International Journal of Architectural, Civil and Construction Sciences
ISSN: 2415-1734
Vol:12, No:3, 2018

Resistance to Sulfuric Acid Attacks of Self-Consolidating Concrete: Effect Metakaolin and Various Cements Types

Kianoosh Samimi, Farhad Estakhr, Mahdi Mahdikhani, Faramaz Moodi

***Abstract*—**Due to their fluidity and simplicity of use, self-compacting concretes (SCCs) have undeniable advantages. In recent years, the role of metakaolin as a one of pozzolanic materials in concrete has been considered by researchers. It can modify various properties of concrete, due to high pozzolanic reactions and also makes a denser microstructure. The objective of this paper is to examine the influence of three type of Portland cement and metakaolin on fresh state, compressive strength and sulfuric acid attacks in self- consolidating concrete at early age up to 90 days of curing in lime water. Six concrete mixtures were prepared with three types of different cement as Portland cement type II, Portland Slag Cement (PSC), Pozzolanic Portland Cement (PPC) and 15% substitution of metakaolin by every cement. The results show that the metakaolin admixture increases the viscosity and the demand amount of superplasticizer. According to the compressive strength results, the highest value of compressive strength was achieved for PSC and without any metakaolin at age of 90 days. Conversely, the lowest level of compressive strength at all ages of conservation was obtained for PPC and containing 15% metakaolin. According to this study, the total substitution of PSC and PPC by Portland cement type II is beneficial to the increasing in the chemical resistance of the SCC with respect to the sulfuric acid attack. On the other hand, this increase is more noticeable by the use of 15% of metakaolin. Therefore, it can be concluded that metakaolin has a positive effect on the chemical resistance of SCC containing of Portland cement type II, PSC, and PPC.

***Keywords*—**SCC, metakaolin, cement type, durability, compressive strength, sulfuric acid attacks.

I. Introduction

TODAY, verification of the durability of concrete is an important issue for the prevention of concrete degradation with respect to aggressive agents in the environment. The mix design of SCC is different from that of a normal concrete and therefore its durability characteristics are still uncertain. In this way, the study of the effective durability effects of SCC against aggressive agents is an important point on the life of concrete structures. The presence of acids such as sulfuric (H_2SO_4) and hydrochloric acids (HCl) usually originates in factories located in industrial areas, otherwise they are sometimes due to urban activities. Concrete infrastructure members can be degraded by the attack of sulfuric acid present in groundwater, such as chemical wastes generated by the oxidation of sulfur compounds (e.g., pyrite) in the embankment [1]. Concrete is a strongly basic medium with a pH of 13. In contact with an acidic medium with a pH of less than 7, the chemical equilibrium of the hydrates is destabilized. In the case of the different hydrates, the stability of the various hydrates is variable [2]. Thereby, portlandite is an element by high solubility which it is very sensitive to an aggressive attack indicating that the dissolution of the portlandite initiates for a pH below 12.5. In acid attack, the flux of transported ions will cause, on the one hand the dissolution of the hydrates previously formed and, on the other, the precipitation of the new compounds leading to the progressive degradation of the concrete [3]. The aggressiveness of the attack depends on the different elements such as the solubility of the salts formed due to the production of the acid-base reaction as calcium, aluminum, iron and magnesium salts, the aggressive acid species and the pH of the solution attack [4]. Mineral additions play an important role in the physical, mechanical, and chemical properties of cementitious composite. The use of cementitious additives modifies the nature and texture of hydrates [5]. The use of cementitious additives is for purpose to reduce the consumption of cement by contributing in a simple and economical way to solve the problems related to the environment. The cementitious additions interact with the cement paste in two forms:

- Hydraulic reaction: in this case, using the filler effect, the particle sizes improve the compaction of the mixture and thereby minimize the transport of fluid in the cementitious matrix.
- The pozzolanic reaction: A siliceous or alumino-siliceous compound reacts in the presence of water with the portlandite created during the hydration of the cement in order to form binder compounds (C-S-H).

The pozzolan influences the structure of the pores, not only because of the pozzolanic reaction, but also because they can infiltrate between the grains of cement and serve as nucleation points for the formation of hydrates. This generates a densification of the structure which leads to an improvement on the properties of the hardened cement paste at the level of

Kianoosh Samimi is with the Research and Development Service, Imen Rah Consulting Engineering Co., No7, 4th.St Khaled Eslamboli (vozara) Ave. Tehran, Iran (phone: 0098-21-88707051; fax: 0098-21-88707052; e-mail: samimi.kianoosh@imenrah.com).
Farhad Estakhr is with the Department of Civil and Engineering, Islamic Azad University, Marvdasht, Iran (e-mail: farestakhr@yahoo.com).
Mahdi Mahdikhani is with the Department of Engineering and Technology, Imam Khomeini international University, Noruzian Blvd., Qazvin, Iran (e-mail: mahdikhani@aut.ac.ir).
Faramaz Moodi (Research Assistant) is with the Department of Civil and Environmental Engineering, Amirkabir University of Technology, Hafez Ave, Tehran, Iran (e-mail: fmoodi@aut.ac.ir).

the mechanical and chemical resistances [3].

This paper investigates and compares the effect of three different cement (Type II Portland Cement, PSC, PPC) and artificial pozzolan such as metakaolin on rheological behavior, compressive strength and resistance to sulfuric acid attack of SCC at early ages and up to 90 days. For this purpose, first, different tests such as slump flow, L-box and sieve, were performed to study the fresh phase of SCC, and then mechanical testing was done on hardened states to evaluate the compressive strength of the different prepared mixtures. Finally, the tests concerning the resistance to sulfuric acid attack were also performed at 28 and 90 days aging in order to evaluate the durability properties with time including visual examination, effect of degradation on weight loss, compressive strength and volume variation.

II. Experimental Program

A. Materials and Mix Proportions

A SCC formulation based on Type II Portland Cement was chosen as control concrete. The same composition was used for the other two SCCs where the Type II Portland Cement was completely replaced by PSC or PPC. In addition, metakaolin was used as an additive with replacement of 15% by Type II Portland Cement, PSC, and PPC. In total, six SCCs were manufactured with a constant water to binder (W/b) ratio of 0.33 and a constant paste quantity of 600 kg/m^3. The gravel and sand contents of the mixtures were kept constant. Only one type of adjuvant was used during this study, a high range water-reducing admixture (HRWRA) based on chains of modified poly-carboxylate ether (PCE 180). The dosage of superplasticizer is experimentally determined from tests on fresh concrete to obtain a slump flow diameter of 685±25 mm for all SCCs. Table I shows the composition of the six SCCs studied and their designations. For all mix designs, the sand used is of granular class 0/4 of alluvial origin having a density of 2.5. In addition, gravel 6/12 from crushing siliceous rocks with a density of 2.58 and a water absorption coefficient of 0.62% is used in this study. Potable water was used for casting all concrete specimens.

TABLE I
MIXTURE PROPORTIONS OF CONCRETE

Composition (kg/m^3)	SCC II	SCC II + MK	SCC PSC	SCC PSC + MK	SCC PPC	SCC PPC + MK
Gravel 6/12	780	780	780	780	780	780
Sand 0/4	780	780	780	780	780	780
Type II Portland Cement	350	297.5	-	-	-	-
PSC	-	-	350	297.5	-	-
PPC	-	-	-	-	350	297.5
Lime stone powder	250	250	250	250	250	250
Metakaolin	-	52.5	-	52.5	-	52.5
Water	200	200	200	200	200	200
Superplasticizer	3.3	4.9	2.5	3.6	3	4
W/b	0.33	0.33	0.33	0.33	0.33	0.33

TABLE II
TEST RESULTS OF FRESH SCCS

Mix name	Slump flow Dia (mm)	L-box H2/H1	Sieve test Segregation (%)
SCCII	680	0.85	8.6
SCCII+MK	670	0.84	7.3
SCC PSC	710	0.89	9.9
SCC PSC+MK	690	0.87	8.7
SCC PPC	690	0.86	8.2
SCC PPC+MK	660	0.83	6.6

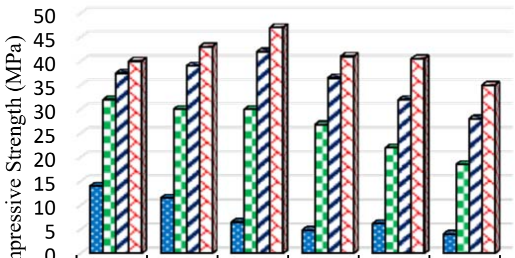
III. Results and Discussion

A. Fresh State

Table II presents the results of the performance tests carried out on the studied SCCs. The results show that the use of metakaolin reduces the fluidity of the mixture, certainly due to the large surface area of this admixture. Also, higher contents of superplasticizer were used. In fact, high open porosity and the irregular surface texture of metakaolin, associated with specific surface area, decreased the available water around particles and resulted in slump reduction. This finding is consistent with that of Paiva et al. [6] who found that using metakaolin decreased the workability of the traditional concrete and self-consolidating concretes, respectively. On the other hand, the use of metakaolin seems to improve the resistance of the SCC to the segregation compared to the cements used. In addition, the use of PSC and, to a lesser measure, PPC requires lower contents of superplasticizer.

B. Compressive Strength

Compressive strength of HSSCC mixes (fc) was measured on a total of 90 cubes of 100×100 mm at 1, 7, 14, 28, and 90 days of aging after curing in saturated lime solution at room temperature (22±2 °C) in accordance with BS 8110: part1: 1997. The evolution of the compressive strength (Rc) as a function of time and the nature of the binder is shown in Fig. 1. The results show that, the metakaolin used seems to produce lower compressive strengths compared to the control SCC. On the other hand, as of 28 days, Rc of SCCI + MK (39 MPa) exceeds that of the control SCC (38 MPa) and continues its increase. This can be explained by the pozzolanic reactivity of the MK on the one hand and by its accelerating effect of the hydration of clinker by nucleation effect on the other hand. For SCCs based on PSC and PPC, the low values of compressive strength at young ages can be explained by the slow hydraulicity and pozzolanicity of slag and fly ash. These results confirm the latent property of hydration of cements containing fly ash and slags.



	SCC II	SCC II+MK	SCC PSC	SCC PSC+ MK	SCC PPC	SCC PPC+ MK
1	14	11,5	6,5	4,8	6,2	4
7	32	30	30	26,8	22	18,5
28	37,5	39	42	36,5	32	28
90	40	43	47	41	40,5	35

Fig. 1 Evolution of compressive strength, Rc, of SCC mixtures with curing time

C. Degradation in Sulfuric Acid

In this study, the immersion test was selected to evaluate the strength of SCCs used in different applications such as foundations, walls, floors, pipes, etc. in the chemical attack by sulfuric acid [1]. The test specimens were immersed in jars filled with equal quantities of 5% sulfuric acid solutions. Each formulation has its own container of aggressive solution (see Fig. 2). This is to provide acidic environments similar to each formulation. Six containers each having a capacity of about 20 liters were used. Sulfuric acid with a concentration of 98.5% was used to prepare the aggressive solution with the concentration of 5%. The pH levels of the acid solutions were monitored at an average interval of 2 days with a portable pH meter. At the beginning of every week, the solution was renewed with a new solution with the same initial concentration (5%), but the maximum pH threshold was set to 1.0 until the end of the test. The test program was concluded after about 8 weeks when some of the test specimens completely disintegrated in the acid solutions. There is currently no standardized procedure for testing the resistance of concrete to sulfuric acid attack. However, ASTM C 267, 1997 provides general guidelines for testing the chemical resistance of mortars and polymer concretes.

Samples were extracted weekly, rinsed three times with tap water to remove the bulk reaction products and left to dry at 20 °C and 50% RH for 30 minutes before weighing and visual inspection. The test was performed on samples of SCC aged 28 and 90 days. The tested samples are cubic (7x7x7 cm^3). Four samples are used per formulation. The resistance of the samples immersed in the sulfuric acid solution was evaluated visually, physically (variation of weight), mechanically (variation of compressive strength) and also chemically (variation of volume).

Fig. 2 Samples of the concrete immersed in the solution of H_2SO_4 acid

- Visual examination

Fig. 3 shows that the state of the samples of all concretes studied before test and after 4 and 8 weeks of immersion in the aggressive solution of 5% H_2SO4 after washing and cleaning the white layer produced on the outside of the surface of sample. This layer is fragile and easily washed. From these figures, a visible degradation can be observed in all of the concrete samples. SCC I concrete presents the highest degradation. The alteration of the samples is presented by loss of aggregates in all surfaces exposed to sulfuric acid. SCCs containing pozzolan more or less retained their cement paste on the surfaces, while for concrete, SCC I, the paste on the all side of the sample was dissolved.

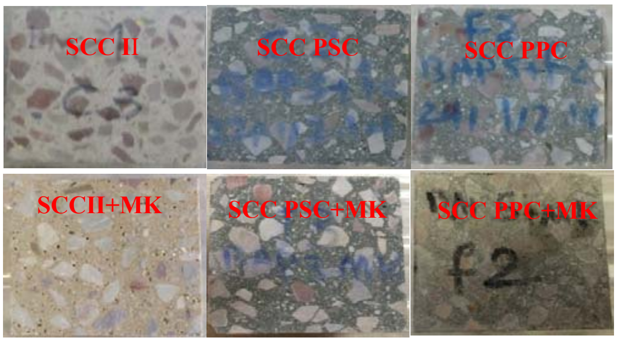


Fig. 3 The visual appearances of specimens before test exposure to sulfuric acid solution at age of 90 days of cure

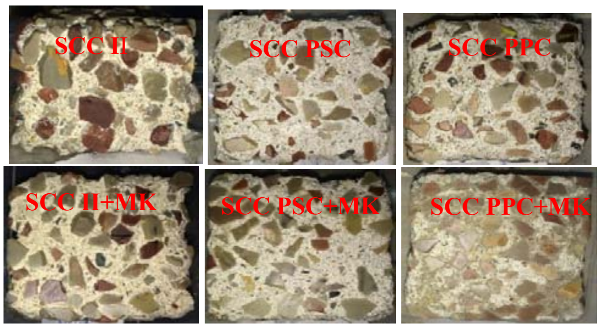


Fig. 4 The visual appearances of specimens after 4 weeks exposure to sulfuric acid solution at age of 90 days of cure

Fig. 5 The visual appearances of specimens after 8 weeks exposure to sulfuric acid solution at age of 90 days of cure

- Variation of weight

The variation of weight of each specimen is calculated from the following equation:

$$\Delta M\% = [\frac{(M0 - Mi)}{M0}] \times 100$$

with ΔM: Variation of weight in (%); M0: The mass of the specimen before exposure to acid attack in g; Mi (i = 1, 2, 3, …, 8): The mass after 1, 2,..., 8 weeks of attack in g.

- Result after 28 days of conservation:

The results relative to the variation of weight the concretes aging of 28 days and immersed in the 5% H_2SO_4 solution are presented as a function of immersion time in Fig. 6.

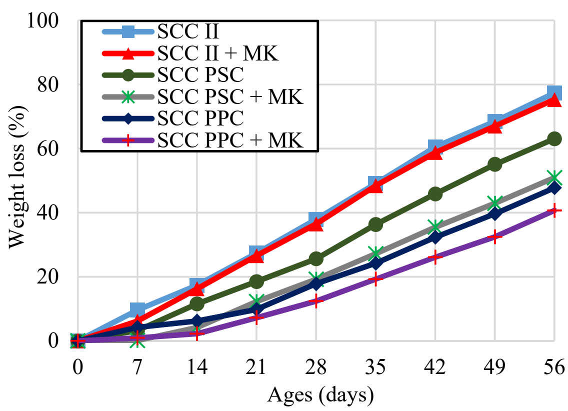


Fig. 6 Weight loss of different SCC aging of 28 days and immersed in H_2SO_4

The results in Fig. 6 show a better resistance for SCCs containing PSC and PPC compared to the control concrete. This fact is more sensitive by using of PPC. According these results, the weight loss of the SCC with metakaolin is lower than that of the concrete without metakaolin. And this is for the all periods of immersion in the sulfuric acid. After 8 weeks of immersion in the sulfuric acid solution, the weight loss for the different SCCs studied is equal to 77.3, 63.1, 47.8, 75.3, 50.9 and 40.7 for SCCI, SCCIII, SCCV, SCCI+MK, SCCIII+MK and SCCV+MK respectively. The weight loss after 8 weeks of immersion for SCCI is 1.23, 1.62, 1.03, 1.52, and 1.9 times higher compared to SCCIII, SCCV, SCCI+MK, SCCIII+MK and SCCV+MK, respectively.

- After 90 days of conservation:

The results relative to the variation of weight of the concretes aging of 90 days and immersed in the 5% H_2SO_4 solution are presented as a function of immersion time in Fig. 7.

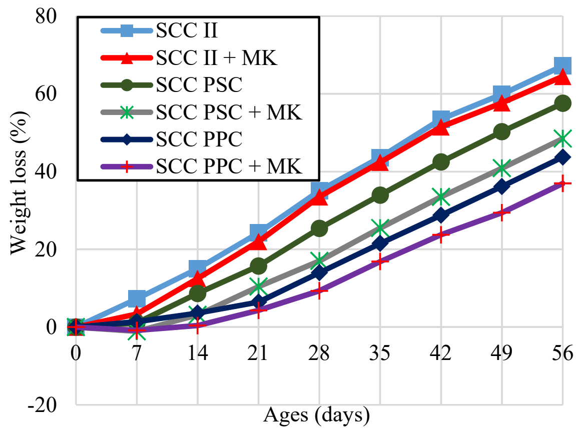


Fig. 7 Weight loss of different SCC aging of 90 days and immersed in H_2SO_4

At age of 90 days, after 8 weeks of immersion, a weight loss of 67.2% was observed for SCCI against 57.5, 43.7, 64.5, 48.5, and 36.9% respectively for SCCIII, SCCV, SCCI+MK, SCCIII+MK and SCCV+MK. From Figs. 6 and 7, it can be seen that the weight loss curve in all SCC at the age of 90 days generally follows the same tendency as that found for the SCC at the age of 28 days. The behavior of SCCI and SCCI+MK at age of 28 and 90 days is very similar. The difference between these SCC is relatively low.

The sulfuric acid resistivity of SCC specimens represents moving ions in pore solution. Therefore, the relationship between sulfuric acid resistivity and diffusion test is reasonable. The results show that sulfuric acid resistivity of all specimens was lower after 56 days of immersion. The degree of concrete deterioration is increased by time of exposure to sulfuric acid. In addition, the rate of concrete deterioration along the penetration depth of sulfuric acid could be described by a variation in chemical properties of cementitious paste. For instance, the sulfuric acid deterioration of Type II Portland Cement after 8-week immersion at the age of 90 days was 67.2 %. Nonetheless, using PPC and 15% of metakaolin decreased sulfuric acid deterioration values by 36.94%.

From Figs. 6 and 7, it is found that the SCCs with metakaolin resist well, as least compared to the control SCC with respect to the acid attack H_2SO_4. A more significant difference is observed for SCCs with PPC compared to the control SCC. The reason of less amount weight loss in SCC containing cement pozzolanic or metakaolin can be explained because, due to pozzolanic reactions, the amount of first sensitive effect such as Ca $(OH)_2$ against to acid attack is lower. On the other hand, the reduction of the diffusion and the densification of the microstructure are two very important effects for this improvement. Also, the decisive effect concerning good behavior in SCCs containing PPC may be due to the residual anhydrous grains on the degraded surface.

- Variation of compressive strength

After 4 and 8 weeks of immersion in the acid solution, two specimens of each formulation were used to determine the compressive strength (ASTM C 267, 1997). The percentage of variation of the compressive strength is calculated according to the following equation:

$$\Delta Rc\% = [\frac{(Rc0-Rci)}{Rc0}] \times 100$$

with ΔRC: Variation of compressive strength in (%); RC0: The compressive strength before immersion, in (MPa); RCi (i= 4 and 8 weeks): The compressive strength after 4 and 8 weeks of immersion, in (MPa).

It is particularly difficult to speak of resistance loss due to H_2SO_4 attack because the highly altered surface does not allow having a plane section which is well defined. Also, the receding surface due to the dissolution of material and the loss of aggregates as well as the precipitation of ettringite in the matrix makes it difficult to evaluate the results in terms of strength. The percentages of strength loss in compression at the age of 28 and 90 days of cure due to degradation by sulfuric acid are given in Table III. According to Table III, the duration of degradation increases resistance loss by compression for all the SCC studied. This loss is significant and reaches the totally degraded state at 56 days of degradation for all SCC at the age of 28 days. This loss is identical for the same concrete after 90 days of curing except for SCCV and SCCV+MK. Generally, a positive effect of the duration of curing on the strength loss in compression is found for the six SCC studied.

According to the results presented relative to mass loss and compressive strength loss in SCC I and SCC I + MK, there is a direct relationship between two last characters for these concretes. On the other hand, despite a greater weight loss in the SCC without metakaolin compared to the SCC with metakaolin, it presents less loss in terms of compressive strength. This fact can be justified because a protective layer can be created in a mixture containing metakaolin, and the diffusion of sulfuric acid in the core of concrete decreases. Then, the amount of weight loss in mixture containing metakaolin is lower compared to that in SCC without metakaolin. On the other hand, this layer is naturally more fragile, so the amount of loss by compression strength in SCC with metakaolin is higher compared to that in SCC without metakaolin. According to the result, relative to the physical and mechanical study in this paper, compressive strength loss is not a determining factor for assessing the rate of degradation by H_2SO_4 attack. In this manner, Fig. 8 shows that there is not a close relationship between weight loss and compressive strength loss of SCCs studied with respect to sulfuric acid attack.

TABLE III
MECHANICAL RESISTANCE LOSS COMPARED TO THE INITIAL VALUES BEFORE IMMERSION IN THE H_2SO_4 SOLUTION

	28 days		90 days	
Concrete	4 weeks of immersion	8 weeks of immersion	4 weeks of immersion	8 weeks of immersion
SCC II	74.7	degraded	71.77	degraded
SCC II +MK	64.95	degraded	62.15	degraded
SCC PSC	59.51	degraded	57.31	degraded
SCC PSC + MK	65	degraded	62.2	degraded
SCC PPC	64.3	degraded	58.3	77.63
SCC PPC + MK	69.44	degraded	63.04	80.24

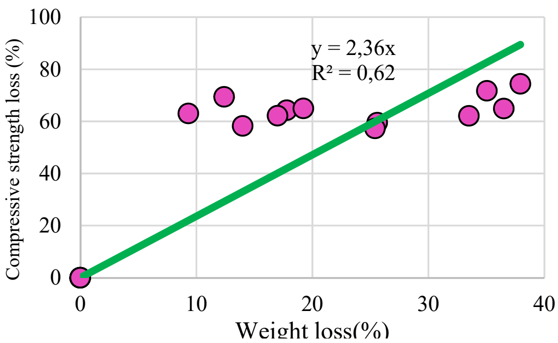


Fig. 8 Variation of compressive strength loss as a function of weight loss during 8 weeks of immersion at the age of 28 and 90 days of cure

- Variation of volume

At the age of 28 and 90 days, after 4 and 8 weeks of immersion in the acid solution, two specimens of each formulation were used to determine volume loss. Fig. 9 shows the manner of volume loss of specimen by acid attack at the age of 28 and 90 days.

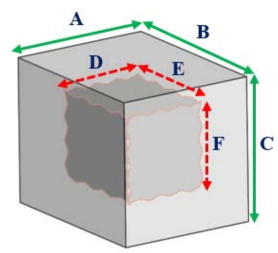


Fig. 9 The manner of volume loss of specimen by acid attack

The volume loss of each specimen is calculated from:

$$\textbf{\textit{Volume loss (\%)}} = [\frac{(V0-Vi)}{V0}] \times 100$$

with: V0: The volume of the specimen before exposure to acid attack in cm^3 (A×B×C); Vi (i = 4 and 8): The volume after 4 and 8 weeks of attack in cm3 (D×E×F).

The results relative to the volume variation of samples immersed in the sulfuric acid solution after 4 and 8 weeks of immersion at 28 and 90 days of cure are presented in Figs. 10 and 11.

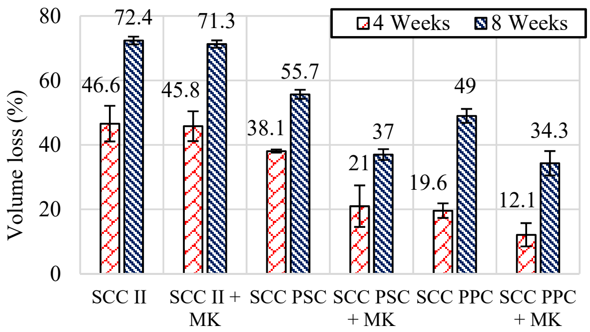


Fig. 10 Volume loss of SCC at the age of 28 days after immersion in 5% H_2SO_4

Fig. 10 shows that, after 8 weeks of immersion in the acid, a significant degradation of the volume causing a decrease of this volume is observed in contact with the aggressive medium. The maximum value and minimum value of the volume loss is equal to 72.4% and 34.3% for SCCI and SCCV+MK, respectively.

For results relative to the age of 90 days of cure illustrated in Fig. 11, a significant difference is also observed between the volume loss after 4 weeks of immersion and the volume loss after 8 weeks of immersion. For SCC based on pozzolans, the volume loss is lower compared to that of the control SCC.

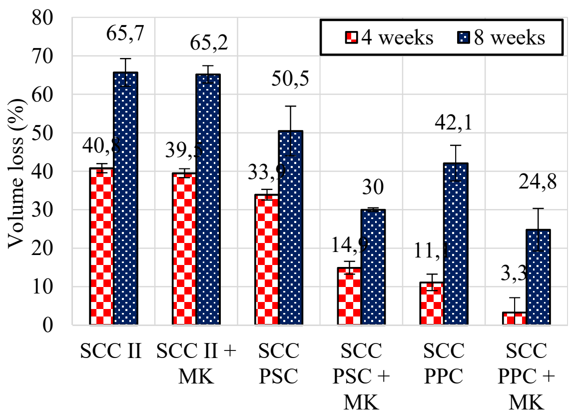


Fig. 11 Volume loss of SCC at the age of 90 days after immersion in 5% H_2SO_4

IV. Conclusions

The main results of this study are presented as follows:

1) Metakaolin can have rheological effects on the workability of SCCs. The performance of SCCs mixture decreased according to 15% metakaolin content.
2) The compressive strength in SCC containing of Type II Portland Cement with metakaolin is higher compared to that in relative to SCC without metakaolin from 28 days of age. On the other hand, the samples containing PSC and PPC with metakaolin had a lower compressive strength than plain samples.
3) As can be seen in the results, due to the densification of the paste microstructure, the highest level of sulfuric acid resistivity was observed at PPC and metakaolin.
4) Taking into account all the results, the use of PSC and PPC as total replacement instead of Type II Portland Cement and also the partial substitution of various cement by 15% of metakaolin is affordable for durability aspect with respect to attack of sulfuric acid.

Acknowledgment

The authors would like to specifically thank Mr. Rahmatolah Hakimi President of the Imen Rah Consulting engineers Company for the financial support of this research. The authors would like to thank Mr. Reza Moinie and Mr.Ghanbar Zamanpoor for its assistance with some laboratory measurements.

References

[1] Samimi K (2016) Contribution to the study of the durability of BAPs in aggressive environments: effects of natural pozzolans. Dissertation, France: INSA de Rennes.
[2] Mehta, P. K., Monteiro, P. J. M., « concrete: Structure, Properties and Materials», Englewood Cliffs, NJ; Prentice Hall, 548, 1993.
[3] Oueslati OLFA., «Durabilité des matériaux cimentaires soumis aux acides organiques, résistance chimique, mécanique et de corrosion», Thèse de doctorat, l'Université Laval, 2011.
[4] Lide D. R., Handbook of Chemistry and Physics, CRC Press, Inc., 72nd edition, 1991-1992.
[5] Baron J., Ollivier J. P., La durabilité des Bétons, Presses de l'école nationale des ponts et chaussées, Paris, 1992.
[6] Paiva H, Esteves L. P, Cachim PB, Ferreira VM. Rheology and hardened properties of single-coat render mortars with different types of water retaining agents. Construction and Building Materials. 2009 Feb 28;23(2):1141-6.