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Research Article

Durability and chemical resistance of nanoparticles fly ash and silica fume belite cement pastes against sulfate and chloride aggressive media- Part II

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Abstract: The durability (chemical resistence) of the Portland cement (OPC), belite cement (BC) and the optimum belite cement (B4), which their physical and chemo/mechanical properties were perviously investigated in Part I, against 4 % $MgSO_4$ and 4% $MgCl_2$ solutions up to 12 months in terms of compressive strength, total sulfate and total chloride was evaluated and studied. Results showed that the optimum belite cement (B4) containing 15 % High pulverized fly ash (HPFA) and 5 % Silica fume (SF) could be resisted up to 6 months, while that of BC could be withstood only up to 5 months, and the OPC could not resist more than three months of immersion in 4% $MgSO_4$ solution. The compressive strength values exhibited by the samples immesed in sulfate solution at 3, 5 and 6 months of immersion were 83.81, 76.38 and 91.13 MPa, respectively. The same trend was displayed when the same samples were exposed to 4% $MgCl_2$ solution. The compressive strength values exhibited by the same samples exposed to chloride solution at 3, 5 and 6 months of immersion were 84.49, 82.23 and 93.32 MPa, respectively. The total sulfate and chloride contents were enhanced with immesion time up to 12 months, but their values were the minimum with B4 and the maximum with OPC, while with BC were the medium. The optimum cement batch (B4) achieved the highest resistance where it recorded the lowest values for sulfate and chloride ions, but the OPC exhibited the lowest resistance where it recorded the highest values of sulfate and chloride contents at all immersion ages till 12 months.

Keywords: Nanomaterials, Belite cement, Fly ash, Silica fume, Durability, Strength, Total sulfate, Total chloride.

1. Introduction

1.1 Scope of the problem

The gradual and continual dominance of cementitious building materials for various constructions is a response due to its increased strength, resistance and versatility when compared with other building materials, e.g. steel, glass, wood and so on. The used raw materials to produce cementing building composites are too cheap and largely available. The exposure of building structures produced by cementing materials to different aggressive media needs to improve the durability performance of these structures. One of the effective methods to improve the performance of cementing composites which is recently gaining an attention is the use of nanotechnology. Generally, materials with sizes ranged between 0.1 to 100 nm are known as nanomaterials. Increasing the durability of cementing composites by the use of nanomaterials could be associated with its smaller size which refines the micro-

and nanostructures of the composites. The used nanomaterials in cementing building composites often possess active pozzolanic characteristics to create some hydrates, and the relatively densification of the micro- and nanostructure were improved [1-5]. Chemical reactions of the nanopozzolanic materials with the evolved calcium hydroxide, or free lime $Ca(OH)_2$ due to hydration in the pore solution of cementing composites often form more calcium silicate hydrate which soon precipitated in the pore structure of the hardened cement pastes. This in turn decreases the total porosity and increases the bulk density. Moreover, this was positively reflected on the mechanical strength of cement structures. The hydration reactions of Portland cement with water have also been found to be expedited in the presence of nanomaterials. This resulted in the formation of more calcium hydroxide [4–9]. This pointed to increase the rate of hydration process. This can be contributed to the nanomaterials that are serving as nucleation site areas for the formation of hydration products due to its

high fineness [10-14]. Many recent studies [15-24] have proved that the existence of nanomaterials inside the cementing composites revealed an enhancement in the formation of calcium hydroxide at early hydration ages [4-6]. Silicate chain is often formed due to the existence of nanomaterials in cementing composites, This has also been found to increase the resistance of the composites against to the various aggressive chemical attacks [7-11]. Not only is the durability improvement of cementing composites due to the use of nanomaterials, but also the expensive cement content is reduced, where the use of about 1 kg of nanomaterials will result in a reduction of about 4 kg of cement to exhibit improved characteristics [6-8].

Very important improvements in the permeability characteristics of cement and/or concrete mixtures containing nano-SiO_2 and nano clay at a very low dosage was reported [14]. The enhancement of durability characteristics of cementing composites with the presence of nanomaterials is generally contributed to the pore filling, good compaction and nuclei activating ability of the nanomaterials [18-23]. Though the benefits due to the use of nanomaterials in cementing composites, it is important to ensure that these nanomaterials are well dispersed in the matrix of cement composites. This has been found to result in consequential creation of weak areas and voids in this cementing matrix [15,24].

1.2. Objectives of the study

To propel more applications of nano materials improve and enhance the durability performance of cementitious composites, the study was conducted to evaluate the influence of nanomaterials on the durability properties of cementing composites. The durability performance of cementing composites was studied in terms of permeability and resistance to some aggressive chemical media attacks as $MgSO_4$ and $MgCl_2$ solutions up to 12 months.

2. Experimental

2.1. Raw materials

The used raw materials in the current research study (Part II) are Ordinary Portland cement (OPC Type I- CEM I 42,5R), High belite cement (HBC), high pulverized fly ash (HPFA) and silica fume (SF). The OPC and HBC samples were provided by the new cement factory, Sohag, Egypt, while HPFA sample was provided from a local plant, Giza, Egypt. The SF sample was supplied by the ferrosilicon alloys company, Edfo, Egypt. The blaine surface areas of the four raw materials were 3400, 3763, 4150 and 19230 cm^2/g, respectively. The blaine surface areas of OPC and HBC cements were carried out by the "Air Permeability Apparatus", while those of PFA and SF were received as it is from the factories.

The chemical analysis of the OPC, HBC, HPFA and SF specimens as measured by X-ray florescence technique (XRF) is shown in Table 1. The mineralogical phase composition of the used OPC and HBC as provided by the factory is given in Table 2, while the batch composition is recorded in Table 3.

Table 1 Chemical analysis of the raw materials, wt.%.

Oxide Materials	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	Na₂O	K₂O	SO₃	Insoluble residue	LOI	Total, %
OPC	20.41	5.51	3.64	61.53	1.60	1.01	1.16	2.07	1.63	1.44	100
HBC	23.62	3.45	4.28	57.54	4.89	0.07	0.13	2.43	0.77	1.82	100
FA	50.53	31.64	6.05	5.13	1.47	0.76	3.14	0.17	0.42	1.51	100
SF	93.15	0.11	0.15	1.12	0.32	0.08	0.41	0.41	----	0.71	100

Table 2 Mineralogical constituents of OPC and HBS cement samples, wt. %.

Phase Cement	C₃S	β-C₂S	C₃A	C₄AF
OPC	48.37	24.72	8.28	11.45
HBC	29.12	42.87	2.03	12.57

Table 3 Mix composition from the used raw materials, wt. %.

Materials Mixes	OPC	HBC	HPFA	SF
P0	100	----	----	----
B0	100	----	----	----
B1	----	95	5	----
B2	----	90	5	5
B3	----	85	10	5
B4	----	80	15	5
B5	----	75	20	5

2.2. Preparation and methods

There are five blended cement batches composed from Belite cement (BC), high pulverized fly ash (HPFA) and silica fume (SF). The belite cement batches were composed of BC, HPFA and SF as 100:0:0, 95:5:0, 90:5:5, 85:10:5, 80:15:5, and 75:20:5 having the symbols: B0, B1, B2, B3, B4 and B5, respectively (Table 3). The blending process of the various cement batches was done in a porcelain ball mill using three balls for two hours to assure the complete homogeneity of all cement batches. The physical and mechanical properties of OPC and HBC blended with different ratios of HPFA and a constant ratio of SF (5%) were previously investigated in Part I [25]. The optimum cement batch (B4) containing 80 % HBC, 15 % HPFA and 5% SF was selected to be subjected to sulfate and chloride attacks for 12 months.

In the present study (Part II), the resistance of the selected optimum batch (B4) pastes from Part I against the attack by 4% $MgSO_4$ and 4 % $MgCl_4$ was evaluated comparing with those of the blank cements (OPC and HBC). There are three cement mixes as OPC, HBC and B4 having the symbols of P0, B0 and B4, respectively. The blending process was mechanically made in a porcelain ball mill containing three balls for one hour to assure the complete homogeneity of all batches. Before casting of cement cubes, all moulds were oiled with a thin film of motor engine oil, to facilitate the release of the cubes from the moulds during the de-moulding. During casting of cement pastes, a certain percentage of Na-lignosulphonate admixture was added to all cement mixtures during mixing to avoid the agglomeration of the nanoparticles of cement powder. Sodium lignosulfonate admixture was applied due to its higher activity than other conventional ones (Figure 1). Each already prepared oil

moulds were filled with the premixed cement composite and rammed 10 minutes to remove all air bubbles tapped within the mixture. The moulds were filled to the top surface and smoothed with a suitable flat stainless-steel trowel or spatula to obtain a flat and smooth surface [26,27].
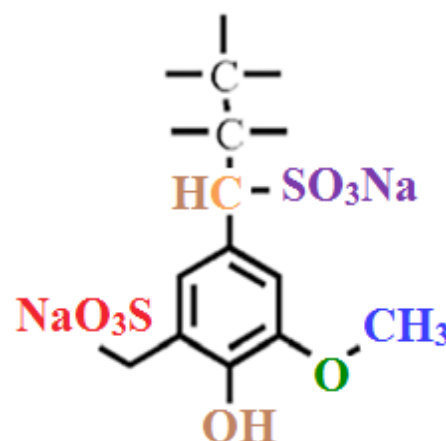
Figure 1 Chemical structure of sodium lignosulphonate.

The cement pastes were mixed using the predetermined water of consistency that was previously determined in Part I [25], then molded into one-inch cubic stainless steel moulds (2.5x2.5x2.5 cm^3), vibrated manually for five minutes, and then on a mechanical vibrator for another five minutes. After casting of all cement cubes, they were covered with a black wet sheet for the first 24 hours to prevent moisture loss. The moulds were kept inside a humidity cabinet for 24 hours at 23±1 °C and 100 % R.H., de-molded in the following day, and soon cured in water up to 28 days. The 28 days hydrated samples were subjected to compressive strength [28], where the loading was applied perpendicular to the direction of

the upper surface of the cubes. The compressive strength was calculated from the following equation:

CS = L (KN)/Sa (cm²) KN/m² x 102 (Kg/cm²)/10.2 (MPa)   (1)

Where, L and Sa are the load taken and the surface area, respectively. After carrying out the compressive strength at each curing time, about 10 g of the broken samples was dried at 105 °C for one hour, and then were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration, and then kept in an airtight bottle [29-32]. Also, the total sulfate and chloride were measured at each hydration interval. The measured values at 28-days for compressive strength, total sulfate and chloride contents for each cement mix were considered as zero readings.

The rest of samples were then immersed in a freshly prepared 4 % MgSO₄ and 4% MgCl₂ solutions up to 12 months noticing that at first, the chloride and sulfate solutions were renewed every 2-3 days so as to keep its concentrations nearly constant [33,34]. The total SO_3 content [35-37] was determined by placing one gram of the dried sample (W_1) in a beaker containing 300 ml freshly prepared half saturated lime water. The content was stirred for one hour using a magnetic stirrer, and then filtered through a sintered glass funnel G. 4. The residue was washed several times with lime water, and then with distilled water. Add 5 ml conc. HCl acid (Sp. gr. 1.18) and drop wise 10 ml $BaCl_2$ (100 g/l) to the boiling filtrate. The mixture was boiled gently for 5 minutes, let to cool gradually, and then filter. Wash several times with hot distilled water till free from chloride. Thus, the total sulfate content precipitated. Ignite the residue up to 850 °C for 30 minutes, cool in a desiccator and weigh (W_2). The total sulfate content was calculated from the following relation:

Total SO₃, % = W₂ x 34.3 / W₁ x 100   (2)

Where, W_1 is the weight of the original sample, W_2 is the ignited weight of the residue and 34.3 is the molecular ratio of SO_3 to $BaSO_4$ (0.343) multiplied by 100. The total Cl^- ions content in the hardened cement pastes was determined by weighing 2 grams of the powdered sample into a stoppered conical flask (M_1). Dispersed with 35 ml dist. water, and then add 10 ml HNO_3 acid (Sp. Gr. 1.42). add 50 ml hot water, heat till boiling and keep warm for 10-15 min. Cool to the room temperature and add standard 0.1 N $AgNO_3$. Add 2-3 ml nitrobenzene, stopper the flask and shake vigorously to coagulate the precipitate. Add one ml of ferric indicator (100 ml saturated ammonium ferric

sulfate solution + 10 ml HNO_3). Titrate using a standard solution of 0.1 N ammonium thiocyanate till the first permanent red color and weigh (M_2). The total chloride content was then calculated from the next relation:

Total Cl⁻, % = M₁ − M2/ M₂ x 100   (3)

Where M_1 is the original weight of the sample, M_2 is the final weight of the sample. The obtained results of chloride contents must be corrected by subtracting the values of chloride contents of the starting raw materials.
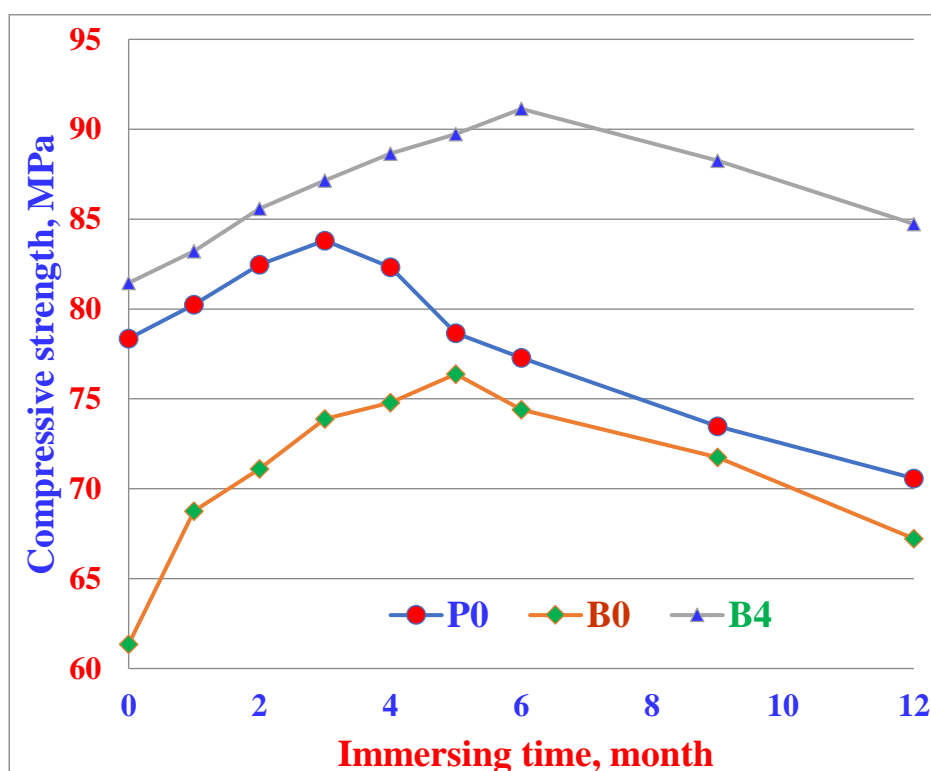
3. Results and Discussion

3.1. Compressive strength (4 % MgSO₄)

The compressive strength of the OPC (P0), HB (B0) and HPFA/SF/HB (B4) cements cured in 4 % MgSO₄ solution till 12 months is represented versus immersing time in Figure 2. The compressive strength of the hardened cement pastes of the OPC (P0) slightly enhanced merely up to three months, and then diminished up to 6 months, but sharply declined till 12 months of immersion, i.e. the 28-compressive strength of the pure OPC pastes (P0) can withstand only up to three months in 4 % MgSO₄. It is essentially attributed to the fact that at early ages of immersion the total porosity of the hardened cement pastes was nearly the maximum. Therefore, the rate of diffusion of SO_4^{-2} ions could be partially eliminated and only form a white coat on the lateral edges of the samples which prevents the further diffusion of the SO_4^{-2} ions through the cement surfaces [38,39]. So, a slight improve in the compressive strength coming from the hydration process and the small activation of SO_4^{-2} ions [40,41]. The decrease of compressive strength after 3 months of immersion is principally due to the aggressive attack of the SO_4^{-2} ions so that the cement pastes could not resist the diffusion of SO_4^{-2} ions inside the cement matrix. This gave a big opportunity to some deleterious reactions to take place. This case was often ended by the formation of ettringite and/or gypsum. These phases always cause expansion accompanied by internal minor cracks and the disintegration of the formed hydrates, which are the centers of binding or cementing properties. These are the main reasons responsible for the strength loss [41-43]. Though the values of compressive strength of BC are lower than those of OPC at all immersing times, the BC could be withstood up to five months, and then decreased. This means that the BC is more resistant against the attack of SO_4^{-2} ions than OPC [33,34].

The compressive strength of the hardened cement pastes of B4 containing FA and SF enhanced with the increase of immersing time till 6 months, and then declined. Improving of compressive strength is essentially attributed to the decrease of C_3A phase because it is very sensitive to SO_4^{-2} ions and it is easily spoiled by these ions. It was in turn compensated with the two pozzolanic mineral admixtures [35], because the FA and/or SF particles are difficult to disintegrate by the sulfate ions due to its high glassy structure and also due to its high contents of silica, and moreover the activation of the BC by HPFA and SF, in addition to the good dispersion by the used admixture, and the good compaction of these pozzolanic materials during moulding. The filling action as well as the relatively lower amount of free lime due to its consumption by the pozzolanic reactions to form CSH and the rate of SO_4^{-2} ions diffusion into the hardened cement matrix was the minimum because it decreases the permeability [44]. The FA can create soft parts of fresh pastes which improve its plasticity, infill gaps between constituents, compress the contact zone between the various grains and the matured cement [45]. Also, the hydraulic characteristics of both components are well contributed to the less permeability to liquids or gases and mechanical strength improvement. Accordingly, the compressive strength improved and enhanced

[38,41]. Lack of compressive strength was related to the evolution of water from the cement matrix into the solution due to the deleterious reactions. It is often followed by an increase in the porosity and permeability. It seemed to speed up the action effect of SO_4^{2-} ions, and hence a strength loss could be expected [40,46]. This higher porosity and permeability often accompanied by a more strength loss [43-46]. This was perfectly agreed with that obtained by many investigators [35,46].

Though the SO_4^{2-} ions aggressively attacked the cement matrix after the 6th month of immersion, no visual cracks or any signs of deterioration on the lateral surfaces or edges could be seen by the naked eyes. At the end of the 12th month of immersion, the SO_4^{2-} ions only deposited or adsorbed on the external surfaces or lateral edges of the hardened cement structures and some horizontal minor cracks and little deformation could be seen on the edges of specimens which is likely due to the decalcification of CSH [35,43-46], while the action effect of these sulfate ions are more effective on the OPC pastes where large cracks and swelling were noted. This means that the degree of damage was in the decreasing order: OPC < HBC < B4. Consequently, it could be concluded that the OPC is more affected by 4% $MgSO_4$ ions, while the B4 is the least.

Figure 2 Compressive strength of the OPC, belite and HPFA/SF belite cements immersed in $MgSO_4$ solution up to 12 months.

3.2. Total sulfate content

The total SO_4^{-2} content of the OPC (P0), BC (B0) and HPFA/SF/BC (B4) cements cured in 4 % $MgSO_4$ solution up to 12 months is represented versus the immersing time in Figure 3. The total SO_4^{-2} content enhanced with the time of immersing up to 12 months. This is mainly due to the migration of SO_4^{2-} ions into the hardened cement matrix. This in turn reacted with C_3A, C_4AF and Ca $(OH)_2$ to form calcium sulfoaluminate hydrates (ettringite) and/or monosulfate hydrate [37,42,47]. The OPC exhibited the highest values of total SO_4^{-2} content, while those of other blended cement pastes (B4) achieved the lowest values nearly at all immersing times, This is principally attributed to the formation of a dense white coat of SO_4^{2-} ions on the lateral surfaces of the immersed specimens. This coat prevents the penetration or diffusion of SO_4^{2-} ions into the matrix of cement pastes. This in turn slows down the aggressive diffusion of the SO_4^{2-} ions [35,37], beside other factors as the good dispersion and good compaction of samples during moulding. Therefore, the pure OPC pastes (P0) are so sensitive to SO_4^{2-} ions that they are highly influenced by these ions [35,37,42,48], noticing that the BC (B0) recorded the medium values of SO_4^{2-} ions contents at all immersing times.

3.3. Mechanism of MgSO₄ attack

During the early ages of immersion in 4 % $MgSO_4$ (MS⁻) solution, the MS⁻ ions directly reacted with the produced Ca $(OH)_2$ (H⁻) from the hydration process to form gypsum $CaCO_3$. 2 H_2O (CS⁻.H_2) and brucite, Mg $(OH)_2$ (MH) as follows:

MS⁻ + CH + 2H   → CS⁻.H₂ + MH   **(4)**

The insoluble MH decreases the pH-value of the hydrates. So, the lower pH-value de-stabilizes either CSH or ettringite. Moreover, no additional ettringite could be formed because the MS⁻ ions further react with CSH to form more gypsum, MH and SiO_2-gel [23,33,34] as follows:

CₓSᵧHᵤ + MS⁻ + (3x+0.5y-z) H   → CS⁻.H₂ + MH + SiO₂-gel   **(5)**
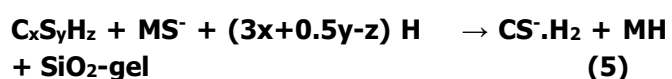
The formed phase (SiO_2-gel) has no or minor cementing properties than CSH. The CSH further hydrates to liberate CH to re-increase the pH-value and establish its equilibrium. But, the liberated lime instead of re-increasing the pH-value, it reacts with MS⁻ ions forming more CS⁻.H_2 and MH and so on. Accordingly, the CS⁻.H_2 and MH contents increase gradually,

whereas the CSH losses its cementing properties leading to further deleterious action. Furthermore, the MH reacts with the SiO_2-gel forming MSH [43] as follows:

4MH + SiO₂-gel → MSH   **(6)**

The resulting product (MSH) is non-cementitious and causes softening of the cement pastes. Hence, the formation of high amounts of gypsum and MH is the main reason responsible for damaging [33,34,49,50].

3.4. Compressive strength (4 % MgCl₂)

The compressive strength of the OPC (P0), HB (B0) and HPFA/SF/HB (B4) cements cured in 4 % $MgCl_2$ solution up to 12 months is graphically drawn against immersing time in Figure 4. In case of $MgCl_2$ solution, the compressive strength displayed the same trend with the same samples up to 12 months. The compressive strength of the OPC (P0) enhanced merely up to 3 months of immersion, and then declined. Increasing of the compressive strength is essentially due to the hydration process of the main cement phases, in addition to the initial activation of cement phases by Cl⁻ ions [35,37]. Furthermore, the nano-grain size particles of the HPFA and SF led to a significant decrease in the diffusion of chloride ions into the hardened cement pastes [29,33,51]. Whereas the reduction of compressive strength is mainly contributed to the aggressive attack of the Cl⁻ ions so that the cement pastes could not resist the diffusion of Cl⁻ ions into the cement matrix, i.e. the P0 could not withstand against the attack of Cl⁻ ions except three months. The compressive strength 0f B0 increased up to 5 months, and then decreased. Though the values of compressive strength of BC are being lower than those of OPC up to 3 months of immersing, the BC could be withstood only up to four months, and then decreased, i.e. the B0 is more resistant against the attack of Cl⁻ ions than OPC [33,34]. Moreover, the compressive strength values after 3 months of immersion were higher than those of P0 onward.
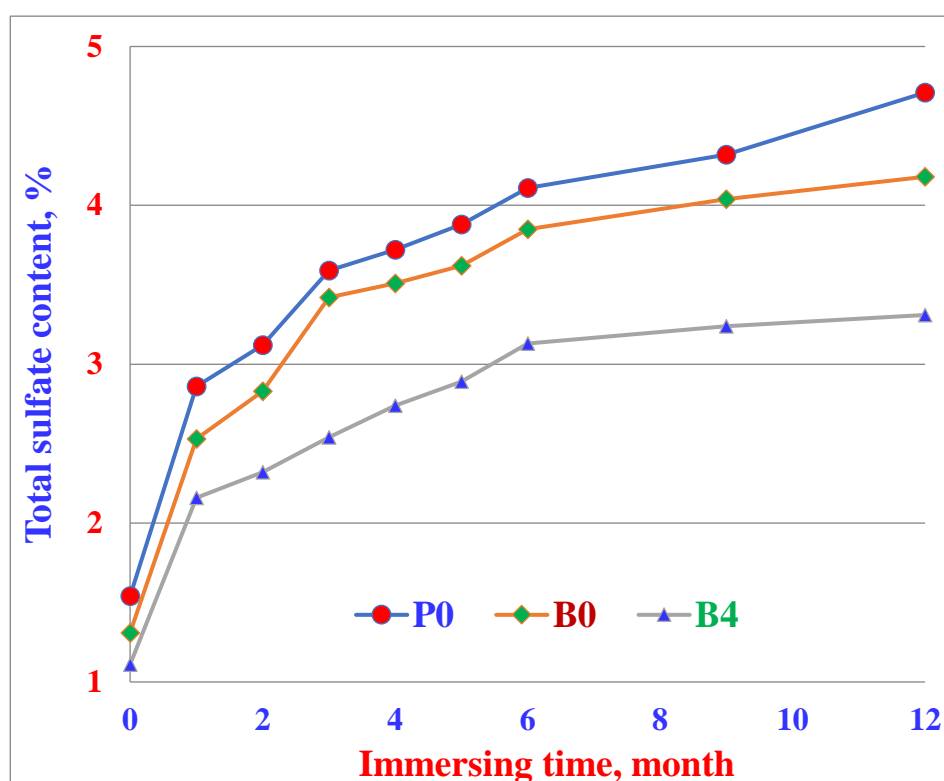
The compressive strength of the hardened cement pastes of B4 containing FA and SF enhanced with immersing ages up to 6 months, and then reduced. The increase of compressive strength is mainly due to the pozzolanic reaction of the HPFA and SF [35]. The FA and/or SF particles are also difficult to decompose by the Cl⁻ ions because of its high glassy structure and its high contents of silica. Moreover, the

activation of the BC by HPFA and SF, in addition to the good dispersion by the used admixture, and the good compaction of these pozzolanic materials due to its filling action as well as the relatively lower amount of free Ca(OH)$_2$ due to its consumption by these pozzolanic materials to form CSH. This made the rate of sulfate ions diffusion into the hardened cement matrix was the minimum because this reduces the permeability to a large extent [44,45]. Also, the hydraulic features of both components are well contributed to the less permeability to liquids or even gases and mechanical strength improvement. As a result, the compressive strength tends to increase [38,41]. A reduction in the Cl$^-$ ions penetration into the hardened cement pastes incorporating nano-sized particles was reported due to the densification capability of the nanomaterials like nanosilica [33,52]. Reduction of compressive strength is perhaps contributed to the release of water from the cement pastes into the solution as a result of the detrimental reactions. This usually accompanied with a consequent increase in the porosity and permeability [53,54].
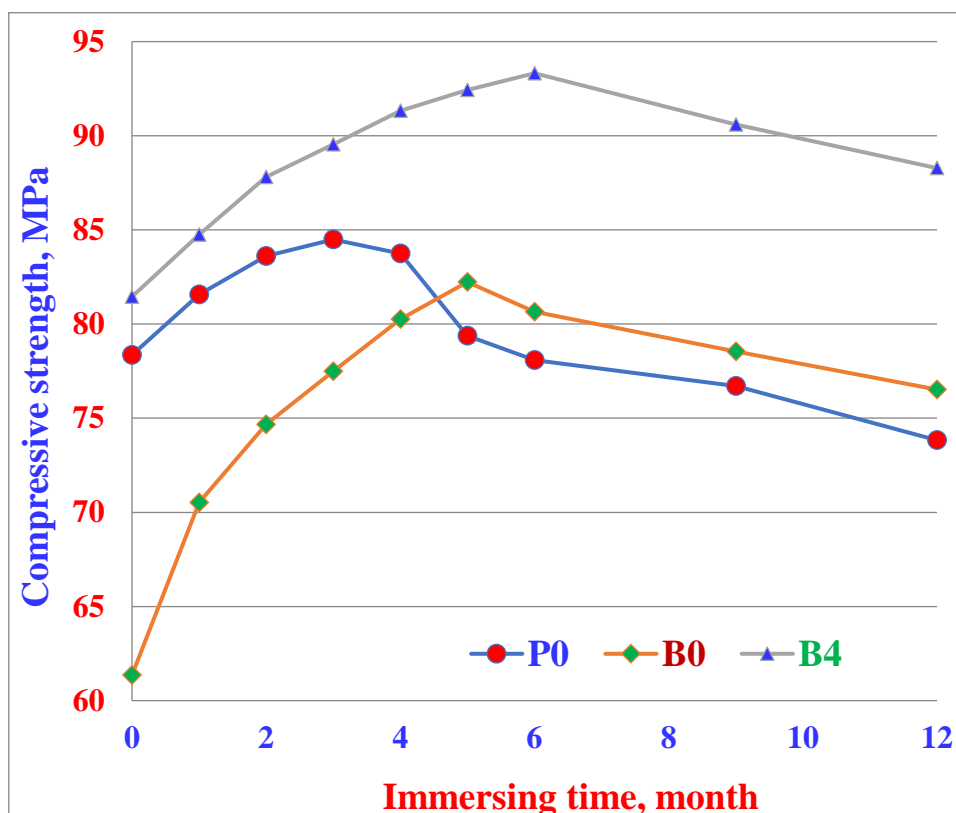
3.5. Total chloride content

The total Cl$^-$ ions content of the OPC (P0), BC (B0) and HPFA/SFBC (B4) cements cured in 4 % MgCl$_2$ solution up to 12 months is represented versus the immersing time in Figure 5. The total Cl$^-$ ions content gradually enhanced with immersing time up to 12 months. It is contributed to the migration of Cl$^-$ ions into the hardened cement pastes. This in turn reacted with C$_3$A and Ca (OH)$_2$ to produce calcium chloro-aluminate hydrate, C$_3$A.CaCl$_2$.H$_{12}$ [37,42,47]. The OPC exhibited the highest values of total Cl$^-$ ions content, while those of other blended cement pastes (B4) achieved the lowest values, nearly at all immersing times. This is essentially attributed to that at early periods of exposure to Cl$^-$ ions (up to 3 months) the Cl$^-$ ions accelerated the rate of hydration due to the formation of CaCl$_2$. After 3 months, the amounts of CaCl$_2$ and Mg (OH)$_2$ were largely and continuously increased, which in turn increased the amount of calcium chloro-aluminate hydrate, C$_3$A.CaCl$_2$.H$_{12}$. This could be increased the diffusion of Cl$^-$ ions by time. The accumulation of these ions was often followed by more dissociation of the formed CSH from the hydration process. The total Cl$^-$ ions of B4 incorporated HPFA and SF achieved the lowest Cl$^-$ ions content. It is principally attributed to the presence of nanosilica particles because it was more resistant to Cl$^-$ ions than in its absence, beside other factors as the good dispersion and good compaction of samples during moulding, i.e. the pure OPC pastes (P0) are so sensitive to Cl$^-$ ions that they are highly affected with these ions [35,37,42,48].

Figure 3 Total sulfate content of the OPC, belite and HPFA/SF belite cements immersed in MgCl$_2$ solution up to 12 months.

Figure 4 Compressive strength of the OPC, belite and HPFA/SF belite cements immersed in MgCl$_2$ solution up to 12 months.
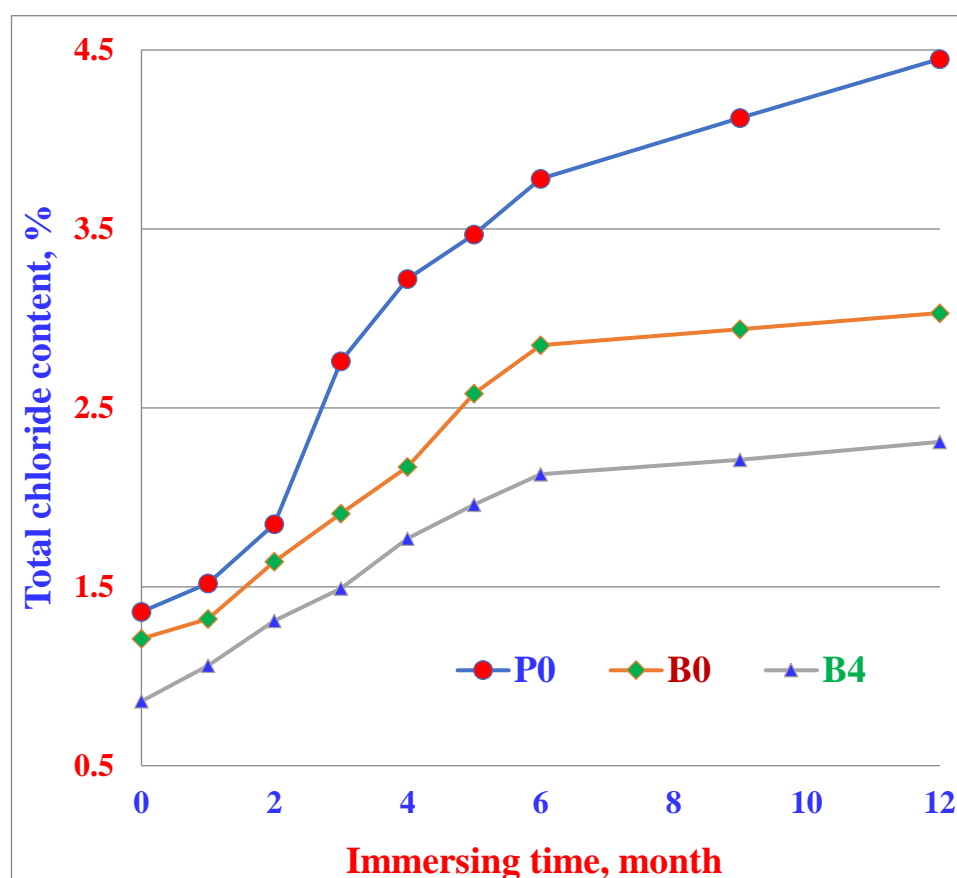
Figure 5 Total chloride content of the OPC, belite and HPFA/SF belite cements immersed in MgCl$_2$ solution up to 12 months.

3.6. Mechanism of MgCl₂ attack

During the early ages of immersion in 4 % MgCl₂ (MC²⁻) solution, the MC²⁻⁻ ions directly reacted with the formed Ca (OH)₂ (H⁻) that is coming from the hydration process to produce calcium chloride (CaCl₂) and brucite, Mg (OH)₂ (MH) as in equation 6. The resulting CaCl₂ could be reacted with alumina-bearing compounds to form chloro-aluminate hydrate (C₃A.CaCl₂.H₁₂) as in equation 7 [23,35,37,55].

$$MgCl_2 + Ca\ (OH)_2 \rightarrow CaCl_2 + Mg(OH)_2 \qquad (7)$$

$$CaCl_2 + C_3A.H_{12} \rightarrow C_3A.CaCl_2.H_{12} \qquad (8)$$

The formed latter hydrate causes a little expansion due to its high crystal growth. It often caused softening of the cement pastes, and its formation is always accompanied by decreasing the compressive strength. This is mainly due to that the Cl⁻ ions were evidently form a more pore volume on the long-term of immersion, i.e. porous CSH. This allows easier diffusion of Cl⁻ ions by the leaching of Ca (OH)₂ and the formation of the very soluble CaCl₂. It also reduces the pH value of the poresolution. Therefore, the net result is a higher degree of deterioration or even the complete damage of the cement structure on the long time, i.e. the excess of the formed CaCl₂ is the increase of the deterioration. Furthermore, on the long time the breakdown or even decay of the hardened cement pastes was expected not only due to the formation of C₃A.CaCl₂.H₁₂ or leaching of Ca (OH)₂, but also associated to the formation of another salts with no cementing or binding properties [33,43,53,55].

4. General Discussion

Generally, the resistance of cementing composites is principally contributed to its ability to withstand against the detrimental reactions in the various chemical media to which it is exposed, i.e. the durability performance of cementing composites is mainly depending on the ease and rate of diffusion of the deteriorating ions and fluids into the hardened cement structures. On account of the nature of the used nanomaterials, the nanoparticles could be acted as fillers that could fill the pore volume between the various grains of the cement. Thereby, this could be resulted in a more densified structure with a higher resistance to the diffusion of any deleterious ions. Moreover, the pozzolanic reactions of the nanoparticles with the released free lime or Ca (OH)₂ from the hydration of calcium silicate phases of the cement (C₃S and β–C₂S) to form CSH–gel. Soon, it precipitated in the pore volume of the hardened cement pastes. It will improve the densification parameters of the hardened cement microstructure as water absorption, bulk density and total porosity, i.e. existence of nanoparticles is always resulted in a pore refinement, filling ability and a lower permeability, in addition to a higher mechanical performance [1,8,13,17,53,56,57].

The use of nanosilica and/or nanoalumina that were present in GPFA and SF decreased the water absorption or permeability of the hardened cement pastes due to its filing ability and pozzolanic reactivity [58-64]. A decrease in water absorption or permeability of cement composites containing nanosilica or nanoalumina or generally nanomaterials was reported due to the pore filling effect of the nanomaterials coupled with enhancement of the interfacial transition zone between the aggregate and cement matrix [59,61,62]. Furthermore, the decline in the rate of permeability of cement and/or concrete containing nanosilica was also due to the important production of other calcium silicate hydrates which results in refinement of the microstructure and the relating reduction in permeability, i.e. the use of nanosilica is more effective in the decrease of the water absorption compared to any nanomaterial [59-63].

5. Conclusions

The physical and chemo/mechanical properties of the Portland cement (OPC), belite cement (BC) incorporated high pulverized fly ash (HPFA) and Silica fume (SF) were perviously studied in Part I, from which it could be selected the optimum belite cement (B4), that achieved the best results. In Part II, the chemical resistence or durability against 4 % MgSO₄ and 4% MgCl₂ aggressive solutions up to 12 months in terms of compressive strength, total sulfate and total chloride was evaluated and studied. The following conclusions could be obtained:-

1. The optimum belite cement (B4) containing 15 % high pulverized fly ash (HPFA) and 5 % silica fume (SF) could be resisted up to 6 months, while that of BC could be withstood only up to 5 months, and the OPC could not be resisted more than 3 months of immersion in 4% MgSO₄ medium.

2. The compressive strength exhibited by the samples immesed in sulfate solution at 3, 5 and 6 months of immersion were 83.81, 76.38 and 91.31MPa, respectively.

3. The same trend was displayed when the same samples were exposed to 4% MgCl₂ solution.

4   The compressive strength exhibited by the same samples exposed to chloride solution at 3, 5 and 6 months of immersion were 84.49, 82.23 and 93.32 MPa, respectively.

5   Both total sulfate and chloride contents were enhanced with immesion time up to 12 months, and their values were the minimum with B4 and the maximum with OPC, while with BC were the midium.

6   Nanomaterials largely improved the resistance of cementing composites. This is essentially contributed to the reduction of the permeability of these composites resulting from its pore filling ability and the pozzolanic reactivity of those nanomaterials with the evolved Ca (OH)$_2$ that is coming from the hydration of di- and trisilicate phases of the cement to form additional CSH.

7   Cementitious composites incorporating nano silica as in HPFA and SF exhibited lower permeability due to their pozzolanic properties together with their capability to act as nucleation sites for cement hydration, i.e. the nanosilica is not sensitive to chemical media. Accordingly, this was positively reflected on physical, chemo/mechanical and durability characteristics.

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Yes

Conflict of interest

The Author has no conflicts of interest to declare that they are relevant to the content of this article.

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