Durability of Concretes with Marble Powder

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Abstract. The aim of this study is to examine the valorisation of mineral residues as addition in building materials with cementious matrix, and contributes to sustainable development. The study is based on experimental work carried out at the Civil Engineering and Mechanical Engineering Laboratory (INSA-Rennes, France) and at the Mineral and Composite Materials Laboratory (University of Boumerdes, Algeria). The use of recyclable industrial waste as a partial replacement of Portland cement in concrete allows reduction of greenhouse gas emissions (GGE) and results in the manufacturing of a concrete with less environmental impact. Applying various experimental techniques, the behaviour of finely crushed marble powder addition with Portland cement, with limestone addition, is studied. This study confirmed the improvement of the physical and chemical properties of concretes with marble powder addition; this indicates the potential advantage of using this supplementary cementitious materials.

Keywords: HPC, marble, durability, sulfate

1. Introduction

The management of waste and industrial by-products is crucial for the technical, economic and environmental benefit of society as a whole and business in particular. These factors should include, for example, the life cycle analysis of products or services, thus integrating into these processes the management of residues and by-products. Engineering and environmental studies can facilitate this management, particularly in civil engineering [1-2]. Moreover, the building materials sector is responsible for 9.5 % of the total anthropogenic emissions of carbon dioxide in Europe. About 80% of this amount comes from cement production, then it seems that reducing the amount of cement in concretes and mortars has become a priority [3]. One way for cement and concrete industries to do so is the substitution of clinker with mineral additions. In recent years, many studies have focused on the ordinary Portland cement supplementation by industrial by-products [4].

The use of industrial waste and reducing the demand for natural resources (such as limestone and iron ore) are beneficial. It is also important to note that the concrete with supplementary cementitious materials (SCMs) generally have a lifespan longer than conventional concrete [5].

The most aggressive environments for concrete are saline and sulfate environments, these represent a major hazard by virtue of chemical attack on the concrete. A survey by the OECD (Organization for Economic Cooperation and Development) conducted in 1989 indicates that the sulfate attack is the second leading global cause of damage; this type of attack being detected on 800 000 structures.

Given the denser structure of high-performance concretes (HPC), these materials exhibit a better behaviour towards aggression mechanisms. Most degradation processes are caused by the penetration of aggressive substances, such as chlorides, carbon dioxide, acids and sulfates. If this penetration is impeded, as in the case of HPC, the degradation processes will not manifest itself until much later in the service life.

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By using various experimental techniques, special care is given to the behaviour of the finely ground marble powder together with Portland cement containing limestone addition. The use of Marble powder as a SCM has already been studied in the recent literature, especially for SCC mix design [6-7-8]. However, none of this study focuses on the durability behaviour containing marble powder. Depending on the nature of SCMs considered, their different behaviour may influence the design of the concrete mixes with an impact on their durability. This study confirmed the improvement of physico-chemical properties of concrete with marble powder, which presents a strong argument for its use as a concrete addition.

2. Materials Used

2.1. Cement

The Portland cement has a Blaine Specific Surface (BSS) of 3830 cm$^2$/g. It is a CEM II / A 42.5 clinker with addition of 10% limestone. The cement is marketed by Egyptian Orascom Group (Algerian Cement Company). The X-ray diffraction analysis of the anhydrous cement is shown on Fig. 1.

The XRD pattern shows the presence of different crystalline phases: the four essential minerals ($C_3S$, $\beta C_2S$, $C_3A$ and $C_4AF$) which are responsible for setting and hardening; gypsum, ($CaSO_4$,$2H_2O$) regulate setting time; and limestone filler addition.

![Fig. 1: XRD pattern of CEM II / A 42,5 ($\lambda$kα Cu).](image)

2.2. Marble powder (PM)

The marble powder used is a waste product from marble masonry. The micro analysis performed over a wide range of points shows identical chemical compositions (Fig. 2).

![Fig. 2: Micro analyse EDS of the marble powder.](image)

The Particle Size Distribution (PSD) was measured in ethanol using a laser granulometer CILAS 1180; the results are shown in Fig. 3. The marble powder has a Blaine specific surface of 12 000 cm$^2$/ g. The key point that emerges from the results, summarized by granulometric fineness, is that the powder is well graded. 50% of the marble powder particles are finer than 4 microns and 77% are finer than 10 microns.
Approximately 95% of particles are finer 20 microns. Based on the coefficient of uniformity (Cu), the powdered marble has a tight distribution.

Fig. 3: Granulometric curve for marble powder.

### 2.3. Aggregates

An optimized concrete mix design necessarily involves the determination of optimum mass ratios of various aggregates. The coarse aggregate are crushed gravel from the Jaubert quarry (Algeria), and is mainly limestone.

In this study, after preliminary tests on both the rheology of concrete mixtures at fresh state and the mechanical behaviour at hardened state, the granular classes 3/8 and 8/15 were chosen.

The sand consists of a mix containing 76% of Akbou Sand and 24% of Boussaâda Sand (Algeria), the final fineness modulus after homogenization is 2.60.

### 2.4. Admixtures

In order to ensure required workability, the incorporation of a water-reducing superplasticizer is necessary. The molecules of superplasticizer are adsorbed on the cement grains surface at the interface with the mix water. Once adsorbed, the superplasticizer molecules induce a steric effect that increases the distance between cement particles. As a consequence, the cement grains network is weakened [9-10]. The resulting dispersion reduces the viscosity and the yield stress of the cement paste and increases workability; the molecular structure of the polymeric superplasticizer - in the form of long chains - reinforces this effect.

The admixture used is Viscocrete 3045, an unchlorinated water reducer plasticizer, based on modified polycarboxylates, it provides a good workability for up to 1h 30.

In fluid concrete, Viscocrete 3045 improves stability of the concrete, reduces the risk of aggregates segregation and makes the mix less sensitive to small variation in water and constituents mass ratio.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Composition</th>
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<tr>
<td>Cement</td>
<td>kg/m³</td>
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<tr>
<td>Sand</td>
<td>kg/m³</td>
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<tr>
<td>Aggregate (3/8)</td>
<td>kg/m³</td>
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<tr>
<td>Aggregate (8/15)</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Water</td>
<td>l/m³</td>
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<tr>
<td>Admixture</td>
<td>l/m³</td>
</tr>
<tr>
<td>Marble (MP)</td>
<td>kg/m³</td>
</tr>
<tr>
<td><strong>CC</strong></td>
<td>400 360</td>
</tr>
<tr>
<td><strong>CMP</strong></td>
<td>612 612</td>
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<td></td>
<td>108 108</td>
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<td>1064 1064</td>
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### 3. Experimental Program
The compositions of concretes with and without powdered marble are used in the experimental program as reported in Table 1. It should be noted that the levels of marble powder addition (MP) and superplasticizer, after optimization, are respectively 10% and 2% of the cement mass. For reported tests the following legend is adopted.

3.1. Types of concrete
- CC: Control Concrete
- CMP: Concrete with Marble Powder

The physical, mechanical and microstructure of concrete with and without addition of marble powder are compared. In addition, mineralogical characterization techniques have been carried out which include X-ray diffraction (XRD), differential thermal analysis and gravimetric analysis (DTA-TGA) and scanning electron microscopy (SEM) combined with a micro analysis (EDS).

4. Results and Analysis

The aim of this study is to examine the durability of concrete exposed to sulfates; the resistance of concrete to sulfate attack being an important factor for durability.

The origin of sulfate contamination of concrete is diverse; internal sources namely the material itself (aggregates containing gypsum or sulphides; gypsum cement used as a retarder ...); external sources of sulfates from exposure to the ambient environment (sewage, industrial pollution, groundwater and seawater ...). In these cases the sulfate migrated into the cement matrix by diffusion thus attacking the integrity of the concrete. The sulfate can alter the concrete in two physico-chemical ways, expansion and / or loss of binding properties of the CSH.

4.1. Strength

It is noted that the compressive strength of concrete with marble powder addition, with a very tight particle size distribution (Fig. 4) as used in this study, has a higher strength than the control one for all stages of maturity. It is concluded that these are high-performance concretes; this property is not altered by the surrounding environment (Fig. 5). This can be attributed to the fact that the specific surface of marble powder is higher than the one of cement. Then, marble powder adsorbs more water than cement. As a result, the ratio of water available for hydration is reduced leading to better mechanical strengths.

![Fig. 4: Evolution of compressive strength with relation to age](image)

4.2. Capillary absorption

Capillary absorption of the samples is determined; the results obtained confirm the low capacity of water absorption for concrete with marble powder addition compared to the control concrete; this is an indication of an increased compactness of the concrete. This can be attributed to the fineness of the marble powder that reduces the pore size distribution compared to control concrete. In addition to their high strength the samples have improved durability. The marble powder addition will retard the penetration of aggressive agents, including the sulfate ions within the concrete matrix.
4.3. Measurement of oxygen permeability

This method is applicable to moulded samples and cores that are within the dimensional tolerance limits imposed by the apparatus. The technique can measure permeability ranging between 10-15 and 10-20 m² [11].

The test consists of submitting a cylindrical sample to a constant pressure gradient of oxygen. The permeability thus is determined from the measurement the oxygen flux at a steady flow. This test is performed on five specimens at three pressures (2, 4 and 6 bar absolute). An average permeability value is computed. The three samples, from the group of five, that exhibit the permeabilities closest to the average are considered as the most representative of the material [12].

Regardless of pressure, the addition of finely crushed marble powder led to a significant decrease in the coefficient of permeability to oxygen. For example, at a pressure of 6 bar, Ka is 2.3 \(10^{-16}\) m² for concrete control, and 1.3 \(10^{-17}\) m² for concrete with marble powder addition (Fig. 6). Those results are consistent with the capillary absorption coefficient.

4.4. Internal Microstructure

The physico-chemical analysis, by XRD shows that the hydration process corresponding to different cement paste phases leads to a more or less well crystallized structure. The components identified after three months conservation in calcium sulfate solution are shown in Fig.s 7 and 8.

For all compositions studied hydration leads to the formation of portlandite CH, calcite CC and a silica-hydrate CSH gel. The three major diffraction peaks of CSH are not clearly identified, reflecting its low degree of crystallization. XRD analysis indicates that ettringite \(C_3A.3CaSO_4.31H_2O\) is present in the hardened paste after a period of three months.
The results indicate that the sulfate attack, initiated by gypsum, induces a weak precipitation of ettringite; the most stable environment for this compound being a pH greater than 10.5. In the sample without marble addition, it appears that the sulfate attack is more pronounced. This reaction occurs in an environment where ettringite is more stable.

Finally, one can note the significant and growing presence of calcite resulting from the carbonation of hydrated phases, mainly portlandite, in the samples; also from mineral limestone and marble powder. The differential thermal analysis is used to verify the XRD observations.

4.5. Thermo-gravimetric Analysis

The thermo-gravimetric analysis (Fig.s 9a and 9b) show essentially three mass losses which respectively characterize the loss of water molecules of $C_xS_yAtH_z$ and $C_6AS_3H_{32}$ without differentiating the portlandite dehydration and the de-carbonation of $CaCO_3$ (initial and newly formed $CaCO_3$). However, this method does not detect the presence of monocarboaluminate $C_4ACH_{11}$ or hydrated alumina.

The endothermic effect at temperature of 450-550 °C, expresses the presence of remaining free hydrated lime crystals [13-14].

The thermo-gravimetric analysis shows the initial loss of free water; for the CEM II paste at a higher temperature (146 °C) than from that CEM II with marble powder addition (127 °C). Conversely, the amount of water released is somewhat higher (24.23%) as opposed to 19.10% for the CEMII plus marble addition; this is a consequence of the fineness of the marble powder, whose demand for water is higher and in parallel evaporation temperature is lower.
The formation of portlandite in the cement paste with marble addition is lower, due to the partial replacement of cement with marble powder. Dehydration for the former being 4.28% compared with 3.28% for latter.

Finally, in the temperature range 740-840 °C progressive de-carbonation of carbonates occurs. In this case, the endothermic peak for the cement paste with addition is more pronounced; marble powder addition causes a mass loss of 5.03% as opposed to 2.32% for cement paste without addition.

These results confirm the beneficial effect of finely crushed powder marble filler. The properties of concrete and cement pastes, in terms of compressive strength, capillary absorption and gas permeability are improved. The impact of marble powder on microstructures, in terms of densification of matrix and modification of porosity is very pronounced.

5. Conclusions

The partial replacement of cement by marble powder does not contribute to the formation of a significant volume of hydrated products capable of reducing porosity, however the compressive strength may be improved to a greater or lesser extent.

The marble powder can efficiently supplement cement in concrete; this structural contribution manifests itself by the reduction of porosity and consequently a greater resistance to chemical attack.

The concrete with the addition of marble powder with a specific surface of 12,000 cm$^2$/g offers interesting advantages over the conventional control concrete: higher strength, improved durability against physico-chemical absorption; the absorption of capillary water is reduced as is the permeability. This should lead to improved freeze-thaw resistance, although this remains to be verified.

In addition to its obvious ecological impact, re-use of waste marble dust and its integration in concrete has great advantages in terms of long-term maintenance resulting from the improved durability of structures.

6. References


