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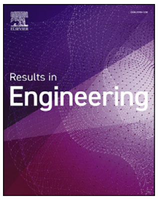

# Mechanical and thermal activation of nickel-laterite mine waste as a precursor for geopolymer synthesis

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ABSTRACT

Geopolymer materials are increasing in scientific interest due to their flexibility in various applications. The geopolymer precursor is a mineral source with reactive Si and Al that is synthesized either mechanically or thermally to improve its cementitious activity. It was found out in previous literature that Nickel-laterite mine waste (NMW) is a prospective geopolymer precursor. However, this potentiality has not been explored in the Philippines, albeit the massive generation of NMW, which is merely dumped as a mining industry downstream process. This paper thus investigates the potential of the NMW as a raw material for geopolymer synthesis. Mechanical activation was performed using a ball mill with the following factors: ball-to-NMW ratio (4:1 and 10:1), mill speed (200 and 500 rpm), and grinding duration (30 and 120 minutes). Thermal activation was performed using a furnace treated at temperatures of 600, 700, and 800 °C. Response Surface Methodology (RSM) of the mechanical activation shows that a ball-to-NMW ratio of 10:1, mill speed of 443 rpm, and grinding duration of 120 minutes achieved optimized leachability of Si and Al. Thermal analysis results showed that NMW could be thermally activated from 600 to 800 °C. The results showed that both activation methods enhanced cementitious activity; hence, NMW could be utilized in geopolymer synthesis after thermal and mechanical activations.

## 1. Introduction

Geopolymers have gained much research interest as a new type of material due to its excellent and exceptional properties in various applications in construction and building materials, additive manufacturing, nanomaterials, ceramic/brick/masonry block sector, and wastewater treatment industry [1–4]. The production of geopolymers are characterized as simple, energy-efficient, and eco-friendly, and the final products have excellent durability and suitable mechanical properties [5]. It is essentially a chemical compound consisting of repeating units of silico-oxide (Si–O–Si), silico-aluminate (Si–O–Al–O-), Ferro-silico-aluminate (-Fe-O-Si-O-Al-O-), or alumino-phosphate (-Al-O-P-O-), created through a process of geopolymerization [6]. It is being studied that the mineral composition of an aluminosilicate is one of the most important factors affecting its process and properties. Thus, it is being investigated that when raw materials are amorphous and contain a significant amount of reactive Si and Al, it can produce a geopolymer with favorable characteristics. These characteristics are activated in different methods like mechanical and thermal activation [5].

To our knowledge, nickel-laterite mine waste (NMW) in the Philippines has not been explored as a potential geopolymer precursor. This shortfall is considered under study since a tremendous amount of NMW is generated in the mining industry at about 136,000 $m^3$/yr, which are washed off downstream, contaminating nearby bodies of water. NMW is a type of clay that primarily consists of minerals of kaolin, illite, montmorillonite, hematite, goethite, and quartz [7]. The matrices of the NMW are also composed of $Fe_2O_3$–$Al_2O_3$–$SiO_2$–$H_2O$, making it a good candidate as a geopolymer precursor [8]. The use of lateritic type as a geopolymer precursor has been demonstrated by several studies. For instance, it was observed that laterites behave similarly with metakaolin when subjected to a thermal activation between 25 and 500 °C. However, poor characteristics of the final geopolymer products have been observed upon activating it at a temperature higher than 500 °C [9]. In another study, a high compressive strength geopolymer was synthesized using laterites calcined at 600 °C and 12 M sodium hydroxide and a molar ratio $SiO_2/Na_2O$ of the silicate solution equal to 0.75 [10]. It was reported that laterite samples which are thermally treated at 700 °C could be utilized as raw material for non-load bearing building materials [7].

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**Table 1**
Chemical composition of raw NMW.

| Components | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | NiO | LOI | Others |
|---|---|---|---|---|---|---|---|---|
| % mass | 20.5 | 2.8 | 47.7 | 5.5 | 4.2 | 1.9 | 15.5 | 2.2 |

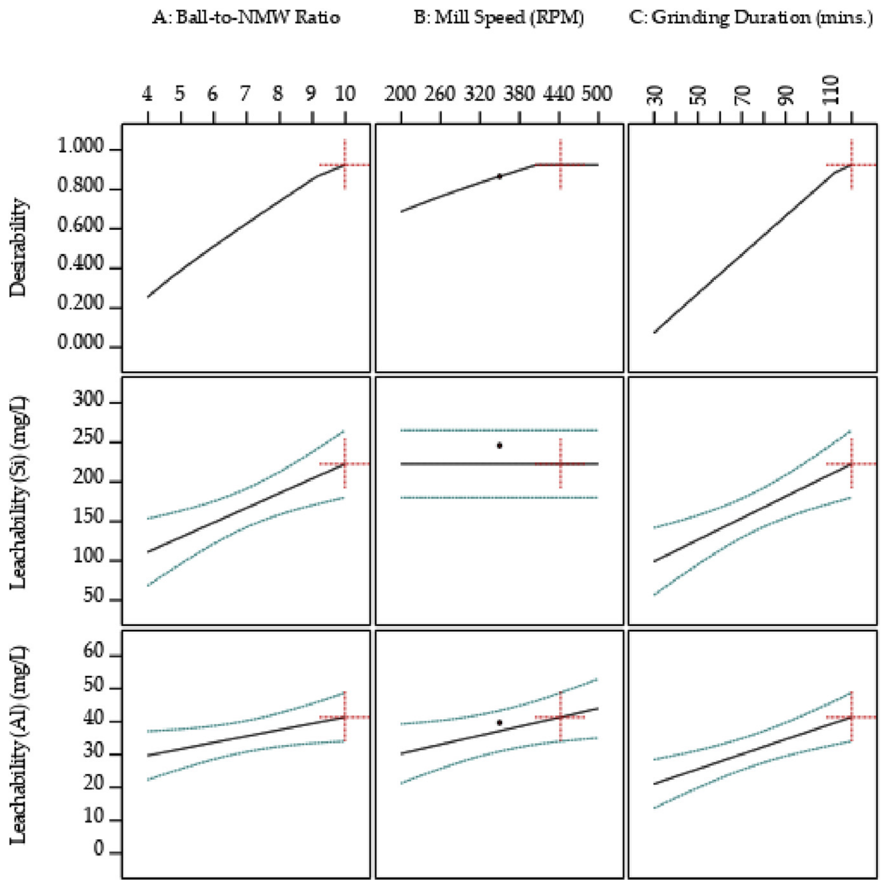

**Fig. 1.** The desirability of the Optimized Parameters.

Thus, this study aims to characterize the suitability of NMW in geopolymer system and investigate the effects of mechanical and thermal activation methods on the improvement of its cementitious activity.

## 2. Materials and methods

NMW was collected from Agata Mining Ventures, Inc., situated at Agusan del Norte, Philippines. It was first oven-dried at 105 °C for 24 hours. The sample was screened, and the particle size used was <50 mesh (297 μm). The NMW chemical composition was determined using X-ray fluorescence spectroscopy (Table 1).

### 2.1. Mechanical activation

To evaluate the mechanical activation of the NMW as a prospective material, an optimization model using a Box-Behnken design of experiment (DoE) and response surface methodology (RSM) was used (through Design-Expert® software 11). DoE was used to determine the relationship between uncertain factors affecting the response of the process. Factors considered include (1) ball-to-NMW mass ratio (4:1 and 10:1), (2) mill speed (200 and 500 rpm), and grinding duration (30 and 200 mins) [11,12]. Seventeen (17) runs were generated, and the samples were milled using the RJM-102 benchtop ball mill. Leaching tests were done to assess the dissolution of silica (Si) and alumina (Al) species. An activated sample was then mixed with 10 mol/L NaOH solution [13] in a polyethylene centrifuge tube for 10 minutes to avoid the formation of $Si(OH)_4$ and $Al(OH)_3$ gel [14]. It was then centrifuged for 15 minutes at 4000 rpm. The solution was analyzed using an inductively coupled plasma optical-emission spectrometer (ICP-OES). Through leachability, the effects of milling factors were evaluated independently. RSM was done to apply different regression models to see the significance of each factor through analysis of variance (ANOVA). Insignificant factors were discarded, and the proposed models are used for response predictions [15].

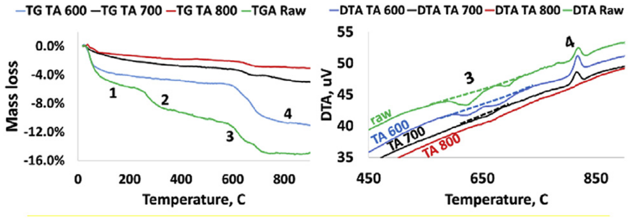

**Fig. 2.** **(a)** TGA and **(b)** DTA thermograms of raw and thermally activated NMW (1: Water removal, 2: Pre-hydroxylation, 3: Hydroxylation, 4: Oxidation).

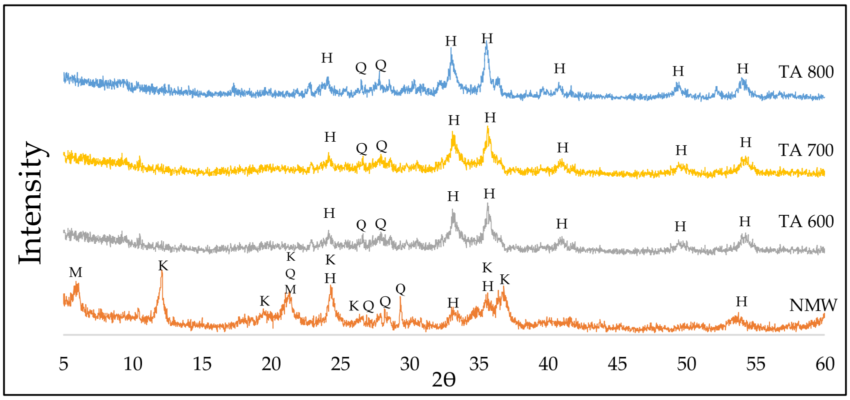

**Fig. 3.** A mineralogical pattern of NMW upon thermal treatment (M – montmorillonite; K- kaolinite; Q-quartz; H- hematite).

### 2.2. *Thermal activation*

To evaluate the thermal activation of the NMW as a prospective material, another set of samples were heat-treated using a programable laboratory furnace from room temperature to different final temperatures (600, 700, and 800 °C) at a ramping rate of 10 °C/min. After heating the sample for 2 h, it was cooled down to room temperature inside the furnace. To evaluate the effect of heat treatment, thermally activated samples were subjected to simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) using Rigaku TG8120. Samples were heated from 20 to 900 °C at a constant heating rate of 10 °C/min in air. The mineralogical composition of the starting and thermally activated NMW were determined using X-ray diffraction (XRD).

## 3. Results and discussion

Mechanical and thermal activation methods were evaluated in this study to describe the suitability of locally sourced NMW as a geopolymer precursor.

### 3.1. *Mechanical activation*

Fig. 1 shows the effect of ball mill parameters on Si and Al leachability through the DoE and RSM method. ANOVA indicated that ball-to-NMW mass ratio and grinding duration significantly affect Si and Al leachability with positive correlations except for mill speed. 2FI model was the significant model with P-values of 0.0031 and 0.0020 ($<0.05$) for the Si and Al leachability, respectively. RSM shows that the optimized leachability of Si and Al had a ball-to-NMW ratio of 10:1, mill speed of 443 rpm, and grinding duration of 120 minutes a 0.92-desirability (Fig. 1).

The effect of leachability to geopolymerization is supported by Ref. [16], which conducted a leaching study of fly ash in varying concentrations of soluble silicate solution. The research determined that calcium (Ca) and silicon (Si) were the first two elements to dissolve, followed by aluminum (Al). It concluded that when soluble silicate solutions of high molarity were utilized, dissolution was greatly enhanced, followed by a gel-phase precipitate being produced like geopolymeric gel. The increase in the leachability of Si and Al with increasing grinding duration may also be attributed as a result of grain refinement of particles. This phenomenon was also demonstrated by the study of [17] wherein Si and Al are easily more leached because the Si–O and $Si(Al^{IV})$–O–Si bonds of the precursor are broken gradually during mechanical activation, thus increasing its cementitious property.

### 3.2. *Thermal activation*

The results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) at varying temperatures are shown in Fig. 2. Likewise, the mineralogical analysis of NMW and thermally treated NMW is shown in Fig. 3 which reveals the presence of montmorillonite, kaolinite, quartz, and hematite.

The TGA and DTA revealed that at temperatures below about 200 °C, the release of adsorbed water occurs [18]. Meanwhile, the mass losses associated between 200 and 450 °C are attributed to the pre-dehydration process. In the range of 450–750 °C, dehydroxylation of kaolinite and formation of metakaolinite takes place [19,20]. The two observed endothermic peaks at 625 and 700 °C in raw NMW samples (Fig. 2b) may be attributed to the dehydroxylation process. NMW heated at 600 °C has smaller endothermic peaks indicating partial or incomplete conversion of kaolin to metakaolin.

However, NMW heated at 700 and 800 °C show no endothermic dehydroxylation peaks indicating complete conversion of kaolin. At about 850 °C, possible oxidation was observed (as can be seen in Fig. 2b). Thermal analysis results showed NMW can be thermally activated from 600 to 800 °C. Further, these results also signify the benefit of thermal treatment at 700 °C compared to 800 °C in terms of lower energy consumption and cheaper materials in constructing the heat treatment equipment.

Furthermore, Fig. 3 shows the XRD pattern of NMW thermally treated at 600 °C (TA 600), 700 °C (TA 700), and 800 °C (TA 800). This reveals that upon a thermal treatment, the disappearance of some peaks of kaolinite and montmorillonite was observed. This result suggests that dehydroxylation of kaolinite occurs, which could lead to the formation of metakaolinite–a geopolymer precursor that has been widely studied due to its excellent pozzolanic property [19]. The result of the XRD pattern is consistent with the result of the TGA/DTA analysis.

## 4. Conclusions

The study shows that thermal activation and mechanical activation can significantly influence and enhance the cementitious activity of the NMW. Hence, nickel-laterite mine waste could be utilized in geopolymer synthesis after thermal and mechanical activation. Future works include the synthesis of a geopolymer using the activated precursors and the effect of iron in the NMW to the geopolymer properties of the final product.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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