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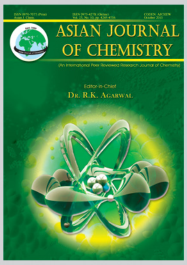

Proportion Dependent Mixing Effects of $CaCO_3$ in Natural Waters

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An interesting phenomenon named proportion dependent mixing effect of $CaCO_3$ in natural waters was discovered and discussed. The proportion dependent mixing effect is defined as mixing corrosion occurring in some of the mixing ratios and mixing precipitation in other ratios when two solutions are mixed. The interesting phenomenon can be produced by mixing of two unsaturated water samples (with respect to $CaCO_3$), two supersaturated water samples or mixing by an unsaturated sample and an oversaturated sample. The proportion dependent mixing effects usually occur under the following conditions: (1) the HCO_3^- concentration in one end member solution is much higher than that in the other solution and the concentration of Ca^{2+} in the former aqueous solution is much lower than that in the latter one; (2) pH value in the higher HCO_3^- concentration solution is higher than that in the lower HCO_3^- concentration solution.

Key Words: $CaCO_3$, Natural water, Equilibrium aqueous model, Proportion dependent mixing effects.

INTRODUCTION

The interesting mixing phenomenon occurring in natural or man made environment has drawn much attention from the world. When two different waters are mixed, the original equilibriums among different species in the water are destroyed and as a result, some specific reactions are induced. These reactions caused by the mixing can make the solubility or precipitability of $CaCO_3$ increase or decrease in the mixed water, which is a complex process to understand because too many things have to be taken into consideration. However, this complexity doesn't constrain the forward steps for science because of the exploration and devotion of many scientists. Since the naissance of mixing corrosion theory by Bogli in 1961[1,2], the mixing corrosion is considered as one of the most important factors controlling the development of littoral karst[3] and much relative work has been done by many scientists from the world[4-9].

However, our recent studies show that when two natural water samples are mixed, mixing precipitation can be produced too[10], which has greatly developed and broadened the mixing corrosion theory. In spite of this, studies are still needed to promote the development of mixing theory. In this study, a proportion dependent mixing effect of $CaCO_3$ is discovered and discussed. The proportion dependent mixing effect refers to mixing corrosion occurring in some of the mixing ratios and mixing precipitation in other ratios when two natural waters are mixed. This is an interesting phenomenon which requires comprehensive and in depth study.

METHODOLOGY

Results of water quality analysis and chemical equilibrium model: A total of 10 water samples are used in this study and of the 10 samples, the first 5 are unsaturated with $CaCO_3$ and the others are supersaturated with $CaCO_3$. Table-1 lists the analysis results of water samples. In Table-1, the SI_c is the saturation index of water samples with respect to $CaCO_3$ (calcite) which is expressed as eqn. 1.

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

where, a $\{Ca^{2+}\}$ and a $\{CO_3^{2-}\}$ are the activities of Ca^{2+} and CO_3^{2-} in the solution, 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.

The chemical equilibrium model listed in Table-2 is used for calculating the chemical equilibrium of aqueous solution systems. The model contains a total of 9 basic components, 17 derivative species.

Computational method

For the calculation of equilibrium distribution of soluble species, many scholars have carried out a wide range of discussions and put forward a number of calculation methods[11-22]. In this paper, the calculation method proposed by Crerar[13] and Qian[17] and the formula expressing the equilibrium constants

TABLE-1
ANALYSIS RESULTS OF WATER SAMPLES

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	8.08	24.0	14.18	9.61	9.60	43.93	8.80	4.20	17.64	1.70	0.456
2	6.65	35.0	4.20	431.00	0	392.00	6.90	26.20	232.00	47.30	0.927
3	6.50	35.5	532.00	441.00	0	1870.00	980.00	98.00	33.20	6.58	0.313
4	6.80	58.0	37.60	39.90	0	1963.60	717.50	62.60	14.00	1.80	0.779
5	6.20	33.0	34.96	134.60	0	2760.00	1000.00	150.00	45.89	8.76	0.241
6	6.50	42.5	244.00	233.00	0	1480.00	497.00	43.60	62.10	28.90	0.699
7	7.00	27.0	2.90	327.00	0	359.00	6.10	19.70	204.00	36.20	1.599
8	6.71	35.0	4.20	431.00	0	393. 00	6.80	26.30	232.00	47.20	1.106
9	7.24	22.0	3.00	244.00	0	276.00	3.70	13.70	159.00	26.10	1.636
10	7.26	25.0	3.40	284.00	0	306.00	4.40	14.40	167.00	28.40	2.155

TABLE-2
CHEMICAL MODEL FOR THE STUDIED WATER

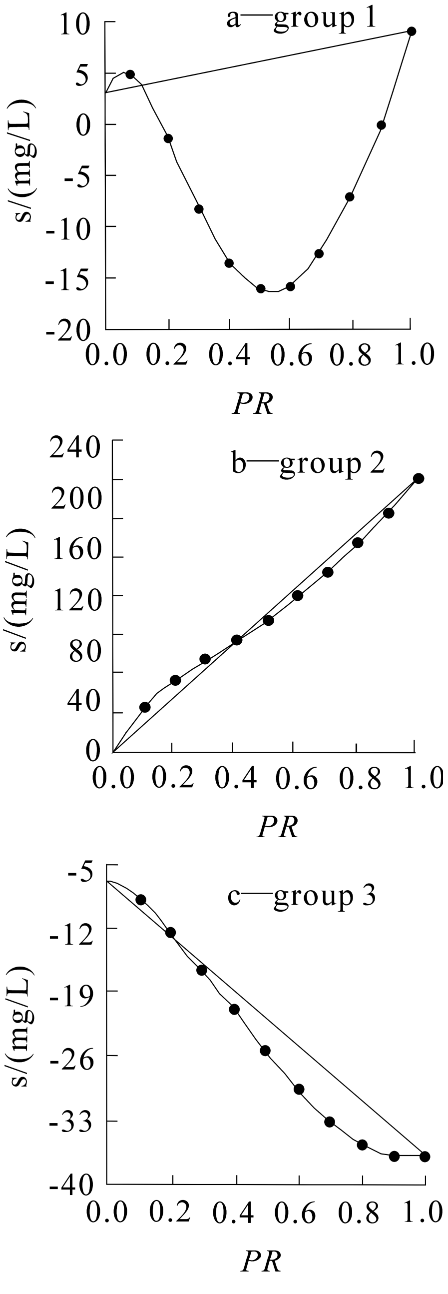
Basic components		Derivative species		
No.	Components	No.	Species	Chemical reactions
1	Cl^-	1	$NaCl^0$	$Na^+ + Cl^- = NaCl^0$
2	SO_4^{2-}	2	KCl^0	$K^+ + Cl^- = KCl^0$
3	CO_3^{2-}	3	$H_2SO_4^0$	$2H^+ + SO_4^{2-} = H_2SO_4^0$
4	Na^+	4	HSO_4^-	$H^+ + SO_4^{2-} = HSO_4^-$
5	K^+	5	$NaSO_4^-$	$Na^+ + SO_4^{2-} = NaSO_4^-$
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	$H^+ + OH^- = H_2O$

varying with temperature proposed by Arnorsson and Sigurdsson[23] are used. Furthermore, Plummer *et al.*[24] have discussed the calculation method of pH for mixed waters. In a previous study[25], we did some modification and improvement to the method, which has been verified by experimental data. In this paper the modified method is adopted.

For the calculation of solubility (precipitability) of $CaCO_3$ in mixed waters, the method introduced by Qian *et al.*[26] is used. The solubility (precipitability) of $CaCO_3$ under different mixing ratios in a closed system is calculated with the method. The calculated results are designated as s_1 with $s_1 > 0$ indicating dissolution and $s_1 < 0$ indicating precipitation. If the mixing corrosion (precipitation) didn't occur, the solubility (precipitability) of $CaCO_3$ in mixed water would show a linear relation with the mixing ratios. The solubility (precipitability) of $CaCO_3$ in mixed waters under no mixing corrosion assumption is designated as s_2. Compare 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 water samples 2 and 9, samples 1 and 7, samples 4 and 10, samples 3 and 8, samples 5 and 8, samples 6 and 7. The calculated results of dissolution (precipitation) of $CaCO_3$ for these mixed waters are listed in Table-3 and corresponding curves are drawn in Fig. 1.



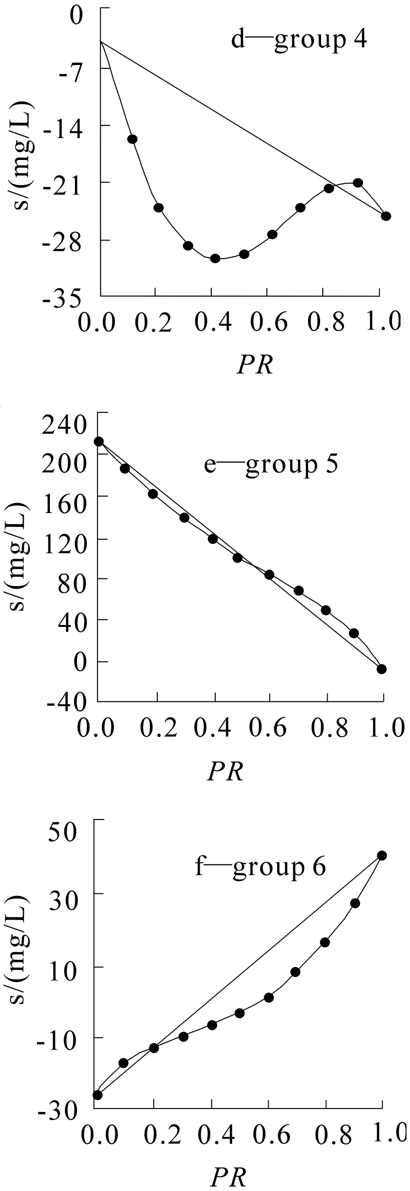


Fig. 1. Dissolution (precipitation) amount of $CaCO_3$ in mixed waters. The x-axis *PR* is the mixing ratio, y-axis s is the dissolution amount of $CaCO_3$ in mixed waters, straight line represents the results under no mixing effects assumption and curve represents the computed results for proportion dependent mixing effects

The mixing between two unsaturated waters can not only produce mixing corrosion or mixing precipitation, but also can produce proportion dependent mixing effects, group 1 and 2 are examples of this case. For group 1, when the mixing ratio is 0.1, the mixing makes the $CaCO_3$ solubility in the solution increased by an amount of 0.50 mg/L. Mean while, it can be seen from Fig. 1a that when the ratio is 0.05, the increased dissolution amount of $CaCO_3$ is even larger. However, when the mixing ratio is 0.2, the mixing makes the saturation state of $CaCO_3$ change from dissolution to precipitation. At this moment, the mixing produces 1.58 mg/L of $CaCO_3$ precipitation. When the mixing ratios are 0.5 and 0.8, the precipitation amounts for mixed waters are, respectively 16.17 and 7.50 mg/L, which means the effects of mixing precipitation are, respectively, 22.15 and 15.50 mg /L. The phenomenon in group 2 is similar to that in group 1, when the mixing ratio is less than or equal to 0.4, the mixing corrosion occurs and when the mixing ratio is larger than or equal to 0.5, the mixing precipitation (mixing precipitation in broad sense) occurs. When the mixing ratios are 0.1, 0.2, 0.3 and 0.4, the increased dissolution amounts of $CaCO_3$ due to mixing are 11.09, 10.75, 61.01 and 0.44 mg/L, respectively and when the mixing ratios are 0.5, 0.6, 0.7, 0.8 and 0.9, the reductions of precipitation amounts are 4.49, 7.94, 9.36, 8.45 and 5.30 mg/L, respectively.

The proportion dependent mixing effects can also occur in mixed waters which are formed by two oversaturated water samples. In group 3, when the mixing ratio is smaller than or equal to 0.2, the mixing dissolution in broad sense occurs and when the mixing ratio is larger than or equal to 0.3, the effect changes into mixing precipitation in strict sense. For example, when the mixing ratio is 0.1 and 0.2, the reductions of $CaCO_3$ precipitation caused by mixing are 0.73 and 0.36 mg/L, respectively. When the mixing ratio is 0.3, the increased amount of $CaCO_3$ precipitation is 0.70 mg/L. In case of the mixing ratio is 0.5, the increase is 3.57 mg/L. It is a little different in group 4 from that in group 3. In group 4, when the mixing ratio is smaller than or equal to 0.8, the mixing precipitation in strict sense occurs and when the mixing ratio is 0.9, mixing dissolution in broad sense takes place. When the mixing ratios are 0.2, 0.5 and 0.8, the increased amounts of $CaCO_3$ precipitation by mixing are 15.77, 15.03 and 0.73 mg/L, respectively. When the mixing ratio is 0.9, the reduction of $CaCO_3$ precipitation is 1.74 mg/L.

When an unsaturated water sample is mixed with an oversaturated water sample, the proportion dependent mixing effects can still take place. Group 5 and group 6 are examples for this case. When the mixing ratio in group 5 is smaller than or equal to 0.5, the mixing precipitation in broad sense occurs. When the mixing ratio is larger than or equal to 0.6, then mixing corrosion in strict sense occurs. For example, when the mixing ratio is 0.1, under no mixing precipitation assumption, the dissolution amount of $CaCO_3$ is 190.96 mg/L and under the influence of the mixing precipitation, the dissolution amount of $CaCO_3$ is 186.44 mg/L, which means the mixing effect makes the dissolution amount of $CaCO_3$ reduced by 4.52 mg/L. Similarly, when the mixing ratios are 0.3 and 0.5, the reductions of dissolution amount of $CaCO_3$ are 7.53 and 2.24 mg/L, respectively. When the mixing ratio is 0.6, the dissolution amount of $CaCO_3$ is 81.246 mg/L assuming no mixing dissolution, under the influence of mixing corrosion, the dissolution amount of $CaCO_3$ is 84.03 mg/L, which indicates that the dissolution amount is increased by 2.79 mg/L due to mixing corrosion. Similarly, when the mixing ratios are 0.7, 0.8 and 0.9, the dissolution amounts of $CaCO_3$ are increased by 8.27, 12.56 and 12.30 mg/L, respectively.

In group 6, when the mixing ratio is 0.1 the mixing corrosion in broad sense occurs, when the mixing ratios are 0.2, 0.3, 0.4 and 0.5, the mixing precipitation in strict sense occurs and when the mixing ratio is larger than or equal to 0.6, the state changes into mixing precipitation in broad sense. For example, when the mixing ratio is 0.1, the precipitation amount of $CaCO_3$ is 18.43 mg/L assuming no mixing corrosion, whereas, under the influence of mixing dissolution, the precipitation amount of $CaCO_3$ is 16.96 mg/L, which indicates the mixing makes the precipitation of $CaCO_3$ reduced by 1.47

TABLE-3
CALCULATED RESULTS FOR MIXED WATER SAMPLES

Groups	Items	Mixing ratios										
		0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
1	pH_0	7.24	7.06	6.98	6.93	6.90	6.87	6.85	6.83	6.82	6.81	6.80
	SI_c	0.91	0.92	1.03	1.12	1.20	1.25	1.26	1.23	1.15	1.00	0.78
	s_1	2.95	4.06	-1.58	-8.30	-13.56	-16.17	-15.95	-12.92	-7.50	-0.05	9.01
	s_2	2.95	3.56	4.16	4.77	5.37	5.98	6.59	7.19	7.80	8.40	9.01
	Δs	0.00	0.50	-5.74	-13.07	-18.93	-22.15	-22.54	-20.11	-15.30	-8.45	0.00
	pH_e	7.27	7.08	6.98	6.91	6.87	6.84	6.83	6.82	6.81	6.81	6.81
2	pH_0	6.65	6.44	6.35	6.30	6.27	6.25	6.23	6.22	6.21	6.21	6.20
	SI_c	0.93	0.69	0.64	0.61	0.58	0.55	0.51	0.46	0.39	0.32	0.24
	s_1	5.05	36.92	57.37	73.50	88.62	104.48	121.81	141.17	162.86	186.80	212.88
	s_2	5.05	25.83	46.62	67.40	88.18	108.97	129.75	150.53	171.31	192.10	212.88
	Δs	0.00	11.09	10.75	6.10	0.44	-4.49	-7.94	-9.36	-8.45	-5.30	0.00
	pH_e	6.67	6.53	6.45	6.40	6.37	6.35	6.33	6.32	6.32	6.31	6.31
3	pH_0	6.71	6.66	6.63	6.60	6.58	6.56	6.54	6.53	6.52	6.51	6.50
	SI_c	1.11	1.13	1.16	1.20	1.24	1.28	1.32	1.35	1.38	1.39	1.39
	s_1	-6.54	-8.85	-12.25	-16.34	-20.79	-25.28	-29.44	-33.01	-35.65	-37.03	-36.89
	s_2	-6.54	-9.58	-12.61	-15.65	-18.68	-21.72	-24.75	-27.79	-30.82	-33.86	-36.89
	Δs	0.00	0.73	0.36	-0.70	-2.11	-3.57	-4.69	-5.23	-4.83	-3.18	0.00
	pH_e	6.68	6.63	6.59	6.55	6.52	6.50	6.48	6.46	6.45	6.45	6.44
4	pH_0	6.50	6.51	6.53	6.55	6.57	6.60	6.63	6.68	6.74	6.83	7.00
	SI_c	1.04	1.15	1.23	1.27	1.29	1.29	1.28	1.27	1.28	1.34	1.60
	s_1	-3.80	-15.59	-23.80	-28.51	-30.14	-29.41	-26.98	-23.91	-21.47	-21.11	-24.97
	s_2	-3.80	-5.92	-8.03	-10.15	-12.27	-14.39	-16.50	-18.62	-20.74	-22.85	-24.97
	Δs	0.00	-9.67	-15.77	-18.36	-17.87	-15.03	-10.48	-5.29	-0.73	1.74	0.00
	pH_e	6.50	6.50	6.50	6.51	6.52	6.55	6.58	6.62	6.68	6.75	6.86
5	pH_0	6.20	6.21	6.22	6.23	6.24	6.26	6.28	6.32	6.37	6.47	6.71
	SI_c	0.24	0.32	0.40	0.46	0.51	0.56	0.60	0.64	0.68	0.76	1.11
	s_1	212.90	186.44	161.88	139.54	119.29	100.94	84.03	67.56	49.91	27.70	-6.54
	s_2	212.90	190.96	169.01	147.07	125.12	103.18	81.24	59.29	37.35	15.40	-6.54
	Δs	0.00	-4.52	-7.13	-7.53	-5.83	-2.24	2.79	8.27	12.56	12.30	0.00
	pH_e	6.31	6.31	6.32	6.32	6.33	6.35	6.37	6.40	6.45	6.53	6.68
6	pH_0	7.00	6.83	6.73	6.67	6.63	6.60	6.57	6.55	6.53	6.51	6.50
	SI_c	1.60	1.26	1.15	1.10	1.06	1.03	0.99	0.94	0.88	0.80	0.70
	s_1	-24.97	-16.96	-12.40	-9.38	-6.60	-3.20	1.46	7.91	16.46	27.25	40.39
	s_2	-24.97	-18.43	-11.90	-5.36	1.17	7.71	14.25	20.78	27.32	33.85	40.39
	Δs	0.00	1.47	-0.50	-4.02	-7.77	-10.91	-12.79	-12.87	-10.86	-6.60	0.00
	pH_e	6.86	6.76	6.70	6.65	6.62	6.59	6.57	6.56	6.55	6.54	6.54

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 dissolution or precipitation amount of $CaCO_3$ for mixed waters, s_2 is the dissolution or precipitation amount for mixed waters under no proportion dependent mixing 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.

mg/L. When the mixing ratio is 0.2, if the mixing precipitation didn't occur, the precipitation amount of $CaCO_3$ would be 11.90 mg/L. However, under the impact of mixing precipitation, the actual amount of $CaCO_3$ precipitation is 12.40 mg/L, which means the mixing increases the precipitation of $CaCO_3$ by 0.50 mg/L. When the mixing ratio is 0.5, the dissolution amount of $CaCO_3$ should be 7.17 mg/L if mixing precipitation did not occur, but under the influence of mixing precipitation, there would be 3.20 mg/L of $CaCO_3$ precipitated in the mixed water. The mixing reduces the dissolution of $CaCO_3$ by 12.786 mg/L when the mixing ratio is 0.6 and when the mixing ratios are 0.7, 0.8 and 0.9, the reduced amounts of dissolution caused by mixing are 12.87, 10.86 and 6.60 mg/L, respectively.

The above example analyses and discussions illustrate that by mixing between two supersaturated water samples, two unsaturated water samples or between an unsaturated water sample and an oversaturated sample, proportion dependent mixing effects can be produced. The end member solution and mixing ratios coherently determine and control the reactions. According to the calculated results of large number of water samples, it is found the proportion dependent mixing effects usually occur under the following conditions: (1) the HCO_3^- concentration in one end member solution is much higher than that in the other solution and the concentration of Ca^{2+} in the former aqueous solution is much lower than that in the latter one; (2) pH value in the higher HCO_3^- concentration solution is higher than that in the lower HCO_3^- concentration solution.

Conclusion

- Mixing of natural water can produce an interesting phenomenon and in this paper, it is named as proportion dependent mixing effects. Just as its name implies, the proportion dependent mixing effects are determined by the mixing ratios of two end member solutions, when mixing ratios are different, the mixing effects are different.
- The proportion dependent mixing effects can be produced by mixing of two unsaturated water samples, two super-

saturated water samples or by mixing of an unsaturated sample and an oversaturated sample.

- The proportion dependent mixing effects usually occur under the following conditions: the HCO_3^- concentration in one end member solution is much higher than that in the other solution and the concentration of Ca^{2+} in the former aqueous solution is much lower than that in the latter one; pH value in the higher HCO_3^- concentration solution is higher than that in the lower HCO_3^- concentration solution.

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