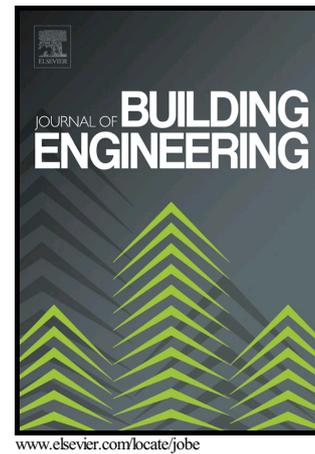


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Chemical activation of slag-blended Portland cement

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Abstract

Chemical activation as one of the most popular methods of activation has been considered for improving hydraulic properties of slags. This work presents chemical activation of blast-furnace slag-blended Portland cement. For this purpose, a number of different chemical activators and two different quality improvers including Triisopropanolamine (TIPA) and Triethanolamine (TEA) were utilized. At first, initial mixes were prepared using different proportions of slag, Portland cement, and insoluble sulfate-based chemical activator. The optimum mix was then selected based on 28- and 60-day compressive strength results. The results indicated that the optimum mix consisted of 48% Portland cement, 43% slag and 9% insoluble chemical activator. In the next stage, various dosages of TIPA and TEA were added to the optimum mix for improving the strength behavior. Based on the results, the addition of 0.04% TEA leads to 8% enhancement in both 28- and 60-day compressive strengths. To induce more improvement in compressive strengths, chlorine soluble chemical activators were incorporated in the mixes. The results showed that, chlorine activators alone or in combination with TEA as quality improver could induce no more improvement in compressive strength. However, the obtained results revealed a set accelerating behavior for chlorine soluble chemical activators. Studies by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy analysis and X-ray diffractometry on 60-day cured hardened paste of the activated mixture have revealed that the microstructure is composed of an amorphous matrix in which plate-like Portlandite crystals are embedded. Application of Fourier transform infrared spectroscopy has confirmed the presence of calcium-silicate hydrates as the main binding compound of the material.

Keywords: Blended cement; Blast-furnace slag; Chemical activation; Quality improver

1. Introduction

Cement industry is faced with serious environmental problems. The production of Portland cement (PC) in the cement industry not only consumes raw materials and large amounts of energy, but also as one of the primary industrial producers of carbon dioxide, contributes to the greenhouse effect and causes acid rain. Actually, this industry generates greenhouse gases (GHGs) both directly through the emission of CO₂ when clinker is produced and also through the consumption of energy [1-4]. On the other hand, the severity of environmental regulations is

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enhanced progressively and has forced the industries to put in a great effort to reduce their pollutants [4].

One of the interesting approaches for reducing environmental problems and also gaining technological and economic advantages is the increasing usage of industrial byproducts and wastes [1-6]. Among the industrial wastes, only slags have latent cementing property and have been converted to an important research area [5, 7, 8]. In fact, the production of slag cements and slag-blended Portland cements results in resource conservation, reducing energy consumption and minimizing emission of GHGs, especially CO₂ [2].

Blast furnace slag (BFS) as one of the industrial solid wastes is formed in a molten state simultaneously with iron in a blast furnace. The chemical composition of the slag is originated from silicate and oxide components of the raw materials used in the smelter feed [9]. The slag exhibits primarily latent hydraulic activity, but may show some pozzolanic character as well.

Nevertheless, BFS adversely affects the early-age strength of PC when used at high replacement levels [10] and as a supplementary cementing material, it is necessary to tailor its reactivity by auxiliary activation techniques [10-12] such as thermal, chemical, and mechanical as the most common activation techniques [11, 12].

Thermal activation or curing at elevated temperatures can improve strength development [12], but at the same time may decrease the ultimate strength [13]. Mechanical activation results from compound effects of particle fracture and other bulk and surface physicochemical changes [14, 15], dislocations and other defects induced by the milling [14, 16]. Mechanical activation of solid dispersed materials leads to accumulation of mechanical energy that is used for enhancement of the specific surface energy of a dispersed material [17, 18]. In mechanical activation, physicochemical properties of solid materials are varied during grinding process [16, 17]. Chemical activation refers to the use of some chemicals to impart cementing properties and/or to activate latent hydraulic properties [11, 18]. There are two types of alkali-activation, including (1) activation with strong alkaline activators that are suitable both for imparting cementing properties to aluminosilicate materials exhibiting no cementing properties and activating industrial slags with latent hydraulic properties, and (2) activation with mild alkaline activators that are applicable only for industrial slags exhibiting some cementing properties [19, 20].

Although, it seems at first glance the problem with using chloride chemicals is that chloride brings corrosion to steel bars in reinforced concretes. But there are two very important points about the type of cement and the chlorine limit: 1) Glass and Buenfeld [21] compiled and analyzed various ranges of chloride threshold levels in concrete and mortars reinforced with steel bars in exposure to different regimes in an excellent review. According to their review, total chloride content must be less than 1.5 wt.%. In the present study, the weight fractions of soluble chlorine activators are 1 wt.% which are below the threshold.

2) Also, in a recent work, Pacheco and Polder [22] found that in BFS concrete specimens the higher resistance to chloride ingress prevented from corrosion initiation after 6 months. Cheng et al. [23] investigated the corrosion behavior of reinforced concrete exposed to sustained loadings (37% and 75% of the ultimate load) and 3.5% NaCl solution and found the slag concretes exhibit lower corrosion rate (relative to the control). The partial replacement of cement by BFS reduced the electrical charge passing through the concrete (during the rapid chloride penetration test) and the water permeability of concrete. This was the result of BFS reacting with water and Portlandite to form extra calcium silicate hydrate (C-S-H) gel and more refined microstructure. A study of slag concrete after 25 years of exposure in a marine tidal zone [24] confirmed the

beneficial role of slag in dramatically reducing the chloride ion penetration, especially at relatively high replacement levels (40–70%).

In addition, the blended cements activated by chloride-based admixtures are widely used for construction in cold weather conditions.

Besides the chemical activators, organic accelerators or grinding aids, also known as quality improvers, are extensively used because of their considerable effectiveness at very low dosages. The most common organic accelerators are alkanolamines such as triethanolamine (TEA) and triisopropanolamine (TIPA) which are the prevalent grinding aids in the comminution process of Portland cement clinker. TEA and TIPA are usually utilized individually or in combination with chemical activators to enhance the mechanical strengths of concrete by hastening hydration reactions [25, 26]. In a study by Huang et al. [25] the effect of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ with and without TEA and TIPA has been investigated. They concluded that these chemical activators and quality improvers can remarkably increase compressive strength of PC, so that a suitable proportioning of $\text{Ca}(\text{NO}_3)_2$ with TIPA and saccharide can improve strengths at all curing ages. In another work, Gok and Klinic [26] evaluated the effect of calcium nitrate, TEA and TIPA on 7- and 28-day compressive strengths of mortars prepared at two different cement compositions. They found that TEA's impact is prominent at later curing ages from the standpoint of compressive strength, whilst TIPA affects both early- and late-age compressive strengths. Alkanolamine-based quality improvers such as TEA and TIPA are also applied not only to efficiently blend admixtures and enhance both early- and late-age compressive strengths, but also to facilitate the grinding process by hindering aggregation and coating at the surface of balls and mill wall [27, 28].

Since most studies have focused on the effects of TEA and TIPA on Portland cement, further experiments are needed to investigate the effects of these two quality improvers on composite cements such as the blended cement considered in this study. Such a study can provide reliable information for the pertinent knowledge.

This study deals with the effectiveness of various soluble chlorine chemical activators and quality improvers (TIPA and TEA) on the improvement of hydraulic property of BFS-blended Portland cement after being activated with the so-called sulfate-based insoluble chemical activator.

2. Experimental

2.1. Materials

BFS used in this study was supplied from Esfahan steel complex. The BFS was ground until cumulative passing of 98.5% from a 90- μm mesh screen. Type II Portland cement (PC2) used in all mix proportions was obtained from Tehran cement plant. Table 1 presents chemical composition and physical properties of these materials as well as Bogue's potential phase composition of PC2.

X-Ray diffractogram of BFS is illustrated in Fig. 1. As can be clearly seen, the XRD pattern of the slag shows the presence of few amounts of tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), and calcite phases, identified based on standard cards of ICDD-00-013-0209, ICDD-00-002-0866, and ICDD-00-003-0569, respectively. Calcite can be originated from the gradual carbonation of CaO content of fresh slag with atmospheric carbon dioxide. The observation of calcium silicates is as the consequence of the reaction between calcium oxide and silicon dioxide existed in the melt during the high temperature production process of the BFS.

In order to increase early- and late-age hydraulic properties of BFS-blended Portland cement, insoluble sulfate-based chemical activator in combination with the most effective soluble chlorine chemical activators and quality improvers was used. According to previous research studies [29, 30], the anhydrite of the composition (in wt.%); CaO-36.00, SO₃-54.38, and SiO₂-5.88 was used as insoluble chemical activator. The optimum proportion of the insoluble chemical activator in PC-BFS paste will be described in section 2.4.

TIPA and TEA as quality improvers were added to the blend at the stage of homogenizing PC2 and BFS using a cylindrical laboratory ball mill with the length and diameter of 0.30 and 0.26 m, respectively. The dosages of 0.02, 0.04, 0.06, 0.08, and 0.01 (wt.%) were utilized for both TEA and TIPA.

Different soluble chlorine chemical activators were used for more effective activation of the BFS. Table 2 presents the used type and dosage of soluble chemical activators. These activators were dissolved into mixing water and then added to the mixture.

2.2. Tests performed

Tests performed were:

2.2.1. Normal consistency of hydraulic paste

Water-to-cement ratio (w/c) of the cement pastes was mensurated according to ASTM standard C187 which is a standard test method for measuring the amount of water needed for normal consistency of hydraulic cement paste. Based on the results, a constant w/c of 0.28, giving normal consistency and appropriate workability was determined for all fresh cement pastes.

2.2.2. Setting times

Initial and final setting times (IST and FST) of the cement pastes were determined according to ASTM C191 that is standard test method for time of setting of hydraulic cements by means of Vicat needle.

2.2.3. Compressive strength

A uniaxial digital hydraulic compression test machine (SCL STD 30) of 300 kN-capacity with $\pm 1\%$ accuracy and a loading rate of 0.4 MPa/s was employed for the measurement of compressive strength of the cured paste specimens. Three paste specimens were used in each compressive strength measurement and the average of them was recorded as the result. The minimum and maximum values of the standard deviations for the measurements were 0.1 and 1.2 MPa, respectively.

2.3. Preparation of initial mixes

Table 3 presents different proportions (by total weight of the binder) of BFS, PC2, and insoluble chemical activator for preparation of initial mixes. The dry mixes were afterwards completely homogenized for 20 min using a laboratory ball mill. After adding water to the dry mixes at the constant w/c of 0.28, the fresh pastes were exhaustively mixed in a planetary mixer for 5 min and afterwards cast into $2 \times 2 \times 2$ cm³ molds. The molds were stored at an atmosphere of more than 95% relative humidity at 25 °C for the first 24 hours and then the specimens were cured in lime-saturated water at 25 °C until the time of testing.

2.4. Specifying the optimal proportions of mixes

To achieve the optimum proportion of the insoluble chemical activator in PC-BFS paste, 28- and 60-day compressive strengths were measured and the mix containing higher amount of slag and exhibiting the highest compressive strength was selected as the reference mix for the rest of the experiments. In the next stage, the effect of both TEA and TIPA as quality improvers on compressive strength of the reference mix was probed by measuring and comparing 28- and 60-day compressive strengths of the hardened paste specimens cured at the same conditions. The effectiveness of the opted soluble chlorine chemical activators on the enhancement of hydraulic properties of PC-BFS paste after being activated with the so-called sulfate-based insoluble chemical activator was evaluated by comparing the achieved 28- and 60-day compressive strengths as the last stage of the experimentation. Finally, the chosen mixes were characterized by some complementary techniques.

2.5. Complementary studies

2.5.1. Mineralogical study

In order to conduct mineralogical study, the X-ray diffractograms of the reference mix and the mix representing the highest improvements in compressive strengths were recorded on a Philips Expert diffractometer using $\text{CuK}\alpha$ radiation. The tests were run in a 2θ range of $10\text{--}90^\circ$ at a scanning rate of $2^\circ/\text{min}$, with a deliverance slit of 1° , an anti-scatter slit of 1° , and a receiving slit of 0.01 mm .

2.5.2. Fourier transform infrared spectroscopy

FTIR spectra of the BFS, reference mix and the mix representing the highest improvements in compressive strengths were provided using a SHIMADZU (IR Spectrophotometer 8400s) FTIR spectrometer in transmittance mode from 400 to 4000 cm^{-1} using standard KBr technique (0.5 mg sample with 250 mg KBr). All spectra were obtained with a sensitivity of 4 cm^{-1} and 64 scans per spectrum taken.

2.5.3. Scanning electron microscopy

Microstructural studies were also performed on the reference mix and the mix representing the highest improvements in compressive strengths using a TESCAN VEGA II (Czech Republic) Scanning Electron Microscope. The morphology of the microstructure of the paste specimens was investigated using secondary electron (SE) mode of the microscope at an accelerating voltage of 20 kV . For this purpose, a number of paste specimens were cut into $2\text{--}3\text{ mm}$ thick slices to expose internal regions. Suitable slices were then dried at 90°C for 24 h and coated with a gold layer to make them conductive.

3. Results and discussion

3.1. Compressive strength

Fig. 2 depicts the values of the compressive strength for all 25 paste specimens after 28 and 60 days of curing. The 28- and 60-day compressive strengths of mix No. 3, mix No. 8, mix No. 17, and mix No. 21 are close together. The 28-day compressive strengths of the mentioned mixes reached 77.5 ± 3.8 , 80.0 ± 4.0 , 80.0 ± 3.2 , and $75.0\pm 3.7\text{ MPa}$, respectively. The same mixes exhibit 60-day compressive strengths of 92.5 ± 4.6 , 91.2 ± 4.5 , 95.0 ± 4.7 , and $92.5\pm 5.1\text{ MPa}$, respectively. Thus, mix No. 17 containing 48% PC2, 43% BFS and 9% insoluble chemical activator parades the highest compressive strengths at both curing times. The mix No. 17 was consequently chosen for the rest of the study and regarded as the reference mix.

As mentioned in *Experimental* section, to investigate the effects of TEA and TIPA as the quality improvers on the compressive strength of the reference mix, the dosages of 0.02%, 0.04%, 0.06%, 0.08% and 0.1% by weight were considered for both TEA and TIPA. Table 4 displays the results of both 28- and 60-day compressive strengths of the reference mix under the effect of various dosages of TEA and TIPA.

As can be deduced from data presented in Table 4, both quality improvers can significantly tailor 28- and 60-day compressive strengths if they are added at the optimum dosages. As found out, when TIPA is added at the optimum dosage, i.e. 0.02 wt.%, 5.0% and 3.7% increases in 28- and 60-day compressive strengths can be attained, respectively. Addition of TEA at optimal dosage, i.e. 0.04 wt.%, however is more effective and can cause about 8% enhancement in both 28- and 60-day compressive strengths. The results in Table 4 reveal that dosages higher than optimum values lead to gradual decline in compressive strengths. Therefore, the dosage of 0.04 wt.% TEA is chosen for the rest of the experiments.

TEA and TIPA are conventional additives for the purpose of facilitating the grinding process of cement by reducing agglomeration of cement particles and also hindering coating formation on the surface of grinding media. This effect, however, causes effectual homogenization of cement components including clinker, gypsum, BFS, which in turn tailor hydration reactions and compressive strengths. Many researchers have investigated the effects of TEA and TIPA on hydration reactions of cements, mainly plain PCs [31, 32]. There is no report on the effect of TEA and TIPA on composite cements and this is considered in the present study for the first time.

Fig. 3 depicts the results acquired for both 28- and 60-day compressive strengths of the reference mix chemically activated by individual soluble chloride activators. As can be observed, compared to the 28-day compressive strength of the reference mix (80.0 ± 4.8 MPa), the addition of 1 wt.% of each of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, NaCl, KCl, MgCl_2 , NH_4Cl , and LiCl to the reference mix, caused the 28-day compressive strengths of 95.0 ± 5.0 , 85.0 ± 5.0 , 92.5 ± 5.5 , 78.5 ± 4.5 , 90.0 ± 5.4 , and 75.0 ± 4.5 MPa, respectively. Also, 60-day compressive strengths of 100.0 ± 6.0 , 98.7 ± 5.9 , 100.0 ± 5.0 , 90.0 ± 5.4 , 101.7 ± 5.1 , and 84.2 ± 5.0 MPa reached after the addition of 1 wt.% of each of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, NaCl, KCl, MgCl_2 , NH_4Cl , and LiCl, respectively to the reference mix. The maximum improvements on 28- and 60-day compressive strengths are 12.50% and 7.01%, respectively, originated from the addition of 1 wt.% NH_4Cl . The addition of 1 wt.% MgCl_2 and LiCl not only does not result in any improvement, but also leads to a remarkable decrease in compressive strength.

Identifying the effective soluble chemical activators, experiments were continued to investigate the combined effects of both effective soluble chemical activators and the most effective quality improver on 28- and 60-day compressive strengths. The compositions designed for the combinations of the effective soluble chemical activators and the best quality improver are listed in Table 5.

The compressive strength values resulted from the combined effect of both chemical activators and quality improver are illustrated in Fig. 4. The 28-day compressive strengths of 82.5 ± 4.1 , 82.5 ± 4.9 , 95.0 ± 4.7 , and 87.5 ± 4.4 MPa were achieved after the addition of the designed compositions of (1% KCl+0.04% TEA), (1% NaCl+0.04% TEA), (1% $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ +0.04% TEA), and (1% NH_4Cl +0.04% TEA), respectively to the reference mix. The 60-day compressive strengths reached 97.5 ± 4.8 , 100.0 ± 6.0 , 100.0 ± 5.0 , and 92.5 ± 4.6 MPa after the incorporation of (1% KCl+0.04% TEA), (1% NaCl+0.04% TEA), (1% $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ +0.04% TEA), and (1% NH_4Cl +0.04% TEA), respectively into the reference mix. The results obviously depict that the

most effective chemical activators and quality improver in combination with each other not only do not yield any more amelioration, but also in the case of composition No. 4 (1% $\text{NH}_4\text{Cl}+0.04\%$ TEA) even results in a small decline in compressive strength.

Inasmuch as a 0.04 wt.% addition of TEA, is more effective than the examined soluble chlorine activators alone or in combination with TEA, the mix with 0.04 wt.% TEA was then selected as the best mix regarding both 28- and 60-day compressive strengths and studied for characterization purposes.

3.2. Setting time

Table 6 presents the IST and FST results obtained for the reference mix, PC2, and the mix containing TEA and $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$. Based on the data given in Table 6, it is clear that in comparison with PC2, the three studied mixes possess relatively long setting times.

It is evident that inclusion of a relatively high percentage of BFS in PC2 prolongs both IST and FST even if the mix is activated with insoluble sulfate-based chemical activator. In accordance with the results of the current study, it can be stated that the addition of 0.04 wt.% TEA to the reference mix slightly enhances the setting times. In plain PCs, TEA accelerates or retards the hydration reactions depending upon its dosage and its different effect on cement phases. However, the effect of TEA on the setting times of BFS-blended cements has not been studied sufficiently. The incorporation of $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$ reveals a set accelerating behavior. The addition of 1 wt.% $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$ can significantly decrease both IST and FST compared to the reference mix and the mix containing 0.04 wt.% TEA. This is due to improved formation of C-S-H as the main binding agent [33].

3.3. X-ray diffractometry

Fig. 5 indicates the X-ray diffraction patterns of hardened pastes of the reference mix and the mix containing 0.04 wt.% TEA after 60 days of curing. The X-ray patterns of both hardened pastes are quite similar comprising mainly amorphous structure with a few amount of Portlandite and tiny bit of tricalcium silicate (C_3S), calcite, and C-S-H (I) as the only crystalline phases. These crystalline phases have been identified based on comparison with PDF standard cards. Portlandite and C_3S are resulted from PC and BFS, respectively. Portlandite is formed as a consequence of hydration reactions of alite and belite phases. The presence of C_3S reveals that even after 60 days of hydration, a few amount of unreacted C_3S can be still found in the material. However, the intensity of C_3S phase in the mix containing 0.04 wt.% TEA is lower than that in the reference mix. It has been proved that TEA accelerates the dissolution of C_3S phase to form hydration products such as Portlandite and C-S-H family gels in early stages, which results in an enhancement in compressive strength [34]. With protraction of hydration reactions, TEA is adsorbed on the Portlandite surface because of its slow steric hindrance and the formation of precipitates along with Portlandite when the Ca^{2+} concentration reaches a saturation level [35].

Portlandite is consumed in prolonged hydration reactions to form more C-S-H gel and this causes a similar trend with C_3S to be true about the intensity of Portlandite. The C-S-H (I) ($\text{CaH}_2\text{O}_4\text{Si}$), having a Ca/Si ratio between 0.8 and 1.3 [36] is a poorly crystalline phase and is formed as the consequence of the hydration of calcium silicate phase. The chemical activation has favored the formation of this phase. All these together indicate a higher degree of hydration because of improved reactions caused by TEA.

3.4. FTIR spectroscopy

To identify the chemical bonds in the cementing compounds, FTIR spectroscopy analyses were also performed. Fig. 6 illustrates the FTIR spectra of the BFS and 60-day cured hardened pastes of the reference mix and the mix containing 0.04 wt.% TEA.

The spectrum of BFS indicates bands at wavenumbers of 476, 513, 945 and 3631 cm^{-1} . The bands appeared at 476 and 513 cm^{-1} are due to Si-O and Si-O-Si vibrations, respectively. The absorption peak at 945 cm^{-1} shows the presence of aluminum oxide and the band observed at 3631 cm^{-1} represents the presence of O-H group in $\text{Ca}(\text{OH})_2$. The spectrum of reference mix exhibits bands at wavenumbers of 435, 644, 877, 977, 1427, 3448 and 3643 cm^{-1} . The peaks at 435 and 644 cm^{-1} are due to the existence of Si-O and Al-O, respectively. The stretching vibrations at 877 and 1427 cm^{-1} are allocated to C-O group of CO_3^{2-} . The band at 977 cm^{-1} shows the presence of C-S-H phase as main product of hydration. The absorption band emerged at 3643 cm^{-1} is due to OH group of $\text{Ca}(\text{OH})_2$ and the band seen at 3448 cm^{-1} is assigned to OH in water. The FTIR spectrum of the mix containing 0.04 wt.% TEA indicates bands at 443, 669, 873, 973, 1423, 3446 and 3645 cm^{-1} . The absorption bands at 443 and 669 cm^{-1} indicate the presence of silicon dioxide and aluminum oxide, respectively. The absorption bands at 873 and 1423 cm^{-1} belong to the presence of carbon oxide in carbonate phase and the band appeared at 973 cm^{-1} indicates the formation of C-S-H gel. The bands at 3645 and 3446 cm^{-1} are due to OH group of $\text{Ca}(\text{OH})_2$ and OH of water, respectively. All bands observed in the reference mix are also present in the mix containing 0.04 wt.% TEA, but intensity of the bands of $\text{Ca}(\text{OH})_2$ and C-S-H phases as hydration products are higher compared to those of the reference mix confirming a higher reactivity caused by addition of TEA.

3.5. Scanning electron microscopy

Figs. 7a and 7b depict plate-like Portlandite crystals in hardened paste of reference mix and the mix containing 0.04 wt.% TEA after 60 days of hydration, respectively. The energy dispersive X-ray spectroscopy (EDX) elemental analyses revealed the dominant presence of Ca and O as the main chemistry, suggesting the formation of Portlandite. The formation and precipitation of plate-like Portlandite crystals can be ascribed to the chemical composition of the reacting materials and conditions of the deposition. In fact, Portlandite has been formed as a consequence of hydration reactions of hydraulic phases originating both from BFS and PC2. Portlandite crystals usually precipitates inside the pores included in the cement matrix during the hydration reactions. Some part of the precipitated Portlandite, however, can be consumed in hydration of reactive silica-rich compounds of the slag and forms C-S-H gel. The existence of partially reacted slag particles in the proximity of Portlandite crystals can be regarded as a sign of protraction of hydration reactions.

4. Conclusions and future work

Hydraulic activity improvement of slag-blended Portland cement using insoluble chemical activators, soluble chlorine activators and two common quality improvers was investigated within the scope of this work. It was found out that enhancement of the hydraulic activity of slag-blended Portland cements with high replacement level by the concerted influences of non-chlorine insoluble chemical activators and quality improvers is possible and both 28- and 60-day compressive strengths can be tailored if optimum proportions are used. Contribution of chlorine soluble chemical activators induces improvements up to about 12% on both 28- and 60-day compressive strengths. But, the combined effect of chlorine activators and quality improvers not only does not yield considerable improvement in both 28- and 60-days compressive strengths,

but also in some cases causes decline in compressive strength. Although the use of chlorine activators for non-reinforced concrete products does not result in any corrosion risk, for reinforced applications however further experimental research is necessary to ensure that chlorine activators do not bring corrosion to steel bars in reinforced concretes and this can be considered as a future program.

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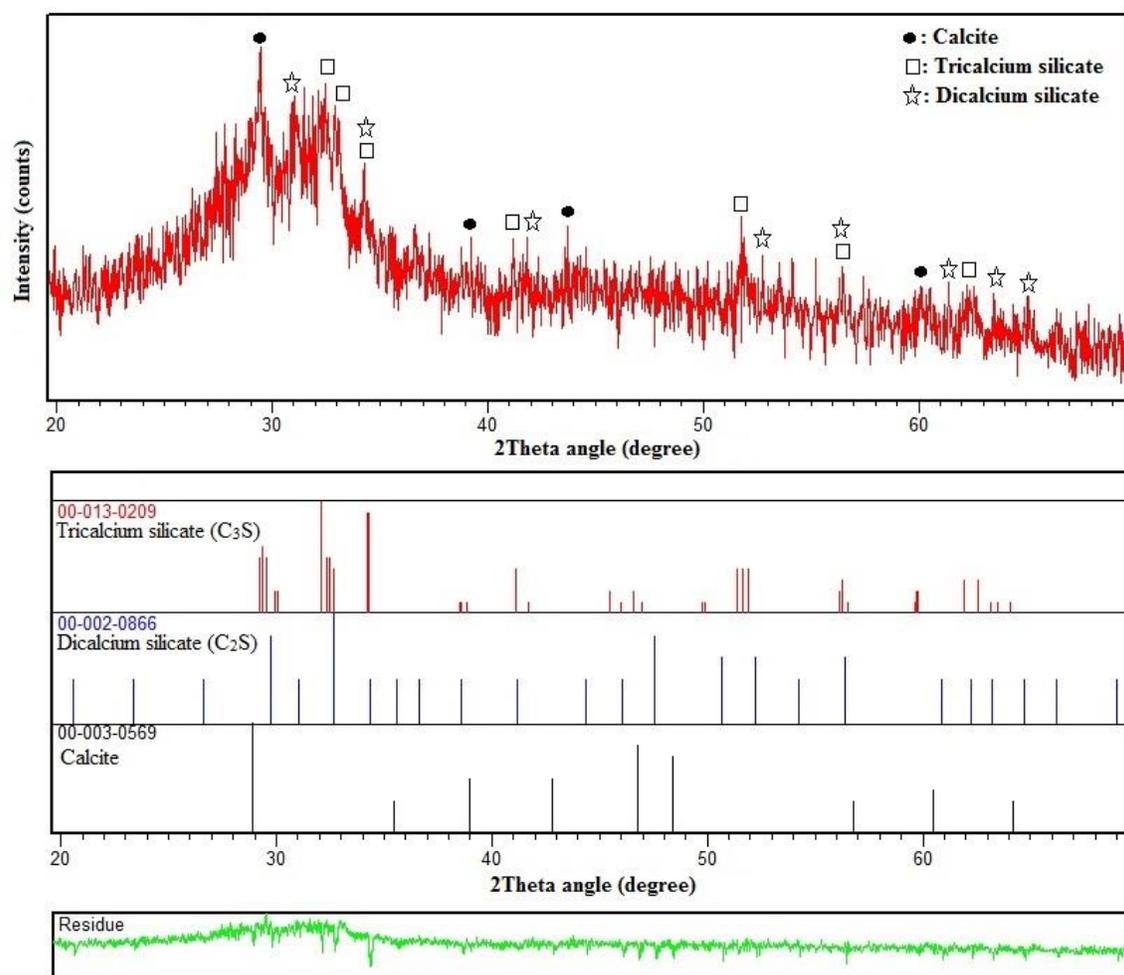


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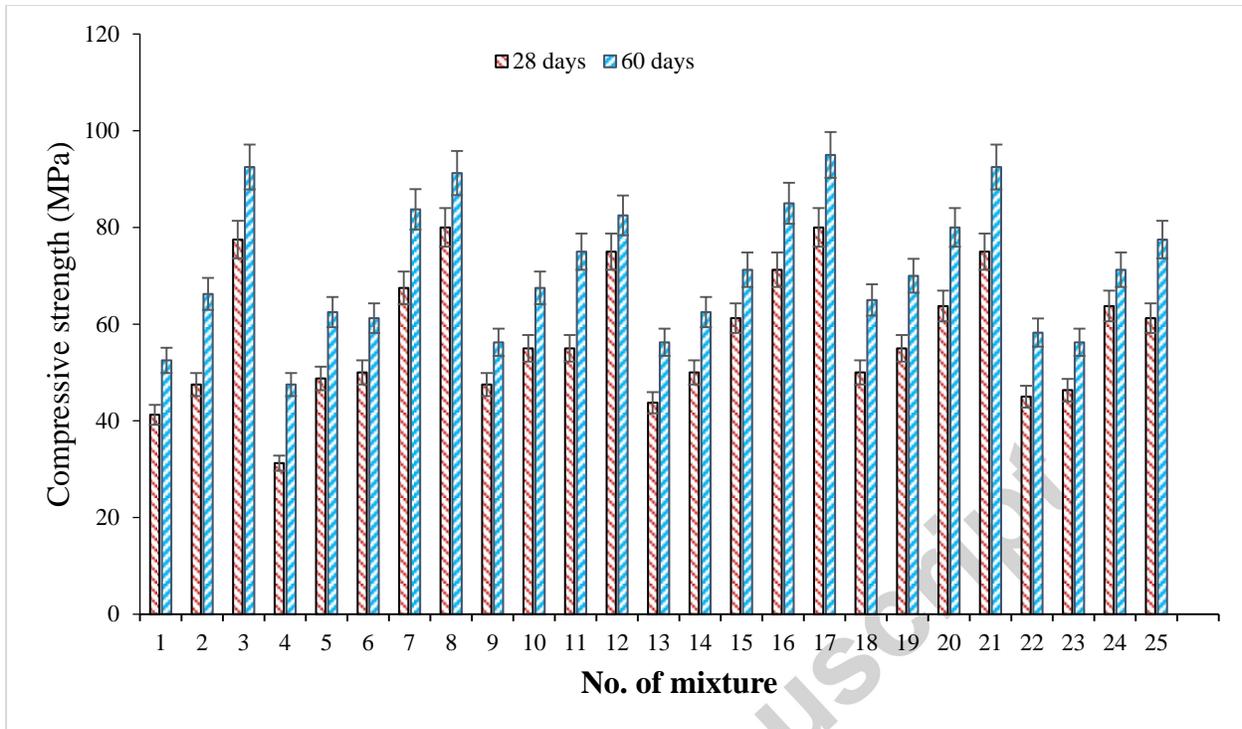


Fig. 2. Compressive strength values of initial mixtures

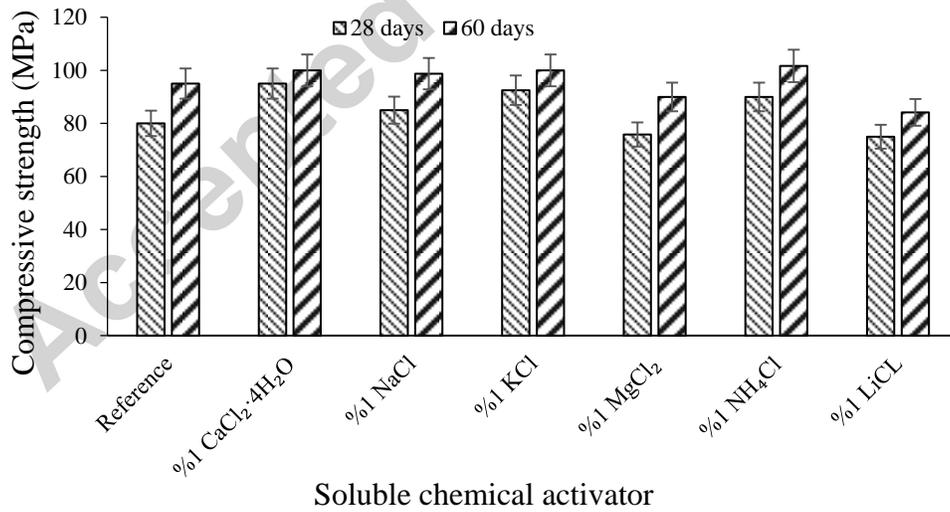


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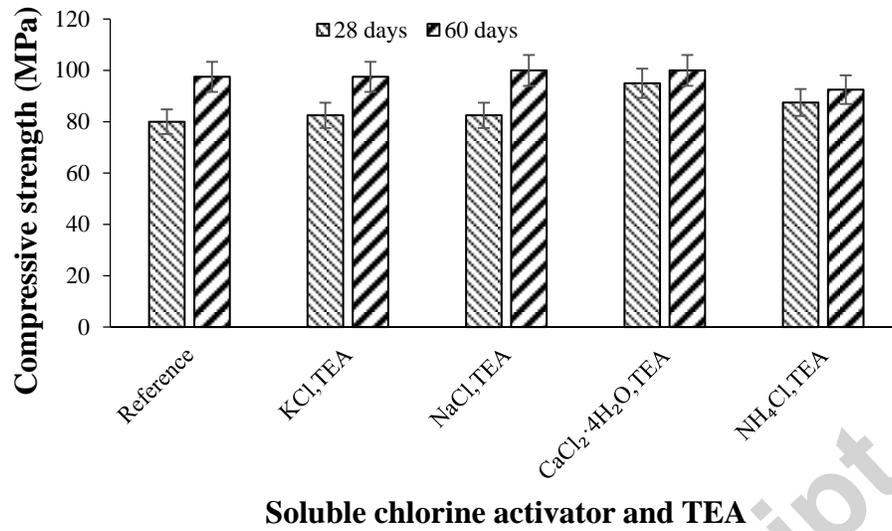


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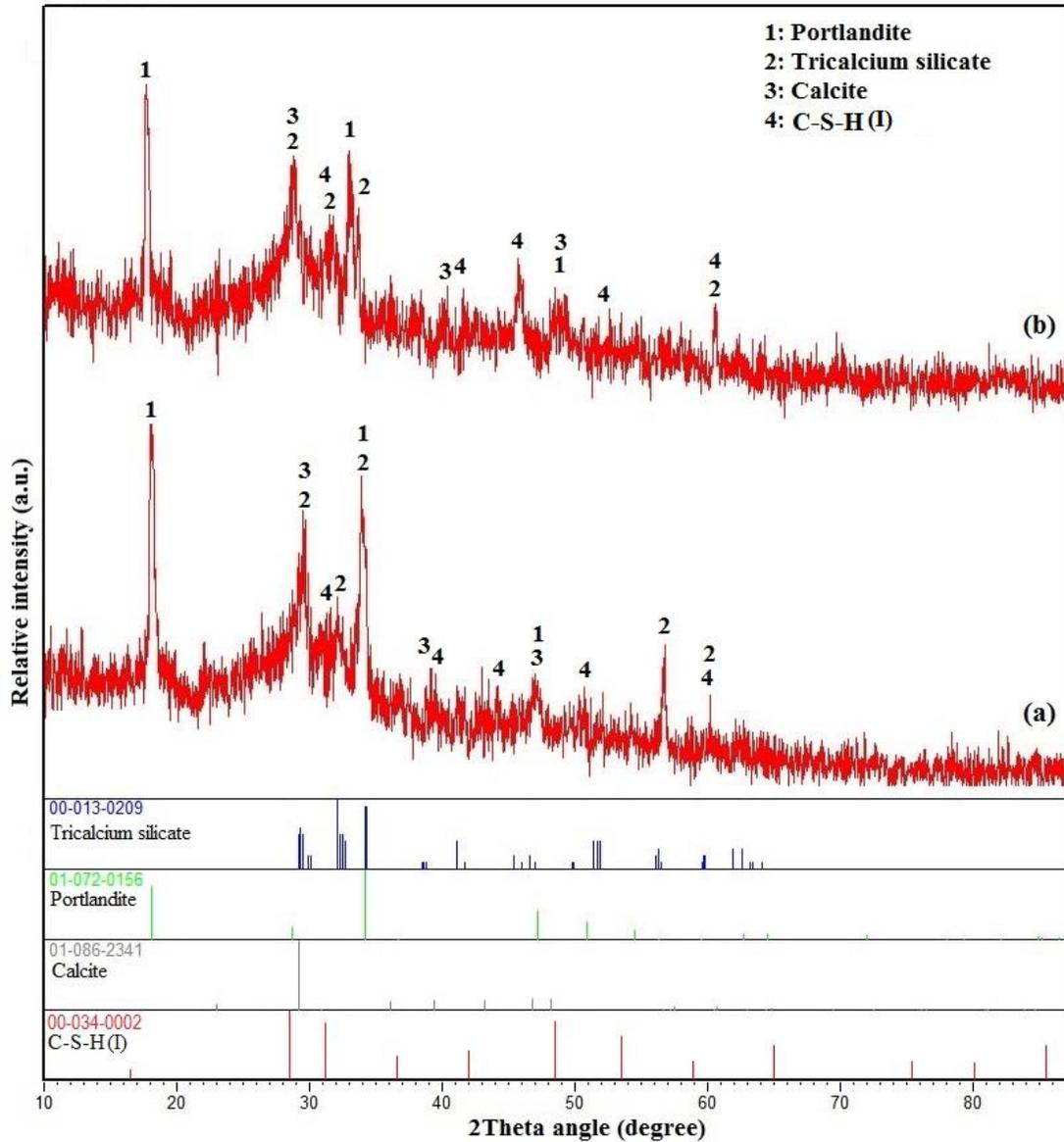


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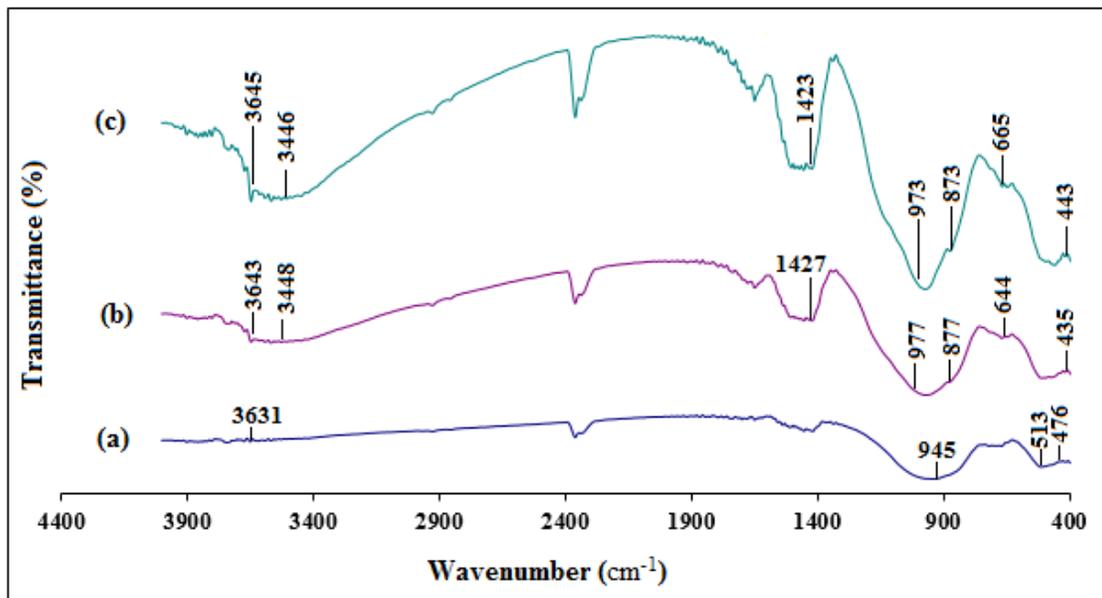
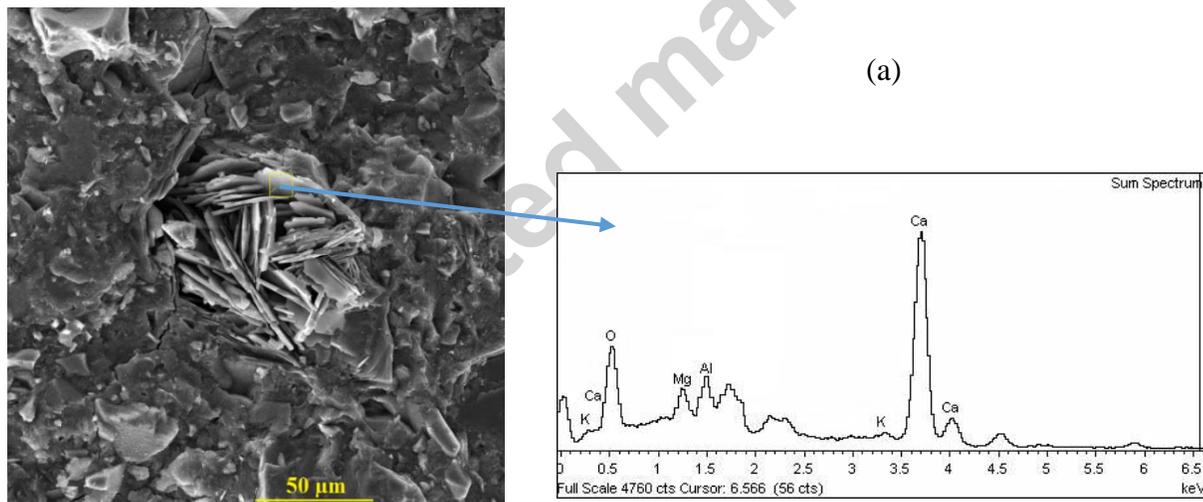


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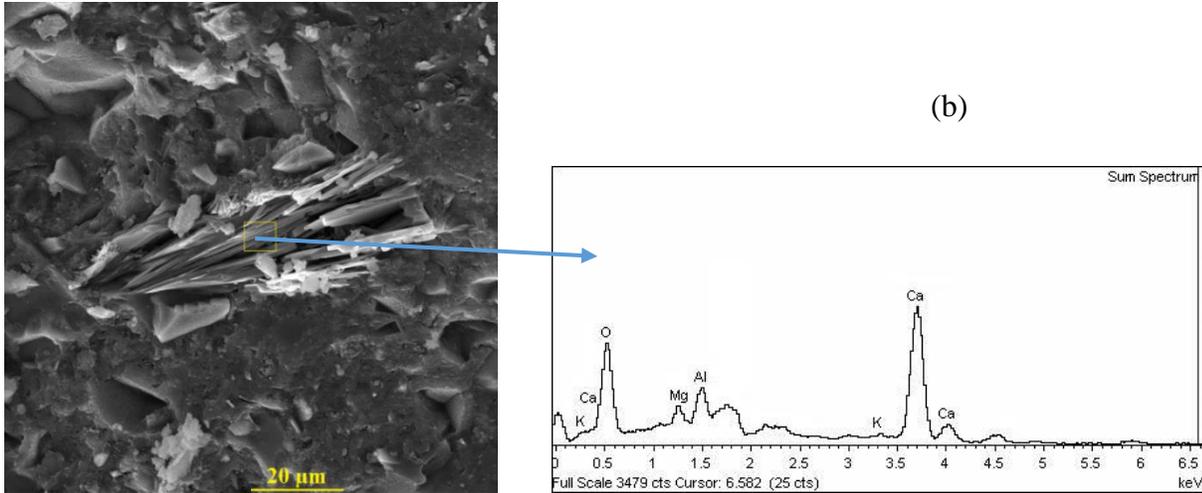


Fig. 7. Plate-like Portlandite crystals and corresponding EDX analysis in the a) reference mix and b) mix containing 0.04 wt.% TEA after 60 days of hydration

Table 1

Chemical composition and physical properties of BFS and PC2.

Physical properties	PC2	BFS
Blaine fineness (m^2/kg)	302	320
Density (kg/m^3)	3120	3090
Chemical composition (wt.%)		
CaO	63.26	36.91
SiO ₂	22.50	36.06
Al ₂ O ₃	4.15	9.16
Fe ₂ O ₃	3.44	0.17
MgO	3.50	10.21
SO ₃	1.80	1.15
K ₂ O	0.67	0.70
Na ₂ O	0.24	0.48
TiO ₂	-	3.50
MnO	-	1.46
V ₂ O ₅	-	0.10
LOI	0.72	-
Free lime	0.66	-
Bogue's potential phase composition (wt.%)		
C ₃ S	53.69	-
C ₂ S	24.07	-
C ₃ A	5.18	-
C ₄ AF	10.47	-

Table 2

Soluble chemical activators and their corresponding dosages.

NO.	Chemical activator	wt (%)
1	CaCl ₂ ·4H ₂ O	1.0
2	NaCl	1.0
3	KCl	1.0
4	MgCl ₂	1.0
5	NH ₄ Cl	1.0
6	LiCl	1.0

Table 3

Initial mix proportions (wt.%).

NO.	PC2	BFS	Insoluble chemical activator
1	6	94	0
2	18	82	0
3	42	58	0
4	0	97	3
5	12	85	3
6	24	73	3
7	36	61	3
8	48	49	3
9	6	88	6
10	18	76	6
11	30	64	6
12	42	52	6
13	0	91	9
14	12	79	9
15	24	67	9
16	36	55	9
17	48	43	9
18	6	82	12
19	18	70	12
20	30	58	12
21	42	46	12
22	0	85	15
23	12	73	15
24	36	49	15
25	48	37	15

Table 4

Effect of TEA and TIPA as quality improvers on compressive strength of reference mix.

Mix	Compressive strength (MPa)	
	28 days	60 days
Ref. mix	80	95
Ref. mix+%0.02 TEA	83.75	95
Ref. mix+%0.04 TEA	86.25	102.5
Ref. mix+%0.06 TEA	82.5	95
Ref. mix+%0.08 TEA	80	93.75
Ref. mix+%0.1 TEA	77.5	90
Ref. mix+%0.02 TIPA	84.16	98.75
Ref. mix+%0.04 TIPA	82.5	95
Ref. mix+%0.06 TIPA	80	93.33
Ref. mix+%0.08 TIPA	77.5	90
Ref. mix+%0.1 TIPA	76.25	83.75

Table 5

Compositions designed for investigating the combined effects of both soluble chemical activators and quality improver.

NO.	Chemical activator	Quality improver
1	NaCl% 1	0.04% TEA
2	CaCl ₂ ·4H ₂ O% 1	0.04% TEA
3	KCl% 1	0.04% TEA
4	NH ₄ Cl% 1	0.04% TEA

Table 6

Setting times of the reference mix, the mix containing TEA and CaCl₂·4H₂O.

Mix type	IST (min)	FST (min)
Reference mix	217	296
Mix containing 0.04 wt.% TEA	246	302
Mix containing 0.04 wt.% TEA and 1 wt.% CaCl ₂ ·4H ₂ O	190	246
PC2	125	165