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Studies on fly ash based geopolymeric coating material compositions incorporated with TiO_2 and Fe_2O_3 nanoparticles for mild steel

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In the present studies, three different compositions of geopolymeric coating material have been developed utilizing fly ash, red mud, alkali activators and sodium dihydrogen phosphate. TiO_2 and Fe_2O_3 nanoparticles are added to the developed coating material compositions as additives. These compositions are applied to mild steel plates by spray coating technique. Further, adhesive strength, water stability and anti-corrosion behavior of geopolymeric coated mild steel plates are determined. Developed geopolymeric coating material compositions are characterized for minerology, bonding behavior and morphology by XRD, FTIR and SEM respectively. Results revealed that among all the three coating material compositions, composition containing nano TiO_2 exhibited best performance in terms of adhesive strength [3.1 MPa at 7th day], water resistance and corrosion resistance characteristics in 3.5 weight % sodium chloride solution by electrochemical measurements.

Keywords: Geopolymeric coating, Adhesive strength, Water stability, Electrochemical measurements

Mild steel is extensively used for different low tech and high tech commercial applications. During the course of time, mild steel surface undergoes excessive corrosion due to different types of aggressive environments including aqueous alkaline or acidic medium resulting in serious economic losses to the industries. Efforts are under progress to mitigate this problem by application of different organic and inorganic coatings on mild steel surface. Such type of coatings act as barrier and delayed or inhibits the corrosion process to provide effective corrosion protection to the substrate[1].

Now-a-days, increased environmental awareness among the researchers leading to the development of greener methods for product synthesis which involves less environmental hazards and also improved properties of the end products. Different studies in the area of corrosion protection of mild steel indicated the application of inorganic alkali activated aluminosilicate materials i.e. geopolymers on mild steel substrate because of its high chemical resistance, superior mechanical properties, possibility of tailoring the composition for specific application and also due to their greener method of synthesis as compared to other commercially available organic coating materials[2-4]. Geopolymers are unique material having Si-O-Si and Si-O-Al linkages in three dimensional framework and they are known to provide corrosion protection to mild steel. The silicate and aluminate network in geopolymers exhibit high adhesion strength with mild steel and the inert nature of N-A-S-H network actively passivates the diffusion of ions from outer to inner environment and vice-versa to protect the surface from being corroded [4]. Work has been done in current years on addition of different types of additives to the geopolymeric gel matrix like silica fumes, nano-SiO_2 and Al_2O_3, nano-clay, carbon nanotubes, $CaCO_3$ nanoparticles and their effect on properties of geopolymers have been studied and reported[5-9].

According to the reported literature, the presence of nanoparticles (viz. SiO_2, Fe_2O_3, TiO_2etc.) in the coating formulations greatly enhanced the corrosion resistant properties as well as mechanical performance[10,11]. In the present studies, three different compositions of geopolymeric coating material for mild steel substrate were prepared utilizing fly ash, red mud, sodium dihydrogen phosphate (NaH_2PO_4),

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sodium hydroxide (NaOH), sodium silicate (SMS), iron oxide (Fe_2O_3) and titanium dioxide (TiO_2) nanoparticles. These compositions were coated on mild steel plates by spray coating technique. Water resistance, Adhesive strengthofcoated mild steel plates weredetermined. Electrochemical measurements were performed on coated mild steel plates using anodic polarization curve.

Experimental Section

Materials

Low calcium class F fly ash was procured from DIRK India Pvt. Limited and used as a starting material. According to supplier's data, the major mineralogical phases of fly ash contained quartz, mullite and hematite along with glassy silicoaluminous phase. Analytical grade sodium silicate and sodium hydroxide pellets were procured from MERCK. Sodium dihydrogen phosphate [NaH_2PO_4] was procured from CDH. Red mud, an industrial waste from aluminium industry was obtained from Hindalco, Renukoot, and was used to along with fly ash to prepare geopolymeric gel. Further, nano-Fe_2O_3 and nano-TiO_2 particles were purchased commercially.

Mild steel substrate in the form of 50 mm × 60 mm coupons with an average thickness 1 mm were purchased from local supplier at Bhopal and selected for the application of geopolymeric coating material by spray technique to carry out present studies.

Preparation of geopolymeric coating material

Red mud used to carry out present studies was preheated at 450°C temperature before use for conversion of goethite to hematite.The raw materials composition (weight%) used for preparation of three different compositions of geopolymeric coating material are shown in Table 1. These compositions are designated as control, FRF and FRT. For preparation of geopolymeric coating material, activator solution was prepared by dissolving NaOH and SMS in water. After this, sodium dihydrogen phosphate added to prepared activator solution. The prepared solution containing NaOH, SMS and sodium dihydrogen phosphate added to premixed solid powder of well dried a) fly ash and red mud for control, b) fly ash, red mud, nano-Fe_2O_3 (FRF)as an additive, and c) fly ash, red mud, nano-TiO_2 as an additive (FRT). The prepared mix then mechanically stirred for 10 min to form thin smooth slurry for coating. In this study, the Si/Al molar ratios, quantity of NaOH, NaH_2PO_4 and solid to water ratios are not altered to observe direct effect of addition of nano particles.

Table 1 — Geopolymeric coating material compositions

Composition	Control	FRF	FRT
	Weight percentage		
Fly ash	83.05	83.05	83.05
Red mud	3.32	3.32	3.32
SMS	4.15	4.15	4.15
NaOH	8.63	8.63	8.63
NaH_2PO_4	0.83	0.83	0.83
Nano-Fe_2O_3	-	0.83	-
Nano-TiO_2	-	-	0.83

Characterization studies

XRD patterns of the prepared geopolymers were obtained from RIGAKU X-ray Diffractometer. The operating conditions included variation of 2θ in the angular range of 5 to 70° using Cu Kα radiation.

FTIR absorption bands of three prepared geopolymer coating material sample were recorded from 4000-500 cm^{-1} wavelength using Bruker Alpha Fourier Transform Infra-Red spectrophotometer. Study of the interface and analysis of synthesized geopolymeric microstructures were carried out using Scanning Electron Microscope JEOL JSM 5600. The thickness of the spray coated samples reported with the help of FESEM model Nova Nanosem-430 of COMFEI.

Coating of prepared geopolymeric material compositions

Mild steel coupons were cleaned by rubbing with sand paper, washed with water, then with acetone and dried. Pre-cleanedand pretreated mild steel coupons were coated with the control, FRF and FRT geopolymeric coating materials using spray gun. Coated plates dried at room temperature which was around 40°C in summer season. Coated plates were then used for further studies.

Determination of adhesive strength

Following ASTM D 4541, the adhesive strength of coating material was determined by Elcometer 106. Elcometer dollies were fixed onto each coated plates using Araldite adhesive A+B, and dried for 24 hours at room temperature. Then, pull off test was performed using Elcometer 106 after 3, 7 and 28 days of curing of the coated material.

Static water immersion test

This test was performed to check the water resistance of the coated materials. At room temperature, the coated plates were immersed in water and weighed after every 24 hours followed by oven drying at 40°C for 1 hour. Change in weight then calculated in percentage as per equation-1. A comparative analysis of control, FRF and FRT coating formulations for water resistance is given in this study.

$$\Delta W = \frac{W_2 - W_1}{W_1} \times 100\% \qquad \text{eq. (1)}$$

where, ΔW= percentage weight loss
w_1= weight of sample before water immersion (gms)
w_2= weight of sample after water immersion (gms)

Electrochemical measurements

Electrical measurements were performed in 3.5 wt% NaCl solution as electrolyte for determination of corrosion of coated mild steel plates using Potentiostat model number CH 1604 C of H CH Instruments Inc., USA. Three electrode electrochemical cell was used for anodic polarization measurements. Coated mild steel plate was working electrode, Ag/AgCl was reference electrode and platinum foil was used as counter electrodes. The potentials have been reported vs Ag/AgCl reference electrode. The current was measured initially, on 1st, 2nd, 5th, 6th, 7th, 19th, 20th, and 21st day respectively at applied potential in the range of 0.6 volt to 1.2 volts at a scan rate of 0.1 volt/second.

Compressive strength analysis

Compressive strength of three geopolymeric coating material compositions was determined as per Indian standard specifications. Mortar paste of three geopolymeric coating material compositions was prepared using fly ash to sand in ratio 1:3. For determination of compressive strengthof control, FRF and FRT samples,mortar pastes of coating material compositions were poured in iron moulds 7.06 ×7.06 ×7.06 cms dimension and compacted on vibratory table for 5 min. After, that samples were oven dried at 60°C for a period of 24 hr, demolded and tested for compressive strength after curing period 3, 7 and 28 days on HEICO compressive strength tester. Three sample cubes were tested for each composition for accuracy.

Results and Discussion

Characterization

XRD Studies

The XRD patterns of the three coating formulations are presented in Fig. 1. The diffraction peaks of samples were almost identical and the common phases in all samples originated from fly ash were quartz SiO_2, JCPDS 02-0458, mullite $3Al_2O_3$. $2SiO_2$, JCPDS 02-0452 and hematite Fe_2O_3, JCPDS 24-0072. The dissolution of glassy silicoaluminous phase from fly ash resulted in formation of geopolymeric phase in the form of sodium aluminium silicate hydrate, herschelite, $NaAlSi_2O_6.3H_2O$, JCPDS 19-1178 in coating samples which was reported as major phase. However, there were some traces of sodium silicate, $Na_2Si_3O_7$, JCPDS 38-0019, which remain unreacted in the compositions reported as minor phase. The XRD analysis also indicated the presence of aluminium phosphate $Al(PO_3)_3$ JCPDS 15-0364 in all geopolymeric samples. In sample FRF, the addition of nano- Fe_2O_3 to the geopolymeric coating composition resulted in the increase intensities of hematite Fe_2O_3 JCPDS 24-0072; whereas in sample FRT, other than above stated phases, anatase TiO_2, JCPDS 02-0387 and sodium titanium oxide, Na_4TiO_4, JCPDS 42-0513 were observed as an additional phase. It is to be noted that the diffraction peak intensities of anatasewas very low as it consumed in formation of sodium titanium oxide.

FTIR Studies

The samples also further characterized for their different chemical bonds using FTIR technique. Various FTIR absorption bands for the coating samples are illustrated in Fig. 2. The strong bands at 1023 cm^{-1} in spectra of control and FRF and band at 1020 cm^{-1} in the spectra of FRT attributed to Si-O-Si asymmetric stretching vibrations. This vibrational band is typical for silicate glassesin geopolymers[12]. Another weak band in lower frequency region of control and FRF at 558 and 559 cm^{-1} respectively, assigned to Al-O bending vibrations was originated

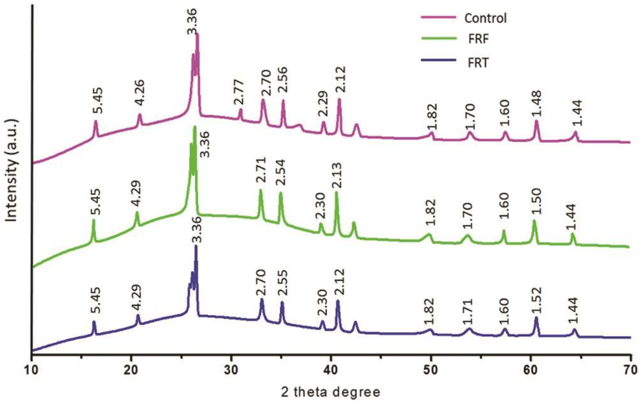

Fig. 1 — XRD patterns of fabricated geopolymeric coating materials with corresponding d values.

from mullite whereas three small diffused bands observed in FRT spectra in lower frequency region at 506 and 554 cm^{-1}were attributed to O-Si-O bending vibrations in quartz and mullite and Al-O bending vibrations[12]. The bands positioned at 3433, 3423 and 3426 cm^{-1} and also bands located at 1604, 1606 and 1605 cm^{-1} in control, FRF and FRT respectively assigned to O-H stretching vibrations of Si-OH and H-O-H bending vibrational modes of water molecules[13].

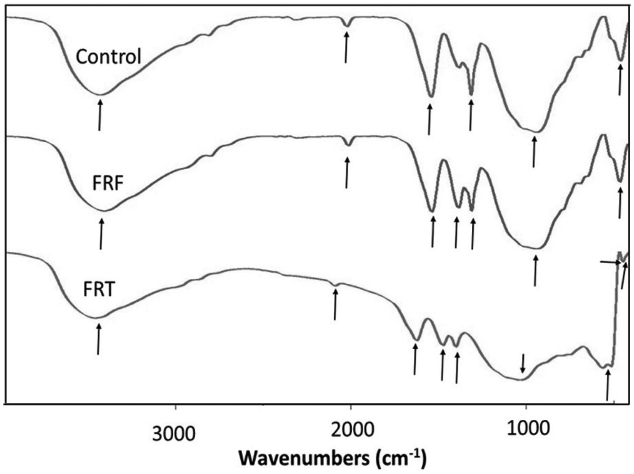

Fig. 2 — FTIR vibrational bands of fabricated geopolymeric coating materials.

In addition, the spectras of control, FRF and FRT also showed the presence of small weak bands at 1384 and 1457 cm^{-1} which specifically assigned to carbonate O-C-O stretching modes originated due to absorption of atmospheric CO_2[14]. Sample FRT indicated occurrence of some overlapping vibrational bands at position 506 and 1457 cm^{-1}and these small diffused bands assigned to stretching vibrations ofTi-O and Ti-O-Tibonds respectively[15]. Similarly, the band at 559 cm^{-1}in the spectra of FRF were assigned to Fe-O stretching vibration mode of Fe_2O_3[16]. One relatively wide small band located at wave number 2070 cm^{-1} in spectra of control, FRF and FRT is attributed to stretching vibrations of P-O-H group[17]. Due to similarities in raw materials and process conditions, no significant changes in the FTIR spectra of samples were observed and the results are also in good agreement with the results of other researchers.

SEM Studies

The SEM images for the study of microstructures and interface bonding of fabricated geopolymer coated mild steel coupons are illustrated in Fig. 3. Micrographs of control (Fig. 3 A) showed the consistent morphology of geopolymer with dense matrix. Only few traces of unreacted relicts of fly ash could be seen throughout the micrographs of

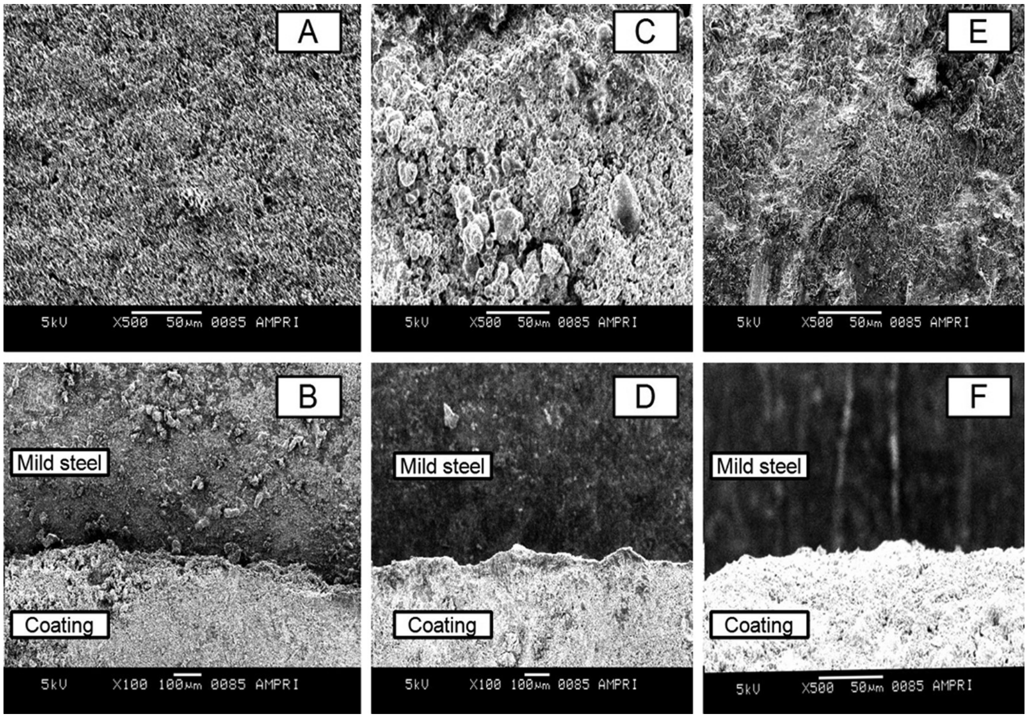

Fig. 3 — Micrographs of geopolymeric coating samples (at 500X). A, C and E are showing microstructures and B, D and F are showing interface bonding between coating material and substrate for control, FRF and FRT respectively.

control, FRF and FRT (Fig. 3 A, C, E). However, the geopolymeric gel seen to be less porous due to the addition of nano particles in FRF and FRT. For all coating formulations, strong bonding between substrate and geopolymeric coating (Fig. 3 B, D, and F) was observed with relatively less number of micro cracks in sample FRT. This suggests that addition of nanoparticles improved the homogeneity of geopolymer matrix and reduced the porosity to some extent by reducing the inter-particle distances due to their nano sizes. The thickness of coated samples determined by FESEM was found to be between 110-130 microns.

Adhesive strength

The results of adhesive strength for geopolymeric coating formulations are relatively compared in Fig. 4. Sample FRF produced maximum adhesive strength of 3.1 MPa at 7th day. FRT produced 2.7 MPa at 7th day which was comparatively more than control but less than FRF. No significant variation observed in the adhesion strength of samples for three aging periods and consistent readings were recorded for 7th and 28th day. This suggests that nano-particles incorporated geopolymeric coating gained its maximum adhesion when reached upto 7th day of ambient curing. No extended curing regime is required to attain bonding strength between coating and underlying substrate. The usefulness of any coating material is specifically dependent on its adhesive properties with the substrate. Geopolymeric coatings, as studied by other researchers, achieved adhesive strength upto 3-4 MPa for mild steel[18-20]. In this study, the spray coated geopolymeric material on mild steel produced thickness upto 120±10 microns and achieved good adhesion with the substrate suggested that nano-particles in geopolymeric matrices effect the adhesion property by reducing gel porosity.

Water immersion test

The static water immersion test for coating samples carried out for 360 hours and the results are reported in Fig. 5. The nanoparticles modified geopolymeric coating samples FRF and FRT showed excellent water resistance as compared to control. As observed, the trend of weight loss was more in control than FRF and FRT. This suggested that incorporation of nanoparticles in geopolymeric framework hindered the dissolution of ions from coating by entrapping them into a closely packed, non-porous geopolymeric matrix which was improved by addition of nano-Fe_2O_3 and nano-TiO_2. These inorganic nanoparticles provided stability to the geopolymeric coating in water. Also the decrease in weight reduces and became constant for samples after 240h, 168h and 144h for control, FRF and FRT respectively. FRT showed maximum improvement in water resistance with minimum weight loss from initial 24h to final 144h of immersion.

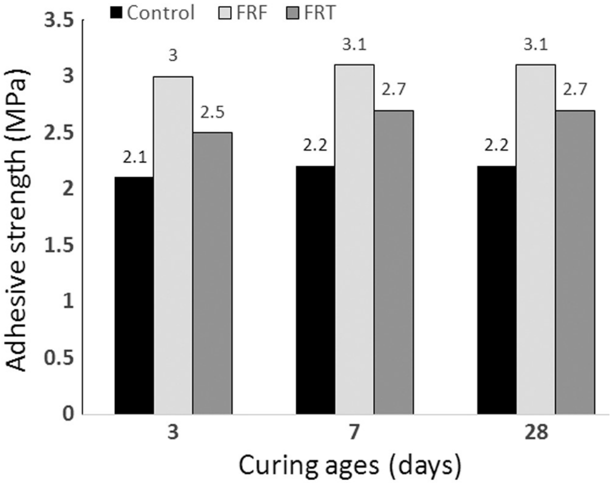

Fig. 4 — Adhesive strength of Control, FRF and FRT geopolymeric coating samples for mild steel for three different ages.

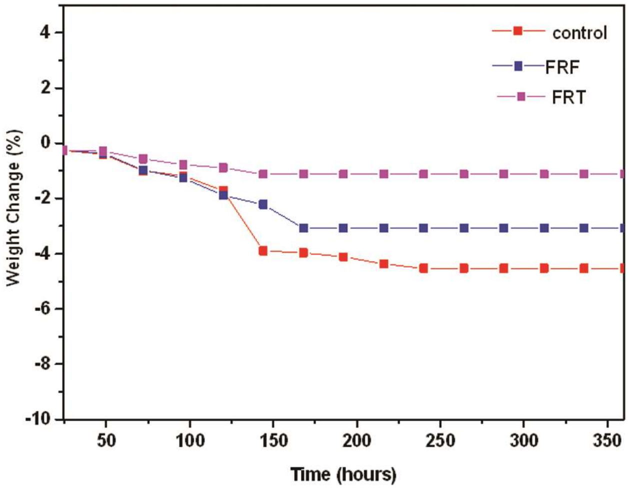

Fig. 5 — Percentage weight change with respect to time curve for geopolymeric coating samples.

Electrochemical Measurements

The anodic polarization curve obtained for Control, FRF and FRT was shown in Fig. 6. Graph between current density (A/cm^2) measured vsnumber of days at a fix potential of 0.2V indicated that current follows zig-zag trend with increase in number of days. However, it achieved almost minimum value after 21 days in Control and FRT and after 20 days in FRF. Decrease in current density in coated samples in the

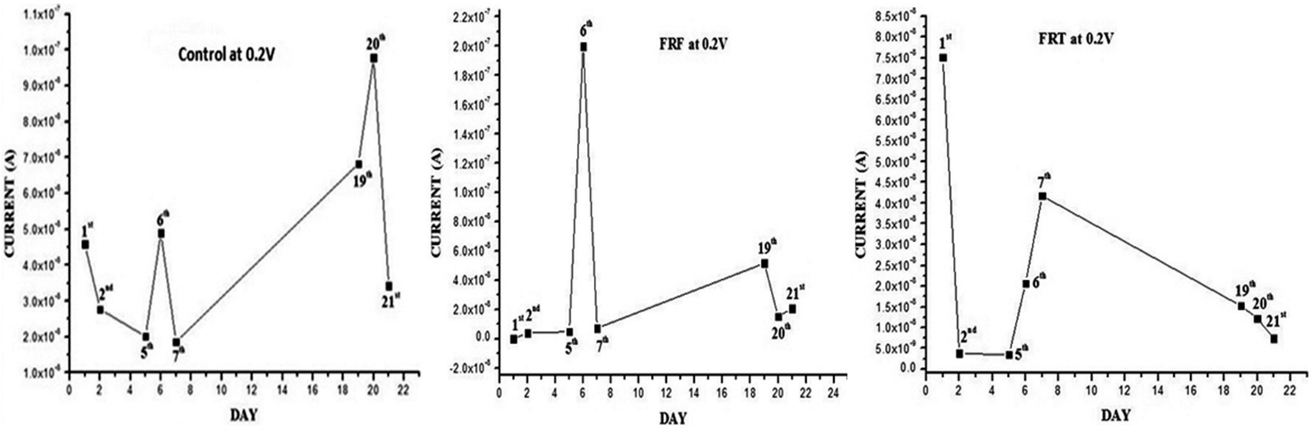

Fig. 6 — Plot of Current density (A/dm^2) vs number of days at fixed potential of 0.2V for Control, FRF and FRT coated mild steel plates.

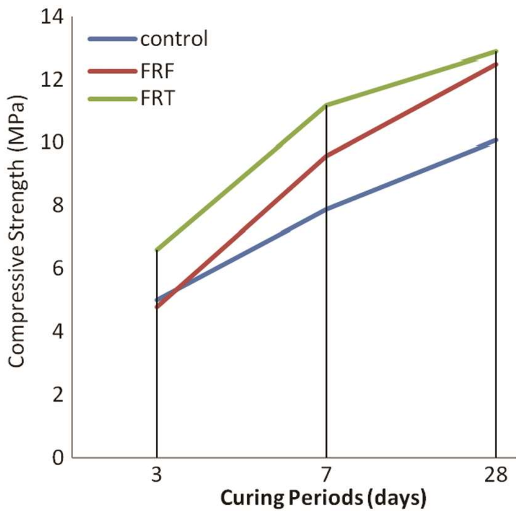

Fig. 7 — Compressive strength variation of geopolymeric material for three different curing periods.

range of 2.2 × 10^{-7} to 5.0 × 10^{-9} A/cm^{2}in comparison touncoated mild steel plates which showed current density ~1 A/cm^2 indicated that coated mild steel plates possess better corrosion resistance. Further lowest current density of FRT indicated that it possesses best corrosion resistance characteristics among control, FRF, and FRT coated mild steel plates.

Compressive strength results

The mechanical strength of fabricated geopolymeric coating material compositions control, FRF and FRT were tested as per Indian standard specifications by preparing geopolymeric mortar, after 3, 7 and 28 days of curing. The results are shown in Fig. 7. The compressive strength of samples increased from 3rd to 28th day curing and FRT exhibited maximum compressive strength at all ages. Although, it was observed that strength of control i.e. 5.0 MPa was little higher then that strength of FRF i.e. 4.8 MPa at 3rd day curing, but the trend changed for 7th day curing for both samples. At 7th day, the compressive strengths of control and FRF were 7.9 MPa and 9.6 MPa respectively. FRT which compositionally contained nano-TiO$_2$ showed highest compressive strength of 12.9 MPa at 28th day curing. These results for FRT were in good agreement with our characterization, water immersion and corrosion test.

Conclusion

Nanoparticles incorporated geopolymeric coating material is fabricated in this study using nano-Fe$_2$O$_3$ and nano-TiO$_2$. These coating materials exhibited good adhesion with mild steel substrate and provided good water resistance. Incorporation of nano-TiO$_2$ effect the performances of coating considerably and found to be best among other two compositions. Nano-Fe$_2$O$_3$ showed contribution in bonding with mild steel substrate and hence indicated higher adhesion to it than the other two coating material compositions. Both the nanoparticles modified coatings showed excellent corrosion protection in 3.5% NaCl but the best corrosion protection was reported for FRT. Thus from this study it can be concluded that the developed nano particles incorporated geopolymeric coating material can be tuned into to desired coating material to protect mild steel structures from early onset of corrosionto enhance their life span and durability after optimization of compositions and process parameters.

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