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Resistance of limestone mortars with quaternary binders to sulfuric acid solution

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ABSTRACT

The synergistic action of three mineral admixtures simultaneously incorporated in cement has a positive effect concerning the durability of limestone mortars. Tests were carried out on limestone mortars made from five quaternary binders (ordinary Portland cement and OPC blended simultaneously with limestone filler, blast furnaces slag and natural pozzolana). The purpose of this investigation was to identify the resistance of five different mortar mixtures to sulfuric acid solutions. The changes in weight loss and compressive strength values measured at 30, 60, 90, 120 and 180 days for each acid solution were studied. The pH variation of the sulfuric acid solution has been monitored during the tests and several phases are determined by XRD.

1. Introduction

It is now well established that the evaluation of the concrete performance is not limited to the determination of its mechanical properties since it is of primordial importance to characterize the material in term of durability. The service life of a reinforced concrete structure and its performance over the time are closely connected with the properties that define durability (permeability to various agents), reaction to sulfates, acids and others [1]. Concrete structures can be exposed to various acids because of the environmental pollution. Therefore changes in physical and chemical properties and also variations in weight, strength and microstructure of the mortars and cements caused by interaction with various acids should be examined [2,3].

It is well known that there are acid attacks in mortars, concrete and many building materials that form part of the urban landscape and Cultural Heritage [4,5]. The reaction of sulfuric acid with calcium carbonate leads to the gypsum deposit. Such gypsum coatings have been studied in natural stones, such as calcareous stones and marbles [6–8]. The ability of the acid to dissociate and the solubility of calcium salts play also an important role in degradation.

Limestone filler and pozzolana also show different durability properties with the content and type of active silica present in their composition. In relation to the effect of pozzolana on concrete strength, it should be stated that the type, amount and fineness of pozzolana, and also the type of cement are factors that affect the strength of concrete [9]. The use of mineral admixtures such as silica fume and fly ash in concretes has been shown to improve the resistance of concrete to sulfuric acid attack in terms of the reduced presence of calcium hydroxide, which is over time vulnerable to acid attack [10].

It was recognized that the use of binary and ternary cement consisting of silica fume and fly ash had a better performance than concretes with other mineral admixtures, toward weight loss of the concrete samples up to 25% after 56 days immersion in 1% sulfuric acid solution [11–14].

The highest resistance to a 0.5% sulfuric acid solution was achieved by a binary binder mixture comprising more than 60% ground granulated blast furnace slag [15]. Conversely, Chang et al. [16] recently reported that binary binder concrete mixtures prepared with 60% slag and ternary binder mixtures with 56% slag and 7% silica fume had inferior performance compared to that of a 100% OPC mixture when immersed in a 1% sulfuric acid solution with a pH of 1.27.

The reaction between the amorphous glassy silica in slag and pozzolana and CH, which is the result of the hydration of cement, produced the CSH. This product is also effective on the durability of concrete [17,18].

Data on the resistance of quaternary binder concrete mixtures to sulfuric acid solutions are extremely limited. In this experimental study, crushed limestone sand was used with a quaternary binder

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to investigate the resistance of mortars to acid attack. Five mortars were investigated using simultaneously limestone filler, granulated blast furnace slag and natural pozzolana. Mortars prismatic samples were immersed in 3% sulfuric acid solution over 180 days and the samples were regularly investigated by mass change, compressive strength, pH and XRD.

2. Experimental investigation

2.1. Materials

Portland cement, limestone filler, blast furnace slag and natural pozzolana, crushed limestone sand, water, and superplasticizer were used in the production of mortar. The cement used in this investigation is the ordinary Portland cement (OPC) prepared from clinker and 5% of gypsum. Clinker with gypsum and all mineral mixtures were ground in a laboratory mill to a specific surface area of 350 m^2/kg and 380 m^2/kg respectively. The chemical analysis of the cement and mineral admixtures are presented in Table 1.

The specific gravities of cement, limestone filler, slag and natural pozzolana are approximately 3, 2.7, 2.6 and 2.8 respectively. The sand used in mortar mixtures was a crushed limestone sand of 2.5 mm maximum size aggregate. SIKA Viscocrete 3045 which is a water reducing plasticizer based on modified polycarboxylates and tap water were employed for the mixing. Sulfuric acid solution (3%), (pH = 1.30) was chosen for formal testing and prepared in order to test the resistance of mortars to the chemicals attack.

2.2. Preparation of specimens and test procedure

All substitutions were made by mass. The water/binder (w/b) ratio was kept constant at the 0.5. The binder/sand (b/s) ratio was 1:3 for all specimens. Plasticizer was added to the mixture in order to obtain a comparable workability. The plasticizer content ranged between 2% and 2.5% of the binder weight. Mortars were mixed according to the EN 196-1 standard and $40 * 40 * 160$ mm prisms were produced. After casting, the mortar samples were cured 24 h in laboratory at 20 ± 2 °C and relative humidity about 50%. After demolding, the specimens were cured in lime-saturated water during 28 days.

Five specimens of mortars for each blended cement were prepared. The mix design of mortars is given in Table 2. After 28 days of curing in lime water, both series of specimens were immersed in lime water and sulfuric acid solutions during 180 days in order to effectuate a comparative study. Samples of each composition were immersed separately in solution tank. Before carrying out the weighings and the mechanical tests, the specimens were washed with water then dried during 3 h in the laboratory.

Changes in weight of mortar specimens and pH of solutions were measured during the testing period of 180 days. All specimens at 28 days of their hardening in lime water, then after 28 days where they have been subjected to different solutions, we determined their compressive strength at 30, 60, 90, 120 and 180 days.

Table 1
Chemical compositions of cement and mineral additions.

Composition	Binder			
	Clinker	Limestone	Slag	Pozzolana
SiO_2	21.38	0.76	39.38	57.10
Al_2O_3	5.59	0.41	5.64	15.82
Fe_2O_3	3.21	0.23	2.3	6.16
CaO	65.26	54.9	40.3	5.95
MgO	1.72	0.61	4.50	2.09
K_2O	0.47	0.24	0.46	2.0
Na_2O	0.19	0.04	0.13	1.1
SO_3	0.56	0.61	0.90	0.28
Cl^-	0.02	0.005	–	1.40
PAF	0.58	36.3	0.8	1.2

Table 2
Composition of different binders.

Composition (%)	C0	C1	C2	C3	C4
Clinker	95	47.5	47.5	47.5	47.5
Gypsum	5	2.5	2.5	2.5	2.5
Limestone	0	30	10	10	16.67
Slag	0	10	30	10	16.67
Pozzolana	0	10	10	30	16.67

3. Results and discussion

3.1. Weight changes

Most investigations have considered weight loss as acceptable indicator for evaluating the resistance of concrete to sulfuric acid attack [17]. Weight change was determined for all mortars stored in 3% sulfuric acid solutions. The results of weight changes of mortars specimens according to exposure time are presented in Fig. 1. As shown in this figure, there was a continuous weight increase for all mortars with exposure age with different extents until 90 days except mortars C2 and C3 showed a weight gain at earlier ages, up to 120 days, then at later age there was a decrease in weight for all mortars.

After 90 and 120 days of immersion, the replacement of part of Portland cement by the mineral admixtures increased the mortar's ability to resist to acid attack. However, the decrease in weight was less with blended cement specimens. The mortar specimens C3, C2 and C4 show a slight weight loss whereas mortars C0 and C1 show an important mass loss especially for the mortar specimen C0 where after 90 days of immersion, the decrease in weight is well marked.

At 180 days immersion, the highest weight increase was found in mixtures containing natural pozzolana C3, with 1.7% weight gain. The specimens of mortars C2 and C4 had 1.2% and 1.0% weight gain respectively, while the mortar C1 has 0.8% weight gain. In contrast, the reference mortar C0 had the smallest weight gain of 0.4%.

It was interesting to note that the relatively higher weight gains occurred with the mortar C3 then C2, all of which had a high proportion of slag and pozzolana in the cement. These results confirm the increasing resistance to acid attack by other pozzolanic materials such as silica fume, metakaolin and fly ash obtained by other

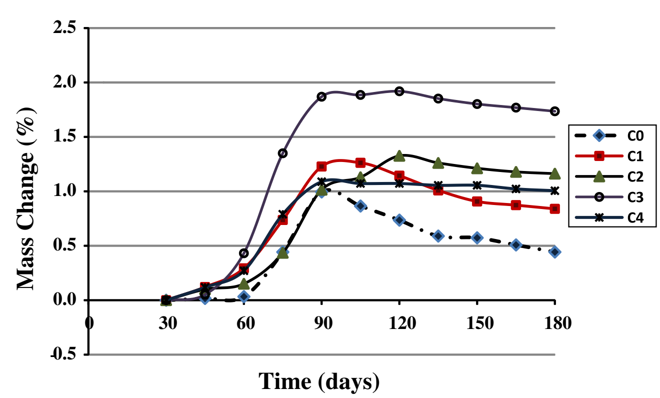

Fig. 1. Weight changes of mortar samples after immersion in sulfuric acid solution.