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Resistance to Chloride Penetration of High Strength Self-Compacting Concretes: Pumice and Zeolite Effect

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***Abstract*—**This paper aims to contribute to the characterization and the understanding of fresh state, compressive strength and chloride penetration tendency of high strength self-compacting concretes (HSSCCs) where Portland cement type II is partially substituted by 10% and 15% of natural pumice and zeolite. First, five concrete mixtures with a control mixture without any pozzolan are prepared and tested in both fresh and hardened states. Then, resistance to chloride penetration for all formulation is investigated in non-steady state and steady state by measurement of chloride penetration and diffusion coefficient. In non-steady state, the correlation between initial current and chloride penetration with diffusion coefficient is studied. Moreover, the relationship between diffusion coefficient in non-steady state and electrical resistivity is determined. The concentration of free chloride ions is also measured in steady state. Finally, chloride penetration for all formulation is studied in immersion and tidal condition. The result shows that, the resistance to chloride penetration for HSSCC in immersion and tidal condition increases by incorporating pumice and zeolite. However, concrete with zeolite displays a better resistance. This paper shows that the HSSCC with 15% pumice and 10% zeolite is suitable in fresh, hardened, and durability characteristics.

***Keywords*—**Chloride penetration, immersion, pumice, HSSCC, tidal, zeolite.

I. INTRODUCTION

PUMICE is one of the natural volcanic pozzolanic materials. Due to frequent volcanic eruption, it is found plentifully in the world and has been used with Portland cement or blended cement either individually or in combinations [1]. In 122 BC, the Romans used the lightweight material made of pumice aggregate to build part of their temples with concrete. Recently pumice, due to its appropriate rheological behavior, mechanical and durability properties as well as its low cost has become of interest for researchers to further investigate their impact on the concrete. However, only few studies related to pumice exist in the literature. According to Ramezanianpour and Samadian, pumice as a pozzolanic material increases the later age compressive strengths of SCC [1]. Application of natural zeolite in manufacture of pozzolanic cements started in the first decades of the 20th century and has been shown to be a growing trend in recent decades. Recently, the use of a large amount of natural zeolite in cement and concrete industry has been reported in China. It is reported that, volcanic material containing 45% of zeolite deposited in the Black Forest in Germany is used in the concrete industry in Germany, Switzerland and France [2]. The use of natural zeolite as a pozzolanic material has grown in recent years in Iran as well [3], [4].

This paper investigates and compares the effect of two different natural pozzolan from Iran (pumice and zeolite) on rheological behavior and compressive strength of HSSCC at early ages and up to 365 days. The impact on the diffusion, migration and resistance to chloride penetration both in immersion and tidal conditions is also investigated. For this purpose, first, different tests such as slump flow, V-funnel, L-box, U-tube, J-Ring and sieve, were performed to study the fresh phase of HSSCC, and then mechanical testing was done on hardened states to evaluate the compressive strength of the different prepared mixtures. The tests concerning the chloride penetration were also performed at different ages in order to evaluate the durability properties with time including chloride ion diffusion in non-steady state, chloride ion migration in non-steady state by electric field (RCMT) and electrical resistivity. Finally, the resistance to chloride penetration of the different mixtures was evaluated in immersion and tidal conditions.

II. MATERIALS

Five concrete mixtures were prepared with the same Portland cement type II content (450 kg/m^3), constant W/Cm ratio of 0.4 and constant gravel to sand ratio of G/S=1. A concrete mixture based on Portland cement was used as the control concrete (HSL). In the other four formulations, HSP10, HSP15, HSZ10, and HSZ15 pumice and zeolite were used respectively as an additive with two different replacement percentages of 10% and 15% by Portland cement. A Portland cement with a specific gravity of 3.15 g/cm^3 and a Blaine fineness of 2900 cm^2/g, in compliance with ASTM C150 was used.

The pumice used in this study has a specific surface area of 4220 cm^2/g and a specific gravity of 2.58 g/cm^3. The used zeolite as shown in Table I is a siliceous zeolite since it contains a high amount of silica. It has a specific surface area of 4060 cm^2/g and a specific gravity of 2.25 g/cm^3. The

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chemical analysis and particle size distribution (PSD) of cementitious materials are shown in Table I and Fig. 1, respectively.

TABLE I
CHEMICAL ANALYSIS OF PORTLAND CEMENT TYPE II, LIMESTONE POWDER, PUMICE AND ZEOLITE

Chemical analysis (% by mass)	Cement (type II)	Lime stone powder	Pumice	Zeolite
Loss on ignition	1.3	42.88	2.26	11.94
SiO_2	21.74	1.19	56.04	69.72
Al_2O_3	5.0	0.85	27.61	13.54
Fe_2O_3	4.0	0.3	0.25	1.26
CaO	63.04	48.82	8.76	0.87
MgO	2	1.58	4.52	2.45
SO_3	2.3	-	-	-
CO_2	-	-	-	-
$CaSO_4$	-	-	-	-
Cl	-	-	-	-
Insoluble residue	0.60	-	-	-
Alkalis (Na_2O%+0.658K_2O %)	1	-	-	-
Na_2O+K_2O	-	4.27	0.41	0.13
Free Cao	1.4	-		
Humidity	-	0.11	0.15	0.09
C_3S	45.5	-	-	-
C_2S	28.0	-	-	-
C_3A	6.5	-	-	-
C_4AF	12.2	-	-	-

For all mix designs, crushed angular material of 6-12 mm nominal size was used as a coarse aggregate (gravel), and natural sand with a maximum size of 4 mm was used as a fine aggregate. The particle size distributions of sand and gravel are shown in Fig. 2. A high range water-reducing admixture (HRWRA), with a specific gravity of 1.11 g/cm^3 based on chains of modified poly-carboxylate ether (PCE 180), was used in all mixtures to produce HSSCC. Potable water was also used to prepare concrete mixes. The balance between high flow and high segregation resistance is made possible by the dispersing effect of HRWRA combined with cohesiveness of high concentration of fine particles in additional filler material. The dosage of superplasticizer is experimentally determined from tests on fresh concrete to obtain a slump flow diameter of 700±30 mm for all HSSCCs. Table II shows the mix proportions of the mixtures. To enhance the stability of SCC mixes, 150 kg/m³ limestone powder was used as filler in the five mixtures. By increasing the replacement level of additives from 10% to 15%, the viscosity of fresh concrete and the amount of superplasticizer required to achieve the desired slump flow is also increased. This last is very significant in the HSZ15 mixture, and therefore, this mixture is considered to be uneconomical (Table II). From this aspect, although natural zeolite is cheaper than Portland cement, the high demand of superplasticizer in concretes containing high levels of natural zeolite may result in more production costs. Some researchers concluded that, a large amount of superplasticizer is required to produce concrete containing high percentage of zeolite replacement [3]-[8]. Ahmadi and Shekarchi [9] and Tokushige et al. [6] concluded that, the dosage of superplasticizer increased substantially with incorporation of zeolite. The large amount of the required superplasticizer can be justified by the following reasons: i) the fine microstructure of zeolite, ii) increase of volume paste and iii) high surface area of natural pozzolan. Other researches on conventional concrete also confirmed that incorporation of natural zeolite increased the demand of superplasticizer.

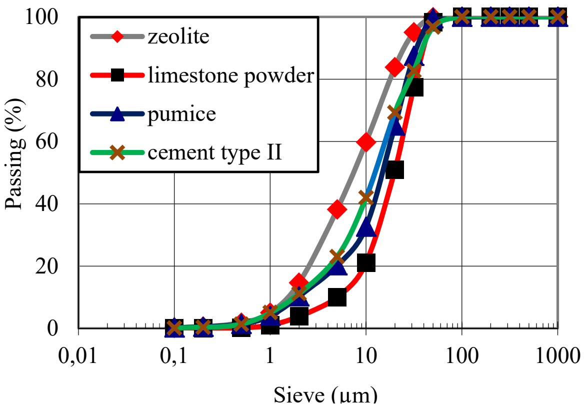

Fig.1 Particle size distribution of fine materials

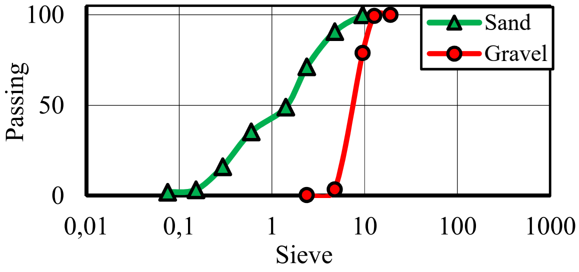

Fig. 2 Particle size distribution of aggregates (gravel and sand)

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TABLE II
MIX DESIGN OF HSSCC MIXTURES (KG/M^3)

Mix name	W	C	w/c	G	S	LP	SP	Z	P
HSL	180	450	0.4	790	790	150	4.85	-	-
HSP10	180	405	0.4	790	790	150	6.2	-	45
HSP15	180	382.5	0.4	790	790	150	6.8	-	67.5
HSZ10	180	405	0.4	790	790	150	8.94	45	-
HSZ15	180	382.5	0.4	790	790	150	21.62	67.5	-

III. EXPERIMENTAL PROGRAM

A. Mix Design

All concrete mixtures were prepared in a 150-liter mixer. The batching sequence consisted of decant total of the fine and coarse aggregate placed into the mixer, and then mixed for 3 minutes. During this period, 2/3 of the water required was added. Next, cementitious materials were added and mixing was continued for one more minute. After this, the superplasticizer and the remaining water were introduced and the blend was mixed for 2 minutes. The mixer was covered with a plastic cover to minimize the evaporation of the mixing water.

B. Casting and Curing

Cubic and cylindrical samples were cast in accordance with ASTM C31 (2012) and ASTM C511 (2013). After casting, samples were covered with two layers of plastic sheets and placed in temperature controlled room at 22±2 °C for 24 hours. All samples were demolded after 24 hours and cured up to the age of testing in saturated lime solution to prevent possible leaching of $Ca(OH)_2$ from these specimens.

IV. RESULTS AND DISCUSSION

A. Fresh State

French National Guidelines [10] characterize fresh SCC, taking into account the three main characteristics: i) mobility in unconfined areas, ii) mobility in confined areas and iii) stability: that means the resistance to segregation and bleeding. In order to evaluate the effects of pozzolan on the fresh properties of SCC, slump flow, V-funnel, and L-box tests were performed according to the procedure recommended by EFNARC Committee and also sieve test, J-Ring test and U-tube were performed according to the procedure recommended by AFGC 2000, ASTM C1621, and BS EN206-1, respectively. The slump flow test is one of the most commonly used experiments to measure the properties of SCC. This type of test can give indications as to the rheology of unconfined environment SCC. Depending on the type of application, the mixes with slump flow values ranging from 550 to 850 mm are considered SCC [10]. The segregation tendency of concrete mixes was also evaluated by visual observation during slump flow test as aggregates separate from cement paste close to the edges of speared out concrete. The slump flow of all HSSCC mixes was near to 700±30 mm, and no segregation was observed in the mixes (Table III). The spreading rate of the concrete is also an indication often taken into account (T50 e.g., time to reach a 500-mm spreading diameter, if it takes more than 5 seconds a large plastic viscosity is concluded and if the measured time is less than 1 second, it shows a lower viscosity. In these cases, the risk of segregation and bleeding and creating aureole will increase). The ability of concrete to flow through a restricted area without blockage and segregation was evaluated using V-funnel test. The time of flow from the opening of outlet to the seizure of flow was recorded, and results are presented in Table III. The V-funnel flow time also depends on the type of application, but it is grouped into two classes [10]. VF1 class: flow time of less than 10 seconds and VF2 class: flow time of between 7 and 27 seconds.

The experimental flows of J-ring for concrete mixes based on ASTM C1621 are indicated in Table III. L-box ratio was carried out on concrete mixes to measure the cohesiveness and ability of SCC to pass through reinforcements without segregation. The L-box ratio is reported to be between 0.7 and 0.9 for normal SCC; however, a range of 0.8 to 1.0 is also proposed by EFNARC guidelines. Results of h2/h1 ratios relative to this study are presented in Table III. It can be seen that the values range from 0.77 to 0.93, which are within the specified limits for SCC. It should be noted that three-bar L-box height was utilized in this study to simulate more congested reinforcements. The test of the U-box allows the mobility of confined concrete to be characterized and verifies that the installation of the concrete will not be opposite by phenomena unacceptable blockages, the value limit is equal H2-H1 = 10 mm. This test was performed for all mixes and the results are presented in Table III. It can be seen that the range of values is almost within the specified limits. The implementation of SCC, under only the effect of gravity requires a very high fluidity of the material but it is also essential that the concrete maintains a satisfactory stable and perfect homogeneity. Various tests can be used to characterize the resistance to static segregation of SCC to remain homogeneous after its placement until it begins to set. One such test is called "stability sieve", developed by GTM to assess the weight percentage milt (Pmilt noted later). The acceptable limitations are as follow: i) 0% < Pmilt < 15%: Satisfactory stability, ii) 15% < Pmilt < 30%: Critical stability (segregation test necessary on site) and iii) Pmilt > 30%: Very poor stability (systematic segregation, unusable concrete).

B. Compressive Strength of HSSCC Mixtures

Compressive strength of HSSCC mixes (fc) was measured on a total of 120 cubes of 100×100 mm at 1, 3, 7, 14, 28, 90, 180, and 365 days of aging in accordance with BS 8110: part1: 1997. The strength development of mixes based on average strength of three samples tested at each age is shown in Fig. 3. The slope of the lines (m) of liners relationship between compressive strength and curing age for different mixes is presented in Table IV. The gradient of strength-age relationship represents the effect of mix design and materials proportions on rate of strength gain for HSSCC mixtures.

TABLE III
TEST RESULTS OF FRESH HSSCCS

Mix name	Slump flow		L-box			V-funnel t (s)		Sieve test	J-ring		U-tube
	Dia (mm)	T_{50} (s)	h_2/h_1	T_{20} (s)	T_{40} (s)	1min	5min	Segregation (%)	Δ_H (mm)	Dia (mm)	h_2-h_1 (mm)
HSL	731.3	2.03	0.93	1.5	2.2	10	9	4.36	15	702.5	10
HSP10	727.5	2.66	0.84	1.5	3.5	9.25	10.85	4.86	10	715	15
HSP15	732.5	2	0.926	0.98	1.88	8.23	15.75	8.19	25	647.5	5
HSZ10	685	3.45	0.77	2.18	4.1	12	22	8.33	8	630	15
HSZ15	695	2.02	0.86	1.4	2.5	5	7.85	11.62	8	667.5	10

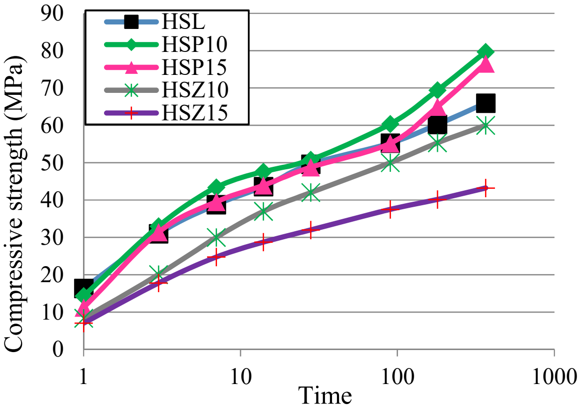


Fig. 3 Evolution of compressive strength, Rc, of HSSCC mixtures with curing time

Compressive strength, fc, of all samples for all ages is in the range of 7.04 to 79.7 MPa. The greatest resistance from 3 to 365 days happened for HSP10. The least resistance happened for HSZ15 at all ages. Concrete content of 10% pumice had a very positive effect on the strength from age of 3 days. On the other hand, their amount at 28 days of aging is almost similar to that of control mix. The compressive strength in concrete containing 10% of pumice is 1.06, 1.12, 1.09, 1.02, 1.09, 1.15, and 1.21 times higher than the one of the control concrete at 3, 7, 14, 28, 90, 180, and 365 days of aging, respectively, whereas the amount of compressive strength in HSSCC containing 15% of pumice is closer to that in control concrete until age of 90 days. After 90 days of aging, the progress of the compressive strength in HSP15 is more remarkable in comparison with the compressive strength in control mix. Indeed, the increase of the compressive strength for SCC containing 10% and 15% of pumice is most visible at the long-term. The rate of increase of the compressive strength in these mixes (HSP10 and HSP15) is more remarkable at 180 and 365 days. On the contrary, zeolite had a negative impact in the process of increasing the compressive strength. Also, this is more impressive in HSZ15. For example, at 28 days of aging, the compressive strength in control concrete is 1.18 and 1.55 times higher than the one of HSZ10 and HSZ15, respectively. In this way, it can be concluded that the use of zeolite as described here has negative effect on compressive strength in HSSCC compared to that of control concrete (HSL). However, this remark cannot be generalized to all mixture using zeolite. Different result could be found with the use of other type of superplasticizer for example.

TABLE IV
THE SLOPE OF COMPRESSIVE STRENGTH DEVELOPMENT AT DIFFERENT AGES

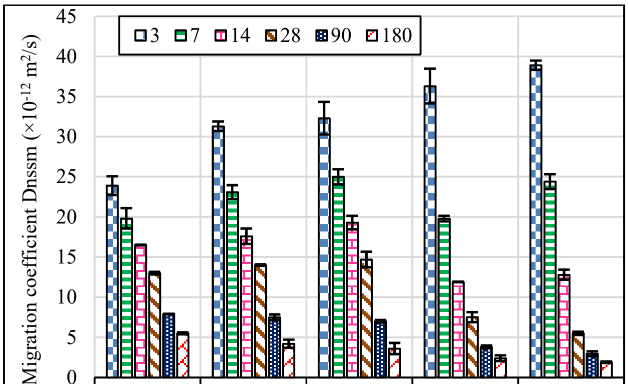
Mix name	**m** $_{1\text{-}3}$	**m** $_{3\text{-}7}$	**m** $_{7\text{-}14}$	**m** $_{14\text{-}28}$	**m** $_{28\text{-}90}$	**m** $_{90\text{-}180}$	**m** $_{180\text{-}365}$
HSL	7.34	1.94	0.69	0.43	0.09	0.06	0.03
HSP10	9.36	2.6	0.6	0.23	0.15	0.1	0.057
HSP15	10.1	2.03	0.63	0.35	0.1	0.11	0.064
HSZ10	5.85	2.49	1	0.36	0.13	0.06	0.03
HSZ15	5.38	1.74	0.57	0.23	0.09	0.03	0.02

C. *Diffusion of Chloride Ions*

- Introduction: Chloride ions penetrate into concrete and cause, from a certain concentration in the pore solution, the local destruction of the passivation of the reinforcement and the initiation of localized corrosion. Chloride penetration in a natural environment takes place under the effect of two mechanisms: capillary absorption and diffusion. Diffusion due to an ionic movement under a concentration gradient between the exposed area and concrete in saturated medium. The penetration of chlorides in concrete depends on different factors, like the exposure conditions and the concrete transport properties:
  - In marine environments, the amount of chloride in contact with the concrete depends on the location of the structure, provided that they are completely submerged or placed in the tidal zone or only in contact with the salt fog.
  - Depending on the exposure conditions, mechanisms of chloride penetration can be a simple diffusion or diffusion combined with convection and advection. The change in temperature, rain and sun introduce variations which should also be taken into account.

In order to qualify the resistance of a concrete against chloride ions penetration, diffusion coefficient measurements are usually recommended.

- Migration in non-steady-state: In this study, migration in non-steady-state conditions under electric fields by NT-BUILD 492 method is investigated. Migration coefficients of the different mixes are presented in Fig. 4. This test was appointed for different ages for 3, 7, 14, 28, 90, 180 days of curing in lime saturated water on slices of 100×50 mm from cast cylinders. At early age, mixtures with natural pozzolan exhibit higher migration coefficient value due to their higher porosities. At 180 days of aging, on the contrary, mixtures with pozzolan present lower migration coefficient values compared to the one of the control mixture. At this age, the difference in coefficient of migration between HSSCCs with pumice and HSSCCs with zeolite is relatively low. Compared to control HSSCC, the migration coefficient value of HSP10, HSP15, HSZ10 and HSZ15 is, respectively, 1.31, 1.52, 2.29 and 2.89 times lower. Fig. 4 shows that the effect of aging in the decrease of migration coefficient is more important in mixtures containing pozzolan. A very fast decrease is observed in mixtures with zeolite while this decrease is slower and less significant in the case of pumice. From the age of 14 days, the zeolite pozzolans with 10% and 15% have a significant influence on the reduction of chloride ions penetration in comparison to that of control concrete. For concretes containing two percentages of pumice, until the age of 28 days, no improvement in the trend of reducing the amount of chloride ions migration is observed, and then at the age of 90 days the improvement is observed. This result can be explained at least partially by the lower connected porosity as can be expected from capillary absorption results. Other explanation of the positive impact of zeolite is related to the pozzolanic reaction of this pozzolan and consequently the consummation of calcium hydroxide which leads to an increase in tortuosity and a reduction of OH- in the pore solution. Consequently, the conductivity and chloride penetration of chloride ions decrease.



	HSL	HSP10	HSP15	HSZ10	HSZ15
3	23,9	31,3	32,3	36,3	38,9
7	19,82	23,1	25	19,8	24,4
14	16,5	17,6	19,3	11,9	12,8
28	13	14	14,7	7,52	5,5
90	7,9	7,5	7	3,81	2,96
180	5,5	4,21	3,61	2,4	1,9

Fig. 4 Migration coefficient of different mixes at different ages

Fig. 5 shows the penetration resistance levels of chloride ions as given in [11]. According to the results illustrated in Fig. 4, all formulations showed good resistance against chloride penetration after 90 days of aging. Moreover, the mixture which contained 15% of zeolite also showed very good resistance against chloride penetration after 180 days of curing.

- $D < 2\times10^{-12}$ m^2/s: Very good resistance against chloride ingress.
- $D < 8\times10^{-12}$ m^2/s: Good resistance against chloride ingress.
- $D < 16\times10^{-12}$ m^2/s: Moderate resistance against chloride ingress.
- $D > 16\times10^{-12}$ m^2/s: Not suitable for aggressive environment.

Fig. 5 Levels of resistance to penetration of chloride ions [11]

The quality of concrete is also evaluated based on the measurement of the current passed through the application of 30 V to the sample. This means that the higher the current, the less the resistance of concrete to chloride penetration is Fig. 6 shows that there is a linear relationship between migration coefficient and initial current. The measurement of initial current seems to be a good durability indicator that can be directly related to the migration coefficient. Fig. 7 presents a linear relationship between the square root of migration coefficient and chloride penetration depth after 24 hours of exposure to migration test. The correlation (R2 = 0.99) suggests between these two parameters that the migration coefficient depends more specifically on depth of penetration. Moreover, from NT BUILD 492 standard, varying parameters such as the initial current, the secondary voltage and test duration are very effective on the quantity of migration coefficient. Chloride depth penetration after RCMT test, highlighted by $AgNO_3$ solution, for the different mixtures is illustrated in Figs. 8 and 9.

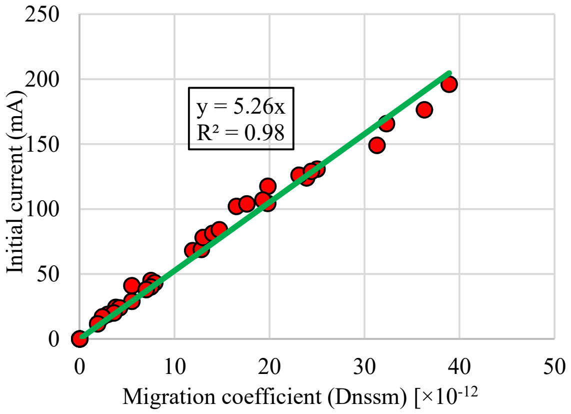


Fig. 6 Evolution of initial current according to migration coefficient of the studied HSSCCs

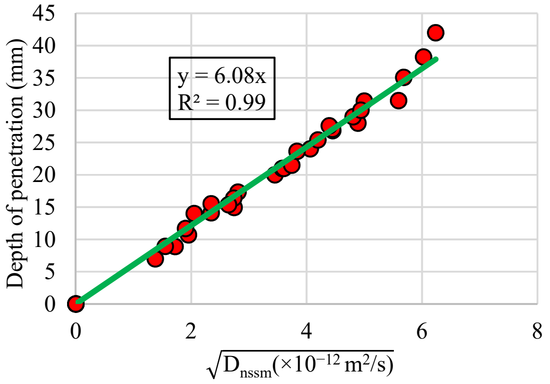


Fig. 7 Evolution of chloride penetration depth according to migration coefficient of the studied HSSCCs

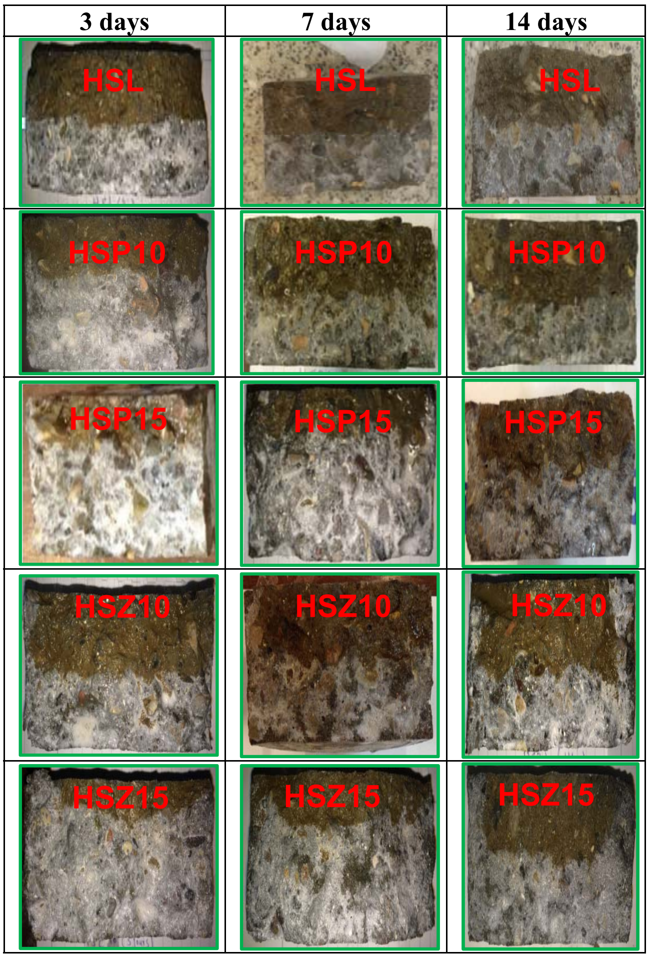


Fig. 8 Chloride penetration depth after RCMT test in the different studied HSSCCs at 3, 7, and 14 days of aging

- Diffusion in non-steady-state: The test of natural diffusion is a tedious test with a longer duration. Natural diffusion test was done according to ASTM C 1543-02 procedure. Free chloride concentration in the samples was measured according to AFREM 1997. The test was carried out on slices of cylinders with dimension of 100×50 mm (three samples per formulation). All surfaces of samples are sealed except the upper one by which chloride diffusion will happen as shown in Fig. 10. This seal is necessary to ensure a one-dimensional penetration of chloride. The unsealed surface is exposed to saline solution for a fixed term. The samples with the age of 90 days are immersed in NaCl solution with the concentration of 165 g/l during 90 and 230 days. At the end of the natural diffusion test, the specimens were removed from the saline solution. In order to measure the free-chloride concentration profile in the tested specimen, different 3-mm slices of concrete (with the precision of 0.2 mm) were cut from the unsealed surface using fully automatic device manufactured in this study (Fig. 11).

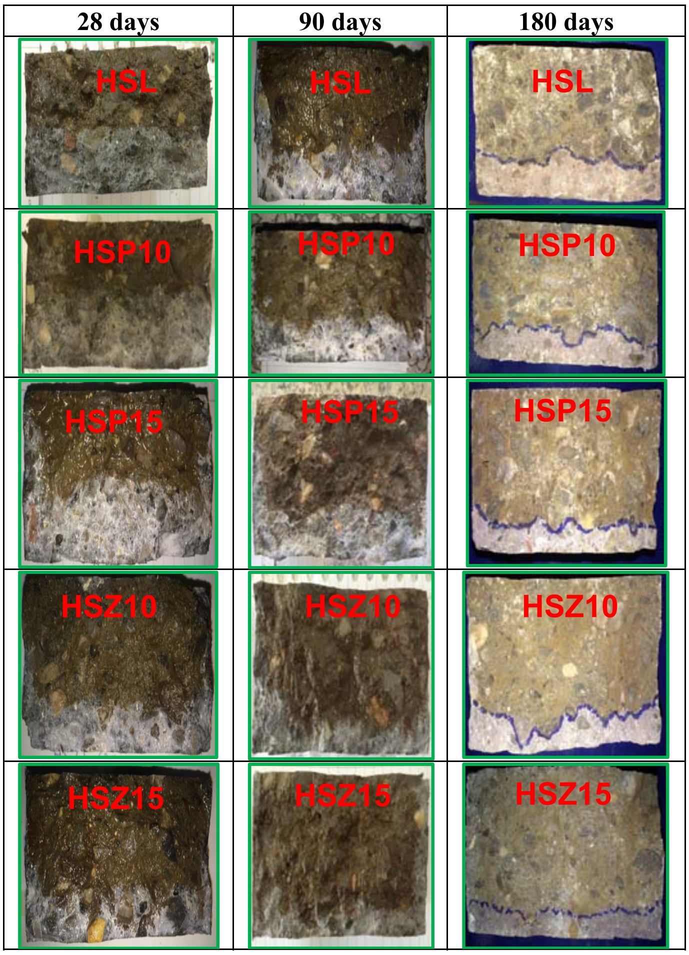


Fig. 9 Chloride penetration depth after RCMT test in the different studied HSSCCs at 28, 90, and 180 days of aging

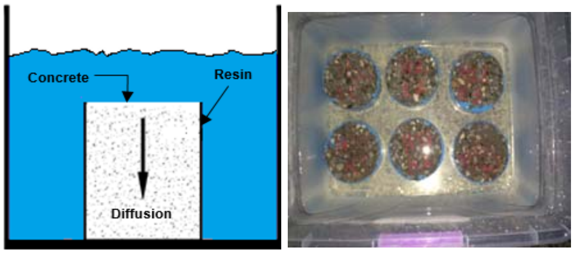


Fig. 10 Illustrations of the used immersion test according to ASTM C 1543-02

Fig. 11 The used devise to obtain concrete powder samples at different depth from the exposure surface [12]

The depth of penetration of chloride ions was measured using $AgNO_3$ solution. The diffusion coefficient is then deduced using the formula proposed by [13]:

$$D_{ns\,(dif)} = \frac{x^2}{4t} \tag{1}$$

where Dns (dif) is the apparent diffusion coefficient of chloride ions in the saturated condition (m2/s), x is the depth of penetration of chloride ions (m), and t is the immersion duration of the specimens in the saline solution (s).

The results relative to the depth of penetration and to the coefficient of chloride diffusion are illustrated in Figs. 12 and 13, respectively. As shown in Fig. 12, the depth of penetration of chloride ions in all HSSCCs increased by increasing the duration of immersion in saline solution. For 90 and 230 days of immersion, the depth of chloride penetration in all HSSCCs containing pozzolan is less than control concrete. This fact is more significant by increasing the percentage of pozzolan. The HSSCC containing 15% of zeolite shows the best performance in comparison with the other formulations. According to Fig. 13, the same conclusions can be done for the different coefficients of the different mixtures. HSSCCs containing pozzolan show remarkable improvement on reducing the coefficient of diffusion compared to that of control mixture.

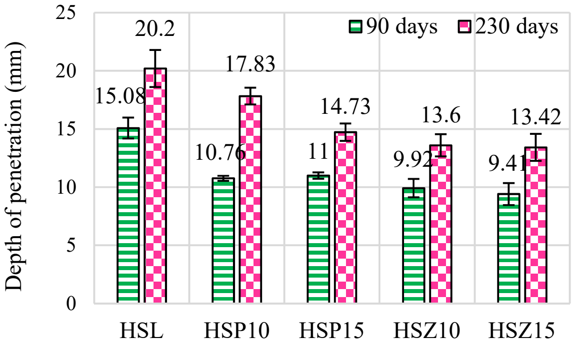


Fig. 12 Depth of chloride ions penetration in the studied HSSCCs at 90 days of aging after 90 and 230 days of immersion in saline solution

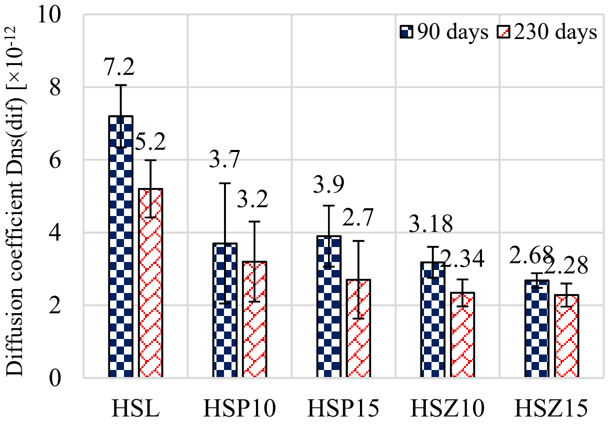


Fig. 13 Chloride diffusion coefficient in HSSCCs at 90 days of aging after 90 and 230 days of immersion in saline solution

The chloride ions exist in concrete in two forms: free chloride and binding chloride. The binding chloride can be found in the form of a complex salt such as calcium monochloroaluminate hydrate, it can be also fixed on C-S-H. It is assumed that this bound chloride cannot initiate corrosion. However, the free chloride ions which are highly mobile have a key role in the corrosion of reinforcement. The free chloride content is usually determined by measuring water-soluble chloride content. In this study, only free chloride content will be considered and analyzed. The water soluble chloride content was measured on concrete powders obtained from the exposure surface using the device illustrated in Fig. 11. The results of water-soluble chloride profile are plotted in Fig. 14, and it is indicated that, comparing to control mixture, HSSCCs with natural pozzolan present lower chloride penetration depths with a value between 30 mm and 33 mm for a control mixture, between 27 mm and 30 mm for HSSCC with 15% of pumice and between 18 mm and 21 mm for HSSCCs with zeolite and HSSCC with 10% of pumice. This in turn means that, the pozzolanic reaction of pumice and zeolite leads to a lower permeability and consequently to lower chloride ingress into the concrete. This effect is more significant when using zeolite. The chloride penetration depths deduced from water-soluble chloride profiles are higher than those measured using a colorimetric method based on $AgNO_3$ solution. This can be explained by the less sensitivity of the colorimetric method to the low values of chloride content and likely to the possible ingress of chloride into sound zone of the sample during the conservation time between the end of the diffusion test and the measurement of water soluble chloride. In terms of water soluble chloride content, control HSSCC exhibited a higher value from 6 mm from the exposure surface. This can be explained by the higher capillary absorption of the control concrete compared to mixtures with pozzolan at 90 days of aging. Higher capillary absorption suggests higher connected porosity and consequently higher free chloride content in the concrete.

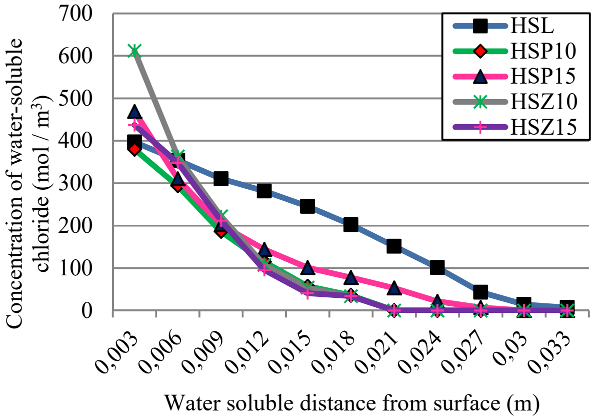


Fig. 14 Water-soluble chloride penetration profile in the different studied HSSCCs

D. Electrical Resistivity

Electrical resistivity is one of durability indicators of cementitious material. Usually, a high electrical resistivity is correlated to high resistance to chloride penetration and consequently high resistance to corrosion. In this study, electrical resistivity was measured on three 100×200 mm cylinders per mixture at the ages of 28, 90, 180 and 365 days according to FM 5-578 method. The results of electrical resistivity for the different mixtures are presented in Fig. 15, and it clearly shows the significant influence of zeolite on the increase of the electrical resistivity at the different tested ages of 28, 90, 180, and 365 days. At the age of 28 days, the electrical resistivity of mixture with 15% of zeolite is 2.8 times higher than the one of the control mixture. The substitution of 10% and 15% of Portland cement by pumice also increases the electrical resistivity of the concrete; this increase is observed at 90 days of aging onward showing the benefic effect of this natural pozzolan too. However, zeolite seems to have higher effect on the increase of the electrical resistivity. This can be related to its pozzolanic reaction leading to dense microstructure and a lower concentration in OH- in pore solution, ultimately increasing electrical resistivity and enhancement durability of concrete against chloride ingress.

According to Fig. 15, aging has a benefic influence on the increase of electrical resistivity which is expected due to the continuous hydration of the binder. However, this increase is more important when pumice and zeolite pozzolan are used. It is also higher with 15% of pozzolan compared to 10% of pozzolan.

The electrical resistivity in concrete is increased when chloride migration coefficient decreased. This can be clearly observed in Fig. 16. These results about the increasing effect of natural zeolite on electrical resistivity are in agreement with the research work done by Ahmadi and Shekarchi [4] and Feng and Peng [8].

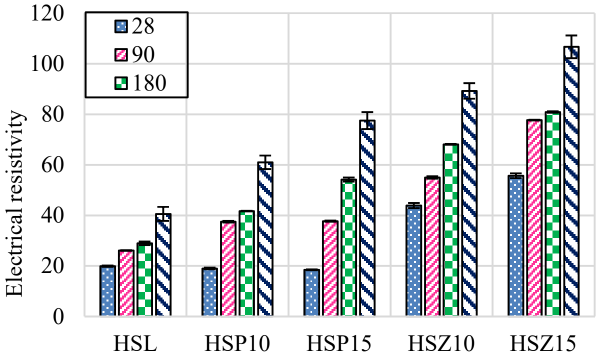


Fig. 15 Evolution of the electrical resistivity with curing time

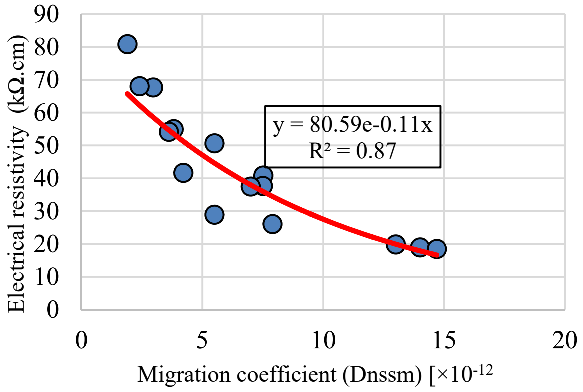


Fig. 16 Evolution of the electrical resistivity according to migration coefficient

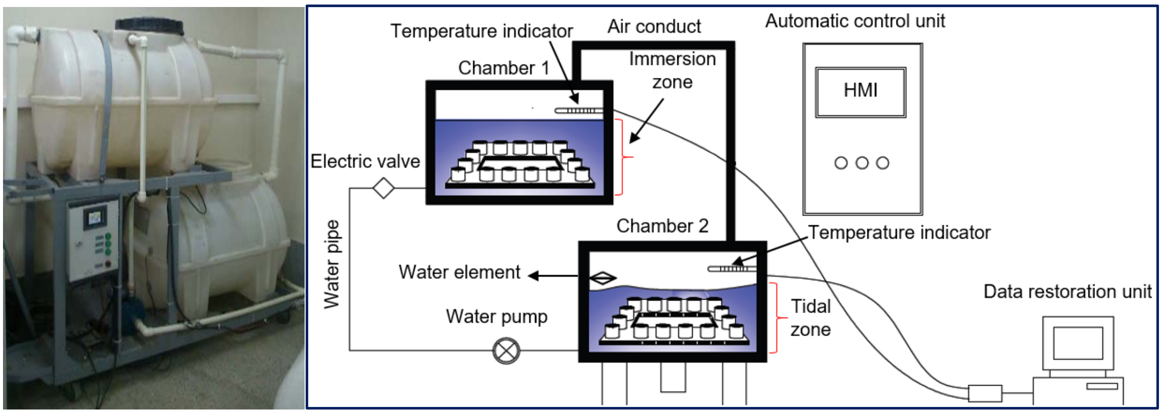


Fig. 17 Apparatus used to simulate chloride ion ingress in immersion and tidal zone [12]

E. Resistance to Chloride Penetration in Marine Environment

To evaluate the resistance to chloride penetration of the studied HSSCCs in marine environment, two different exposure zones are considered and experimentally simulated: tidal zone and immersion zone. Immersion conditions were simulated by a total immersion of SCCs samples in saline solution. Tidal conditions were simulated by imposing wetting and drying cycles. Fig. 17 presents the apparatus manufactured in this study to simulate immersion and wetting drying tests. In chamber 2 (Ch.2), by using a water pump and electric valve, saline water was pumped and drained from chamber 1 (Ch.1) every 6 h to simulate tidal conditions. The test was carried out on slices of cylinders at 430 days of aging with dimensions of 100×50 mm (three samples per formulation). All surfaces of samples are sealed except one, the upper surface by which chloride diffusion will ingress in order to ensure a one-dimensional penetration of chlorides. The samples sealed by resin are saturated in lime water for almost a week (up to arrival at the constant mass). The concentration of the saline solution prepared for tidal and immersion medium is identical and equal to 50 g/l. The duration of this test for both immersion and tidal conditions is fixed to 90 days in this study. At the end of the test, the depth of penetration of chloride ions was determined by spraying $AgNO_3$ solution with the concentration of 0.1 M on split surfaces. The results are given in Fig. 18 and illustrated in Fig.19. The chloride penetration depth in all the mixtures is higher in tidal conditions compared to immersion conditions due to the concrete surface drying. Its value for HSL, HSP10, HSP15, HSZ10 and HSZ15 is respectively, 1.1, 1.11, 1.04, 1.13 and 1.27 times higher in wetting – drying conditions compared to saturated conditions. This increase in chloride penetration should be higher in more severe drying conditions like in the case of the presence of wind and sun. Compared to control HSSCC, mixtures with natural pozzolan exhibit higher resistance to chloride ingress both in immersion and tidal conditions, showing the beneficial use of pumice and zeolite.

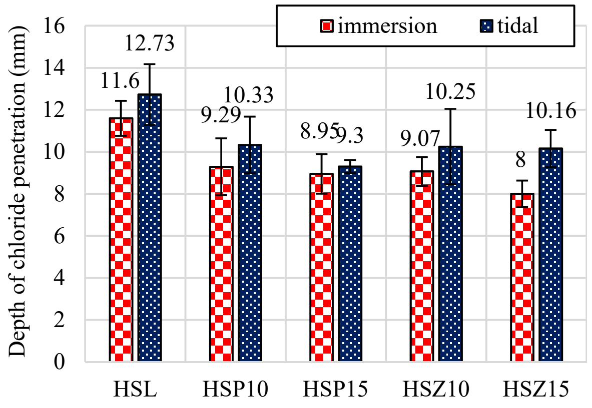


Fig. 18 Depth of chloride ions penetration in HSSCCs at age of 430 days after 90 days of immersion and tidal in saline solution

V. CONCLUSIONS

The main results of this study are presented as follows:

1) Pumice but more zeolite, enhances the viscosity and demand in superplasticizer; this demand increases with increasing the percentage replacement of pozzolan.
2) There is a close relationship between different transport properties such as chloride diffusion coefficient, electrical resistivity, capillary absorption and profoundness of water penetration.
3) The depth of penetration of chloride ions in all mixtures is more important in tidal condition compared to that of the immersion condition. However, compared to control mixture, mixtures with natural pozzolan exhibit higher resistance to chloride penetration both in immersion and tidal conditions. Zeolite pozzolan gives better performances compared to pumice.

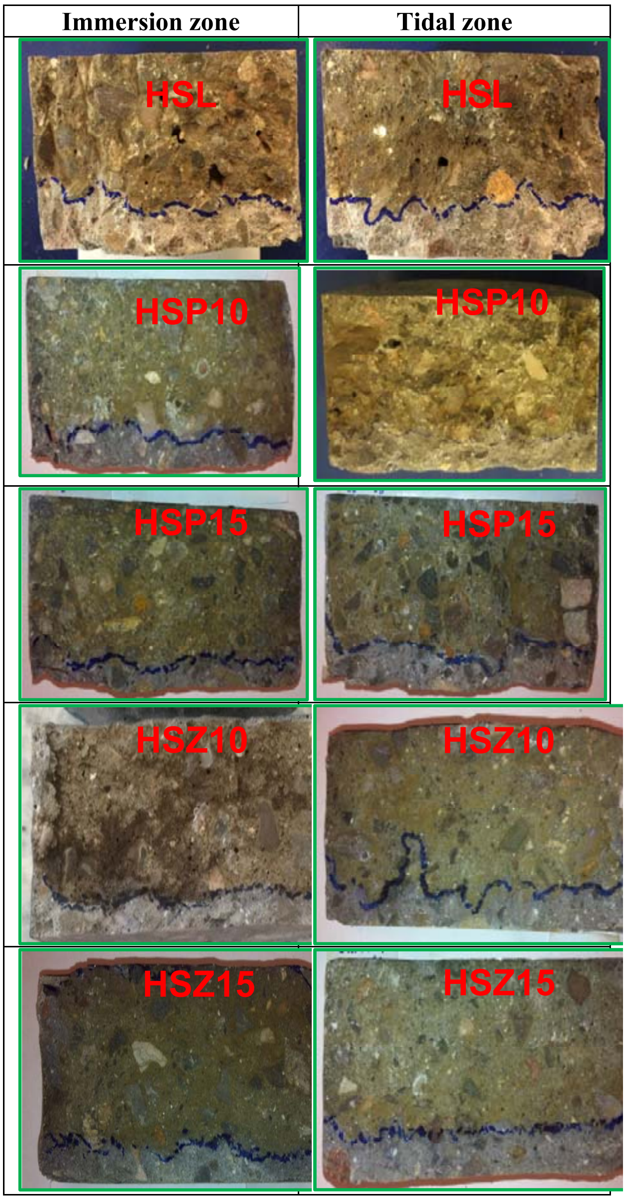


Fig. 19 Chloride penetration depth of HSSCCs samples after 90 days of test highlighted using $AgNO_3$ solution, left): in immersion condition, right): in tidal condition

4) Taking into account all the results, the partial substitution of OPC by 15% of pumice or 10% of zeolite is affordable for all aspects including economic and environmental issues. An improvement in the mixture design when using zeolite by the use of other type of superplasticizer should be an interesting way to maintain good durability properties without decreasing the mechanical strength.

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