

An advanced cured high carbon ferrochrome slag (HCFCS) geopolymer (GP): A constructional materials

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Abstract

In the recent past, investigations are reported on Geopolymer concrete. Geopolymer is known as inorganic polymer. Such materials are useful materials which are capable of replacing constructional materials such as conventional cement. In present investigations, Geopolymer is made from chromium bearing slag obtained from a ferrochrome industry (BRG steel). The mechanism involved is that the silicon and aluminium present in the high carbon ferrochrome (HCFC) slag reacts with alkali liquid, forming Geopolymer which binds other non-reactive materials in the slag. The highest strength level achieved for as-prepared Geopolymers are 11 and 15 MPa by curing 7 days and 28 days, respectively. X-ray diffraction patterns reveal that there is a gradual transformation from crystalline phase to non-crystalline phase which is due to polymeric transformation with increase in curing time. SEM micrographs confirm formation of glassy phases at a higher curing time which also corroborate with mechanical properties such as compressive strength. Distinct changes are observed in FTIR spectra *i.e.*, increase in peak height as well as appearance of many other peaks if compared with FTIR spectrum of virgin material. This strength is due to polymeric reactions and formation of chains with the monomeric structure. Striking features of the TGA pattern is observed for the two materials *i.e.*, uncured and cured samples. DSC isotherms show oozing out of inbuilt water which has accumulated during condensation polymerization reaction. The strength level achieved for optimum combination of variable is found to be comparable to that of standard mortar of grade (M15) as is used for constructional purpose.

Key words: Geopolymer, Slag, Cement and Compressive strength

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1. Introduction

Portland cement (PC) is a common structural material, widely used for construction purposes [1,2]. However, its production causes environmental problems owing to release of CO₂ in the atmosphere and there by polluting our universe [3]. The production of PC is extremely energy intensive process. Therefore, many researchers have used FA as resource material for production of Geopolymer, which can replace PC in the long run [1,3]. It is no wonder why researches are being carried out for the replacement of PC with new generation material, *i.e.*, GP. As a result of this GP technology has emerged out as an alternative route or means for replacement of PC [4].

GPs are described to be a chain of network of inorganic molecules [4]. In the year of 2008, Davidovits has described GP to be a future constructional material which is predicted to replace PC in concrete construction [5]. The material can be prepared from FA or slag, which essentially contains silicon and aluminum bearing oxides [4]. These oxides are polymerized with chain of nucleus by the action of active alkali metal solution such as sodium or potassium [4]. Thus, GP material can now be considered to be an innovative material of 21 century [6]. Many researchers have described the polymer structure, consisting of Silicon-oxygen-Aluminium backbone [4]. The advantage of GP lies in a fact that it is cheaper, unhazardous, fire resistance and environmental friendly materials [4]. There exist some reports on the use of micro silica in ferrochrome slag for the preparation of conventional low castable cements [7,8]. Ferrochrome slag essentially is procured from stainless steel industries.

In the present investigation, a slag is chosen from a ferrochrome industry. The slag contains ingredients such as Al₂O₃, SiO₂, MgO, CaO, Fe₂O₃, Cr₂O₃, etc [9]. Chromium present in

the slag is in the form of chromium oxide which is around 4-5% [10]. The slag also contains high carbon since it is produced during carbothermal reduction of chromium oxide in an arc furnace. There is a disposal problem of this material, experienced by the industry and hence it is thought better to utilize it for the production of a use material such as GP. Attempt is also made to optimize process parameters for maximizing strength properties. Wherever, required detail investigations are carried out to explain structure of the developed material.

2. Experimental Details

2.1. Source of Materials

HCFC slag, the main ingredient for Geopolymer, is collected from **Shyam ferroalloys** (Durgapur, West Bengal, India). Sodium hydroxide (NaOH) is used as an activator, which is obtained from M/S Loba Chemicals, India. Sodium silicate (Na_2SiO_3) is used for the purpose of polymerization and is procured from Merck, India. Water soluble plasticizer (Sika) is purchased from a reputed firm located in the southern parts of India (Visakhapatnam market). Plasticizer usually enhances plasticity of the product *i.e.*, Geopolymer.

2.2. HCFC slag based Geopolymer (GP) preparation

Geopolymer is prepared from HCFC slag used sodium silicate, and alkali as additives. HCFC slag is crushed and ground to 240 mesh size. The fine particles are then dried in an oven for 2 h at 120 °C. The ground and dried materials are mixed with requisite amount of NaOH (8 M), Na_2SiO_3 and water soluble plasticizer (Sika). The semi-solid liquid materials, thus formed, are placed in a mould which is cylindrical in shape (55 mm diameter and 70 mm height). The mixture is rammed in the mould, then uniformity of which is ensured by continuous ramming the mass in the mould three times. Following ramming of the mass in the mould, the samples are left for 3 min for setting before demoulding the green sample [11]. The entire process is shown in

Fig. 1. The green samples are then cured at different temperature *i.e.*, 60, 70, 80 °C for different length 7 days and 28 days. Prepared samples are then characterized by XRD, FTIR TGA, DSC, etc.

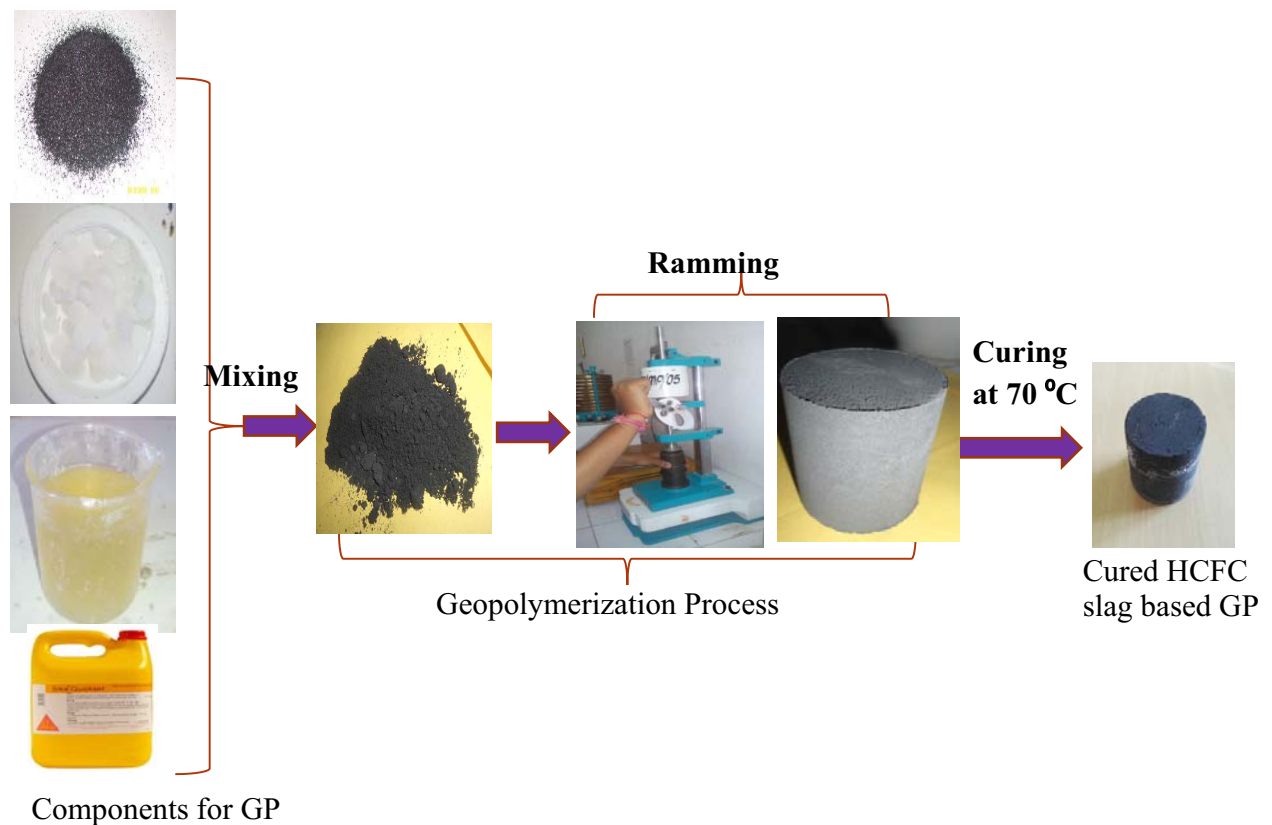


Figure 1 Schematic diagram of process for preparation HCFC slag based GP product

2.3. Characterization techniques.

X-rays diffraction studies are made with treated GP samples at different stages of curing. Similar analysis is also made with the as received HCFC slag for comparison purpose. 1710 advance wide angle XRD is used with $\text{CuK}\alpha$ radiation for all XRD diffraction studies.

Samples are further characterized in **FTIR** (Thermo Nicolet Nexus 870 spectrophotometer). The settings for the instruments are kept constant (50 scan at 4 cm^{-1} resolution, absorbance mode) during entire examination.

For SEM studies of virgin HCFC sample as well as the cured HCFC samples are coated with gold before examining in a scanning electron microscopy (**SEM**, Carl Zeiss Supra 40). The elemental analyses are carried out with the help of EDX attached to the microscope.

The uncured and cured materials are also run in a thermogravimetric (TG) analyser Perkin Elmer Pyris Diamond analyzer. Heating rate is kept $10\text{ }^{\circ}\text{C}/\text{min}$ and experiments are performed in an inert atmosphere (N_2 gas). The entire TGA experiments are carried out in the temperature range of $50\text{--}300\text{ }^{\circ}\text{C}$. For comparison purpose, TG run is also taken from as-received HCFC slag.

Differential scanning calorimetric (**DSC**, Perkin Elmer Pyris Diamond) study is made for measurement of enthalpy of the two materials *i.e.*, as-received HCFC slag and GP prepared with HCFC slag. The parameters such as heating rate ($10\text{ }^{\circ}\text{C}/\text{min}$), run temperature ($50\text{ to }300\text{ }^{\circ}\text{C}$), and nitrogen environment (N_2) are set while run is taken.

Compressive strength of prepared HCFC slag based GP is determined following ASTM standard in a tensile testing machine (**AIMIL COMPTTEST 2000**, India). Maximum load is taken at the point of fracture of the sample.

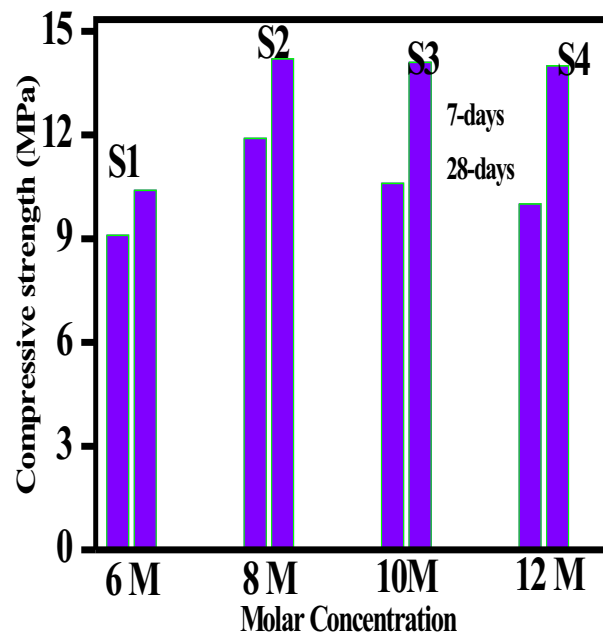
3. Results and Discussion

The **Table 1** shows constituents such as SiO_2 , Al_2O_3 , Fe_2O_3 , and Cr_2O_3 , which are present in major quantities and CaO , Cr_2O_3 , FeO in minor quantities [10]. The ground slag (240 meshes) is dried for 2 h at $120\text{ }^{\circ}\text{C}$ to make it free from moisture.

Table 1 Chemical composition of HCFC slag

Constituents of HCFC slag with percentages	SiO ₂ =28-31	
	MgO=26.0-26.5	
	Al ₂ O ₃ =23.5-24.5	
	CaO =7.5-8.5	
	Cr ₂ O ₃ =4.5-5.4	
	FeO= 2.5-3.0	
Sources	Syam	Ferroalloys,
	Durgapur	

Effect of molar concentration on compressive (MPa) study is shown in **Figure 2**. Subscribes 1, 2, 3, and 4 attached to S in the **Fig. 2** represent Geopolymer prepared with different molar concentration of NaOH *i.e.*, 6, 8, 10, and 12 which are cured at 70 °C. It is well known that sodium plays an important role for polymerization of alumina (Al₂O₃) and silica (SiO₂) present in the slag [4-8].

**Figure 2** Compressive strength vs molar concentration at 7-days and 28-days curing

Each pair of bar drawn is showing data on comparative scale for a Geopolymer prepared with some molar concentration and cured for 7 days and 28 days. It is evident that maximum strength is obtained for the Geopolymer formed with 8 M NaOH concentration.

Similar bar diagram is shown in **Figure 3**. Here subscribes attached T designated Geopolymer prepared with 8 M NaOH and cured for different temperature for two curing time *i.e.*, 7 days and 28 days. The maximum strength is obtained for 15 MPa cured at 70 °C for 28 days [12].

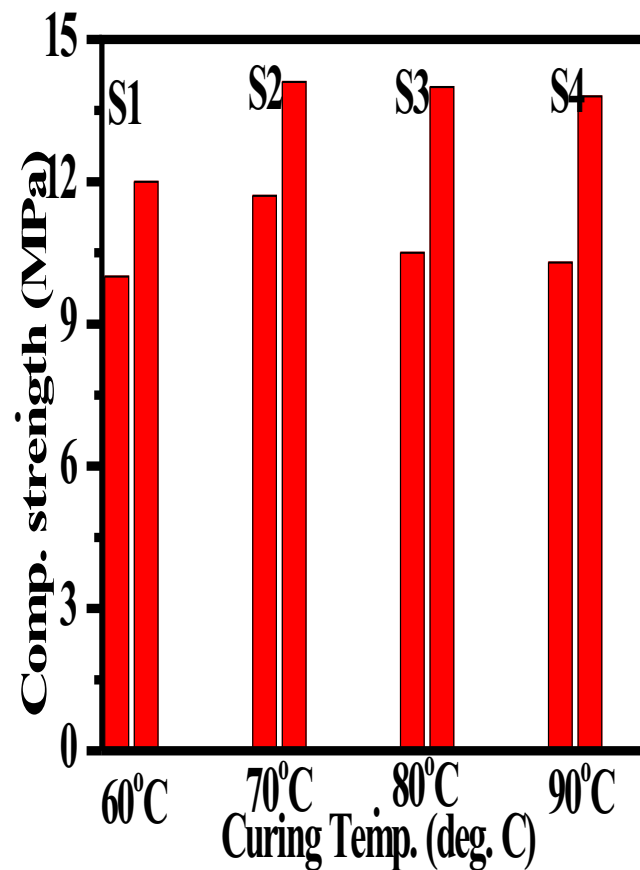


Figure 3 Compressive strength vs temperature at 7-days and 28-days curing

Thus, optimum combination of cured parameter obtained is curing 70 °C for 24 h and with NaOH of 8 M concentration.

Fig. 4 shows superimposed XRD pattern obtained from three different samples, designated 4A and 4B. **XRD** for as-received HCFC slag (**Fig.4A**) shows presence of sharp peaks, indicating crystalline phases, identified as quartz and mullite. Sharp peaks without line broadening essentially show crystallinity of those phases. XRD pattern for GP after curing at 70 °C is shown in **Figs.4B**. Sharp crystalline peaks have disappeared after curing at 70 °C. The disappearance of crystalline phases and appearance of non-crystalline phase are striking features of the diagram. There are broadened line profiles occurring at different Bragg's angles. This is co-related with polymerization process of slag, during curing.

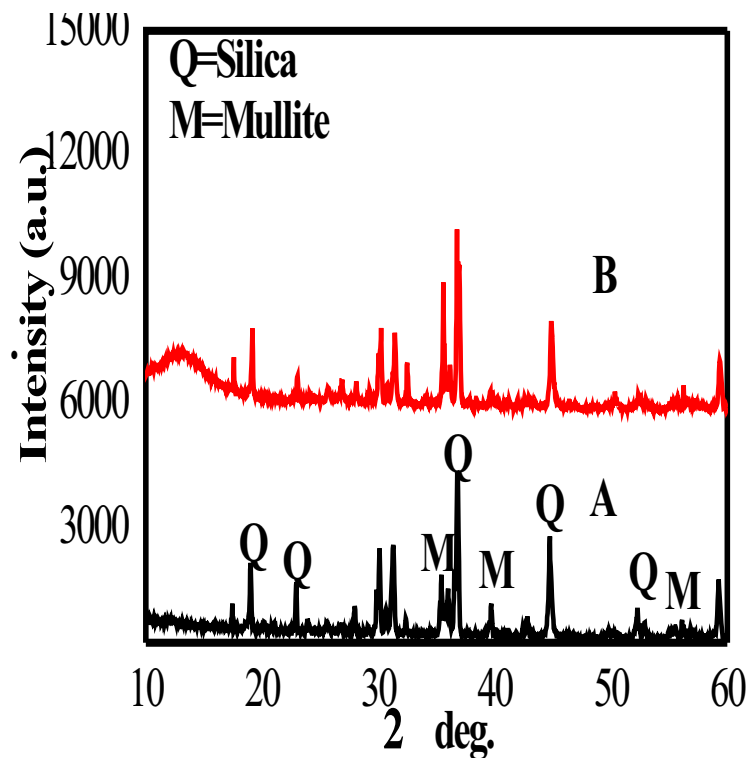


Figure 4 XRD pattern of as received HCFC slag (A) and as-prepared HCFC slag GP

The **microstructural features** of HCFC slag and corresponding slag based GP samples are observed under Scanning Electron Microscopy (SEM). The electron micrograph of unreacted slag and cured HCFC slag based GP are shown in **Figure 5**. **Fig. 5(A)** shows SEM micrograph of HCFC slag.

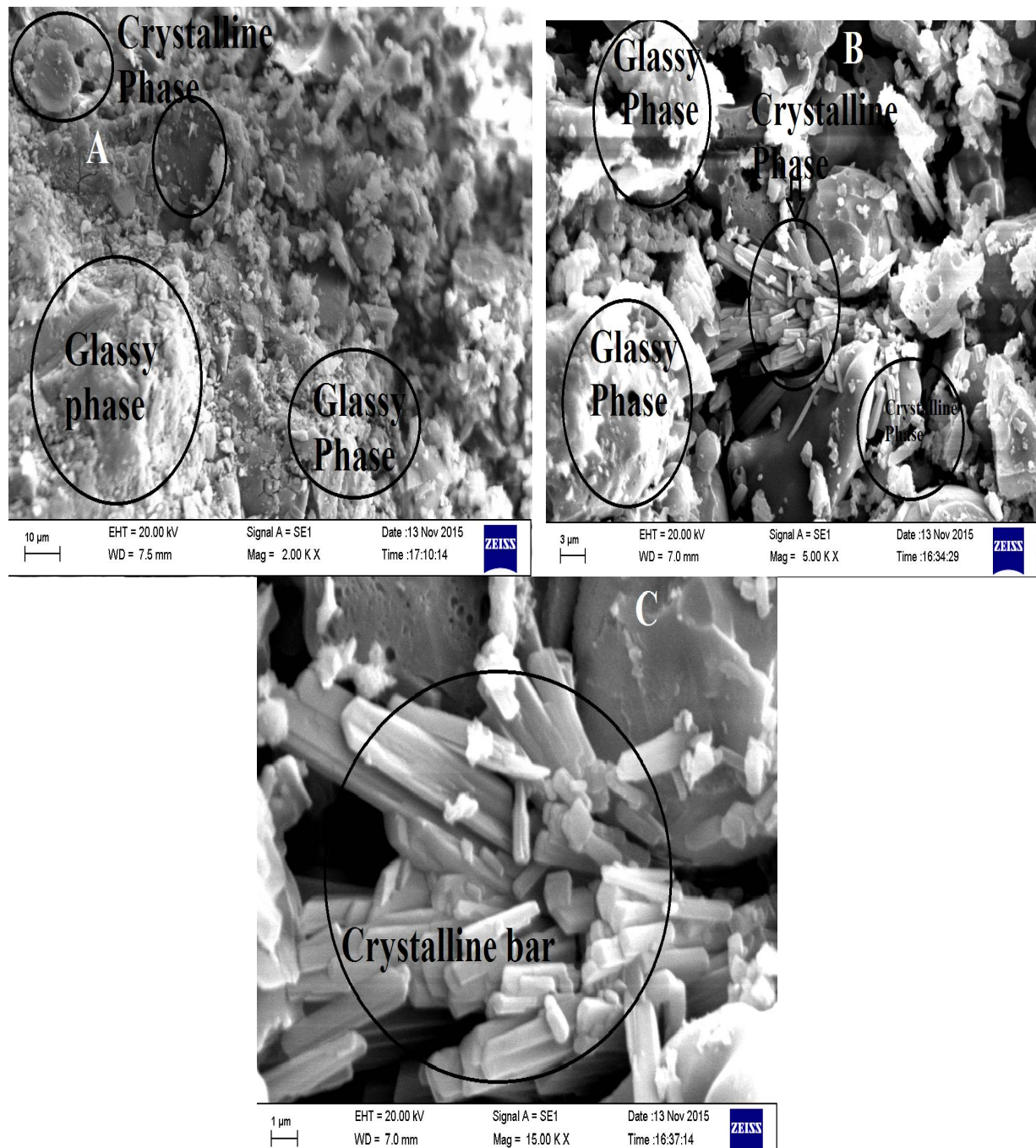


Figure 5 SEM images of as-received HCFC slag (A), Cured HCFC slag based GP

It indicates fused mass of oxide with some glassy phase spread over the matrix. Since the materials are obtained from stainless steel industries, therefore different minerals are fused and

are appearing in the microstructure. There is a someplace marked is as existing glassy phase owing to faster cooling of molten slag to room temperature.

Fig. 5(B) shows micrograph of Geopolymer prepared by curing of a green samples. The material after treatment with alkali materials cured at 70 °C and 24 h have yielded different microstructure. At lower magnification, it shows some crystalline-needle shape phase in random direction and marked. There is some region of glassy phase co-existing with the crystalline phase. The **Fig. 5(B)** looks very interesting, therefore further investigated as different location at higher magnification.

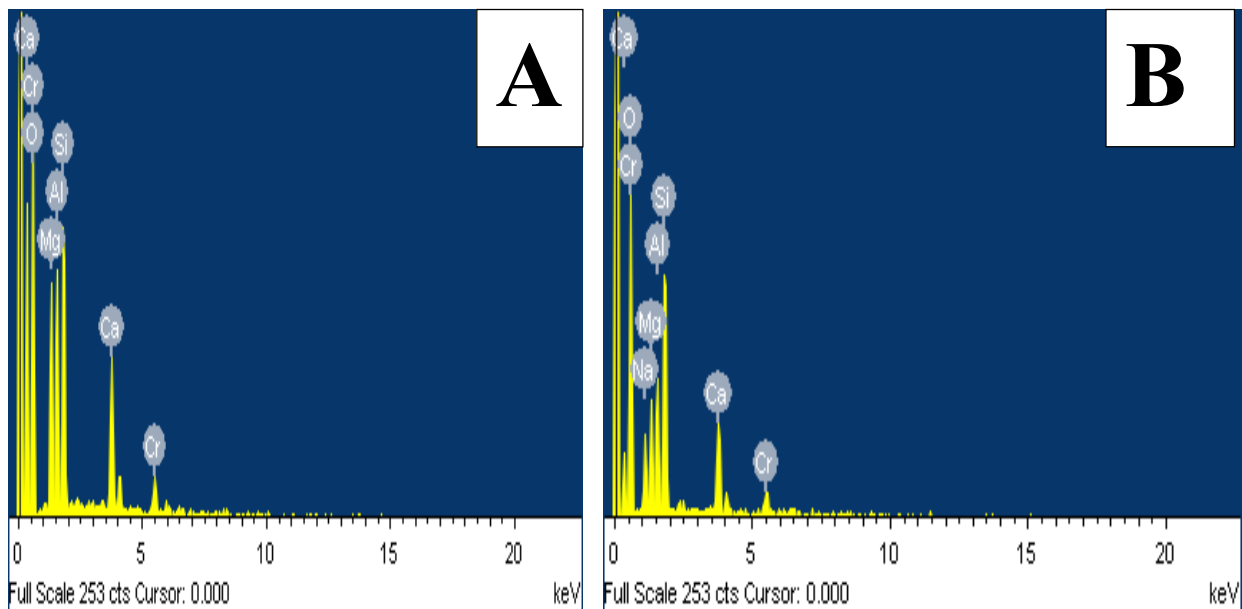


Figure 6 EDS of as received HCFC slag (A) and Cured HCFC slag based GP (B)

At higher magnification, there are bundles of rod-shaped crystalline phase orienting in same direction proving or the polymerization process [13]. Similar structure is also observed by S.D. Muduli et al. [13]. This crystalline phase occurred due to crosslinking of alumino-silicate Geopolymer phase and the process is assisted by sodium. The clearly glassy phases are visible adjacent to crystalline phase.

The in-situ EDS analysis is done on crystalline and glass phases and is shown in Figure 6. The presence elements such as Na, O, Al, Ca, Mg, Cr, etc are present both in crystalline and glassy phases of cured HCFC slag based GP (B), whereas O, Al, Ca, Mg, Cr, etc are present in as-received HCFC slag. Presence of Na and intensity ratio of element present signifies the chemical reaction.

FTIR spectrum of HCFC slag (**Fig. 7A**) and as-prepared GP (**Fig. 7B**) are shown in **Fig. 7**. The spectra indicate the presence of different bands appeared in each category of materials. For HCFC slag, bands occur at different wave numbers *i.e.*, 3441, 2918, 1638, 1442, and 887 cm^{-1} .

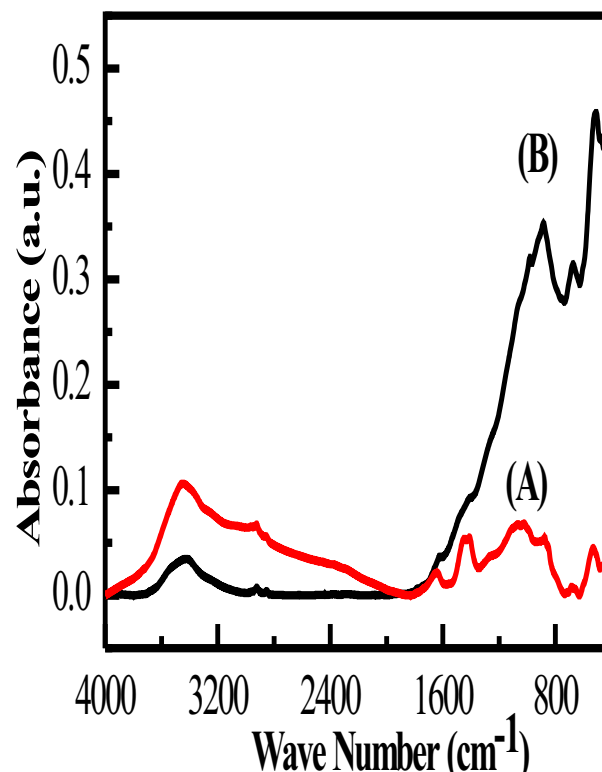


Figure 7 FTIR spectra of as-received HCFC slag (A) and Cured HCFC slag based GP (B)

Bands corresponding to 3441 and 1638 wave number are attributed to the stretching vibrations of O-H bonds and H-O-H bending vibrations of interlayer adsorbed H_2O molecule,

respectively [14]. The water hydroxyl-stretching plays an important role and so the intensity and peak shift of the infrared spectra is significant. Bands occur at 887 cm^{-1} is attributed Si-O band and it signifies the presence of silicate groups. Presences of $\text{Al}^{3+}\text{O}^{2-}$ bonds are also observed near 805 cm^{-1} [14]. Stretching vibrations is found at 440 cm^{-1} signifies the presence of Fe-O bonds [15]. Similarly, the peaks are not found for the as-received samples. This is attributed to the formation of Geopolymer due to treating and curing of as-received samples.

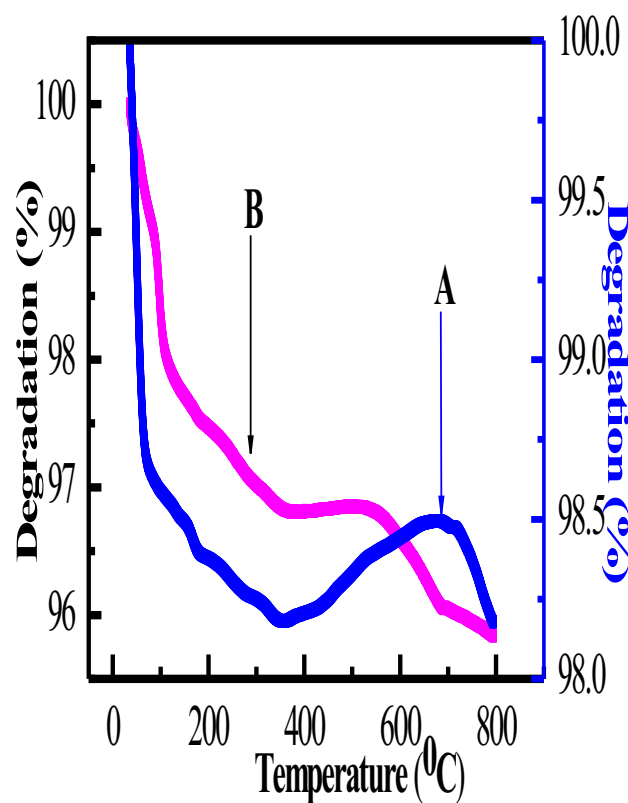


Figure 8 TGA curve of as-received HCFC slag (A) and Cured HCFC slag based GP (B)

In the TGA experiment, the weight loss was measured with increasing temperatures from 50-800 C and is shown in **Fig 8**. Looking to the above results **TGA run** is taken from two samples *i.e.*, as-received materials and cured GP materials striking difference can be observed. From the Fig. 8, Pure HCFC slag shows two types of weight loss. The sharp decrease in weight

after 100 °C as recorded in the TGA thermograms, which is attributed to the loss of evaporable water presence in the form of moisture in pure HCFC slag. After the rapid decline of pure HCFC slag, the rate of weight loss stabilized between 100 °C-350 °C. Little change occurred in the percentage of weight remaining beyond 350 °C. The average total percentage of weight increase and decrease within the range of temperature 350 °C-700 °C exposures was 96% [16].

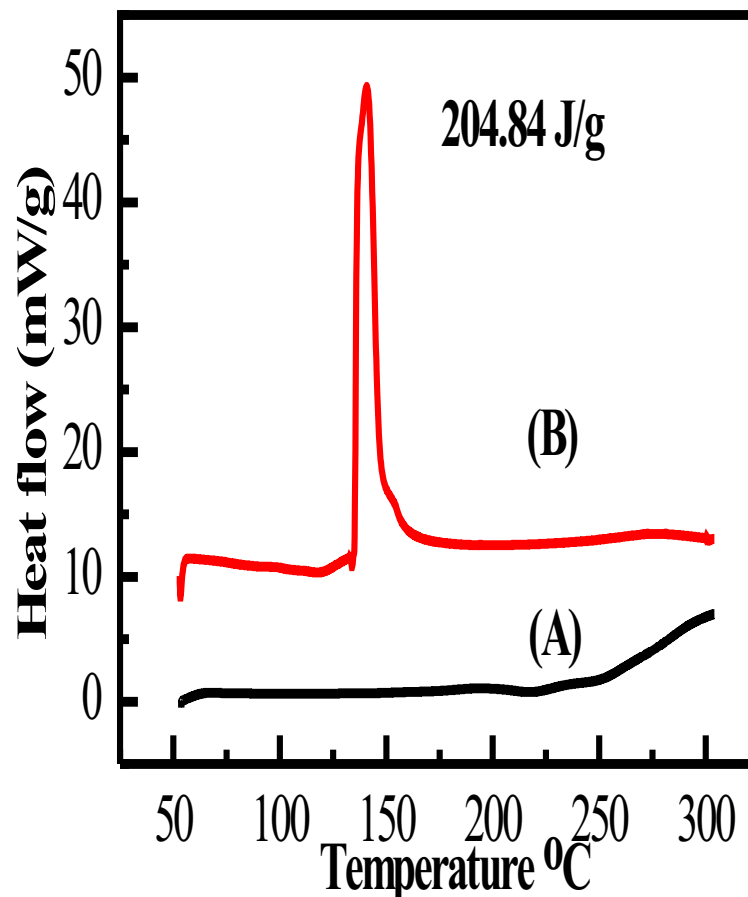


Figure 9 DSC isotherm of as-received HCFC slag (A) and Cured HCFC slag based GP

Figure 9 shows DSC isotherms for untreated and treated HCFC slag. It can be observed that there is no change of heat flow for the untreated slag (**Fig. 9A**), whereas there is a significant change in heat flow curve at around 141 °C in the treated one. This is due to the expulsion of physically bound water within the materials [17].

4. Conclusions

Geopolymers are developed from HCFC slag by treating with sodium silicate, sodium hydroxide, and water soluble plasticizers. The microstructures reveal formation of new glassy phase as reaction product with crystalline phase in between. XRD patterns shows decrease in the intensities of the phases as identified for the as-received samples. In a few phases, some peaks are conspicuously absent. Some line-broadening curves have seen indicating formation of glassy phase in place of crystalline phase. There is a marked difference observed in the FTIR spectrums. The number of peaks of as-prepared samples are much more comparison with as-received samples. This is due to formation of new bonds within the phases. TGA curves have revealed that both materials there are a gradual degradation with temperature. However, Geopolymer materials are more stable as compared to the as-received samples. DSC results shows that there is a exothermic peak in Geopolymer at 150 °C which results of elimination of water form during condensation polymerization process. The compressive strength is maximum curing at 70 °C and 8 M sodium hydroxide keeping other variables are constant.

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