

Synthesis of geopolymer composites from a mixture of ferronickel slag and fly ash

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Abstract. The synthesis of geopolymers using ferronickel slag and fly ash under alkaline activation was studied. In order to study the effects of different fly ash content on the mechanical properties of the geopolymers produced, the compressive strength of samples was tested at 3, 7, 28 days. The results showed that when the fly ash content was 40%, the compressive strength reached the highest (110.32MPa) at 28 days. XRD analysis showed that the ferronickel slag geopolymers had amorphous aluminosilicate phase formation, indicating that the hydration reaction occurred. FTIR analysis showed the reaction of the geopolymers generated at Si-O-T (Si, Al) and Al-O-Si three-dimensional network. In SEM images, the structure of the geopolymers with 40% fly ash was more compact and cohesive.

Keywords: ferronickel slag, fly ash, alkali activation, geopolymers

1. Introduction

Davidovits initially reported geopolymer in 1978 [1]. Geopolymer is three dimensional inorganic polymer with ceramic-like properties and amorphous microstructure [2, 3]. Geopolymeric reaction was applied to use solid aluminosilicate materials (naturally occurring minerals, industrial by-products or waste) [4-6] to produce a wide range of revolutionary materials. Geopolymerization involves a heterogeneous chemical reaction between aluminosilicate solid materials and alkali metal silicate solutions while the geopolymeric network consists of alternately linked SiO₄ and AlO₄ tetrahedra [7,8], under highly alkaline conditions. Geopolymer possesses excellent physical, chemical and mechanical properties such as good compressive strength, outstanding chemical resistance against acids, fire and heat, high thermal resistance, comparatively low emission of greenhouse gases, low shrinkage, quick setting and hardening time and more precise mouldability. In recent decades, geopolymer has attracted worldwide attentions for their low CO₂ emissions and excellent properties.

Ferronickel slag is the solid residues generated in production of ferronickel from laterites [9]. Compared with other metallurgical slag, large slag emissions and low utilization rate have made ferronickel slag becoming a serious problem of metallurgical slag processing. Fly ash is one of the solid residues composed of the fine particles that are driven out of the boiler with flue gases in coal-fired power plants [10]. The stockpiling of fly ash not only occupies a lot of land area, but also pollutes the environment [11,12]. Therefore, new technologies have to emerge aiming at the utilization



of the ferronickel slag and fly ash as raw materials for the production of added-value products. The geopolymer technology provides a new good and green solution to the utilization of the slags, avoiding their negative impact on environment and ecology. Geopolymers synthesized by ferronickel slag and fly ash not only suppresses the environmental hazards, but also improves the ecological cycles [13].

2. Experimental

2.1. Materials

The ferronickel slag used in the present study comes from Shandong Xinhai Technology Co., Ltd with specific surface area of 461m²/kg and 45μm sieve of 7.03%. The fly ash used comes from Shandong Hongyi Technology Co., Ltd with specific surface area of 547m²/kg and 45μm sieve of 5.27%. Table 1 presents the chemical composition of ferronickel slag and fly ash in the form of oxides and trace elements. The mineralogical characterizations of the slags determined with the X-ray diffraction method are shown in figure 1. Ferronickel slag mainly contains dicalcium silicate, tricalcium silicate minerals and a large amount of vitreous, and the main crystalline component of fly ash is mullite and quartz.

The alkali activator is mixtures of industrial liquid sodium silicate with the chemical composition: 26.2% SiO₂, 8.2% Na₂O and 65.6% H₂O (silica molecular modulus, Ms = 3.3) and granular sodium hydroxide.

Table 1. Chemical analysis of raw materials/ wt %.

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Cr ₂ O ₃	Loss
Ferronickel slag	48.85	15.94	9.71	17.45	5.98	0.71	0.23	0.15	0.12	0.76
Fly ash	51.12	28.31	4.38	6.92	1.21	0.32	1.11	0.44	0.89	5.29

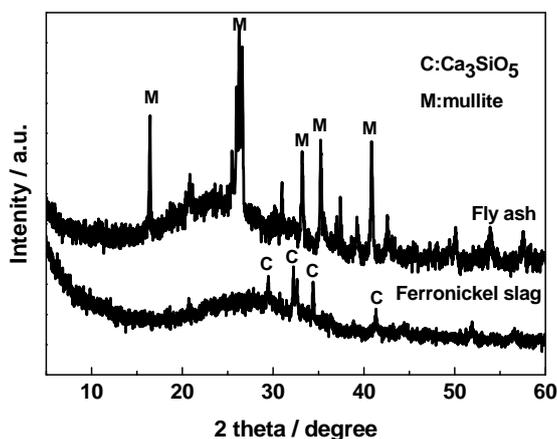


Figure 1. X-ray diffractogram of the raw materials.

2.2. Experimental procedure

2.2.1. Preparation of activator. The activator was prepared by premixing the liquid sodium silicate with sodium hydroxide 24h earlier before the preparation of geopolymer. The activator was mixed in certain proportions making the modulus fixed at 2.2.

2.2.2. Preparation of geopolymer. The alkaline activator content kept constant at 12% (calculated as solids content) and water/solid ratio kept constant at 0.30. Geopolymer samples were synthesized by following stages. Firstly, a homogeneous viscous paste was obtained by mixing the solid phase with the alkaline aqueous phase mechanically. The solid phase was consisted of ferronickel slag and fly ash. Then the fresh paste was poured in the cubic molds with size of $20 \times 20 \times 20$ mm and vibrated for 1min on a vibrating table. Finally, the moulded paste was cured in a laboratory oven for 24h at temperature $20 \pm 2^\circ\text{C}$ and relative humidity 95%. After curing, the geopolymer samples were demolded and left more days at ambient conditions for further hardening.

3. Results and discussion

3.1. Compressive strength

The compressive strength of the geopolymer samples was tested at 3, 7 and 28 days. As shown in figure 2, the compressive strength of all the specimens grows fast as the curing period extending. Initially, with the increase of fly ash content, the compressive strength of the sample increases. When the fly ash content is 40%, the compressive strength of the geopolymer reaches the highest 110.32 MPa, which is 1.5 times of the strength of the ferronickel slag-based geopolymer without fly ash. But, when the fly ash content continues to increase, the compressive strength of the specimens begins to decrease. Fly ash with smaller particle size can fill the fine pores generated by the evaporation of water and make the structure more compact and cohesive without discontinuities. But, because of the low activity of fly ash, adding too much fly ash will reduce the compressive strength.

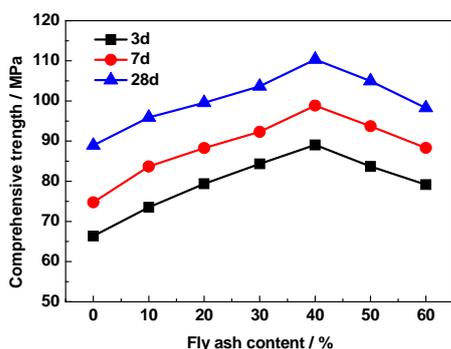


Figure 2. Compressive strength of the different fly ash content geopolymers.

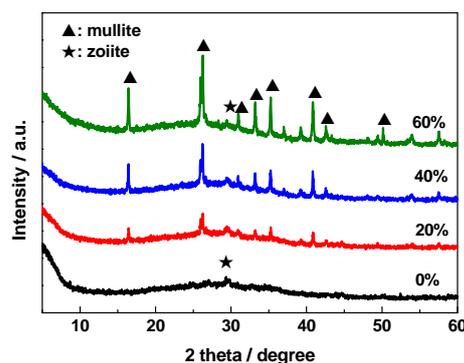


Figure 3. X-ray diffractograms of the different fly ash content geopolymers.

3.2. XRD analysis

In order to investigate the compositions of the reaction products, reacted pastes were analysed with X-ray diffraction (XRD) technique. Figure 3 shows the compared diffractograms for different fly ash content geopolymers. It is clearly observed that the only crystalline mineralogical phase of the geopolymer without fly ash is zoisite ($\text{Ca}_2\text{Al}_3\text{SiO}_4\text{SiO}_2 \cdot 7 \text{H}_2\text{O}$) belonging to the zeolite substances. This peak is attributed to an aqueous aluminosilicate that was formed during the geopolymerization as the result of the polycondensation phenomena. The geopolymers added fly ash also contain mullite peaks, the crystalline mineralogical phase of the fly ash, and has not undergone any substantial change during the geopolymerization process. With the fly ash content increasing, the mullite peaks gradually become sharp.

3.3. FTIR analysis

The FTIR spectra of different fly ash content geopolymers is presented in figure 4. Significant broad bands of O-H stretching and O-H bending are observed in the range of $3410\text{--}3455 \text{ cm}^{-1}$ and 1645 cm^{-1} in all FTIR spectra of geopolymers [6]. These bands indicate the presence of water molecules which

are surface absorbed or entrapped in the large cavities of the polymeric framework. The bands located between 1380 cm^{-1} and 1500 cm^{-1} are attributed to stretching vibrations of O–C–O bond [6]. These absorption bands indicate the presence of sodium bicarbonate which is suggested to due to atmospheric carbonation. The peaks located at wavenumbers lower than 1300 cm^{-1} and includes absorption bands ascribed to asymmetric stretching Si–O–Si ($970\text{--}1090\text{ cm}^{-1}$) [14–16], symmetric stretching Si–O–Si and Al–O–Si ($500\text{--}750\text{ cm}^{-1}$) vibrations [6]. All the above results proved the phase transformations that occurred during the geopolymerization.

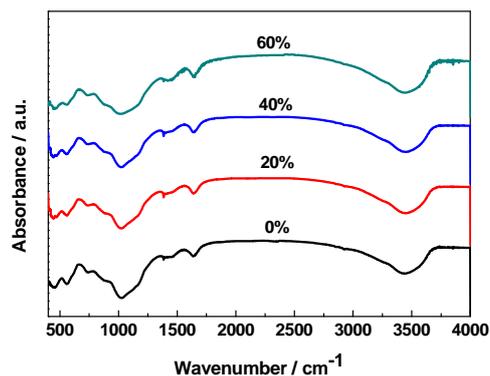


Figure 4. FTIR spectra of the different fly ash content geopolymers.

3.4. SEM observation

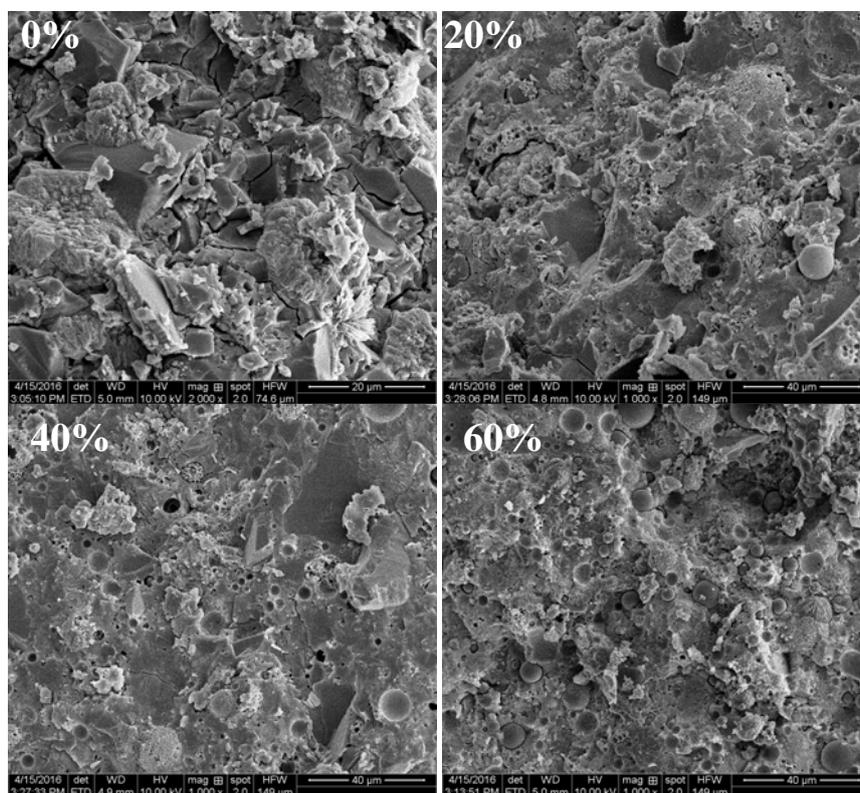


Figure 5. SEM images of the different fly ash content geopolymers.

The SEM images of the produced geopolymers are shown in figure 5. It appears that all samples are composed of a large amounts of gelatinous substance and trace particulate matter. With the fly ash

content increasing from 0 to 40%, the structure of geopolymer gradually becomes more and more compact and cohesive. This is ascribed to the fact that fly ash with smaller particle size can fill the fine pores generated by evaporation of water and make the structure dense. When the fly ash content is 60%, from the figure it can be observed that the surface of samples decline in compactness and increase in unreacted particles. This is related to the fly ash with low activity makes the polymerization and hydration degree of geopolymer reduced.

4. Conclusions

The geopolymer has been prepared using ferronickel slag and fly ash as raw materials under activation of sodium silicate solution. The geopolymer technology provides a new good and green solution to the utilization of the slags. When the fly ash content was 40%, the compressive strength reaches the highest 110.32MPa. Amorphous aluminosilicate phase founded in the XRD analysis indicates that hydration also occurred in the geological polymerization reaction. The FTIR analysis shows that the Si-O-T (Si, Al) of three-dimensional network generates in the reaction of the geopolymers. In SEM microstructure images, the structure of the geopolymer with 40% fly ash is more compact and cohesive. Fly ash with small particle size can fill the fine pores generated by evaporation of water and make the structure dense.

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