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Reaction kinetics of dolomite and portlandite

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ABSTRACT

The reactions of dolomite with portlandite have been studied at well-spaced temperatures between 20 °C and 85 °C using XRD Rietveld, TG and SEM methods. The results show quantitatively the faster rates of reaction at higher temperature. Isothermal reaction has, at most, a short induction period after which the degree of reaction is linear with time. An exponential equation is presented to predict the initial rate of reaction as a function of temperature. The microstructure shows that large equant calcite crystals, up to 30 μm, develop on the rhomboid cleavage surfaces of dolomite. Pressed pellets of dolomite develop calcite at both exterior surfaces and in the interior, where calcite develops as a secondary phase but is not morphologically well-formed crystals. Pellets remain coherent in the course of reaction. The porous pellets have much unfilled space inside and often exhibit portlandite agglomerates with development of Hadley grain structures at the sites of former dolomite crystals, especially when reacted at lower temperatures. The reaction is not topotactic but requires dissolution, transport, nucleation and growth. Transport occurs often over considerable distance relative to the sizes of crystals.

1. Introduction

Dolomite, ideally $CaMg(CO_3)_2$, is widely distributed in nature. Its crystal structure is derived from that of calcite by ordered replacement of half the calcium cations in calcite by magnesium, forming alternate sheets of 6-coordinate Ca and Mg.

Dolomite-containing rock is frequently used as concrete-making aggregates. However under some circumstances, not well defined, dolomite aggregates react slowly with Portland cement. The reaction appears to be physically expansive.

Saline water, high pH, low Ca^{2+}/Mg^{2+} ratio and elevated temperatures favour dolomite formation in nature [1]. Dolomite has only been made synthetically at very high pressures, although it is believed to be stable relative to calcite and magnesite ($MgCO_3$) at 25 °C and 1 bar pressure.

The reaction mechanism of dolomite with portlandite has been much studied [2–4]. Reaction proceeds with formation of brucite according to the equation [2,3]

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

In the range of 0–85 °C the free energy of reaction (1) is favourable for reaction to proceed and, as a consequence of the free energy differences between products and reactants of the constituent phases, the 25 °C solubilities must decrease in the order:

$$Ca(OH)_2 > CaCO_3 > Mg(OH)_2 > CaMg(CO_3)_2.$$

The reaction rate is reported to be controlled by the dissolution of dolomite. At high pH values, typical of environments conditioned by Portland cement, $pH > 10$, the main reaction is

$$CaMg(CO_3)_2 + 2OH^- \leftrightarrow CaCO_3 + Mg(OH)_2 + CO_3^{2-}. \qquad (2)$$

Temperature influences the solubility of carbonate and hydroxide phases. Counter to the typically observed increase of mineral solubility with increasing temperature, the relevant carbonate minerals (Table 1) are more soluble in cold water than hot, because their dissolution reaction is exothermic [5]. The solubilities of portlandite and brucite, Table 1 [5–8] show the same trend with increasing equilibration temperature. As can be seen, the hydroxides are more soluble than the carbonates by several orders of magnitude.

According to the study by Gali et al. [3], both temperature and alkalinity of the media influence the dissolution rate of dolomite. At 75 °C in initially pure water, the dissolution rate was found to increase by more than one order of magnitude relative to 25 °C. The influence of alkali (Na, K) content on dissolution also depends on temperatures: at room temperature, soluble alkali reduces the dissolution rate of dolomite whereas at high temperature, it increases the rate of "dedolomitisation"—a general descriptive term applied to any process

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Table 1
Solubility data for relevant phases [5–8].

	Temperature	$CaMg(CO_3)_2$	$Ca(OH)_2$	$CaCO_3$	$Mg(OH)_2$
Solubility product Ksp	0 °C		$10^{-4.84}$	$10^{-8.02}$	
	25 °C	$10^{-(17-19)}$	$10^{-5.30}$	$10^{-8.42}$	$10^{-11.25}$
	50 °C			$10^{-8.63}$	
Solubility (mol/l)	0 °C		0.024970		0.0001543
	100 °C		0.01039		0.0006859

whereby Mg is selectively removed from dolomite, leaving calcite [3]. The morphology of brucite formed in the course of dedolomitisation is also sensitive to temperature.

Garcia et al. [4] conducted experiments on dolomite reactions in sealed containers to prevent access of carbon dioxide but used stirring, to prevent local stagnation and concentrations. They observed brucite and calcite as reaction products but with large variation in morphology. Fibrous brucite formed as a characteristic reaction product at low temperature, 25 °C, but at 75 °C a much greater variety of brucite morphologies were observed: it grew as platelets, and stacks of platelets, sometimes as truncated ditrigonal pyramidal forms but often in sponge-like growths. However, experiments described in Ref. [4] used either $Ca(OH)_2$ solutions or (Na, K)OH solutions as sources of calcium and alkali respectively, with the result that the pH of the aqueous phase did not remain constant throughout the process. For example, when dolomite was contacted with either 0.1 M NaOH or 0.1 M KOH, pH values, initially 13, had decreased to 11.84 and 12.00 respectively at the end of the experiment. Thus the experiments were not conducted at constant pH, leading to some doubts concerning the significance of the dissolution rates and growth morphologies deduced from the data, given the known sensitivity of reaction constants to pH.

The title study was undertaken to measure the rate of reaction and microstructure of dolomite at different temperatures, to improve our understanding of the reaction kinetics and provide some insight on the potential use of dolomite as a reactive admixture in cementitious formulations. Because synthetic material was not available it was necessary to use natural dolomite in the course of this study. Dolomite rhombs were obtained commercially, crushed, sieved and used as the source of dolomite.

In general we used solid activators and limited the liquid water: solid ratio, to simulate conditions encountered in cementitious systems. In experiments with portlandite reactant an excess of solid was used to buffer pH, so the experiments reported here were made at constant pH, essentially that of saturated $Ca(OH)_2$ at the relevant temperature.

2. Experimental

2.1. Materials

The dolomite material used here was mainly a commercial ground dolomite. Some work (see Section 3.3) was done on crushed fragments from a translucent single crystal of dolomite obtained from a mineral dealer and confirmed as dolomite by XRD, but all the other works were done using “Microdol H600” from Omya UK. X-ray diffraction verified that it was dolomite (as distinct from magnesian calcite) (Fig. 1). Data from supplier show that its chemical composition is close to theoretical (Table 2). The particle size distribution and packing density of powdered commercial dolomite are also listed in Table 2 and Fig. 2. The specific surface area of the as supplied dolomite was found to be 1.96 m^2/g by BET, using nitrogen as the sorbate.

Calcium hydroxide was a chemical reagent grade (Fisher scientific). Only newly-opened bottles were used to avoid introducing carbonate.

As calcium hydroxide is easily carbonated by even traces of air, the molar ratio of dolomite and calcium hydroxide was fixed at 1:2 to ensure sufficient calcium hydroxide supply for reaction at constant concentration. Every effort was made to exclude atmospheric carbon dioxide, but minor carbonation may have occurred.

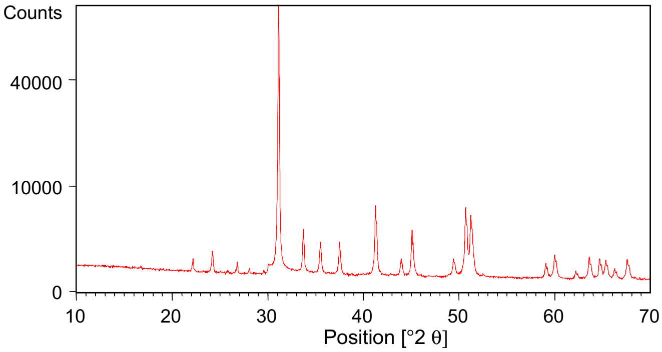

Fig. 1. XRD pattern of microdol H600 (Y axis is in a square root scale).

The large differences in bulk densities of the reactants make it difficult to slurry the raw materials homogeneously. To prevent segregation, wafers ~25 mm in diameter and ca 1 mm thick were prepared using a commercial press; the reactants were dry mixed and pressed in CO_2-free conditions. The wafers were put into a solution of activator in distilled water, with an excess of portlandite not in physical contact with wafers, sealed in thick walled gas-tight polymer bottles and cured isothermally at 20, 40, 55 and 85 °C respectively until the time of measurement, at which point they were filtered, washed with CO_2-free water and dried under nitrogen.

2.2. Experimental techniques

The reaction of dolomite commenced when the pellets or cleavage fragments were immersed in solution. The progress of reaction was monitored by a combination of appropriate techniques: for quantitative studies of reaction kinetics, both X-ray powder diffraction with Rietveld analysis of the diffractograms and DTA/TG of products following reaction were used. The combination of techniques gives valuable confirmation and better confidence than could be obtained by using a single technique. Electron microscopy with microanalysis was used to characterise the evolution of microstructure and identify phases. Both surfaces and interior sections of pellets were imaged.

2.3. XRD Rietveld analysis

The crystalline phases can be quantified from XRD patterns with Rietveld analysis. Its principle [9] is iteratively to compare the experimental pattern with a simulated pattern based on the presumed amounts and from knowledge of the crystal structure, using constant equipment parameters and calibrated using an unreacted mixture of pure phases in known proportions. The Rietveld parameters may be adjusted between iterations to minimise the difference between experimental and simulated patterns by means of a least square fitting.

The reacted pellets were ground into fine powders and put into a standard sample holder. The X-ray diffraction patterns were obtained at 2θ angle (CuKalpha radiation) from 10 to 70° using a step size of 0.02° with a dwell time of 5 s, with the X-ray generator power of 40 kV and 40 mA. A D8 Advance (Bucker AXS) diffractometer was used. Quantitative Rietveld analysis was performed with the X'pert Highscore Plus software with control files developed in EPFL-LMC [10,11].

2.4. Thermogravimetric analysis (TG)

TG curves are used to measure the weight loss corresponding to thermal decomposition. Fig. 3 shows an example of a TG/DTA curve obtained from a partially reacted dolomite–portlandite mixture. To avoid carbonation of portlandite during the heating process, a flowing N_2