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# High volume limestone alkali-activated cement developed by design of experiment

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## ABSTRACT

Herein, we report on the development of a cement comprising ground granulated blast furnace slag, soda ash (sodium carbonate), and up to 68 wt.% granular limestone. Mixture Design of Experiment (DOE) was utilized, with analysis of compressive strength, modulus of elasticity, hydraulic properties, cost, $CO_2$ production, and energy consumption. Models were derived to understand the impact of mix design on performance and for optimization. Successful formulations are hydraulic and cure at room temperature, with strengths as high as 41 MPa at 3 d and 65 MPa at 28 d. These formulations, compared to OPC, are competitive in cost and performance and can reduce both $CO_2$ production and energy consumption by up to 97%.

## 1. Introduction

The manufacture of one tonne of the Ordinary Portland Cement (OPC) generates 900 kg of $CO_2$ and requires 1510 kW h of energy [1]. While this is, on a unit weight basis, considerably less than other options like steel or treated wood, the enormous volume of cement produced (2.6 billion tons in 2007 [2]) is responsible for approximately 5% of global anthropogenic $CO_2$ production.

As environmental sustainability becomes a greater priority, solutions are being sought to reduce the $CO_2$ and energy burden of cement without sacrificing economic viability. These include emissions sequestration, concretes with lower OPC content, blends of OPC with pozzolans, magnesia cements, alumino-silicate based geopolymers, and more [3]. Efforts are also underway to measure the environmental impact of OPC and its alternatives, for example those introducing novel metrics such as binder intensity and $CO_2$ intensity [4], and those performing life cycle analysis [5].

Due in part to its low energy and $CO_2$ burdens, the use of limestone to replace OPC is an increasingly popular path [6,7]. Originally thought to be an inert filler, recent research has shown, to varying extents, limestone to be chemically and physically active in hydraulic cement [8]. Current standards allow a replacement, of up to 5 wt.% OPC in the US (ASTM C150-04) and up to 35 wt.% in Europe (EN-197-1-2000) [9]. Compared to the energy-intensive kiln-firing process of OPC, maximizing the use of limestone would be desirable to minimize environmental impact.

Another approach to ecological cement is that of geopolymer or alkali-activated cement (AAC), which generally use no OPC. Their advantages over OPC may include: (i) drastically less $CO_2$ production; (ii) longer life and better durability; (iii) better defense against chemical attack (e.g. chlorides, sulfates); (iv) rapid strength gain; (v) better performance in marine environments; and (v) repurposing of industrial waste [3,10–17].

The present work was designed to combine the two above approaches to develop high-volume limestone AACs. Analysis was conducted with respect to key characteristics of performance (strength, modulus, hydraulic stability) and economy and ecology (cost, $CO_2$ production, energy requirement). Design of Experiment (DOE), a statistical method of designing and analyzing multi-variable experiments, was used to extend earlier work [18–21]. Most statistical investigations of AACs have used factorial DOE, with typical variables being raw material specifications (e.g. specific slag surface areas), processing (e.g. curing temperature), categorical factors (e.g. activator chemical), and certain chemical ratios (i.e. amounts of activator) [22–27]. In contrast, this work relies on mixture DOE, thus focusing on the roles and interactions of the system components, and mixture optimization.

This study was intended not only to better understand the impact of mix design on high volume limestone AAC performance, but also to aid in the development of cements for markets in both developed and developing countries. Four ingredients were used: ground granulated blast furnace slag (GGBFS), granular limestone,

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sodium carbonate ($Na_2CO_3$), and water. These ingredients were chosen partially for their real-world practicality. For example, the limestone used was a widely available consumer-grade, granular limestone instead of lab-grade $CaCO_3$. Of common activators, $Na_2CO_3$ is one of the most ubiquitous, inexpensive, and environmentally benign. No admixtures or fibers were included and, hoping to leverage the advantages of AACs, no OPC. The result is novel high volume limestone AACs, which are competitive in performance with OPC, some of which have a $CO_2$ and energy consumption reductions approaching 100% instead of the more common Portland Cement Association (PCA) goal of 10 % [28].

## 2. Material and methods

### 2.1. Experimental methods

As noted above, four raw materials were used. The first was slag (GGBFS) (St. Lawrence Cement, Camden, NJ) with a Blaine fineness of 498 $m^2/kg$ (as tested by the authors per ASTM C204-07 [29]). X-ray Fluorescence (XRF) analysis of the GGBFS was carried out by Arkema, Inc. in King of Prussia, PA (Table 1). Second is sodium carbonate, $Na_2CO_3$ (Brenntag Pacific, Inc., Santa Fe Springs, CA). Third is granular limestone with a $CaCO_3$ content of 89.3 wt.% and a $MgCO_3$ content of 10.7 wt.% (Oldcastle Stone Products, Atlanta, GA). The cumulative particle size distribution of the latter is: 23% < 75 μm, 48% < 150 μm, 68% < 300 μm, 100% < 1000 μm. Fourth, tap water.

A strict interpretation of ASTM C125-07 and ASTM C219-07a would, respectively, define the limestone used as a fine aggregate and the mixture as a mortar [30,31]. However, since the granular limestone in this case is chemically active [18,19], the material could be used as a cement, as it meets the ASTM definition for hydraulic cement, except for the limestone particle size. Nevertheless, henceforth it is labeled a hydraulic cement.

ASTM C192/C192M-07 guided the preparation of 2 in. × 4 in. cement paste (not mortar or concrete) cylinders for compression testing [32]. The four components were weighed, dry mixed, and the water added. The mixture was then mixed by hand for approximately 2 min. Each cylinder was half-filled and rodded in two lifts then struck off with a trowel. The two curing conditions, both at room temperature, were ASTM C192 standard 100% RH – henceforth referred to as moist cure - and submerged in a plain water bath (without lime), where the water was changed every 24 h to avoid possible equilibrium effects due to leaching.

Samples were stored in the molds for 24 h, covered by plastic sheets, after which they were removed from the molds and placed in their respective curing conditions until testing. The compressive strength was measured according to ASTM C39/C39M-09a, using unbonded rubber caps (ASTM C1231/1231M-10), on a load frame (Instron 5800R, Norwood, MA) [33,34]. The strain was measured using an extensometer and the modulus of elasticity calculated according to ASTM C469-02 [35]. For each age, 3 or 28 d, and curing condition, three cylinders were tested for each DOE run, and six for each validation run. The weight of each cylinder was measured immediately after removal from the mold and immediately before compression testing.

Cost, $CO_2$ production, and power consumption were calculated for each run. The bulk costs of components were determined from government and industry data, as listed in Table 2. The $CO_2$ production and power consumption were calculated from studies of cement production; details are provided in Appendix A. The costs, $CO_2$ production, and energy consumption for each component are listed in Table 2 [36–39].

### 2.2. Design of Experiment (DOE)

Prior to the DOE, initial one-factor-at-a-time (OFAT) experiments were performed to establish the system boundaries (Table 2) and to begin to understand the system's trends. Boundaries were intentionally wide to include unconventional ratios (e.g. up to 80 wt.% limestone), while still limited enough to provide sufficient detail for modeling. The boundaries represent ratios of $Na_2CO_3$ spanning hydraulic stability to detrimental leaching; ratios of water for spanning the limits of workability (very dry to very wet), and GGBFS and limestone (with equal boundaries) to produce strength in the range of OPC.

DOE experiment design and analysis was performed on Design-Expert v7.1.5 (Stat-Ease Inc., Minneapolis, MN). A D-optimal mixture design was used, with the four components for each run totaling a fixed weight of 6200 g. A special-cubic Scheffe model was used for the design in order to include tertiary interactions, if any were present. The design comprised 14 model points, 3 lack of fit points, 3 replicates, and 2 additional center points, for a total of 22 runs. In keeping with best practices of DOE, efforts were made to minimize variance, such as keeping the operator, preparation and curing procedures, and test equipment as consistent as possible for all runs.

To determine the model for each response, the model terms were determined by stepwise selection (α in and out: 0.10). Transformations were selected and outliers were removed, as appropriate, to generate the model with the highest statistical significance, determined by Analysis of Variance (ANOVA) and other diagnostic tools such as Box Cox, Cook's Distance, and Normal Plot of Residuals plots. Numerical optimization of variables and responses were performed by assigning criteria to each response as desired. In order to verify the accuracy of the models, three additional formulae

**Table 1**
Slag XRF (wt.%). One sample was analyzed; errors shown are typical relative accuracies for each element, as determined by calibration.

| CaO | $SiO_2$ | $Al_2O_3$ | MgO | $SO_3$ | $TiO_2$ | $Fe_2O_3$ | $Na_2O$ | MnO | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| 39.4 ± 4.0 | 38.4 ± 0.8 | 12.9 ± 1.4 | 6.2 ± 1.0 | 2.1 ± 1.1 | 0.4 ± 0.0 | 0.4 ± 0.1 | 0.2 ± 0.0 | 0.4 ± 0.1 | 0.2 ± 0.0 |

**Table 2**
Cost, $CO_2$ production, and DOE mixture boundaries. Calculations for $CO_2$ and energy are provided in Appendix A.

| Material | Cost/tonne | $CO_2$ produced (kg/tonne) | Energy consumed (kW h/tonne) | DOE mixture boundaries | |
|---|---|---|---|---|---|
| | | | | Constraints | Resulting ranges, total wt.% |
| GGBFS | $80.00 [36,37] | 28.8 | 47.2 | 25–80% of total weight | 25–56 |
| Limestone | $8.60 [38] | 12.2 | 20.1 | 25–80% of total weight | 25–56 |
| $Na_2CO_3$ | $105.00 [39] | 110.8 | 374.1 | 25–100% of slag + limestone | 4–35 |
| Water | – | – | – | 18–25% of dry components | 15–20 |