Compressive Strength and Leaching Characteristic of Geopolymer Composite from Coal Fly Ash and Nickel Laterite Mine Spoils

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Geopolymer, also referred to as "alkali-activated material" or "zeocement", is an emerging sustainable material to replace Portland cement-based binder. It requires a straightforward process and has the potential for large-scale waste valorisation and utilisation and a lower carbon footprint. Several aluminosilicate materials as geopolymer precursors have been explored, such as coal fly ash and metakaolin, among others. However, the characteristics of raw materials vary depending on the source. Hence, this study aims to synthesise geopolymer composite from raw materials that are available locally. Coal fly ash and nickel laterite mine spoils were explored as a potential geopolymer precursor. Optimal mix formulation of 50 % nickel laterite mine spoils / 50 % coal fly ash, sodium hydroxide to sodium silicate ratio of 1:2, and activator to precursor ratio of 0.44:1 yielded a 28 d compressive strength of 22.1 ± 4.4 MPa and a 180 d compressive strength of 32.3 ± 7.4 MPa. The result implies that this eco-friendly geopolymer material can be potentially used for pedestrian pavers, light traffic pavers, and plain concrete for levelling and structural applications. Before any field-scale application, investigating the leachability of material is imperative. Hence, the toxicity characteristic leaching procedure (TCLP) was employed to evaluate the leachability behaviour of both the raw materials and developed geopolymer composite in this study. The results revealed that the concentration of the trace metals released pose no significant environmental and leaching hazard into the soil, surface, and groundwater sources based on the threshold limit as defined by USEPA.

1. Introduction

The Philippines has about 17 % of the world's nickel laterite resources (Ashcroft, 2014). An estimated amount of 341,300 metric tons of nickel ore production was recorded in 2019, making the Philippines one of the top producers of nickel worldwide (Sanchez, 2020). Waste generated by the nickel mining industry may originate from various activities such as mining, minerals processing, and metallurgical processing (Lèbre et al., 2017). At the mine site level, wastes such as waste rock and nickel laterite silt are being generated. These mine spoils may cause an environmental burden if not properly managed. The considerable amount of nickel laterite mine spoils (NMS) generation is one of the significant concerns of the nickel mining industry. The problem arises during the rainy season as these wastes are being washed off downstream, contaminating nearby bodies of water.

Similarly, coal fly ash (CFA), a by-product of thermal power plants, is usually disposed of in landfills, contributing to air and water pollution. Hence, upcycling such wastes into high-value products can solve pollution problems and provide an additional revenue stream to the mining and power sectors. Geopolymers, which other researchers also referred to as "alkali-activated materials" or "zeocements", has become an increasingly attractive alternative to Portland cement-based binder because of their simple process, potential waste valorisation, large-scale utilisation and lower carbon footprint. Geopolymer binder can be synthesised from the

reaction of aluminosilicate solids and alkali activators, such as an aqueous solution of alkali hydroxides and alkali silicates. Various aluminosilicate precursors have been explored and found to be a sustainable solution to the increasing demand of the construction industry (Karayannis, 2018). Geopolymer has captured the interest of researchers due to its exceptional properties such as high early strength, resistance to acid, and thermal stability (Van Jaarsveld and Van Deventer 1997). This study thus extends the work of Longos et al. (2020) by characterising the geopolymer product synthesised from the locally sourced nickel laterite mine spoils (NMS) and coal fly ash (CFA). To our knowledge, evaluation of engineering properties, including microstructure characterisation and leachability of such material, has not been reported yet.

2. Materials and method

Nickel laterite mine spoils (NMS) and coal fly ash (CFA) were collected from a mining company and a coal-fired power plant situated in Mindanao, Philippines. The nickel laterite mine spoils were pretreated by thermal activation at 700 °C for 2 h with a ramping rate of 10 °C to attain the desired temperature and cooled down to room temperature. Coal fly ash samples were used as received. Experimental methods such as raw material characterisation, geopolymer synthesis, geopolymer composite evaluation were employed.

2.1 Raw material characterisation

The chemical composition of raw materials was analysed using X-ray fluorescence spectroscopy (XRF) with X-ray beam generation of 50 kV voltage and 35 A current. The results of the study are shown in Table 1 (Longos et al., 2020).

Table 1: Chemical composition of NMS and CFA

Mass %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	NiO	Cr_2O_3	MnO	TiO_2	K_2O	Ag_2O	SrO	SO_3	LOI
NMS	20.54	2.79	47.68	5.46	4.23	1.94	0.85	0.38	0.25	0.35	0.04	-	-	15.50
CFA	26.12	8.01	22.70	29.35	1.98	0.03	-	0.23	0.97	0.89	0.12	0.30	5.31	4.00

2.2 Geopolymer synthesis

The mix formulation of geopolymer composite considered was based on Longos et al. (2020). A mix formulation of NMS to CFA precursor of 1:1, SH to SS activator of 1:2, and activator to precursor of 0.44:1 ratio was prepared. The alkali activator was prepared by mixing 12M of SH and SS (water glass solution with 34.13 % SiO_2, 14.65 % Na_2O, 51.22 % H_2O) with a silica modulus of 2.33. Mixing was done manually for 5 minutes until the mixture became homogenised. The geopolymer composite was then moulded in 50 mm x 50 mm x 50 mm polyethylene material. The samples were then allowed to be moulded for at least 24 h at ambient temperature. After which, samples were demolded, placed in a zip bag, and pre-cured at 80 °C in an oven for another 24 h. Finally, the samples were then cured for 28 d and another set for 180 d at ambient temperature before compressive testing.

2.3 Geopolymer composite evaluation

The compressive strength of geopolymer samples cured at 28 d and 180 d were evaluated using a universal testing machine following ASTM C109 / C109M. The morphological property of geopolymer composite was also investigated with a FESEM Dual Beam Helios Nanolab 600i having a voltage of 2.0 kV equipped with energy-dispersive X-ray spectroscopy (EDS) with a voltage of 15.0 kV and a beam current of 0.17 nA. Moreover, the leachability of these geopolymer composites was investigated using the toxicity characteristic leaching procedure (TCLP) Method 1311. For the parameters of TCLP, a liquid to solid ratio of 20:1 and an agitation speed of 30 rpm for 12 h using extraction fluids 1 (pH= 4.9) and 2 (pH= 2.9) were used. Leachates were then analysed using Teledyne Leeman Labs Prodigy 7 for inductively coupled plasma – optical emission spectrometry and Techcomp UV 2500 Double Beam Spectrophotometer for ultraviolet-visible spectroscopy method.

3. Results and Discussion

3.1 Compressive strength and surface morphology of geopolymer composite

Table 2 summarises the compressive strength of geopolymer composite developed in this study and the acceptable standard. The results revealed that geopolymerization has continuously occurred, developing a material with high strength as curing time increases. The 28 d and 180 d compressive strength were 22.1 ± 5.4

MPa and 32.2 ± 7.4 MPa, respectively. An increase in the compressive strength by almost 1.5 times has been observed after 180 d curing. The strength gain may be attributed to the continuous reaction between the available aluminosilicate source and the free alkali activator present in the matrix. A similar study by Hoy et al. (2016) in which a strength gain has also been observed on geopolymer samples after curing for a longer period. The measured compressive strength of this study has been promising as this implies that the developed material can comply with the local standard strength requirement as set by the Department of Public Works and Highways and American Society for Testing and Materials (Association of Structural Engineers of the Philippines, 2010).

Table 2: Comparison of strength of geopolymer composite against standard

Material	Mixture	Application	Compressive Strength, MPa
Class A Concrete	OPC-sand mixture	Concrete structures and concrete pavements	20.7
Class C Concrete	OPC-sand mixture	Pedestrian & Light Traffic Paver	20.7
Class B Concrete	OPC-sand mixture	Plain concrete for structure (curbs, gutter, sidewalks)	16.5
Class F Concrete	OPC-sand mixture	Plain concrete for levelling	11.8
Geopolymer Composite	50 % NMS / 50 % CFA (28 d curing)		22.1 ± 5.4
	50 % NMS / 50 % CFA (180 d curing)		32.2 ± 7.4

3.2 Surface morphology of geopolymer composite

The morphological characteristics of geopolymer composite cured for 28 d and 180 d were illustrated in Figure 1. The manifestation of the strength gained in geopolymer composite at longer curing time can be further observed with the SEM images. The etched surfaces that were observed in Figure 1 may be attributed that the unreacted CFA continues to react with the free alkali activator present in the sample. Sample cured at 28 d has shown to have more voids which leads to a lower value of compressive strength in comparison with sample cured at 180 d. Meanwhile, samples cured at a more extended period have resulted in having a more compact and cemented structure.
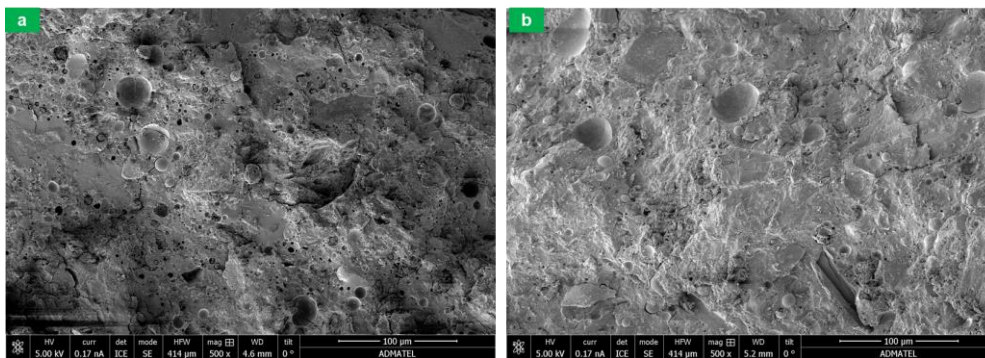

Figure 1: SEM images of a) geopolymer composite cured at 28 d and; b) geopolymer composite cured at 180 d
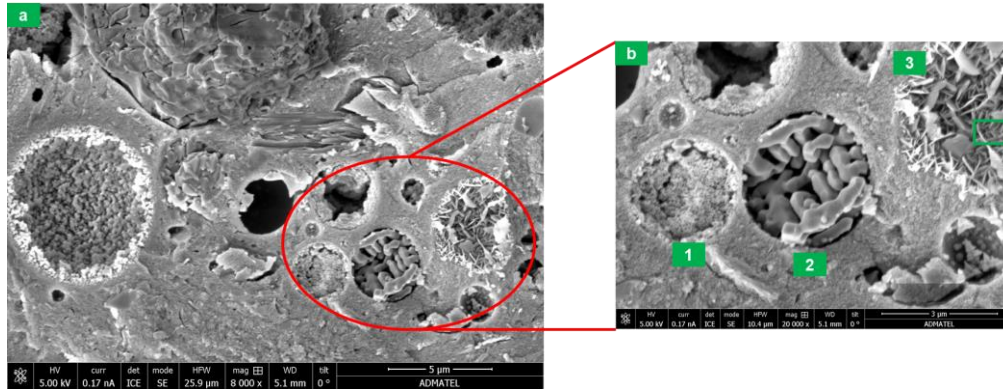
Figure 2: SEM images of geopolymer composite cured at 28 d at magnification a) 8,000x and b) at 20,000x with features etched surface (1) rod-like structure (2) and; needle-like structure (3)

Interesting structures were also observed in Figure 2 and Figure 3. A needle-like structure in Figure 2b may have come from the broken cenosphere of CFA. The broken cenospheres partially react with the available alkali activator, hence forming needle and rod-like structures. Meanwhile, the structures shown in Figure 3 have shown that the surfaces are iron-rich as confirmed by EDS analysis in Table 3. This implies that the iron content of the precursor may have been participated in forming the framework. A similar structure has been observed in the study conducted by Kumar et al. (2016) in which the geopolymeric gel resembles the typical compositions of poly (ferro-sialate-siloxo) and poly (ferro-sialate-disiloxo).
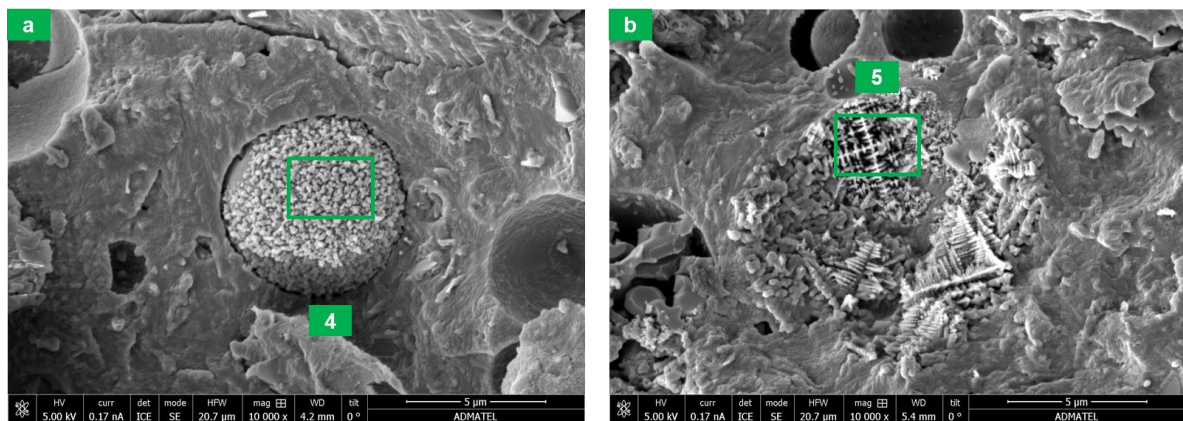

Figure 3: SEM images of geopolymer composite cured at 180 d with features a) partially reacted cenosphere (4) and b) partially reacted needle-structure (5)

Table 3: EDS analysis of geopolymer composite

Component (Mass %)	Spectrum 3	Spectrum 4	Spectrum 5
Si	14.9	5.7	15.0
Al	13.1	1.0	5.0
Fe	6.4	64.4	17.0
Na	4.3	1.3	5.9
Ca	2.7	9.6	2.7
Mg	2	0.5	3.3
O	42.8	6.6	40.5

The presence of Si, Al, Fe, and Na in significant amounts in the EDS analysis supports the agreement that these components have been participating in geopolymerisation.

3.3 Leachability characteristics of geopolymer composite

The geopolymer composite with 28 d and 180 d curing were studied for leachability behaviour, and the results were summarised in Table 4. The concentration of Cr (VI) for both samples at 28 d and 180 d curing conditions is worthy to note as it yielded high-value results but still below the threshold limit. It was also observed that Cr (VI) concentration has decreased upon the decrease in pH. The As behaviour for extraction fluid 1 with a pH of 4.9 for both samples were negligible. The results were observed to be significantly higher in extraction fluid 2 with a pH of 2.9. This result may be attributed to increased mobility as the release of leachates in heavy metals depends mainly on the pH and environment. A similar study conducted by Miccio et al. (2014) has also been observed wherein a significant amount of As and Cr has been released compared to other heavy metals present in the sample. Nevertheless, the release of heavy metals (Cd, Pb, As, Ba, Co, Se, Zn, Cr (VI)) below the TCLP limit revealed that the contaminants present in the sample are non-hazardous. This result implies that the material can be safely deployed for field application as far as leachability behaviour is concerned. Investigating the effect of pH is recommended to determine the possibility of heavy metals increasing mobility upon pH variation. This aspect deserves thorough investigation as some heavy metals are more toxic depending on their form and environment.

Table 4: Leaching of geopolymer composite with 28 d and 180 d curing using extractant fluid 1 and 2

Contaminants	Units	Detection Limit	28 d Curing		180 d Curing		Standard Limit
			Extraction Fluid 1	Extraction Fluid 2	Extraction Fluid 1	Extraction Fluid 2	
Cadmium	mg/L	0.001	0.003	0.005	0.008	0.009	1.0
Lead	mg/L	0.001	<0.001	<0.001	<0.001	<0.001	5.0
Arsenic	mg/L	0.004	0.362	<0.004	0.536	<0.004	5.0
Barium	mg/L	0.002	0.128	0.672	0.121	0.770	100.0
Copper	mg/L	0.006	0.012	0.017	0.015	0.027	5.0
Selenium	mg/L	0.004	0.156	0.016	0.105	<0.004	1.0
Zinc	mg/L	0.002	<0.002	0.002	<0.002	0.009	300.0
Chromium Hexavalent	mg/L	0.002	3.64	4.27	3.45	3.91	5.0

4. Conclusions

This work evaluated the compressive strength and leachability behaviour of geopolymer composite synthesised from nickel laterite mine spoils and coal fly ash. A strength gain has been observed for samples cured after 180 d. The measured compressive strength yielded 22.1 ± 4.4 MPa (28 d curing) and 32.3 ± 7.4 MPa (180 d curing). This value is comparable with the standard compressive strength, making it a promising alternative as a construction material. The compressive strength results are further supported by the morphology of the samples, which showed that the structures were observed to have cemented surfaces. The leaching behaviour on geopolymer was below the regulatory limits, meaning that the developed geopolymer developed in this study can be safely deployed for field application. However, it is recommended to evaluate the effect of varying pH conditions to simulate the actual environment in which it can be applied. This finding is important as some heavy metals are potentially more toxic if present in other forms.

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