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An Aspect on Interfacial Characteristics of Carbonate Minerals in Water

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Abstract

When a carbonate mineral comes in contact with water, the process through which equilibrium between solid, liquid and air is established is grouped into two types: (1) the solid-liquid system monotonously reaches its equilibrated state with air in a short time; (2) the solid-liquid system approaches the apparent system closed to air, after which it reaches its equilibrium state with air after a lengthy period. Manganese carbonate and lead carbonate belong to type(1), and calcium carbonate, barium carbonate and strontium carbonate belong to type(2). The difference between type(1) and type(2) is caused by the magnitude of the solubility product. The pH values at "zero H^+ and OH^- demand" of the carbonate minerals were measured by potentiometric titration. The variation of the pH values at "zero H^+ and OH^- demand" with time and variation of the isoelectric points reported by many reseachers are related to the variation of the IEP(aq) values calculated by chemical thermodynamics under particular conditions.

1. Introduction

Compared with the majority of oxides and silicate minerals, salt-type minerals are characterized by their higher solubilities in an aqueous system. When a mineral coexists with a salt-type mineral, the behavior of the former mineral suspension is affected by the ions derived from the salt-type mineral, where the surface and flotation properties of each mineral in the mixed minerals system differ from those in the single mineral systems. In particular, carbonate minerals considerably influence the behavior of other salt-type minerals such as fluorite and apatite, thus making selective flotation difficult^{1,2,3,4,24}. When carbonate minerals are present in water, two extreme systems, namely, a closed and open system may be considered. The former is closed to atmospheric CO_2 and the later is open to atmospheric CO_2 . When calcite is brought into contact with water, in the initial short period the system approaches a steady state in a similar situation to the closed system, then gradually shifts to and arrives at the steady state in the open system after a lengthy period^{1,2,15}. In the case of rhodochrosite, in a short time the system reaches a steady state in the open system⁵. It is important to study this difference in behavior of carbonate mineral suspension and the change in interfacial characteristics of carbonate minerals with time. Less work has been done on this subject.

In this paper, pH measurements of carbonate mineral suspension as a function of

mixing time and potentiometric titrations were carried out using five types of carbonate mineral, and interfacial characteristics thereof were discussed.

2. Experimental Materials and Methods

Chemical reagents of calcium carbonate, manganese carbonate, barium carbonate, strontium carbonate and lead carbonate were used in this investigation. Perchloric acid and potassium hydroxide were used for pH adjustments. All chemicals used were of analytical grade.

The potentiometric titration technique was essentially that of Parks and de Bruyn²⁷⁾, and the apparatus and method used were previously described in detail⁹⁾. The experimental conditions of the potentiometric titration were as follows: a 2 g of carbonate mineral was suspended in 150 ml of 0.01 mol/l KNO_3 or KClO_4 solution and the titration was carried out under atmospheric conditions at 25.0 ± 0.2 °C using a thermostatic vessel. Blank tests were similarly carried out using 150 ml of the appropriate KNO_3 or KClO_4 solution flushed with CO_2 -free N_2 gas. As the amount of H^+ or OH^- required by the carbonate mineral suspension corresponds to the amount of H^+ or OH^- consumed by both its adsorption on carbonate mineral surface and reactions with dissolved ions in the solution, the amount is referred to as " H^+ and OH^- demand" by the present writers.

The pH measurement of the suspension as a function of mixing time was carried out as follows. A 2 g of carbonate mineral was added to 150 ml of aqueous solution adjusted to different initial pH values, then the suspension was agitated under atmosphere, and the pH value of the suspension was continuously measured as a function of time. The ionic strength of the suspension was kept constant with 0.01 mol/l of KNO_3 or KClO_4 , and the temperature of the system was also kept constant at 25.0 ± 0.2 °C.

3. Results

The changes in pH of calcium carbonate suspensions with time are shown in Fig. 1.

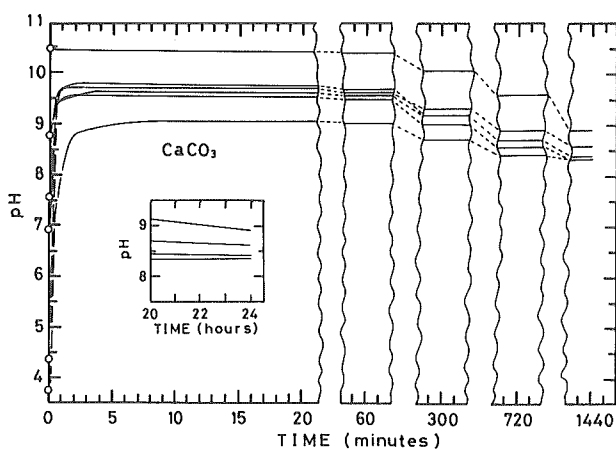


Fig. 1. Change in pH of the aqueous solutions with mixing in presence of CaCO_3 and air.
Supporting electrolyte: 0.01 mol/l KNO_3 .
Initial pH: 3.7, 4.3, 6.8, 7.5, 8.8, 10.5.

When initial pH was adjusted to below pH 8.8, immediately after adding calcium carbonate to the aqueous solution, the pH of the suspensions suddenly increased and arrived at pH 9.0 ~9.8, then decreased very slowly, and converged into pH 8.3~8.6 after 24 hours. In the case of initial pH 10.5, the pH of the suspension decreased gradually and arrived at pH 8.9 after 24 hours, showing a tendency to reach pH 8.3~8.6 after a lengthy time.

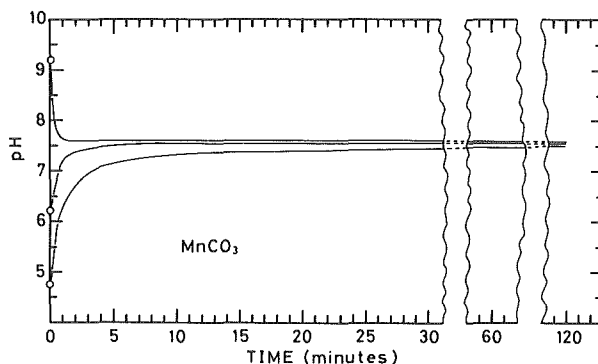


Fig. 2 . Change in pH of the aqueous solutions with mixing in presence of MnCO_3 and air.
Supporting electrolyte : 0.01 mol/l KNO_3 .
Initial pH : 4.8, 6.2, 9.2.

Fig. 2 shows the results for manganese carbonate. The pH of the suspensions changed monotonously compared with that of calcium carbonate suspensions, and converged into pH 7.5~7.6 after 2 hours. Figs. 3, 4 and 5 show the results for barium carbonate, strontium carbonate and lead carbonate respectively. The changes in pH of the suspensions of barium carbonate and strontium carbonate with time were similar to those of calcium carbonate. The pH of the suspensions converged into pH 8.3~8.5 for barium carbonate after 40 hours, and into pH 8.1~8.2 for strontium carbonate after 20 hours. The pH

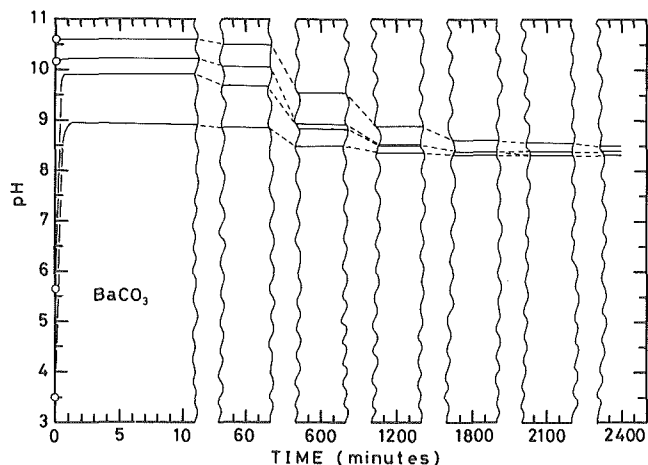


Fig. 3 . Change in pH of the aqueous solutions with mixing in presence of BaCO_3 and air.
Supporting electrolyte : 0.01 mol/l KClO_4 .
Initial pH : 3.5, 5.6, 10.2, 10.6.

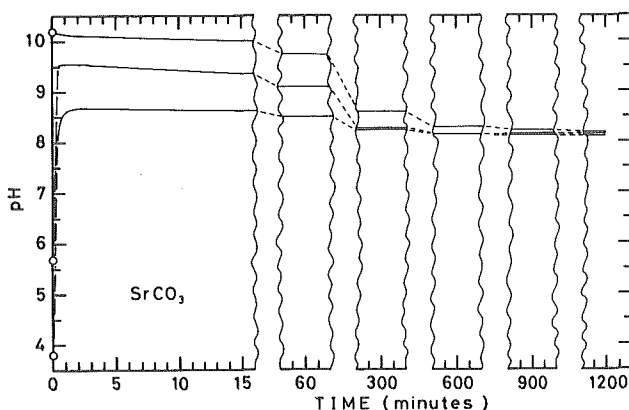


Fig. 4. Change in pH of the aqueous solutions with mixing in presence of SrCO_3 and air.
Supporting electrolyte: 0.01 mol/l KClO_4 .
Initial pH: 3.8, 5.7, 10.2.

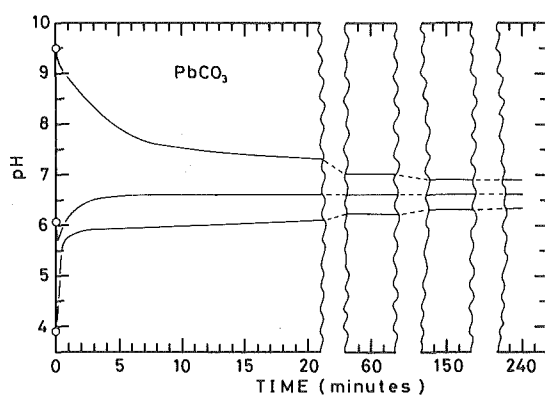


Fig. 5. Change in pH of the aqueous solutions with mixing in presence of PbCO_3 and air.
Supporting electrolyte: 0.01 mol/l KClO_4 .
Initial pH: 3.9, 6.1, 9.5.

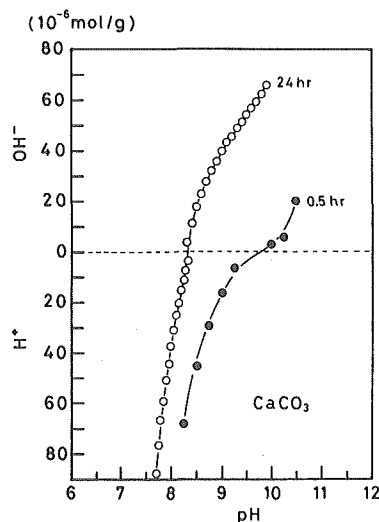


Fig. 6. Relation of H^+ and OH^- demand in suspension to pH value.
Supporting electrolyte: 0.01 mol/l KNO_3 .

changes of lead carbonate suspensions were similar to those of manganese carbonate, and the pH converged into pH 6.3~6.9 after 4 hours.

The H^+ and OH^- demands in calcium carbonate suspension are shown in Fig. 6. The pH values at zero H^+ and OH^- demand were 9.8 and 8.3 when measured at 30 minutes and 24 hours after calcium carbonate addition, respectively.

Figs. 7, 8, 9 and 10 show the results of H^+ and OH^- demand for manganese carbonate, barium carbonate, strontium carbonate and lead carbonate respectively. The pH values at zero H^+ and OH^- demand in the carbonate mineral suspensions were 7.8 (after 30 minutes) for manganese carbonate, 9.8 (after 30 minutes) and 8.3 (after 40 hours) for barium carbonate, 9.3 (after 30 minutes) and 8.2 (after 24 hours) for strontium carbonate, and 6.6

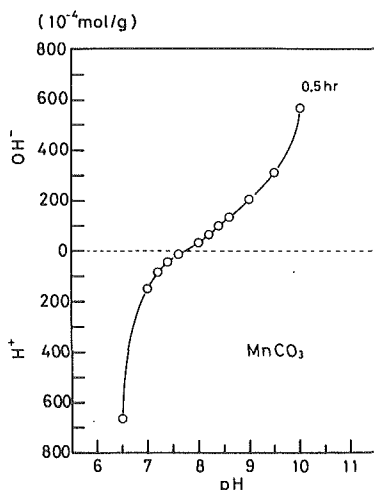


Fig. 7. Relation of H^+ and OH^- demand in suspension to pH value.
Supporting electrolyte : 0.01 mol/l KNO_3 .

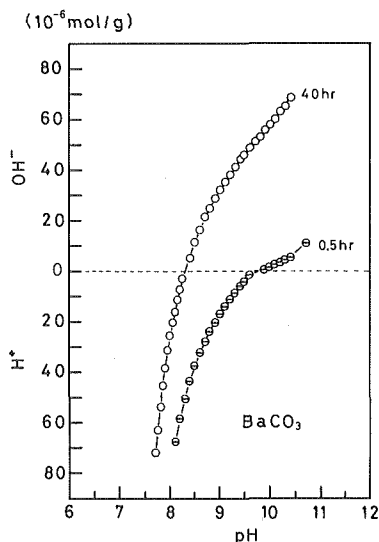


Fig. 8. Relation of H^+ and OH^- demand in suspension to pH value.
Supporting electrolyte : 0.01 mol/l $KClO_4$.

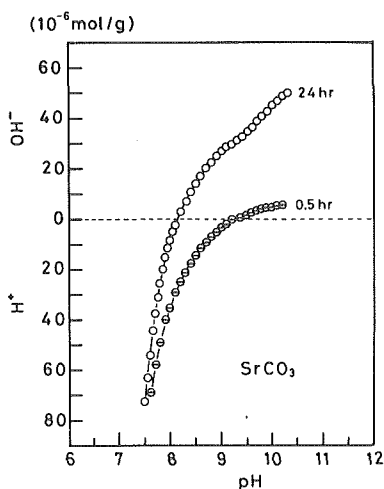


Fig. 9. Relation of H^+ and OH^- demand in suspension to pH value.
Supporting electrolyte : 0.01 mol/l $KClO_4$.

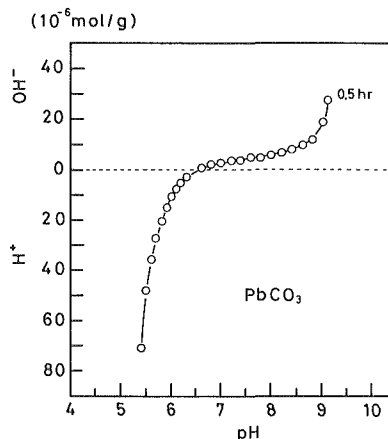
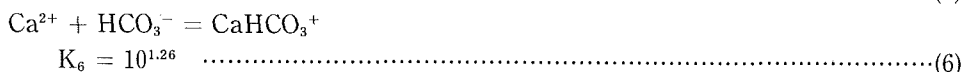
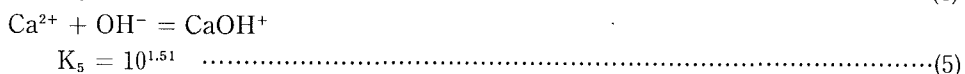
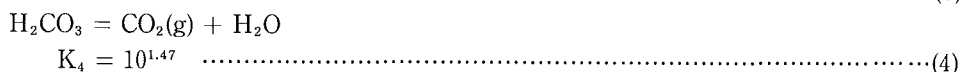
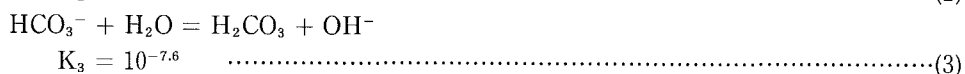
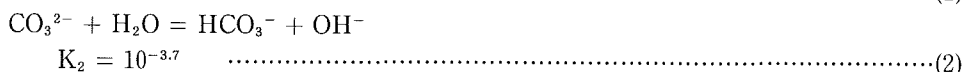
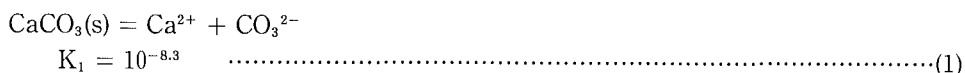


Fig. 10. Relation of H^+ and OH^- demand in suspension to pH value.
Supporting electrolyte : 0.01 mol/l $KClO_4$.

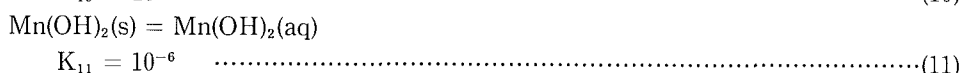
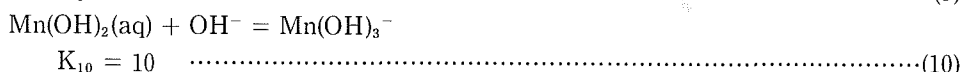
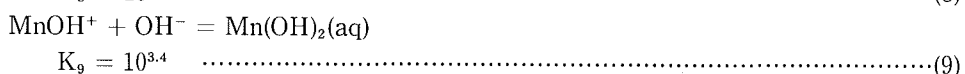
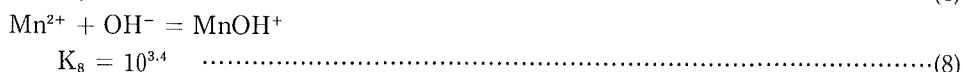
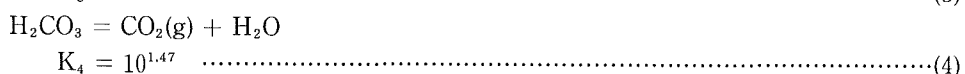
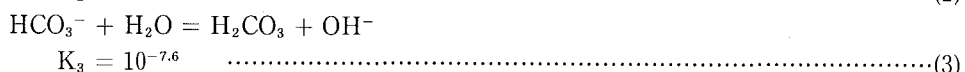
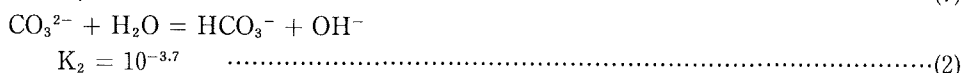
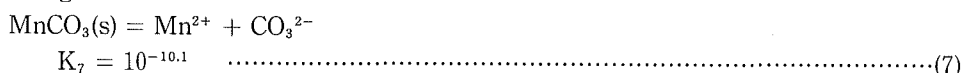
(after 30 minutes) for lead carbonate, respectively.

4. Discussion

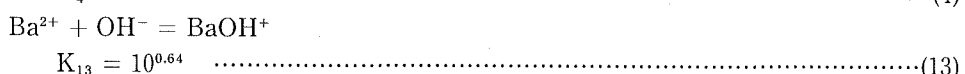
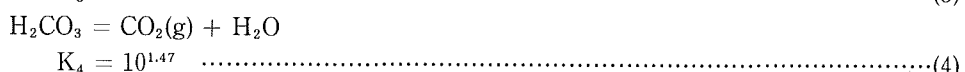
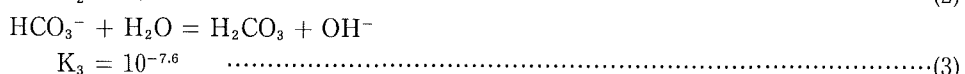
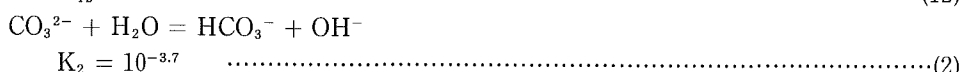
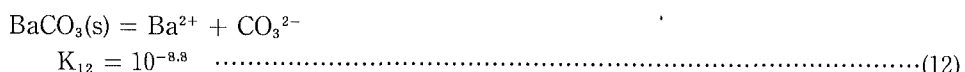
As carbonate minerals are fairly soluble, it is necessary to evaluate the concentrations of chemical species in aqueous phase of the carbonate suspensions as a function of pH. The following reactions will occur when carbonate minerals are suspended in water^(6,7,8,9). For calcium carbonate



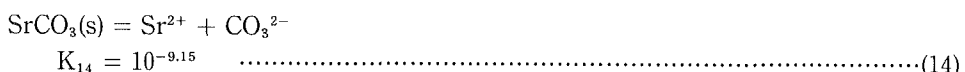
For manganese carbonate

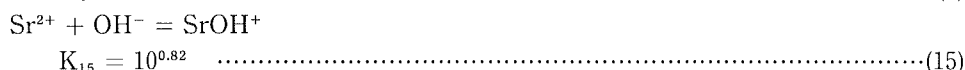
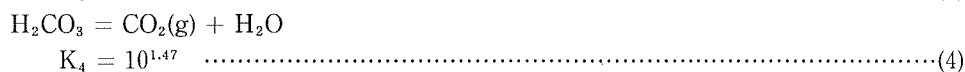
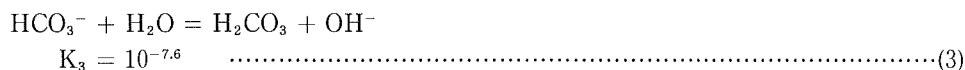
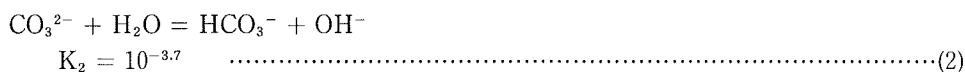


For barium carbonate

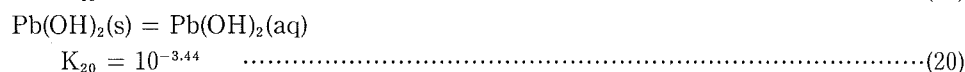
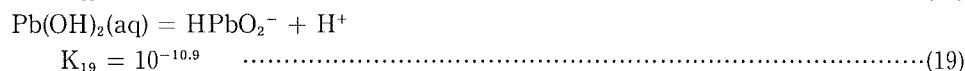
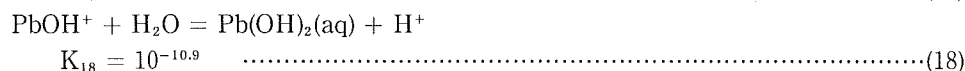
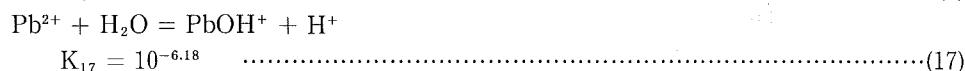
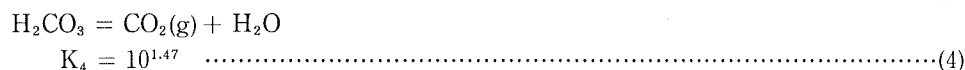
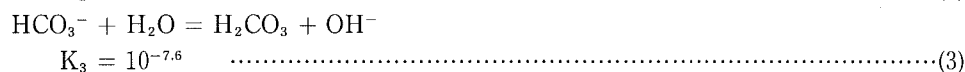
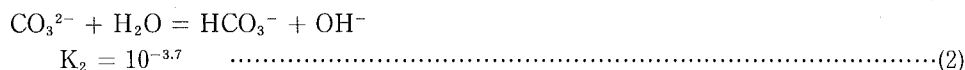
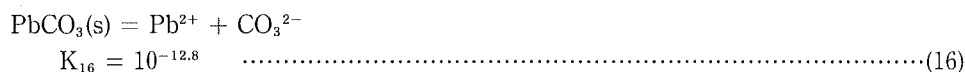


For strontium carbonate





For lead carbonate



The carbonate mineral-water system could be classified as an open or closed system. The open system is when the aqueous suspension system is open to the atmosphere with a constant partial pressure of CO_2 (P_{CO_2}), and in contrast the closed system is closed to the atmosphere. The experiments in this study were carried out under the atmospheric air with P_{CO_2} of $10^{-3.5}$ atm. It is possible to calculate the activities of different chemical species in equilibrium with carbonate minerals at different pH values, using the equilibrium constants given in Eqs. (1)~(20) and $P_{\text{CO}_2} = 10^{-3.5}$ atm. The results calculated are shown in Figs. 11~15. When IEP(aq) is defined as the condition at zero point of total electric charge of chemical species regarding constituent ions of a particular mineral, the values of IEP(aq) were pH 8.35 for calcium carbonate, pH 7.75 for manganese carbonate, pH 8.18 for barium carbonate, pH 8.06 for strontium carbonate, and pH 7.07 for lead carbonate. Table 1 shows the results obtained in this work and the isoelectric points published in the literature.

The equilibrium pH values calculated for carbonate mineral-pure water-atmospheric air system should coincide with the pH values of the IEP(aq) obtained at $P_{\text{CO}_2} = 10^{-3.5}$ atm. As shown in Table 1, the pH values finally attainable by each carbonate mineral system were in accord with the corresponding IEP(aq) values and consequently the pH values finally attainable could be the equilibrium pH values.

As the concentration of chemical species present at the solid-solution interface and in

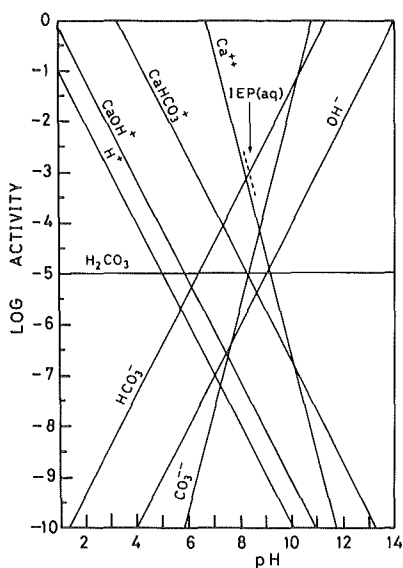


Fig. 11. Logarithmic activity diagram for CaCO₃-water-air system ($P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$).

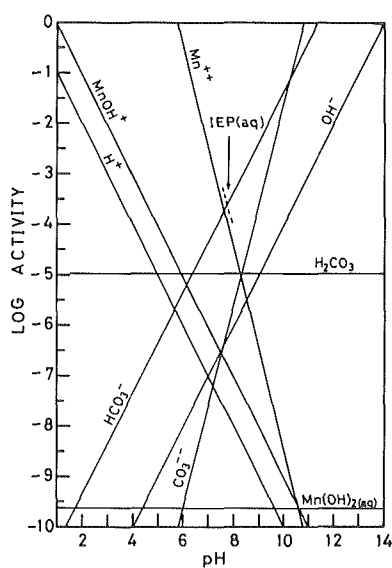


Fig. 12. Logarithmic activity diagram for MnCO₃-water-air system ($P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$).

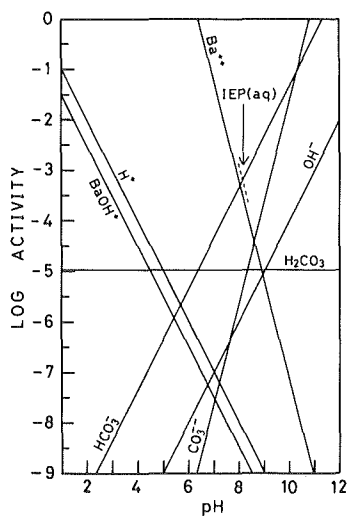


Fig. 13. Logarithmic activity diagram for BaCO₃-water-air system ($P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$).

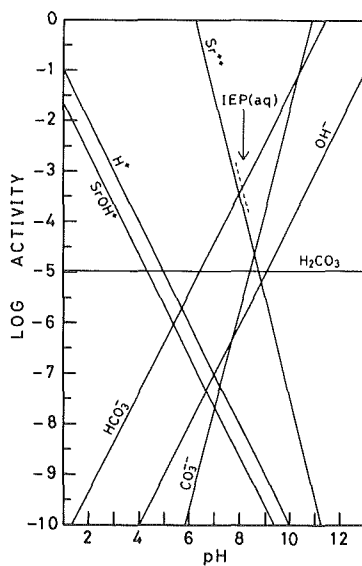


Fig. 14. Logarithmic activity diagram for SrCO₃-water-air system ($P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$).

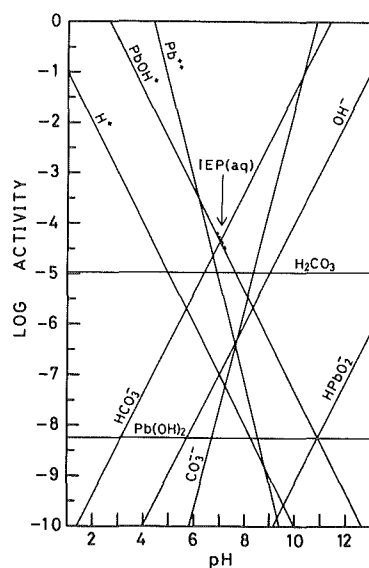


Fig. 15. Logarithmic activity diagram for PbCO_3 -water-air system ($P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$).

Table 1. Summary of investigations of interfacial characteristics of carbonate minerals in aqueous solution.

Material	IEP(aq)		pH drift test		pH value at zero H^+ and OH^- demand	Isoelectric point (References)
	$10^{-3.5} \text{ atm}$	$10^{-6.13} \text{ atm}$	a) Max.pH	b) Equ.pH		
CaCO_3	pH 8.35	pH 10.00	pH 9.8	pH 8.3 ~8.6	pH 9.8 after 0.5h	pH 10.8~9.5 (12)
					pH 8.3 after 24h	pH 10.8 (13)
						pH 10.6 (28)
						pH 10.5 (24)
						pH 10.3 (14)
						pH 9.8 (15)
						pH 9.6 (16)
						pH 9.5 (17, 18, 25)
						pH 9.3 (26)
						pH 8.7 (19)
						pH 8.2 (20)
						pH 8.1 (21)
						pH 7.4 (22)
						pH 5.4 (23)
BaCO_3	pH 8.18	pH 9.86	pH 9.9	pH 8.3 ~8.5	pH 9.8 after 0.5h	
					pH 8.3 after 40h	
SrCO_3	pH 8.06	pH 9.75	pH 9.5	pH 8.1 ~8.2	pH 9.3 after 0.5h	pH 8.7 (16)
					pH 8.2 after 24h	

MnCO ₃	pH 7.75	pH 9.47	c)	pH 7.5 ~7.6	pH 7.8 after 0.5h	pH 7.6 (5)
PbCO ₃	pH 7.07	pH 9.58	c)	pH 6.3 ~6.9	pH 6.6 after 0.5h	

- a) Max. pH: Maximum pH value attainable in a short time when adjusting initial pH to pH 5.5~7.5.
b) Equ. pH: Equilibrium pH value attainable in a long run when adjusting initial pH to pH 3.5~10.5.
c) The pH of the suspension changed monotonously.

the solution depends on pH, when adding carbonate mineral to aqueous solution, the mineral-solution system would proceed with the reactions given in Eqs. (1)~(20) until they achieved a stable state as shown in Figs. 1~5, namely, the release and uptake of H⁺ and OH⁻ occur in carbonate mineral suspensions, and the pH values of the suspensions change and finally converge into the equilibrium pH values. The process of the approach to the equilibrium pH may be grouped into two types: (1) in the case of manganese carbonate and lead carbonate, the pH values of the suspensions change monotonously and arrive at the equilibrium pH in a short time; (2) in the case of calcium carbonate, barium carbonate and strontium carbonate, the changes in pH of suspensions with time are not monotonous and it takes a lengthy time to arrive at the equilibrium pH.

Calcium carbonate-water system first is considered here in relation to type(2). When calcium carbonate is placed in pure water isolated from a gaseous phase, the equilibrium pH of the suspension is calculated to be 9.95⁷⁾. On the other hand, calculation using Eqs. (1)~(6) shows that the value of pH 9.95 corresponds to the equilibrium pH of the suspension open to the atmosphere with $P_{CO_2}=10^{-6.13}$ atm. As shown in Fig. 1, the maximum pH values of suspensions were reached within 5 minutes when adding calcium carbonate to water, and their maximum pH values approached pH 9.95. Then, the pH values of the suspension decreased slowly and after 24 hours arrived at pH 8.3~8.6 which were the equilibrium pH of the system open to the atmospheric air with $P_{CO_2}=10^{-3.5}$ atm. This result indicates that the reaction rate for attaining the equilibrium between solid and liquid is much faster than that between gas and liquid, thus the equilibrium between gas and liquid could be a rate-determining step in this system. An attempt to analyze this phenomenon under the following hypothesis was made. The suspension contacts with such gaseous phase as the partial pressure of CO₂ gradually changes from $10^{-6.13}$ to $10^{-3.5}$ atm and the equilibrium between gaseous phase and liquid phase is rapidly accomplishes. The values of IEP(aq) obtained at $P_{CO_2}=10^{-6.13}$ atm are shown in Table 1. The IEP(aq) of calcium carbonate-water-air system would be expected to change from pH 10.0 to pH 8.35 with time. Our experimental results show that the pH values at zero H⁺ and OH⁻ demand after 30 minutes and 24 hours mixing correspond to the IEP(aq) values at P_{CO_2} of $10^{-6.13}$ atm and $10^{-3.5}$ atm. As shown in Table 1, the values of isoelectric point of calcite reported by many reseachers scatter over a wide range, and most of the values are in the pH range from 8 to 10, which is in rough accord with the pH range of IEP(aq) variation (pH 8.4~10.0). In reference to the behavior of calcium carbonate suspension (Fig. 1), we can assume that the variation in the reported values is probably caused by the differences with regard to the experimental condition under which each researcher carried out isoelectric point measur-

ment. On the other hand, it should be also remembered that lattice defects and ionic impurities can have a great influence on the isoelectric point¹¹⁾.

The behavior of suspension of barium carbonate and strontium carbonate is similar to that of calcium carbonate and can also be interpreted in the same way mentioned above. When these carbonates come in contact with water, these solid-solution system would rapidly approach the steady state in the closed system or in the open system to the gaseous phase with apparent $P_{\text{CO}_2} = 10^{-6.13}$ atm, then it would proceed to the steady state in the system open to the atmospheric air and arrive at after a lengthy time. From Fig. 1, Fig. 3 and Fig. 4 the rate to attain to the equilibrium between solid, liquid and air is faster for strontium carbonate compared with calcium carbonate and barium carbonate. The apparent values of P_{CO_2} calculated from the values at zero H^+ and OH^- demand after 30 minutes mixing, are $10^{-5.39}$ atm for strontium carbonate, $10^{-6.04}$ atm for barium carbonate and $10^{-5.79}$ atm for calcium carbonate. For strontium carbonate, its apparent partial pressure was significantly higher than $P_{\text{CO}_2} = 10^{-6.13}$ atm. An isoelectric point of strontium carbonate is in the pH range of IEP(aq) variation (pH 8.1~9.8).

In the case of manganese carbonate and lead carbonate, the IEP(aq) at $P_{\text{CO}_2} = 10^{-3.5}$ atm agreed well with the pH value at zero H^+ and OH^- demand even after 30 minutes mixing, and the isoelectric point of manganese carbonate also agreed with the IEP(aq) at $P_{\text{CO}_2} = 10^{-3.5}$ atm. When these carbonates come in contact with water, these solid-solution systems would directly approach the steady state in the system open to the atmospheric air and arrive at in a short time. Good agreements between theoretical and experimental results are obtained for these carbonate minerals.

The order of solubility product of carbonate minerals used in this work is as follows⁸⁾.



It is seen that the carbonate mineral with a solubility product higher than that of manganese carbonate belong to type(1). The solubility product of strontium carbonate is the lowest in three of type(1) minerals.

5. Summary

When a carbonate mineral comes in contact with water, the process through which equilibrium between solid, liquid and air is established may be grouped in two types: (1) the solid-liquid system reaches monotonously its equilibrium state with air in a short time; (2) the solid-liquid system approaches the apparent system closed to air, then reaches its equilibrium state with air after a lengthy time.

Carbonate minerals with lower solubility product such as manganese carbonate and lead carbonate belong to type(1). The pH value at "zero H^+ and OH^- demand", and isoelectric point of both minerals are in good agreement with the IEP(aq) at $P_{\text{CO}_2} = 10^{-3.5}$ atm. Calcium carbonate, barium carbonate and strontium carbonate, which have relatively high solubility product belong to type(2). For these minerals, solid-liquid system can be analyzed by the hypothesis that the system is equilibrated with a gaseous phase whose apparent P_{CO_2} gradually changes from $10^{-6.13}$ atm to $10^{-3.5}$ atm. Both the pH value at "zero H^+ and OH^- demand" and isoelectric point depend on experimental methods and conditions, and most of them are in the pH range of IEP(aq) variation mentioned in the present paper.

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