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A novel green approach for making hybrid inorganic- organic geopolymeric cementitious material utilizing fly ash and rice husk

Sudhir S. Amritphale*, Deepti Mishra, Manish Mudgal, Ramesh K. Chouhan, Navin Chandra

Materials for Radiation Shielding and Cement Free Concrete Division, Council of Scientific and Industrial Research- Advanced Materials and Processes Research Institute, Hoshangabad Road, Bhopal (M.P.) 462 064, India

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ABSTRACT

A novel green process[1] has been presented in this paper for preparation of hybrid inorganic −organic geopolymeric cementitious material utilizing fly ash, and rice husk which helps in reduction of greenhouse gas (GHG) carbon dioxide thus addressing the issue of global warming. The process involves synergistic and simultaneous chemical reactions among glassy silico- aluminous phase present in fly ash and amorphous silica and organic molecules present in rice husk in presence of alkali. This results in in −situ synthesis of sodium silicate and transformation of tetra coordinated silicon complexes originally present in fly ash and rice husk to penta coordinated silicon complexes in hybrid inorganic −organic geopolymeric material. This has been confirmed by ^{29}Si NMR spectra of hybrid inorganic −organic geopolymeric material. The organic molecules present in rice husk resulting in development homogenous, non brittle hybrid inorganic −organic matrix. Hybrid inorganic −organic geopolymeric material possess 25% more flexural strength with a value of 2–4 MPa in comparison to conventional geeopolymeric material which possess flexural strength of 1–2 MPa only. The formation of hybrid inorganic −organic matrix is confirmed by presence of peaks of organic and inorganic phases in XRD. The presence of organic and inorganic linkages in FTIR spectra of hybrid inorganic organic geopolymeric material further confirms formation of hybrid matrix. The presence of characteristic ^{27}Al NMR signal of geopolymeric material at around 59 ppm in both conventional as well as in hybrid inorganic-organic geopolymeric material confirmed the formation of geopolymeric material in both the cases.

1. Introduction

In the recent years there is an increasing concern on energy saving and reduction in greenhouse gas (GHG) emissions. Much emphasis is given to bulk utilization of industrial waste as resource material for development of value added materials.

Fly Ash, a coal combustion residue, is generated in bulk quantity from thermal power plants. It contain amorphous glassy silico-aluminous phase. It is also rich in mineralogical values in the form of quartz, mullite and hematite. Further, the rice husk is a unique biopolymeric material. It contain significant amount of inorganic amorphous silica (upto 20%) in combination with organic molecules cellulose, hemicelluloses and lignin. In contrary, other biopolymeric materials like maize, wheat etc containing cellulose, hemicellulose and lignin, but are devoid of significant amount of amorphous silica. It is therefore useful to exploit these values of fly ash and rice husk for making value added materials by innovative methodologies [1,2].

The present research work involves development of a novel green process for preparation of functionally designed hybrid inorganic organic geopolymeric cementitious material. This material is useful for broad application spectrum. Fly ash, rice husk and sodium hydroxide were used as raw materials [3]. Need of sodium silicate is obviated in developed novel process.

The novel process resulting in formation of hybrid inorganic-organic matrix in developed geopolymeric cementitious material unlike conventional geopolymeric cementitious materials possessing inorganic matrix only. It involves complete conversion of tetra coordinated and penta coordinated silicon complexes which are originally present in conventional geopolymeric cementitious material to penta coordinated silicon complexes in developed hybrid inorganic −organic geopolymeric cementitious material. It also obviates the need of sodium silicate which is otherwise

* Corresponding author.
E-mail address: ssamritphale@hotmail.com (S.S. Amritphale).

[1] Patented in India and USA: US 9120, 701 B2, Date of Patent September 1, 2015.

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necessary to be added externally in conventional geoplymeric cementitious materials as one of the raw materials. It is synthesized in-situ within matrix of developed hybrid inorganic −organic geopolymerc cementitious material.

2. Materials and method

2.1. Raw materials

Class F fly ash (ASTM C-618 and IS 3812), collected from Thermal Power Plant, Sarni, Madhaya Pradesh, India is used as a base material in the present studies. It is low lime fly ash and pozzolanic in nature. It contains SiO_2 63–65%, Al_2O_3 27–29%, Fe_2O_3 3–4% as major constituents and CaO below 1%. Sodium hydroxide pellets and sodium metasilicate of GR grade were procured from Merck and used for the preparation of alkali activator solution. Rice hulls, procured from Mandideep region in Bhopal, Madhaya Pradesh, India were used as source material for making hybrid inorganic-organic geopolymeric cementitious material.

2.2. Preparation of conventional geopolymeric cementitious material

The alkali activator solution of 12.5 molar strength was prepared by dissolving sodium hydroxide pellets in water (100 gms in 200 ml) and subsequently adding sodium metasilicate (50 gms) to the prepared sodium hydroxide solution. Paste of conventional geopolymeric material was made by mixing of fly ash (500 gms) in already prepared alkali activator solution(200 ml). SiO_2/Na_2O ratio was 3.52. The paste of conventional geopolymeric material dried at room temperature was subjected to detailed characterization studies.

2.3. Preparation of advanced hybrid inorganic-organic geopolymeric cementitious material

2.3.1. Preparation of novel hybrid inorganic- organic alkali activator solution

For preparation of novel hybrid inorganic- organic alkali activator solution, rice hulls (20 gms) were refluxed with prepared alkali solution of 12.5 M (100 gms sodium hydroxide pellets in 200 ml water) for 2 h at 85 °C temperature. This resulting in formation of dark brown coloured solution. Prepared dark brown coloured solution was filtered through number 40 whatmann filter paper. This solution is termed as hybrid inorganic- organic alkali activator solution as it contains both inorganic phase and organic phases viz. sodium silicate, α D-glucose, native cellulose, phenolic compounds and sucrose.

2.3.2. Preparation of novel hybrid inorganic- organic geopolymeric cementitious material

Paste of advanced hybrid inorganic-organic geopolymeric material was prepared by mixing fly ash (500 gms) with prepared novel hybrid inorganic- organic alkaline activator solution. SiO_2/Na_2O ratio was 4.04. The paste of novel hybrid inorganic- organic geopolymeric material dried at room temperature was subjected to detailed characterization studies.

2.4. Preparation of sample cubes of conventional and hybrid inorganic- organic geopolymeric cementitious material for evaluating mechanical properties

Specimen cubes of 5 cms × 5 cms × 5 cms dimensions of conventional and hybrid inorganic- organic geopolymeric cementitious material were prepared in the laboratory. Prepared cubes were used for evaluation of compressive and flexural strength as per Indian standard specifications using digital compressive strength testing machine model no. AIM 308E-DG of AIMIL Ltd., India.

2.5. Sample characterization

Different phases present in geopolymeric material were determined using XRD technique. The XRD intensity was recorded as a function of Bragg's 2θ in the angular range of 5–70^0 on D8 advance X-ray diffractometer. FTIR spectral analysis was performed between 500 and 4000 cm^{-1} to determine the functional group present in the samples using Bruker alpha Fourier Transform Infra Red Spectrometer at Sagar Institute of Research & Technology, Bhopal, Madhaya Pradesh, India. Morphology and elemental composition (weight%) was determined using Field Emission Scanning Electron Microscope (FESEM), model NOVA NANOSEM-430 of COMFEI and Energy-dispersive X-ray spectroscopy (EDX), Model X-MAX of Oxford. ^{29}Si NMR and ^{27}Al NMR studies have been carried out using facilities available at Council of Scientific & Industrial Research – National Chemical Laboratory, Pune, Maharashtra, India.

3. Results and discussion

3.1. XRD studies

Peaks observed in XRD pattern were matched with standard JCPDS (joint committee on powder diffraction standards) data-ICDD (International centre for diffraction data) 1997 using PCPDFWIN JCPDS software (A programme to view powder diffraction files from ICDD database).

3.1.1. Fly ash

XRD pattern of fly ash shown in Fig. 1 indicated presence of peaks of quartz (syn silicon oxide, SiO_2, JCPDS 46-1045), mullite (aluminium silicate, $3Al_2O_32SiO_2$, JCPDS 06-0258) and hematite (iron oxide, Fe_2O_3, JCPDS 01-1053) phases. Glassy silico- aluminous phase is observed as diffused pattern from 2θ value 5–15°.

3.1.2. Conventional geopolymeric cementitious material

XRD pattern of conventional geopolymeric cementitious material shown in Fig. 2 indicated presence of peaks of cancrisilite (sodium aluminium carbonate silicate hydrate, $Na_7[Al_5Si_7O_{24}]CO_3{\cdot}3H_2O$, JCPDS 46-1381), sodium aluminium silicate ($NaAl_3Si_3O_{11}$, JCPDS 46-0740) and herschelite (sodium aluminium silicate hydrate, $NaAlSi_2O_6{\cdot}3H_2O$, JCPDS 19-1178) phases in addition to peaks of quartz (silicon oxide, SiO_2, JCPDS 46-1045), mullite (Aluminium silicate, $3Al_2O_32SiO_2$, JCPDS 06-0258) and hematite (Iron oxide, Fe_2O_3, JCPDS 01-1053). Presence of new peaks of aluminosilicate and hydrated aluminosilicate phases, in addition to peaks of quartz (syn silicon oxide, SiO_2, JCPDS 46-1045), mullite (aluminium silicate, $3Al_2O_32SiO_2$, JCPDS 06-0258) and hematite (iron oxide, Fe_2O_3, JCPDS 01-1053) initially observed in fly ash confirmed formation of geopolymer matrix [4].

3.1.3. Hybrid inorganic-organic geopolymeric cementitious material

XRD pattern of hybrid inorganic −organic geopolymeric cementitious material shown in Fig. 3 indicated presence of peaks of organic phases namely sucrose ($C_{12}H_{22}O_{11}$, JCPDS 01-0528), α D-glucose ($C_6H_{12}O_6$, JCPDS 24-1964), native cellulose ($(C_6H_{12}O_6)x$, JCPDS 3-0289) and phenol ($C_6H_6O_5$, JCPDS 37-1618) in addition to peaks of inorganic phases viz. cancrisilite (sodium aluminium carbonate silicate hydrate, $Na_7[Al_5Si_7O_{24}]CO_3{\cdot}3H_2O$, JCPDS 46-1381), sodium aluminium silicate ($NaAl_3Si_3O_{11}$, JCPDS 46-0740) and herschelite (sodium aluminium silicate hydrate, $NaAlSi_2O_6{\cdot}3H_2O$, JCPDS 19-1178) already present in conventional geopolymeric cementitious material and quartz (syn silicon oxide,