

## **PROPERTIES OF ALKALI ACTIVATED MATERIALS MADE WITH BAUXITE REFINING RESIDUE (RED MUD-RM) AND BLENDS OF RM WITH FLY ASH (FA)**

**O. Alelweet<sup>1</sup>**

**S. Pavia<sup>1</sup>**

<sup>1</sup>Department of Civil Engineering. Trinity College Dublin. Museum Building. Dublin 2. IRELAND.  
Corresponding author: pavias@tcd.ie

### **Keywords**

Low carbon cement; red mud; fly ash; geopolymers; alkali activation.

### **Abstract**

A bauxite refining residue (RM), both alone and blended with FA at 30% and 50%, is activated with alkalis ( $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ) to produce geopolymer cements. Alkali-activated materials (AAMs)/geopolymers are a more sustainable alternative to Portland cement (PC) products because they largely consist of waste. They can save energy (consumed for the calcination of raw materials and the grinding of PC clinker) and reduce carbon emissions (emitted on combustion of fossil fuels and decarbonisation of the raw materials for PC clinker production). They can provide an alternative route to transform waste into construction materials. They can also reduce landfill use, lowering soil and water contamination, and lessen the exploitation of non-renewable resources such as the shale, limestone and clay use for PC production. The RM geopolymers achieved significant strengths. Even the materials made with RM alone reached significant strengths up to  $\sim 7\text{MPa}$  at 90 d. Replacing RM with FA increased strength. The compressive strength of the 30% FA materials at 28 d.:  $\sim 7$  to  $11\text{MPa}$ , increased to  $\sim 9 - 12\text{MPa}$  with 50% FA substitution, reaching over  $15\text{MPa}$  at 90 days. Using a blend of activators at high silica ratio ( $\text{Na}_2\text{SiO}_3/6\text{M NaOH}=2.5$ ) provides the greatest strengths and the maximum durability under accelerated weathering. The  $\text{Na}_2\text{SiO}_3$  activator alone delivers low strengths and reduces the resistance to weather, probably due to an excess of unreacted Si preventing polymerisation. The setting times are within workable limits. Initial setting times range from 340 to 660 minutes, and the pastes with the highest FA content are the slowest to set. The geopolymers made with RM alone form scarce cementing hydrates, hence the RM acted as a filler during polymerisation. However, the RM-FA geopolymers show abundant hydrates including low crystallinity gels and needle-shaped phases-probably AFm. The gels contain significant Na that hints to the presence of N-A-S-H.

## **1. INTRODUCTION**

To decarbonise the construction industry and lower its environmental impact, there is a need for high-performance materials that can replace Portland cement (PC) products. PC is probably the construction material most widely used in the world. It is the most common binder in concrete, pre-cast units, blocks, mortars, structural columns and beams and other construction elements. However, it carries a substantial environmental impact. Most of the impact of PC comes from the decarbonisation of the raw materials and the burning of the fossil fuels which are required to produce the PC clinker. On another hand, millions of tonnes of waste are generated annually worldwide, spoiling valuable land which is used as landfill, and contaminating the soil and groundwater.

Alkali-activated materials (AAMs) / geopolymers are a more sustainable alternative to PC goods because, rather than clinker, they largely consist of waste. They are inorganic polymers produced when alkaline solutions react with aluminosilicate precursors to create cementitious material [1-2]. (Davidovits, 1994; Duxson et al., 2007). The designations AAMs and geopolymer are often used unclearly. Some authors consider geopolymers a subset of AAMs, made with an aluminosilicate precursor of low calcium content [3] (Provis, 2018). However, others claim that geopolymers form 3-D polymer structures, while AAMs are monomers or dimers of Si tetrahedra [4-6]. (Davidovits, 1976; Lecomte et al. 2006; Davidovits 2018). Nevertheless, geopolymers are AAMs, and AAMs are polymer structures.

This paper uses bauxite residue (red mud-RM), an aluminosilicate with low calcium content, as a precursor. Therefore, we refer to AAMs and geopolymers randomly. The use of geopolymers in lieu of PC based products can save significant energy (consumed for the calcination of raw materials and the grinding of the PC clinker) and can also reduce carbon emissions (those emitted on combustion of fossil fuels and decarbonisation of the raw materials for PC clinker production). It can also reduce the use of landfill,

lower soil and water contamination, and lessen the exploitation of non-renewable natural resources such as the shale, limestone and clay use for PC production. Furthermore, it can provide an alternative route to transform waste into construction materials.

The RM used in this research was produced, as a by-product of aluminium production, by the Ma'aden Mining Industries of the Kingdom of Saudi Arabia which are one of the main world producers. They generate circa 6,000 tonnes of RM per day which results in disposal problems and high land decommissioning costs for landfill disposal. RM contains Si and Al which can be active in an alkali media. This indicates potential for use in alkali activation technology [7] (Dimas et al., 2009). RM can be high in silica inherited from the parent bauxite impurities. It can also include some residual Al [8] (Provis et al., 2014). However, the typically low Si/Al ratio may result in a weak final product [2,9]. (Duxson et al., 2007; Hajjaji et al., 2013). The RM used to generate the alkali activated cements was studied by Alelweet et al. (2021) [10]. According to the authors, the RM is pozzolanic, and the pozzolanic activity is mainly due to the reaction of feldspathoids and the formation of zeolitic and feldspathoid-based hydrates.

## 2. MATERIALS AND METHODS

The RM waste is produced as a by-product by the Ma'aden Mining Industries during the refining of bauxite for aluminium production. Fly ash (FA)-class F, from a coal-burning power plant in Moneypoint, Co. Clare, Ireland, was also used as a precursor. The chemical composition was determined by XRF elemental quantitative analysis, with a ThermoFisher Scientific and Edwards Analytical using a Quant'X EDX Spectrometer and UniQuant analysis package. The results were expressed as a % oxide by weight. The carbon content was estimated by measuring the loss on ignition (LOI). The mineral composition was studied with X-Ray diffraction (XRD), using a Phillips PW1720 XRD with a PW1050/80 goniometer and a PW3313/20 Cu k-alpha anode tube at 40kV and 20mA. All measurements were taken from 3 to 60 degrees ( $2\theta$ ) at 0.02 degrees/second. The particle size was analysed with a Malvern Mastersizer 2000 apparatus based on laser diffraction. The specific surface area (SSA) was measured using a Quantachrome Nova 4200e apparatus and the Brunauer-Emmett-Teller BET theory, which relates the physical adsorption of gas molecules on the particles surface with their specific surface area.

A SEM/EDX system was used to investigate the microstructure of the geopolymers and their cementing hydrates. The elemental composition of the hydrates was determined with EDX. The qualitative nature of the technique does not deliver enough resolution to clearly determine the nature of the hydrates. However, an indication of the nature of the hydrates was established.

The setting times of the geopolymers were measured with the Vicat test EN 196-3:2016, which determines the stiffening rate of a paste by dropping a needle from a fixed height and measuring its penetration. The initial and final setting times are standard references which provide comparative data.

Flexural strength tests were performed using the centre point loading method According to EN 196-1:2016. The prisms (160 x 40 x 40 mm) were mounted on fixed supports with the longitudinal axis perpendicular to them when the load was applied. The compressive load is applied to the half prisms by loading the sides. EN 196-1: 2016 was used to test this property.

A material must show resilience under salt crystallization, wet-dry and freeze-dry cycles. Accelerated durability cycles were performed according to RILEM recommendations. These tests aimed to assess the resistance of the materials to weathering agents and quantify the extent of damage that they cause. To this end, the variation in strength after cycling and the macroscopic damage were evaluated, and the performance compared with a standard CEM II mix. After each cycle, the condition of the specimens was recorded, and the results were reported in terms of weight loss (expressed as a percentage of the initial dry weight) and the number of cycles required to induce failure.

## 3. RESULTS

### 3.1. CHARACTERIZATION OF THE RM AND FA PRECURSORS

According to Alelweet et al. 2021 [10], the RM consists of gibbsite and boehmite inherited from the parent bauxite, and cancrinite, chantalite and sodalite formed during the refining (Bayer) process. The presence of feldspathoids, instead of zeolites, is owed to the high available silica and high alkali content of the RM [10]. According to the authors, the Saudi RM has high SiO<sub>2</sub> and high alkalinity, and an abundant specific surface area available for reaction; the chloride and carbon contents are low, and no environmental toxicity is inferred from its chemistry. The geopolymer was made with RM calcined at 400°C because the thermal treatment enhanced reactivity. According to Alelweet et al. (2021) [10], at 400°C, the RM is most amorphous and has the greatest activity due to the transformation of gibbsite (Al (OH)<sub>3</sub>) into boehmite (Y- AlO(OH)) and amorphous alumina polymorphs, and the presence of maximum cancrinite. According to the authors, the 400°C RM consists of hematite (Fe<sub>2</sub>O<sub>3</sub>), cancrinite (Na<sub>6</sub>Ca<sub>2</sub>[(CO<sub>3</sub>)<sub>2</sub>]Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>·2H<sub>2</sub>O) and sodalite (Na<sub>4</sub>Si<sub>3</sub>Al<sub>3</sub>O<sub>12</sub>Cl), highly reactive phases that should facilitate polymerisation. Previous authors also noted that calcination improves the dissolution of aluminosilicate phases in RM enhancing geopolymerization [11] (Ye *et al.*, 2012).

### 3.2. DESIGN OF THE GEOPOLYMER CEMENT

According to Provis et al.(2014) [8], low Al in RM is the most significant challenge for the use of RM in alkali activation technology. However, the Saudi RM has significant silica (20%) and alumina (30%) and low Ca (5%). Therefore, it is possible that the Saudi RM may produce polymers alone if suitably activated. Nevertheless, to enhance polymerisation, the RM was blended with FA as a supplementary source for Si and Al. According to Alelweet and Pavia (2020) [12], the FA (table 1) is highly reactive including

abundant glass (40-60%); it is ultrafine (with 90% of the particles under 100  $\mu\text{m}$  and 50% under 15  $\mu\text{m}$ ), and it has high specific surface area, at 6500 $\text{m}^2/\text{kg}$ . Therefore, the FA should contribute abundant reactive Si and Al.

Table 1. Chemical composition of the precursors used to make the RM geopolymers (%wt). CEM II: SSA = 1880  $\text{m}^2/\text{kg}$ ; D50  $\mu\text{m}$  = 24.9.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Si/Al	Ca/Si	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	SO <sub>3</sub>	TiO <sub>2</sub>	MnO	SSA m <sup>2</sup> /kg	D50 $\mu\text{m}$	LOI 450 °C
RM	19.6	29.8	5.0	0.6	0.25	12.9	24.0	0.09	0.0	1.6	5.1	0.02	9347	3.8	5.0
FA	53-65	22.5	3.0	2.5	0.07	6.0	0.7	1.70	1	1	1	0.07	6500	15	1.6

The activators were chosen based on the literature. In general, an increase in NaOH content or concentration increases alkalinity which escalates the dissolution rate of aluminosilicates [13,14] (Fernández-Jiménez and Puertas, 2003; Ke *et al.*, 2015) and encourages setting and strength development. However, at high NaOH concentration, an excess of OH<sup>-</sup> and Na<sup>+</sup> lowers mechanical strength. NaOH at 6M has been proposed as the optimum activator to enhance reaction and mechanical properties of RM based geopolymers [15] (Kumar and Kumar, 2013). Higher NaOH concentrations promote the dissolution of the Si and Al in the precursors which normally facilitates polycondensation because of the increase of the SiO<sub>2</sub>/Na<sub>2</sub>O mass ratio in the aqueous phase. However, very high initial NaOH concentrations damage polycondensation because, over a threshold, the amount of dissolved Si and Al remains almost constant while the free Na<sup>+</sup> increases, resulting in lower SiO<sub>2</sub>/Na<sub>2</sub>O mass ratios in the aqueous phase that lower polycondensation [7] (Dimas *et al.* 2009). Furthermore, the Na<sup>+</sup> excess can form sodium carbonate due to atmospheric carbonation which may disrupt the polymerization process [16,17] (Barbosa *et al.*, 2000; Al Bakri *et al.*, 2013). Singh *et al.* (2016) [18] studied 30-50% RM geopolymers, blended with FA and GGBS and activated with NaOH 6-10M and Na<sub>2</sub>SiO<sub>3</sub>/NaOH at 2.5. The results showed compressive strength ranging from 6 to 12 MPa, and that increasing RM substitution and NaOH molarity lowered strength. The optimum NaOH molarity was 6M for maximum strength. According to Singh *et al.* (2018) [19] geopolymers made with 30% RM, FA (class-F) and 10% GGBS activated with NaOH 6 M exhibited maximum strength. Therefore, polycondensation is best at intermediate NaOH concentration of around 6M.

The activators were blended as it is generally recommended to blend Na<sub>2</sub>SiO<sub>3</sub> with NaOH to minimize the disadvantages of NaOH activation such as heat generation. Singh *et al.*, 2016 [18] developed a RM-FA geopolymer with NaOH/Na<sub>2</sub>SiO<sub>3</sub> (1 /2.5). The RM content varied from 10 to 100% and the NaOH concentration from 6 to 12 M. The geopolymer containing 30% RM, activated with a 12M NaOH solution obtained the best 28-day strength at 38 MPa.

Table 2. Composition of the RM geopolymer materials (3:1 – sand: RM+FA). NaOH concentration =6M; Sand (59-66%); water (9.8-11.5%).

Notation	RM %wt	FA %wt	Na <sub>2</sub> SiO <sub>3</sub> / NaOH	NaOH %	Na <sub>2</sub> SiO <sub>3</sub> %	Activator / b	w/b
RM1	100	—	1	1.74	4.71	0.88	0.43
RM2	100	—	2.5	1.08	7.30	0.97	0.39
RM3	100	—	Na <sub>2</sub> SiO <sub>3</sub>	—	11.14	1.08	0.33
RM-FA1	70	30	1	1.69	4.59	0.85	0.42
RM-FA2	70	30	2.5	1.05	7.12	0.94	0.38
RM-FA3	70	30	Na <sub>2</sub> SiO <sub>3</sub>	—	10.89	1.05	0.32
RM-FA4	50	50	1	1.65	4.47	0.82	0.41
RM-FA5	50	50	2.5	1.02	6.95	0.91	0.37
RM-FA6	50	50	Na <sub>2</sub> SiO <sub>3</sub>	—	8.16	1.08	0.34

### 3.3. MECHANICAL STRENGTH

Even the materials made with RM alone reached significant flexural and compressive strengths at 90 days up to ~7MPa, and the strengths increased significantly between 28 and 90 days. Using a blend of activators at high silica ratio (Na<sub>2</sub>SiO<sub>3</sub> / 6M NaOH = 2.5) provides the greatest mechanical strengths agreeing with the authors above. The Na<sub>2</sub>SiO<sub>3</sub> activator alone delivers lower strengths, but the values are still significant when part of the RM has been replaced with FA.

The significant strength upsurge between 28 and 90 days, can be related to the conversion of the initial hydrates into phases of greater strength. During the hydration of calcium aluminates (e.g. in CACs) metastable hydrates can form that may persist for

many years before they convert into stable phases [20] (Lawrence and Hewlett, 1988). Risdanareni et al. (2015) [21] and other authors also report that geopolymer binders do not reach full strength at 28 days.

Table 3. Mechanical strength of AA RM materials at 28 and 90 days. COVs=0.001-0.19 (flexural strength). COVs=0.015-0.22 (compressive strength).

Notation	FA %	Na <sub>2</sub> SiO <sub>3</sub> / 6M NaOH	flexural strength (N/mm <sup>2</sup> )		compressive strength (N/mm <sup>2</sup> )	
			28d	90d	28d	90d
RM1	0	1	0.10	2.70	4.53	6.73
RM2	0	2.5	1.03	5.14	4.68	6.85
RM3	0	Na <sub>2</sub> SiO <sub>3</sub>	0.86	1.28	1.69	2.30
RM-FA1	30	1	1.70	4.11	6.87	7.72
RM-FA2	30	2.5	4.36	4.67	10.85	11.70
RM-FA3	30	Na <sub>2</sub> SiO <sub>3</sub>	2.21	3.83	5.74	5.89
RM-FA4	50	1	4.17	4.39	9.90	13.22
RM-FA5	50	2.5	5.98	7.08	11.54	15.53
RM-FA6	50	Na <sub>2</sub> SiO <sub>3</sub>	3.95	6.68	8.90	10.30

Replacing RM with FA increased the flexural and compressive strengths. The compressive strength of the 30% FA materials: ~7 to 11 MPa at 28 days, increased to ~9 - 12 MPa with 50% FA substitution; and reached over 15 MPa at 90 days. The superior strength of the FA materials compared to the RM alone is probably related to the contribution of the Al in the FA to the production of cements [15] (Kumar and Kumar, 2013). Mudgal *et al.* (2021) [22] confirmed a high dense structure in a RM-FA geopolymer, with Al participating in the geopolymerization.

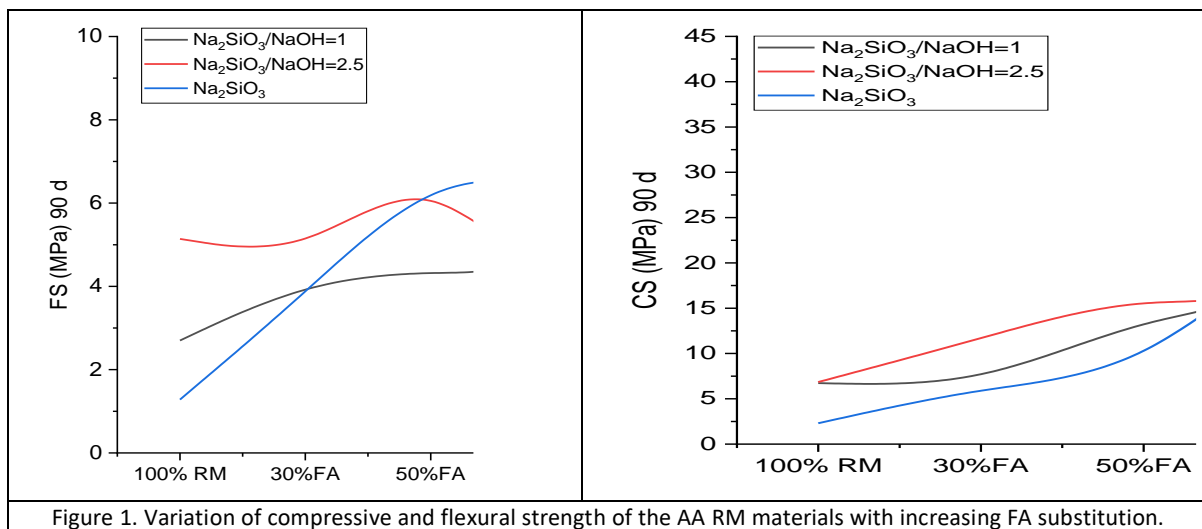


Figure 1. Variation of compressive and flexural strength of the AA RM materials with increasing FA substitution.

The lower strength provided by the Na<sub>2</sub>SiO<sub>3</sub> activator alone can be attributed to an excess of Si in the mix which results in unreacted Si that prevents to enhance the formation of geopolymer cement agreeing with Provis *et al.* (2014) [8]. The silica provided by the activator is more active in geopolymerization than the silica in the RM precursor [9] (Hajjaji *et al.*, 2013). However, an excess of silica may hinder polymerisation, hence the optimum Si/Al ratio for a given geopolymer matrix varies with the amount of soluble silica in the raw material [19] (Singh *et al.*, 2018).

### 3.4. SETTING

The setting times of the alkali activated RM pastes appear in table 4. The initial setting times vary greatly, ranging from 340 to 660 minutes. The pastes with the highest FA content take the longest to set. The final set follows a similar trend. The RM materials take longer to set than CEM II because geopolymerization is generally slower than PC hydration.

The initial and final setting times tend to increase when increasing the FA content. This agrees with former authors. Kumar and Kumar (2013) [14], using blends of FA with 0–40% RM, showed that the initial and final setting times increased when increasing the FA content (210 and 310 minutes for the initial and final set respectively). Similarly, Lin *et al.* (2020) [23] found that the initial

setting time increased from 4.6 h to 5.5 h and the final setting time from 7.5 to 9.5 h when increasing FA content from 5 to 25% in RM. The author attributed this to the presence of inert FA cenospheres. According to Kuenzel and Ranjbar (2019) [24], reactive FA cenospheres dissolve completely during geopolymerisation while, in partially reactive FA cenospheres, only the outer vitreous Si shell dissolves and the inert material remains un-reacted.

Table 4. Setting time of the alkali-activated RM materials. CEM II is a 3:1 mix at w/b=0.50.

Notation	FA %	Setting times (min)		Na <sub>2</sub> SiO <sub>3</sub> / 6M NaOH
		Initial set	Final set	
RM1	0	340	400	1
RM2	0	400	490	2.5
RM3	0	410	510	Na <sub>2</sub> SiO <sub>3</sub>
RM-FA1	30	400	460	1
RM-FA2	30	420	480	2.5
RM-FA3	30	440	500	Na <sub>2</sub> SiO <sub>3</sub>
RM-FA4	50	570	620	1
RM-FA5	50	610	660	2.5
RM-FA6	50	560	610	Na <sub>2</sub> SiO <sub>3</sub>
CEM II	-	130	140	-

### 3.5. MICROSTRUCTURE AND CEMENTING HYDRATES IN THE RM AND RM-FA GEOPOLYMERS

In general, alkali-activated cements have low Ca/Si molar ratios (0.7-0.3) that are consistent with longer, more polymerised, aluminosilicate chains [5] (Lecomte *et al.*, 2006). The low calcium system of the RM and RM-FA geopolymers (Ca/Si = 0.07-0.26 - table 1) may result in a lack of calcium silicate hydrate (C-S-H) cements. The low Ca content can disable the synthesis of C-A-S-H cement, as the Ca/Si ratio must be at least 0.6 [25] (Martín-Garrido *et al.*, 2020), being generally over 2 in PC. SEM analyses were carried out in pastes aged 28 days.

**In the geopolymer cements made with RM alone**, a scarce cementing phase grows outwards into the pore space (figure 2). These cements are semi amorphous, and their accurate composition couldn't be recorded. However, some representative compositions and morphologies are included in figure 2B and table 5. Many of the typical particles and irregularly-shaped aggregates comprising the RM seem unchanged (figure 2) agreeing with Dimas *et al.* (2009) [7], who claim that RM mainly acts as a filler during polymerisation. Dimas *et al.* (2009) [7] studied the mineralogical phases of RM+metakaolin polymers during geopolymerization. They observed that the initial RM phases did not change during geopolymerization. The authors conclude a negligible solubility of RM in caustic solutions, and that the RM mainly acts as a filler. They claim that it was the metakaolin's illite and amorphous aluminosilicates that dissolved, providing Al and Si to form cements during geopolymerization, and found a zeolite cement ( $2\theta=18^\circ$ ) agglomerating the RM particles. No significant changes were apparent with varying Na<sub>2</sub>SiO<sub>3</sub>/NaOH activators.

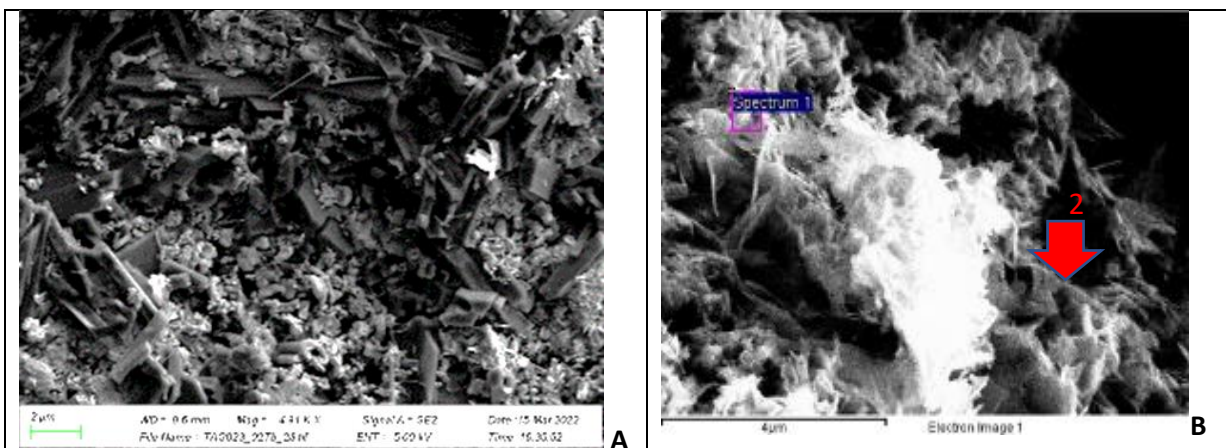


Figure 2. Cementing hydrates and microstructure of geopolymers made with RM alone, activated with Na<sub>2</sub>SiO<sub>3</sub>/NaOH =2.5.

Figure 2A. RM particles largely unchanged with scarce cementing gels.

Figure 2B. Detail of cementing hydrates.

Table 5. Chemical composition %wt of 1 and 2 in figure 2B.

Spectrum	Na	Al	Si	Ca	Fe
1	2.98	1.43	1.32	1.24	47.90
2	2.69	1.38	1.12	0.92	39.46

In the geopolymer cements made with RM and FA, the FA provided active Si and Al, hence more profuse cementing hydrates were expected. The SEM evidenced abundant cementing hydrates including low crystallinity gels and needle-shaped phases (figures 3 and 4). It also evidenced fan-shaped sprays of zeolite crystals like the zeolitic cements found on pozzolanic activation of the RM by Alelweet et al. (2021) [10]. The chemical EDX analyses suggest that the needles are probably AFm phases (figure 4A and table 7). The crystallinity of the gel is too low to obtain reliable EDX analyses. It has a morphology like C-S-H, but the RM+FA material is a low Ca system. According to former authors, this typically produces N-A-S-H hydrates, an alkali aluminosilicate structure different from the C-S-H gel typical of PC hydration [26] (García-Lodeiro *et al.*, 2013) which agrees with the high %wt Na in the spectrums of the gels (figure 4B and table 8). Increasing the amount of silica in the activator slightly raised the Si content of the hydrates, but the SEM / EDX didn't provide enough resolution to determine a clear change in the nature of the hydrates.

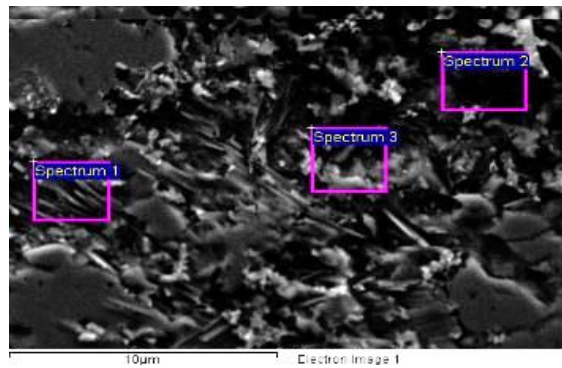
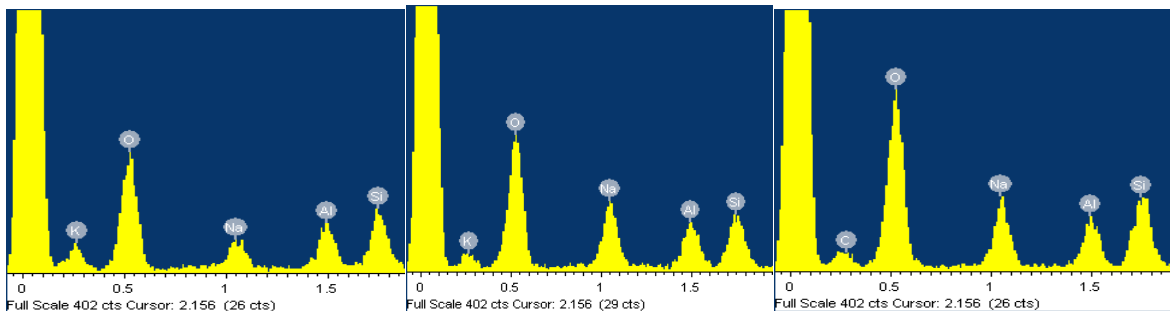


Figure 3. Cementing hydrates and microstructure of geopolymers made with 70% RM and 30% FA activated with  $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2.5$

Table 6. Chemical composition of spectrums 1, 2 and 3 in figure 3 (from left to right); and their main constituents - %wt.



Spectrum	C	O	Na	Al	Si	K
1	9.82	49.98	7.63	13.75	22.82	5.82
2	-	48.06	15.20	11.75	18.16	6.84
3	17.08	44.43	11.11	9.37	18.02	-

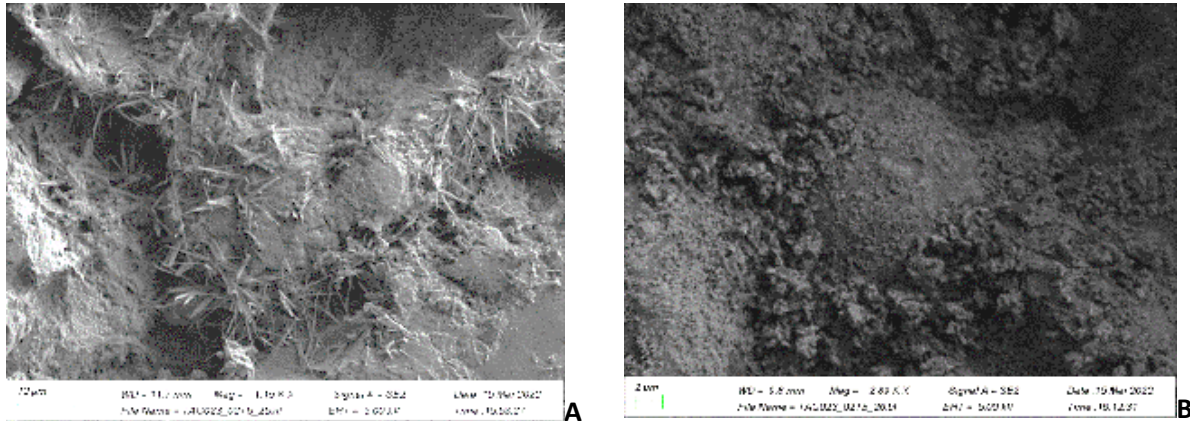


Figure 4. Cementing hydrates and microstructure of geopolymers made with 50% RM and 50% FA activated with  $\text{Na}_2\text{SiO}_3/\text{NaOH}=2.5$ .

Figure 4A. Needle-shaped hydrates, likely AFm phases.

Figure 4B. Low crystallinity hydrates, likely N-A-S-H.

Table 7. Chemical composition (%wt) of the needle-shaped hydrates in figure 4A. From left to right spectrums 1, 2 and 3; and their main constituents - %wt.

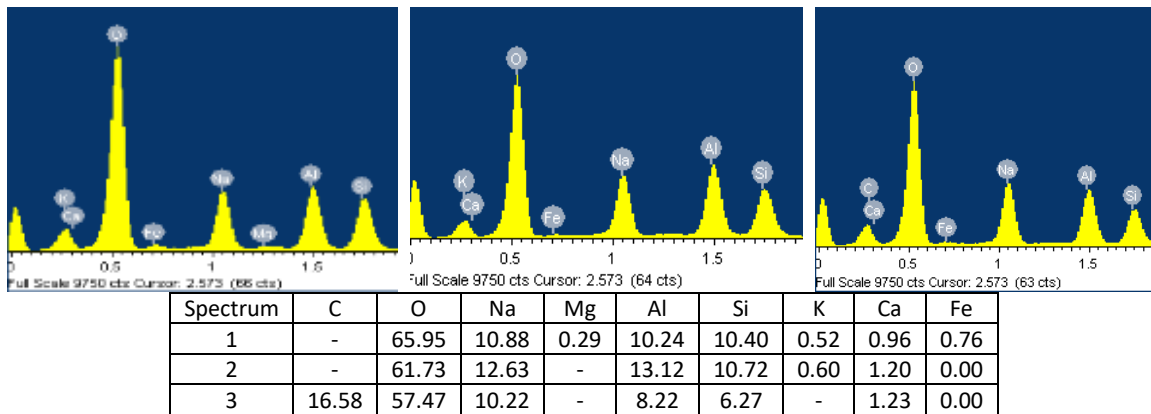
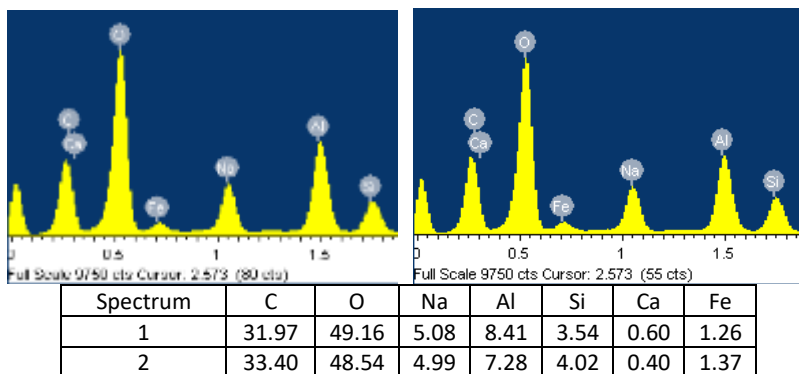


Table 8. Chemical composition (%wt) of the semi amorphous gels in figure 4B shown in EDX spectrums 1 (left) and 2 (right) and their main constituents - %wt.



### 3.6. DURABILITY BY ACCELERATED CYCLING

The specimens were subject to weathering cycles after 28 days of curing, and the strength and mass loss, as well as the physical damage, were assessed after cycling. Despite reaching substantial strengths, many of the AAMs made

with RM alone did not resist weathering cycles, and they were particularly vulnerable to frost action. The specimens suffered cracks and swelling after cycling, some after one cycle (RM-1) and others after 15-20 cycles, and they lost considerable strength after cycling (tables 9 and 10).

The type of activator impacts durability: the RM-FA polymers (both with 30 and 50%FA) activated with  $\text{Na}_2\text{SiO}_3 / \text{NaOH} = 2.5$  survived all the durability tests, and using the silicate activator alone tends to lower the resistance to weather (RM-FA-3 and RM-FA-6 failed after hygrothermal and frost cycling). Increasing the amount of NaOH activator lowers the resistance to frost action. Both lowering the silica activator to  $\text{Na}_2\text{SiO}_3 / \text{NaOH} = 1$ , and using the silicate as the only activator, caused failure regardless of the amount of FA replacement.








Table 9. Mass loss and strength after accelerated weathering (N/mm<sup>2</sup>).

Notation	Wet-dry cycling			Freeze-thaw cycling			Salt-crystallization			Control: un-weathered		$\text{Na}_2\text{SiO}_3 / 6\text{M NaOH}$
	Mass loss%	FS	CS	Mass loss%	FS	CS	Mass loss%	FS	CS	FS	CS	
RM1	-	-	-	-	-	-	-	-	-	0.10	4.53	1
RM2	-14.50	0.60	1.41	-	-	-	1.30	2.65	4.05	1.03	4.68	2.5
RM3	-19.80	0.60	0.43	-	-	-	-	-	-	0.86	1.69	$\text{Na}_2\text{SiO}_3$
RM-FA1	-8.80	2.70	11.00	-	-	-	1.80	3.95	12.64	1.70	6.87	1
RM-FA2	-9.60	2.80	5.33	-1.30	0.76	3.41	1.70	8.14	14.69	4.36	10.85	2.5
RM-FA3	-	-	-	-	-	-	-6.50	2.22	4.97	2.21	5.74	$\text{Na}_2\text{SiO}_3$
RM-FA4	-8.30	3.10	13.07	-	-	-	2.20	3.60	21.04	4.17	9.90	1
RM-FA5	-8.60	2.70	8.20	-2.60	0.52	2.80	2.60	6.89	22.06	5.98	11.54	2.5
RM-FA6	-14.00	2.70	2.31	-	-	-	-16.10	1.15	4.70	3.95	8.90	$\text{Na}_2\text{SiO}_3$
CEM II	-4.50	5.60	25.78	-0.70	6.08	23.39	-5.30	6.87	33.07	6.02	37.18	-

Partial RM replacement with FA, tends to improve the resistance to hygrothermal and salt cycling, but only c. 33% of the specimens survived frost action. The RM-FA materials activated with  $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2.5$  lost considerable strength on wet-dry and freeze-thaw cycling but reached significantly higher strengths than the control material after salt cycling. The raise in strength because of the salt crystallization cycles can be due to the crystallization of sodium salts. If this is the case, it cannot be considered a reinforcement of the structure but a weakness, as the salts would readily dissolve with moisture supply to cause further damage.

The low durability is likely due to the need for a longer time for geopolymerization to be completed. Dimas et al. (2009) [7] also found insufficient resistance in RM geopolymers activated with NaOH. They attribute the lack of resistance to weak cross-linking between the polymer layers which could also explain the low flexural strength, and they state that the weak links are due to insufficient aluminium being dissolved during the polymer synthesis, not enough to form strong 3D structures hence forming weak cross-linked 2D structures instead.

Table 10. Deterioration of RM geopolymer mortars after wet-dry cycling.

			
RM1 Spalling	RM2 Cracking, swelling	RM3 Cracks + material loss	
			
RM-FA1 micro cracks + material loss	RM-FA2 microcracks	RM-FA3 Delamination, cracks + material loss	RM-FA6 slight material loss



## 4. CONCLUSION

A bauxite refining residue (RM), both alone and blended with FA at 30% and 50%, is activated with  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  at varying ratios to produce geopolymer cements of low embodied carbon and low environmental impact.

Even the materials made with RM alone reached significant flexural and compressive strengths, up to  $\sim 7\text{MPa}$  at 90 days, and the strengths increased significantly between 28 and 90 days. However, replacing RM with FA increased the flexural and compressive strengths and enhanced durability under accelerated weathering cycles. The compressive strength of the 30% FA materials at 28 days:  $\sim 7$  to  $11\text{MPa}$ , increased to  $\sim 9 - 12\text{MPa}$  with 50% FA substitution; reaching over  $15\text{MPa}$  at 90 days. The setting times vary within workable limits: initial setting times range from 340 to 660 minutes. They take longer to set than CEM II because polymerization is slower than PC hydration. The pastes with the highest FA content take the longest to set.

Using a blend of activators at high silica ratio ( $\text{Na}_2\text{SiO}_3 / 6\text{M NaOH} = 2.5$ ) provided the greatest mechanical strengths and the greatest durability under accelerated weathering. The  $\text{Na}_2\text{SiO}_3$  activator alone delivers lower strengths and tends to lower the resistance to weather, probably due to an excess of unreacted Si preventing polymerisation.

The geopolymer cements made with RM alone display scarce cementing hydrates hence the RM has acted as a filler during polymerisation. The geopolymers made with RM and FA include abundant cementing hydrates of semi-amorphous gels and needle-shaped (probably AFm) phases. The crystallinity of the gel is too low to obtain reliable analyses, but the EDX includes abundant Na that hints to the presence of N-A-S-H phases.

## Acknowledgements

The authors thank Abdul Malik Shaheen of Ma'adem for providing valuable information of the processing and refining process of the bauxite ore in the Ma'adem refineries. The authors also thank the Government of Saudi Arabia, Technical & Vocational Training Corporation and the Saudi Arabian Cultural Bureau for their support and for financing the project. We thank our colleagues in the Civil Engineering laboratories in particular, M. Grimes, our Chief Technician D. McAuley and M. Gilligan for their assistance with testing. The authors thank Dr R. Goodhue of ICRAAG / Geochemistry TCD, and Dr J. Canavan, Geography Department, TCD, Dr. A. Rafferty, of the Centre for Adaptive Nanostructures and Nanodevices and D. Daly of AMBER, Centre for Advanced Materials and CRANN, TCD, for their assistance with the analyses.

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