Mixing Corrosion of CaCO$_3$ in Natural Waters

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Abstract: The methods of aqueous speciation calculation, pH calculation and the solubility (precipitability) calculation of CaCO$_3$ were used to study the mixing corrosion of CaCO$_3$ in natural waters. Mixing processes were done between two unsaturated (with CaCO$_3$) solutions, two oversaturated solutions and between an unsaturated solution and an oversaturated solution, respectively. Results show that the mixing corrosion can be divided into two different levels: mixing corrosion in strict sense and mixing corrosion in broad sense. When mixing corrosion occurs, the HCO$_3^-$ concentration in one end member solution is usually higher than that in the other solution, and the Ca^{2+} concentration in the former solution is also usually higher than that in the latter one.

Keywords: CaCO$_3$, Natural water, Equilibrium model, Mixing corrosion

Introduction

The mixing between fresh water and salt water around the coastal area has drawn much attention from the world these years. However, the interesting phenomenon caused by mixing of waters was noticed many years ago. The phenomenon of corrosion caused by water mixing (named mixing corrosion) was first found in 1932 by Buneyew and in 1961, Bogli recognized the phenomenon once again and interpreted it with the solubility curve of CaCO$_3$ in CO$_2$ solution[1,2]. The mixing corrosion is considered as one of the most important factors controlling the development of littoral karst[3]. The interesting mixing phenomenon has been studied by many scholars around the world. For example, Savchenko *et al.*[4] did some work on the microelements' behavior under the mixing of acid riverine water and sea water with a physicochemical modeling with the Selektor software package. Şebnem Elçi[5] studied the thermal stratification and mixing effects on reservoir water quality by field observations and statistical analysis. Chudaeva and Chudaev[6] studied the behavior of rare earth elements during mixing of different types of waters.

At present, the interpretation method proposed by Bogli[1] has been widely referred and has produced profound influences. Gong[7] pointed out according to a mixing corrosion

experiment in Guilin karst area that mixing corrosion theory is derived from the solubility curve of $CaCO_3$ in pure carbonate-water system and should be cautiously used in explaining the mixing corrosion of natural waters. In fact, there are some serious problems when using the Bogli corrosion theory to explain the mixing corrosion of natural waters and sometimes can even produce opposite results[8]. Only when the species and mixing ratio of the two aqueous solutions are suitable can the mixing corrosion in strict sense occurs and in natural systems, the mixing corrosion in strict sense is rare. In this paper, the author simulated and computed the mixing corrosion effects with aqueous solution equilibrium model based on the analysis results of water samples and found that it was the compositions of end member solutions that determined the dissolution or precipitation of $CaCO_3$ after mixing.

Methodology

Data collection and analysis

For this study, 10 water samples were used, the first 4 samples were unsaturated with $CaCO_3$ and the last 6 samples were oversaturated with $CaCO_3$. Since the difficulties in collecting the samples in nature, all these samples were from a previous study conducted by Tong *et al.*[9] in Tibetan geothermal regions. All these samples were collected in different geothermal regions in Tibet. Table 1 lists the physiochemical analysis results of water samples.

Table 1. Analysis results of water samples

Sample No.	pH	t ^oC	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	8.08	24.0	14.18	9.61	9.60	43.93	8.80	4.20	17.64	1.70	0.456
2	7.36	19.0	4.25	9.61	0	139.13	0.00	0.00	49.70	0.73	0.452
3	6.65	35.0	4.20	431.00	0	392.00	6.90	26.20	232.00	47.30	0.927
4	7.24	18.5	2.13	0.96	0	258.72	0.20	0.00	80.56	2.68	0.906
5	8.60	18.0	2.84	14.41	4.80	112.28	0.30	0.00	44.09	1.00	5.973
6	7.38	17.0	2.13	4.80	0.00	241.63	0.30	0.00	78.16	1.46	1.116
7	7.35	44.2	127.00	1.63	0	764.00	238.00	31.00	87.50	15.60	6.797
8	8.24	31.0	2.84	0.00	4.80	61.02	0.60	0.30	20.04	2.92	1.193
9	7.00	27.0	2.90	327.00	0	359.00	6.10	19.70	204.00	36.20	1.599
10	7.24	22.0	3.00	244.00	0	276.00	3.70	13.70	159.00	26.10	1.636

SI_c - *The solution saturation index with respect to $CaCO_3$ (calcite) which is expressed as equation 1.*

$$SI_c = \frac{a\{Ca^{2+}\} \cdot a\{CO_3^{2-}\}}{K_c} \tag{1}$$

Where, $a\{Ca^{2+}\}$ and $a\{CO_3^{2-}\}$ are the activities of Ca^{2+} and CO_3^{2-} respectively, K_c is the solubility product of calcite. Apparently, the solution is unsaturated with calcite when $SI_c < 1$, when $SI_c > 1$, the solution is supersaturated with calcite and when $SI_c = 1$, the solution is in equilibrium with calcite.

Methods

During the mixing processes, the calculation of $CaCO_3$ dissolution (precipitation) involves the equilibrium distribution calculation of soluble species, the mixed water compositions and pH values calculation as well as the calculation of $CaCO_3$ dissolution (precipitation) in mixed water. The specific methods for solving these problems are as follows:

1) For the equilibrium distribution of soluble species calculation, many scholars have carried out a wide range of discussions and put forward a number of calculation methods[10-21]. In this paper, the calculation method proposed by Crerar[12] and Qian[16] and the formula expressing the equilibrium constants varying with temperature proposed by Arnorsson[22] were used. When calculating the chemical equilibrium of aqueous solution systems, the chemical equilibrium model listed in Table 2 were used. The model contains 9 basic components and 17 derived species.

Table 2. Chemical model for the studied water

| Basic components		Derived species		
No.	Components	No.	Species	Chemical reactions
1	Cl^-	1	$NaCl^0$	$Na^+ + Cl^- = NaCl^0$
2	SO_4^{2-}	2	KCl^0	$K^+ + Cl^- = KCl^0$
3	CO_3^{2-}	3	$H_2SO_4^0$	$2H^+ + SO_4^{2-} = H_2SO_4^0$
4	Na^+	4	HSO_4^-	$H^+ + SO_4^{2-} = HSO_4^-$
5	K^+	5	$NaSO_4^-$	$Na^+ + SO_4^{2-} = NaSO_4^-$
6	Ca^{2+}	6	KSO_4^-	$K^+ + SO_4^{2-} = KSO_4^-$
7	Mg^{2+}	7	$CaSO_4^0$	$Ca^{2+} + SO_4^{2-} = CaSO_4^0$
8	H^+	8	$MgSO_4^0$	$Mg^{2+} + SO_4^{2-} = MgSO_4^0$
9	OH^-	9	$H_2CO_3^0$	$2H^+ + CO_3^{2-} = H_2CO_3^0$
		10	HCO_3^-	$H^+ + CO_3^{2-} = HCO_3^-$
		11	$CaCO_3^0$	$Ca^{2+} + CO_3^{2-} = CaCO_3^0$
		12	$MgCO_3^0$	$Mg^{2+} + CO_3^{2-} = MgCO_3^0$
		13	$CaHCO_3^+$	$Ca^{2+} + H^+ + CO_3^{2-} = CaHCO_3^+$
		14	$MgHCO_3^+$	$Mg^{2+} + H^+ + CO_3^{2-} = MgHCO_3^+$
		15	$CaOH^+$	$Ca^{2+} + OH- = CaOH^+$
		16	$MgOH^+$	$Mg^{2+} + OH^- = MgOH^+$
		17	H_2O	$H^+ + OH^- = H_2O$

2) Plummer *et al.*[23] have discussed the calculation method for mixed water compositions and pH values. In a previous study[24], we did some modification and improvement to the method, which has been verified by experimental data. In this paper the modified method was adopted.

3) The amounts of the dissolution (precipitation) of CaCO$_3$ under different mixing ratios in a closed system were calculated. The calculated results are designated as s_1 with $s_1 > 0$ indicating dissolution and $s_1 < 0$ indicating precipitation. If the mixing corrosion didn't occur, the dissolution (precipitation) amounts of CaCO$_3$ in mixed water would show a linear relation with the mixing ratios. The dissolution (precipitation) amounts of CaCO$_3$ in mixed waters under no mixing corrosion assumption are designated as s_2. Comparing the results of s_1 and s_2, if Δs ($= s_1 - s_2$) > 0, it shows the mixing corrosion has occurred, and if the contrary, mixing precipitation has occurred.

Results and Discussion

Six groups of mixed water were obtained by mixing between water sample 1 and 2 (Group 1), sample 3 and 4 (Group 2), sample 5 and 6 (Group 3), sample 7 and 8 (Group 4), sample 10 and 3 (Group 5), sample 1 and 9 (Group 6). The first 2 groups are mixed waters between two unsaturated water samples, group 3 and group 4 are mixed waters between two oversaturated samples and group 5 and group 6 are mixed waters between an unsaturated water

sample and an oversaturated water sample. The calculated results of the mixing corrosion for the 6 groups of mixed waters are listed in Table 3 and corresponding curves are drawn in Figure 1.
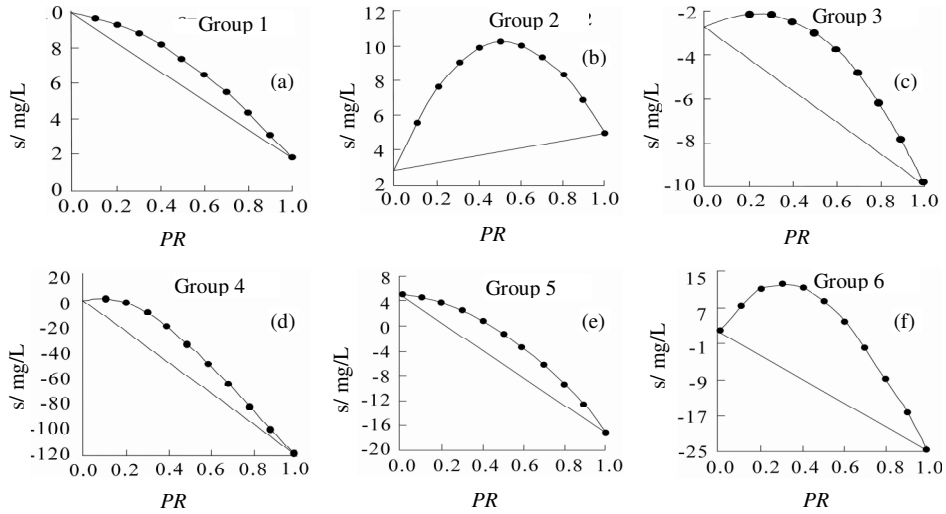
The x-axis PR is the mixing ratio, y-axis s is the dissolution amount of CaCO₃ in mixed waters.
Straight line represents the results under no mixing corrosion assumption and curve represents the
computed results for mixing corrosion

Figure 1. Dissolution (precipitation) amount of CaCO$_3$ for mixed waters

Table 3. Calculated results for mixed water samples

Groups	Items	Mixing ratios										
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1	pH$_0$	7.36	7.38	7.39	7.42	7.45	7.48	7.53	7.59	7.68	7.83	8.08
	SI_c	0.45	0.42	0.40	0.37	0.35	0.33	0.31	0.30	0.30	0.34	0.46
	s_1	9.90	9.70	9.34	8.85	8.23	7.47	6.58	5.57	4.42	3.15	1.83
	s_2	9.90	9.09	8.29	7.48	6.67	5.87	5.06	4.25	3.44	2.64	1.83
	Δs	0.00	0.61	1.05	1.37	1.56	1.61	1.52	1.32	0.98	0.51	0.00
	pH$_e$	7.64	7.68	7.73	7.78	7.83	7.90	7.97	8.05	8.15	8.26	8.40
2	pH$_0$	7.24	7.13	7.05	6.97	6.91	6.86	6.81	6.76	6.72	6.68	6.65
	SI_c	0.91	0.85	0.82	0.81	0.81	0.82	0.83	0.85	0.87	0.90	0.93
	s_1	2.95	5.66	7.70	9.12	10.00	10.31	10.16	9.53	8.45	6.95	5.06
	s_2	2.95	3.16	3.37	3.58	3.79	4.01	4.22	4.43	4.64	4.85	5.06
	Δs	0.00	2.50	4.33	5.54	6.21	6.31	5.94	5.10	3.81	2.10	0.00
	pH$_e$	7.27	7.18	7.11	7.04	6.97	6.91	6.86	6.81	6.76	6.71	6.67
3	pH$_0$	7.38	7.41	7.45	7.49	7.55	7.62	7.71	7.84	8.03	8.30	8.60
	SI_c	1.12	1.11	1.11	1.12	1.16	1.23	1.37	1.63	2.22	3.57	5.97
	s_1	-2.72	-2.32	-2.11	-2.12	-2.39	-2.91	-3.71	-4.79	-6.16	-7.85	-9.84
	s_2	-2.72	-3.43	-4.14	-4.86	-5.57	-6.28	-6.99	-7.70	-8.42	-9.13	-9.84
	Δs	0.00	1.11	2.03	2.74	3.18	3.37	3.28	2.91	2.26	1.28	0.00
	pH$_e$	7.34	7.38	7.41	7.45	7.50	7.54	7.60	7.65	7.72	7.79	7.87

Contd…

Groups	Items	Mixing ratios										
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
4	pH$_0$	8.24	7.69	7.56	7.49	7.46	7.43	7.41	7.39	7.38	7.36	7.35
	SI_c	1.19	0.86	1.16	1.59	2.10	2.69	3.36	4.10	4.92	5.82	6.80
	s_1	-0.54	1.20	-2.18	-9.74	-20.49	-33.64	-48.58	-64.88	-82.21	-100.30	-119.00
	s_2	-0.54	-12.39	-24.23	-36.08	-47.92	-59.77	-71.62	-83.46	-95.31	-107.15	-119.00
	Δs	0.00	13.59	22.05	26.34	27.43	26.13	23.04	18.58	13.10	6.85	0.00
	pH$_e$	8.17	7.74	7.51	7.35	7.24	7.16	7.09	7.03	6.99	6.95	6.92
5	pH$_0$	6.65	6.68	6.72	6.76	6.81	6.86	6.91	6.97	7.05	7.13	7.24
	SI_c	0.93	0.93	0.94	0.96	0.98	1.02	1.07	1.14	1.24	1.40	1.64
	s_1	5.06	4.53	3.68	2.46	0.91	-1.03	-3.37	-6.11	-9.31	-12.96	-17.12
	s_2	5.06	2.84	0.62	-1.59	-3.81	-6.03	-8.25	-10.47	-12.68	-14.90	-17.12
	Δs	0.00	1.69	3.06	4.05	4.72	5.00	4.88	4.36	3.37	1.94	0.00
	pH$_e$	6.67	6.70	6.74	6.77	6.81	6.85	6.89	6.93	6.98	7.03	7.08
6	pH$_0$	8.08	7.43	7.26	7.18	7.13	7.09	7.07	7.05	7.03	7.01	7.00
	SI_c	0.46	0.28	0.36	0.46	0.59	0.73	0.88	1.05	1.22	1.41	1.60
	s_1	1.83	7.65	11.23	12.35	11.34	8.48	4.07	-1.65	-8.50	-16.32	-24.97
	s_2	1.83	-0.85	-3.53	-6.21	-8.89	-11.57	-14.25	-16.93	-19.61	-22.29	-24.97
	Δs	0.00	8.50	14.76	18.56	20.23	20.05	18.32	15.28	11.11	5.97	0.00
	pH$_e$	8.40	7.91	7.63	7.44	7.31	7.20	7.11	7.03	6.97	6.91	6.86

Note: Units for s_1, s_2 and Δs are mg/L, pH$_0$ is calculated pH values for mixed waters, SI_c is the saturation indices for mixed waters, s_1 is the calculated results of CaCO$_3$ dissolution or precipitation amount for mixed waters, s_2 is the dissolution or precipitation amount for mixed waters under no mixing corrosion assumption, Δs (=s_1- s_2) is mixing corrosion amount, pH$_e$ is the calculated pH values for mixed waters after s_1 dissolution or precipitation

Group 1 and group 2 are obtained by mixing between unsaturated water samples. In Figure 1a and Figure 1b, the curves PR-s_1 of mixed waters are above the corresponding straight lines PR-s_2, which indicates that the mixing corrosion has occurred in group 1 and group 2. Taking group 1 as an example, when the mixing ratio is 0.2, the dissolution amount of CaCO$_3$ in the mixed water is 9.34 mg/L. If there were no mixing dissolution, that is to say, take 0.2 L of water sample 1 and 0.8 L of water sample 2 and make CaCO$_3$ dissolve in them, respectively, the total amount of dissolved CaCO$_3$ would be 8.28 mg/L, which indicates the mixing makes the dissolution of CaCO$_3$ increased by 1.054 mg/L. When the mixing ratio is 0.5, the increased dissolution amount by mixing is 1.605 mg/L and when the mixing ratio is 0.8, the increased amount is 0.98 mg/L. The increased amounts of CaCO$_3$ due to mixing in group 2 are even larger, when the mixing ratios are 0.2, 0.5 and 0.8, respectively, the increased dissolution amounts of CaCO$_3$ are 4.33, 6.31, 3.81 mg/L, correspondingly. This shows that the increased dissolution amount of CaCO$_3$ due to mixing not only changes with the mixing ratios, but is also closely related with the compositions of end member solutions.

Group 3 and group 4 are obtained by mixing between two oversaturated water samples. The values of Δs in group 3 listed in Table 3 are bigger than 0, which means the mixing corrosion has occurred. This is also proved in Figure 1c by the curve PR-s_1 of mixed water being above the corresponding straight line PR-s_2. For Group 3, when the mixing ratio is 0.2, the precipitation amount of CaCO$_3$ is 2.11 mg/L, whereas, if the mixing corrosion didn't occur, namely, 0.2 L of water from sample 5 and 0.8 L from sample 6 would produce a total of 4.14 mg/L of CaCO$_3$ precipitation, which means the mixing reduces the precipitation amount of CaCO$_3$ by 2.03 mg/L. Similarly, when the mixing ratio is 0.5 and 0.8, the reductions

of $CaCO_3$ precipitation caused by mixing are 3.37 and 2.26 mg/L, respectively. In all mixing ratios, the mixing procedure doesn't cause the state of $CaCO_3$ to change from precipitation to dissolution. Hereby, some new concepts can be proposed. The effect of mixing which makes the dissolution amount of $CaCO_3$ increase, or makes the state of $CaCO_3$ change from precipitation into dissolution is named as mixing corrosion in strict sense. And the effect of mixing that causes the precipitation amount of $CaCO_3$ to reduce is named as mixing corrosion in broad sense. According to the concepts, group 1 and group 2 are both mixing corrosion in strict sense and group 3 is mixing corrosion in broad sense.

Actually, in the mixed aqueous solution by two oversaturated samples, the mixing corrosion in strict sense can also occur. For instance, the values of Δs in group 4 listed in Table 3 are bigger than 0, which means mixing corrosion has occurred while mixing. This finds expression in Figure 1d by the curve PR-s_1 of mixed water being above the corresponding straight line PR-s_2. The two end member solutions are both oversaturated with $CaCO_3$, 110.00 mg of $CaCO_3$ can be precipitated from 1 L of water sample 7 and 0.54 mg of $CaCO_3$ can be precipitated from 1 L of water sample 8. That is to say, when we take 0.1 L of sample 7 and 0.9 L of sample 8 (indicating the ratio is 0.1) separately, a total of 12.39 mg/L of $CaCO_3$ should be precipitated from the solution. However, as a result of mixing, no $CaCO_3$ precipitation was produced in the mixed water but 1.12 mg/L of $CaCO_3$ was dissolved in it. When the mixing ratio is larger than or equal to 0.2, the mixing effect changes from corrosion in strict sense into corrosion in broad sense. When the mixing ratio is 0.2, the reduction amount of $CaCO_3$ precipitation caused by mixing is 2.05 mg/L and when the mixing ratio is 0.5 and 0.8, the reduced amounts are 26.13 and 13.10 mg/L, respectively.

Group 5 and group 6 are both obtained by mixing from an unsaturated water sample and an oversaturated water sample. In group 5, when the mixing ratio is smaller than or equal to 0.4, mixing corrosion in strict sense occurs, while in other ratios, mixing corrosion in broad sense occurs. When mixing ratios are 0.1, 0.2, 0.3 and 0.4, the corresponding amounts of mixing corrosion (Δs) are 1.688, 3.06, 4.05 and 4.72 mg/L, respectively. When the mixing ratios are 0.5, 0.7 and 0.9, the reduction of $CaCO_3$ precipitation caused by mixing are 5.00, 4.36 and 1.94 mg/L. If mixing corrosion didn't occur, equilibrium should have reached when the ratio is 0.23. However, because of the impact of mixing corrosion, when the mixing ratio is 0.23, still another 3.33 mg/L of $CaCO_3$ can be dissolved by the mixed water.

There is some kind of similarity in group 6 to that in group 5. Mixing corrosion in strict sense occurs when the mixing ratio is smaller than or equal to 0.6 and when the mixing ratio is equal to or larger than 0.7, mixing corrosion in broad sense occurs in the mixed water. For example, when the mixing ratio is 0.4, 11.34 mg/L of $CaCO_3$ dissolved in the mixed water instead of precipitation. When the mixing ratio is 0.8, the precipitation amount of $CaCO_3$ should be 19.61 mg/L when there is no mixing dissolution, but the fact is that the actual precipitation amount of $CaCO_3$ in the mixed water is 8.50 mg/L, which means the mixing reduced the $CaCO_3$ precipitation by 11.11 mg/L. If mixing corrosion didn't occur, equilibrium should have reached when the ratio is 0.07. However, because of the impact of mixing corrosion, when the mixing ratio is 0.07, still another 6.00 mg/L of $CaCO_3$ can be dissolved by the mixed water.

The above example analyses and discussions illustrate that the mixing between two unsaturated water samples, mixing between two oversaturated samples and mixing between an unsaturated sample and an oversaturated sample all can produce mixing corrosion, either mixing corrosion in strict sense or mixing corrosion in broad sense.

We have implemented plenty of mixing corrosion simulations and calculations, based on which we concluded that the mixing corrosion has close relations with the compositions of end member water samples.

According to the calculated results of large number of water samples, it is found that if mixing corrosion (including mixing corrosion in strict sense and mixing corrosion in broad sense) occurs, the two end member solutions generally possess the following characteristics: when the HCO$_3^-$ concentration in one aqueous solution is higher than that in the other solution, the Ca^{2+} concentration in the former solution is also usually higher than that in the latter one. The above 6 groups of mixtures occurring mixing dissolution all belong to this situation.

Conclusion

1)   According to the results of the study, the mixing corrosion can be divided into two different levels: mixing corrosion in strict sense and mixing corrosion in broad sense. Mixing corrosion in strict sense refers to the effects that makes the state of CaCO$_3$ change from precipitation into dissolution, or makes the dissolution amount of CaCO$_3$ increase. Mixing corrosion in broad sense refers to the effect causing the precipitation of CaCO$_3$ to reduce due to mixing.

2)   According to the different compositions of end member water samples, the mixing corrosion, either mixing corrosion in strict sense or mixing corrosion in broad sense, can be produced by mixing between two unsaturated water samples, mixing between two oversaturated samples or mixing between an unsaturated sample and an oversaturated sample.

3)   When mixing corrosion 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 Ca^{2+} concentration in the former solution is also usually higher than that in the latter one.

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