Construction and Building Materials 115 (2016) 555–564

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of up to 12% substitution of clinker with limestone on commercial grade concrete containing supplementary cementitious materials

James Mohammadi *, Warren South

Research and Technical Services, Cement Concrete & Aggregates Australia (CCAA)

HIGHLIGHTS

- A comprehensive industrial test program for cement with up to 12% limestone.
- Intergrinding limestone and cement in plants instead of blending them in laboratories.
- Concrete durability properties were similar or improved with 12% limestone cement.

ARTICLE INFO

Article history:
Received 15 February 2016
Received in revised form 4 April 2016
Accepted 17 April 2016

Keywords:
Cement
Limestone
Fly ash
Slag
Amorphous silica
Concrete durability

ABSTRACT

This paper presents the results of a test program conducted to determine the effect of up to 12% limestone addition in cement on properties of concrete for durable applications. Cement samples with 5%, 7.5%, 10% and 12% limestone content were used and concretes were made with different binder combinations incorporating one or more of fly ash, slag and amorphous silica, applicable for durable applications. Fresh concrete properties including slump, air content, bleed and setting time were investigated and no adverse effects were found. Hardened properties examined included compressive strength, drying shrinkage, chloride resistance and volume of permeable voids. The results revealed a minor effect on concrete strength, though performance depended on the binder composition. Drying shrinkage of concrete was found to be similar for all concretes investigated. For mixes containing slag, chloride resistance was improved with increasing limestone content.

1. Introduction

Concrete is the most widely used construction material on earth and the manufacture of cement is an energy intensive process producing large amounts of CO_2 emissions as well as being a major consumer of natural resources. In a continuing effort to improve the sustainability of our cement manufacturing processes and concrete infrastructure and buildings, the focus on increased use of mineral additions in cement including fly ash, slag and ground limestone is developing [1].

Limestone is defined in AS3972 [2] as a naturally occurring inorganic mineral material, containing not less than 75% by mass of $CaCO_3$. It is a relatively inert filler, in that unlike supplementary cementitious materials (SCM's), it does not show pozzolanic properties and, consequently, does not produce C-S-H gel [3]. It, however, can influence binder hydration and concrete properties. When used in cementitious material, it causes changes in the capillary porosity of the binder matrix due to three main physical effects: the dilution effect, the filler effect and heterogeneous nucleation [3]. The dilution effect results in an increase in the amount of limestone that decreases the amount of cement and consequently, increases the effective water:cement ratio. The filler effect refers to the improvement of the particle packing of the cementitious system which generally reduces initial porosity and water demand of the mix. Heterogeneous nucleation is thought to occur when limestone is added to cement as it provides nucleation sites for the products of hydration reactions, thus marginally accelerating the early hydration rate of the cement [4,5].

Ground granulated iron blast furnace slag (slag) and fly ash have been used in Australia since the early 1970's for enhancing concrete properties [6,7] and more recently for reducing embodied energy in concrete. Limestone provides an additional option to reduce embodied energy in concrete. As well as being relatively inert, it is readily available at cement plants and its inclusion in binder systems reduces embodied energy of the resulting product.

There has been a significant amount of research undertaken worldwide on the use of ground limestone in cement and concrete

* Corresponding author at: Cement Concrete & Aggregates Australia (CCAA), PO Box 124, Mascot, NSW 1460, Australia.

E-mail address: James.Mohammadi@ccaa.com.au (J. Mohammadi).

http://dx.doi.org/10.1016/j.conbuildmat.2016.04.071
0950-0618/

and on optimised levels of limestone in Portland cement and for Portland-limestone cement systems [4,5,8–20].

Limestone has been commonly used in Europe and other countries for several decades. The European Standard EN 197-1-2000 permits up to 5% limestone as a minor additional constituent and classifies four types of Portland-limestone cements containing up to 35% limestone. The Canadian Standard has allowed the inclusion of up to 5% limestone addition in Portland cements since 1983. As a result of recent extensive studies and trials by Thomas and Hooton [21], the 2008 version of the Canadian cement Standard (CSA A3001-08) introduced a Portland-limestone cement (PLC) classification allowing up to 15% limestone. The only limitation is that this Standard does not currently allow PLC to be used to produce sulfate-resisting cement and cannot be used in concrete exposed to sulfate environments. This is because there is research that indicates that PLC, when used as the sole cementitious material, is more susceptible to the thaumasite form of sulfate attack [22–25]. It has been shown that thaumasite sulfate attack can be prevented when typical levels of SCM's that would normally be used to provide sulfate resistance are adopted in a concrete mix [26]. Limestone as an ingredient in cement is used in many countries outside of Europe at various levels and under various classifications, including Latin American countries such as Argentina, Brazil and Mexico [3]. New Zealand (NZS 3125) has a published specification for 'Portland-limestone filler cement' with up to 15% limestone which was developed in 1991.

Detailed research by Hooton [27] and recent state of the art reports [28,29] on use of limestone in cement provide a comprehensive review of technical data and published literature on its effects on cement and concrete. Generally it has been found by researchers that up to levels of 15% of cement, fresh and hardened properties of concrete are similar to those of concretes without limestone [21,27]. It has also been found that control of limestone particle size distribution and overall fineness of cement provides for equivalent strength and durability benefits when limestone is used in amounts up to 15% [28,29]. Results on the effects on durability parameters such as chloride ion penetration, sorptivity, charge transfer resistance and sulfate resistance are found dependent on limestone fineness, whether it is inter-ground or blended, the water:cement ratio of the mix and the type and proportion of SCMs that are used [30].

A major study on the effects of ground limestone addition into cementitious systems has been conducted in Australia over the last 5 years [31,32]. This paper provides information from that study on the effects of up to 12% limestone addition in Australian cement and its influence on the fresh and hardened properties of concrete prepared by commercial mix-designs for durable applications. An upper limit of 12% was chosen for the test program based on past literature findings and manufacturing considerations. Typical commercially available cements produced from various manufacturing facilities in Australia were used in the study with different limestone supply sources and properties. Concretes made using the limestone cements in conjunction with combinations of fly ash, slag and amorphous silica were also investigated to better understand the influence of the increased limestone addition on fresh, hardening and hardened properties.

2. Research significance

Using limestone as an ingredient in cement at higher levels that currently allowed reduces the amount of clinker that needs to be produced for an equivalent amount of cement, which results in less energy consumption and carbon dioxide (CO_2) emissions and presents a significant opportunity for sustainability benefits. CO_2 emissions from cement plants are emitted due to two main processes: calcination of the limestone, a primary raw ingredient for clinker manufacture, and fuel consumption needed to heat the raw materials to the required temperature for clinker production. Generally, even when taking into consideration that Portland-limestone cements may require higher grinding effort, the net change is a reduction in CO_2 emissions, roughly proportional to the decrease in the amount of clinker in the blended cement [28].

Australian Standard AS3972 was updated in 2010 to allow up to 7.5% mineral additions in Type GP cement which can be limestone, up from 5% in the previous version of the Standard. The new Standard also makes provisions for a new classification, Type General Purpose Limestone (Type GL) cement which permits between 8 to 20% limestone addition. This study was undertaken in order to better understand the influence of ground limestone on concrete properties to facilitate its wider use in construction. Important in this investigation was to identify where higher limestone additions would provide engineering benefits to concretes and instances where such additions may be unfavourable. Furthermore, the study focussed on highlighting the benefits of using higher limestone cements in conjunction with SCMs properties of concrete such as long-term durability.

3. Experimental program

3.1. Materials

Most cements used in studies on limestone influence on cementitious systems in the literature are typically either purpose made in laboratories or blended. However, cements used in this study were produced as part of a full-scale production grinding using Type GP cements (conforming to AS3972) with limestone being inter-ground with clinker and gypsum at the cement plant. The limestone was obtained from a range of sources and in all cases met requirements as specified in AS3972 clause 3.4 as detailed below:

- 75% $\leqslant$ $CaCO_3$ content $\leqslant$ 80% by mass,
- Clay content (determined by EN 933-9) <1.20%, and
- Total organic carbon (TOC) content (as given in EN 13639) <0.50% by mass.

Table 1 provides more general information regarding the chemical and physical properties of cement, fly ash and slag used in this program.

The manufactured cement samples were combined with other binder materials and concrete component materials in laboratories where testing was carried out. In all laboratory trials, a control cement containing 5% limestone content was used. This was compared with cement samples containing 7.5%, 10% and 12% limestone content by mass. The overall cement particle size distribution and fineness varied for each sample according to the combined Portland cement and limestone system properties. Generally, the overall cement fineness increased with increasing limestone content.

3.2. Concrete mixes

Concretes grades investigated ranged between 40 MPa to 65 MPa. The cementitious content ranged between 420 kg/m^3 and 470 kg/m^3 and water:binder ratios ranged between 0.35 and 0.40. Water contents ranged between 150 kg/m^3 and 180 kg/m^3. Total aggregate contents were within those for commercial mix designs between 1650 kg/m^3 and 1850 kg/m^3, respectively. More details relating to the mix designed used are provided in Table 2.

Aggregates complied with provisions described in AS2758.1. Normal range water reducing admixtures complying with AS1478 provisions were used to achieve a constant target slump of 120 mm for control samples with 5% limestone content. A total of 16 different binder combinations were tested. These included binders containing limestone as described previously and containing one or more supplementary cementitious materials (SCMs) including fly ash, slag or amorphous silica at varying proportions, and complying with provisions described in AS3582.

Concrete testing was undertaken across 5 different laboratories located within the respective cement manufacturing facilities as shown in Table 3. For each trial, the performance of concrete made with cements incorporating 7.5%, 10% and 12% limestone addition was compared with control concrete made with cement containing 5% limestone addition.

3.3. Testing undertaken

Tests undertaken in this investigation included both fresh and hardened concrete properties. Fresh concrete properties were investigated in terms of slump to AS1012.3.1, air content to AS1012.4.1, bleed to AS1012.6 and setting time to AS1012.18. Hardened concrete properties investigated included compressive