

# Synthesis and Characterization of Geopolymer from Bayer Red Mud with Thermal Pretreatment

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A composite geopolymeric material was synthesized from Bayer red mud combined with granulated blast-furnace slag. Thermal pretreatment was applied to improve the solubility of red mud in alkaline solution to promote geopolymerization. The dissolution efficiencies of alumina and silica reached a maximum when red mud was calcined at 800°C, resulting in the highest compressive strength of binders. It was demonstrated that a higher solubility of calcined red mud led to a higher strength of the composite binders. The characteristic microstructures of hydration products were studied to illustrate the geopolymerization process by XRD, FTIR and SEM. The results showed that aluminosilicates were dissolved in the alkaline solution to form nanostructural particulates during the early dissolution process, and then accumulated to form highly dense geopolymeric matrices through solidification reaction. The coexistence of geopolymer and C-(A)-S-H is suggested to contribute to the good performance of the composite binders.

# I. Introduction

 ${f B}$  AYER red mud (RM) is a solid waste residue from caustic soda digestion of alumina from bauxite ores by the Bayer process. It is estimated that approximately 2.7 billion tons of RM has been generated in about 120 yr of alumina extraction history, with an increase in 120 million tons per annum currently.<sup>1</sup> RM is classified as a toxic waste because of its high basicity and leaching potential,<sup>2</sup> which make it hard for disposal. Generally, most of RM still ends up in landfills throughout the world. High alkaline slurry and leachate pose a potential risk to the environment.

Beneficial reuse of RM is of great interests.<sup>3</sup> Recovery of valuable elements such as Na, Al, Fe, and Ti from RM has been reported.<sup>4–6</sup> However, the cost is high and a large quantity of residues after the extraction still need disposal. Preparation of ceramic, glasses-ceramic or tiles<sup>7–9</sup> from RM by calcination is a high value-added approach, but this approach only consumes a small quantity of RM due to the limited market demand. Adding RM to portland cement or concrete,<sup>10</sup> and making RM brick<sup>11</sup> or special cements<sup>12,13</sup> are restricted by the less pozzolanic activity of Bayer RM. In addition, sodium in RM is detrimental that may cause alkaliaggregate reaction. Consequently, while the presence of sodium restricts the use of RM in construction materials, synthesizing geopolymer from RM is a favorable disposal approach away from this problem as alkali is a necessary component for geopolymer.

Geopolymeric materials are a class of aluminosilicate binders that differ substantially from ordinary portland cement, and exhibit high performance, such as high mechanical strength and excellent stability in high temperature, acidic or alkaline environments.<sup>14</sup> They are synthesized by activating solid aluminosilicate sources with alkali metal hydroxide or silicate solutions.<sup>14</sup> Geopolymerization is a promising technology that can transform industrial solid wastes containing aluminosilicates into useful products. Any pozzolanic compounds or materials containing silica and alumina that are readily soluble in an alkaline solution, can serve as precursors of geopolymer.<sup>15</sup>

RM contains an amount of alkali and aluminosilicates, so it poses a potential for synthesis of geopolymeric materials. Some researches in synthesis of geopolymer with RM have been carried out.<sup>16</sup> However, the activity or solubility of aluminosilicates in RM is poor, which limits the geopolymerization process. In the research of Dimas *et al.*<sup>16</sup>, the solubility of the aluminosilicate phases in RM under alkaline conditions was low, and RM particles mainly played as fillers with metakaolin playing a leading role. Thus, the final products were poor in the flexural strength and not resistant to freezing-thawing cycles. Therefore, improving dissolution of silica and alumina from RM is a pivotal matter in synthesis of geopolymer from RM.

Thermal treatment is commonly used to improve pozzolanic properties of raw materials containing zeolite clay minerals before geopolymerization.<sup>17</sup> This study tried to improve the solubility of Bayer RM in alkaline environment by thermal treatment. In addition, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of  $RM^{18,19}$  is usually much less than the scope of 3.3–4.5 for the satisfactory formulation of geopolymer.<sup>20,21</sup> Therefore, to produce a geopolymer with stable structure, it is necessary to utilize some other active silicates or aluminosilicates as a partial substitute of RM to regulate the formulations. In this study, granulated blastfurnace slag (GBFS) was used as a partial substitute of thermally pretreated RM in synthesis of high-value geopolymer. GBFS is a byproduct made from the extraction of iron from iron ore in blast furnace. It has a latent hydraulic activity, which can be catalyzed by alkali salts to make clinker-free binders that are called alkali-activated slag (AAS) materials.<sup>22</sup> GBFS is also used as a raw material for partially substituting metakaolin or fly ash to synthesize high-value geopolymer.<sup>23–26</sup>

In this study, a local Bayer RM with low  $Fe_2O_3$  content of about 9.5 wt% was used to eliminate the negative effect of Fe. It is a typical Bayer residue from the leaching of Chinese local diaspore bauxite ores in Bayer process.<sup>18</sup> The flowchart of the process is shown in Fig. 1. The RM samples were calcined at different temperatures to get phase transformations of the aluminosilicates. The solubility of RM samples under alkaline conditions was determined to evaluate the latent activity of calcined RM samples through alkaline leaching test. Then, the calcined RM was blended with GBFS and

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20 of approximately 29°.

of 10°C/min in air atmosphere.

(3) Alkaline Leaching Test

900°C, and 1000°C for 3 h, respectively.



Fig. 1. Flowchart of the process for recycling of RM through geopolymer technology.

activated by sodium silicate to prepare geopolymer. Main parameters affecting the reaction and their effects on the compressive strength of the binders were investigated. The

Dissolution efficiency =  $\frac{\text{The amount of Al}_2\text{O}_3\text{or SiO}_2\text{in the filtrate}}{\text{The amount of Al}_2\text{O}_3\text{or SiO}_2\text{in RM raw material}}$ 

(1)

microstructure characterizations of the geopolymerization products were also studied.

# **II. Experimental Procedure**

### (1) Raw Materials

A local Bayer RM was provided by an alumina plant of Chalco Co. in Zhengzhou, China. It was dried to constant weight at 100°C for subsequent experiments. GBFS was provided by Wuhan Iron and Steel Corp. (Wuhan, China), and was ground to pass 200 mesh sieves. The chemical compositions of RM and GBFS samples are presented in Table I.

The main chemical components of the RM are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub>. Therefore, RM can be considered as an alkaline aluminosilicate source with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.41. It is a typical Bayer waste with a relatively low Fe<sub>2</sub>O<sub>3</sub> content due to the low Fe Chinese bauxite, but its alumina and silica contents are in the common scope of China<sup>18</sup> and the world.<sup>19</sup> GBFS mainly consists of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO.

The mineral phases of the raw materials were analyzed by powder X-ray diffractometry (XRD), using an X'Pert Pro XRD (Philips, PANalytical B.V., Almelo, Holland) with CuK $\alpha$  radiation and  $\lambda = 1.5418$  Å, operated at 300 mA, 40 kV with scanning rate of 0.2785°/s for 2 $\theta$  in the range

# (4) Synthesis of Geopolymer Binders

were calculated according to Eq. (1) below:

The preparation process of the geopolymer binders included three steps. Firstly, the solid phase consisting of RM and GBFS was mechanically blended with water and an activator to obtain a homogeneous viscous paste. The activator was a strong alkaline solution containing sodium silicate prepared by dissolving sodium hydroxide in an original sodium silicate solution (initial solid content = 38.11%, SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio = 3.15). Then, the pastes was molded in steel molds (40 mm × 40 mm × 40 mm) and cured at  $20 \pm 1^{\circ}$ C and relative humidity of 95% for 24 h. The binders were then demolded and cured again under the same condition. Afterwards, the compressive strengths of the binders cured for 3, 7, and 28 d were measured. Each set of binders had triplicates, and every compressive strength data were the mean value of three parallel samples.

from 5° to 75°. The XRD patterns are shown in Fig. 2. The

mineral phases of the raw RM include gibbsite, hematite,

cancrisilite, muscovite-2, and katoite, while GBFS shows an amorphous material characterization with a broad hump at

Thermal analysis of the raw RM sample was performed in a

Pt crucible by the thermo gravimetric analysis (TG), using

Diamond TG-DTA (PerkinElmer Co. Ltd., Waltham, MA). The temperature was raised up to 1000°C at a ramping rate

RM samples were calcined in a muffle furnace under static

air at 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C,

To determine the solubility of the aluminosilicate phases in RM samples under an alkaline condition, alkaline leaching

tests<sup>16</sup> were carried out. The tests were carried out by using

5*M* sodium hydroxide solution, with a solid/liquid ratio of 1:10, in a constant-temperature shaker bath ( $25 \pm 2^{\circ}$ C) for

24 h. The residual solids were separated using vacuum filtra-

tion and then washed. The alumina and silica contents in the filtrate were determined according to Chinese standard YS/T

575-2007. The dissolution efficiencies of Si and Al from RM

(2) Thermal Analysis and Calcination Procedure

Four groups of the experiments labeled as group I, II, III, and IV, respectively, were designed to evaluate the effects of modulus  $SiO_2/Na_2O$  molar ratio and dosage of sodium silicate, RM/GBFS mass ratio, and calcination temperature for RM on the compressive strength of the composite binders. The experimental conditions are shown in Table II. The dosage of various sodium silicate (Na<sub>2</sub>O·mSiO<sub>2</sub>) was presented simply as the mass ratio of the contained Na<sub>2</sub>O to the solid mixture consisting of RM and GBFS. In group III, with increased RM content, the paste became stiff, which made

Table I.	Chemical	Compositions	of RM	and	GBFS
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Components (wt%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	TiO <sub>2</sub>	K <sub>2</sub> O	MgO	LOI
RM	20.38	24.50	9.48	11.46	12.86	2.92	0.88	1.00	15.40
GBFS	32.85	14.96	0.55	0.41	37.46	0.98	0.57	9.27	0.62

LOI: loss on ignition, mass loss at 1200°C.









#### (5) Microstructure Characterization

The mineral phases of the calcined RM samples and the hydration products were investigated by the powder XRD at the same experimental conditions described in Section II(1). Fourier-transform infrared spectroscopy (FTIR) tests were performed by Vertex 70 (Bruker Co., Karlsruhe, Germany) with a wavelength of 400–4000 cm<sup>-1</sup>. The morphology of the typical binders was examined by scanning electron microscope (SEM) after coating with Au, using Nova Nano SEM 450 (FEI Co., Eindhoven, Holland).

### III. Results and Discussion

#### (1) Thermal Analysis and Calcination Process

The TG and DTG curves of the raw RM specimen are shown in Fig. 3. The TG curve declined continuously as the temperature rose from 20°C to 1000°C. The weight loss of RM presented in the curve can be separated into four stages: 147°C–285°C, 285°C–550°C, 550°C–700°C, 720°C–950°C, referred to as stage I, II, III, and IV, corresponding to peaks at 260°C, 322°C, 641°C, and 843°C in the DTG curve, respectively. The weight losses result from the transformation of different minerals, which will be discussed in the following section.

<b>Fable II.</b>	Conditions	for	Preparing	the	Geopol	ymer	Binders
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	Sodium silicates		Solid phases			Molar ratio of binders			
No.	SiO <sub>2</sub> /Na <sub>2</sub> O molar ratio	Addition <sup>†</sup> (Na <sub>2</sub> O, wt%)	RM/GBFS (wt/wt)	Calcination temperature of RM (°C)	Water/solid (g/g)	(Na <sub>2</sub> O + K <sub>2</sub> O)/SiO <sub>2</sub>	CaO/SiO <sub>2</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Na <sub>2</sub> O
RM-I-1	1.3	6.90	5:5	800	0.45	0.37	0.76	3.04	11.64
RM-I-2	1.4					0.36	0.75	3.10	11.64
RM-I-3	1.5					0.35	0.74	3.16	11.64
RM-I-4	1.6					0.35	0.72	3.21	11.64
RM-I-5	1.7					0.34	0.71	3.27	11.64
RM-I-6	1.8					0.33	0.70	3.33	11.64
RM-I-7	1.9					0.33	0.69	3.39	11.64
RM-II-1	1.7	3.45	5:5	800	0.45	0.30	0.83	2.78	15.71
RM-II-2		4.60				0.31	0.79	2.95	14.07
RM-II-3		5.75				0.33	0.75	3.11	12.74
RM-II-4		6.90				0.34	0.71	3.27	11.64
RM-II-5		8.05				0.35	0.68	3.43	10.72
RM-II-6		9.20				0.36	0.65	3.60	9.93
RM-II-7		10.35				0.37	0.62	3.76	9.25
RM-III-0	1.7	6.90	10:0	800	0.55	0.57	0.43	2.20	10.00
RM-III-1			9:1		0.53	0.52	0.50	2.38	10.25
RM-III-2			8:2		0.51	0.47	0.56	2.58	10.53
RM-III-3			7:3		0.49	0.42	0.61	2.79	10.84
RM-III-4			6:4		0.47	0.38	0.66	3.02	11.21
RM-III-5			5:5		0.45	0.34	0.71	3.27	11.64
RM-III-6			4:6		0.43	0.30	0.75	3.55	12.15
RM-III-7			3:7		0.41	0.27	0.80	3.86	12.77
RM-III -8			2:8		0.39	0.23	0.84	4.20	13.52
RM-III-9			1:9		0.37	0.20	0.87	4.59	14.46
GBFS-III			0:10		0.35	0.17	0.91	5.02	15.69
RM-IV-1	1.7	6.90	5:5	_	0.45	0.34	0.71	3.27	11.64
RM-IV-2				200		0.34	0.71	3.27	11.64
RM-IV-3				300		0.34	0.71	3.27	11.64
RM-IV-4				400		0.34	0.71	3.27	11.64
RM-IV-5				500		0.34	0.71	3.27	11.64
RM-IV-6				600		0.34	0.71	3.27	11.64
RM-IV-7				700		0.34	0.71	3.27	11.64
RM-IV-8				800		0.34	0.71	3.27	11.64
RM-IV-9				900		0.34	0.71	3.27	11.64
RM-IV-10				1000		0.34	0.71	3.27	11.64

<sup> $\dagger$ </sup>The dosage of various sodium silicate (Na<sub>2</sub>O·mSiO<sub>2</sub>) was presented simply as the mass ratio of the contained Na<sub>2</sub>O to the solid mixture consisting of RM and GBFS.



Fig. 3. TG-DTG curves of the raw RM specimen.

# (2) Phase Transformation

The XRD patterns of calcined RM samples are shown in Fig. 4. When the calcination temperature rose to 1000°C, minerals transformed successively except hematite, corresponding to the four stages on TG curve. In stage I, gibbsite decomposed at 147°C -285°C according to Eq. (2). The intensity of its characteristic peaks in XRD patterns decreased at 200°C, and disappeared at 300°C. In stage II, katoite dehydrated partly when the temperature rose over 200°C, and transformed into hibschite (Ca<sub>3</sub>Al<sub>2</sub>(- $SiO_4$ )<sub>1.53</sub>(OH)<sub>5.88</sub>). In stage III, the intensity of the characteristic peaks of muscovite-2 decreased at 600°C and disappeared at 800°C. In stage IV, hibschite dehydrated from 700°C to 1000°C. Cancrisilite decomposed at 800°C, with the formation of nepheline (NaAlSiO<sub>4</sub>), sodium alumina silicate  $(Na_6(AlSiO_4)_6)$  and some amorphous materials, identified by the amorphous peak at 20 of about 28°-38°. Moreover, gehlenite (Ca<sub>2</sub>(Al(AlSi)O<sub>7</sub>)) was formed at 800°C, and its content increased from 800°C to 1000°C.

The dehydroxylation of katoite, muscovite-2 and hibschite can cause the formation of Al atoms in fourfold or fivefold coordination,<sup>14</sup> which could contribute to the depolymerization of aluminosilicates and improve their dissolution in alkaline environment. The transformation of cancrisilite is proposed as Eq. (3). NaAlSiO<sub>4</sub> and Na<sub>2</sub>SiO<sub>3</sub> are both more readily to dissolve in alkaline solution.

At 
$$147 - 285^{\circ}C : 2Al(OH)_3 \rightarrow Al_2O_3(s) + 3H_2O(g)$$
 (2)

$$\begin{array}{l} \operatorname{At 800 ^{\circ}C}: 2\operatorname{Na_{7}[Al_{5}Si_{7}O_{24}](CO)_{3} \cdot 3H_{2}O} \\ \to 5\operatorname{NaAlSiO_{4}(s)} + \operatorname{Na_{2}SiO_{3}(s)} + \operatorname{CO_{2}(g)} \\ + 3H_{2}O(g) \end{array}$$
(3)

The phase transformation of RM was also well-identified by FTIR spectra shown in Fig. 5. There were several common absorption bands for different pretreated RM samples, such as those attributed to asymmetric stretching vibrations of Si–O–Si and Al–O–Si (~1200–950 cm<sup>-1</sup>), symmetric stretching vibrations of Si–O–Si and Al–O–Si(~700–680 cm<sup>-1</sup>), and bending vibrations of Si–O–Si and Al–O–Si(~470–460 cm<sup>-1</sup>).<sup>14,27</sup> The intensity of the band attributed to stretching vibrations of Al–OH at 1385 cm<sup>-1</sup> decreased when the RM was calcined above 200°C because of the dehydration of gibbsite. At 600°C, the



**Fig. 4.** XRD patterns of RM samples calcined at 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C, and 1000°C for 3 h.

decomposition of muscovite-2 led to the decrease in absorption band attributed to bending vibrations of Si–O–Al in the region of 500–550 cm<sup>-1</sup>.<sup>14</sup> The absorption bands attributed to stretching vibrations of O–C–O (~1510–1410 cm<sup>-1</sup>, ~873 cm<sup>-1</sup>) and bending vibrations of HOH (~1650– 1630 cm<sup>-1</sup>)<sup>27</sup> disappeared at 800°C because of the transformation of cancrisilite. The absorption bands attributed to symmetric stretching vibrations of Si–O–Si and Al–O–Si (~650–550 cm<sup>-1</sup>, 770–760 cm<sup>-1</sup>), and Si–OH bending (~880– 870 cm<sup>-1</sup>)<sup>14,27</sup> also decreased and then disappeared in the range of 800°C –1000°C, which are mainly caused by decomposition of hibschite or amorphous phases.

# (3) Effect of Thermal Pretreatment on Leaching by Alkaline Solution

The effect of calcination temperature on the solubility of RM in sodium hydroxide solution is shown in Fig. 6. There were two peak values for alumina at about 200°C and 800°C. As shown in Fig. 4, a large amount of Al existed as gibbsite in the raw RM sample. It decomposed easily at 200°C–300°C, and transformed into amorphous phase more readily to dissolve in alkaline solution. But as the temperature rose over 300°C, the dissolution efficiency of alumina declined on the contrary, possibly because of the further transformation of the dehydration product. From 600°C to 800°C, muscovite-2, hibschite and cancrisilite transformed into phases which are more readily to dissolve. When the temperature rose over 800°C, the main aluminosilicate phases transformed into a

more stable phase of gehlenite. Thus, the dissolution efficiency of alumina decreased. The dissolution efficiency of silica increased from 100°C to 800°C and reached a maximum at approximately 800°C. The variation in dissolution efficiency of silica was also attributed to the transformation of muscovite-2, hibschite and cancrisilite. It is suggested that the optimum calcination temperature is about 800°C by



Fig. 5. FTIR spectra of raw RM sample and RM samples calcined at 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C, and 1000°C for 3 h.



Fig. 6. Dissolution efficiencies of alumina and silica from RM in 5M sodium hydroxide solution with a liquid/solid of 10 mL/g.

considering the dissolution efficiencies of both alumina and silica.

From the results of the alkaline leaching test, it can be concluded that thermal pretreatment can greatly improve the solubility of RM in a strong alkaline environment. Generally, more soluble aluminosilicates significantly enhance the geopolymeric reaction. Therefore, thermal pretreatment is an effective method for the application of RM to make geopolymeric materials.

# (4) Compressive Strength of the Geopolymer Material Made From RM

(A) The Effect of SiO<sub>2</sub>/Na<sub>2</sub>O Molar Ratio of Sodium *Silicate:* The effect of the initial soluble silica concentration in the sodium silicate solution on the compressive strength of binders is shown in Fig. 7. The compressive strength increased when the SiO2/Na2O molar ratio increased from 1.3 to 1.7, and then decreased beyond this range. The optimum SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of sodium silicate was 1.7. This effect can be explained from the extent of dissolution of aluminosilicates. Dissolved silica initially present in the alkaline activating solution enhanced depolymerization of Si-O-Al and Si-O-Si bonds from the solid surface.<sup>28,29</sup> Thus, the addition of soluble silicate accelerated the dissolution of alumina and silica, and promoted the conversion of solid aluminosilicate sources to geopolymer gel. In addition, the sodium silicate served as a silica supplement to the formulation of the binders, which reached a satisfactory Si<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio of 3.27 when the SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of sodium silicate was 1.7. However, high silicate concentration could contribute to the formation of cyclic silicate species and reduce the interaction of tetrahedral  $Al(OH)_4^-$  and  $H_3SiO_4^-$  monomers or larger linear silicate anions during condensation.<sup>30</sup> Therefore, excessive silica was detrimental which reduced the strength of the binders.

(B) The Effect of Dosage of Sodium Silicate: Alkali concentration is the most significant factor for geopolymerization.<sup>30</sup> The compressive strength versus the dosage of Na<sub>2</sub>O from the sodium silicate (Na<sub>2</sub>O·1.7SiO<sub>2</sub>) is shown in Fig. 8. It is obvious that the compressive strength increased with the increase in dosage of Na<sub>2</sub>O from 3.45 to 6.90 wt%, and reached a maximum of about 49.2 MPa at 28 d at approximately 6.90 wt%. The strength variation can be explained based on the theory that geopolymerization consists of a series of dissolution–reorientation–solidification



Fig. 7. Compressive strength of the binders versus the SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio in sodium solicate. (Na<sub>2</sub>O dosage of 6.90 wt%; RM calcination temperature of 800°C; and RM/GBFS mass ratio of 5:5).



Fig. 8. Compressive strength of the binders versus dosage of sodium silicate. ( $SiO_2/Na_2O$  molar ratio of 1.7; RM calcination temperature of 800°C; and RM/GBFS mass ratio of 5:5).

reactions.<sup>31</sup> The solubility of aluminosilicates increases with increasing hydroxide ion concentration,<sup>32</sup> forming more aluminate and silicate monomers for subsequent reactions, which leads to a higher strength of the geopolymer. Therefore, the compressive strength of the binders increased as the dosage of Na<sub>2</sub>O increased from 3.45 to 6.90 wt%. However, excessive alkali may result in undesirable morphology and nonuniformity of hydration products in the pastes,<sup>33</sup> which partially explains the reduction in strength when the dosage of Na<sub>2</sub>O further increased beyond 6.90 wt%.

(C) The Effect of Calcined RM Content: The compressive strength versus the RM/GBFS mass ratio is shown in Fig. 9. The compressive strength of RM-III-0 binders which was prepared without addition of GBFS was poor. Although the dissolution efficiency of alumina and silica from RM in alkaline solution are greatly improved after thermal pretreatment, the total contents and activity of alumina and silica of RM are still lower than that of GBFS. Therefore, it is necessary to combine RM with other reactive aluminosilicate materials such as GBFS and metakaolin for synthesis of geopolymer. Generally, the compressive strength of the binders increased as the content of calcined RM in the composite binders decreased. But the compressive strength of RM-III-9



Fig. 9. Compressive strength of the binders versus RM/GBFS mass ratio. (Na<sub>2</sub>O dosage of 6.90 wt%; SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 1.7; and RM calcination temperature of 800°C).

binders with 10 wt% calcined RM was even higher than GBFS-III binders with 100 wt% GBFS at the same curing days. It is consistent with the result of Yip et al.<sup>25</sup> who also found that the coexistence of geopolymer and AAS showed better performance than those made from individually raw materials. Therefore, the strength tendency indicated that RM is a beneficial additive rather than a harmful or useless one in the composite materials and synthesizing geopolymer is a potential approach of RM reuse and disposal. From Table II, all of the  $(Na_2O + K_2O)/SiO_2$ ,  $SiO_2/Al_2O_3$  and  $H_2O/(Na_2O + K_2O)$  molar ratios of the binders reached the scope of satisfaction for a geopolymer<sup>20,21</sup> when the content of RM ranged from 10% to 50%. The produced materials had a  $CaO/SiO_2$  ratio less than 1, which is different to an ordinary geopolymer. However, GBFS is now a valuable solid waste mostly used as concrete additive. It was suggested that to achieve broad-based market penetration, a geopolymer concrete need to be low cost with low slag mixing amount.<sup>34</sup> To reuse as much RM as possible, the RM/GBFS ratio of 5:5 with a compressive strength of 49.2 MPa was acceptable for the potential application in construction materials.

(D) The Effect of Calcination Temperature of RM: The compressive strength versus the RM calcination temperature is shown in Fig. 10. The compressive strength of the binders increased with the increase in calcination temperature from 100°C to 800°C, and reached a maximum at 800°C. It is known that more soluble aluminosilicates can significantly contribute to the geopolymeric reaction. The solubility of aluminosilicates in RM was greatly improved after calcination at 800°C, thus the corresponding binders posed a higher compressive strength. As shown in Fig. 6, although the dissolution efficiency of silica from RM increased from 100°C to  $600^{\circ}$ C, the solubility of alumina decreased in this range. As a result, the compressive strength did not change significantly from 100°C to 600°C.

#### (5) Microstructure of the Geopolymeric Materials

(A) XRD Analysis: To illustrate the alkali activation process of RM and GBFS, the XRD patterns of RM-III-0, GBFS-III, and RM-III-5 binders are shown in Fig. 11. RM-III-0 binders contained a poorly crystalline C–(A)–S–H phase,<sup>35</sup> cancrinite, hematite, hibschite, and gehlenite. The content of C–(A)–S–H phase, which acts as a microaggregate in the structure of binders, increased along with the hydration process. Cancrinite is a zeolitic mineral that sometimes occurs in alkaline massifs as a rock-forming mineral.<sup>36</sup> It was formed according to Eq. (4) by absorbing CO<sub>2</sub> from air in a



Fig. 10. Compressive strength of the binders versus the RM calcination temperature. (Na<sub>2</sub>O dosage of 6.90 wt%; SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 1.7; and RM/GBFS mass ratio of 5:5).



Fig. 11. XRD patterns of RM-III-0, GBFS-III, RM-III-5 binders and RM sample calcined at 800°C at different curing days.

highly alkaline environment. While hematite, hibschite, and gehlenite from the RM sample remained stable during the hydration process, sodium aluminum silicate and nepheline disappeared after alkali activation.

Geopolymers are known to be a class of amorphous aluminosilicate materials that have the same outstanding feature in diffractograms with a broad hump centered at  $2\theta$  of 27°-29°.<sup>14</sup> This amorphous peak seemed to be weak in the absence of GBFS as shown in Fig. 11 as for the RM-III-0 binders, which implied that geopolymerization was difficult to take place in the presence of only RM, probably because of low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. However, the amorphous phase in the RM-III-5 binders became more and more obvious as the curing time increased from 3 to 28 d, which implied the formation of geopolymer in the produced materials. On the other hand, the GBFS precursor and its hydration products had the same amorphous peak which remained unchanged as the curing time increased. Therefore, it can be inferred that the increasing amorphous phase in RM-III-5 samples should be concerned with RM in the presence of GBFS.

$$\frac{2\text{CO}_2 + 6\text{Na}^+ + 2\text{Ca}^{2+} + 6\text{H}_3\text{SiO}_4^- + 6\text{Al}(\text{OH})_4^- \rightarrow}{\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O} + 18\text{H}_2\text{O} + 2\text{OH}^-}$$
(4)

The mineral phases of RM-III-5 binders were similar to RM-III-0 binders at 28 d, except for a more significant broad hump centered at around 27°–29°. But large quantities of



**Fig. 12.** FTIR spectra of (a) RM sample calcined at 800°C and the different binders: (b) RM-III-5 cured for 3 d; (c) RM-III-5 cured for 28 d; (d) RM-III-0 cured for 28 d; and (e) GBFS-III cured for 28 d.

alumina and silica were identified in RM-III-5 binders cured for 3 d. It is inferred that the alumina and silica were formed from dehydroxylation of  $Al(OH)_4^-$  and  $H_3SiO_4^-$  monomers under the action of alcohol during the specimen preparation for XRD test. The  $Al(OH)_4^-$  and  $H_3SiO_4^-$  monomers are precursors of the geopolymerization process, which are formed through the dissolution of aluminosilicate sources in the alkaline solution.<sup>15</sup> The peaks of alumina disappeared in RM-III-5 binders cured for 7 d, and the peaks of silica disappeared in the sample cured for 28 d.

(B) FTIR Analysis: The geopolymerization of the binders was also identified by the FTIR spectra shown in Fig. 12. The absorption bands attributed to the asymmetric stretching vibrations of Si-O-Si and Al-O-Si (~1200-950 cm<sup>-1</sup>) in RM-III-5 and RM-III-0 binders became broader with lower intensity than those of the calcined RM sample. The bands attributed to symmetric stretching vibrations of Si–O–Si or Al–O–Si (~689 cm<sup>-1</sup>, ~622 cm<sup>-1</sup>, and ~577 cm<sup>-1</sup>) weakened in RM-III-5 binders cured for 3 d, but became stronger again in the sample cured for 28 d. These transformations implied the dissolution of RM and the formation of new phases during the geopolymerization process. The band attributed to stretching vibrations of O–C–O ( $\sim$ 873 cm<sup>-1</sup>) in the binders implies the formation of cancrinite. The FTIR spectrum of RM-III-5 binders was similar to that of RM-III-0 binders, but different from that of GBFS-III binders in the region of 500–700  $\text{cm}^{-1}$ , which can be attributed to the difference between geopolymer and AAS.

(C) SEM Analysis: The morphological transformations during the geopolymerization process of RM-III-5 and GBFS-III binders are shown in Fig. 13. As shown in Figs. 13(a) and (d), large quantities of nanosized particulates were formed through the dissolution and reorientation reactions of the aluminosilicate sources in alkaline solution. Nanosized particulates, which are called geopolymeric micelles<sup>14</sup> have been observed in many reports.<sup>30,37,38</sup> In Figs. 13(b) and (e), some matrices were formed through the aggregation of the nanosized particulates during the solidification process. At last, most nanosized particulates transformed to homogeneous and highly dense matrices as shown in Figs. 13(c) and (f). The increase in strength of the binders along with curing time can be attributed to the growth of the homogeneous and dense matrix microstructure.

By comparing the SEM images of two binders cured for 3 d, it can be found that there were some undissolved raw material particles in RM-III-5 binders [in Fig. 13(a)], but homogeneous nanosized particles were distributed in the



Fig. 13. SEM images of RM-III-5 binder cured for different ages: (a) 3 d, (b) 7 d, and (c) 28 d; and GBFS-III binder cured for different ages: (d) 3 d, (e) 7 d, and (f) 28 d.

whole microstructure in GBFS-III binders, as shown in Fig. 13(d). In Fig. 13(b), many flocculent gels were also observed in the microstructure, which implied poorly crystalline C-(A)-S-H phase. The C-(A)-S-H gels acted as a bridge or formed a framework for geopolymeric matrices. In a study of the effect of GBFS addition on the microstructure and properties of metakaolin-based geopolymeric materials, Yip et al.<sup>25</sup> found the coexistence of geopolymeric gel and C-S-H gel, which was similar to the structure of ancient concrete. C-S-H gel within the geopolymer worked as a microaggregate and thus produced dense binders, which presented better performance. Similarly, the produced composite materials in this research are also the composite of geopolymer and AAS. This explains why the compressive strength of RM-III-9 binders was higher than that of GBFS-III binders.

# IV. Conclusions

The work demonstrated the feasibility of synthesizing a composite geopolymeric material by the use of calcined RM and GBFS. Synthesizing geopolymer from Bayer RM is a potential disposal and reutilization approach for RM, which could eliminate the negative effect of sodium in RM on its application in other construction materials.

The conclusions are drawn as follows:

- 1. Thermal treatment has a great influence on the aluminosilicate phase transformation of RM. Mineral phases in the raw RM transformed successively with an increase in temperature, forming new phases with different solubility. The optimal condition of thermal treatment for RM was approximately 800°C for 3 h by which the highest dissolution efficiencies of both alumina and silica were obtained.
- To reuse as much RM as possible, the RM/GBFS mass ratio of 5:5 with a satisfactory compressive strength was acceptable for the potential application in construction materials. The optimum dosage of sodium silicate is 6.90 wt% of Na<sub>2</sub>O, with a SiO<sub>2</sub>/Na<sub>2</sub>O molar

ratio of 1.7. The 28-d compressive strength of the composite binders reached the highest value of 49.2 MPa with RM calcined at 800°C, which demonstrated that a higher solubility of the calcined RM leads to a higher compressive strength of the binders.

3. XRD, FTIR, and SEM results well-presented the geopolymerization process of the composite binders made from calcined RM and GBFS. The aluminosilicate materials dissolved in the alkaline solution, forming nanosized particulates for the subsequent reactions. The nanosized particulates accumulated to form highly dense geopolymer matrices in the following solidification process. The main hydration products were poorly crystalline C-(A)-S-H and amorphous geopolymeric materials. It is suggested that the coexistence of geopolymeric gel and C-(A)-S-H gel contributes to a good performance of the composite binders.

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#### References

<sup>1</sup>G. Power, M. Gräfe, and C. Klauber, "Bauxite Residue Issues: I. Current Management, Disposal and Storage Practices," *Hydrometallurgy*, **108** [1–2] 33–45 (2011).

<sup>2</sup>A. R. Hind, S. K. Bhargava, and S. C. Grocott, "The Surface Chemistry of Bayer Process Solids: A Review," *Colloids Surf. A: Physicochem. Eng. Aspects*, **146** [1–3] 359–74 (1999).

<sup>3</sup>R. U. Ayres, J. Holmberg, and B. Andersson, "Materials and the Global Environment: Waste Mining in the 21st Century," *MRS Bull.*, **26** [6] 477–80 (2001).

<sup>4</sup>Y. Cengeloglu, E. Kir, M. Ersoz, T. Buyukerkek, and S. Gezgin, "Recovery and Concentration of Metals from Red Mud by Donnan Dialysis," *Colloids Surf. A: Physicochem. Eng. Aspects*, **223** [1–3] 95–101 (2003).

<sup>5</sup>W. Liu, J. Yang, and B. Xiao, "Application of Bayer Red Mud for Iron Recovery and Building Material Production from Alumosilicate Residues," J. Hazard. Mater., 161 [1] 474-8 (2009).

<sup>6</sup>L. Piga, F. Pochetti, and L. Stoppa, "Recovering Metals from Red Mud Generated during Alumina Production," *J. Miner.*, **45** [11] 54–59 (1993).

Y. Pontikes, P. Nikolopoulos, and G. N. Angelopoulos, "Thermal Behaviour of Clay Mixtures with Bauxite Residue for the Production of Heavy-clay

Ceramics," J. Eur. Ceram. Soc., 27 [2] 1645–49 (2007). <sup>8</sup>N. YalÅIn and V. SevinÅ, "Utilization of Bauxite Waste in Ceramic Glazes," Ceram. Int., 26 [5] 485-93 (2000).

<sup>9</sup>J. Yang, D. Zhang, J. Hou, B. He, and B. Xiao, "Preparation of Glass-Ceramics from Red Mud in the Aluminium Industries," Ceram. Int., 34 [1] -30(2008).

<sup>10</sup>C. Klauber, M. Gräfe, and G. Power, "Bauxite Residue Issues: II. Options <sup>67</sup> Franker Karley and State (1997) and State (1997)

from Red Mud Wastes Produced in the Sintering Alumina Process," *Constr. Build. Mater.*, **22** [12] 2299–307 (2008).

<sup>12</sup>M. Singh, S. Upadhayay, and P. Prasad, "Preparation of Special Cements from Red Mud," *Waste Manage.*, 16 [8] 665–70 (1996).
<sup>13</sup>M. Singh, S. Upadhayay, and P. Prasad, "Preparation of Iron Rich Cements using Red Mud," *Cem. Concr. Res.*, 27 [7] 1037–46 (1997).
<sup>14</sup>J. Davidovits, *Geopolymer Chemistry and Applications*, 2nd edition. Geo-

<sup>15</sup>H. Xu and J. S. J. Van Deventer, "The Geopolymerisation of Alumino-Silicate Minerals," *Int. J. Miner. Process.*, **59** [3] 247–66 (2000).
<sup>16</sup>D. D. Dimas, I. P. Giannopoulou, and D. Panias, "Utilization of Alumina

Red Mud for Synthesis of Inorganic Polymeric Materials,' Miner. Process.

 Extr. Metall. Rev., **30** [3] 211–39 (2009).
<sup>17</sup>D. Bondar, C. J. Lynsdale, N. B. Milestone, N. Hassani, and A. A. Ramezanianpour, "Effect of Heat Treatment on Reactivity-Strength of Alkali-Acti-

<sup>20</sup>C. K. Yip and J. S. J. Van Deventer, "Microanalysis of Calcium Silicate Hydrate Gel Formed Within a Geopolymeric Binder," *J. Mater. Sci.*, **38** [18]

<sup>21</sup>D. Khale and R. Chaudhary, "Mechanism of Geopolymerization and Factors Influencing its Development: A Review," *J. Mater. Sci.*, 42 [3] 729–46 (2007).
<sup>22</sup>I. Lecomte, C. Henrist, M. Liégeois, F. Maseri, A. Rulmont, and R. Clo-

"(Micro)-Structural Comparison Between Geopolymers, Alkali-Activated ots, Slag Cement and Portland Cement," J. Eur. Ceram. Soc., 26 [16] 3789-97

<sup>(2006)</sup>. <sup>23</sup>A. Buchwald, H. Hilbig, and C. Kaps, "Alkali-Activated Metakaolin-Slag Blends-Performance and Structure in Dependence of their Composition,' Mater. Sci., 42 [9] 3024-32 (2007).

<sup>24</sup>M. Izquierdo, X. Querol, J. Davidovits, D. Antenucci, H. Nugteren, and C. Fernandez-Pereira, "Coal Fly Ash-Slag-Based Geopolymers: Microstructure and Metal Leaching," J. Hazard. Mater., **166** [1] 561-6 (2009).

C. K. Yip, G. C. Lukey, and J. S. J. Dean, "Effect of Blast Furnace Slag Addition on Microstructure and Properties of Metakaolinite Geopolymeric Materials"; pp. 187-209 in Advances in Ceramic Matrix Composites IX, Vol. 153. Edited by N. P. Bansal, J. P. Singh, W. M. Kriven, and H. Schneider. John Wiley & Sons, Inc., Hoboken, NJ, 2006.

Y. Zhang, W. Sun, Q. Chen, and L. Chen, "Synthesis and Heavy Metal Immobilization Behaviors of Slag Based Geopolymer," J. Hazard. Mater., 143 [1-2] 206–13 (2007).
<sup>27</sup>D. Panias, I. P. Giannopoulou, and T. Perraki, "Effect of Synthesis

Parameters on the Mechanical Properties of Fly Ash-Based Geopolymers,' Colloids Surf. A: Physicochem. Eng. Aspects, 301 [1-3] 246-54 (2007)

<sup>28</sup>A. Hajimohammadi, J. L. Provis, and J. S. J. van Deventer, "The Effect of Silica Availability on the Mechanism of Geopolymerisation," *Cem. Concr.* 

<sup>20</sup>V. D. Sindhunata, J. S. J. Van Deventer, G. C. Lukey, and H. Xu, "Effect of Curing Temperature and Silicate Concentration on Fly-Ash-Based Geopolymerization," *Ind. Eng. Chem. Res.*, 45 [10] 3559–68 (2006).

F. Puertas, S. Martínez-Ramírez, S. Alonso, and T. Vázquez, "Alkali-Activated Fly Ash/Slag Cements: Strength Behaviour and Hydration Products,'

Cem. Concr. Res., **30** [10] 1625–32 (2000). <sup>31</sup>J. G. S. Van Jaarsveld, J. S. J. Van Deventer, and L. Lorenzen, "The Potential Use of Geopolymeric Materials to Immobilise Toxic Metals: Part I. Theory and Applications," *Miner. Eng.*, **10** [7] 659–69 (1997). <sup>32</sup>H. A. Gasteiger, W. J. Frederick, and R. C. Streisel, "Solubility of Alumi-

nosilicates in Alkaline Solutions and a Thermodynamic Equilibrium Model, Ind. Eng. Chem. Res., 31 [4] 1183–90 (1992).

W. Kejin, S. P. Shah, and A. Mishulovich, "Effects of Curing Temperature and NaOH Addition on Hydration and Strength Development of Clin-

ker-Free CKD-Fly Ash Binders," *Cem. Concr. Res.*, **34** [2] 299–309 (2004). <sup>34</sup>P. Duxson and J. L. Provis, "Designing Precursors for Geopolymer Cements, *J. Am. Ceram. Soc.*, **91** [12] 3864–69 (2008). <sup>35</sup>I. Ismail, S. Bernal, J. L. Provis, S. Hamdan, and J. J. Deventer, "Micro-

structural Changes in Alkali Activated Fly Ash/Slag Geopolymers with Sulfate osure," *Mater. Struct.*, **46** [3] 361–73 (2013). <sup>1</sup>L. P. Ogorodova, L. V. Mel'chakova, M. F. Vigasina, L. V. Olysich, and I. Exposure,

V. Pekov, "Cancrinite and Cancrisilite in the Khibina-Lovozero Alkaline Complex: Thermochemical and Thermal Data," *Geochem. Int.*, **47** [3] 260–67 (2009). <sup>37</sup>P. Duxson, A. Fernández-Jiménez, J. Provis, G. Lukey, A. Palomo, and J

S. J. van Deventer, "Geopolymer Technology: The Current State of the Art,"

J. Mater. Sci., 42 [9] 2917–33 (2007). <sup>38</sup>W. M. Kriven, J. L. Bell, and M. Gordon, "Microstructure and Microchemistry of Fully-Reacted Geopolymers and Geopolymer Matrix Composites"; pp. 227-50 in Advances in Ceramic Matrix Composites IX, Vol. 153. Edited by N. P. Bansal, J. P. Singh, W. M. Kriven, and H. Schneider. John Wiley & Sons, Inc., Hoboken, NJ, USA, 2006.