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# **Analysis of Chloride Penetration Into High Performance Concrete**

#### Abstract

Corrosion of reinforcement is one of basic destruction mechanisms of reinforced concrete structures. In that sense, the most affected structures are those by the sea, especially their parts subjected to cycles of wetting and drying. Chlorides penetrate to concrete mostly by diffusion, faster if the concrete is more permeable, destructing reinforcement passive protection and causing its corrosion, reduction of reinforcement cross section and bearing capacity of the structure. Retardation of chloride corrosion that causes structure degradation in marine environment can be achieved by the usage of quality concrete with enhanced strength and permeability parameters in regards to ordinary concrete. Mixes of ordinary and high performance concrete with different ratio of silica fume have been made. Compressive strength and resistivity to chloride penetration have been tested on the specimens 28 days after mixing. The resistivity to chloride penetration has been determined by fast chloride penetration test according to ASTM C1202 standard, using appliance that measures electrical conductivity of concrete specimens. Based on test results, the suitability of building reinforced concrete structures by the sea using high performance concrete has been analysed.

**Keywords:** chloride corrosion, marine environment, high performance concrete, compressive strength, chloride penetration

#### 1. Introduction

Corrosion of steel in concrete caused by chloride is one of the main causes of degradation of reinforced concrete structures built by the sea. Chloride ions can enter concrete by the process of capillary absorption, pressure flow and, most commonly, diffusion. Steel in concrete (reinforcing bars, steel fibres), under normal conditions of use, is protected from corrosion by a passive oxide layer which does not further corrode due to the high alkalinity of the concrete. The penetration of aggressive substances

from the environment into concrete reduces its pH factor and, in the presence of water and oxygen, creates conditions for the chloride corrosion process of steel. Chemical reactions produce iron (III) oxide (rust) on the surface of reinforcing steel, whose volume is two to four times larger than the initial volume of steel [1]. Higher volume causes tensile stresses in the concrete around the steel. When these stresses exceed the tensile strength of the concrete, cracking, crushing and, in the worst case, breaking of the protective layer of concrete, occur.

Since penetration of chloride into the structure of concrete is possible due to its porosity, it is important for the durability of concrete structures to achieve as thick a concrete structure as possible. In [2 - 4], the advantages of using mixed cements with a certain proportion of pozzolan (silica fume, fly ash, blast-furnace slag, metakaolin, rice husks) over ordinary Portland cement were analysed to prepare concrete more resistant to chloride penetration. Except for the production of mixed cements, pozzolan can be used, in a certain percentage, as a substitute for cement in concrete. A certain proportion of cement replacements with pozzolan gives an advantage in terms of concrete price, energy efficiency, environmental impact as well as strength and durability properties [2]. According to [5], silica fume is the most effective mineral admixture that can improve the durability, workability, cohesiveness and strength of concrete due to its extremely fine round particles and high content of amorphous silica. The increase in strength depends on the addition of silica fume as a substitute for a part of the cement whereby the increase in strength will be insignificant (in some cases even annulled) or on top of a certain amount of cement, when the increase in strength will be noticeable.

High Performance Concrete (HPC) concrete is a type of concrete of greater durability and strength than ordinary concrete, which has been used in recent decades as a structural material in aggressive coastal and sea environments. Improved properties are achieved by a customized concrete composition with a water-cement ratio of less than 0.35, higher cement content (450 to 550 kg/m³), high content of silica fume (5 to 15% of cement weight) and superplasticizer (5 to 15 l/m³) which gives a dense microstructure of low permeability [6].

The aim of this study was to consider the possibility of replacing a portion of cement with 10%, 20% and 30% of silica fume and to analyse the effect on strength and durability parameters in terms of resistance to chloride corrosion. A total of 34 specimens were made and compressive strength and permeability for chloride ions are tested.

The results of the tests showed that the replacement of a part of cement with silica fume had little effect on increasing the compressive strength of concrete, up to a certain percentage of replacement, and significantly reducing the permeability of concrete for chloride ions.

### 2. Testing methods of chloride penetration

There are various methods of measuring the content of chloride ions in concrete, which have their advantages and disadvantages. Long-term test methods, such as AASHTO T 259 [7] and ASTM C1556 [8] tests, provide real models for the penetration of chloride ions, but the drawback is the long test duration. Tests according to both methods are performed by immersing the samples in sodium chloride solution for 90 days for AASHTO T 259 and 35 days for ASTM C1556 method. Short-term methods, such as rapid chloride penetration tests, have the advantage of velocity of testing, but the test method is not directly related to the proportion of chloride ions in concrete [9]. Short-term method or rapid chloride penetration test ASTM C1202 "Standard Test Method for Electrical Indication of Concrete Resistance to Chloride Ion Penetration" [10] requires approximately 24 hours for sample preparation and an additional 6 hours for chloride ion penetration testing, which is relatively quick in relation to the aforementioned long-lasting methods. For all the above methods, treatment of the samples has started at 28 and 56 days of age, respectively. The age of the samples at the beginning of the test depends on whether it is ordinary concrete or concrete with the addition of pozzolan [11, 12]. Due to the diversity of methods, many studies have been conducted that tended to correlate the results of individual methods. In the paper [13], based on comparative tests with a long-term ASTM C1556 and a short-term ASTM C1202 test, the authors propose criteria for evaluating chloride penetration based on a rapid chloride penetration test. Table 1 shows the permeability for chloride ion classes through concrete, defined by the limits of electric charge passage through concrete specimens.

Table 1: Permeability classes of chloride ions through concrete [10]

Electric charge passage Q (C)	Permeability for chloride ions
> 4000	visoka
2000 – 4000	srednja
1000 – 2000	slaba
100 – 1000	vrlo slaba
< 100	beznačajna

## 3. Laboratory testing

At the Laboratory for Materials of the Faculty of Civil Engineering in Rijeka specimens of high-performance reference concrete and HPC specimens with the replacement of cement by silica fume were made and tested.

#### 3.1. Composition and preparation of HPC mixtures

A total of four mixtures, the reference mixture (REF) and the mixtures where part of the cement was 10% (SF10), 20% (SF20) or 30% (SF30) replaced by silica fume, were prepared. The amounts of silica fume, water, superplasticizers and viscosity regulators are the same for all mixtures. The amount of aggregate varies slightly as the difference between the density of silica fume and cement affects the volume occupied by the aggregate.

Table 2 lists the constituents used to make HPC mixtures in quantities per 1 m<sup>3</sup> of concrete.

Component (kg)	REF (kg)	SF10 (kg)	SF20 (kg)	SF30 (kg)
cement CEM I 52,5R	800	720	640	560
silica fume	0	80	160	240
water	272	272	272	272
superplasticizer	20	20	20	20
viscosity regulator	4,8	4,8	4,8	4,8
grounded limestone 0 – 2	608	600	590	560
quartz sand $0.1 - 0.6$	552	548	530	512

Table 2: Composition of HPC mixtures

All HPC mixtures were prepared in a 150 l volume mixer (Figure 1). For the sake of repeatability, the procedure for mixing, casting, compacting and curing of concrete is defined as follows:

- mixing dry ingredients, aggregates and silica fume for 5 min
- adding cement and mixing for 5 min
- adding 80% water and mixing for 2.5 min
- adding 10% water with superplasticizer and 10% water with viscosity regulator and mixing for 2.5 min
  - pouring of concrete to moulds in three layers and vibrating each layer for 10 s
  - curing concrete in moulds in air at 20°±2° C for 24 h (Figure 2)
  - curing concrete in water for 55 days at a water temperature of 20°±2° C





Figure 1: Fresh concrete mixture SF20 [14]

Figure 2: HPC in moulds

## 3.2. Testing of fresh concrete

The density of fresh concrete mixtures specimens has been tested according to HRN EN 12350-6 [14], the proportion of pores in fresh concrete according to HRN EN 12350-7 [15] (Figure 3) and the consistency of concrete by flow test according to HRN EN 12350-5 [16] (Figure 4).



Figure 3: Porosity meter [17]

Figure 4: Testing of consistency of concrete [17]

### 3.3. Testing of hardened concrete

#### 3.3.1. Compressive strength testing

A total of 18 hardened specimens, four of the REF, SF10 and SF30 mixtures and six of the SF20 mixture, were tested for compressive strength according to HRN EN 12390-3 [18] at a 28-day age. The compressive strength of cube-shaped specimens measuring 150 x 150 x 150 mm was tested using a 3000 KN hydraulic press (Figure 5).





Figure 5: Testing of compressive strength of HPC [17]

#### 3.3.2. Testing of concrete resistivity to chloride ion passage

Resistance of concrete 56 days old to penetration of chloride ions according to ASTM C1202 was tested on a total of 16 hardened specimens, four for each mixture. For testing, specimens of the shape of a cylinder with a diameter of 100 mm were used, which, after curing, were cut from concrete specimens 200 mm high to those  $50 \pm 3$  mm high. The specimens with side surface coated with electrically non-conductive, fast-drying silicone were placed in a desiccator which is a part of the specimen vacuuming and saturation device (Figure 6).

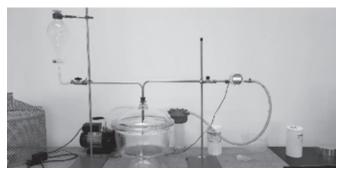


Figure 6: Specimen vacuuming and saturation device

Extraction of air from the samples by means of a vacuum pump (pressure of 0.3 to 0.5 bar) lasted for three hours after which the samples were saturated with demineralised water for 4 h. After saturation, the samples were left under water for  $18\pm2$  h.

Saturated concrete specimens were placed between cells with solution tanks of an electrical conductivity measuring device according to ASTM C1202 (Figure 7).

The positive voltage cell tank was filled with 3% NaCl solution, and the negative voltage cell tank was filled with 0.3N NaOH solution. A 60 V DC electrical voltage is released through the sample bases. Electrical conductivity through concrete samples was measured for 6 hours and data on the total electric charge passage through the sample, expressed in the Coulomb unit were obtained.

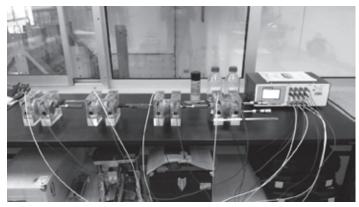


Figure 7: Apparatus for chloride ion conductivity measurement

According to ASTM C1202 [10], if the passage of current is recorded at 30 min intervals, the total electrical charge that has passed through the sample is calculated according to the expression (1) based on the trapezoidal rule.

$$Q = 900 \cdot (I_0 + 2I_{30} + 2I_{60} + \dots + 2I_{330} + 2I_{360}) \tag{1}$$

where is:

Q – total electric charge (C),

 $I_0$  – amperage at the test start (A),

 $I_t$  – current intensity at 30 min intervals (A).

## 4. Analysis of testing results and conclusion

Table 3 shows the mean test results of fresh concrete samples: density, pore content, and flow consistency for HPC mixtures. As expected, due to the lower volume mass of silica fume, mixtures with a higher proportion of it have a slightly lower density. The proportion of pores in all mixtures is the same, which is in accordance with the properties of concrete with the addition of silica fume, in which the proportion of pores remains at the same level, but their size changes. Because the water-cement ratio and additive amount are the same for all mixtures, mixtures with a higher silica fume content show a significantly lower workability due to the higher water requirement caused by

the higher fineness of the silica fume particles than those of the cement as shown by the consistency test results given in Table 3.

Characteristic	REF	SF10	SF20	SF30
volume mass (kg/m³)	2200	2137	2135	2106
porosity (%)	4,3	4,4	5,3	5,9
flow consistency (flow class)	F4	F4	F1	F1

The mean values of the density of hardened concrete, the results of the compressive strength test and the total passage of chloride ions are shown in Table 4.

*Table 4: Hardened concrete testing results* 

Characteristic	REF	SF10	SF20	SF30
density (kg/m³)	2212	2169	2160	2052
compressive strength (MPa)	83,5	85,8	86,2	68,4
total electric charge (C)	5084	856	560	141

The diagram in Figure 8 shows the trend of the amount of leaked current through HPC samples over time.

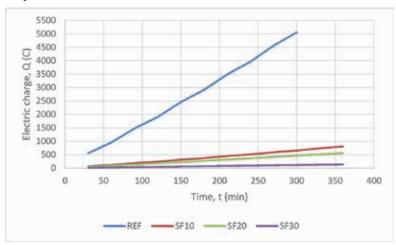


Figure 8: Passed electric charge in time

For samples with a silicon fume content, the measurement was carried out according to the standard with a duration of 360 min. In the test of chloride penetration through the reference samples, the test was stopped after 300 min because the temperature in the solutions arose above the set point of 85° C. All specimens with silica fume show, according to Table 1, very poor permeability for chlorides as opposed to the reference sample whose permeability is high. This is explained by the fact that smaller particles of silicon fume, by hydration, create products that fill the space between larger particles of cement, that is, their products of hydration.

Figure 9 shows the achieved mean compressive strength depending on the silica fume content of HPC mixtures. The results are consistent with those in [4], where it was concluded that replacing a portion of cement with up to 20% silica fume had an effect on increasing the compressive strength of concrete. Concrete with 30% silicon fume has a compressive strength drop and does not satisfy the HPC strength according to [6].

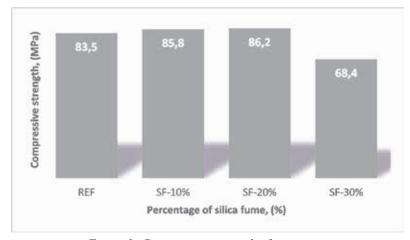


Figure 9: Compressive strength of specimens

Figure 10 shows the mean total amount of charge that passed through samples with a single silica fume content in 300 min of testing. Permeability for chloride ions is as expected, high for reference concrete with 0% silica fume and significantly lower for concrete with 10%, 20% or 30% silicon fume as a replacement for cement.

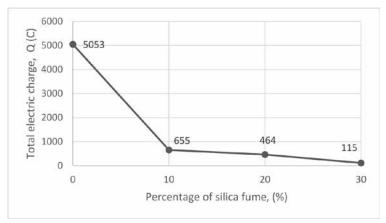


Figure 10: Passed total electric charge vs. Percentage of silica fume in HPC

Comparison of concrete compressive strength and total charge data for concrete mixes shows that mixtures with 10% and 20% silica fume are satisfactory as for the low permeability for chloride ions as well as for high strength classification.

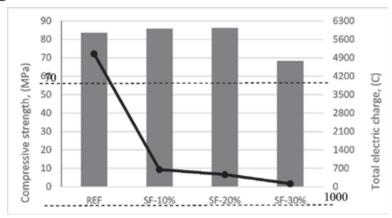


Figure 11: Achieved compressive strength and total charge passed

In conclusion, because of their low permeability to aggressive substances, concrete with high performance properties is suitable for the construction of structures by the sea and in the sea. In order to obtain satisfactory compressive strengths and low permeabilities, concrete compositions with between 10% and 20% silica fume should be optimized. Further research could go towards improving the concrete formulation with 30% silica fume, which is very poorly permeable to chloride ions but does not satisfy the high compressive strength.

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