Pergamon

Cement and Concrete Research, Vol. 28, No. 1, pp. 19–24, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(97)00193-2

ACID DEPOSITIONS AND CONCRETE ATTACK: MAIN INFLUENCES

R. Sersale,* G. Frigione,[1]† and L. Bonavita†
*Dipartimento di Ingegneria dei Materiali, Università di Napoli, Naples, Italy
†Dipartimento di Ingegneria Chimica e Materiali, Università della Calabria, Rende, Italy

(Received August 6, 1997; in final form September 15, 1997)

ABSTRACT

The results of an experimental research on the factors responsible to a greater extent for the action of simulated acid precipitations on cement concrete works, both in static and in dynamic conditions, are discussed. The influence of the cement type, the role of calcium hydroxide, the influence of water-cement ratio, and the retard effect on assault, owing to a surface treatment with a water repellent agent, are emphasized. *© 1998 Elsevier Science Ltd*

Introduction

The phenomenon of the polluting depositions (acid rains and mists) is known from a long time. Over the past twenty years, however, their effects have become worrying, owing to the increase of the activity in the urban and industrial areas. Such acid precipitations, with a pH level ranging between 3.0 and 5.0, are an aggressive agent for cement concretes. Such a fact was not taken into consideration at the time of the buildings construction, so that they are now exposed to an unexpected type of attack.

A bibliographical research by the Brookhaven National Laboratory (1), showed the existence of a wide documentation on the composition and distribution of acid precipitations, but there is only sporadic information on their effects on concrete works. In this case, the wide bibliography on corrosion phenomena of concrete due to different inorganic and organic agents, waste waters, and gases is missing.

Responsible to a greater extent for the origin of acid depositions are sulphur and nitrogen compounds, both wrapped in clouds (moist depositions) and directly transferred (dry depositions). Industrial emission, combustion, volcanic activity, fill in fact the atmosphere with sulphur dioxide, which later changes into sulphuric acid.

Similarly, nitrogen oxides (NO_x) undergo some changes that originate nitric acid.

Sulphuric and nitric acids are therefore to be considered the main aggressive agents of acid precipitations in the molar ratio H_2SO_4:HNO_3 = 2:1 (2).

Concrete attack begins with the reaction of acid compounds with calcium hydroxide, present in the works owing to the course of cement hydration process. From the limited bibliography on the effect on concretes of acid depositions, one can infer that decay increases

Communicated by F.W. Locher.

[1]To whom correspondence should be addressed.

TABLE 1
Composition of the cements (weight percent).

	Portland Clinker	Type I Portland Cement	Type III/B Slag Cement	Type IV/B Pozzolanic Cement
C_3S	56			
C_2S	18			
C_3A	12			
C_4AF	9			
Portland Clinker		94	26	55
True Pozzolana				40
Blastfurnace Slag			70	
Gypsum		6	4	5

with the lowering of the pH of the solution simulating acid precipitation and is more deep in those works showing higher strength, owing to a higher cement content (3).

We have therefore considered interesting to start a preliminary experimental investigation, with the purpose of selecting now the main factors responsible for the decay and suggesting later suitable prevention and restoration procedures.

Materials and Procedures

Binders

Portland cement (CEN Type I), slag cement (CEN Type III/B), and pozzolanic cement (CEN Type IV/B) (4) were used. The cements were manufactured with the same Portland clinker and of the same class (32.5 MPa) (4). Portland clinker composition and addition amounts are reported in Table 1.

Aggregates

Crushed basaltic stone has been employed as coarse aggregate, 25 mm maximum diameter, and as sand that of dunes, after suitable washing. Size distributions have been modelled upon a Fuller curve.

Concrete

Cement content has been 300 kg/m^3. Three water-cement ratios were used, 0.55, 0.71, and 0.77 by weight, respectively.

Concrete Specimens

Cylindrical concrete, (15 cm diameter $\times$ 30 cm height) were cast. They were moist cured for 14 days before placing on the external exposure for 9 years (75 $\pm$ 20% R.H. and 15 $\pm$ 15°C.

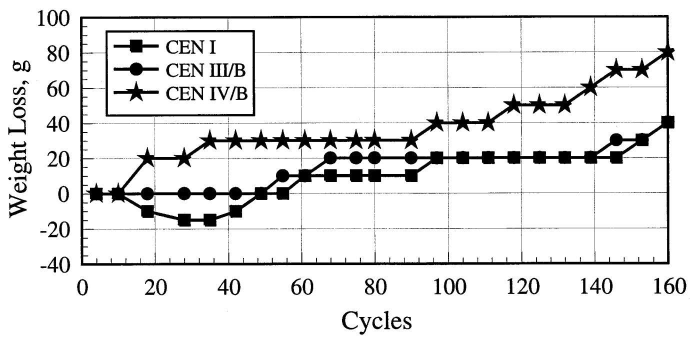

FIG. 1.
Concretes manufactured with different types of cement (w/c = 0.71).

The reported results are the average of three specimens. A series of specimens was submitted to a surface saturation treatment with a commercial water repellent, suitable for reacting with the moisture inside the concrete, in order to originate a coating of hydrophobic molecules both on the pore surface and in the depth.

Solution

A water solution of sulphuric and nitric acid, molar ratio 2:1, has been used as acid rain, diluted until a pH 3.5 was reached, measured and adjusted with a glass electrode instrument, with a calomel electrode as reference. pH has been kept constant as much as possible in order to counteract its increase due to lime leaching from cementitious matrix.

The effects of the rain simulation have been investigated both in static and dynamic conditions. In the first case, specimens have been exposed to a stagnant solution, measuring at recurrent expirations weight losses. Solutions-specimen volume ratio was 5:1. Rain and serene days alternations have been simulated by plunging specimens in the solution for 24 hours, successively extracting and drying them, at room temperature, for 24 hours before the new immersion according to programmed cycles.

On the second case, the same solution has been sprayed as small drops, by means of a proper ejector, on specimen surface, combining in this way corrosion effects of the solution with the impact of drops action. We sprayed 50 mL/h of acid solution at 0.2 atm pressure. Rain and serene alternations were simulated, too, with cycles of 120 h spraying the acid solution and 48 h drying up.

Results

In Figure 1, the results of the acid resistance, in static conditions and at the same water-cement ratio (0.71), of concrete specimens manufactured with three different types of cement are shown. The abscissa indicates the number of immersion-drying cycles; ordinate, weight loss of specimens. It can be seen that all the specimens suffer the attack. Those manufactured with pozzolanic cement show a higher attack than those with slag cement. Specimens prepared with Portland cement reveal a behaviour similar to the latter.

Figure 2 shows the influence of the water-cement ratio for specimens manufactured with

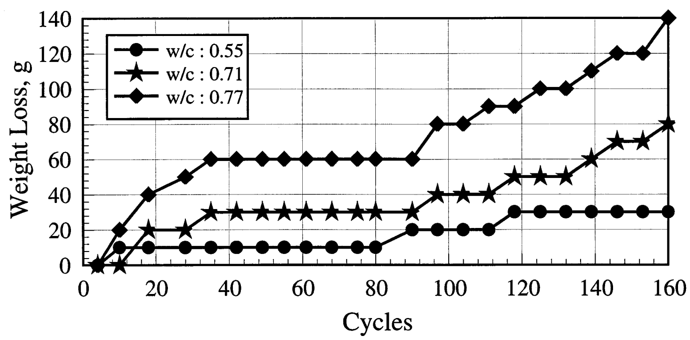

FIG. 2.
Concretes manufactured with pozzolanic cement at different w/c.

pozzolanic cement. It can be seen that when the ratio increases, also attack increases, probably owing to its influence on porosity of the concrete.

Figure 3 makes reference to specimens manufactured with slag cement. The significant influence of the water-cement ratio on the attack, showed for pozzolanic cement specimens, is confirmed. The slight weight increase of the specimens at a lower water-cement ratio might be attributable to the lesser permeability and therefore to the higher ability to bear the attack.

Figure 4shows the influence of the impregnation with a water-repellent agent on specimens manufactured with pozzolanic cement, at the same water-cement ratio, with the term of reference being untreated specimens. It can be seen that impregnation leads to an initial weight increase, attributable to a more difficult penetration of the solution, on account of the presence of a water-repellent coating. When this protection begins to weaken, decay proceeds. Water-proofing treatment allows therefore only a slowing-down but not a removal of the acid attack.

In Figure 5 the histogram of the intensity of the attack is reported, made both on the basis of a visual observation and on the residue collected after immersion of specimens in the acid bath. It is confirmed that pozzolanic cement shows the worse behaviour, whereas that of Portland and slag cements is more or less similar. The significant influence of the water-cement ratio is confirmed, too. In fact, its increase enhances the attack. The delay effect, attributable to impregnation treatment, is stressed, too.

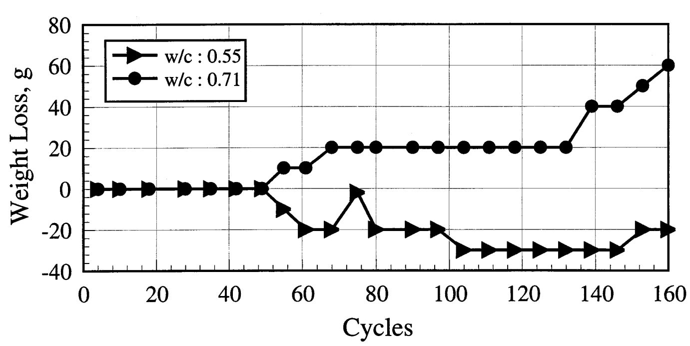

FIG. 3.
Concretes manufactured with slag cement at different w/c.

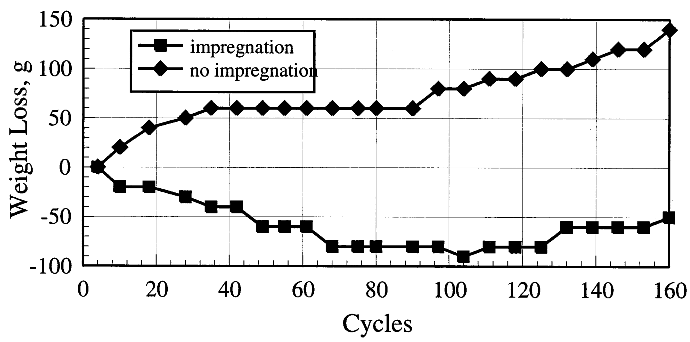

FIG. 4.
Effect of impregnation with a water-repellent agent. Concretes manufactured with pozzolanic cement (w/c = 0.77).

Conclusion

The whole of the experimental results indicates the following:

1) In our experimental conditions, the immersion of concrete specimens in a sulphuric and nitric bath, in the molar ratio 2:1 and with a pH level of 3.5, supplies results agreeing with those in dynamic conditions, namely simulating a driving rain. Static method (stagnant immersion) supplies nevertheless data able for an easier differentiation of the factors responsible for the decay, even though in a higher length of time;

2) Cement type, at a parity of water-cement ratio and strength grade, is an essential factor. A fundamental role for attack progression appears in fact to be attributable to calcium hydroxide in the hardened concrete. It has been pointed out a better behaviour of Portland cement, in comparison to pozzolanic cement, in a middle position being slag cement.

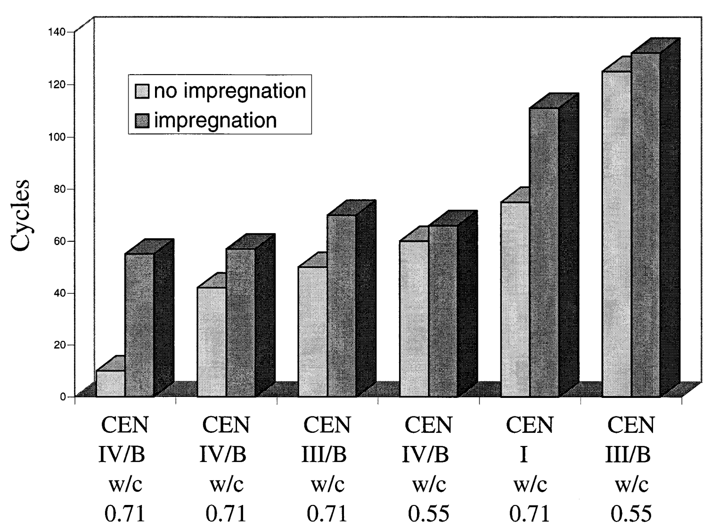

FIG. 5.
Intensity of the attack on the basis of a visual observation.

Calcium hydroxide, being in fact the compound to be readily attacked, could represent therefore a bulwark against assault of the silicate framework, which would be attacked only later. The higher amount of calcium hydroxide in Portland cement could therefore represent a defence against the attack of the hydrated silicates. On the contrary, their attack could start soon in those cements free, in practice, from calcium hydroxide (pozzolanic cement) and later in slag cement, characterized by a higher delay in the diffusion of aggressive ions;

3) Surface treatment with a water repellent agent represents a provisional remedy able to delay concrete attack, owing to the loss of effectiveness due to a progressive consumption.

References

1. G.E. Linken, Acid precipitation: Our understanding of the problem, EPA-902,9–75-001, pp. 45–75. New York, 1975.
2. I. Allegrini, A. Febo, and C. Perrino, Inquinamento, 4 (1992).
3. H.L. Kong and J.G. Orbison, ACI Mater. J. March-April (1987).
4. CEN ENV 197–1. Cem. Compos. Bruxelles (1992).