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Durability of high-strength concrete in ammonium sulfate solution

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Abstract

This paper considers the ammonium sulfate attack of high-strength concrete (grade 100). An accelerated attack consisting in wetting–drying cycles was adopted throughout this study. Compressive strength, mass loss, and length variations were measured before and after sulfate attack. The microstructure was investigated by scanning electron microscopy (SEM). No swelling was observed after six cycles of degradation and the chemical attack was limited to a superficial zone of 5 mm thick. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pore size distribution; SEM; Compressive strength; Degradation; Sulfate attack

1. Introduction

Calcium, sodium, magnesium, and ammonium sulfates are, in increasing order of hazard, harmful to concrete [1] as they can cause expansion, loss of strength, and eventually transform the material into a mushy mass. Calcium sulfate reacts on calcium aluminate hydrates, thus forming expansive ettringite. Sodium sulfate reacts on calcium hydroxide and forms expansive gypsum, which, in the presence of aluminates, may produce ettringite. Magnesium sulfate reacts on all cement compounds, including C-S-H, forming brucite and gypsum, which, at a later age, can give ettringite [2]. The concrete deterioration by ammonium sulfate covers the most aggressive corrosion on concrete: only expansive gypsum is formed and no protective layer like brucite is created. There occurs not only expansion due to the formation of gypsum and ettringite [3], but also intensive dissolution of cement hydrates.

There are little data available concerning ammonium sulfate attack; however, some of it indicates that this salt is very harmful to concrete [4–7]. The role of admixtures such as silica fume, fly ash, or blast furnace slag on the improvement in the ammonium sulfate resistance of concrete has not yet been clearly established; some researches report a negative effect [1–4], while others claim their effectiveness [5]. In a previous study, Péra et al. [7] have shown that silica fume was more efficient than metakaolin with regard to the resistance of concrete to ammonium sulfate, at a level of 10% Portland cement replacement. Nevertheless, some swelling occurred and the mass loss was important (10–15%).

Therefore, in order to obtain a satisfactory solution, the behavior of high-strength concrete exposed to ammonium sulfate solution was investigated.

2. Experimental

2.1. Materials

A high-strength concrete presenting a 28-day strength of 100 MPa was investigated in this study. The binder content was fixed at 515 kg/m^3, which is a value in the range of those presented in the literature [8]. The binder was a mixture of 75% ordinary Portland cement (OPC) type CPA CEM I 52.5 R and 25% blended cement type CHF CEM III A 52.5, containing 37% OPC and 63% ground granulated blast-furnace slag. Such mixture presented a lower heat of hydration than plain Portland cement. The temperature rise measured by the Langavant's calorimeter method according to the French standard NFP 15-436 reached 47°C instead of 55°C for plain Portland cement.

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Table 1
Physical and chemical properties of cements and ultrafine particles

Properties	OPC CEM I 52.5 R	Slag cement CEM III A 52.5	Metakaolin	Silica fume	Ground slag
Oxides (mass%)					
SiO_2	20.4	28.8		96.8	39.3
Al_2O_3	5.1	8.3	39.3	0.1	22.6
Fe_2O_3	3.6	1.9	1.5	0.1	0.7
MnO	–	–	–	–	10.9
MgO	1.6	5.8	–	0.2	8.7
CaO	65.4	50.5	–	0.3	17.6
Na_2O	–	–	–	–	0.3
K_2O	–	–	1.3	0.5	1.2
TiO_2	–	–	1.5	–	0.1
P_2O_5	–	–	–	0.1	0.2
SO_3	3.6	4.4	–	–	2.0
LOI (%)	1.0	1.3	2.0	2.0	2.1
Specific gravity (g/cm^3)	3.16	2.97	2.5	2.1	2.9
Fineness					
Blaine (cm^2/g)	3900	5000	–	–	–
BET (m^2/g)	–	–	19.0	16.2	1.3

Table 2
Mixture proportions of high-strength concrete

Constituents (kg/m^3)	Control (C)	Silica fume (SF)	Metakaolin (MK)	Ground granulated slag (GGS)
OPC CEM I 52.5 R	387	387	387	387
Slag cement CEM III A	129	129	129	129
Ultrafine particles	–	51.5	51.5	51.5
Sand 0/4 mm	681	656	660	662
Gravel 6/10 mm	1049	1010	1016	1021
Water (W)	129	129	129	129
Superplasticizer	29.4	29.4	29.4	29.4
W/CM[a]	0.28	0.26	0.26	0.26
Unit weight (kg/m^3)	2420	2410	2420	2430
Slump flow (mm)	650	610	610	690
28-day strength (MPa)	99.3 ± 7.0	108.4 ± 6.4	117.2 ± 7.8	111.9 ± 4.8

[a] CM = OPC + slag cement + ultrafine particle.

In order to densify the matrix, three types of ultrafine particles were introduced in the different types of mixtures: metakaolin, silica fume, and ground granulated slag from the ferroalloy industry. The mineral admixtures were added at a content of 51.5 kg/m^3, which is 10% of the cementitious material content. The physical and chemical properties of cements and ultrafine particles are given in Table 1.

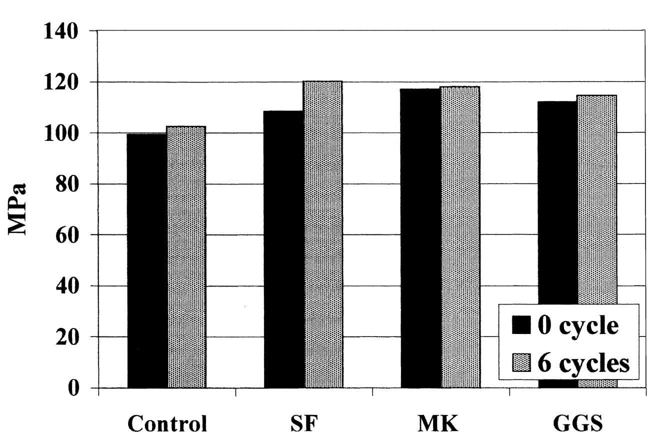

Fig. 1. Compressive strength of concrete after six cycles of degradation.

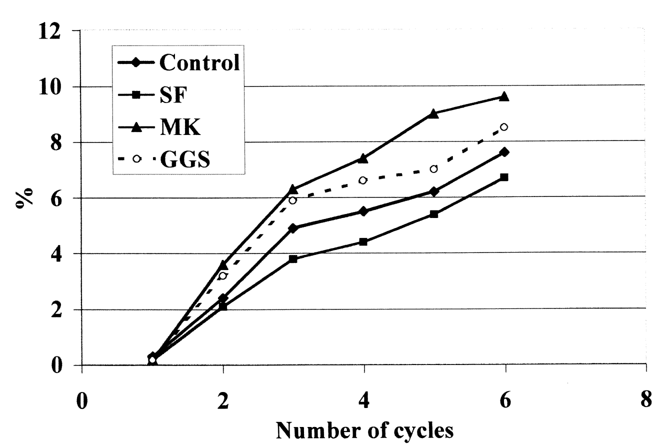

Fig. 2. Mass loss after six cycles of degradation.

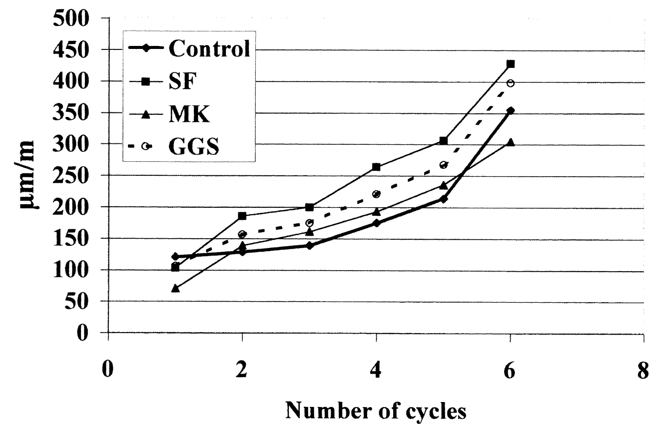

Fig. 3. Length variations (shrinkage).

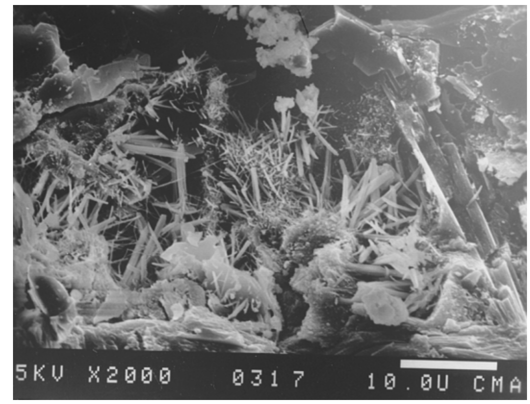

Fig. 5. Control concrete (C) after six cycles in lime-saturated water.

The properties of the Si–Mn slag containing 10.9% MnO have been described in previous papers [9,10]. The results obtained show that such slag ground to a Blaine fineness of 500–600 m^2/kg can be used as additional ultrafine material in concrete, instead of silica fume.

A calcareous, crushed quarry sand 0/4 mm with an absorption of 2.4% was used. The gravel (6/10 mm) was crushed limestone with an absorption of 1.0%. Different combinations of gravel and sand were tested to determine the optimum packing of the granular skeleton. A gravel-to-sand ratio (G/S) of 1.5 was adopted in this study.

A solution of polycarboxylate (Glenium 51 from MBT) was used as superplasticizer. The solids content was 34 mass%.

The different mixture proportions are shown in Table 2. A control concrete without ultrafine particle was also prepared. The amount of mixing water was kept constant at 129 l/m^3 and that of superplasticizer at 29.4 l/m^3, which means 10 kg/m^3 of active matter (1.94% of the cement content). The fluidity of fresh concrete was measured by means of the static spread of a truncated cone having the following dimensions:

$$\emptyset_{sup} = 170 \text{ mm}; \ \emptyset_{inf} = 225 \text{ mm}; \ h = 120 \text{ mm}.$$

All the mixtures presented a flow higher than 600 mm, which is the value generally recorded for self-compacting concrete [11,12]. The lower fluidity was obtained with silica fume and metakaolin.

2.2. Testing

The 28-day compressive strength of the different mixtures was measured on cylinders ($\emptyset = 70$ mm; $h = 140$ mm) cured in lime-saturated water. The different values obtained are reported in Table 2.

Concrete prisms ($70 \times 70 \times 280$ mm^3) were prepared, kept in molds for 24 h, then stored in lime-saturated water at 20 ± 2°C for 27 days. At 28 days of age, those specimens were immersed in a 20% ammonium sulfate solution. The ratio between the volume of the samples and the surrounding solution was 0.08. The different specimens were subjected to six cycles of degradation, each one consisting of 4 weeks of immersion in the aggressive solution followed by 1 week of drying at 20°C.

After each cycle, the compressive strength, mass loss, and length changes were measured. The microstructure was investigated by means of scanning electron micro-

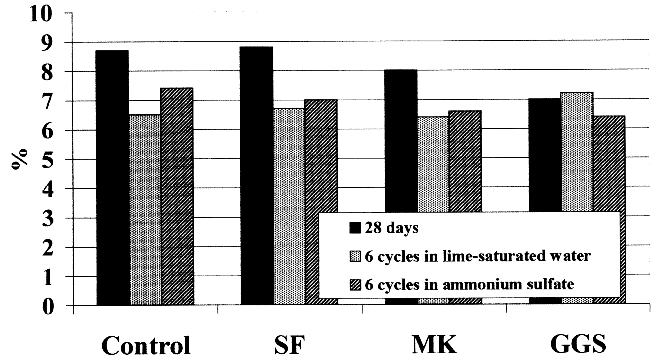

Fig. 4. Total porosity of the different concretes.

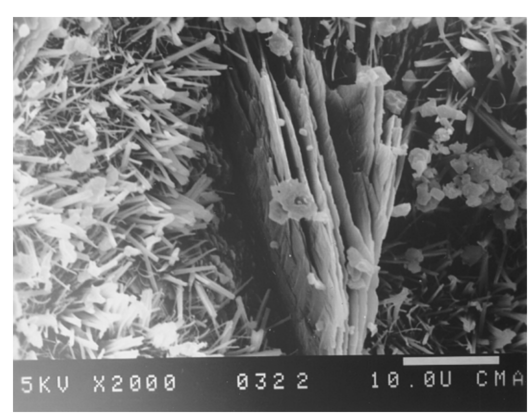

Fig. 6. Silica fume (SF) concrete after six cycles in lime-saturated water.

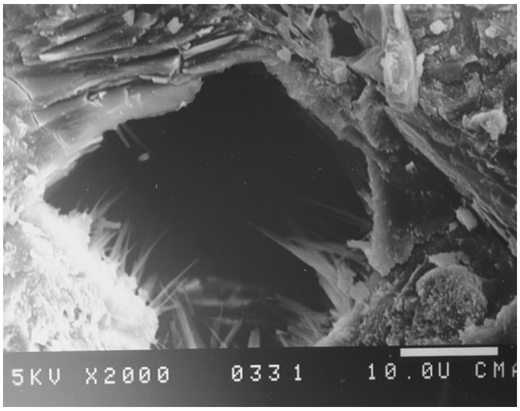

Fig. 7. Metakaolin (MK) after six cycles in lime-saturated water.

scopy (SEM, JEOL 35 CF) associated with energy dispersive X-ray analysis (TRACOR system).

3. Results and discussion

3.1. Compressive strength

The results obtained after six cycles are presented in Fig. 1. They show that no degradation was observed regardless of the composition of the concrete.

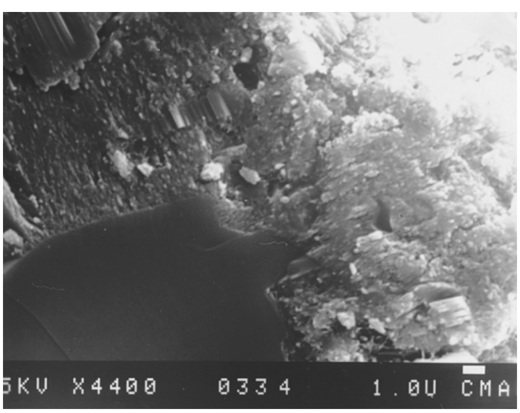

Fig. 8. Slag concrete (GGS) after six cycles in lime-saturated water.

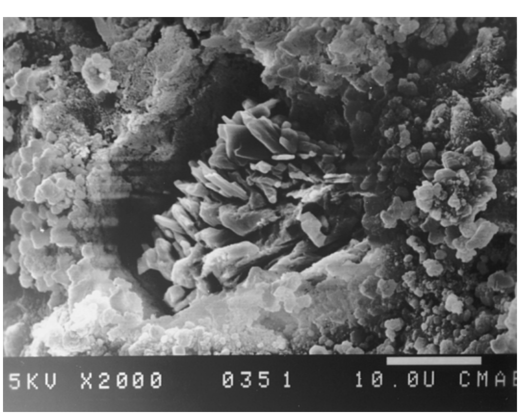

Fig. 9. Superficial zone of C concrete after six cycles in ammonium sulfate.

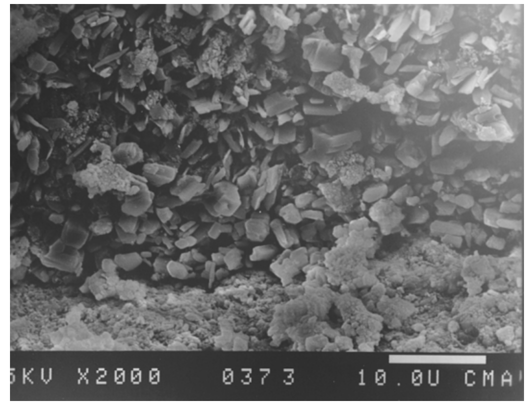

Fig. 10. Superficial zone of SF concrete after six cycles in ammonium sulfate.

3.2. Mass loss

After six cycles, the mass loss was in the range of 6–10%, depending on the nature of the fine particles used (Fig. 2). Silica fume led to the lowest mass loss, while metakaolin generated higher values.

Previous results reported in Ref. [7], show that the mass loss recorded for a grade 45 concrete was about 17%

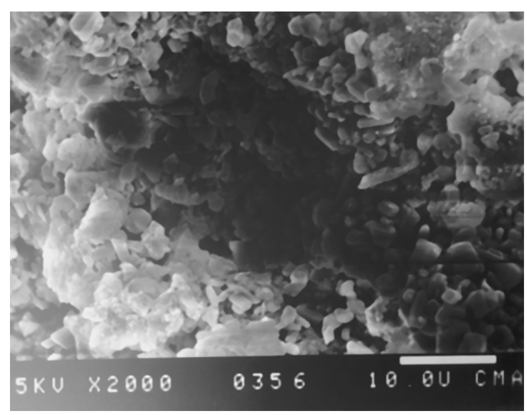

Fig. 11. Superficial zone of MK concrete after six cycles in ammonium sulfate.

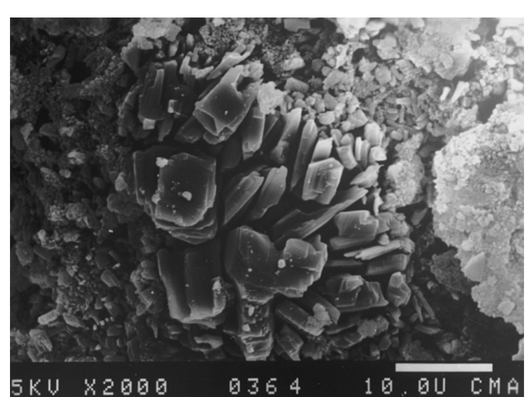

Fig. 12. Superficial zone of GGS concrete after six cycles in ammonium sulfate.

3.3. Length variations

As shown in Fig. 3, no swelling occurred after six cycles of degradation. Only shrinkage was recorded and its value was limited (300–450 μm/m). In grade 45 concrete, a swelling of 20,000 μm/m was recorded [7].

3.4. Porosity

The total porosity assessed by mercury intrusion porosimetry (Micromeritics 930) is shown in Fig. 4. It was directly measured on concrete cylinders ($\emptyset = 23.7$ mm, $h = 40$ mm) cored in specimens subjected to durability tests. The cylinders were dried at 50°C until they reached constant weight, and then subjected to the MIP test.

The results obtained point out a general decrease of porosity after 28 days.

3.5. Microstructure

The SEM examination of samples subjected to six wetting–drying cycles in lime-saturated water (Figs. 5–8) show the presence of C-S-H and calcium hydroxide in the cementitious matrix. In matrices containing pozzolanic admixtures (metakaolin and silica fume), there is a lack of pozzolanic material to ensure a total consumption of calcium hydroxide.

After six cycles in the 20% ammonium sulfate, both the external zone of concrete directly in contact with the aggressive solution and the core were submitted to SEM investigations. In the superficial zone (Figs. 9–12), small crystals of gypsum were detected and certain aggregates were pushed out by the gypsum crystals. This zone presented a thickness of 5 mm.

In this zone, calcium hydroxide still present in the matrix reacts with ammonium sulfate to form gypsum:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4,\ 2H_2O + 2NH_3$$

In the core of concrete, gypsum was not detected.

4. Conclusions

From this limited investigation, the following conclusions can be drawn:

1. High-strength concrete (grade 100) is durable in a 20% ammonium sulfate solution due to its very low porosity and permeability.
2. Sulfate attack remains very superficial and gypsum is not found in the core of specimens.
3. No swelling is observed during the durability cycles.
4. The nature of the fine particle used has a slight influence on the behavior of concrete. Generally, silica fume leads to the best results.

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