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Influence of natural pozzolan, silica fume and limestone fine on strength, acid resistance and microstructure of mortar

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ABSTRACT

Based on an ongoing experimental programme, this research focuses on the effect of various supplementary cementitious materials (SCMs) (natural pozzolan (NP)/silica fume (SF)/limestone fine (LF) at various substitution levels) on the microstructure and mechano-chemical resistance of blended mortar. The paper primarily considers the characteristics of these materials, including their strength and the effects of aggressive chemical environments, by using sulphuric acid and nitric acid. The porosity and pore size distribution of the mortars are also examined using mercury intrusion porosimetry (MIP).

The microstructural changes in pastes caused by SCMs and the acid attack of the solution are analysed and related to the phase composition found by X-ray diffraction (XRD). Microstructural investigations, such as scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), were also used to support the explanation for these mechanisms.

The results, according to ASTM C267, showed that the addition of natural pozzolan or limestone fine would improve the acid resistance of mortar, but at different rates depending on the proportion of SCMs. On the other hand, mortars with silica fume are severely damaged in the sulphuric acid environment.

1. Introduction

Supplementary cementitious materials can be either self-cementing or pozzolanic, or both, depending on their chemical composition [1]. They can be obtained as industrial by-products such as silica fume, fly ash, and ground granulated blast-furnace slag or from agricultural wastes such as rice husk ash [1–3]. Furthermore, several SCMs, such as volcanic tuffs, pumice, calcined clay and others, can be obtained naturally [2,3] and SCMs such as high reactivity metakaolin can be manufactured industrially [4]. Some SCMs contain silica in amorphous form, which would react with calcium hydroxide (C–H) to form more cementitious calcium silicate hydrate (C–S–H, C═CaO; S═SiO_2 and H═H_2O) and contribute to the concrete strength. These materials include volcanic ash, diatomaceous earths, condensed silica fume, pulverised fly ash, natural pozzolan and rice husk ash [5].

Today, the incorporation of SCMs has gained in importance because it improves the durability of concrete [6–8], leads to a significant reduction in CO_2 emissions, and reduces the unit cost of concrete production [9]. The use of SCM can lead to densification of the mortar [10] and cannot only contribute to the decrease or disappearance of calcium hydroxide but also modify the chemical composition of the cement matrix, thus improving resistance to acid attack [11,12]. In a word, SCMs contribute greatly to the production of economic and durable concrete structures. Moreover, according to Hidalgo et al. [13], the capability of pozzolanic materials to enhance the strength of concrete is more closely associated with physical than chemical effects.

From the literature review, it is clear that, in the context of durability and especially of resistance to acid attacks, there is debate over the incorporation of mineral admixtures in concrete. First, the addition of mineral admixtures may have little influence on the chemical resistance. Second, the lower water requirement of concrete containing mineral admixtures (except silica fume) coupled with pore refinement through the formation of additional C–S–H may lead to a denser microstructure of the cement matrix, thus reducing the rate of diffusion of aggressive solutions [8,14]. Third, the pozzolanic reaction consumes calcium hydroxide (C–H) from the cement paste and thereby reduces the amount of C–H available per unit area to react with the acidic solution, which may result in faster movement of the corrosion front. For instance, Durning and Hicks [15] and Mehta [16] reported that the incorporation of silica fume increased the resistance of concrete to 1% sulphuric acid attack through reduced C–H content and lower permeability. Conversely, Monteny et al. [17] reported a negative effect of silica fume incorporation in concrete specimens exposed to 0.5% sulphuric acid. They stated that a refined pore structure with higher capillary suction would cause deeper penetration of acidic solutions into concrete and increase the surface area in contact with acid [17].

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Other research [7,11] has shown that the action of acid attack is dependent on the type of acid present. In the case of attack by hydrochloric and nitric acids, the calcium salt formed is soluble in water, leading to higher mass loss. On other hand, in the case of sulphuric acid attack, the calcium salt formed is not soluble in water. It becomes deposited in voids and causes internal stresses that lead to disruption and loss of strength of the matrix.

In a series of chemical tests with a range of SCC mixtures, Bassuoni and Nehdi [6] reported that the resistance to sulphuric acid attack of self-consolidating concrete (SCC) incorporating combinations of SCMs was moderately improved by addition of an organic corrosion inhibitor (OCI), while sulphate resistant Portland cement (SRPC) and air-entrainment offered little improvement in strong and very strong sulphuric acid solutions.

In Algeria, most of the cement is blended with additions such as limestone and natural pozzolan. Natural pozzolan is currently used in cement manufacture by at least eight of the fourteen Algerian cement plants while two cement plants use limestone. These cement plants usually add between 15 and 20% of natural pozzolan and 10% of limestone filler as cement replacement by weight. Apart from the internal quality control testing for conformity to standards requirements, no detailed investigation has been made to evaluate the effect of the interaction between limestone and natural pozzolan additions on the properties of cement mortar and concrete [18].

The present study is aimed at evaluating the response to sulphuric and nitric acid of local SCM mortars prepared with ordinary Portland cement and natural-pozzolan/silica fume/limestone at various replacement levels. The chemical degradation caused by dilute solutions of nitric and sulphuric acids is intended to simulate the deterioration of mortars exposed to the aggressive environments. A specific method standardised in ASTM C267 [19] was a major tool used in the current study to evaluate resistance to acidic chemical environments.

The effects of SCMs and exposure to these media on these cements were investigated by using mercury intrusion porosimetry tests and by the visual and chemical information provided by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Hence, the objective of the present investigation is to address some of the uncertainties concerning the acid attack of mortar containing mineral admixtures.

2. Materials and methods

2.1. Constituent materials

The physical and chemical properties of the various materials used in the present work are highlighted below. The choice of local Algerian materials was based on their abundant availability and their moderate cost.

2.1.1. Cement

The cement used was a local ordinary Portland cement type (CEM I 42.5 R), manufactured by the Zahana Cement Company located in the west of Algeria. The cement factory conforms to the Algerian standard NA 442 [20] (which is mainly based on the European Standard EN 197-1). The physical properties of clinker, and its mineralogical and chemical composition data are presented in Table 1.

2.1.2. Natural pozzolan (NP)

The natural pozzolans used as mineral admixtures in Portland cement must meet certain chemical and physical requirements. For instance, ASTM C 618 [21] Class N admixtures must have a minimum content of 70% in $SiO_2 + Al_2O_3 + Fe_2O_3$, whereas Algerian natural pozzolan 76%. Although, the importance of the content ($SiO_2 + Al_2O_3$) is emphasised by the fact that the active vitreous phases generally are richer in silica and alumina content. NP used in this study was obtained from natural deposits in the west of Algeria. The pozzolan was ground in a laboratory mill to a specific surface of 350 m^2/kg. The chemical composition of the cement and NP are given in Table 1. The Algerian natural pozzolan shows a strong acidic character, having a ($SiO_2 + Al_2O_3$) content ranging around 57% of the total.

Table 1
Chemical and physical properties of cement and supplementary materials.

Oxides in clinker (%)		OPC	Natural Pozzolan	Silica fume	Limestone
SiO_2		21.35	47.21	88.10	7.89
Al_2O_3		4.59	18.85	5.39	2.58
Fe_2O_3		5.52	9.99	0.84	1.13
CaO		63.89	10.84	1.49	45.45
MgO		1.37	4.38	1.50	1.72
SO_3		2.72	0.50	0.06	0.95
K_2O		0.41	0.20	0.08	0.21
Na_2O		0.13	0.81	0.52	0.00
Cl		–	–	–	–
LOI		2.47	3.91	1.70	42.48
Calcite content ($CaCO_3$)		–	–	–	86.98
Mineralogical compounds in clinker (*Bogue calculation*)					
C_2S, %		25.69			
C_3S, %		47.15			
C_3A, %		2.84			
C_4AF, %		16.70			
Physical properties					
Setting time (min.)	Initial set	105			
	Final set	225			
Specific gravity [kg/m^3]		3.10	2.62	2.24	2.70
Fineness, [m^2/kg] (EN196-6)		325	430	23,000[a]	456

[a] According to the data sheet.

2.1.3. Silica fume (SF)

Condensed silica fume has been classified as a pozzolan by the American Concrete Institute (ACI) Committee 226 on cementitious materials [22]. ASTM C 618 [21] recognises three classes of pozzolan: N, F, and C. Silica fume is somewhat closer to the N class. However, particular provision is needed to classify silica fume appropriately. The superfineness of SF (specific surface area 15,000–30,000 m^2/kg compared to 200–500 m^2/kg for cement) and its high silica dioxide content enhance its pozzolanic action. The silica fume used in this experimental programme was a commercial product called Sikacrete HD from Sika Algeria. Its chemical composition and selected properties are shown in Table 1.

2.1.4. Limestone fine (LF)

Crushed limestone is the main source of aggregates used in concrete. However, its production is associated with high percentages of fines that can make these aggregates unacceptable in the concrete mix design. As a result, over 20% of such products cannot be used and become hazardous to the environment. Many studies have shown that the main effects of limestone filler are of a physical nature. It leads to better packing of the cement granular skeleton and a large dispersion of cement grains [23]. The crushed limestone used here was obtained from limestone quarries in Oran City. It was ground to a specific surface area of 456 m^2/kg, with a maximum nominal size of 80 μm. The basic properties of crushed limestone are shown in Table 1.

The granulometric study of the three mineral additions was carried out using CILAS 1090 apparatus, which analyses particle sizes from 0.02 to 500 μm by laser diffraction. The particle size distributions are shown in Fig. 1.

2.1.5. Sand

Local, well graded, crushed sand from a quarry at Kristel (Oran) was used. Its physical proprieties were as follows: relative specific density, 2650 kg/m^3, water absorption, 1.5%, bulk density, 1500 kg/m^3 and maximum grain size, 3 mm.