FTIR Analysis of Nanomodified Cement Concrete Incorporating Nano Silica and Waste Marble Dust

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Abstract

In present study, different compositions of concrete mixes with marble dust and nano-silica have been prepared and studied with Fourier Transform Infrared (FTIR) spectroscopy to evaluate different phases formed during hydration reaction. Formation and extent of phases formed during hydration reaction occurring for different curing days can be successfully correlated with the shifting of FTIR bands in various concrete samples. FTIR results demonstrate the shifting in peaks in presence of marble dust and nano-silica as compared to control mix. Decrease in intensity of Raman bands at 1636 and 3400-3650 cm\(^{-1}\) with curing time was observed due to hydration of C-S and CaS. The bands observed at 1475 and 890 cm\(^{-1}\) also shift towards lower wave number side 1450-1460 cm\(^{-1}\) with increasing nano-silica content. These peaks are correlated with extent of carbonation which gets decreased in the presence of nano-silica. In addition to this, bands corresponding to ettringite, monosulphate and C-S-H molecules at 1180, 1120 and 980 cm\(^{-1}\) also shift towards lower number side with increase in concentration of nano-silica and marble dust.

Keywords: Waste marble dust; Nano-silica; Nanomodified concrete; FTIR.

1. Introduction

Cement industry has emerged as one of biggest industry with an annual production of 2.6 billion tons [1] due to increasing industrialization and civilization. This industry uses most of natural resources, generates huge amount of solid waste and also contributes in 6-7% of annual production of CO\(_2\) [1][2]. In the current scenario it is highly recommended that recycled materials should be used in place of cement for concrete mixes as it will reduce the production and use of cement. Among different types of industrial waste materials, marble waste generated from marble cutting and shaping is a huge problem. Marble waste can cause breathing and skin issues due to its small sized particles. Its dumping on earth surface and in water bodies cause reduction in water permeability and water pollution, respectively [3]. All over the world, this waste is produced in huge amount and it is really a difficult task to dump or reutilize it. It has been observed that marble dust powder or slurry can get easily substituted in the voids of cement and generates a dense structure resulting in dense matrix with better mechanical properties. In addition to this, it is also highly effective in controlling the alkali silica reaction by accelerating the hydration of C-S and aluminosilicate formation that also results in interconnected matrix and less porous structure [4]. Use of marble dust and nano silica in replacement to cement has their own advantages and disadvantages. Marble dust is observed to have positive effect on setting time and workability of concrete mixes but it negatively impacts the mechanical properties, especially compressive strength. On the other side, nano-silica negatively affects the water requirement but enhances the compressive strength due to its pozzolanic properties. From literature, it can also concluded that addition of both marble dust and nano-silica directly or indirectly affects the hydration reaction and the formation of tricalcium silicate, aluminosilicate and C-S-H gel which finally affects the mechanical and durability properties of the concrete mix. Thus, it would be interesting to explore the combined effect of nano-silica and marble dust on the structural changes occurring in concrete mixes after hydration at different time intervals. In the present study, the different concrete mixes with varying compositions were synthesized and studied with Fourier transform infrared spectroscopy to evaluate the various structural changes occurring in concrete mixes after hydration of 28 and 90 days.

2. Literature Review

Talah et al. [5] have observed that maximum of 15% of marble dust can be added in place of cement without making any compromise with compressive strength and durability. Rana et al. [6] have studied durability properties of concrete mixes with 25% of marble dust slurry and found that optimum concentration of marble dust...
slurry for durability enhancement is only up to 10%. Li et al. [7] have demonstrated that addition of marble dust in the form of paste reduce the cement content up to 33% in concrete mixes and also significantly enhance the water resistance and carbonation. To enhance the mechanical properties further, nano silica was incorporated. Due to its nano size and high surface area it was observed to provide better density and high chemical reactivity. Incorporation of nano silica was found to form fine hydrated phases like C-S-H gel due to its pozzolanic properties which results into highly dense microstructure and better mechanical properties. However, there are some controversial statements in literature regarding maximum substitution limit of nano silica in cement matrix. Some authors have claimed that concentration of nano silica in cement matrix should be kept in between 1-5% to avoid any agglomeration [8][9], whereas in some other reports it has been observed that substitution of nano silica up to 10 wt% can enhance the properties of concrete mixes [10][11].

2. Experimental Technique

For the present experimental work, different concrete mixes were formed by mixing ordinary Portland cement (OPC), marble powder, nano-silica, fine and coarse aggregates with water in different concentrations. OPC of 43 grade as per Indian standards IS 8112:1989 [12], was used in the present study. Marble dust was procured from local marble cutting industry located at Jaipur, Rajasthan, India. Before mixing with other constituents, it was dried in oven at 100 ± 5 °C for 24 hrs and the sieved through IS 90 µm sieve. The density, specific gravity and surface area of marble dust was determined to be 2.74 g/cm³, 2.63 and 364 m²/kg, respectively. Commercially available nano-silica of particle size 20-30 nm was used in present study. The crushed stone and river sand were used as coarse and fine aggregates in the concrete mixes as per IS 8112:1989 [13].

From the above mentioned constituents materials, different concrete mixes were formed according to IS 10262:2009 [14] by varying the concentration of marble dust powder and nano silica. The different compositions of concrete mixes are given in table 1. Water content in all the concrete mixes was fixed to be 158 kg/m³ and the water binder ration (w/b) of 0.4 was selected to cast different specimens. To mix all the constituents completely and uniformly, laboratory pan mixer was used. These mixes were cast into IS steel moulds and kept at room temperature of 23°C for 24 hrs. After this said timings, the samples were demould and cured in water at a temperature of 20°C for 28 and 90 days of hydration. A small portion of the specimen was collected after the mechanical test from the fractured area and was then instantly saturated in the acetone to stop the further hydration. It was then finely ground for FTIR characterization. The specimens were then mixed with KBr and the measurements were carried out in the frequency range of 500-4000 cm⁻¹ in total attenuated reflection mode. Specimens were tested for their structural changes with Fourier transform infrared spectroscopy (FTIR) (Bruker ALPHA spectrophotometer).

Table: 01 Mix proportions

| Water (kg/m³) – 158, W/b Ratio – 0.4 | Binder (kg/m³) | Notes |
|--------------------------------------|----------------|-------|
| Mix ID | Mix Series | Cement % | Nano Silica % | Marble Dust % |
| C100 | NS0-MD0-C100 | Control Mix | 100 | 0 | 0 |
| C99 | N1-M0-C99 | Nano Silica replacement | 99 | 1 | 0 |
| C98 | N2-M0-C98 | 98 | 2 | 0 |
| C97 | N3-M0-C97 | 97 | 3 | 0 |
| C95 | N0-M5-C95 | Marble Dust replacement | 95 | 0 | 5 |
| C90 | N0-M10-C90 | 90 | 0 | 10 |
| C85 | N0-M15-C85 | 85 | 0 | 15 |
| C94 | NS1-MD5-C94 | 94 | 1 | 5 |
| C89 | NS1-MD10-C89 | 89 | 1 | 10 |
| C84 | NS1-MD15-C84 | 84 | 1 | 15 |
3. Results and Discussion

The overall hydration reaction taking place in concrete mixes when cement and other constituents where mixed with water can be explained as follows: Tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF) are the main constituents of Portland cement. During formation of concrete mixes, when water is added to the cement, hydration reaction takes place which mainly involves conversion of C₃S and C₂S into calcium silicate hydrate (C-S-H) and calcium hydroxide (Ca(OH)₂). However, during hydration, C₄AF and C₃A produces calcium sulpho aluminate known as ettringite. The whole reaction involved during hydration can be summarized as [15]:

\[
2Ca₃SiO₅ + 6H₂O \rightarrow Ca₃Si₂O₆·3H₂O + 3Ca(OH)₂
\]

\[
2Ca₃SiO₄ + 4H₂O \rightarrow Ca₃Si₂O₆·3H₂O + 3Ca(OH)₂
\]

\[
Ca₃Al₂O₆ + 3CaSO₄·2H₂O + 26H₂O \rightarrow Ca₆Al₂[O₆(SO₄)₂]₃ + 32H₂O
\]

This hydration reaction produces two major products 5-60% quasi-amorphous C-S-H and 20-25% crystalline calcium hydroxide. Presence of pozzolanic materials like SiO₂ accelerates this hydration reaction and reacts with calcium hydroxide to produce secondary long chain of C-S-H. The pozzolonic reaction can be represented as follows [16]:

\[
Ca(OH)₂ + SiO₂ \rightarrow C - S - H
\]

The reaction decreases the water content in the cement and also Ca/Si ratio. But the production of secondary C-S-H depends upon the concentration of portlandite after hydration reaction. Apart from these reactions, marble dust reacts with aluminium particles and forms a phase comprising aluminum oxide, ferric oxide and carbonate. All these phase or structural changes occurring during hydration reaction can be more elaborated with the help of FTIR spectroscopy.

The FTIR spectra of different concrete mixes with only marble dust and nano-silica as a replacement of cement were recorded after 28 days and 90 days of curing and are shown in Fig. 1 and Fig. 2, whereas the results for concrete mixes having combined nano-silica and marble dust in different compositions of the same after 28 days and 90 days of curing are shown in Fig. 3 to Fig. 5. Si-O asymmetric stretching bonds are identified near 1000 cm⁻¹ are attributed to the generation of hydraulic compounds such as C-S-H [17]. The IR spectrum acquired can be classified into three basic zones [18]. The first zone is having a wavelength of around 850–1200 cm⁻¹ subjected to stretching vibrations. The second zone has a band around 750-800 cm⁻¹ it is because of the asymmetric stretching band these bonds are wide and are weak. The third zone is around 500 cm⁻¹ they are because of the bending vibration of Si-O-Si bonds. Most of bands are commonly observed in all the concrete samples like the bands at wavenumber of 1636 and 3400 to 3650 cm⁻¹ which are present in all the samples. H-O-H bending, and H-O-H vibrations are responsible for generation of these bands. Both these bands are associated with adsorbed water on surface of concrete mixes and due the end products of hydration of C-S and C-S. Intensity of these bands decreases with the increase in curing time and decrease in available free water due to the formation of complex C-S-H gel. That is why a decrease in intensity of these bands is observed after 90 days of curing as compared to 28 days. Even the decrease in these bands is more for samples containing marble dust and nano silica as compared to control concrete mix. The change in these bands are more prominent for specimens with combined substitution of marble dust and nano silica as compared to specimens having individual marble or nano-silica [19].
Fig. 1. FTIR spectra of concrete mixes with nano-silica replacement with cement.

Fig. 2. FTIR spectra of concrete mixes with marble dust replacement with cement.

Fig. 3. FTIR spectra of concrete mixes with 1% nano-silica and 5, 10 & 15% marble dust replacement with cement.

Fig. 4. FTIR spectra of concrete mixes with 2% nano-silica and 5, 10 & 15% marble dust replacement with cement.
Fig. 5. FTIR spectra of concrete mixes with 3% nano-silica and 5, 10 & 15% marble dust replacement with cement.

The other two bands at 1475 and 890 cm\(^{-1}\) are due to the C-O stretching vibration of carbonate molecules. Carbonate molecules are formed due to the reaction between calcium hydroxide and carbon dioxide present in the air [20]. These bands are indirectly linked to extent of carbonation [21]. These bands are found to shift towards lower wavenumber side of 1450-1460 cm\(^{-1}\) with increasing nano-silica content, whereas no shift or very minor shift in these bands is observed for control mix and specimens without nano silica (Fig. 1 left). This can be attributed to the pozzolonic property of nano-silica due to which hydration reaction is accelerated and more calcium hydroxide is consumed to form C-S-H phase. Presence of tricalcium silicate and tricalcium aluminate in concrete matrices can be confirmed due to the presence of bands at 626 and 528 cm\(^{-1}\) in FTIR spectra. Other than this, monosulphate, ettringite and C-S-H molecule formation during hydration reaction can be correlated with the presence of FTIR bands at 1180, 1120 and 980 cm\(^{-1}\)[22]. Intensity of these bands decreases with the increase in curing time from 28 days to 90 days. FTIR band present at 980 cm\(^{-1}\) also exhibits shifting towards lower wave number side (950-970 cm\(^{-1}\)) in all the samples. This shifting in bands is an indicator for formation of C-S-H phase due to the hydration reaction. Thus, overall hydration reaction and role of different substituents can successfully be explained with the help of FTIR spectra [23]. FTIR bands observed in various concrete samples are summarised as in table 3.

Table 2. FTIR bands observed in Fig. 1 to Fig. 5

| Wave number [cm\(^{-1}\)] | Functional bond | Assigned to | Refs. |
|---------------------------|-----------------|-------------|-------|
| 3637–3644                 | O-H             | Portlandite – Ca(OH)\(_2\) | [24], [25], [26], [27] |
| 3452, 3485, 3600 and 3400 | O-H stretching vibrations | inorganic layers and the interlayer water. | [28], [29], [30] |
| 3420                      | O-H             | existence of crystal or absorbed water produced during the reaction procedures. | [29] |
| 2873                      | C-H stretching  |                           | [29] |
| 1726                      | overlapping of C-O|                      | [29] |
Conclusions

In present work, recycling of waste marble powder and nano-silica has been studied as replacements for cement in concrete mixes by using FTIR spectroscopy. FTIR results clearly demonstrate shifting in peaks in presence of marble dust and nano-silica as compared to control mix. Decrease in intensity of Raman bands at 1636 and 3400-3650 cm$^{-1}$ with curing time is observed due to hydration of C-S and C-S. The bands observed at 1475 and 890 cm$^{-1}$ also shift towards lower wave number side 1450-1460 cm$^{-1}$ with increasing nano-silica content. These peaks are correlated with extent of carbonation which gets decreased in the presence of nano-silica. In addition to this, bands corresponding to ettringite, monosulphate and C-S-H molecules at 1180, 1120 and 980 cm$^{-1}$ also shift towards lower wave number side with increase in concentration of nano-silica and marble dust.

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| 1640 - 1650 | C-H bending | chemically bound water in the hydrated calcium silicate phases | [24], [27] |
| 1636 - 1646 | H-O-H bending | | [26], [27] |
| 1631 | O-H bending | Bond in water | [28] |
| 1475 | $\mathrm{C}-\mathrm{O}$ stretching | residual $\mathrm{Ca(OH)}_2$ | [24] |
| 1434 - 1440 | Asymmetric stretching of CO$_3^{2-}$ | | [26], [27] |
| 1180 | Si-O stretching | Monosulphate | [24] |
| 1120 | Si-O stretching | Ettringite | [24], [27] |
| 972 and 1111 | Si-O stretching | Pristine and modified nano-SiO$_2$ | [27], [28] |
| 980 and 1000 | Si-O asymmetric stretching vibration strong bond | C-S-H | [24], [26], [27], [31], [32] |
| 898 | C-O and O-H Stretching | Hemicellulose | [33] |
| 882 – 890 | CO$_2$ | Carbonates | [26] |
| 779 - 881 | Out-of-plane bending of CO$_3$ | | [26], [27] |
| 523 - 535 | Si-O out-of-plane bending | | [26], [27] |
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