



Influence of Using Fly ash and Silica Fume on the Concrete Performance against Chloride Attack

Received 24 May 2022; Revised 24 August; Accepted 24 August 2022

M. Anwar¹
A. Shokir²
M. Omar³

Keywords

Ternary, Fly ash, Silica fume,
Fresh and Hardened
Properties, Concrete, Total,
Soluble, Chloride attack.

Abstract

This paper is part of a research project deals with the study of the possible use of by-product materials such as fly ash (FA) and silica fume (SF) with Ordinary Portland Cement (OPC) in ternary system in different applicable measured properties of concrete. In this research, six concrete mixtures with water/cement ratios 0.4 and 0.5 have been investigated. Trial mixes were carried out to produce concrete with same slump and air content percentage. Also, the influence of using fly ash and silica fume with Portland cement on the concrete performance against chloride attack has been studied. The potentiometric apparatus was used to measure the chloride concentrations through the concrete samples by titration chemical analysis. In addition, the diffusion coefficients were determined for the tested specimens. It is concluded that the addition of fly ash and silica fume to Portland cement in ternary system improved concrete resistance to chloride attack and reduced its diffusion coefficient as well as can be reasonably used in concrete industry with considerable proportions. Moreover, the change in the cementitious materials content, type and their replacement percent have significant effect in the studied properties of concrete. Furthermore, results show that the total and soluble chloride content for zone 10~20 mm and zone 20~30 mm are very low. This result leads that such type of concrete needs less concrete cover depth which leads to protect the reinforcement.

1. Introduction

Concrete is a durable construction material. Generally Concrete durability is defined as the concrete ability to resist severe conditions such as chemical attack, weathering action, abrasion and keeping its main required engineering properties. However, reinforced

¹ Professor, Construction Research Institute, NWRC, Delta-Barrage 13621, Egypt. maelsayedos@yahoo.com

² Researcher, Construction Research Institute, NWRC, Delta-Barrage 13621, Egypt. eng.samal212@yahoo.com

³ Researcher, Construction Research Institute, NWRC, Delta-Barrage 13621, Egypt. mohamed_omar@nwrc.gov.eg

concrete structures deteriorate when exposed to aggressive conditions and its durability are influenced by internal and external factors. In addition, damage due to deterioration of structures can vary depending on the degree of exposure to severe conditions. When concrete is exposed to aggressive actions such as chloride penetration, sulphate attack and carbonation, its strength is significantly affected [1].

The concrete resistance to chemical attack and abrasion or any process of deterioration was defined as the durability of hydraulic-cement concrete by ACI Committee 201.2R-2 [2]. The deterioration process occurs due to external or internal factors. The various actions can be physical, chemical, or mechanical. Mechanical destruction occurs due to impact, abrasion, erosion, or cavitation. The exposure to harmful chemicals and sea water are considered as one of the important causes of chemical deterioration in concrete structures. The sulfates and chlorides are the aggressive chemicals that affect durability of concrete structures. When the chloride attacked the concrete leads to increase porosity and decreasing strength and concrete stiffness. Magnesium, sodium, and calcium sulfates are causes of hazard-harmful to concrete [3]. Some studies found that chloride threshold limits should evenly be expressed in items of free (soluble) chloride content and the free chlorides are the main reason for the initiation of corrosion [4].

Some research studied the effects of chloride ion attack on the diffusion and durability of concrete structures [5]. The influence of chloride penetration and its change in concrete cover on corrosion probability was evaluated in that research [6]. The chloride ions penetration in concrete structures was described as a significant threat to the main engineering properties of concrete structures, especially, its durability. It has been revealed that corrosion takes place when the passive protective layer is destroyed by chloride ingress in structures constructed using reinforced concrete [7]. Therefore, to maintain long service life of concrete structures, it is required to design and construct using materials with high resistance to chloride penetration and has sufficient concrete cover. Supplementary cementitious materials have been used as replacement to cement materials in concrete industry for which now. Maintaining concrete properties in appropriate degree especially its durability needs more attention to resistance of concrete to chloride penetration. The replacement percent of cement content in concrete by supplementary materials shall depend on the reactivity of the pozzolanic and its efficiency with respect to durability aspects [8].

Concrete engineers and corrosion scientists have become polarized with respect to both chloride limitations and the significance of water-soluble chloride determinations. Marusin mentioned that [9] the corrosion threshold limit for soluble chloride ion concentration in normal weight reinforced concrete is about 0.03 percent by weight of concrete. Moreover, when chlorides penetrate the concrete and reach a concentration approximately equal to 0.2 percent of total chloride ions by weight of cement, corrosion will be initiated. Federal Highway Administration (FHWA) determined that approximately 75 percent of the total chlorides will be water-soluble chlorides. Thus, the American Concrete Institute (ACI) Committee 201 suggested a limit of 0.15 percent by weight of cement as the limit for water-soluble chlorides in conventionally reinforced concrete in a moist environment not exposed to chloride [10].

Y. Zhang and others [11] studied the roles of pore features in relative chloride diffusion coefficient of mortar specimens at various degrees of water saturation based on mercury intrusion Porosimetry and resistivity tests. The study resulted that the higher w/b ratio of OPC mortar has a larger chloride diffusion coefficient. It is also found that the role of pore structure in the diffusion coefficient - water saturation relationship is a result of its effect on the water continuity.

2. Experimental Program

Six concrete mixtures investigated in this research prepared with cementitious materials contents of 410, 330 kg/m³. The used sand/aggregate ratio was 0.4 and water/cementitious materials ratios were 0.4 and 0.5. Chemical admixtures were added to the mixtures to achieve slump of 10± 2 cm and air content of 4± 1%. Several trials have been carried out using air entraining agent (AE) and high-performance superplasticizer and high range water reducer agent includes air entraining effect (Ad) to obtain the required slump and air content of concrete. The silica fume was used as a partial replacement of used cement with 5% and 10% as well as fly ash with (25%) as listed in Table 1.

The slump, air content, and unit weight were measured for fresh concrete according to JIS A 1101[12], JIS A 1128 and [13] JIS A 1116[14], respectively. For hardened concrete, compressive strength (JIS A 1108[15]), dynamic elastic modulus (JIS A 1127[16]), and pulse velocity were measured at ages of 3, 7, 28, 90 and 180 days. The properties of used aggregates and cementitious blends as well as mixing details, casting, curing, and testing are available in Ref. [18].

Table 1: Details of Mix Proportions

Mix No	W/Cm	(Kg/m ³)			(%)		
		CMC	Ad	AE	OPC	FA	SF
1	0.40	410	3.895	1.025	100	0	0
2			3.690	3.280	70	25	5
3			3.690	2.050	65	25	10
4	0.50	330	3.960	1.155	100	0	0
5			3.300	2.805	70	25	5
6			3.465	2.640	65	25	10

W/Cm: water to Cementitious material ratio, CMC: Cementitious Materials content, Ad: High performance Superplasticizer and High range water reducer agent includes air entraining effect, OPC: Ordinary Portland Cement. AE: Air Entraining Agent, FA: Fly Ash, SF: Silica Fume. After 28 days of water curing, samples were submerged in 5% sodium chloride (NaCl) solution up to 5 months. The chloride ions contents, total and soluble, were measured using the titration analysis after immersion periods of one, three and five months ([JIS K 0113 17]). Chloride ingress can be measured directly by determining chloride contents as a function of position and time in concrete subjected to chloride environments, or indirectly through conductivity or resistivity measurements. The total chloride content is generally obtained by removing the chloride from a sample by titration analysis (using nitric acid). On the other hand, the water-soluble chloride content is determined by immersion of the sample in hot water. Furthermore, the diffusion coefficients were determined for the tested samples.

3. Fresh Concrete Properties

As mentioned above, the measured values of fresh concrete include slump, air content and unit weight; the values are listed in Table 2. The results of air contents were ranged from 3.3% to 4.3% and slump ranged from 9.0 cm to 11.0 cm. The resulted values of the unit

weight varied due to the change in the cementitious material content, type of by-products materials and its replacement percent as well as the dose of used chemical admixtures.

Table2: Measured Slump, Air Content and Unit Weight.

Mix No.	Slump (cm)	Air content (%)	Unit weight (t/m ³)
1	11.1	3.6	2.398
2	10.7	3.6	2.347
3	9.7	3.3	2.339
4	9.7	4.0	2.385
5	11.0	3.7	2.359
6	10.6	4.3	2.368

4. Hardened Concrete Properties

The obtained results of the hardened concrete are represented in Figs. 1 to 3. Generally, mixes 1, 2, and 3 of water/cementitious materials ratio of 0.4 and cementitious materials content 410 kg/m³ show better compressive strength than mixes 4, 5, and 6 of water/cementitious materials ratio 0.5 and cementitious materials content 330 kg/m³. Moreover, from results of Fig. 1, mixes containing FA and SF show increase in compressive strength with time. Furthermore, it noticed that compressive strength values for mixes containing FA and SF are relatively low compared to OPC mixes in the early ages but with time the compressive strength increasing (equivalent or higher than those of OPC mixes) after 28 days. This increase is due to the use of relatively high content of FA and the increase in silica fume content from 5% to 10%.

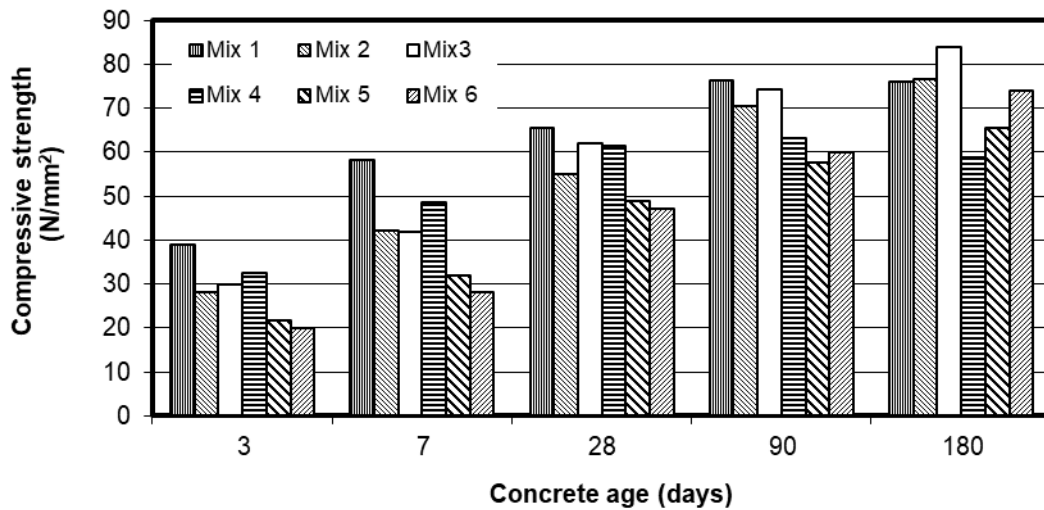


Fig. 1: Compressive Strength of Tested Mixes.

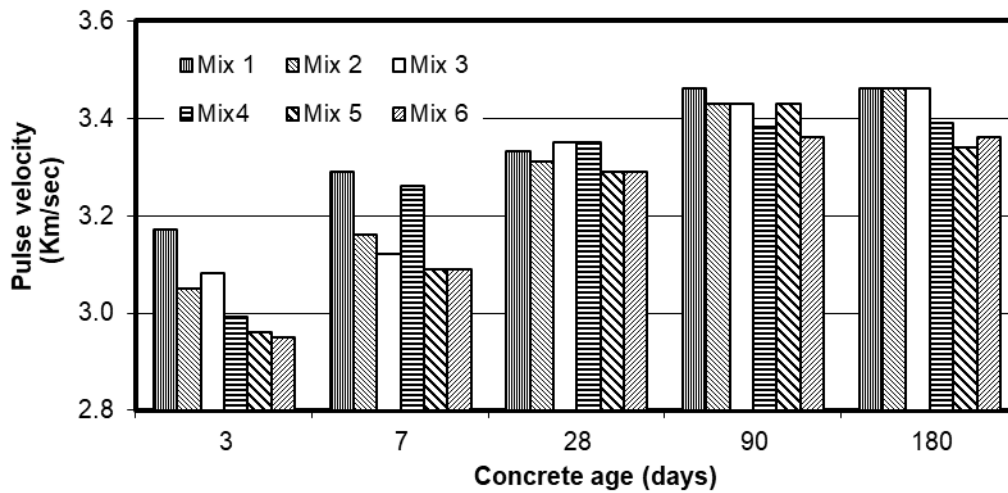


Fig. 2: Pulse Velocity of Tested Mixes.

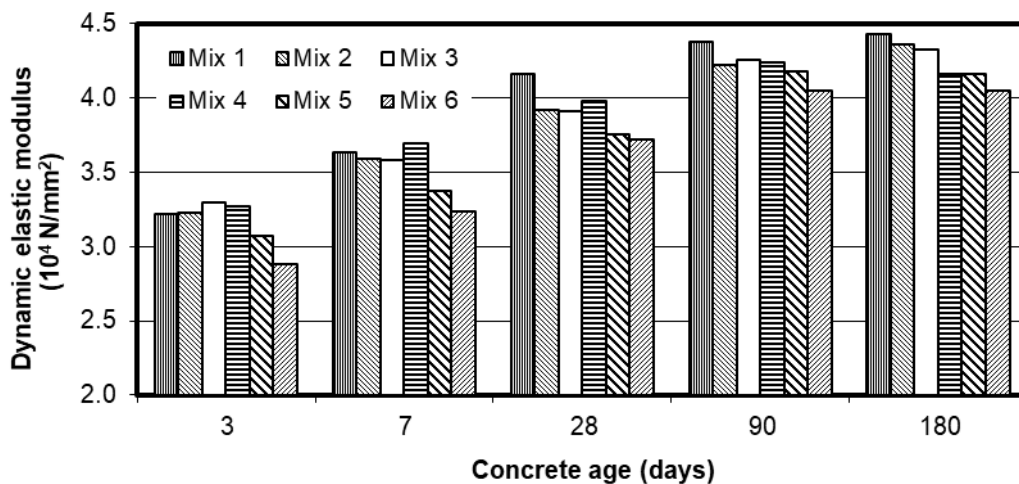


Fig. 3: Dynamic Elastic Modulus of Tested mixes.

Fig. 2 represent results of pulse velocity of the mixes containing FA and SF which is relatively low comparing to OPC mixes in the early ages. The measured pulse velocity results were slightly improved at age of 90 and 180 days. It is expected that pulse velocity values will be comparable or higher than those of OPC mixes with time. Moreover, Fig 3 shows the results of dynamic elastic modulus. The result of mixes 2 and 3 containing FA and SF is approximately equivalent to them of OPC mix at age of three days. Later, they showed relatively same or lower values than those of OPC one (mix1). Where, mixes 5 and 6 indicate lower dynamic elastic modulus than OPC one (mix 4) up to 28 days. Later, they showed improvement in the measured values but still lower than the OPC (mix 4). The same as mentioned with pulse velocity, it is expected that values of dynamic elastic modulus will be equivalent or higher than those of OPC mixes

Generally, values of measured pulse velocity and dynamic elastic modulus show almost the same trend as the measured compressive strength. In addition, as mentioned above with compressive strength, mixes 1, 2, and 3 of water/cementitious materials ratio of 0.4 and cementitious materials content 410 kg/m^3 show higher values of pules velocity and dynamic elastic modulus than those of mixes 4, 5, and 6 of water/cementitious materials ratio 0.5 and cementitious materials content 330 kg/m^3 .

5. Chloride Contents

Concrete specimens cured for 28 days, after which they were immersed in salt water (5% sodium chloride solution). For one, three and five months, the concentrations of chloride (total and soluble) measured. The obtained contents of total chloride are shown in Figs. 4 and 5 for the studied six mixes. While the soluble chloride contents are shown in Figs. 6 and 7. The results after 1, 3, and 5 months indicate that chloride contents decrease with the increase in the tested depth and measured values of depths 10~20 mm and 20~30 mm of Portland cement samples are higher than those of ternary cementitious blends samples.

The results after five months show that using fly ash with 5% of silica fume decrease the total and soluble chloride ion by about 40% and 50% respectively, while increasing silica fume to 10% decrease total and soluble chloride contents by about 55% and 60% respectively. The results of cementitious blends mixes show lower value of soluble/total chloride than the control mixes. Further, results indicate that there are no significant differences between soluble and total chloride ions for zone 10~20 mm and zone 20~30 mm.

From the measured values, it is possible to report that the use of cementitious blends results in the decrease the chloride concentrations (soluble and total) except the content of total chloride at depths 0~10 mm for mixes 4, 5, and 6 after one month. The rates of increase in chloride contents with time for OPC samples are greater than those of cementitious blends samples after 5 months. Further, the chloride contents at 5 months indicate that OPC samples showed higher values than those of the other studied mixes. Furthermore, results show that the values of both measured chloride concentrations (total and soluble) for zone 10~20 mm and zone 20~30 mm are approximately same and very low. The cementitious blends mixes showed lower soluble chloride contents. This result leads that such type of concrete needs less concrete cover depth which leads to protect the reinforcement.

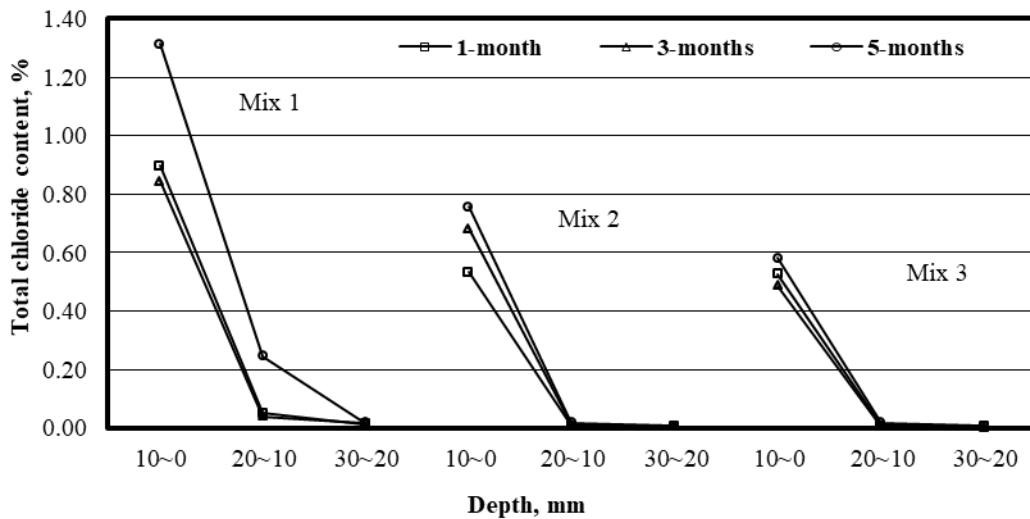


Fig 4: Profiles of Total Chloride Contents of Mixes 1, 2, and 3.

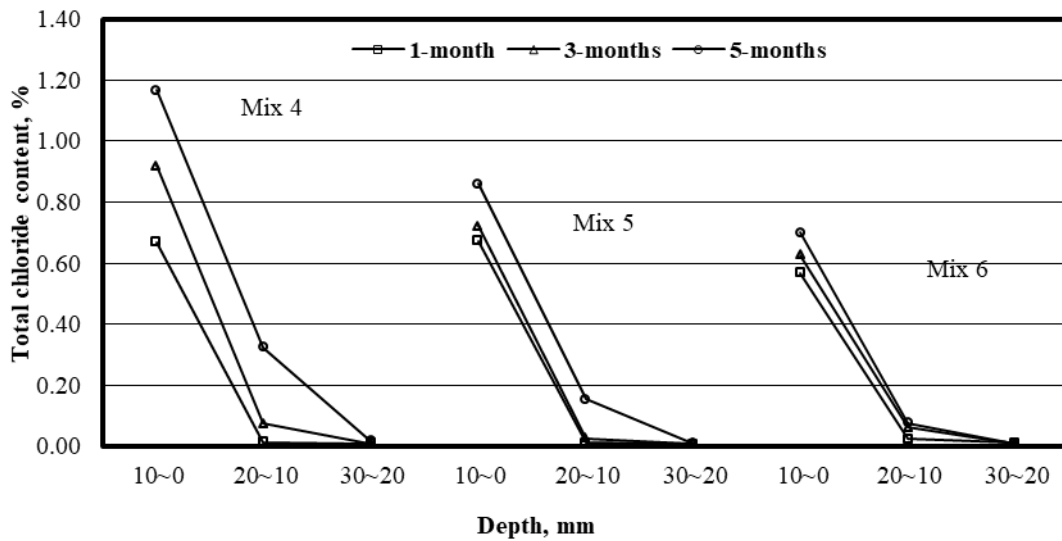


Fig 5: Profiles of Total Chloride Contents of Mixes 4, 5, and 6.

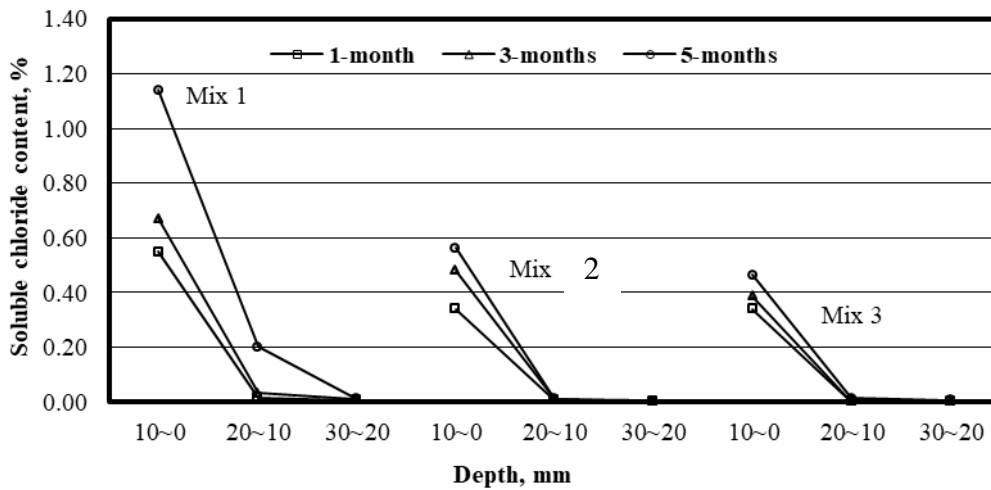


Fig 6: Profiles of Soluble Chloride Contents of Mixes 1, 2, and 3.

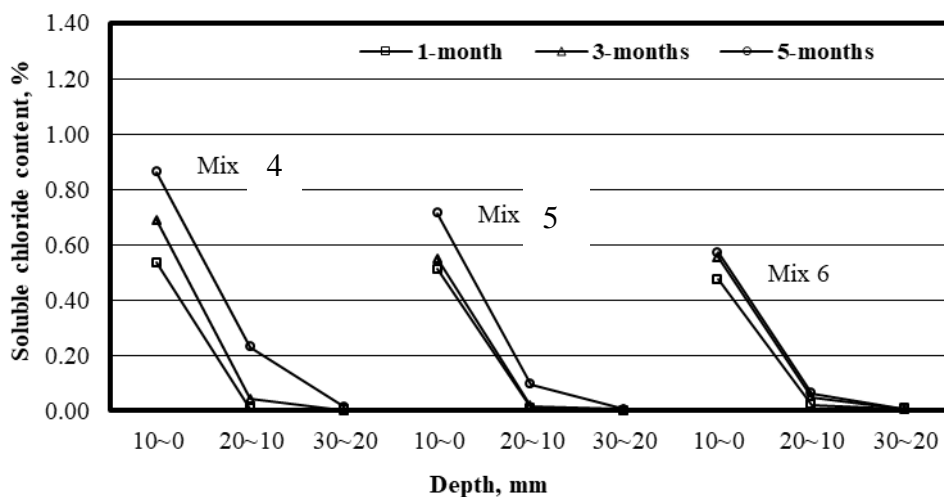


Fig 7: Profiles of soluble chloride contents of mixes 4, 5, and 6.

The obtained results display that with decreasing the water to cementitious ratio the chloride contents decreasing. This research results agreed with the research findings which verified that the greater the water/cementitious ratio of the concrete, the higher chloride content

values [19]. In addition, the obtained results of this study comply with the main findings of the research work [20], where the change in cementitious materials type and their replacement ratio affect the chloride contents and the lower water/cementitious materials ratio show lower chloride contents than those of high ratios. The results reported in the research [7] that chlorine showed clear diffusion profiles up to 10–20 mm depth, whereas ingress of sodium was limited to the outer 10 mm at the surface agreed with the main concept of this study.

6. Diffusion Coefficient

In marine environment, the chloride ions penetrate through the concrete by a solution diffusion process in which the solution in the pore water. Therefore, the diffusion coefficients of the studied concrete mixes were calculated using the measured total chloride contents and results are shown in Fig. 8. The method which used to calculate the diffusion coefficient was established by Japanese researchers and the details of such calculations are described in Ref. [21].

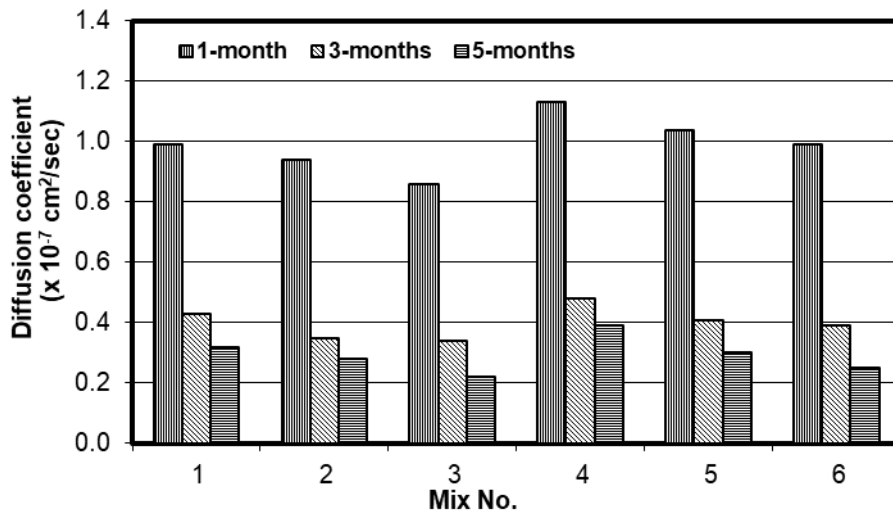


Fig. 8: Diffusion coefficient of tested concrete mixtures.

Results in Fig. 8 showed that diffusion coefficient values of the six mixes after one month are higher than those of the same mixes after 3 and 5 months. Moreover, mixes 1, 2, and 3 of water/cementitious materials ratio of 0.4 and cementitious materials content 410 kg/m^3 show lower values of diffusion coefficients than those of mixes 4, 5, and 6 of water/cementitious materials ratio 0.5 and cementitious materials content 330 kg/m^3 . Furthermore, the obtained results show that the diffusion coefficient decreases with increasing the concrete age due to the hydration process as well as the effect of using FA and SF.

7. Conclusion

- The results of ternary cementitious materials mixes show better values of the studied properties than Portland Cement Mixes.
- The results indicate that the measured values of depths 10~20 mm and 20~30 mm of Portland Cement Samples are higher than those of ternary cementitious blends samples.

- The change in cementitious materials type and their replacement ratio affect the measured values of chloride contents. The samples of water/cementitious materials ratio of 0.4 and cementitious materials content 410 kg/m^3 show lower chloride contents than those of water/cementitious materials ratio 0.5 and cementitious materials content 330 kg/m^3 .
- The change in the cementitious materials content, cementitious materials type, and their replacement ratio as well as the water/cementitious ratios has a noticeable effect in measured properties of concrete.
- The results indicate that the use of ternary cementitious systems in concrete showed a significant improvement in resistance of concrete to chloride penetration and can be reasonably used in concrete industry with considerable proportions.

References

1. D. Nahirwa, H. Qiao, C. Mahame, "Effect of Carbonation, Chloride and Sulphate Attacks on Reinforced Concrete: A Review", *International Journal of Civil Engineering, Construction and Estate Management* Vol.6, No.2, pp.59-64, July 2018.
2. ACI Committee, "Guide to Durable Concrete 201.2R-2", 2000.
3. T. Wee, K. Arvind, S. Suryavanshi, F. Wong, and A. Anisur Rahman., "Sulfate Resistance of Concrete Containing Mineral Admixtures", *ACI Material Journal*, Vol. 97 (5), PP. 536- 549, 2000.
4. M. Anwar, A. Makhoulf, "The Relationship between Soluble and Total Chloride Contents in Concrete Containing Cementitious Materials", *Civil Engineering Research Magazine*, CERM, Al-Azhar University, Cairo, Egypt, pp. 190-197, January 2005.
5. J. Prabakar, P. Manoharan, A. Chellappan, "Diffusion Characteristics of OPC Concrete of Various Grades Under Accelerated Test Conditions" , *Construction and Building Materials*, Vol.24, No. 3, PP. 346- 352, 2010.
6. S. K. Verma, S. S. Bhaduria, S. Akhtar, "Evaluating Effect of Chloride Attack and Concrete Cover on the Probability of Corrosion", *Front. Structure Civil Engineering*, 7(4), PP.379–390, 2013.
7. K. De Weerdta, B. Lothenbacha, M. R. Geiker, "Comparing Chloride Ingress from Seawater and NaCl Solution in Portland Cement Mortar", *Cement and Concrete Research*, 115, PP 80-89, 2019.
8. N. John, B. S. Choo, "Advanced Concrete Technology", Vol. 1, Oxford, UK: Butterworth-Heinemann an imprint of Elsevier Linacre House, Jordan Hill, Oxford OX2 8DP 200-Wheeler Road, Burlington MA01803, 2003.
9. Marusin, S. L., "Influence of Length of Moist Curing Time on Weight Change Behaviour and Chloride Ion Permeability of Concrete Containing Silica Fume", 3 rd Int. Conf. on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Trondheim, Norway, SP-114, 1989, pp. 929-944.
10. Gaynor, R., "Understanding Chloride Percentages", *steel Corrosion in Concrete causes and restraints*, ACI SP-102, 1987, pp. 161-165.
11. Y Zhanga, b, c, Z Yanga, b, G Yec, "Dependence of unsaturated chloride diffusion on the pore structure in cementitious materials ", *Cement and Concrete Research*, vol. 127, 105919,2020.
12. JIS A 1101. Method of Test for Slump of Concrete. JIS: Tokyo, Japan 2020.
13. JIS A 1116. Method of Test for Unit Weight and Air Content (Gravimetric) of Fresh Concrete 2020.
14. JIS A 1128. Method of test for air content of fresh concrete by pressure method. JIS: Tokyo, Japan 2020.
15. JIS A1108. Method of test for compressive strength of concrete. JIS: Tokyo, Japan 2018.
16. JIS A 1127 Method of Test for dynamic modulus of elasticity, rigidity, and dynamic Poisson's ratio of concrete specimens by resonance vibration. JIS: Tokyo, Japan 2020.
17. JIS K 0113. General rules for methods of potentiometric, amperometric, coulometric, and karl-fischer titrations. JIS: Tokyo, Japan 2015.
18. M. Anwar, "Concrete Properties of Ternary Cementitious Systems Containing Fly Ash and Silica Fume", *HBRC Journal, Housing & Building National Research Center*, Giza, Egypt, Vol. 2, No. 1, pp. 1-10, Jan. 2006.
19. M. H. Medeiros, F. Rocha, F. C. Medeiros-Junior, R. A., P. Helene, "Corrosion Potential: Influence of Moisture, Water-Cement Ratio, Chloride Content and Concrete Cover", *Ibraco11 Structures and Material Journal*, Vol. 10, No. 4, PP. 864-885, 2017.

20. S. Shashi and S. Nacer, "Interaction of Silica Fume and Water Content on Strength and Permeability of Concrete", TRB. Annual meeting, 2012.
21. Anwar, M., "Use of Rice Husk Ash as Part of Cement Content in Concrete", Ph.D. thesis, Cairo University, 1996.

تأثير استخدام الرماد المتطاير والسيليكا فيوم على أداء الخرسانة ضد هجوم الكلوريدات

الملخص العربي

هذا البحث جزء من مشروع بحثي شامل يتناول بالدراسة امكانية استخدام المواد ذات الخصائص الاسمنتية مثل الرماد المتطاير والسيليكا فيوم مع الأسمنت البورتلاندي العادي في خليط اسمنتي ثلاثي وتأثير هذا الخليط على مختلف خواص الخرسانة. ففي هذا البحث تم تصميم ست خلطات خرسانية بنسب مياه/اسمنت ٠,٤ و ٠,٥, حيث تم اعداد مجموعة من الخلطات الخرسانية التجريبية للحصول على خرسانة لها هبوط قيمته 2 ± 10 سم مع نسبة محتوى هواء قيمتها $1 \pm 4\%$. وكانت نسب السيليكا فيوم المستخدمة 5% و 10% مع نسبة 25% من الرماد المتطاير. وقد اشتملت الدراسة على قياس الهبوط ونسبة محتوى الهواء والوزن الحجمي للخرسانة الطازجة بالإضافة الي قياس مقاومة الضغط ومعايير المرونة الديناميكي وسرعة الموجات فوق الصوتية للخرسانة المتصلدة عند اعمار ٣ و ٧ و ٢٨ و ٩٠ و ١٨٠ يوم. وبعد مرور ٢٨ يوم على معالجة العينات الخرسانية تم تعريض مجموعة منها لمحلول كلوريد الصوديوم (تركيز 5%) لمدة خمسة شهور وقياس المحتوى الكلي والذائب للكلوريدات ومعامل الانتشار لأملاح الكلوريدات خلال الخرسانة بعد مرور شهر وثلاثة شهور وخمسة شهور عند اعماق $0 \sim 10$ و $10 \sim 20$ و $20 \sim 30$ مم من سطح العينة. واستخدمت الطريقة الكيميائية (Titration Analysis) لاستخلاص أملاح الكلوريدات من الغطاء الخرساني وقياس المحتوى الكلي والذائب للكلوريدات كنسبه مئوية من وزن الخرسانة ومعامل الانتشار لأملاح الكلوريدات خلال العينات الخرسانية طبقاً لما جاء بالمواصفات القياسية اليابانية. وأظهرت النتائج أن استخدام خليط أسمنتي ثلاثي من الأسمنت البورتلاندي العادي والرماد المتطاير والسيليكا فيوم بالخرسانة يزيد من مقاومتها لاختراق الكلوريدات ويقلل من معمل الانتشار خلالها، بالإضافة الي انها أبدت نتائج أفضل من تلك التي أبدتها خرسانة الأسمنت البورتلاندي العادي. بالتالي يمكن استخدام كل من الأسمنت البورتلاندي العادي والسيليكا فيوم والرماد المتطاير معاً كخليط أسمنتي ثلاثي في صناعة الخرسانة بنجاح. كما اظهرت النتائج ان التغيير في محتوى المواد الأسمنتية ونوعها ونسبة استبدالها له تأثير واضح على خواص الخرسانة التي تناولتها الدراسة. وقد اتضح من النتائج أن محتوى الكلوريد الذائب عند عمق $10 \sim 20$ مم وعمق $20 \sim 30$ مم من سطح الخرسانة منخفض جداً، مما يؤدي إلى أن هذا النوع من الخرسانة قد يحتاج إلى سمك أقل للغطاء الخرساني لحماية حديد التسليح.