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Marl-based geopolymers incorporated with limestone: A feasibility study

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ABSTRACT

The expanding raw materials base is one of the drivers for the further development of inorganic binders, including alkali-activated cements. This research focuses on studying marl with a high calcite/aluminosilicates ratio as a geopolymer precursor, and limestone as a mineral addition to this geopolymer. The calcination of marl at 800 °C resulting in the formation of reactive Si, Al, and Ca due to the dehydroxylation of clay minerals and decarbonation of calcite makes marl suitable for use as a geopolymer precursor. Calcined marl activated with sodium silicate and cured at ambient temperature had a 28-day compressive strength of 34 MPa. When incorporated with 50% limestone, the compressive strength became 39.2 MPa. XRD, TG/DSC, FTIR, optical and SEM have been used to investigate the reaction products, as well as the microstructure of the geopolymer hardened pastes.

1. Introduction

Geopolymerization, as a non-fire or low-temperature production method of binders based on various natural and technogenic aluminosilicate materials that are not inferior to the properties of Portland cement, increasingly appeals both in theory and practice [1,2]. Progress in this area is also driven by the constant expansion of the raw material base and the possibilities of using a wide range of both natural and waste aluminosilicate materials [3,4]. The use of different aluminosilicate precursors and ways to improve the performance of the geopolymers based on them through the introduction of chemical additives and mineral additions are also being researched and developed [5–8].

The increasing importance of thermally activated clays as supplementary cementitious materials for Portland cement [9–13] and as precursors for alkali-activated materials [1,2] should be noted. The most valuable clay for both Portland cement-based and alkali-activated cements is metakaolin, which is produced by heating kaolin clays. However, the scarcity of their reserves and the associated high costs have led to research in different countries involving feasibility studies on the use of the more common low-grade kaolin clays and other clays consisting of different minerals [14–18] including calcined marl [19]. Many studies stated the possibility of transforming a wide range of clays or natural and synthetic aluminosilicates like the smectite and the smectite/illite-types of clays [20,21], 16 aluminosilicate minerals with different structures and compositions (albite, illite, sillimanite, andalusite, and others) [22,23], halloysite [24], feldspars [17], etc. into alkali-activated cements. The mechanical performance of the alkaline cements obtained with common clay and feldspar is lower as a rule than that of the cements synthesized from fly ash or metakaolin (MK) [1].

The combination of calcined clays with calcium aluminosilicates (high-calcium fly ash, or slag) [25–30] and fillers is an effective way to reduce the dependence on aluminosilicate clay sources and manage the macro-, micro-, and nanostructures, as well as the technological and physical and technical characteristics of such blended activated systems.

One of the most used mineral additions, both for the blended Portland cements and non-clinker cements, is limestone [31–44]. In the case of alkali-activated cements, a combination of aluminosilicate precursors with physically or chemically active supplementary materials or with materials that are both physically and chemically active is effective because alkali activation allows not only the production of alkali-activated cements of superior technical efficiency in matrices, but also allows for an effective interaction between the alkali-activated cement paste and the fillers, as well as compatibility with mineral

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blending materials of various compositions and structures [6].

As to MK and limestone LS, several studies have been conducted on the beneficial results of their combination.

According to Yip's study [44], the introduction of 20 wt%. of calcite into MK activated by a sodium silicate solution (SiO_2/Na_2O ratio of 1.2:2) is found to improve the mechanical strength of the geopolymer. The authors explained that the results obtained were due to the contributions of the calcium and magnesium ions to the increased adhesion between the particles and the polymeric gel. However, the contribution of these ions in the polymerization process wasn't found to be significant.

In a study of the MK-LS-NaOH system, Cwirzen [36] stated that the presence of LS enhances the release of Al and Si ions from MK. The amount of leached Ca was generally low in all cases, independent of the LS/MK ratio. The concentration of dissolved calcium decreased with time probably due to solution saturation effects and a reduction in the solubility of Ca as the dissolved Si concentration increased. From these data, it was concluded that a small amount of Ca released from LS at an early stage hindered the initial release of Al and Si from MK. However, the authors believe that the actual mechanism is more complex, and involves a complexation and reprecipitation/gel formation process rather than direct hindrance. The newly formed precipitates may be forming on the unreacted particle surfaces, thus creating a degree of hindrance, but this is likely to be a secondary effect. Later, when the dissolved Ca concentration is lower, the release of Al and Si increases. The main alkali-activation product in the investigated pastes is a geopolymer gel with inclusions of unreacted MK, LS particles, zeolite A, and calcium aluminate monosulphates, with different zeolites such as faujasite-like and hydrosodalite phases also identified at higher reaction temperatures. The replacement of MK by 50% LS increased the strength of the hardened paste from 4 to 5 MPa at a curing temperature of 20 °C and from 5 to 7 MPa at a curing temperature of 80 °C.

Aboulayt [45] found that a highly basic environment does not promote the dissolution of calcite, the latter acts as an inert filler in replacing MK. Low amounts of Ca^{2+} ions in the initial mixture do not cause variations in the activation energy.

Qian and Song [46] reported that the addition of up to 10% LS to MK activated by potassium hydroxide improved the mechanical properties and the workability of the fresh geopolymer. The authors attributed this to the formation of a more compact structure and a better particle size distribution and refer to it as the "filler effect".

This research aims to study the properties, the reaction products and the microstructure of a sodium silicate activated geopolymer based on calcined marl (CM) with a high calcite/clay minerals ratio that also incorporates LS.

2. Experimental details

2.1. Materials

The marl and LS used in this study were obtained from deposits from the Republic of Tatarstan (Russian Federation). The marl had the following mineral composition (wt%): kaolinite – 3.45%, montmorillonite – 6.45%, clinochlore – 1.12%, calcite – 57.08%, quartz – 12.58%, orthoclase – 8.42%, muscovite – 6.37%, gypsum – 4.57%, amorphous phase – 34%. The LS had the following mineral composition (wt%): calcite – 90%, quartz – 9%, albite – 1%. The chemical compositions of the starting materials are shown in Table 1, and the details of the size distributions are given in Fig. 1. The specific surface area of marl was 5000 cm^2/g, and that of limestone was 3700 cm^2/g (Blaine). SEM images of the marl are shown in Fig. 2.

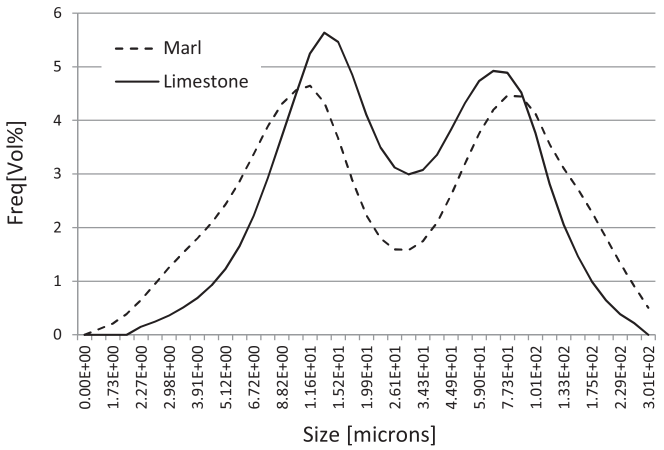

Fig. 1. Particle size distribution of the raw materials measured by laser granulometry.

The alkaline activator commercial hydrous sodium metasilicate $Na_2SiO_3{\cdot}5H_2O$ (NSH_5) was obtained from Meterra (Russian Federation), the molar ratio of silica to sodium ($M_s = SiO_2/Na_2O$) is 1.

2.2. Methods

The marl was calcined at 600, 700, and 800 °C using heating rates of 1.7, 2.5 and 3.3 °C/min, respectively. A dwell time of 3 h was used.

The starting materials were milled in a MPL-1 laboratory planetary mill.

The NSH_5 solution was obtained by dissolving NSH_5 in deionized water and cooling down to room temperature during 24 h prior to use.

The reference sample was prepared by 2 min mixing of CM and NSH_5 solution. The mixed compositions of CM and LS were dry-premixed for 2 min, the NSH_5 solution was then added and the pastes were mixed for a further 2 min. Mixture proportions of the pastes are presented in Table 2. A liquid/solid ratio of 0.4–45 provided a workable and appropriate flowability of the fresh pastes and decreased with the increase of the LS content. The geopolymer paste samples were prepared in cubic moulds (2 × 2 × 2 cm) for compressive strength tests and then demoulded after two days. The cubes were stored in sealed plastic bags in a chamber at room temperature and 98% relative humidity for 28 days. Compression tests were performed by applying a load between the two surfaces that were vertical during casting. Each strength determination quoted is based on an average of six measurements from the same cast.

Calorimetry experiments were carried out using a "Thermochron" measuring device. The pastes were mixed externally, placed in sealed glass ampoules, and loaded into the calorimeter. The time elapsed between the addition of the activating solution to the powder and the loading of the paste into the calorimeter was approximately 3–4 min. The tests were run for 24 h.

Table 1
Chemical composition of starting materials.

Starting material	Component (mass % as oxide)												
	SiO_2	CaO	Al_2O_3	MgO	MnO	Fe_2O_3	TiO_2	Na_2O	K_2O	P_2O_5	SO_3	CO_2	LOI
Raw marl	40.30	40.00	9.04	0.82	–	4.40	0.41	0.51	0.93	0.40	0.05	–	3.55
Calcined marl	40.56	40.26	9.3	1.08	–	4.66	0.67	0.77	1.19	0.66	0.31	–	0.60