated results are listed in Table 3.

Table 3. Calculated results for mixed water from two unsaturated samples (group 1: water samples 1 and 2; group 2: water samples 1 and 3).

Group	Item	Mixing ratios										
		0	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**
1	pH_0	6.50	6.50	6.51	6.51	6.52	6.53	6.54	6.55	6.57	6.60	6.65
	SI_c	0.31	0.48	0.62	0.74	0.84	0.91	0.97	0.99	0.99	0.97	0.93
	s_1	115.36	86.99	62.06	41.06	24.39	12.26	4.61	1.14	1.04	3.00	5.02
	s_2	115.36	104.33	93.29	82.26	71.22	60.19	49.16	38.12	27.09	16.05	5.02
	Δs	0.00	−17.34	−31.23	−41.20	−46.83	−47.93	−44.55	−36.98	−26.05	−13.05	0.00
	pH_e	6.59	6.58	6.57	6.56	6.55	6.54	6.54	6.55	6.57	6.61	6.67
2	pH_0	6.80	6.79	6.79	6.78	6.78	6.77	6.76	6.75	6.73	6.70	6.65
	SI_c	0.78	1.72	2.35	2.74	2.90	2.87	2.69	2.38	1.96	1.47	0.93
	s_1	9.01	−32.72	−69.33	−98.65	−118.01	−124.96	−118.28	−98.72	−69.07	−33.04	5.02
	s_2	9.01	8.61	8.21	7.81	7.41	7.02	6.62	6.22	5.82	5.42	5.02
	Δs	0.00	−41.33	−77.54	−106.46	−125.42	−131.98	−124.90	−104.94	−74.89	−38.46	0.00
	pH_e	6.81	6.76	6.72	6.67	6.63	6.59	6.57	6.56	6.57	6.60	6.67

Notes: pH_0 and SI_c are calculated pH values and saturation indices of $CaCO_3$ for mixed waters, respectively; s_1 (mg/L) is the calculated solubility (precipitability) of $CaCO_3$ for mixed waters; s_2 (mg/L) is the dissolution or precipitation amount of $CaCO_3$ for mixed waters under no mixing precipitation assumption; $\Delta s = s_1 - s_2$; and pH_e is the calculated pH values for mixed waters after solubility (precipitability) of s_1.

It can be seen from Table 3 that Δs are all negative because of mixing effects, the solubility of mixed waters decreased. In other words, the mixing precipitation takes place during the mixing process. For example, for group 1 (Figure 1a), the solubility of $CaCO_3$ in the mixed water was 62.06 mg/L at the mixing ratio of 0.2 (mixture of 0.2 L water sample 1 and 0.8 L water sample 2). However, using the calculated solubility of water samples 1 and 2 in Table 3, if they were not mixed, the total dissolution of 0.2 L of water sample 1 and 0.8 L water sample 2 should be 93.29 mg/L (0.2 × 5.02 mg/L + 0.8 × 115.36 mg/L = 93.29 mg/L). Therefore, the dissolution amount of $CaCO_3$ was decreased by 31.23 mg/L under the mixing precipitation effect. Similarly, when the mixing ratios were 0.5 and 0.8, the decreases of $CaCO_3$ solubility were 47.93 mg/L and 26.05 mg/L, respectively. However, the

mixing effect does not change $CaCO_3$ from the state of dissolution to precipitation in all mixing ratios. Another thing which should be stressed is that both the mixing and subsequent dissolution (precipitation) of $CaCO_3$ change the pH of the solution. The column pH_0 in Table 3 shows the pH values of mixed waters before $CaCO_3$ dissolution (precipitation). The figures for pH_e are the pH values after s_1 (mg/L) of $CaCO_3$ is dissolved (precipitated) into (from) the mixed waters. It can be seen from group 1 that the pH_e is greater than pH_0, which indicates that the dissolution of $CaCO_3$ will increase the pH values of solution and can be explained by the following reactions:

$$CaCO_3 \leftrightharpoons Ca^{2+} + CO_3^{2-} \tag{2}$$

$$H^+ + CO_3^{2-} \leftrightharpoons HCO_3^- \tag{3}$$

$$HCO_3^- + H^+ \leftrightharpoons H_2O + CO_2 \tag{4}$$

The dissolution of $CaCO_3$ caused the concentration of H^+ to decrease, which increased the pH values of the mixed water in group 1 after the dissolution of $CaCO_3$ as a result.

According to the above discussion, a new concept, mixing precipitation in a broad sense, can be proposed. This refers to the mixing effect that causes the solubility of $CaCO_3$ to decrease in mixed water and does not change the dissolution states of $CaCO_3$ at the same time. Correspondingly, the mixing effect which changes the state of $CaCO_3$ from dissolution to precipitation, or increases the precipitability of $CaCO_3$ in mixed water is named mixing precipitation in a strict sense.

The mixing between two unsaturated samples can also lead to mixing precipitation in a strict sense. Group 2 is such an example, which is mixed by water samples 1 and 3 (Figure 1b). Before mixing, the solubility of $CaCO_3$ in sample 1 and 3 were 5.02 and 9.01 mg/L, respectively. However, when water samples 1 and 3 were mixed at the ratio of 0.2, the mixed water produced 69.33 mg/L of $CaCO_3$ precipitation instead. Similarly, when the mixing ratio was 0.5, the solubility of $CaCO_3$ in mixed water should be 7.02 mg/L if there was no mixing precipitation, whereas the mixing process produced 124.96 mg/L of $CaCO_3$ precipitation instead. When the mixing ratio was 0.8, the precipitation amount of $CaCO_3$ caused by mixing precipitation was 69.07 mg/L. The pH_e values are less than the pH_0 in group 2. This is because the mixing process precipitated some $CaCO_3$ from the water and the concentration of H^+ increased in the solution.

3.2.2. Mixing Precipitation between Two Oversaturated Water Samples

Groups 3 and 4 were mixed with two oversaturated water samples. The solubility (precipitation) of $CaCO_3$ at different mixing ratios are listed in Table 4.

It can be seen from Table 4 and Figure 1 (Figures 1c and 1d) that mixing precipitation in a strict sense was observed in groups 3 and 4. In group 3, when the mixing ratio was 0.2, 109.24 mg/L of $CaCO_3$ precipitation was formed in the mixed water, whereas if there was no mixing precipitation, only 36.858 mg/L of $CaCO_3$ should be precipitated at the same mixing ratio. In other words, the mixing effect increased 72.38 mg/L of $CaCO_3$ precipitation. When the mixing ratio was 0.5 and 0.8, the increased amounts of $CaCO_3$ precipitation were 117.27 and 64.698 mg/L with mixing precipitation, respectively. In group 4, the increased amounts of $CaCO_3$ precipitation were relatively less than those

in group 3. When the mixing ratios were 0.2, 0.5 and 0.8, the mixed waters produced 52.93, 86.79 and 47.83 mg/L of $CaCO_3$ precipitation, respectively.

Because the two end member samples were all oversaturated, the mixing precipitation in a strict sense can be only obtained from the mixed waters.

Table 4. Calculated results for mixed water from two oversaturated samples (group 3: water samples 4 and 5; group 4: water samples 4 and 6).

Group	Item	Mixing ratios										
		0	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**
3	pH_0	7.00	7.02	7.02	7.02	7.02	7.02	7.01	7.01	7.01	7.00	7.00
	SI_c	1.60	2.47	3.22	3.83	4.32	4.65	4.83	4.85	4.68	4.31	3.72
	s_1	−24.97	−68.42	−109.24	−141.95	−163.23	−171.96	−169.14	−156.73	−137.22	−112.62	−84.41
	s_2	−24.97	−30.91	−36.86	−42.80	−48.75	−54.69	−60.63	−66.58	−72.52	−78.47	−84.41
	Δs	0.00	−37.51	−72.38	−99.15	−114.48	−117.27	−108.51	−90.15	−64.70	−34.15	0.00
	pH_e	6.86	6.77	6.73	6.71	6.72	6.75	6.78	6.81	6.85	6.88	6.92
4	pH_o	7.25	7.16	7.12	7.09	7.07	7.05	7.04	7.02	7.02	7.01	7.00
	SI_c	2.07	2.61	3.12	3.56	3.91	4.16	4.32	4.36	4.29	4.08	3.72
	s_1	−28.08	−60.13	−92.28	−118.38	−135.48	−143.03	−142.04	−134.11	−120.97	−104.07	−84.41
	s_2	−28.08	−33.71	−39.35	−44.98	−50.61	−56.25	−61.88	−67.51	−73.14	−78.78	−84.41
	Δs	0.00	−26.42	−52.93	−73.40	−84.87	−86.79	−80.16	−66.60	−47.83	−25.29	0.00
	pH_e	7.01	6.89	6.83	6.80	6.80	6.81	6.83	6.85	6.87	6.90	6.92

Notes: pH_0 and SI_c are calculated pH values and saturation indices of $CaCO_3$ for mixed waters, respectively; s_1 (mg/L) is the calculated solubility (precipitability) of $CaCO_3$ for mixed waters; s_2 (mg/L) is the dissolution or precipitation amount of $CaCO_3$ for mixed waters under no mixing precipitation assumption; $\Delta s = s_1 - s_2$; and pH_e is the calculated pH values for mixed waters after solubility (precipitability) of s_1.

3.2.3. Mixing Precipitation between an Unsaturated Water Sample and an Oversaturated Water Sample

Group 5 was obtained by mixing samples 3 and 8, and group 6 was mixed with samples 2 and 7. The mixing precipitation between an unsaturated sample and an oversaturated sample were calculated using the aforementioned model. The results are listed in Table 5.

For group 5 when the mixing ratio was less than or equal to 0.2, mixing precipitation in a broad sense can be observed. The state of $CaCO_3$ changes from dissolution to precipitation under the mixing effect. For example, when the mixing ratio was 0.1, if there was no mixing precipitation, 5.17 mg/L of $CaCO_3$ should be dissolved in the mixed water. However, under the influence of the mixing precipitation18.93 mg/L of $CaCO_3$ was precipitated from the mixed water. This is the type of mixing precipitation which changes the states of $CaCO_3$ from dissolution into precipitation; it is a kind of mixing precipitation in a strict sense. When the mixing ratio was larger than 0.2, the precipitation amount of $CaCO_3$ was increased by the mixing precipitation effect. When the mixing ratio was 0.8, for instance, the mixing effects increased the precipitability of $CaCO_3$ by an amount of 38.29 mg/L.

The phenomena in group 6 are different from those in group 5. When the mixing ratio was less than or equal to 0.5, the mixing precipitation in a broad sense occurs. The mixing effect only reduced the solubility of $CaCO_3$, it did not change the saturation state of $CaCO_3$. When the mixing ratio was larger

than or equal to 0.6, the mixing effect changed the state of $CaCO_3$ from dissolution to precipitation, thus, mixing precipitation in a strict sense occurs. For example, when the mixing ratio was 0.3, if there is no mixing precipitation, 78.78 mg/L of $CaCO_3$ will be dissolved in the mixed water, but because of the impact of mixing precipitation, only 38.16 mg/L of $CaCO_3$ dissolved. When the mixing ratio is 0.8, 17.82 mg/L of $CaCO_3$ can be dissolved in the mixed water under the assumption of no mixing precipitation, but under the influence of mixing precipitation, 7.01 mg/L of $CaCO_3$ is precipitated instead. In this case, mixing precipitation in a strict sense occurs.

Table 5. Calculated results for mixed water from an unsaturated sample and an oversaturated sample (group 5: water samples 3 and 8, group 6: water samples 2 and 7).

Group	Item	Mixing ratios										
		0	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**
5	pH_0	6.80	6.81	6.81	6.83	6.84	6.86	6.89	6.92	6.97	7.06	7.26
	SI_c	0.78	1.42	1.87	2.15	2.31	2.36	2.32	2.22	2.09	1.97	2.16
	s_1	9.01	−18.93	−43.54	−63.65	−77.87	−84.83	−83.75	−74.85	−60.03	−42.89	−29.43
	s_2	9.01	5.17	1.32	−2.52	−6.37	−10.21	−14.05	−17.90	−21.74	−25.59	−29.43
	Δs	0.00	−24.10	−44.86	−61.13	−71.50	−74.62	−69.70	−56.95	−38.29	−17.30	0.00
	pH_e	6.81	6.79	6.77	6.75	6.73	6.73	6.73	6.75	6.79	6.87	7.01
6	pH_o	6.50	6.51	6.51	6.52	6.53	6.54	6.55	6.57	6.59	6.64	6.71
	SI_c	0.31	0.48	0.62	0.75	0.86	0.94	1.00	1.05	1.07	1.08	1.11
	s_1	115.36	86.47	60.94	39.16	21.60	8.36	−0.51	−5.35	−7.01	−6.69	−6.57
	s_2	115.36	103.17	90.97	78.78	66.59	54.40	42.20	30.01	17.82	5.62	−6.57
	Δs	0.00	−16.70	−30.03	−39.62	−44.99	−46.04	−42.71	−35.36	−24.83	−12.31	0.00
	pH_e	6.59	6.58	6.57	6.56	6.55	6.55	6.55	6.56	6.58	6.62	6.68

Notes: pH_0 and SI_c are calculated pH values and saturation indices of $CaCO_3$ for mixed waters, respectively; s_1 (mg/L) is the calculated solubility (precipitability) of $CaCO_3$ for mixed waters; s_2 (mg/L) is the dissolution or precipitation amount of $CaCO_3$ for mixed waters under no mixing precipitation assumption; $\Delta s = s_1 - s_2$; and pH_e is the calculated pH values for mixed waters after solubility (precipitability) of s_1.

It can be concluded that when an unsaturated water sample and an oversaturated water sample are mixed, the mixing precipitation both in a strict sense and in a broad sense can be produced. Which of these phenomena occurs depends on the hydrochemical characteristics of the end member solutions and the saturation states before and after mixing.

3.2.4. General Characteristics of End Member Samples for Mixing Precipitation

The above analyses and discussions illustrate that mixing precipitation is a common phenomenon in natural waters. It can be produced by mixing between two supersaturated water samples, between two unsaturated water samples or between an unsaturated water sample and an oversaturated water sample. The mixing precipitation in a strict sense can be observed in all three mixing types, while the mixing precipitation in a broad sense cannot be produced by mixing between two oversaturated samples. Therefore, it can be concluded that mixing precipitation in a broad sense can only be observed when at

least one of the end member solutions is unsaturated, and the solubility or precipitability of $CaCO_3$ is controlled by the saturation index in mixed water. Besides, the mixing precipitation is also influenced by the hydrochemical characteristics of end member solutions. A large number of calculations reveal that if mixing precipitation (including mixing precipitation in strict sense and in broad sense) occurs, the two end member aqueous solutions generally possess the following characteristics: when the HCO_3^- concentration in one aqueous solution is higher than that in the other solution, the concentration of Ca^{2+} in the former aqueous solution is usually lower than that in the latter. That is to say, when two water samples are mixed, if one solution contains a large amount of HCO_3^- and the other contains a lot of Ca^{2+}, mixing precipitation of $CaCO_3$ will occur when they are mixed.

4. Conclusions

According to the discussions above, the following conclusions can be derived:

(1) Precipibility (Solubility) can be calculated based on a chemical equilibrium model for mixed waters considering mixing precipitation. The calculated results show that mixing precipitation can be classified into two major types: mixing precipitation in a strict sense and mixing precipitation in a broad sense. Mixing precipitation in a strict sense refers to the effect that makes the state of $CaCO_3$ change from dissolution to precipitation, or increases the precipitability of $CaCO_3$. Mixing precipitation in a broad sense refers to the mixing effect that reduces the solubility of $CaCO_3$.

(2) Mixing precipitation is a common phenomenon in natural waters system. It can be observed by mixing between two unsaturated water samples, two oversaturated water samples, or an unsaturated and an oversaturated sample. Mixing precipitation in a broad sense cannot be observed when two oversaturated samples are mixed.

(3) The mixing precipitation is controlled by the simultaneous chemical equilibria that are established, which can be expressed in terms of saturation indices of the end member solutions and influenced by their hydrochemical characteristics. Generally, if the HCO_3^- concentration is higher in one solution and the Ca^{2+} concentration is higher in the other, mixing precipitation of $CaCO_3$ will be produced when they are mixed.

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Conflicts of Interest

The authors declare no conflict of interest.

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