Study of Pozzolanic Admixtures Effects in the Concretes Under Chemical Attack

Henrique Catuzzo, Giovanna Patricia Gava and Camila Salvi Malacarne

Abstract The alkaline nature of concrete makes it highly vulnerable to acidic attack. The chemical attack occurs due to the decomposition of hydration products, forming soluble products that can be leached, or insoluble products than can expand in their formation site. The use of cements with pozzolan and blast furnace slag in concrete mixtures reduces their permeability, as well as their porosity, besides consuming part of the calcium hydroxide. These characteristics are signs of benefits for the reduction of the effects of corrosion caused by acid in the concretes. In this study, the effect of the presence of pozzolanic materials on the resistance of concrete against acidic attack had been investigated by considering two different acids. The concretes studied were inserted in lactic and formic acid solutions, thus simulating environments commonly found in the dairy, paper and cellulose industries, respectively. The tests were made with concretes with two water/cementitious materials ratios and two different content of replacement of cement by silica fume, 8 and 15 %, apart from pozzolanic cement. Test specimens with 100 mm × 200 mm cylindric dimensions were immersed in acid solutions after the curing process, and then subjected to cycles of wetting and drying. Mass loss and compressive strength tests were carried out between cycles of exposure to the acids. At each water/cementitious materials ratio, the mass loss and compressive strength loss of concrete with silica fume were less than the concrete without pozzolan. The presence of pozzolan decreased the detrimental effect of both acids in concrete. And besides, it was verified that formic acid is more aggressive for all concrete mixtures.

Keywords Chemical Attack · Concrete · Acidic attack · Lactic acid · Formic acid · Sílica fume · Mass loss

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1 Introduction

Concrete is an alkaline material that presents low resistance to the attack of strong acids, such as: lactic, formic and acetic acids, commonly found in industrial environments. In most times, the acids attack calcium hydroxide and some hydration products of the cement matrix, forming compounds that, when soluble, can be leached or causing decomposition of these products and consequent degradation of the mechanical properties of concrete (Goyal et al. 2009).

The resistance of the cement matrix to acid corrosion depends primarily on its pore structure characteristics, the ability of matrix components to neutralize acid and also on the products of acid corrosion (Shi and Stegemann 2000).

The use of pozzolanic materials such as fly ash and silica fume is believed to increase the durability of concrete through pore refinement and the reduction of calcium hydroxide content of the cement paste matrix. However, the beneficial effect of these materials on acidic attack is still under review (Goyal et al. 2009). While some research works point towards improvement through the use of silica fume or fly ash (Kim et al. 2007; Roy et al. 2001) other works report that pozzolanic materials have only little or no effect on the durability of concrete under acid attack (Pavlik 1996; Pavlik and Uncik 1997).

In this study, the effect of the water/cementitious materials ratio and the presence of pozzolanic materials on the resistance of concrete against acidic attack had been investigated by considering two different acids: lactic and formic acids. It was investigated the mass loss and the compressive strength loss of concretes.

2 Experimental Program

The experimental program, including test solution and measurements, to carry out the chemical attack process was based on researches performed by Dal Molin (1996) and Kulakowski (1997), which resistance of concrete under acidic attack were evaluated by mass loss and compressive strength tests.

2.1 Materials

2.1.1 Aggregates

Crushed basalt with a maximum nominal size of 19 mm was used as coarse aggregate, natural river sand with a fineness modulus of 1.95 and a crushed basalt with a fineness modulus of 3.15 were used as fine aggregates. The properties of the aggregates are listed in Table 1.

Table 1 Properties of aggregates

Property	Natural sand	Fine crushed basalt	Coarse aggregate
Maximum characteristic dimension (mm)	2.36	4.75	19.50
Minimum characteristic dimension (mm)	0.15	<0.15	6.30
Fineness modulus	1.98	3.15	6.81
Material finer than 75 μm (n° 200 sieve) (%)	0.30	18.20	0.50
Specific gravity (g/cm^3)	2.65	2.94	2.96
Absorption (%)	1.33	1.10	1.10

2.1.2 Cementitious Materials

Two types of cement were used throughout the investigation, CP IV—Portland Pozzolan Cement and CP V ARI RS—Portland Cement with High Early Strength and Sulfates Resistance, whereas only in the latter silica fume was added. The silica fume used as a pozzolanic addition presented a pozzolanic activity index of 79 %, features of amorphous material. The most important characteristics of all cementitious materials are presented in Table 2. Figure 1 shows the X-ray diffractogram of the silica fume.

2.1.3 Additive

The additive used was Muraplast FK 110, produced by MC-Bauchemie Brasil, which acts as a dispersal agent to the cement particles, preventing its agglomeration and reducing the superficial tension of the mixing water. It has a density of 1.20 g/cm^3.

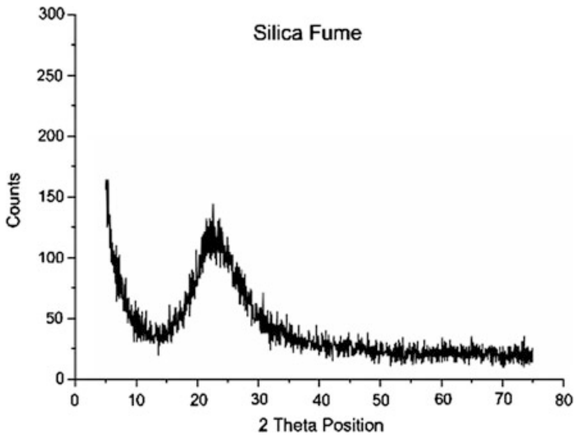
2.1.4 Acids

The acids used were lactic acid, found in dairy industries, and formic acid, present in the paper and cellulose industries, with densities of 1.21 and 1.20 g/cm^3, respectively.

Table 2 Characteristics of cementitious materials used in this study

Cement	Loss on ignition (%)	Insoluble residue (%)	Specific gravity (g/cm^3)	Alkali content Na_2O_{eq} (%)
CP IV	2.90	24.27	2.73	0.65
CP V ARI RS	2.71	8.58	2.94	0.70
Silica fume (SF)	–	–	2.22	0.74

Fig. 1 X-ray diffraction analysis of silica fume



2.2 Preparation of Test Especimens

A total of eight concrete mixtures were prepared through a combination of two different types of cement (CP IV—Portland Pozzolan Cement and CP V ARI RS—Portland Cement with High Early Strength and Sulfates Resistance), two water/cementitious materials ratios (0.45 and 0.55) and silica fume as cement replacement, used in two different content levels (8 and 15 %). The concrete mixtures were attacked separately by two different acid solutions, one with lactic acid and other with formic acid, both with 6 % concentration.

The consumption of materials per cubic meter of fabricated concrete is presented in Table 3.

2.3 Test Methods

100 mm × 200 mm test specimens were cast for all mixtures, for the performance of mass loss and compressive strength tests. The specimens were cured for 21 days, immersed in a water and lime solution. After that period, 12 test specimens were exposed to air curing in the lab environmental for 7 days, and in the end of that period, they were immersed in acid solution. Before the immersion in acid, the specimens were coated with colored paraffin in their upper and lower surfaces to guarantee that the attack would happen only in its side and also help in its identification, then the specimens were weighed and placed in groups of 6 in each type of acid.

The acid attack test consisted of two immersion cycles in lactic or formic acid solution, where the solution presented a pH equal to 1.73. Each cycle of immersion in acid lasted 7 days, in the seventh day the specimens were removed from the acid solution for washing with a polypropylene bristle brush. After the wash, the specimens were kept out of the solution for air drying, in the lab environmental, for 7 days.

Table 3 Consumption of material per cubic meter of fabricated concrete

Concrete (water/cementitious materials ratio)	Cement (kg)	Silica fume (kg)	Natural sand aggregate (kg)	Fine crushed basalt aggregate (kg)	Coarse aggregate (kg)	Water (l)	Additive (l)
CP V (0.45)	438	–	556	258	1064	197.2	0.39
CP V–8 % SF (0.45)	403	25.8	556	258	1064	197.2	1.42
CP V–15 % SF (0.45)	372	48.3	556	258	1064	197.2	1.43
CP V (0.55)	357	–	604	286	1065	196.6	0.00
CP V–8 % SF (0.55)	328	21.0	604	286	1065	196.6	0.31
CP V–15 % SF (0.55)	303	39.4	604	286	1065	196.6	0.67
CP IV (0.45)	433	–	550	255	1052	195.0	0.91
CP IV (0.55)	354	–	598	283	1055	195.0	0.00

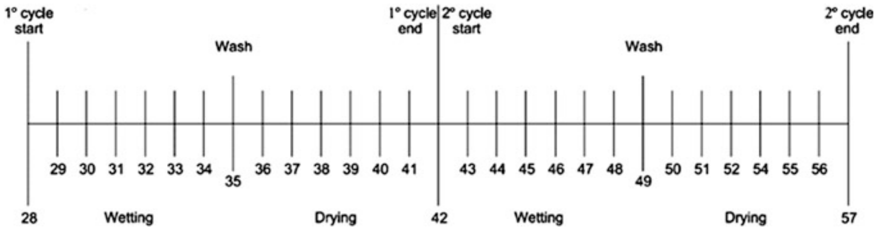


Fig. 2 Exposure cycles with time scales in days

Once the drying period was over, the specimens were weighed to determine the amount of mass loss, and compressive strength tests were carried out in 2 specimens. At the end of this first process, 3 specimens were returned to the recipient containing acid to start the second cycle. Figure 2 exemplifies the process of aggression.

The compressive strength tests were carried out in accordance with recommendations from ABNT NBR 5739 (2007), and the absorption and void ratio tests according to ABNT NBR 9778 (2009) recommendations.

3 Results

The compressive strength test and absorption test results of the concretes at 7 and 28 days, before immersion in acids solution, were presented in Table 4.

Figures 3 and 4 present the percentage of mass loss of the concretes when exposed to 6 % latic acid or formic acid in relation to the voids ratios in the concretes, for the mixtures with water/cementitious materials ratios of 0.45 and 0.55, respectively.

Table 4 Compressive strength and absorption test results

Concrete (water/cementitious materials ratio)	Compressive strength at 7 days (MPa)	Compressive strength at 28 days (MPa)	Absorption (%)	Void ratio (%)
CP V (0.45)	47.0	56.8	5.35	12.85
CP V–8 % SF (0.45)	48.5	69.4	4.57	10.96
CP V–15 % SF (0.45)	42.3	59.3	4.57	10.83
CP V (0.55)	36.2	41.8	6.32	15.16
CP V–8 % SF (0.55)	35.0	53.1	5.64	13.39
CP V–15 % SF (0.55)	33.1	54.9	4.96	11.94
CP IV (0.45)	37.1	48.0	4.05	9.80
CP IV (0.55)	24.1	34.3	4.53	11.01

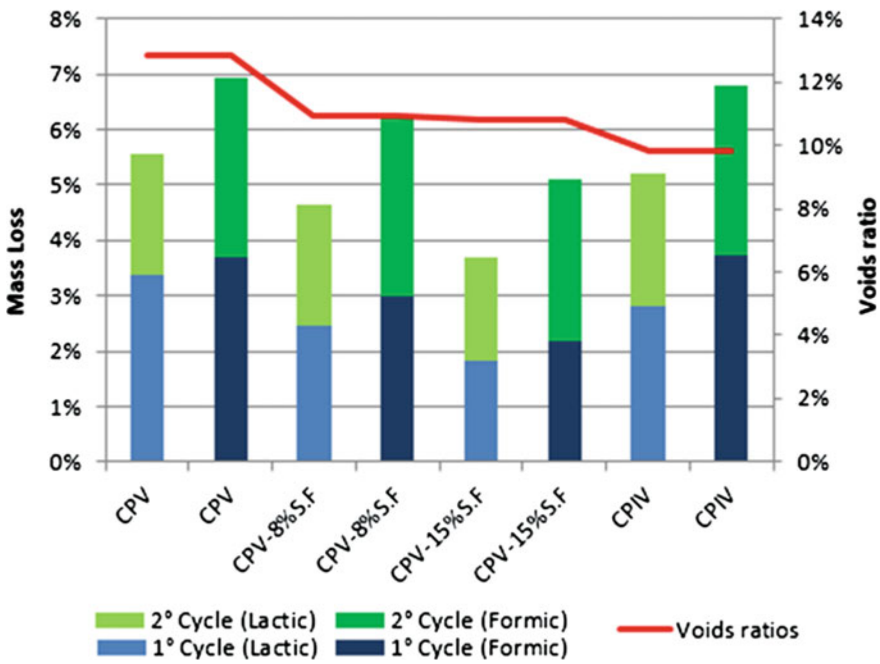


Fig. 3 Mass loss of concretes with water/cementitious materials ratio of 0.45

Figures 5 and 6 present the results of the compressive strength loss of the concretes when exposed to 6 % latic acid or formic acid in relation to the mass loss of concretes with water/cementitious materials ratios of 0.45 and 0.55, respectively.

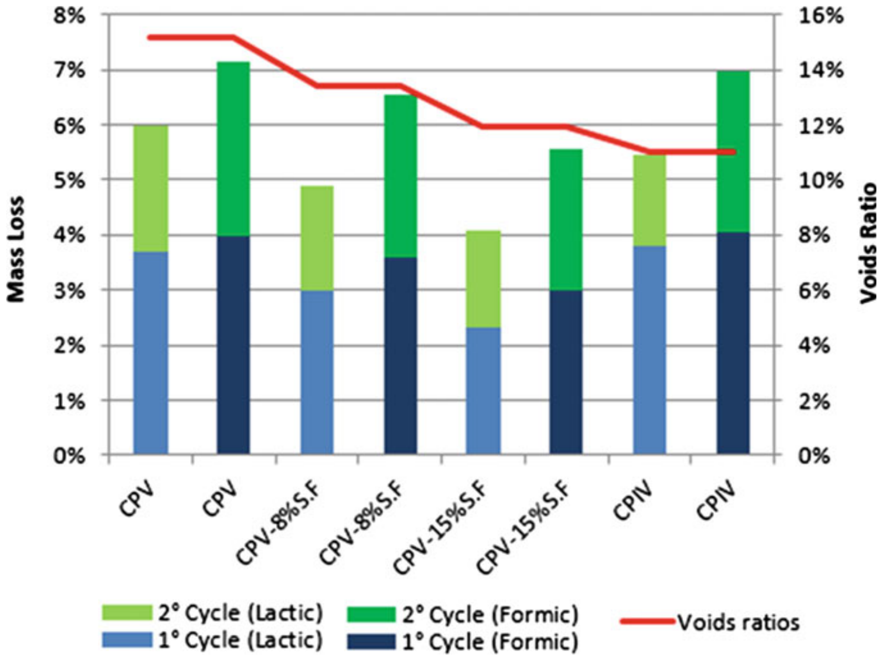


Fig. 4 Mass loss of concretes with water/cementitious materials ratio of 0.55

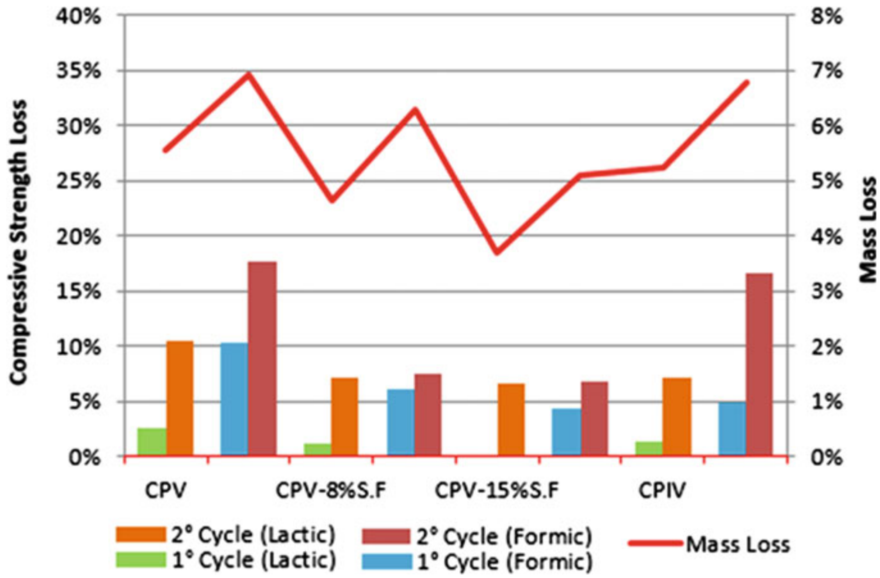


Fig. 5 Compressive strength loss of concretes with water/cementitious materials ratio of 0.45

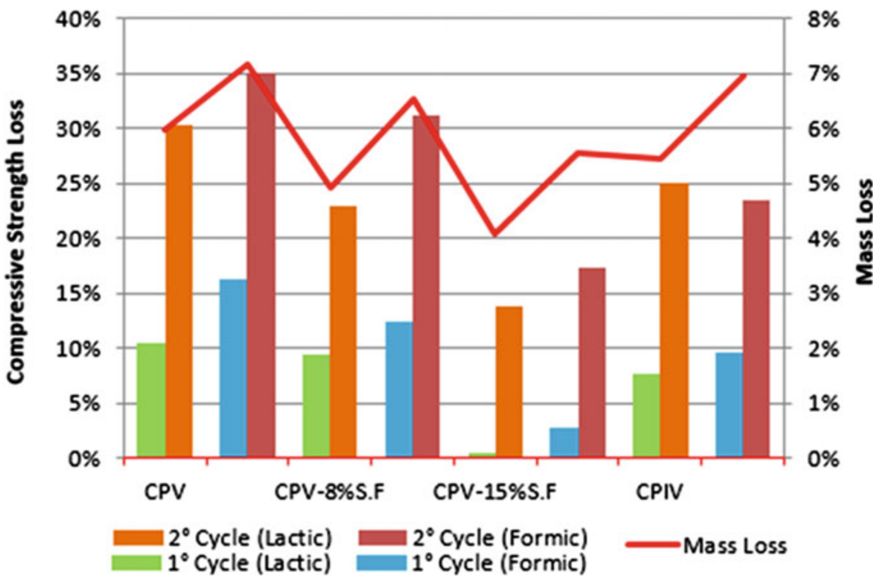


Fig. 6 Compressive strength loss of concretes with water/cementitious materials ratio of 0.55

3.1 Results and Discussion

The additions of silica fume decreased the mass loss of concretes. It was observed that the as the silica fume content increased, the mass loss of concretes decreased, as well as the absorption values and the void ratios decreased. The effect of silica fume in decreased mass loss of concrete can be seen in Fig. 7.

Concretes with Portland Pozzolan Cement (CP IV) presented mass loss values intermediary between concretes with Portland Cement with High Early Strength and Sulfates Resistance (CP V ARI RS) without addition and with replacement of 8 % silica fume, however, with the smallest void ratios found. These results show that the silica fume is more efficient than pozzolan present in Portland Pozzolan Cement, in that case fly ashes, to reduce the detrimental effect of the acids over concrete.

The mass loss caused by the second cycle of aggression was smaller compared to the first cycle. That can be explained by the fact that from the first process of degradation, some aggregates are already exposed, thus decreasing the attack's area of influence (cement paste). It is important to emphasize that acids react directly with the cement paste compounds such as calcium hydroxide.

There was a great contribution of silica fume to improve the acid resistance of concrete. For both acids analyzed, lactic and formic, the concretes with 15 % of cement replaced by silica fume, even after two cycles of exposure to acid, practically did not present compressive strength loss (values of compressive strength loss inferior to 7 %).

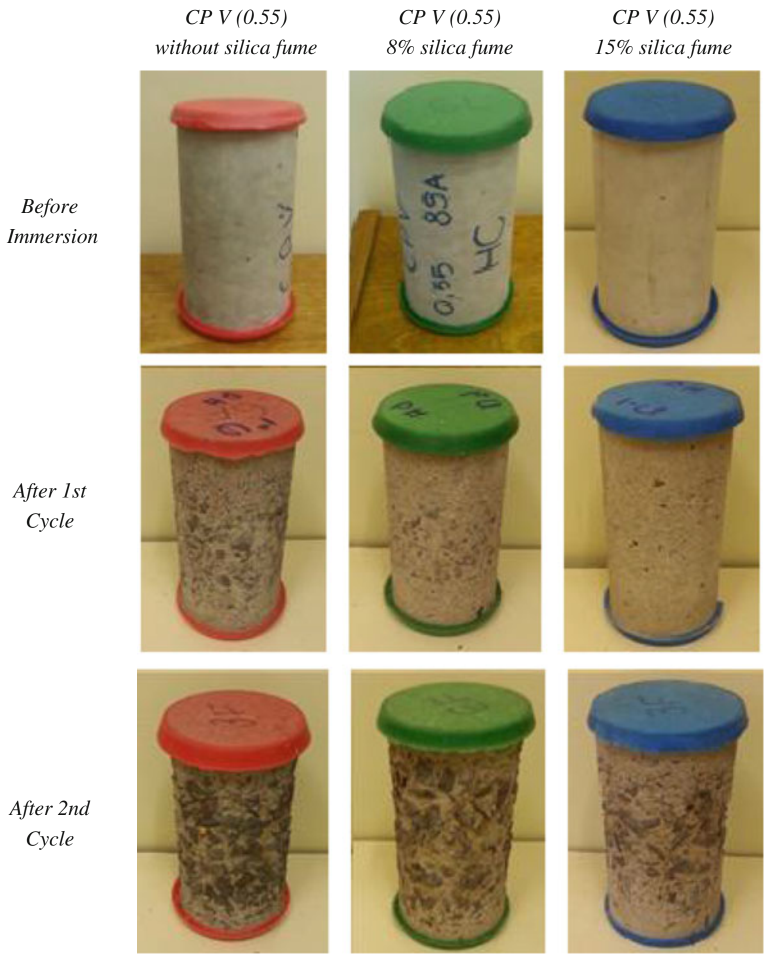


Fig. 7 The effect of silica fume in the specimens

It was observed that with increased in water/cementitious materials ratio, mass loss increased and compressive strength loss increased. It occurs because concretes with water/cementitious materials ratio of 0.55 are more porous and consequently the acid effects are less superficial than in the concretes with water/cementitious materials ratio of 0.45.

Formic acid, commonly found in industrial paper and cellulose installations, dye houses and food industries, was more aggressive to concrete than lactic acid, present in dairy products.

4 Conclusions

The accelerated test of degradation by acid, among other tests, provided results that showed that the presence of silica fume lowers the detrimental effect of lactic and formic acids on concrete and increase the durability of concrete. With the addition of silica fume, due to the pozzolanic reaction, voids ratios were reduced, contributing with to the decrease of particles leaching and decreasing the compressive strength loss. The silica fume is more efficient than pozzolan present in Portland Pozzolan Cement, in that case fly ashes, to reduce the detrimental effect of the acids over concrete.

The water/cementitious materials ratio also proved itself as an important asset in the control of acid attack. Among the eight mixtures tested, it was noticed that the most efficient combination for the control of the effects of degradation by acid was concrete that used CP V ARI RS with 15 % of cement replaced by silica fume and water/cementitious materials ratio equal to 0.45, considerably reducing the mass loss and almost inhibiting the compressive strength loss.

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