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INFLUENCE OF SUBSTITUTION OF ORDINARY PORTLAND CEMENT BY SILICA FUME IN THE DURABILITY OF SLAG PORTLAND CEMENT PASTES IN SEA WATER

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ABSTRACT

Effect of gradually substitution of ordinary Portland cement by a few percent of silica fume (0.0, 2.5, 5.0 and 7.5 wt.%) on the durability of slag-Portland cement pastes up to 12 months immersed in sea water was investigated. The results show that the substitution of Portland cement by silica fume in the granulated slag-Portland cement pastes improves the physico-mechanical properties of the hardened cement pastes especially at early ages as well as gives a better resistance of cement stone to sea water attack at all immersing time. Also, the composite cement pastes containing 7.5% silica fume showed a maximum durability than other samples.

Keywords: composite cement, silica fume, slag, sea water.

1. INTRODUCTION

Silica fume has been used as high pozzolanic reactive cementitious material to make high-performance concrete in the sever conditions [1, 2]. This mineral admixture has highly been used in severe environmental conditions despite its several mixing and curing problems, because of its acceptable early age strength development [3, 4]. The hydration mechanism and properties of secondary C-S-H made by pozzolanic reaction have been studied by many investigators [3]. However, pozzolanic reaction might be different in respect of the amount of molecular water, C/S ratio and density [5].

The service life of concrete structures depends on the environmental conditions and on the quality of concrete. Durability of concrete to sulfate attack is one of the environmental problems. As a result of sulfate attack the cementitious matrix is damaged through the formation of ettringite and gypsum. According to one theory, the formation of ettringite is expansive (it has a density of 1.73 g/cm^3 compared with an averaged density of 2.5 g/cm^3 for the other products of hydration). Therefore expansion and cracking of concrete happen as a result of sulfate attack caused by sulfate solutions [6]. Sulfate attack is a problem generally associated with buried concrete structures exposed to soils or ground waters containing soluble sulfates. Since usage new type of chemicals for agricultural purposes was extended during the last decades, underground water pollution has increased and sulfate attack is of great importance for the long term service life of such structures.

The principal method available to limit sulfate attack is the use of ASTM Type II or Type V Portland cements instead of Type I Portland cement [7] or the use of additives; such as natural pozzolanas, fly ash or silica fume. Pozzolanic materials have an important role in the long term durability of mixtures exposed in sulfate environments because they contribute chemically and physically to their properties. Their effect is thought to be explained by two primary mechanisms [8]: the "dilution

effect' (decrease of the C$_3$A content of the binder when they replace a portion of Portland cement) and the "pozzolanic effect" (formation of secondary CSH). The later results are in a less permeable concrete, from which the excess calcium hydroxide has been consumed and prevent the formation of ettringite and gypsum compounds [8-10].

High-performance concrete mixes containing various proportions of natural pozzlan and silica fume (up to 15% by weight of cement) were prepared and stored in sodium and magnesium sulfate solutions, in Dead Sea and Red Sea waters. The progressive deterioration and the relative sulfate resistance of these mixes were evaluated through visual observations, ultrasonic pulse velocity measurements, and relative strength determinations. The results indicate that the concrete mix containing 15% natural pozzolan, and 15% silica fume showed the best protection in sulfates solutions and sea waters. It retained more than 65% of its strength after one year of storage in sulfates solutions and sea waters. The superior resistance of that mix against sulfate attack is attributed to the pore refinement process and further densification of the transition zone occurring due to the conversion of lime forming from the hydration of cement into additional binding materials through lime-pozzolan reaction. This investigation recommends the use of silica fume in combination with natural pozzlan for better performance in severe sulfate environments [11].

The aim of the present work is to study the effect of substitution of Portland cement by silica fume on durability of Portland slag cement pastes in sea water.

2. EXPERIMENTAL WORK

The materials used in this work were ordinary Portland cement, supplied from National Cement Company, Silica fume from Egyption Company producing ferrosilicon alloys, Edfo; granulated blast furnace slag from the Iron and Steel Company, Hellwan, Egypt. The

chemical analysis of the starting materials is given in   Table-1.

Table-1. Chemical analysis of the starting materials, (wt, %).

Materials	Oxides							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Portland Cement	21.3	5.41	3.77	63.14	1.21	2.35	0.09	0.4
Silica fume	96.89	1.03	0.56	0.21	0.15	0.16	0.62	0.17
Granulated slag	39.89	13.72	2.56	26.38	3.47	1.22	1.06	1.0

Different mixes were made from OPC, silica fume and granulated slag as seen in Table-2. Each dry mix was homogenized for 1/2 hour in a porcelain ball mill using two balls to assure complete homogeneity. The mixing of cement pastes was carried out with the water required for normal consistency [12], that in the case of OPC with 0, 2.5, 5.0 and 7.5 silica fume and 45% granulated slag was 26.0, 26.5, 27.5, and 28.0%, respectively. The increase of the mixing water with silica fume content is mainly due to its high surface area.

Table-2. Mix composition of different prepared cements, wt %.

Mix no.	Granulated slag	Silica fume	OPC
C_o	45	0.0	55.0
C_1	45	2.5	52.5
C_2	45	5.0	50.0
C_3	45	7.5	47.5

The mixing of the cement with the required water amount was completed by continuous mixing by hand for 4 minutes by gauging trowels. Immediately, after mixing the cement paste was poured in one inch cubic moulds and pressed until homogeneous specimen was obtained. The moulds were manually shaken to remove any air bubbles, and then smoothed by spatula. The moulds were cured in a 100% R.H. chamber at 23±2˚C for 24 hour, then demoulded and cured under tap water for 28 days. After 28 days (zero-time) curing in tap water, the samples were immersed in sea water for 1, 3, 6, 9, and 12 months. The sea water was renewed every month to keep the concentration of the attack salts as much as possible constant. The progress of the attack was determined through the measurements of compressive strength, free lime content [13], and total porosity [14]. After the compressive strength determined, a representative sample of about 10 g was taken, ground in a porcelain mortar with 50 ml solution [(1:1 v) methanol/acetone] and then filtered through sintered glass funnel G4. The paste was washed for two times with the stopping solution and finally with 50 ml fresh diethyl ether and dried at 70˚C for 20 minutes then kept in an airtight bottle. Some selected samples were examined by X-ray diffraction to identify the phase products in their cement pastes.

3. RESULTS AND DISCUSSIONS

3.1 Compressive strength of composite cement

The compressive strength of the hardened cement pastes cured up to one year in sea water illustrated as a function of immersing time is graphically represented in Figure-1. The compressive strength sharply increases at early immersing time (0-3months) for all cement pastes, then enhances with a lower rate up to 6 months for cement pastes containing 5.0 and 7.5% silica fume. The samples with 0 and 2.5% silica fume enhance up to 3 months then decreases up to one year. It can be concluded that as the proportion of the replacement of Portland cement by silica fume increased, the sea water resistance of the cement pastes enhanced. The super resistance of the cement pastes containing pozzolanic products against sulfate attack is attributed to the pore refinement process occurring due to the conversion of lime forming from the hydration of cement into additional binding materials through lime-pozzolan reaction [11]. In addition to the pozzolanic reaction, the filler action due to the finer particle size of silica fume (0.1-0.2 µm) further densifies the pore structure to enhance the resistance to sulfate attack [15-16]. Furthermore these pozzolanic materials play an important role in improving the aggregate-paste bond though the densification of the transition zone and formation of more calcium silicate hydrates [17].

3.2 Apparent porosity of composite cement

The apparent porosity of the cement pastes cured up to one year is plotted as a function of time in Figure-2. The apparent porosity of the cement pastes containing silica fume decreases up to 6 months, while the cement paste without silica fume decreases up to 3 months then increases till 12 months. The porosity of cement pastes decreases at early immersing time due to the filling up a part of the available pores with the hydration products. Also, the results show that the sample without silica fume gives a lower value of porosity than other samples at early ages of immersion (one month), while it has a higher value at later ages (6-12 months). It is evident that, as the silica fume content of the cement pastes increases, the porosity decreases at later ages (6-12 months). This indicates the positive effect of silica fume addition on the cement pastes i.e., the presence of silica fume in the cement pastes improves the durability as well as the physical properties of the cement pastes exposed to sea water. On the other

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hand, the free lime drops from normal in the bulk to zero in the vicinity of the surface, showing a direct evidence of Ca (OH) $_2$ leaching by the sea water attack [15]. The removal of $Ca(OH)_2$ not only weakens the solid phase, but also increases the porosity of the cement paste at later ages (6-12) months. On the other hand, the gypsum, and sulfoaluminate hydrates are considered to be the main part of the products of the chemical reaction due to the penetration of the chloride and sulfate ions into the paste. They are responsible of the further increase of the porosity especially at later ages of immersion time. It can be seen that when silica fume is added to cement pastes, it acts both as chemically inert filler, improving the physical structure, and as a pozzolan, reacting chemically with CH formed during hydration of cement.

3.3 Free lime of composite cement

The free lime contents of the composite cement pastes immersed in sea water up to one year are given in Figure-3. The results show that the free lime of the cement pastes decreases with increasing silica fume contents and later ages of immersing time. The free lime contents of the control cement paste (C_0) increase with immersed time up to 3-months then decreases up to 12-months. The increase of the free lime at early ages is due to its liberated during the hydration of the silicates phases of Portland cement. The decrease of the free lime contents of the control samples at later ages is mainly due to the acidic attack of $MgSO_4$ and $MgCl_2$ which present in sea water involving the conversion of Ca (OH) $_2$ to gypsum and sulfoaluminate phases. On the other side, the free lime contents of the pastes containing silica fume are lower than the control sample (C_0). Also, as the amount of silica fume increases, the free lime decreases at all immersing time. The silica fume is assumed to be as the reactant to produce secondary CSH by consuming calcium hydroxide. The formation of pozzolanic gel begins with hydration of elite and belite during hardening process. Decreased calcium hydroxide content of the cement matrix and increased amount of CSH gel together with filler effect of silica fume contribute to safeguarding of the matrix against external ingressive ions.

3.4 XRD of composite cement

The XRD patterns of the samples containing 0, 2.5, and 7.5% silica fume and cured for one-month in sea water are shown in Figure-4. The XRD results of the control sample (without silica fume) show the presence of calcium hydroxide, gypsum, calcium carbonate as well as C_4AH_{13}. In addition, quartz peaks were detected as a main constituent of slag-cement. The intensity of calcium hydroxide as well as gypsum decrease with increasing of the silica fume content in the composite cement pastes. On the other side, the data show that the intensity of calcium hydroxide and gypsum peaks were completely disappeared

with 5.0 and 7.5% silica fume. The disappearance of calcium hydroxide and the presence of higher amounts of CSH are evidenced that silica fume consumes calcium hydroxide forming CSH gel which fill some of open pores leads to enhancing the durability of the hardened cement pastes.

The XRD patterns of cement pastes containing 0, 2.5, and 7.5% silica fume and immersed for 6 month in sea water are seen in Figure-5. The main phases detected in the patterns of control sample are gypsum, sulfoaluminare as well as C_4AH_{13} and small peaks of Ca (OH) $_2$. This is attributed to the leaching of Ca (OH) $_2$ to the surrounding medium and/or to the chemical reaction between the free lime which liberated during the cement hydration and the chloride and sulfate ions of the solution to produce gypsum and sulfoaluminate products. On the other hand, the silicate phases of the cement component liberate lime to the surrounding medium to establish their equilibrium pH, but when magnesium sulfate is present, the lime reacts with it, forming magnesium hydroxide and calcium sulfate as well as reducing the pH value to 10.5 again, more lime passes into solution to re-establish pH, and so the reaction proceed [18]. The calcium sulfate accumulates in the solution till becomes saturated and crystals of the gypsum separate out for cement paste in contact with sulfate and chloride ions in sea water. The attack is attributed to the chemically reaction between their ions and hydrated Portland cement phases to form the more insoluble sulfoaluminate products. It is clear that the intensity of Ca (OH) $_2$, gypsum peaks were decreased in the presence of silica fume till completely disappearance with 7.5%.

Figure-6 shows the XRD patterns of the composite cement pastes immersed for 12 months in sea water. The main phases detected in the patterns are gypsum, sulfoaluminate and C_4AH_{13} as well as quartz. The results show that as the silica fume contents increase the deleterious products such as gypsum and sulfaoaluminate, phases decrease in the composite pastes. Also, the intensity of the deleterious phases peaks were completely disappeared with 7.5 silica fume content. The disappearance of $Ca(OH)_2$ in the composite pastes containing silica fume and the presence of a valuable amounts of CSH are evidenced that silica fume plays an important role consumes $Ca(OH)_2$ forming additional CSH gel which fill some of open pores enhancing the durability of the composite cement pastes in sea water. These results are in a complete agreement with the physico-mechanical results.

4. Energy requirement

Energy requirement in the production of different composite cement types, where secondary components are added in the proportion usually employed in the industry is reported in Table-3.

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**Table-3.** Energy required for the production of composite cement in comparison to Portland cement.

OPC		Different types of composite cement			
	OPC	**C_0**	**C_1**	**C_2**	**\C_3**
	Clinker, 95 % Gypsum 5 %	OPC 55% Slag 45% SF 0%	OPC 52% Slag 45% SF 2.5 %	OPC 50% Slag 45 % SF 5 %	OPC 47.5% Slag 45% SF 7.5%
OPC, MJ/ton	3230	1870	1760	1700	1632
Cost $/ton	10.0	5.8	5.5	4.5	2.5

The values are based on the total energy required of 3400 MJ/ton of clinker produced. Also, it can be supposed that grinding, handling and packing need 40 kwh (364MJ) and 45 kwh (409MJ) of Portland cements and portland pozzolanic or Portland filler cement, respectively, and 55 kwh (500 MJ) per tone of Portland slag. The energy employed for the transportation of secondary constituents and raw materials necessary for the manufacture of the substituted clinker has been considered in this computation. This energy varies from 6 to 60 MJ/tone of cement, depending on the distance and the kind of transportation [19].

The difference between the energy required by the different composite cements and Portland cement is between 1310-2330 MJ/tone.

It can be concluded that the difference of the cost saving between the production of Portland cement and composite cement between 10 to 2.4 $/tone, respectively.
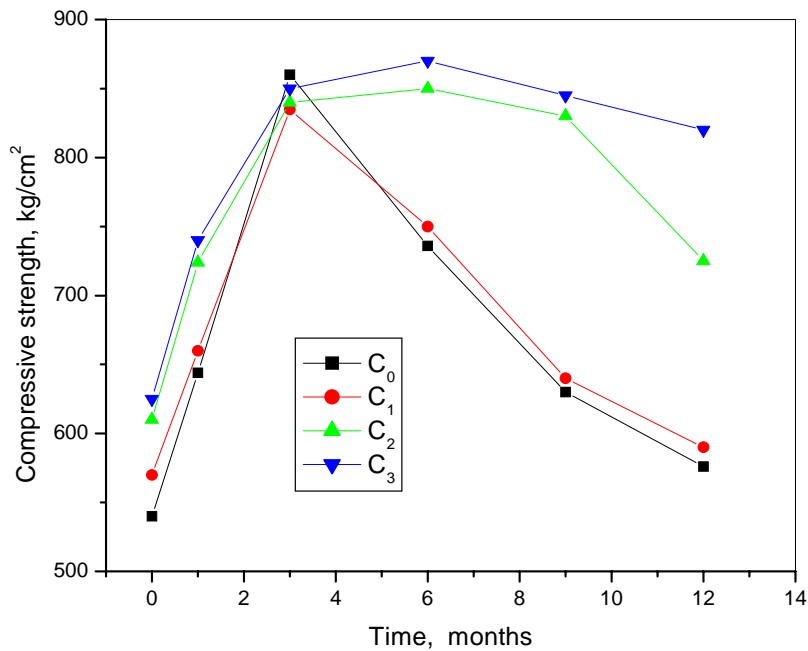
Figure-1. Compressive strength of different hardened composite cement pastes as function of immersing time in sea water.
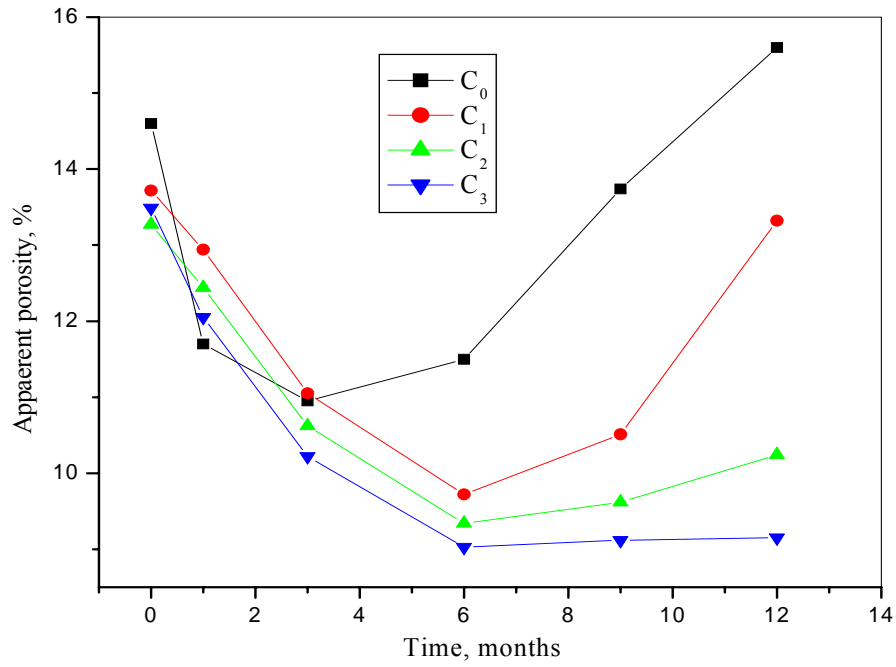
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Figure-2. Apparent porosity of the different hardened composite cement paste as function of immersing time in sea water.
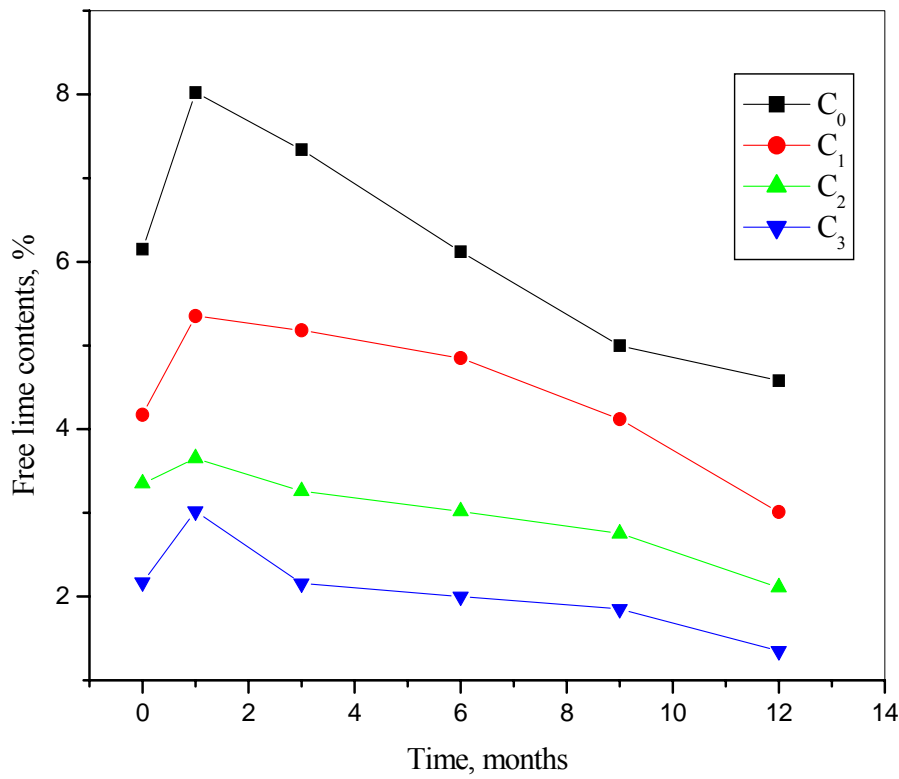

Figure-3. Free lime contents of different composite cement pastes as function of immersing time in sea water.
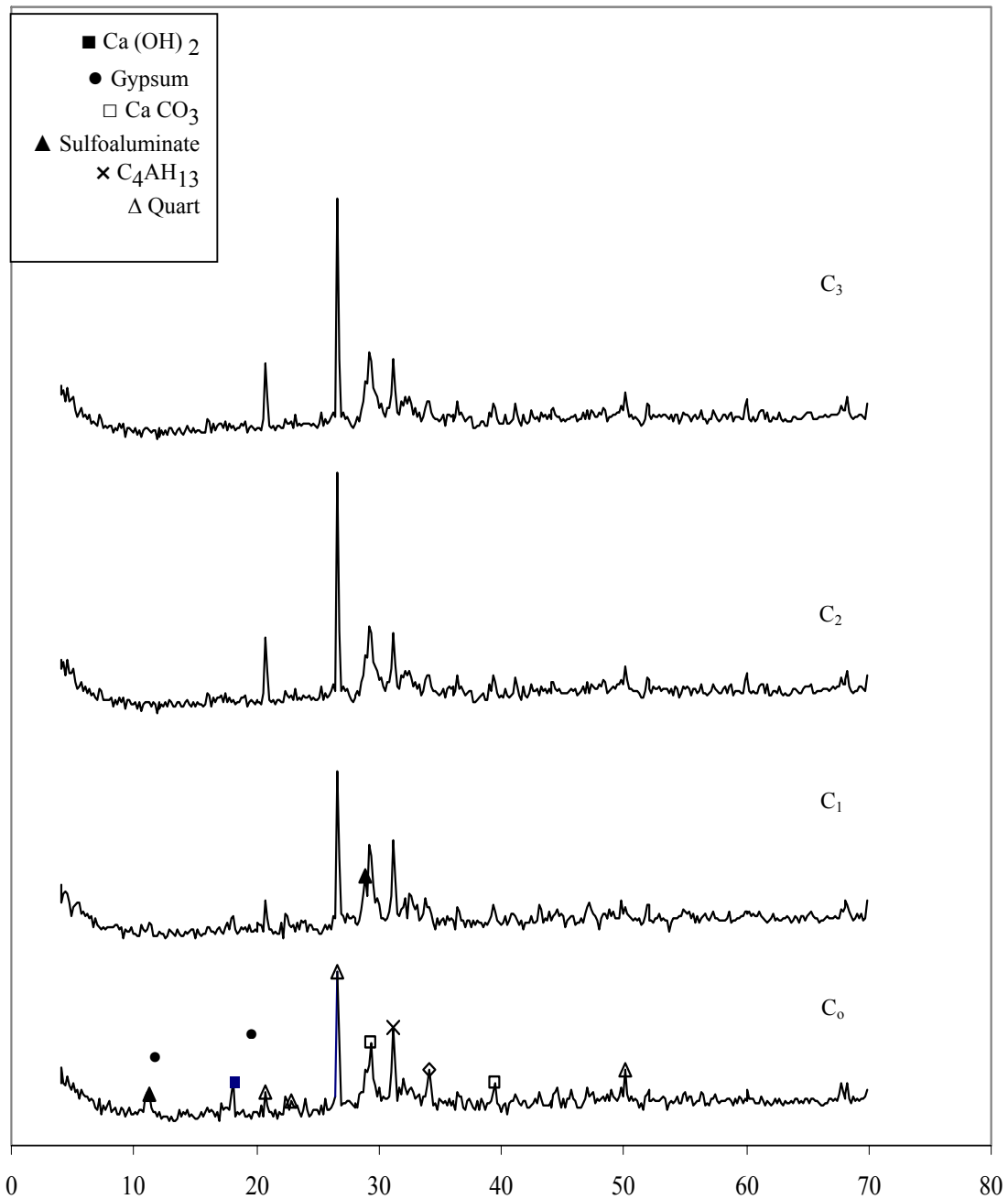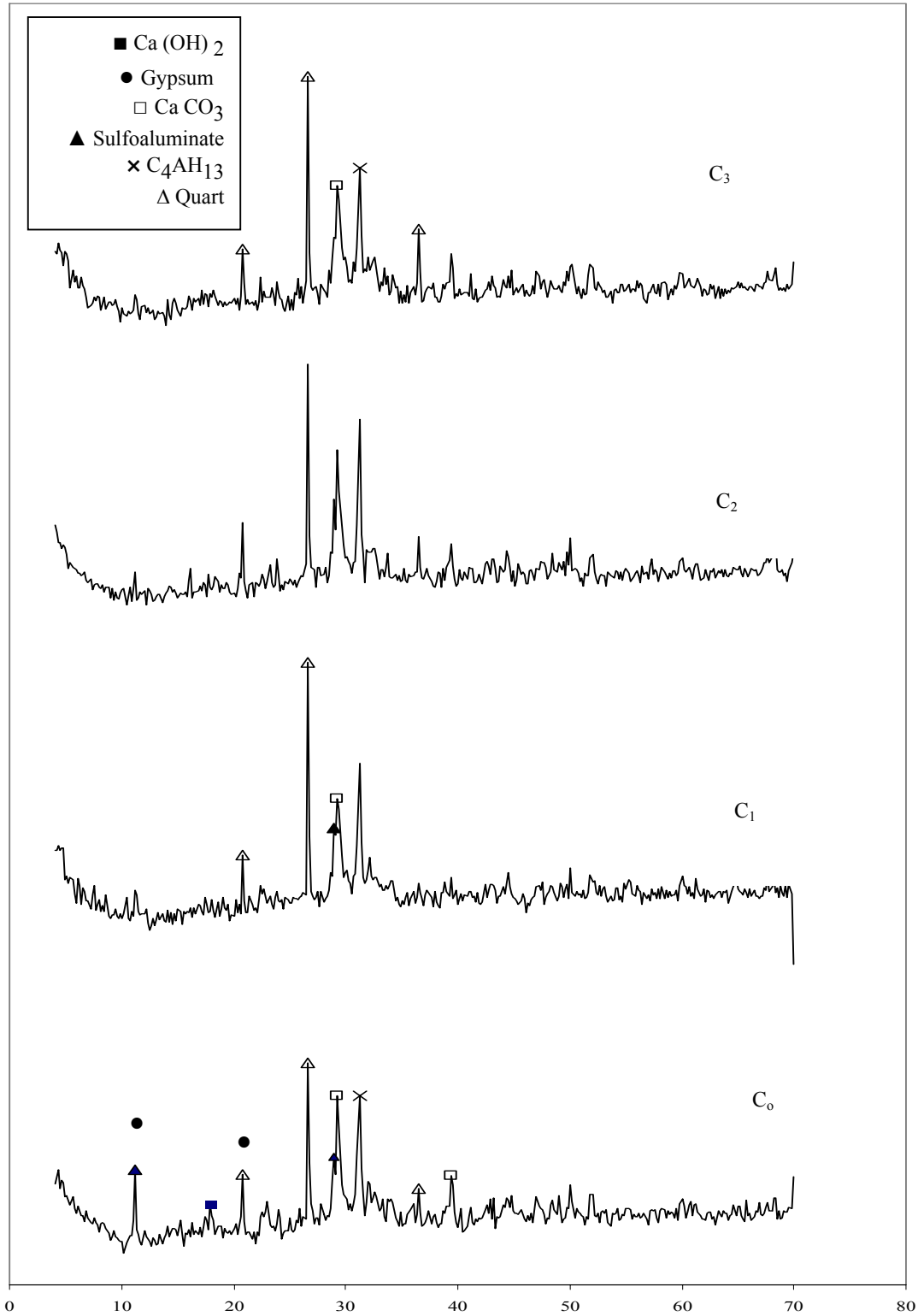
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Figure-4. XRD patterns of different cement composite pastes immersed in sea water for one-month.

Figure-5. XRD patterns of different cement composite pastes immersed in sea water for 6-month.
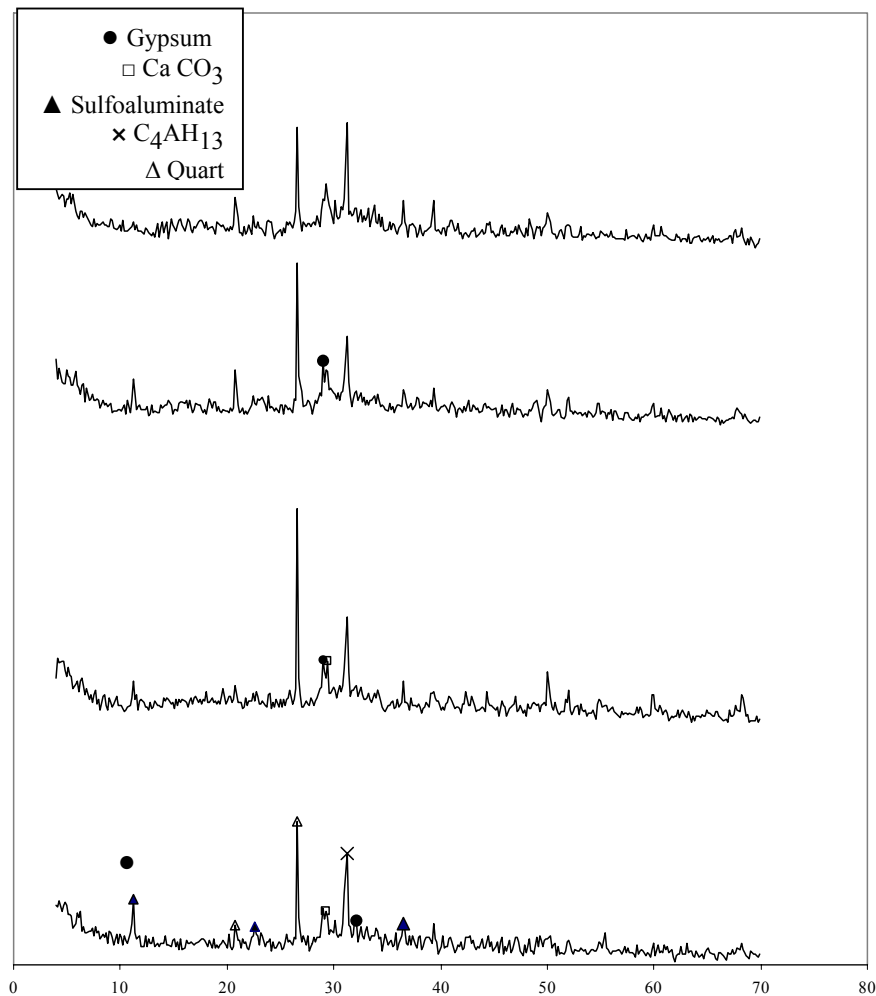
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Figure-6. XRD patterns of different cement composite pastes immersed in sea water
for 12-month

5. CONCLUSIONS

Based on the results of this study, it can be concluded that:

- The substitution of Portland cement by silica fume in the granulated slag-Portland cement pastes improves the physico-mechanical properties of the hardened cement pastes especially at early ages as well as gives a better resistance of cement stone to sea water attack;
- With increasing the silica fume contents in the composite pastes the durability of the cements enhances at all immersing time;
- The XRD results show that the intensity of Ca (OH) 2, sulfoaluminate and chloroaluminate peaks are completely disappeared in presence of 7.5% silica fume; and
- After one year immersion, the composite cement pastes containing 7.5% silica fume showed a maximum durability in sea water.

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