Effect of Fly Ash on Setting Mechanism and Strength of Commercial Cement: A Chemical Approach

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Research Article

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Abstract

The chemistry and mechanism of mechanical strength-development at different setting-times in different weight-ratios of proclaimed commercial-cement and fly-ash mixture is studied. The main content of fly-ash is the quartz (SiO2). According to our results, as the setting time increases, the quartz present in fly-ash gets utilized during setting of the cement to form the well known C-S-H gel ($3CaO.2SiO_2.3H_2O$). Our analysis suggests that the addition of fly-ash reduces the water requirement for the hydration-process. Furthermore, the fly-ash inhibits the formation of $CaCO_3$ phase from portlandite ($Ca(OH)_2$) through atmospheric CO_2, and more importantly, it promotes the transformation of portlandite to form the C-S-H network which provides strength and long term stability to the set cement. As the commercial cement already contains optimum amount of fly-ash, any further addition of fly ash leaves the fly-ash partially unreacted which drastically decreases the compressive strength.

1. Introduction

Ordinary Portland cement is the most commonly used binder in concrete.[1–11] Cement is made up of four most important components known as Bogue's compounds. These components are: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) or alite, belite, celite and brown-millerite, respectively. The compositions of ordinary Portland cement, including the Bogue's compounds, is: ~ 30–70 wt% of C_3S, ~ 20–45 wt% of C_2S, ~ 5–15 wt% of C_3A and ~ 5–10 wt% of C_4AF, ~ 0–5 wt% of Gypsum ($CaSO_4 \cdot 2H_2O$), ~ 0–2 wt% of alkalies (Na_2O, K_2O). It has been identified that tricalcium silicate and dicalcium silicate are largely answerable for providing mechanical strength due to hydration process of cement.[1] Moreover, tricalcium silicate is responsible for temporary strength development, while dicalcium silicate contributes to better long term strength development. The hydration process starts with the reaction of these Bogue's compounds with water. Reaction of C_3S and C_2S with water forms C-S-H network or C-S-H gel ($3CaO \cdot 2SiO_2 \cdot 3H_2O$), which is the main product responsible for strength of cement. Along with the C-S-H gel, calcium hydroxide ($Ca(OH)_2$), called as portlandite, also forms as a by-product during the hydration process. The portlandite ($Ca(OH)_2$) is highly unstable and it reacts with atmospheric CO_2 to form calcium carbonate ($CaCO_3$),which makes the cement/concrete brittle. As this brittleness reduces the durability of concrete, formation of calcium carbonate ($CaCO_3$) from $Ca(OH)_2$ should be avoided. This can be achieved by transforming portlandite ($Ca(OH)_2$) to some other useful compound before it reacts with the atmospheric carbon-dioxide.[1,2] Fly ash is the main materials which is attractive in this regard, as discussed below.

Fly ash is the coal ash particles produced as a by-product during the combustion of coal used for the production of electricity in thermal power plants. Fly ash is considered as a major global pollutant, because the nanoparticles of the ash floats in air and are easily carried to the human habitats causing health problems. Hence, the fly ash is usually allowed/restricted to settle in the power plants and is collected.[12–15] The collection of fly ash is increasing year by year, but a high percentage of the collected fly ash remains unutilized. Presence of silica, alumina and ferrous minerals in the form of nanoparticles in fly ash renders their use for the revitalization of cement. Most importantly, addition of fly ash in cement reduces the formation of calcium carbonate ($CaCO_3$) because the silica (SiO_2) present in the fly ash reacts with portlandite and produces C-S-H gel which is the main component of set-cement providing increased strength to the hardened cement through their C-S-H network. This can be rationalized from the following reaction:

$3Ca(OH)_2 + 2SiO_2 \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$ (C-S-H gel)

Furthermore, the addition of fly ash decreases the amount of water requirement for setting of cement, high ultimate strength, improves the workability, reduces bleeding, reduces heat of hydration, reduces permeability, increases resistance to sulphate attack, increases resistance to alkali-silica reactivity, lower costs, reduces shrinkage, increases durability [16–28]. Hence, it can be said that the use of fly ash in the cement will enhance the properties of cement, particularly, in increasing the strength, leading to cement with longer durability and strength. Here, we have studied the phase transformation and mechanical strength of cement by preparing pellets of different compositions of cement-fly ash paste and allowing them to set for different time durations.

2. Materials And Methods

The dry powder of proclaimed cement was collected from a local company near the Gulburga region of India. Fly ash was collected from the thermal power plant Raichur, India. The Dry cement and fly ash were characterized by X-ray diffraction (XRD) using '*PANalytical X'Pert PRO'* diffractometer, and by Fourier Transformed Infra-Red (FTIR) spectroscopy using a *Frontier (Perkin Elmer)* spectrometer. For all XRD experiments, Cu-K_α radiation and Ni filter was used, and the data were collected in the 2θ range of 20–90° with the step size of ~ 0.0263°. All the FTIR transmission spectra were measured in the wave number scan range of 400–4000 cm^{-1} for all the cement samples before and after hydration. To study the hydration process, different proportions of fly ash was first dry mixed with cement. The different proportions of fly ash added to cement were 5, 10, 20, 30, 40 and 50 wt%. These dry mixtures are thoroughly mixed and then distilled water was added to make a paste. Water to cement ratio was kept constant at 4:10 for all the proportions of cement and fly ash. This paste is then used to make small pellets of diameter ~ 10 mm and thickness of ~ 6 mm by using a hollow cylindrical plastic mould. The plastic mould was then removed and pellets were kept on a plastic salver in ambient atmosphere to set. A day after the preparation of the pellets, they were cured by pouring distilled water on it daily. After 7 days, 14 days and 28 days of curing, the samples were characterized using XRD and FTIR techniques. In addition, the strength of each pellet was examined after various aging periods using a universal testing machine (UTM) from KIC-2-1000C, *Kalpak Instruments & Controls*, Pune, India. Note that the pellets used in our study are a much smaller than those normally used for measuring the strength of the samples. However, as our goal is to reveal the atomistic understanding of the fundamental aspects of strength development, unlike the strength originating due to microstructure/voids/fatigue, the relative strengths measured using our smaller sample sizes won't violet the scientific understanding. Note further that, for the compression tests, the load was applied until the used pellets broke into powders.

3. Results And Discussion

The XRD patterns of the dry commercial cement (BSC) and fly ash (from the thermal power plant, Raichur, India) are shown in Fig. 1 (a, b). The XRD pattern of the commercial cement (Fig. 1(a)) shows the Bragg peaks of all the four Bogue's compounds (A: alite, B: belite, C; celite and D: brown-millerite)[1] and quartz (Q). A rough estimation of the intensity of the Bragg peaks corresponding to different Bogue's compounds indicates the following percentages: $C_3S \approx 60$ %, $C_2S \approx 25$ %, $C_3A \approx 10$ % and $C_4AF \approx 4\%$ and Gypsum ≈ 1%. However, the intensity of the Bragg peak observed at about 2θ = 26.5°, in Fig. 1(a), is much more intense than the normal intensity observed in C_3S (alite) phase.[1] This peak is identified, in fact, as the peak of quartz (SiO_2, Q) which overlaps with the C_3S peak. It indicates the presence of excess amount of quartz in our commercial cement, BSC. This creates ambiguity over the composition of commercial cements, which will be clarified below.

As discussed earlier, the cement industries commonly add fly ash to improve the strength of cement during hydration (setting) and also other properties. As the behaviour or properties of fly-ash depends on the source from where the fly-ash is obtained[12–13], it is very important to understand the composition of fly-ash. First of all, to verify the presence of fly-ash in our BSC cement, we have studied the content of fly ash (collected from the thermal power plant, Raichur, India). The XRD pattern of this fly-ash, shown in Fig. 1(b), confirms the presence of high amount of quartz (Q, JCPDS file # 01-074-1811) along with mullite (M, $2Al_2O_3 \cdot SiO$▯ or $3Al_2O_3 \cdot 2SiO$▯, JCPDS file # 01-074-4143) and hematite (H, α-Fe_2O_3, JCPDS file #01-071-5088). The presence of aluminosilicate (mullite) in fly ash is due to the aggregation and fast cooling of the individual components (SiO_2 and Al_2O_3) from a high temperature in the thermal power plant. A rough estimation of alumina to silica ratio in this mullite phase is found to be about 5:2. The sharp peak of quartz (Q) observed in Fig. 1(b) confirms that quartz is the most dominant phase in this fly-ash, which is also commonly observed in fly ashes collected from other industries.[6, 12]

Now, it can be rationalized that the sharp peak at 2θ = 26.5° of quartz in fly ash adds to the intensity of the C_3S Bragg peak to result in the observed high net intensity for the proclaimed BSC cement. Hence, it confirms the presence of fly ash (along with the Bogue's compounds) in our proclaimed BSC cement. Due to the overlap of this Bragg peak of quartz with that of C_3S (alite) and the different content of quartz in fly ashes obtained from different firms[12], estimating the exact content of fly ash in our studied BSC cement will be erroneous. Moreover, it will be clear later that optimum amount of fly ash is already present in the proclaimed commercial cement (BSC) studied here.

The XRD patterns after setting time of 7, 14 and 28 days for the pellets prepared using the BSC cement only (without any fly-ash addition) is shown in Fig. 1(c) and the corresponding FTIR spectra are given in Fig. 1(d). Note that, to study the cement specimens after 7 days, 14 days and 28 days of setting time is chosen based on previous studies,[1] as discussed below. As ~ 99% strength development occurs through setting of the cement within 28 days, this is fairly sufficient time to analyse the setting mechanism of cement, i.e., the Bogue's compounds and the fly-ash phase transform during this 28 days time. Furthermore, as the commercial cement used here is not a fast setting cement, the study before 7 days is not considered, but we have chosen the specimens after 7, 14 and 28 days of setting. From the XRD patterns it is clear that the hydration reaction is gradually occur until 14 days, but after 28 days the intensities of the XRD peaks corresponding to the Bogue's compounds are decreased drastically. The mechanism of hydration or setting of cement is fairly understood in the literature,[1–11, 29–30] which suggests that the reduction in intensity of the XRD peaks of Bogue's compounds is due to the formation of amorphous C-S-H gel.[1, 29–31] Similarly, the FTIR spectra for the pellets obtained after setting times of 7, 14 and 28 days show the reduction of the FTIR peaks corresponding to the O-H vibrations of water (observed at wavenumbers of 3400 cm^{-1} and 1075 cm^{-1}). This clearly suggests the formation of C-S-H gel ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) through the hydration reaction.[1]

Setting Mechanism of Commercial Cement and Fly Ash Mixture

There are several attempts to understand the setting mechanism of fly-ash blended cement.[17–21, 32–34] However, the atomistic understanding of the setting mechanism and strength development is not explored. A huge amount of literature is available on ternary blended concrete. The main focus of most the previous studies is given in the development of strength and mechanical property from engineering perspective.[14, 25, 35–47] For instance, in a cement-fly ash-lime stone ternary blended concrete, Wang[19] demonstrated that lime stone improves the early age strength whereas fly-ash enhances the late age strength of concrete due to pozzolanic reactions. Chi and Hunag[38] demonstrated that binding of alkali (Na_2O) activated fly-ash/slag mortar improves for a particular concentration of ~ 6% of Na_2O addition. Hu et al.[28] demonstrated that with increase in slag and fly ash content, the shrinkage of cwmwnt-fly ash-slag ternary blends decrease linearly. Tkaczewska[36] studied the effect of the type of superplasticizer on fly ash blended cement and concluded that the water requirement for the reaction was reduced and the hydration heat, setting time and the mechanical properties improved. Kaja et al. [22] studied the effect of Portland cement addition on improvement in reaction kinetics and setting time of class-F fly-ash geopolymer cured under ambient conditions. Zhang et al.[35] studied that due to grain size refinement and pore size refinement, the setting time of ternary blended cement was decreased and, both late and early age strength was increased considerably. Freeman and Carasquillo[20] have demonstrated that resistance of Portland cement concrete against sulphate attack was increased by incorporating fly ash. Krishnaraj et al.[24] demonstrated that an efficient usage of ultrafine fly-ash increases the mechanical strength and improves the thermal behaviour of brick masonry. Singh and Garg[27] observed the increase in strength of a cement binder based on phosphogypsum, fly ash, hydrated lime and Portland cement, and observed a remarkable increase in strength at 50°C than that at 27°C. Li et al.[21] studied the effect of unburnt carbon in fly-ash in hardened cement pastes. Han et al.[17] extensively studied the effect of size of the ultrafine fly ash on the hydration heat of fly ash – cement composites. Lee and Lee[32] demonstrated that the setting of alkali activated fly ash/slag concrete almost achieves its full mechanical strength in about 28 days of setting time. Kocak et al.[37] demonstrated that addition of fly ash in cement improves the formation of concrete product (C-S-H gel) by consuming $Ca(OH)_2$. Ramachandra et al.[26] have further demonstrated that addition of fly ash eliminates the carbonation process in cement, which helps in improving the mechanical strength and durability of cement. Jiang et al.[23] demonstrated that about 10–20 % addition of fly-ash and lime stone in blended cement optimizes the rheological properties, mechanical strength and hydration characteristics of ternary blends. In most of the above cases an atomistic understanding on the development of strength in cement-fly ash mixture is lacking. Hence, the atomistic understanding is the aim of this work.

The cement contains mainly the amorphous CS-H phases, but, by using the changes in the XRD patterns of the crystalline compounds, we demonstrated here the atomistic nature of the setting mechanism of cement. The XRD patterns of the pellets prepared using different percentages of fly ash-cement mixture, after 7, 14 and 28 days of setting time is shown in Fig. 2. Comparing the XRD patterns after 7, 14 and 28 days of setting, for any particular composition of cement-Fly ash mixture, it is clear that, when the setting time increases the intensity of the XRD peaks of the crystalline Bogue's compounds is decreasing drastically. This intensity reduction is more pronounced for the samples of 28 days of ageing. Furthermore, the intensity of the quartz peak observed at 2θ = 21° (and 26.5°), are reducing after 28 days of hydration/setting. However, comparing the XRD patterns of the pellets for different compositions of cement-fly ash mixture, it is clear that when the amount of fly ash content increases the XRD peaks corresponding to quartz becomes intense, which is the common phenomenon. Another important observation is that, as the fly ash content increases the intensities of the quartz peaks increase even after 28 days of setting time. This can be easily conceived by comparing the relative intensity of the quartz peaks observed at 2θ = 21° for different composition of the pellets set for 28 days. As we have not observed the quartz peak at 2θ = 21°, up to ~ 5 to 10 wt% of fly ash, it indicates that ~ 5–10 wt% of fly ash can be incorporated into this commercial BSC cement, which can be utilized in the formation the C-S-H gel. However, beyond ~ 10 wt% of fly-ash addition, the XRD results clearly show that the fly-ash is not fully utilized in the formation of the C-S-H network. As it will be discussed later, it has strong influence on the strength of the commercial cement. The left over extra fly ash which is un-utilized in the hydration process shows up as the Bragg peak (Fig. 2) of the set cement, even after 28 days of setting. This can be understood form the following discussion.

Let's first consider the influence of the setting mechanism to understand the development of mechanical strength in cement due to fly ash addition. At the first stage of setting of cements, hydration of alite and belite leads to the formation of portlandite (calcium hydroxide). Without presence of quartz (fly-ash), this calcium hydroxide reacts with the atmospheric carbon dioxide (CO_2) to form calcium carbonate.[26] The gradually increased absorption of atmospheric CO_2 (over time) and formation of calcium carbonate, leads to a local expansion of the regions having portlandite ($Ca(OH)_2$) which makes the cement brittle as the time progresses. However, when some amount of quartz (SiO_2) (such as fly ash) is present/added in the cement, this extra quartz reacts with calcium hydroxide to form amorphous C-S-H (calcium silicate hydrate) network. This contributes to the enhancement of strength of the hardened cement through the formation of C-S-H network. More importantly, this also helps in reduction of brittleness of the cement through the unavailability of portlandite for any calcium carbonate formation in the hardened cement. Hence, addition of fly ash (quartz) is advantageous in a number of ways. The above discussed mechanism of setting of cement and fly-ash mixture can be written in the form of the following equations:

Reaction of Alite and Belite to form portlandite:

C_3S (Alite) + H_2O (water) $\longrightarrow$ C-S-H + $Ca(OH)_2$ (portlandite) .....(1)

C_2S (Belite) + H_2O (water) $\longrightarrow$ C-S-H + $Ca(OH)_2$ (portlandite) .....(2)

In the absence of extra quartz:

$Ca(OH)_2$ (portlandite) + CO_2 (gas) $\longrightarrow$ $CaCO_3 + H_2O$ .....(3)

(expansion leads to crack formation)

In the presence of extra quartz:

$3Ca(OH)_2$ (portlandite) + $2SiO_2$ (Quartz) $\longrightarrow$ $3CaO{\cdot}2SiO_2{\cdot}3H_2O$ (C-S-H) ..(4)

With very high content of fly ash (SiO_2):

$3Ca(OH)_2 + (N+2)SiO_2 \longrightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + (N)\ SiO_2$ .....(5)

From the above equation, it is clear that the formation for same volume of the C-S-H network (cement) the amount of required water would be less, because the hydration is achieved through the transformation of the (−OH ions) present in portlandite. From Eq. 3, it is clear that release of water from the cement can also lead to the shrinkage of cement and also increased permeability of cement (for corrosion (sulphate) attack). Hence, addition of fly ash increases the durability of cement, in addition to increase in strength and decrease in brittleness. Furthermore, it can be envisaged from Eq. 4 that excess addition of fly ash (SiO_2) would lead to aggregation of SiO_2 within the network of C-S-H. This is the main reason behind the observation of increased intensity of the quartz peak in Fig. 2 when the content of fly ash increases beyond a certain value. It is clear that the aggregation of SiO_2 within the network of C-S-H would increase the brittleness and decrease in mechanical properties, such as strength of cement.

The FTIR spectra taken after 7, 14 and 28 days of ageing for different compositions of cement and fly ash mixture are shown in Fig. 3. All the observed FTIR peaks are assigned to the corresponding vibrations of different moieties present in cement-fly ash mixture, as listed in Table 1.[48–54] Note that the broad peaks observed at about 3000–3600 cm^{-1} corresponds to the O-H stretching vibrations of water and the peaks of ~ 1420–1495 cm^{-1} are due to the C-O vibrations of $(CO_3)^{2-}$. Also the peaks observed between from ~ 450–525 cm^{-1} are vibrations of Si-O at set, the peaks between 1058–1100 cm^{-1} corresponds to S-O vibrations of SO_4^{2-} of Gypsum ($CaSO_4$). Interestingly, in the above FTIR spectra, we observe that the intensity of the peaks corresponding to O-H vibrations (3000–3600 cm^{-1}) of portlandite ($Ca(OH)_2$) and water (H_2O) reduces as the aging time increases; and the intensity of this peak is the minimal for the samples set for 28 days. This supports our XRD results that addition of fly ash helps in consuming the portlandite for the formation of C-S-H gel and thus helps reducing the brittleness of cement, which will be discussed below. Furthermore, the reduction in the peak intensity corresponding to the symmetric stretching vibrations of Si-O-Si (at 1050–1100 cm^{-1}) confirms the transformation of quartz to the C-S-H phase, as in Eq. 4.

Table.1 Assignment of the FTIR peaks to their respective vibrational modes, as in Fig. 3.

Wave number (cm^{-1})	Assignment	Ref.
450–525	Bending Si-O-Si vibrations	[48]
710–715	Symmetric stretching vibration of Al-O-Si	[48]
840–870	Al–O and Al–OH vibration mode	[49]
874	v_3 out of plane vibration of CO_3^{2-}	[50]
916–980	v_3 Si–O asymmetric stretching ofC_3S/C_2S	[51, 52]
1084	Symmetric stretching vibration of CO_3^{2-}	[50, 53]
1050–1100	Symmetric stretching vibration of Si-O-Si	[48]
1420–1495	Asymmetric stretching of $CO3^{2-}$	[53]
3405–3448	v_1 Vibrations of H_2O	[54]

Variation of Compressive Strength with Fly Ash Content and Ageing Time

Although, several reports on the measured compressive strength of cement-fly ash mixture are available,[14, 20, 25, 35–47] the demonstration on atomistic understanding of strength development is lacking in the literature. As demonstrated earlier, the formation of C-S-H phase provides the strength of cement; and the SiO_2 present in fly-ash helps in promoting the formation of this C-S-H phase through decreasing in the formation of $CaCO_3$ from portlandite (denying the Eq. 3 to proceed!). This enhances the strength and durability of the cements. The compressive strengths, of all our studied samples, are measured using a universal testing machine. The typical load verses compression (length) plot, for the pellet with 60 wt%

BSC cement and 40 wt% of fly ash, after setting times of 7, 14 and 28 days, as indicated, are shown in Fig. 4(a). The length values, given in X-axis of Fig. 4(a), represent the displacement of the crosshead position. Note here that, as it can be observed from the successive data points, the statistical variation is estimated to be less than ~ 5–7%. Figure 4(a) clearly indicates that the pellet breaks into powders after the compressive strength is achieved.

Note that the provided statistical error bar (5–7%) would be the maximum estimated value. This is because, for bigger (ASTM standard) samples the microstructure and specimen in-homogeneity along with the voids play important role in deciding the strength of these materials for their direct application. However, from a closer look at the relative strength variations of the nearby points in Fig. 4(b), one can fairly understand the low statistical deviation, unless unexpectedly very big voids are present with fully inhomogeneous microstructures in different samples. We have carefully prepared the small specimens, hence, those speculations can be avoided.

The compressive strength results for all our samples are plotted in Fig. 4(b). We observe that, as the setting time increases there is a progressive increase in the compressive strength for all compositions of commercial cement + fly ash, i.e., for the aging time of 7, 14 and 28 days, the compressive strength gradually increases. This is due to the gradual formation of the C-S-H gel in the cement which is the setting process. During setting, the formation of C-S-H gel network[1,7] enhances the strength of the cement. Furthermore, for pure cement (without any fly ash addition) the compressive strength is the maximum, and as the fly ash content is increases, we observe a sudden decrease in the compressive strength (Fig. 4(b)) for each set of data. As discussed earlier in this section, the addition of fly-ash to cement should increase the compressive strength, because this should facilitates formation of better C-S-H network and block the formation of $CaCO_3$ (according to Eq. 4).[7, 55–56] This is against our expectation. To understand this aspect, let's first consider the following observations. It is clear in Fig. 4(b) that, as the fly ash content increases beyond 20 wt%, the compressive strength values remain constant (within the error bar) for all specimens having the same setting time. Furthermore, as we have discussed earlier in this section, Eq. 5 suggests that, addition of excess (N + 2) fly ash can lead to retention of (N) SiO_2 particles within the C-S-H network. As formation of no other phase was observed in XRD, considering the above two aspects, i.e., decrease in compressive strength with gradually more and more fly-ash addition, and presence of silica (SiO_2) particles within the C-S-H network, it can be understood that our sample already contains optimum amount of fly-ash in the cement. By adding more and more fly-ash, as in our case, we are going far beyond the optimum amount of Fly ash that should be added to obtain highest compressive strength. Hence, it can be rationalized that optimum amount of fly ash was already present in our commercial cement, i.e., the cement industry has already added optimum amount of fly ash before packaging. Further addition of fly ash, as in our present case of study, reduces the strength of the cement after setting due to retention of the excess unreacted fly ash in the C-S-H network of our specimen. This can be easily inferred from the presence of the Bragg peak of quartz (at $2\theta = 20.5^o$) in the XRD pattern of dry cement (Fig. 1(a)), which becomes more intense as the fly ash content increases (Fig. 2). Hence, the reason behind the drastic decrease of compressive strength with increase in fly ash in our specimens is due to the non-transformation or retention of excess Fly-ash particles within the C-S-H network. This excess fly-ash retained within the C-S-H network facilitates breaking of the pellets at a very low compression load.

4. Conclusion

The effect of fly-ash addition on the mechanical strength and setting mechanism of a commercial-cement is studied here using a chemical atomistic approach. In the commercial cement, we added different weight ratios of fly ash, and the mixture was allowed to set for different durations. The fly ash was obtained from the thermal power plant, Raichur, India. The XRD patterns confirm the presence of quartz as the major phase in fly ash, along with minor amounts of mullite and lime. As setting time increases, the intensity of XRD peaks corresponding to quartz (present in fly-ash) along with that of the Bogue's compounds decrease. This decrease in content of quartz and the Bogue's compounds is assigned to the formation of amorphous C-S-H ($3CaO.2SiO_2.3H_2O$) network, which provides strength and reduces the brittleness of cement. Furthermore, our XRD results affirms that even after 28 days of setting time, some amount of quartz present in fly ash remains unreacted. This indicates that for those compositions the fly ash content is much higher than the optimum. Interestingly, we observed that the carbonation of portlandite phase, i.e., calcium carbonate formation from calcium hydroxide (portlandite), the cause behind brittleness of cement, is reduced due to fly-ash addition. The FTIR results suggest that expansion of fly ash decreases the water necessity for the hydration procedure. Generally, addition of fly ash does not allow the carbonation process to occur; rather it promotes the development of C-S-H phase giving good quality and strength to the concrete, which is in line with the XRD results. From the compression test result, we observed that the compressive strength of the cement-fly ash mixture increases with setting time due to formation of C-S-H network. However, optimum amount of fly ash seems to be already present in commercial cement, and hence, fly-ash addition decreases the mechanical strength of the set commercial cement. Our work explored the atomistic structural mechanism of strength development in cementeous materials due to addition of cement.

Declarations

Conflicts of Interest

The authors declare no conflicts of Interest.

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Figures

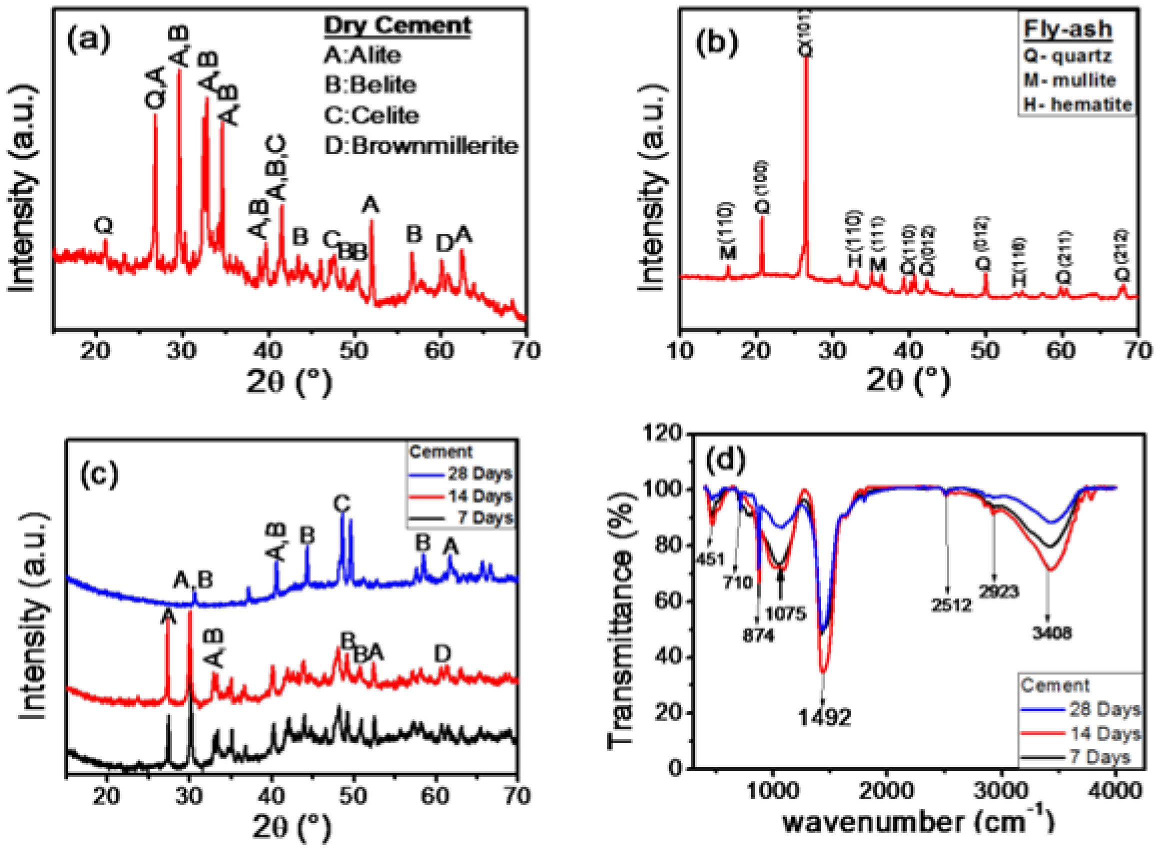

Figure 1

XRD patterns of (a) Dry cement (BSC) powder, (b) Fly ash, (c) proclaimed BSC cement taken after 7, 14 and 28 days of setting time, and (d) FTIR spectra of the proclaimed cement taken after 7, 14 and 28 days of setting time, as indicated.

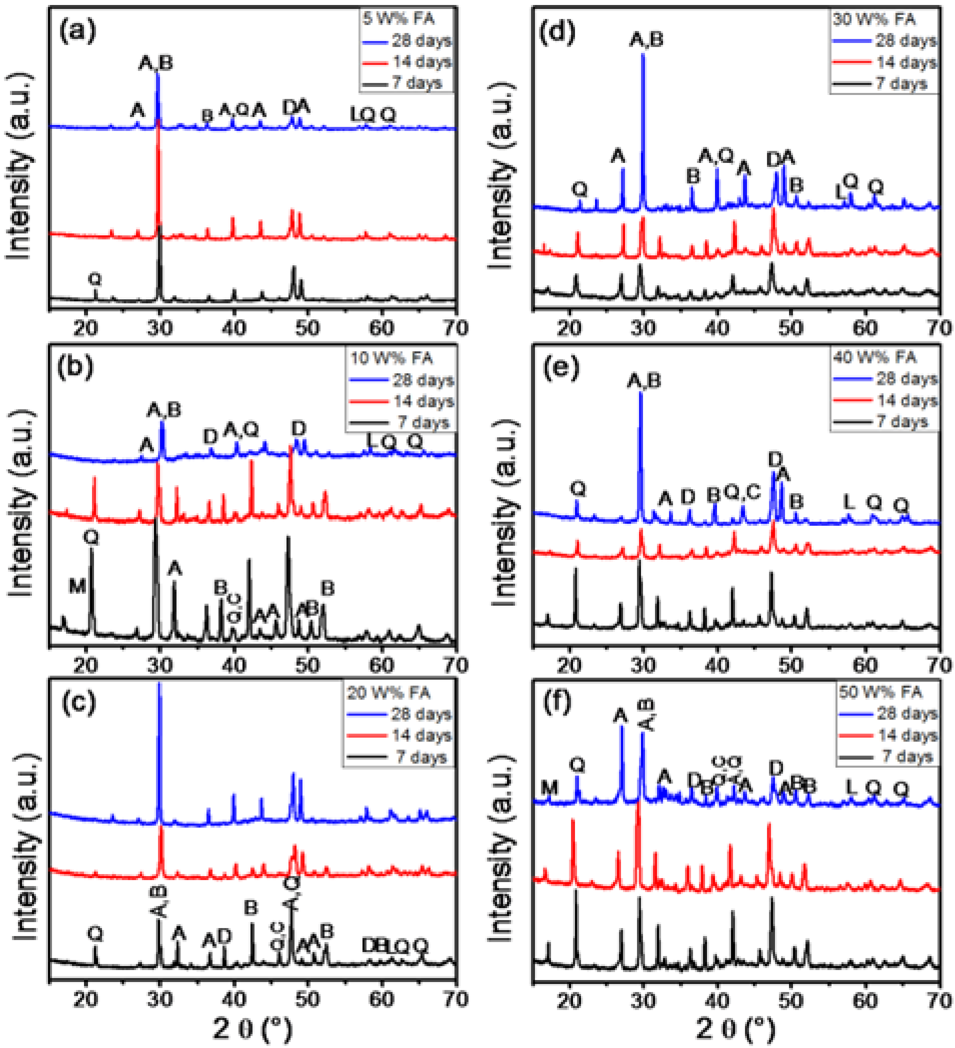

Figure 2

The XRD patterns of the pellets prepared by using different proportions of fly ash (FA) and BSC cement mixture: (a) 5 wt% FA, (b) 10 wt% FA, (c) 20 wt% FA, (d) 30 wt% FA, (e) 40 wt% FA and (f) 50 wt% FA. In each set, the XRD patterns of the pellets taken after 7, 14 and 28 days of setting time are given (as indicated).

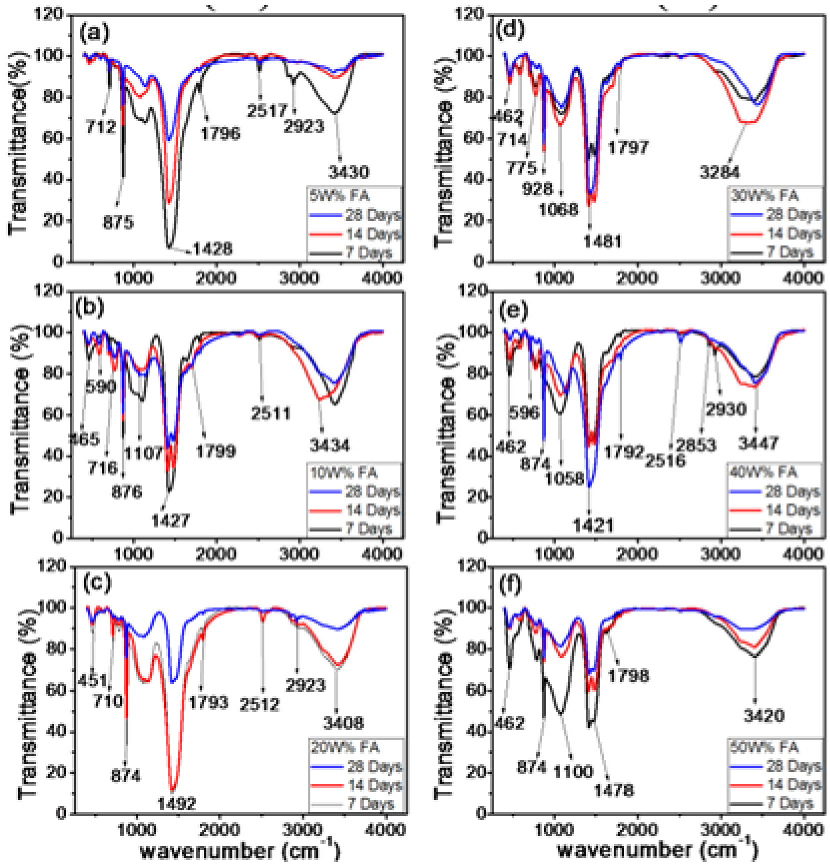

Figure 3

The FTIR spectra of the pellets prepared by using different proportions of fly ash (FA) and BSC cement mixture: (a) 5 wt% FA, (b) 10 wt% FA, (c) 20 wt% FA, (d) 30 wt% FA, (e) 40 wt% FA, and (f) 50 wt% FA. The spectra were taken after 7, 14 and 28 days of setting time (as indicated).

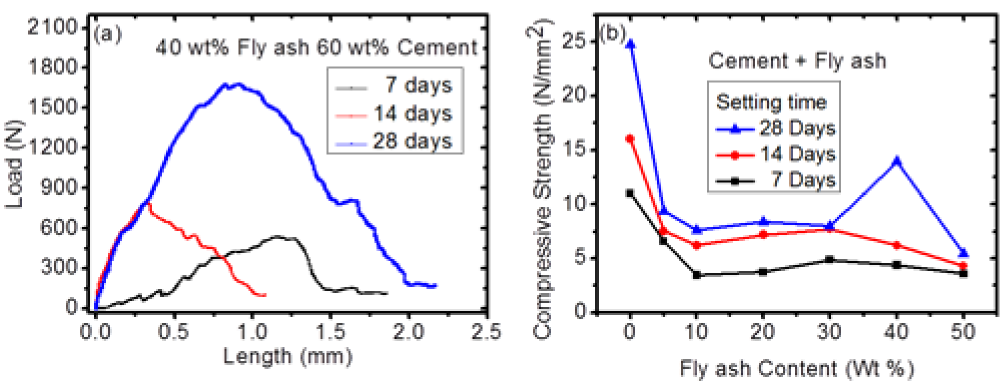

Figure 4

Compressive strength of the pellets of different proportions of fly ash (FA) and BSC cement mixture: measured after 7, 14 and 28 days of setting time (as indicated): (a) Load versus compression plot for 40 wt% FA sample, (b) Compressive strength versus fly ash content (wt%).