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The influence of ion chloride on concretes made with sulfate-resistant cements and mineral admixtures

J. Bernal Camacho *, S. Mahmoud Abdelkader, E. Reyes Pozo, A. Moragues Terrades

E.T.S.I. de Caminos, Canales y Puertos, Department of Civil Engineering: Construction, Universidad Politécnica de Madrid, C/ Profesor Aranguren, sn, 28040 Madrid, Spain

HIGHLIGHTS

- We compared concretes cured in saturated calcium hydroxide versus sodium chloride solution.
- The change in the mechanical and microstructural properties was not significant.
- The free, bound and total chloride content was computed experimentally.
- The proposed model, called Langmuir–Freundlich, showed the best fit to the experimental results.
- The concretes with blast furnace slag cement and with silica fume showed the best performance.

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ABSTRACT

The aim of this work is to study the influence of chloride ion in the mechanical, microstructural and chemical properties of concrete. For this purpose, four concrete mixes were designed, with two types of sulfate-resistant cement and two mineral admixtures (silica fume and fly ash). Furthermore, a chloride binding isotherm is offered that is compared with Freundlich and Langmuir models. This provides certain advantages in reproducing experimental results. According to such results, the properties do not present significant changes in all cases. The concretes with blast-furnace slag cement and with silica fume are those that present the best performance.

1. Introduction

The study of chloride penetration into concrete is considered complex topic, given that it depends on many factors. The presence of chlorides in the reinforced concrete can provoke initiation and acceleration of corrosion of the steel bar [1]. There exist distinct conditions where ion chloride is present, with the most important being marine and high-mountain (with use of de-icing salts) environments. The main transport mechanisms of chloride ions in concrete are diffusion, capillary suction and convection [2]. The chloride ions in the concrete can be free, bound or adsorbed into calcium silicate hydrate [3].

Use of mineral admixtures improves the durability of the concrete, mainly due to an increased bounding chloride capacity [4], a reduction of permeability and total porosity, and an improvement of the distribution porosity of the cement matrix [5,6]. Admixtures such as fly ash and silica fume are used as a partial replacement of the cement, improving significantly resistance of the concrete significantly [7,8]. In addition, admixtures from ground-granulated blast-furnace slag are used because of a capacity of hydraulic reaction that provides hydrated products which increase mechanical strength.

Use of fly ash is considered to be effective in reducing corrosion induced by chlorides. Such a use generates an increase of bound chlorides due to an appreciable content of alumina [9] which results in the formation of Friedel's salt [10]. The silica fume is recognised for reducing permeability through the refinement of the microstructure by means of chemical and physical processes, reducing substantially risk of corrosion. Regarding blast-furnace

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* Corresponding author. Tel.: +34 913366721.

E-mail addresses: jesusmanuel.bernal.camacho@alumnos.upm.es (J. Bernal Camacho), safwat.mahmoud@upm.es (S. Mahmoud Abdelkader), ereyes@caminos.upm.es (E. Reyes Pozo), amoragues@caminos.upm.es (A. Moragues Terrades).

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slag, published research has shown an improved performance against chloride penetration due to a reduction of the concrete pore network, a bonding capacity increase and a diffusion coefficient reduction [11,12].

The penetration of chloride in the concrete depends on the characteristics of the cement matrix such as bonding capacity, total porosity, pore size distribution, connectivity and tortuosity. The ingress of chloride has been studied by calculating the diffusion coefficient (D) which determines the penetration rate of chlorides [13], considering a constant surface concentration in the material (Cs) and assuming that chloride penetration capacity does not change over time. However, the chloride penetration profiles obtained in real structures show a different behavior due to the complexity of the phenomenon. The study and modeling of the penetration process under natural conditions is an interesting research topic [14,15]. Recent research [16] has studied the dependence of D and C_s over time. Change in these values can be attributed to the continuous hydration of cement paste and chemical bonding of chloride ion during the penetration process. One published study, for example, defined that D decreases while C_s increases [17]. In order to examine the chemically bound and free chloride content at constant temperature, so-called binding isotherms are used. These isotherms express the bound chloride content as a function of the free chloride concentration in the porous medium, with the commonest models being the Langmuir and the Freundlich isotherms [18].

As mentioned above, in the case of concrete the two main aggressive examples in which the ion chloride is present are the marine and high- mountain environments. In order to increase durability in the marine environment, the literature [19,20] recommends using cement with a low concentration of aluminates (sulfate-resistant cement) or mineral additions (mainly cements with fly ash and silica fume) to improve impermeability. The second option would be that advisable in cases with aggressive agents, including high-mountain environments. Hence, in this work four concrete mixtures were prepared by using two sulfate-resistant cements. The cements used were CEM I 42.5 R/SR and CEM III/B 42-5 L/SR, with the latter including a mineral admixture of ground-granulated blast-furnace slag. Two dosages were prepared by using only the abovementioned cement. The rest of the dosages were made with CEM I 42.5 R/SR plus two different mineral admixtures, silica fume and fly ash, as cement replacements. In this case, two replacements, due to the weight of cement were examined: 10% in the case of silica fume and 20% for the fly ash within the limits allowed by current standards in Spain [21].

In order to characterise the concrete, several tests were performed that considered mechanical and microstructural aspects. In addition, an experimental programme was designed to study the behavior of the mixtures under chloride penetration, in which the concrete samples were submerged in a NaCl solution with a molar concentration of one. The tests were carried out at different ages (182 and 546 days) to obtain the development of penetration profiles of chloride, considering the hydration degree of the cement and pozzolanic reactions of the admixtures. The main objective was to examine the relationship between the microstructure generated in different concretes with admixtures and the chloride transport within it. The free, bound and total chlorides were identified and the values fitted in four chloride-binding isotherms: Langmuir Linear, Langmuir, Freundlich and a combination of the last two that was denoted Langmuir–Freundlich. In this work, the latter isotherm model is proposed to provide a model that conserves the properties of the two originals on which it is based, avoiding the difficulties that can occur in some cases and providing a good fit and correlation.

2. Materials and methods

2.1. Materials

The behavior of two types of sulfate-resistant cement, namely Type I 42.5 R/SR sulfate-resistant Portland cement and Type III/B 42.5 L/SR blast-furnace slag Portland cement with 66% of mineral admixture [22] was evaluated. The two types were used in the design of four different concrete mixes: one for each cement type and two more by using Type I plus two admixtures, silica fume and fly ash, as cement replacements. In these cases two replacements relative to the weight of cement within the limits allowed by the current standards were examined: 10% in the case of silica fume and 20% for the fly ash. Table 1 summarises the chemical composition and physical properties of the cements, silica fume and fly ash used. The fine aggregate used was a natural siliceous sand with a 2.8 fineness modulus. The coarse aggregate was crushed limestone with a maximum size of 20 mm and a 6.88 fineness modulus. With the aim of achieving an appropriate workability, a superplasticizer was used as a high-range water-reducing agent.

From now on, the four concrete mixes will be termed as the following: sulfate-resistant Portland cement (SRPC), blast-furnace slag Portland cement (BFSPC), sulfate-resistant Portland cement with silica fume (SRPC + 10%SF) and sulfate-resistant Portland cement with fly ash (SRPC + 20%FA). The proportioning was carried out in accordance with recommendations made by the Spanish Instrucción *de* Hormigón Estructural (EHE) [21]. Table 2 shows the compositions of the mixtures. The concrete was designed by using the method offered by La Peña [1]. In the cases of SRPC + 10%SF and SRPC + 20%FA, the authors followed the recommendations of the EHE, replacing the cement contents (C) with cementitious material ($C + KF$), where F was the content of the admixture and K the coefficient of effectiveness. In this work $K = 2$ is used for the silica fume and $K = 0.3$ for the fly ash. The concrete mixtures were prepared with a water-to-cementitious materials ratio (w/cm) of 0.45.

The procedures identified in standard UNE-EN-12390-2 were used for casting, curing, and testing the concrete specimens. A typical steel cylinder mold of 150 mm in diameter and 300 mm in height was used for the test samples. The casting and finishing of the specimens were performed in a laboratory at a temperature of 20 °C. The specimens were then demoulded approximately 24 h after casting and then placed in a curing chamber at a temperature of 20 ± 2 °C and a relative humidity (RH) of 95–98% until testing. A total of 72 cylindrical specimens were made from each mixture for the characterisation of the mechanical properties, permeability and porosity, and the assessment of the hydrated compounds of the concretes in the conditions studied.

Table 1
Chemical composition and physical properties of cementitious materials.

Parameters (%)	I 42.5 R/SR	III/B 42,5 L/SR	Silica fume	Fly ash
SiO_2	21.58	26.70	85.0	40.66
Al_2O_3	3.48	7.40	–	30.02
Fe_2O_3	4.78	1.80	–	19.93
CaO	67.64	50.20	1.0	8.09
MgO	1.00	6.80	–	1.70
Na_2O	–	0.23	1.5	0.22
K_2O	–	0.78	–	1.13
SO_3	3.3	3.03	2.0	0.85
Cl^-	0.01	0.03	0.1	0
Loss to fire	–	1.50	–	1.14
Loss due to calcinations	3.16	–	4.0	–
Insoluble residue	1.25	1.48	–	–