



Optimization studies and characterization of advanced geopolymer coatings for the fabrication of mild steel substrate by spin coating technique

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Advance inorganic fly ash – metakaolin- phosphatic geopolymer has been developed via greener approach and deposited on mild steel substrate using spin-coating method, to improve the substrate-matrix interaction. The present research investigates the effect of incorporation of metakaolin and phosphate to geopolymer matrix to assess the performance of coating and optimization of spin coating parameters are performed as well to achieve maximum adhesion strength. XRD, FTIR, and SEM studies coupled with energy dispersive spectroscopy (EDX) have been carried out for determination of mineralogical phases, bonding interactions, substrate–matrix interface, and microstructural and chemical analysis. Results indicated that spin coating method produced well-ordered thin geopolymeric coating (thickness 13-20 micrometres), therefore spin coating deposition is the simplest way to obtain thin coatings of visibly thick materials. Maximum adhesion strength of material with substrate is 2.5M.Pa. which is obtained at optimized water to precursor ratio 0.5 at 500rpm spinning speed. It is concluded that new inorganic phases (originated from mutual contribution of phosphate, metakaolin and fly ash) like sodium iron aluminium phosphate, aluminium phosphate and sodium iron phosphate were responsible for good adhesion of material to the substrate and then related properties. The developed and optimized method can be used to produce homogeneous coating of heterogeneous geopolymer material on low carbon steel to indorse its advanced applications.

Keywords: Adhesion strength, Optimization studies, Spin-coating, Substrate–matrix interface

Geopolymers are amorphous to semi-crystalline three-dimensional silica-aluminate materials prepared by alkali hydroxide and alkali silicate activation of amorphous alumina and silica containing materials such as fly ash, metakaolin, red mud^{1,2}. Geopolymers are eco-friendly, green, competent building material developed from cast-aside of energy efficient process³⁻⁵. The alkali activation of alumino-silicious material like fly ash follows the bimolecular nucleophilic substitution (S_N2) mechanism⁶. This conventional sol-gel technology of manufacturing geopolymer using coal combustion residue is considered as user unfriendly approach as it is associated with different handling and safety issues⁷⁻⁹. In order to reduce the alkali hazards and making the synthesis process risk free, advanced geopolymeric material were developed by a novel process of mechano-chemical co-grinding of raw materials and adding water only in appropriate quantity to solid precursor powder obtained to prepare geopolymeric material^{6,10}. The advanced geopolymer undergoes solid state chemical route and follows

unimolecular nucleophilic substitution mechanism (S_N1)^{6,11}. The new chemical route mechanism enhances the gelation property of the geopolymer and expand the application zone of the material. The developed innovative and inexpensive material has multifunctional applications along with benefits over the conventional methodology, and can be used to make low cost bricks, panels, tiles, coating material etc with tailored properties. Geopolymer based coatings demonstrate efficient protective property and enhance the efficiency of metal surface¹². Various coating techniques are conventionally used to fabricate the metal substrate to improve the protective efficiency of the coating material like spray coating, spin coating and dip coating¹³. Spin coating technique proves highly efficient for reproducible fabrication of coating material on metal substrate and has the potential to develop uniform coatings even in the micrometre range which is not possible with other techniques¹⁴. Slurry viscosity is one of the considerable parameters which affect the thickness and ultimately performance

of the coating¹⁵. Less number of coating cycles and temperature exemption make the technique more beneficial over other. The uniform thin coatings are the foremost requirement for the adhesion studies which will not obtain in any of the coating techniques like paint and dip coating techniques. The important parameters of the technique include the determination of effect of viscosity and composition of slurry on the coatings and adhesion studies¹⁶⁻¹⁸. The instrumental parameters like spinning speed, spinning cycles and rotation time also plays an important role in this technique. The present study, investigated the effect of these parameters on film performance in detail. This technique also provides an industrial application in future to deposit multi-layer film of different or same materials for properties enhancement.

Fly ash as aluminosilicate source, is used as a raw material having Si: Al in the ratio 2:1^{19,20}. Obviating the use of sodium metasilicate, making the material with low Si/Al ratio and for high Al₂O₃ content, metakaolin was added which led to increased chemical interaction at metal-coating interface²¹⁻²⁵. The addition of sodium hexa meta phosphate to the coating material decrease the porosity of the geopolymer gel matrix and enhance fire protective property of the coating material^{26,27}. Metakaolin; a dehydroxylated form of clay mineral kaolinite; calcined at 800°C for 2 h is considered to be a suitable precursor for geopolymer production due to its reactivity and predictable properties both during preparation and in property development^{28,29,12}. It is a highly pozzolanic and reactive material having Si: Al ratio of 1:1³⁰. High Si: Al ratio improves the adhesion of developed fly ash based geopolymer to mild steel substrate³¹. The developed material precursor as well as gel characterized by XRD, FTIR, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis. The study aimed to examine the feasibility of the developed novel geopolymer as a coating material on mild steel substrate along with determination of optimum spin parameters for the potential application of the material as a protective coating material.

Experimental Section

Materials

Materials for formation of slurry included advance phosphatic geopolymer material of optimized composition - sodium hydroxide (AR Grade, Rankem Co., 98%), sodium hexa meta phosphate SHMP (CDH) and class-F Fly ash (DIRK India Private Limited, ASTM C618).

It is to be noted that the used material was prepared using novel solid-state route^{6,10}. Class F Fly ash used in this study compositionally contained (weight %) SiO₂ -53%, Al₂O₃ -33%, Fe₂O₃ -6.8% CaO - 2.8% and TiO₂ - 2.01%, moisture content 0.5%. Metakaolin (Si: Al ratio 1:1) added to the material with the following composition (weight %) SiO₂ -49%, Al₂O₃ -48%, Fe₂O₃ -1.6% CaO - 0.48% K₂O - 2.2% and TiO₂ - 2.1%. Performance studies were accomplished using mild steel specimen as coating substrate with the plate size 2 x 3 cm.

Methods

Synthesis of advanced geopolymeric coating material

Advanced geopolymeric precursor was developed by mixing the raw materials fly ash: NaOH: SHMP in 50:6:0.5 proportion by mass. Metakaolin was also added to the mixture (5 % of the amount of fly ash) and mechano-chemically grinded in a ball mill. The milling was accomplished using 6 steel balls (350gm wt. and 50mm diameter each) for the duration of 8 h. The dry mix powder obtained kept in air tight sealed poly bags to prevent moisture. To prepare geopolymer coating slurry, water was added to the above precursor powder (water to precursor ratio 0.21) resulted in the formation of viscous geopolymeric gel suited for spin coating technique. Further, for experimental procedures, the viscosity of slurry was varied by varying the water content. Homogeneity of prepared geopolymeric slurry achieved through mechanical agitation. The schematic flowchart for the process followed is represented in Figure 1.

Pre-treatment of metal substrates

Mild steel coupons were pretreated before coating to make the surface free from contamination. The treatment was initiated by rubbing the metal substrates with sand paper to remove any type of corrosion. Then the substrates were dipped in 1M HCl for 5-10 min followed by neutralization with 1M NaOH. Then coupons were dipped in organic solvent like acetone to remove oil from the surface. The treated plates were again rubbed with sand paper to make the surface rough for better coating adhesion. Then the plates were exposed to high pressure steam blasting to open the pores of the metal surface^{12,32}.

Optimization of parameters for spin coating

Developed advance geopolymer material were spin coated on treated metal steel surface using spin coating instruments pinNXG-P1 apex. The study examines different parameters like spinning speed, time of rotation

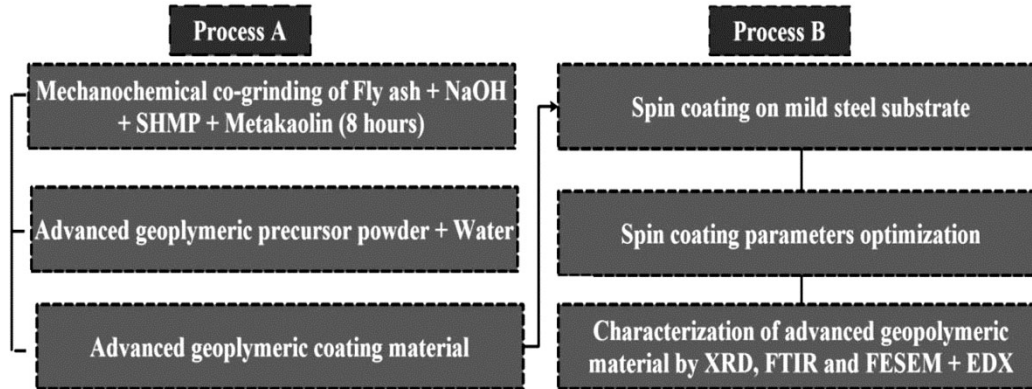


Fig. 1 – Schematic flowchart for the development of coating material and its application.

and number of coating cycles and effect of these parameters on the coating thickness, coating appearance and coating performance. The investigation yields the optimized parameters for further studies. During analysis, viscosity of the material and the amount used were considered. To obtain the uniform thin layer coatings, the less viscous material was used.

Water to precursor ratio

One of the dominant parameters is viscosity of slurry and its optimization, for the optimization process three different gels with different water to precursor ratios were prepared- 0.3, 0.5, 0.7 (w/v) and used for the spin coating technique. Developed different gels were coated onto substrate and adhesive strength was determined. The coating which provided the good value of adhesion (in MPa) used for further studies.

Amount of inorganic geopolymeric gel

For homogeneous uniform coating, the complete planar surface of the substrate should be covered by the coating material. In view of this, the optimization of the amount of coating material sufficient enough for regular smooth coating texture is required. We used micropipettes to vary volume upto 1, 3 and 5 mL, and these specified amounts poured over the metal substrate followed by spin coating. The dried coating was tested for adhesion strength and the optimized amount was further used for the coating purpose.

Spinning speed of rotation

Spinning speed is a very crucial parameter in spin coating technique. Low spinning speed will decrease the spreading velocity which leads to incomplete development of surface coating on metal substrates. To optimize the spinning speed for the uniform and smooth coatings, the developed material was coated on the substrate using spin technique at different spinning

speeds. Although the coatings were done at various spinning speeds, the noticeable results were obtained at 500 rpm, 1000 rpm and 1500 rpm spinning speed for different water to precursor ratio and adhesive strength was determined at all these variable parameters.

Rotation time

During the application of inorganic coatings over mild steel substrate time of rotation also plays significant role. Too short and too long spin time can adversely affect the coating thickness and performance. For uniform coating the time of rotation was also optimized. Spin coating rotation time acquired were 10, 15 and 20 sec and the results for adhesive strength were observed.

After number of systematic experiments, the optimized amount of developed advanced geopolymeric gel was deposited on the metal substrate using micropipette and simultaneously spun for different time with varying spin speed. After spinning, the obtained wet films were dried at room temperature and then oven cured at 60°C for 24 h. The spun films were evaluated for thickness, hardness and adhesive strength.

Determination of Adhesion strength, thickness and coating hardness test

Adhesion strength of the coating material was determined using an Elcometer 106 as per ASTM D 4541³³. The dollies were fixed on coating surface using epoxy adhesive (Araldite A and B) at ambient temperature for 24 h for drying (Fig. 2). Elcometer 106 was used to pull off the dollies using hydraulic mechanism²⁷. Thickness of the samples was examined by analyzing the cross-section of the samples through FESEM images. The hardness was determined by pencil hardness test. The set of calibrated wood pencils composed of 9 pencils, ranging hardness from 6H to B. The 6H was hardest followed by 6H, 5H,

4H, 3H, 2H, H and HB. F was at the middle of the hardness scale; B was the softest.

Characterization studies

The X-ray Diffraction (XRD) patterns of the final geopolymeric coating material with improved adhesion strength were obtained using RIGAKU X-ray Diffractometer, at CSIR-AMPRI, Bhopal (M.P). The operating conditions included continuous scanning angular range of 5° - 70° . Fourier Transform Infra-Red (FTIR) spectral studies of the sample were performed by BRUKER-ALPHA FTIR in 400 - 4000 cm^{-1} range to determine the linkages evolved by mechano-chemical co-grinding of raw materials. Surface and microstructure

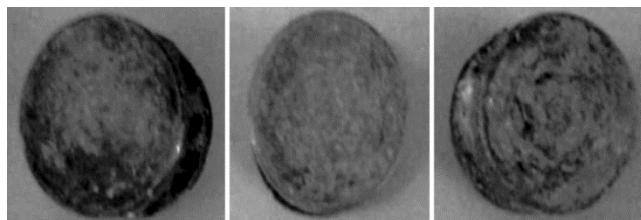


Fig. 2 — Spin coated mild steel coupons tested for adhesion as per ASTM D4541 using Elcometer 106.

analysis were carried out using JOEL-JSM-5600 Scanning Electron Microscope at CSIR-AMPRI. Energy dispersive X-ray spectroscopy (EDS or EDX) were also determined by the SEM. To observe the microstructure of surface interaction between mild steel plates and geopolymer coating material; Field Emission Scanning Electron Microscopy (FESEM) –instrument Nova NANOSEM430 was employed.

Results and Discussion

Effect of concentration of coating material [C] and amount of geopolymeric gel [A]

Parameters like slurry viscosity and slurry amount are important to geopolymeric coating thickness. During the spreading process, if slurry viscosity is too thick, it will affect the radial flow of the material. On the other hand, less viscous slurry renders the surface of the substrate appeared with streaks or flares. In that case, concentration of coating material and its appropriate amount was significantly adjusted to obtain a uniform and performable coating. The C and thickness of coatings were linearly dependent as evident from Fig. 3 (A-2, B-2, and C-2). Although it

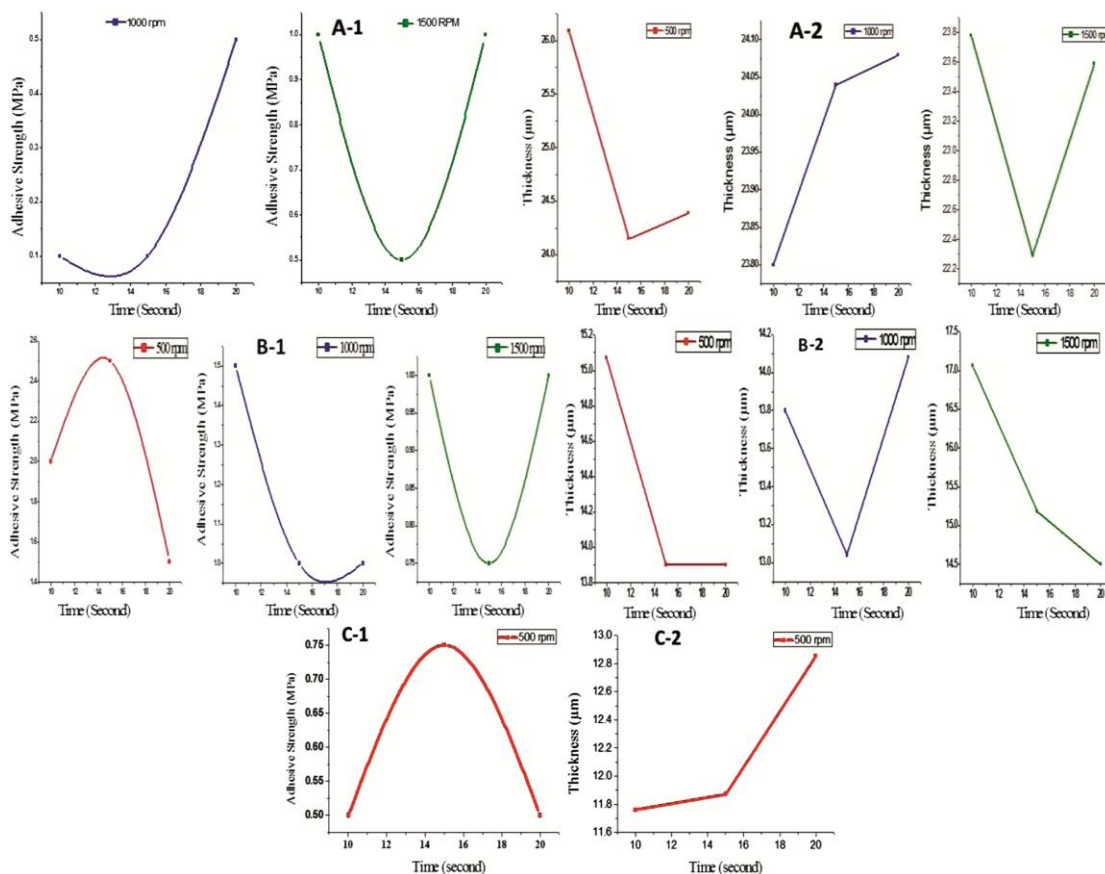


Fig. 3 — Spin coated mild steel coupons tested for adhesion as per ASTM D4541 using Elcometer 106.

is to be noted that the geopolymeric slurry at all concentrations got thickened as water from geopolymeric matrix started getting dry but it hardly affected the spin process during experimentation. Further, the relationship showed that as the concentration increased, the coating thickness also increased. The thickness ranged between 13 μm to 27 μm for the different C 0.7 to 0.3(w/v). Further saturating the coating geopolymeric material was not found to be very effective as it became difficult to apply the thick coating material on the metal substrate. The coating slurry with concentration 0.5(w/v) and 3 mL of geopolymeric gel has been optimised as evident from the results that the adhesion strength achieved with the 0.5 concentration was maximum (Fig. 3 B-1). The amount of coating material deposited from micropipettes produced uniform coating over metal substrates. Coating material, 1 mL, was insufficient to cover the surface of metal substrate and 5 mL produced uneven thick coating layer with comets and flares. Therefore, by the analysis above, the optimised valuable parameters for spin coating for the developed material were 0.5 (w/v) concentration and 3 mL of geopolymeric coating material.

Effect of spinning speed and rotation time

The spinning speed (rpm) has a marked effect on degree of radial force which is applied to the coating material slurry and it is the spinning speed which finally decides the thickness of the coating onto the substrate surface. As the spinning speed increased, thickness of geopolymeric coating decreased (Fig. 3, A-2, B-2, and C-2). From the observations, it was found that the dependency of thickness on spinning speed became negligible beyond 1500rpm. The thickness ranged between 13 μm to 27 μm at spinning

speed of 500 rpm to 1500 rpm. Hence, the optimised spinning speed was 500 rpm for 15 sec as the coating obtained at these values were uniform with thickness 15 ± 2 μm (Fig. 3 B-2) and strength reached to its maximum (Fig. 3 B-1). Considerably, these parameters prevent multilayer coatings.

Adhesion study

Adhesion studies are the most valuable parameter for the study of coating materials. The adhesion strength of different compositions at different parameters was evaluated after 24 h. On the basis of the maximum adhesion strength achieved, the parameters were optimised. The optimised composition and parameters were further studied for evaluating adhesion strength for 3, 7, and 28 days to explore the effects of curing period over adhesion strength. It was observed that maximum adhesion strength of 2.5 MPa (Figure 3. B-1) was observed for the optimised composition after 7 days and 28 days of curing at room temperature. Interestingly, no significant change was observed in the adhesion strength when the curing period was extended above 28 days. Therefore, 7 days of curing period was optimum for getting adhesion strength of geopolymer based coating material.

Thickness

The results of thickness analysis showed that the adhesion strength of the coating increased as the thickness decreased. Venkataraman *et al* and Rico *et al* also reported that increase in the porosity will lead to the decrease the coating hardness^{34,35}. Therefore, coating thickness should be less for getting acceptable adhesion strength. The coating thickness of geopolymer coating sample were between 13 to 27 μm by spin coating technique. Figure 4 is more clearly illustrating

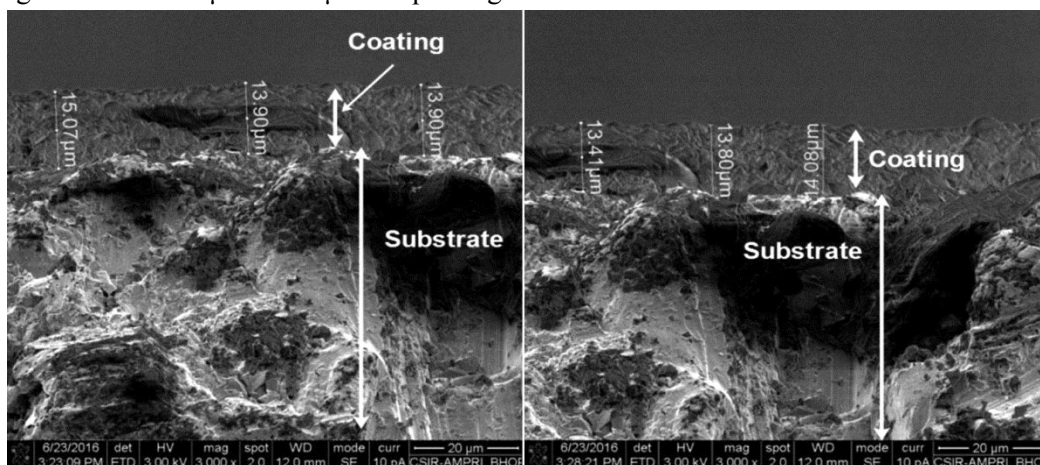


Fig. 4 — Thickness of spin coated material onto mild steel substrate analyzed with FESEM.

Table 1 — Pencil hardness test of spin coated geopolymeric coating.

Property	Coating cured for 3 days	Coating cured for 7 days	Coating cured for 28 days
Pencil Hardness	3H	4H	4H

the coating thickness of the optimised composition i.e. 0.3(w/v).

Hardness study

Table 1 represents hardness study for 3, 7, and 28 days of the optimised geopolymer coated mild steel substrates. The results demonstrated that maximum hardness 4H was observed after 7 days and 28 days of curing period. More ambient curing to geopolymeric coating material enhanced the coating hardness but remain unaffected for 28 day curing duration. In view of this, it can be speculated that no significant change in the hardness was observed when the curing period was extended to 28 days. Therefore, in this study, 7 days curing duration was found to be optimum for achieving 4 H hardness of geopolymer based coating.

Characterisation studies

XRD analysis

X-ray diffraction pattern of the optimised composition of developed coating material is presented in Fig. 5. The main crystalline components of fly ash i.e. quartz, mullite and hematite also appeared in the XRD of developed precursor material but with low intensities. The declining intensity of these crystalline components corresponded to the amorphization phenomena occurred during mechanochemical co-grinding of raw materials. For the improved substrate – matrix interaction, the decreased crystallinity played an important role. Presence of sodium aluminium silicate hydrate ($\text{NaAlSi}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$, JCPDS 19-1178), sodium aluminium oxide hydrate ($2\text{NaAlO}_2 \cdot 3\text{H}_2\text{O}$ JCPDS - 02-1025) and sodium silicate hydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, JCPDS. - 19-1239) phases in the developed coating material revealed the hydration of the geopolymeric phases evolved on grinding. The rapid hydration of these phases attributed to the higher degree of reaction process, followed during mechanochemical co-grinding of raw materials. The appearance of phases like aluminium silicate hydrate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, JCPDS 01-0527), sodium iron aluminium phosphate ($\text{Na}_2\text{Fe}_2\text{Al}(\text{PO}_4)_3$, JCPDS 39-0409), aluminium phosphate ($\text{Al}(\text{PO}_3)_3$, JCPDS 15-0364), silicon phosphate ($\text{Si}_5\text{P}_6\text{O}_{25}$, JCPDS 40-0425) and sodium iron phosphate ($\text{Na}_3\text{FeP}_8\text{O}_{23}$, JCPDS 42-0292) indicated the solid state chemical transformation reactions followed during mechanochemical co-

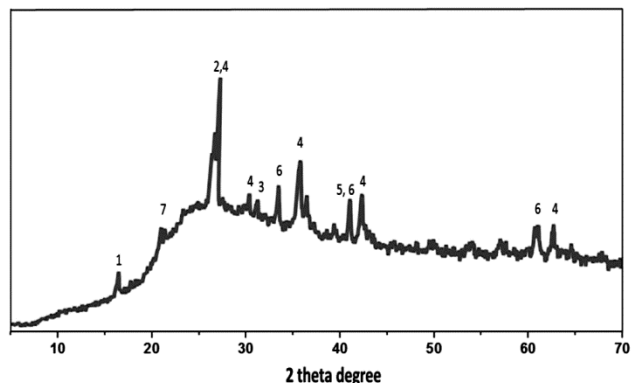


Fig. 5 — XRD pattern of optimized composition of geopolymer coating material. Key 1-Mullite, 2-Quartz, 3-Haematite, 4- Sodium aluminium silicate hydrate, 5- sodium aluminium oxide hydrate, 6- Aluminium phosphate, 7- sodium iron aluminium phosphate.

grinding of raw materials out of which sodium iron aluminium phosphate and aluminium phosphate were recorded as major phosphate containing inorganic phases. The evolution of less crystalline phases and dense matrix confirmed the formation of geopolymeric network, on geopolymerisation with improved properties. The incorporation of phosphate in the oligomeric linkages (Al-O-P) were confirmed by the evolution of phosphate containing phases like aluminium phosphate and silicon phosphate which improved the fire resistance properties of the developed coating material.

FTIR analysis

The bonding in geopolymer composition was analysed by Fourier Transform Infrared spectroscopy. Figure 6 showed absorption bands in FTIR spectra of optimised composition of developed geopolymer coating material. A broad and intense band in the high frequency region appeared at around 1009 cm^{-1} corresponded to stretching and bending vibrations of Si-O-Si³⁶. This band showed great amount of shift towards lower frequency synergistically indicates amorphization of the material on mechanochemical co-grinding of raw materials and association of Na metal ion to the polymeric unit.

A well-defined peak at 865 cm^{-1} associated with Al-OH bond²⁹. This band shows the octahedral coordination of Al with hydroxyl group. The intense band at 900 cm^{-1} ascribed to the asymmetric stretching of Si-O-M⁺ (where M⁺ is metal ion, Si or Al) due to the evolution of hydrated sodium aluminosilicate phases evolved on

gelation. The low intensity peaks at 687 cm^{-1} was due to the presence of mullite (Al_2O_3) and peak at 738 cm^{-1} corresponded to Si-O-Si of quartz SiO_2 . The evolution of new weak band in the range of 2319 cm^{-1} and 1451 cm^{-1} was due to the stretching vibrations of P-O-H group and P-O stretching due to the incorporation of phosphate group in the polymeric chain²⁵. The weak band corresponded to the less amount of phosphate group present in the developed composition of geopolymer. A small peak at 1645 cm^{-1} attributed to bending and deformation vibrations of OH group. These phases were responsible for the dense matrix formation contributing to the enhanced adhesive strength between geopolymeric coating material and metal substrate.

Morphology and microstructural analysis

SEM and EDX studies were performed to determine the microstructural changes in the geopolymer matrix elemental analysis of the developed material respectively (Fig. 7). The SEM images (at different magnifications) displayed formation of dense geopolymer matrix with homogeneous morphology.

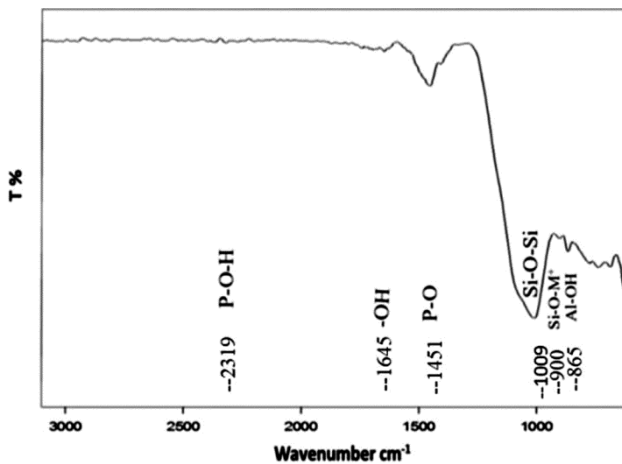


Fig. 6 — FTIR spectral bands of studied geopolymer coating composition.

The particles and geopolymer matrix cannot be distinguished clearly due to outstanding unification of water and geopolymer. This indicated enhanced geopolymerisation by using the advanced technique of mechanochemical co-grinding of raw materials which produced active reaction sites resulting in agglomeration phenomena.

The EDX of uncoated substrate showed presence of large percentage of element iron (Fig. 8 A). The weight percentages of iron and carbon were 91.67 % and 8.33 % respectively. This percentage of carbon can be attributed to the surface contamination in mechanical polishing. While EDX of mild steel samples coated with developed material of optimised

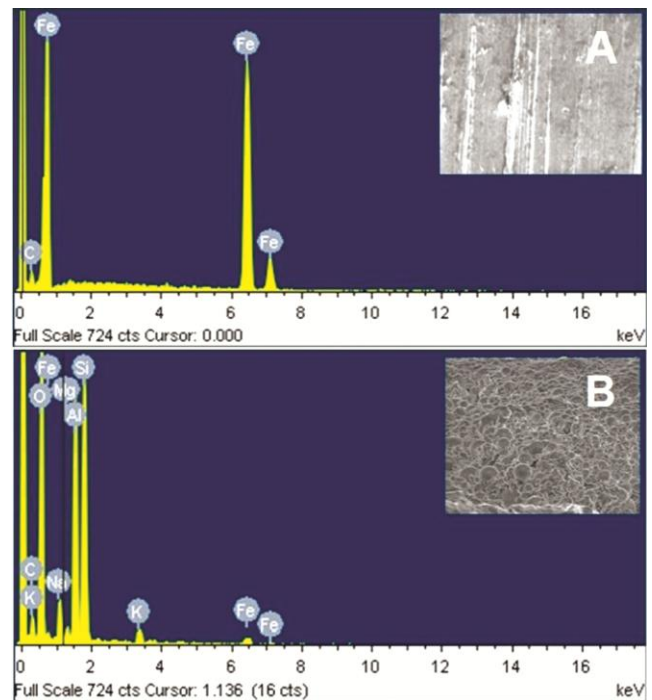


Fig. 8 — EDX analysis and micrograph of (A) uncoated sample (B) geopolymer coating material.

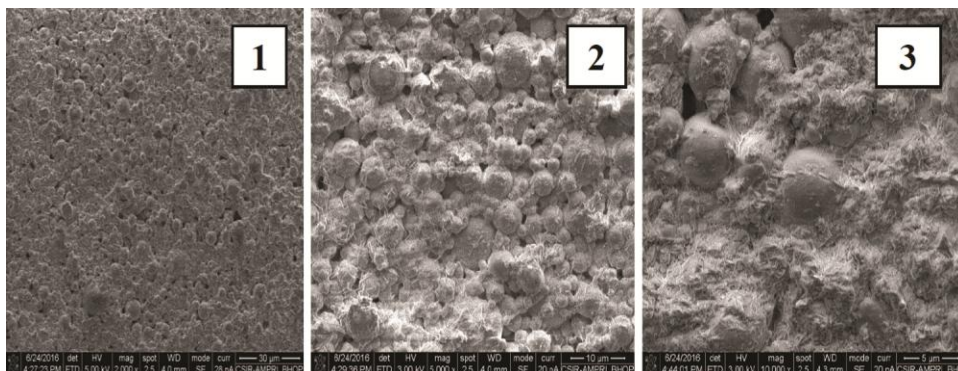


Fig. 7 — SEM images of coating material at three different magnifications. 1) 30μm, 2) 10 μm and 3) 5μm

Table 2 — Summary of experimentally optimized parameters for geopolymeric coating using spin coating technique.

Geopolymeric coating composition	Spin coating parameters	Experimentally optimized notes
Fly ash + NaOH + SHMP + Metakaolin	Slurry viscosity	0.5 (water to precursor powder ratio)
	Slurry amount	3 mL
	Spinning speed	500 rpm
	Rotation time	15 seconds
	Acceleration	5 seconds
	Adhesive strength	2.5 MPa
	Coating thickness	15±2 µm
	Hardness	3H

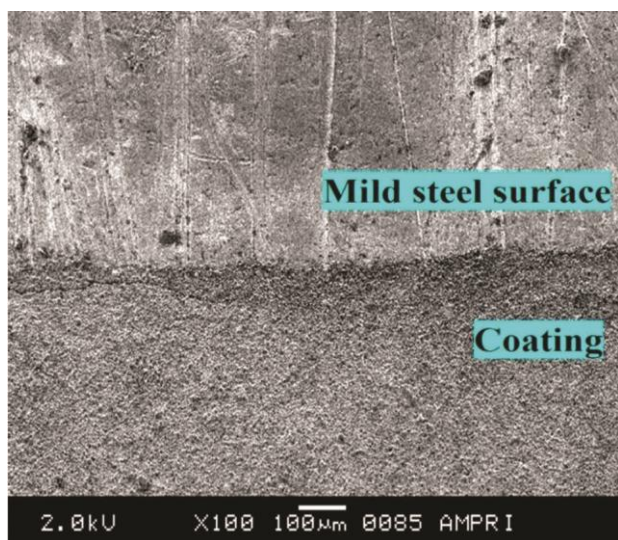


Fig. 9 — SEM image of mild steel and coating interface.

composition revealed less percentage of iron. This illustrated that a well dense geopolymer matrix forms through a novel technique of grinding, potentially good to protect the surface from external exposure (Fig. 8 B). The homogeneous geopolymer significantly covered the whole exposed surface of the mild steel substrate. The presence of Na, Si, Al, K, Fe and O elements in EDX spectra corresponded to the elemental composition of the geopolymeric material developed by grinding of raw materials. The weight percentages of these elements were respectively 2.39, 13.86, 10.69, 1.07, 1.58 and 58.58. Beside these, small fractions of impurities like Mg (0.46 wt %) and C (11.38wt %) appear in the EDX spectra of the coated samples. These impurities were acquired from the respective composition of flyash which was the basic component of the developed coating material. Accordingly, improved properties were shown by the coated samples as evident from adhesion studies.

Steel-geopolymer interface

The interface between mild steel plates and developed coating material was observed by FESEM

studies. FESEM images of the developed coating material of optimised composition with mild steel substrate is displayed in Fig. 9. Good adherence with less pores and cracks were observed at the interface. FESEM images of the coating samples showed the good contact between geopolymer matrix and substrate. It is well evident from the images that the mild steel surface exposed to atmospheric conditions is more prone to corrosion while the coated surface develops a barrier between the mild steel surface and the atmospheric factors causing corrosion. The developed geopolymer coating material was dense enough, well intact and less porous. This material reduces the active surface sites for corrosion process. The evolved phases in the novel material promote the enhanced adhesion properties of the developed material with the metal substrate.

Conclusion

In this study, a well-defined; uniform geopolymeric coating employed on the mild steel surface using spin coating technique and the spinning parameters for well and effective deposition of geopolymeric coating material onto substrate were optimized and summarized in Table 2.

On the basis of results obtained, it can be concluded that the best spin conditions for getting maximum adhesion strength of advanced geopolymeric coating on mild steel were slurry viscosity-0.5, slurry amount-3mL and spinning speed- 500 rpm. Additionally, for the developed advanced geopolymeric coating material, maximum adhesive strength obtained was 2.5 MPa and coating thickness achieved was 13.9 micrometers. Coating was found to be good for scratch resistance as it resisted hardness upto 3H by pencil hardness test. Further, detailed characterization of the coating material revealed the occurrence of inorganic phases like aluminium silicate hydrate, sodium iron aluminium phosphate, aluminium phosphate. These phosphatic phases resulted in better

adhesion of material with the substrate and contributed to the pencil scratch resistance. Similarly, from the microstructural analysis of coating material, it can be concluded that the novel process for the formation of geopolymeric material contributed to the evolution of less porous, intact and more amorphous gel responsible for showing improved adhesion properties along with improved coating performance.

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