



Understanding the hydration of dolomite in cementitious systems with reactive aluminosilicates such as calcined clay

Sreejith Krishnan*, Shashank Bishnoi

Department of Civil Engineering, Indian Institute of Technology Delhi, 110016, India



ARTICLE INFO

Keywords:

Dolomite
Limestone
Brucite
Hydrotalcite
Carboaluminates

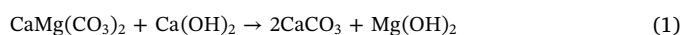
ABSTRACT

This study investigates the hydration of dolomite, $\text{CaMg}(\text{CO}_3)_2$, with calcined clay in presence of calcium hydroxide and ordinary Portland cement. The hydration products as well as the microstructure at various ages were characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), and mercury intrusion porosimetry (MIP). Isothermal calorimetry was used to understand the reaction kinetics. The systems with dolomite were compared against control systems with limestone and quartz. It was seen that, the formation of carbonate – AFm phases takes place in the dolomite systems similar to limestone systems. No formation of brucite ($\text{Mg}(\text{OH})_2$) was observed till 90 days of hydration, with Mg^{2+} ions most likely being incorporated into hydrotalcite phase ($\text{Mg}_4\text{Al}_2(\text{OH})_{14}$). The synergetic effect observed in the Portland cement – calcined clay – dolomite system was found to result in a refined pore structure at early ages and improvement in the mechanical properties such as compressive strength.

1. Introduction

Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are two important carbonate minerals found in nature. Limestone and dolostones are sedimentary carbonate rocks that are composed mainly of calcite and dolomite respectively. Formation of dolomite can occur via two possible mechanisms – i) direct precipitation from solution to form primary dolomite, and ii) dolomitization process in which calcite undergoes dissolution supplying the Ca^{2+} ions followed by the precipitation of dolomite from a solution rich in Mg^{2+} ions [1,2]. Therefore, it is not uncommon to observe dolomite coexisting with calcite. The presence of dolomite renders limestone unsuitable for the production of clinker, as the dolomite will decompose in the rotary kiln to form periclase (MgO), which forms brucite ($\text{Mg}(\text{OH})_2$) during the later stages of cement hydration. The formation of brucite from periclase is an expansive reaction and makes the cement unsound. Dolomite can be used in cement in two ways. First, as aggregate for the production of concrete and second, as a partial replacement of Portland cement i.e. as reactive cementitious addition. It has been reported [3] that dolomitic aggregates might cause expansion in concretes due to its reaction with portlandite called dedolomitization reaction (Eq. (1)). Higher alkalinity content and higher temperatures are said to favour this dedolomitization [4,5]. But recent studies suggest that mechanism of dedolomitization is still not well understood and the deterioration in concretes attributed to the ACR might not have been caused by the dedolomitization reaction [6–8].

Studies have indicated that this reaction cannot lead to expansion since it is accompanied by a reduction in the solid volume. The rate of dissolution of dolomite is seen as the limiting factor in the dedolomitization reaction.



The hydration reaction of ordinary Portland cement in the presence of limestone has been well documented [9–13]. The CO_3^{2-} ions are able to react with the reactive alumina present (primarily from C_3A) in the Portland cement system forming carboaluminate phases. In the presence of SCMs such as calcined clay, additional alumina is available for the carbonate ions to bind with, and form these phases. Ternary cements that utilize the synergetic effect between the calcined clay and limestone is a green alternatives to ordinary Portland cements, and are especially suited for the developing countries such as Brazil, India, China, and Cuba due to wide availability of calcined clay [14–18]. Limestone is a critical resource in the cement industry as it is the primary raw material for the production of clinker. Dolomite and lower grade limestone such as dolomitic limestone cannot be utilized for clinker production, making them a potential carbonate source that can be utilized together with calcined clay and Portland cement. It is seen that dolomite blended cements perform comparably to Portland limestone cement [19,20] with no negative effect such as unsoundness, which is associated with clinkers produced from limestones containing dolomite. Its addition to cement can therefore, provide a means to

* Corresponding author.

E-mail addresses: sree1111@gmail.com, sreejith.krishnan@civil.iitd.ac.in (S. Krishnan).

Table 1
Chemical composition and specific gravity of the raw materials.

Oxide composition (%)	Clinker	Calcined Clay	Dolomite	Limestone
CaO	65.16	0.06	29.68	44.24
SiO ₂	21.07	54.93	0.75	11.02
Al ₂ O ₃	4.65	39.75	1.02	2.53
Fe ₂ O ₃	4.32	4.16	0.64	1.55
MgO	2.13	0.02	21.26	1.96
Na ₂ O	0.38	0.18	0.1	0.5
K ₂ O	0.20	0.17	0.05	0.28
SO ₃	0.77	0.1	–	–
LOI	0.96	0.24	46.09	36.96
Specific gravity (g/cm ³)	3.1	2.60	2.88	2.64

gainfully utilize dolomitic limestones and increase mine life.

The synergistic effect observed in limestone calcined clay cements has been investigated in detail by various researchers [14,21–24]. The pozzolanic reaction of calcined clay produces additional C-(A)-S-H gel. The limestone present in these systems is able to release carbonate ions that forms carboaluminate phases. Formation of carboaluminate phases prevents the transformation of ettringite (water rich, low density Aft phase) to monosulphate. The formation of additional C-(A)-S-H gel and carboaluminates, combined with stabilization of ettringite phases ensure better space filling and well-refined pore structure. The well refined pore structure is primarily due to the presence of calcined clay [25–27]. Even clays with low kaolinitic content are seen to produce a well refined microstructure compared to ordinary Portland cement at later ages [25]. The well refined pore structure leads to improved durability performance of calcined clay limestone cements.

This article tries to explore the use of dolomite as an alternate carbonate source to limestone in calcined clay - limestone systems. The hydration process and possible reaction mechanisms of dolomite with calcined clay are studied with: 1) calcium hydroxide and, 2) ordinary Portland cement.

2. Materials and methods

2.1. Materials

Two naturally occurring carbonate rocks – limestone and dolomite were used in this study. Raw clay (with an estimated kaolinite content

of 60%) was procured from a mine in the western Indian city of Bhuj, and calcined in a rotary calcination unit to produce calcined clay. Quartz was found to be the major impurity present in the clay along with minor quantities of hematite and anatase. Clinker was purchased from a clinker production unit of a major Indian cement company, located in the state of Gujarat, India. The specific gravity of the raw materials (Table 1) was determined using Le Chatelier's flask.

The composition of the clinker was determined using Rietveld analysis (Table 3). There are two ways to prepare ternary cement blends - i) intergrinding of raw materials together in a ball mill or ii) grinding each raw material separately to a fixed fineness followed by interblending the raw materials together. Intergrinding results in the production of homogenous blends but it is difficult to control the fineness of individual components of the blended cements, especially due to the different relative hardness of clinker, calcined clay, quartz, limestone and dolomite. On the other hand, the fineness of the individual raw materials can be controlled during interblending but it would be difficult to produce a homogenous blend. In this study, ternary cements were prepared both by intergrinding as well as interblending for isothermal calorimetric studies. Similar grinding protocols were used for grinding the blended cements as well as the individual raw materials. Isothermal calorimetry measures the rate of evolution of heat as the cement hydrates and can be useful in identifying the difference between interblending and intergrinding. Further tests and studies were only carried out on blends produced by intergrinding as it was believed that intergrinding would more representative of the blends produced in a commercial ball mill. The particle size distributions of the raw materials as well as interground blends were measured on a laser diffractometer (Malvern Mastersizer 3000) (Figs. 1 and 2).

Reagent grade calcium hydroxide (from CDH Company) was used to prepare calcium hydroxide + calcined clay + carbonate blends. Crushed quartz was used as a filler to replace carbonate source. The chemical compositions of the raw materials used in the study are given in Table 1. The X-ray diffractograms of the limestone and dolomite are shown in Fig. 3. It is important to note, as observed in the diffractograms, that the dolomite used in the study did not contain any calcite impurity. The limestone used contained around 85% calcite with quartz being the major impurity. The details of the blends studied are given in Tables 2 and 3. The blends produced by interblending were differentiated from blends produced by intergrinding by adding a suffix "IB" (LC3 - IB, DC3 - IB and QC3 - IB). The ratio of calcined clay to

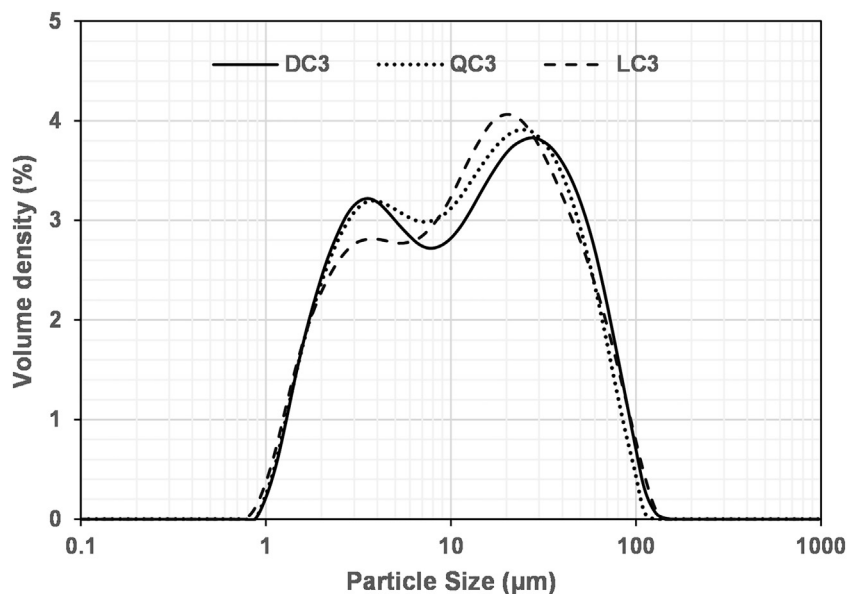


Fig. 1. The particle size distribution of blends produced by intergrinding in a laboratory ball mill.

Download English Version:

<https://daneshyari.com/en/article/7884689>

Download Persian Version:

<https://daneshyari.com/article/7884689>

[Daneshyari.com](https://daneshyari.com)