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Use of silica fume and natural volcanic ash as a replacement to Portland cement: Micro and pore structural investigation using NMR, XRD, FTIR and X-ray microtomography

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HIGHLIGHTS

- Natural volcanic ash and silica fume as a replacement to Portland cement.
- Micro and pore structure characterization using XRD, NMR, FTIR and X-ray Micro CT.
- Silica fume along volcanic ash helps to densify the cementitious matrix with OPC.

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ABSTRACT

This work investigates the effectiveness of the use of volcanic ash along with silica fume as a partial replacement for Portland cement. Multiple mix combinations of volcanic ash, silica fume and Portland cement were examined using various pore and microstructure characterization techniques. Hardened cement pastes were cured for 28 days and their pore and microstructures were examined using X-ray Microtomography, Magic Angle Spinning (MAS) Nuclear magnetic resonance (NMR) for ^{27}Al and ^{29}Si, X-ray Diffraction (XRD) and Fourier transform infra-red spectroscopy (FTIR). Microstructure examination of mixes prepared with volcanic ash, silica fume and Portland cement revealed the co-existance of calcium silicate hydrate (C-S-H) and calcium–alumino-silicate-hydrate (C-A-S-H) gels, along with other hydration products that led to a reduction in porosity and densification of the cement matrix. These findings indicate that volcanic ash along with silica fume is a viable substitute for Portland cement up to 40% and provides a sustainable, cost effective and environmentally friendly solution to volcanic ash disposal.

1. Introduction

Volcanic ash (VA) has been used in the past as an admixture for concrete applications [1–4]. The Romans were the first to use natural aluminosilicates to prepare highly durable cements [5]. Volcanic materials are found abundantly in areas around the world, and new and improved ways to utilize these materials in construction is becoming widespread. The motivation for the use of volcanic ash materials as replacement of Portland cement is due to the significant carbon footprint of concrete materials [6–10], the regional availability of VA, and its capability to be used as an additive for high-performance materials [3,5,11].

There are two types of VA, one which erupts from molten rock and primarily consists of basaltic compositions, and the other type which originates from the more explosive pyroclastic flow eruptions that develop to form secondary pozzolanic clays and zeolitic phases [3,11,12]. Recent studies have utilized the basaltic ash type as a supplementary cementitious material in concrete and found that it complies with ASTM C 618 and is categorized as a class N natural pozzolana [4]. Further work is needed to better understand the factors controlling the incorporation of VA within a concrete mixture as well as the reaction mechanisms controlling hydration.

Not all ash materials are suitable for usage within blended cements [13,14]. The ability of an ash material to replace Portland cement is partly a function of its pozzolanic activity, which depends on the amount of reactive silica and the amorphous content of the ash [3]. A recent study by Contrafatto [14] suggests that

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Notations

A	average area occupied by one molecule of adsorbate
AFm	aluminate-ferrite-monosubstituent
Al_o	octahedral coordinated aluminum
Al_T	tetrahedral aluminum
BET	Brunauer-Emmett-Teller
C-A-S-H	Calcium-Alumino-Silicate-Hydrate
C-S-H	Calcium-Silicate-Hydrate
D	density conversion factor
D(t)	self-diffusivity in the porous environment
D_0	diffusion coefficient of the bulk fluid in free space without solid grains
D_{avg}	average pore diameter
DP	pore diameter
EDS	Energy Dispersive Spectra
FTIR	Fourier Transform Infrared Spectroscopy
LP_1	Length of pore
MAS	Magic Angle Spinning
N	Avogadro constant
NMR	Nuclear Magnetic Resonance
OPC	Ordinary Portland Cement
OPC35VA50SF15	OPC (35% by wt) + VA (50% by wt) + SF (15% by wt)
OPC60VA30SF10	OPC (60% by wt) + VA (30% by wt) + SF (10% by wt)
OPC60VA40	OPC (60% by wt) + VA (40% by wt)
OPC80VA10SF10	OPC (80% by wt) + VA (10% by wt) + SF (10% by wt)
OPC80VA20	OPC (80% by wt) + VA (20% by wt)
PSD	Particle Size Distribution
Q	denotes a silicon bonded to four oxygen atoms forming a tetrahedron
Q^0	silicon bonded through oxygen to no other network forming elements
Q^1	silicon bonded through oxygen to one other silicon (end group of chains also known as "dimers")
Q^2	middle group of chains
Q^3	branching group that consists of sheets
Q^4	silicon bonded through oxygen to four other silicon (three-dimensionally cross-linked groups)
Q^n	number of bridging oxygens per tetrahedron (n represents connectivity, i.e. the number of Q units attached to the SiO_4 tetrahedron)
$r(\tau)^2$	mean-square displacement as a function of dimensionless time integer τ
SA	Surface Area
SCM	Supplementary Cementitious Materials
SF	Silica Fume
V_1	amount of gas adsorbed per gram of sample
VA	Volcanic Ash
V_{CUM}	cumulative pore volume
V_M	molar volume
V_m	volume of gas adsorbed when the entire surface area is covered by a monomolecular layer
VOI	volume of interest
VP_1	internal pore volume
X-ray μCT	X-ray Microtomography
XRD	X-ray Diffraction
XRF	X-ray Florescence
α	Lattice constant
τ_D	Diffusion Tortuosity

the pyroclasts produced by the explosive activity of Mt. Etna, Italy did not have sufficient reactive SiO_2 hence unable to produce sufficient pozzolanic reactivity to achieve the required strength and thus could not be used as an SCM for producing cement pastes. Several methods of increasing the overall pozzolanic reactivity have been investigated. This includes reducing the mean size of ash particles to provide a higher specific surface area, or by reducing the quantity of clay minerals while increasing the zeolitic mineral composition in the ash [15]. In one study, vibratory milling was used to increase the amorphous composition which resulted in higher pozzolanic activity [16]. In addition, the pozzolanic activity is enhanced by the amount of cations present in the aluminosilicate precursor and the ease with which these cations are exchanged [17]. Calcination, acid [18,19] and thermal treatments [20] have also been used to assist with the preparation of blended cements.

These blended cement pastes prepared with Supplementary Cementitious Materials (SCM) form a complex composite of hydration product, and to decipher this binder a multi-scale analysis using advanced experimental techniques is required. The microstructural growth of these hydration products is at intermittent scales ranging from angstrom to microns, hence; a combination of experimental techniques is required for understanding evolution and growth of these hydration products [21]. Pure OPC and Tricalcium Silicate (C_3S) mixtures have been well studied using advanced micro and pore structural techniques such as Magic Angle Spin (MAS) Nuclear Magnetic Resonance (NMR) [22–24] and X-ray Microtomography (X-ray μCT) [25–30]. However, limited data is available using these characterization techniques when SCM's are used with natural pozzolans (volcanic ash) for preparing sustainable and durable cement pastes [31–39]. These studies mostly focus only on usage of volcanic ash with Portland cement, however, considering the current needs incorporation of silica fume with volcanic ash is required, since silica fume is currently being commercially used for developing high strength concretes [40].

For this study, we will evaluate the mineralogical nature of VA as a partial substitute to Portland cement, and assess the resulting hydration products of various cement paste mixtures incorporating the silica fume additive. VA was obtained from a pozzolan factory located in Jeddah, Saudi Arabia. Our investigation utilizes experimental techniques of NMR, X-ray microtomography, X-ray Diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR) and nitrogen adsorption to study the feasibility of VA as a partial replacement for Portland cement to obtain denser and less porous cementitious microstructures. This study examines the effect of silica fume, along with VA, by examining the type and nature of hydration products using multiple micro-characterization techniques. A new insights into micro- and pore-structure formation is observed as a basis for developing engineered cement pastes when Portland cement is partially replaced with VA and silica fume. Silica fume is a common additive used with OPC for densifying the matrix; however, the current study investigates the interaction of silica fume with VA in terms of hydration products that influences the pore structure of the resulting cementitious binder.

A microstructural insight from angstrom level using XRD and the hydration products formation was examined via ^{29}Si and ^{27}Al NMR along with bonding mechanism was studied via FTIR analysis. The pore structure and porosity was examined by X-ray microtomography. Furthermore, adsorption-desorption isotherms and