Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 1443–1448

CEMENT AND CONCRETE RESEARCH

Dedolomitization in different alkaline media: Application to Portland cement paste

E. García[*], P. Alfonso, M. Labrador, S. Galí

Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, C/Martí i Franquès s/n,
08028 Barcelona, Catalunya, Spain

Received 6 December 2002; accepted 28 February 2003

Abstract

The dedolomitization reaction kinetics is studied through several long-term experiments consisting of an aqueous dispersion of fine powders of dolomite and portlandite with alkalinity between 0.1 and 1 M KOH, at 25 and 75 °C. The experimental results are numerically simulated to calculate the apparent dissolution constant rates for dolomite, k_{dol}. At low temperature, two dissolution stages were observed. In an early stage, part of dolomite powder dissolves quickly until an apparent steady is reached. After several days, the reaction continues at a lower rate. The calculated dissolution rate for dolomite in the first stage is one order of magnitude higher than that of the second stage. At 75 °C, the k_{dol} is two orders of magnitude higher than at 25 °C. The addition of alkali increases the k_{dol} at high temperature, but reduces it at room temperature.

Keywords: Kinetics; Alkali–aggregate reaction; KOH; Dolomite–portlandite; Simulation

1. Introduction

Dolomite represents an important reserve of carbonate rocks that could be used as aggregate in the manufacture of concretes. Dolomite aggregates, in some cases, could be associated with expansion and cracking processes that can deteriorate the concrete structure [1,2]. However, it is demonstrated that this problem only occurs in some kind of dolostones that contain clays, which provide silica to the system [3,4]. For most dolomitic rocks used as aggregate, the main aspect to consider is the dedolomitization reaction and their effect on the durability of concrete.

Dolomite in most natural environments is thermodynamically unstable and dedolomitization reaction occurs in different conditions [5].

The proposed dedolomitization reaction in alkaline media is:

$$\mathrm{CaMg(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + Mg(OH)_2} \qquad (1)$$

It has been postulated [6] that this reaction takes place through two steps and needs the presence of alkali:

$$\mathrm{CaMg(CO_3)_2 + 2Na(OH) = CaCO_3 + Mg(OH)_2 + Na_2CO_3}$$

$$\mathrm{Na_2CO_3 + Ca(OH)_2 = 2CaCO_3 + 2NaOH} \qquad (2)$$

However, a recent work [7] has demonstrated that NaOH is not a necessary compound for the reaction. Indeed, at room temperature, the reaction is faster in pure water solution, while at higher temperatures, alkali accelerates the reaction. Furthermore, it is not clear whether $\mathrm{Na_2CO_3}$ could play a role in the dedolomitization.

Most of experiments on alkali–carbonate reaction (ACR) related in the literature are performed with alkaline NaOH solution. In this paper, we present several dedolomitization experiments similar to those reported in a previous paper [7] but using KOH and mixed NaOH + KOH solutions to imitate the pore water solutions in the Portland cement paste, which, on average, is approximately 0.15 + 0.45 M KOH (0.6 M KOH equivalent) [8].

---

[*] Corresponding author. Tel.: +34-93-402-1354; fax: +34-93-402-1340.
E-mail address: engarcia@natura.geo.ub.es (E. García).

0008-8846/03/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00095-4

Increasing the alkalinity up to 1 M KOH gives rise to a different way of dedolomitization through the reaction

$$2CaMg(CO_3)_2 + 6K(OH) = CaCO_3 + Ca(OH)_2 + 2Mg(OH)_2 + 3K_2CO_3 \quad (3)$$

which produces portlandite and a potassium carbonate. This reaction is not observed when NaOH substitutes KOH at similar concentration.

As stated in a previous work [7], the limiting step of these reactions is the dissolution of dolomite. To obtain the apparent constant rates for the dissolution of dolomite, long-term experiments on the evolution of alkaline media saturated with portlandite and dolomite were undertaken. These experiments include quantitative control of dissolution–precipitation of phases in different potassium hydroxide solutions at room temperature and at 75 °C. All these results have been reproduced by computer simulation, and the estimated kinetic parameters allow the extension of the simulation to a wide variety of conditions.

2. Experimental procedure

The basic batch experiments consisted of an aqueous dispersion of fine powders of dolomite and portlandite. Two different initial alkaline water solutions were used: (1) 0.1 M KOH solution and (2) 0.6 M KOH equivalent solution (0.45 M KOH + 0.15 M NaOH). Experiments with each composition were performed at 25 and 75 °C. Moreover, a series of similar experiments at higher alkali concentrations and without the addition of portlandite was undertaken to find the conditions for reaction (3). These included solutions with alkali concentration between 0.1 to 1 M KOH and NaOH performed at 25 and 75 °C.

The starting materials were finely powdered (below 25 μm in diameter) gem quality crystals of dolomite and "Alfa" commercial $Ca(OH)_2$ powders from Johnson and Matthey. The measured BET specific surface areas were 3.0 and 16.5 $m^2\ g^{-1}$, respectively.

The amount of portlandite and dolomite added to the solution had a volume ratio of 1/100 (mass ratio of 1/400). Portlandite was introduced in slight excess to obtain a complete reaction. The starting water solution and mineral powders were introduced in Teflon bottles provided with a cap to avoid atmospheric carbonation. About 20–25 bottles were prepared with the same initial composition, for room temperature experiments, and 5 bottles for those at 75 °C. The content was stirred every 30 min. Bottles were extracted from the thermostatic bath after different periods of time. The period between extractions was increased as the rate of the reaction slowed down. Each extracted sample was filtered using a millipore filter with 0.22 μm pore diameter. The solid particles retained in the filter were identified by X-ray powder diffraction. Quantitative analyses of the crystalline solids were achieved by the full-diffraction profile-matching method (quantitative Rietveld analyses) using the FULLPROF program [9].

Characterisation of the filtered solution included pH measurement with a standard high-alkalinity electrode and cation analyses of the metals by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The spectrometer used was a Perkin Elmer Elan 6000.

The chemical model used is widely explained in Ref. [7]. This model considers that calcite and brucite precipitate in equilibrium [10]. The involved reactions and their equilibrium constants are shown in Table 1.

Table 1
Chemical reactions considered in the chemical model

	Log *K*
Primary aqueous species	
Ca^{2+}, Mg^{2+}, K^+, Na^+, OH^-, CO_3^{2-}	
Aqueous complexes	
$OH^- + H^+ = H_2O$	14.000
$HCO_3^- + OH^- = CO_3^{2-} + H_2O$	3.666
$CaCO_3(aq) = Ca^{2+} + CO_3^{2-}$	− 3.327
$CaOH^+ = Ca^{2+} + OH^-$	− 1.145
$KOH = K^+ + OH^-$	0.465
$NaOH = Na^+ + OH^-$	0.1849
Minerals	
$CaMg(CO_3)_2 = 2CO_3^{2-} + Ca^{2+} + Mg^{2+}$	− 17.090
$CaCO_3 = CO_3^{2-} + Ca^{2+}$	− 8.480
$Ca(OH)_2 = Ca^{2+} + 2OH^-$	− 5.435
$Mg(OH)_2 = Mg^{2+} + 2OH^-$	− 11.690

The values of the equilibrium constants are those of the EQ3NR database [11].

3. Results

The amount of dissolved and precipitated solid phases, the composition of the solution, and the pH were simulated as a function of time. Experimental results and the corresponding numerical simulation of each experiment are plotted in Figs. 1 and 2.

Numerical simulation of the experimental results allows the estimation of the apparent dissolution rate constant of the phases involved in the different experiments.

In long-term experiments at room temperature, two different dissolution stages were observed from the experimental data. In the first stage, part of dolomite powder dissolved very quickly until an apparent steady state was reached. After some days, in the second stage, the reaction continued until the dolomite was completely exhausted.

In the following sections, we give a brief account of the main features of each group of experiments.

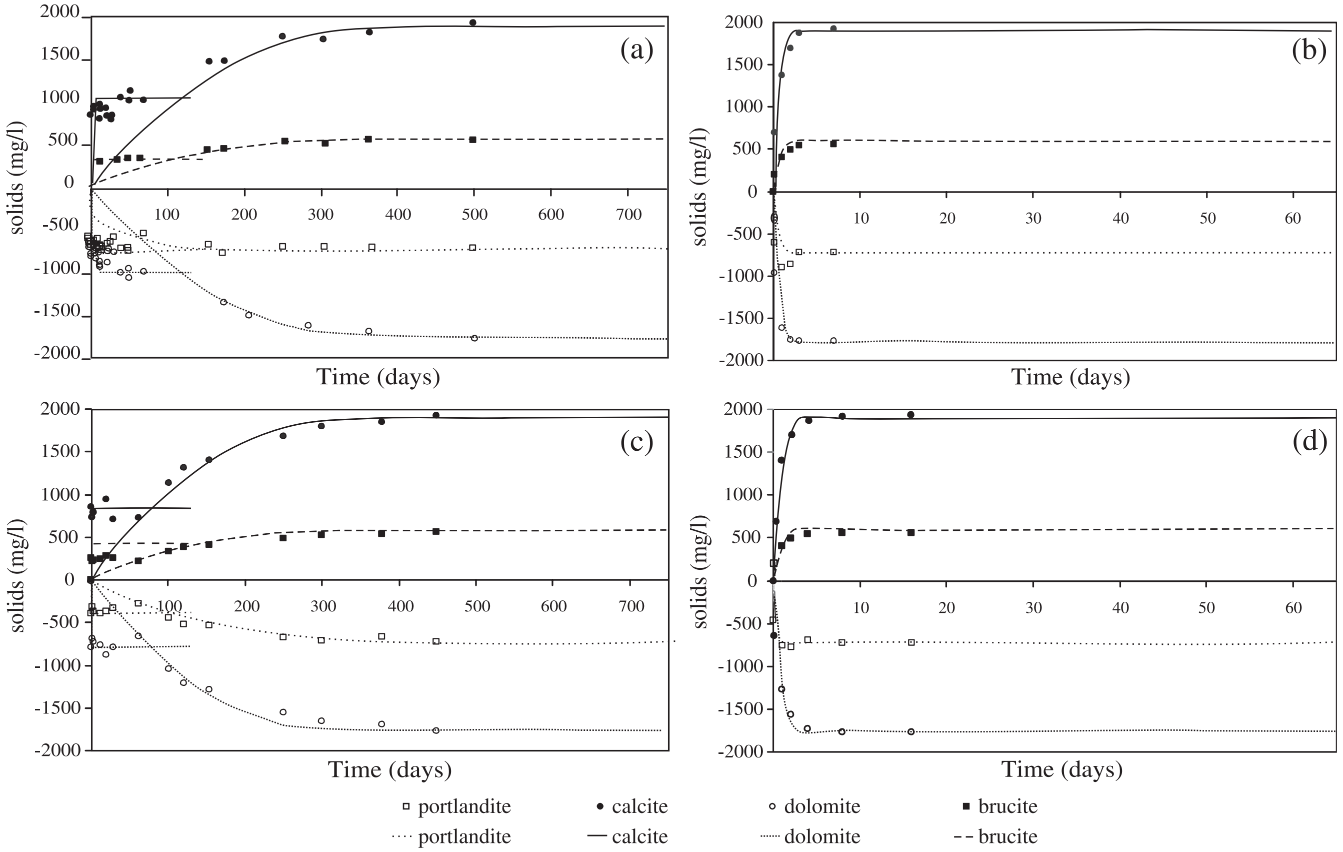

Fig. 1. Dissolved and precipitated solids. (a) Solution 0.1 M KOH, 25 °C; (b) Solution 0.1 M KOH, 75 °C; (c) solution 0.6 M KOH equivalent, 25 °C; (d) solution 0.1 M KOH, 75 °C. Different symbols indicate experimental values. Lines indicate simulated results.

3.1. Solution 0.1 M KOH, 25 °C (Figs. 1a and 2a)

At the beginning, the reaction takes places very quickly, probably consuming the finest fraction of dolomite powders. After about 20–25 days, the reaction slows down, until reaching a first apparent steady state that remains for 100 days. At this moment about 60% of the starting dolomite is consumed. The solution is subsaturated ($\Omega_{dol} = 0.2 \times 10^{-6}$) and the calcium concentration dissolved in the solution remains constant during this period of time (Fig. 2a).

In the second stage, the reaction continues for 400 days when dolomite is completely exhausted ($\Omega_{dol} = 0.3 \times 10^{-5}$). Calcium concentration decreases considerably in the solution until it reaches very low values. At the end of the experiment, the 17 wt.% of the starting portlandite remains in the solution forming a laminate aggregate ($\Omega_{port} = 1.0$).

From the experimental results and numerical simulation calculated for each stage, two different apparent dissolution constant rates were estimated for dolomite. In the first stage, the apparent constant dissolution rate calculated was 1.1×10^{-9} mol m^{-2} s^{-1} and the dissolution rate obtained from the second stage was 1.2×10^{-10} mol m^{-2} s^{-1}.

3.2. Solution 0.1 M KOH, 75 °C (Figs. 1b and 2b)

In this experiment, the reaction ends after 4 days when dolomite is completely consumed ($\Omega_{dol} = 0.1\ 10^{-3}$). The apparent dissolution rate constant obtained from the experimental results is 1.8×10^{-8} mol m^{-2} s^{-1}. It is about two orders of magnitude higher than the value estimated from the previous experiment.

3.3. Solution 0.6 M KOH equivalent, 25 °C (Figs. 1c and 2c)

About 44% of the starting dolomite is consumed in very few hours and the solution remains subsaturated ($\Omega_{dol} = 0.7 \times 10^{-6}$). An apparent rate constant of 5.8×10^{-9} mol m^{-2} s^{-1} is obtained for dolomite dissolution in this first stage. From this moment until 76-day time, the reaction remains in an apparent steady state, similar to that observed in the first experiment. Afterwards, the dissolution of dolomite goes on for 370 days until it is completely dissolved ($\Omega_{dol} = 0.2 \times 10^{-5}$) and 18 wt.% of the starting portlandite is forming a laminate aggregate similar to that in experiment with 0.1 M KOH solution.

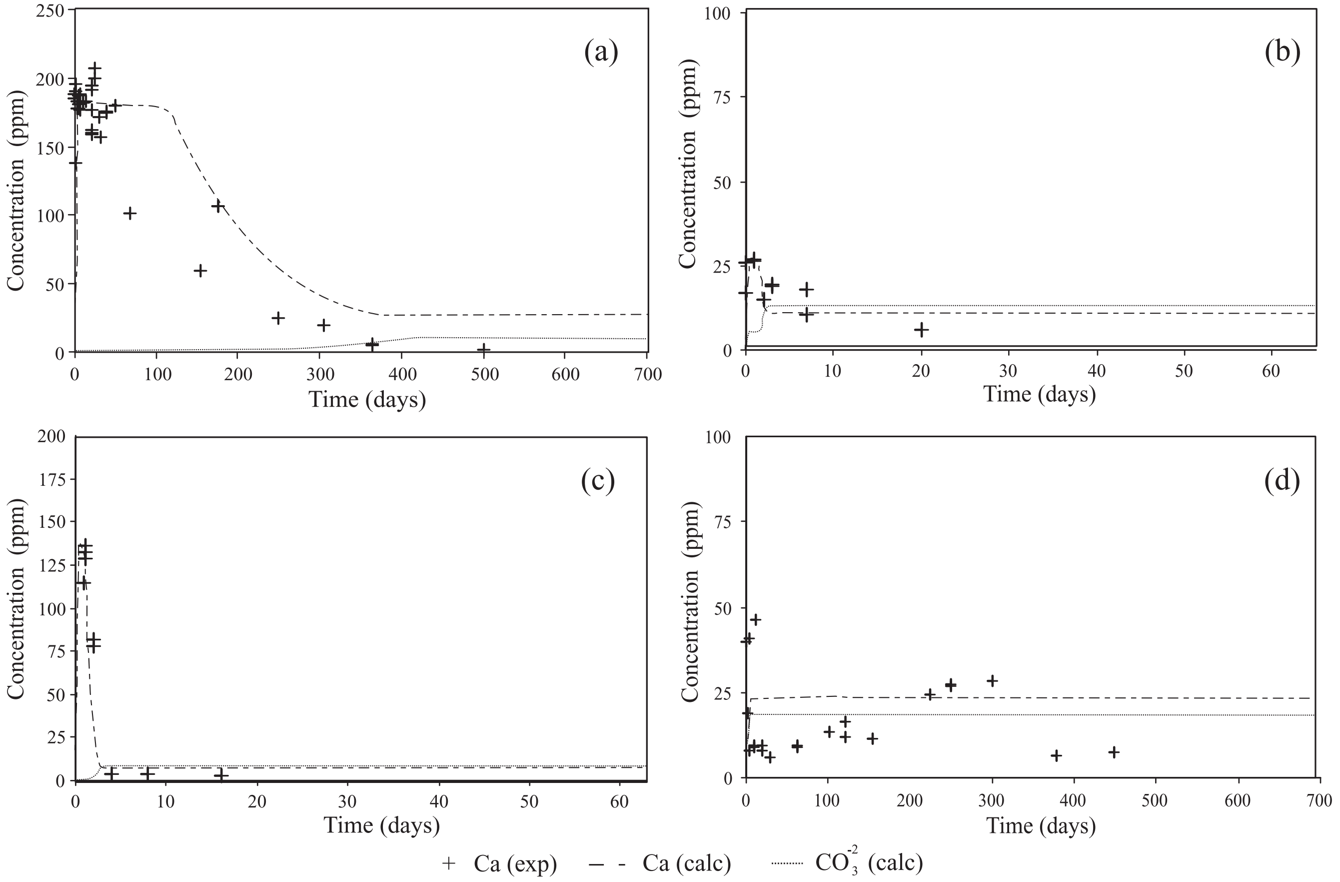

Fig. 2. Concentration of Ca^{2+} and CO_3^{2-}. (a) Solution 0.1 M KOH, 25 °C; (b) solution 0.1 M KOH, 75 °C; (c) solution 0.6 M KOH equivalent, 25 °C; (d) solution 0.1 M KOH, 75 °C.

The second apparent rate constant estimated was 1.2×10^{-10} mol m^{-2} s^{-1}, the same as that obtained for the 0.1 M KOH solution.

3.4. Solution 0.6 M KOH equivalent, 75 °C (Figs. 1d and 2d)

The reaction ends after 2 days, when dolomite is completely exhausted ($\Omega_{dol} = 0.6 \times 10^{-4}$). The dissolution rate constant calculated from the experimental data is 2.3×10^{-8} mol m^{-2} s^{-1}.

3.5. Alkaline solutions without added portlandite

In experiments without portlandite, the main results are different depending on the alkaline cation used. In presence of KOH, reaction (3) is observed: dissolution of dolomite produces calcite, portlandite, brucite, and potassium carbonate. On the contrary, portlandite is never observed in solutions with NaOH.

The saturation indexes for portlandite after 30 days at room temperature are listed in Table 2. Portlandite becomes supersaturated in KOH concentrations higher than 0.6 M. In NaOH solutions, portlandite always remains subsaturated.

Fig. 3 synthesizes the evolution of the reaction at 75 °C for the experiments with 1 M KOH solution. In this case, experimental points are not included because the mass balance of solids is difficult on account of the metastability of portlandite. The reaction is completed after 3 days, when dolomite is absolutely exhausted. At the beginning, portlandite precipitates before calcite, but in the end, the

Table 2
Saturation index obtained for portlandite at 25 °C in experiments without added portlandite

	Ω_{port}
0.1 M KOH	0.0
0.3 M KOH	0.9
0.6 M KOH	1.3
1 M KOH	3.1
0.1 M NaOH	0.0
0.3 M NaOH	0.0
0.6 M NaOH	0.1
1 M NaOH	0.1

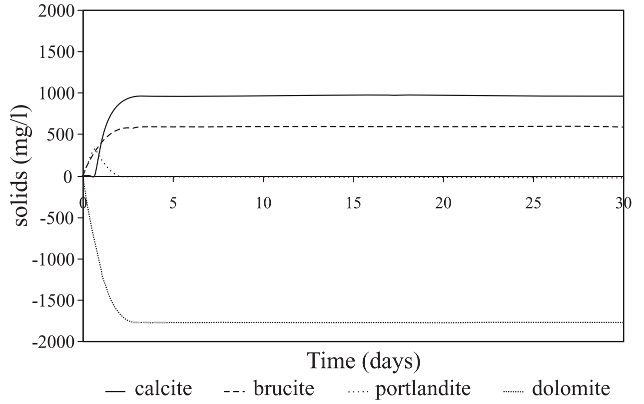

Fig. 3. Dissolved and precipitated solids in experiment without starting portlandite and 1 M KOH solution.

calcite–brucite pair becomes the most stable pair. Potassium carbonate is always undersaturated.

4. Discussion

In all the experiments, the dedolomitization reaction proceeded with the complete consumption of dolomite powder. As a result, calcite and brucite precipitated and some portlandite, which was introduced in excess, remained as a solid phase forming laminate aggregates of big crystals (low temperature experiments). These have grown at the expenses of the small fraction, according to the Ostwald ripening mechanism [12,13], indicating that portlandite has been in equilibrium with solution during all the experiment.

In the early stage, dolomite reactive surface included in the simulation corresponds to the measured BET surface, but when dedolomitization reaction takes place, the reactive surface decreases considerably. At the beginning this reduction of the reactive surface is due to the fastest dissolution of the finest fraction of dolomite powder and reduction of the volume fraction of this phase on the system. This process is accounted for in the numerical simulation. In addition, another important process that contributes to the reduction of the dolomite surface is the precipitation of the new phases on dolomite particles. This point has been confirmed by Scanning Electron Microscopy (SEM) observation of the solids retained on the filters. SEM images show that brucite and/or calcite cover the dolomite powder. To gain some understanding about this process, single crystals of dolomite were immersed in portlandite-saturated alkaline solution with the same composition and temperature as the experiments in the present work. SEM observation and DRX of the crystals corroborate that calcite and brucite grow on the dolomite surface [14].

The two stages of dissolution at low temperature represented by two different apparent dissolution rate constants can be explained as follows. In the first stage, as pointed out above, there is an elimination of dolomite surface and creation of new calcite and brucite surface. Since the dissolution of dolomite provides CO_3^{2-}, Ca^{2+}, and Mg^{2+} for the reaction, the reduction of its surface slows down the dedolomitization. During the apparent steady state, a new surface of dolomite is created by corrosion, and the process continues until the complete consumption of dolomite. In this second stage, newly precipitated calcite and brucite crystallises mainly on calcite and brucite surfaces created in the first stage and do not cover dolomite any more [14].

Table 3
Saturation index for the different phases involved at the end of the dedolomitization reaction

	Ω_{dol}	Ω_{port}	Ω_{cc}[a]	Ω_{bru}[a]
0.1 M KOH 25 °C	0.3×10^{-5}	1.0	1.0	1.0
0.6 M KOH equivalent 25 °C	0.3×10^{-5}	1.0	1.0	1.0
0.1 M KOH 75 °C	0.1×10^{-3}	0.0	1.0	1.0
0.6 M KOH equivalent 75 °C	0.6×10^{-4}	0.3	1.0	1.0

[a] According to the chemical model, calcite and brucite are in equilibrium.

The apparent dissolution constant rate for dolomite (k_{dol}), estimated from simulated experimental data, is about one order of magnitude lower than in the early stage for each experiment.

Table 3 summarises the saturation index of the different phases involved at the end of the experiments. Dolomite always remains subsaturated; portlandite is either subsaturated or saturated (solution 0.6 M equivalent at 25 °C); calcite and brucite, as observed throughout all the experiments, are always in equilibrium with the solution. Then, we can consider that the process that controls the overall reaction is the dissolution of dolomite because this is the slowest step. To explain the kinetics of the reaction in different solutions it is necessary to take into account the dissolution rate constant of dolomite.

Table 4 shows the estimated k_{dol} from experiments. By comparison, the apparent dolomite constant rates estimated in a previous work [7] and in the present paper, the addition of alkali in the solution at room temperature has an opposed effect than that at 75 °C. At room temperature, alkali addition slightly slows the dedolomitization reaction. On the contrary, in experiments at 75 °C, the alkaline solution increases k_{dol} by about one order of magnitude. The different behaviour at high and low temperature, as compared with solutions without addition of alkali, could be explained in the way that the surface charge of dolomite changes with the temperature. The solids, when immersed in water solutions, acquire a surface charge, which may be strongly affected by pH, ionic concen-

Table 4
Apparent constant rate (mol m^{-2} s^{-1}) of dolomite in different solutions and temperature, and activation energies (kJ mol^{-1})

	k_{dol} (25 °C)	k_{dol} (75 °C)	E_a
Pure water[a]	4.5×10^{-10}	3.9×10^{-9}	37.2
Silica[a]	2.3×10^{-10}	–	–
0.1 M NaOH[a]	2.1×10^{-10}	1.9×10^{-8}	76.5
0.1 M KOH	1.2×10^{-10}	1.8×10^{-8}	86.8
0.6 M equivalent	1.2×10^{-10}	2.3×10^{-8}	91.0

[a] Ref. [7].

tration, and temperature. At low pH, the surface charge tends to be positive. On the contrary, at high pH, it becomes negative. For each solid in a water solution, there exists a pH value (pH_{pzc}) where the surface charge is zero. As a result, the surface charge depends on whether the solution have higher or lower pH than the pH_{pzc}. It has been proved that the dissolution rate as a function of pH has an absolute minimum at the pH_{pzc} [15,16]. It is assumed then, that at 25 °C, increasing pH approach pH_{pzc} point, while at 75 °C moves away from it.

5. Conclusions

1. Dolomite is always unstable in contact with the average alkaline pore solutions of Portland cements.
2. The mechanism of the dedolomitization reaction is different according to the temperature. At low temperature, regardless of alkaline concentrations, two different stages are observed. In the first stage, k_{dol} is about one order of magnitude higher. At the end of this stage, there is a significant reduction of dolomite surface. In the second stage the rate is lower.
3. At 75 °C, the mechanism of dedolomitization is simple, and the rate is only slightly affected by the alkali concentration.
4. For low alkaline concentrations, there are no significant differences in the dedolomitization mechanism between NaOH and KOH solution, as compared with previous results [7]. However, in this previous work, the authors were not completely aware of the two-stage mechanism operating at low temperature.
5. For alkaline solutions higher than 0.6 M, the dedolomitization reactions at room temperature start to show a different behaviour, with portlandite being saturated for KOH and unsaturated for NaOH solutions.

Acknowledgements

The ICP-AES analyses were performed at the Serveis Científico-Tècnics (SCT) de la Universitat de Barcelona. X-ray diffraction analyses were performed at the X-ray unit at the SCT (X. Alcobé). E. García acknowledges the receipt a FPU fellowship from the Spanish Ministerio de Educación y Cultura. This research was sponsored by the CICYT Spanish research project MAT2001-3345 and contract RED99-57.

References

[1] E.G. Swenson, J. Gillott, Characteristics of Kingston carbonate rock reaction, Highw. Res. Board Bull. 275 (1960) 18–31.
[2] J.E. Gillott, Alkali reactivity problems with emphasis on Canadian aggregates, Eng. Geol. 23 (1986) 29–43.
[3] M. Tang, Z. Liu, S. Han, Mechanism of alkali–carbonate reaction, in: Grattan-Bellew (Ed.), Proceedings of the 7th International Conference on the Alkali Aggregate Reaction, Noyes Publications, Otawa, 1986, pp. 275–279.
[4] T. Katayama, A critical review of carbonate rock reaction—Is their reactivity useful or harmful? The 9th International Conference on Alkali–Aggregate Reaction in Concrete, 1992.
[5] M. Deng, M. Tang, Mechanism of dedolomitization and expansion of dolomitic rocks, Cem. Concr. Res. 23 (6) (1993) 1397–1408.
[6] H. Wang, J.E. Gillot, Alkali–carbonate reaction: Significance of chemical and mineral admixtures, Mag. Concr. Res. 170 (1995) 69–75.
[7] S. Galí, C. Ayora, P. Alfonso, E. Tauler, M. Labrador, Kinetics of dolomite–portlandite reaction. Application to Portland cement concrete, Cem. Concr. Res. 31 (6) (2001) 933–939.
[8] K. Andersson, B. Allard, M. Bengtsson, B. Magnusson, Chemical composition of cement pore solutions, Cem. Concr. Res. 19 (3) (1989) 327–332.
[9] J. Rodriguez-Carvajal, FULLPROF, v. 3.2, Laboratoire Leon Brillouin (CEA-CNRS), 1998.
[10] W.P. Inskeep, P.R. Bloom, An evaluation of rate equations for calcite precipitation kinetics at pCO_2 less than 0.01 atm and pH greater than 8, Geochim. Cosmochim. Acta 49 (1985) 2165–2180.
[11] T.J. Wolery, EQ3NR, a Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide and Related Documentation (Version 7.0), Publ. UCRL-MA-110662 Pt III, Lawrence Livermore Lab, California, USA, 1992.
[12] I.M. Lifshitz, V.V. Slyozov, The kinetics of the precipitation from supersaturated solid solutions, J. Phys. Chem. Solids 19 (1961) 35–50.
[13] W. Otstwaldt, Z. Phys. Chem. 34 (1900) 495.
[14] E. García, P. Alfonso, E. Tauler, S. Galí, Surface Alteration of Dolomite in Dedolomitization Reaction in Alkaline Media, Cem. Concr. Res. (In press).
[15] W. Stumm, Chemistry of the Solid–Water Interface, Wiley-Interscience, Wiley, New York, 1992.
[16] J.M. Zachara, J.A. Kittrick, J.B. Harsh, The mechanism of Zn^{2+} adsorption on calcite, Geochim. Cosmochim. Acta 52 (1988) 2281–2291.