Durability performance and microstructure analysis of a road base material prepared from red mud and flue gas desulfurization fly ash

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Abstract: The present study aimed to investigate the durability and microstructure evolution of a road base materials (RBM) prepared from red mud and flue gas desulfurization fly ash. The durability testing showed that the strength of RBM with the blast furnace slag addition of 1\%, 3\%, and 5\% reached 3.81, 4.87, and 5.84 MPa respectively after 5 freezing–thawing (F–T) cycles and reached 5.21, 5.75, and 6.98 MPa after 20 wetting–drying (W–D) cycles, respectively. The results also indicated that hydration products were continuously formed even during W–D and F–T exposures, resulting in the increase for the strength and durability of RBM. The observed increase of macropores (>1 μm) after F–T and W–D exposures suggested that the mechanism for RBM deterioration is pore enlargement due to cracks that develop inside their matrix. Moreover, the F–T exposure showed a greater negative effect on the durability of RBM compared to the W–D exposure. The leaching tests showed that sodium and heavy metals were solidified below the minimum requirement, which indicates that these wastes are suitable for use as a natural material replacement in road base construction.

Keywords: red mud; road base material; durability; microstructure; damage mechanism

1. Introduction

Red mud is a solid waste generated during alumina production from bauxite ores [1–5]. Worldwide production of red mud was nearly 160 million tons in 2015, with China being the top contributor, accounting for more than 88 million tons in 2016; red mud stockpiles were approximately 4 billion tons by 2015 [6]. Its safe disposal is still a global challenge in terms of both environmental pollution concerns [3,4,7–9] and high disposal costs [2,3,10]; the disposal cost is nearly 2\% of the alumina price in addition to an extensive disposal land area of approximately 1 km\textsuperscript{2} in 5 years for a 1 million tons per year alumina plant [10–11]. However, a huge amount of natural materials specifically, gravel and crushed stone, as well as cementitious materials (cement, bitumen, and lime) are depleted by road construction projects [12]. For instance, approximately 25000 tons aggregates per kilometer are required to build a two-lane bitumen road [13], showing how aggregates are one of the most mined resources in the world. Therefore, the replacement of a large amount of natural materials with solid wastes in road base construction would represent a substantial economic and environmental advantage.

In recent years, much effort has been devoted to effectively recycling red mud and mitigate its disposal-related issues [14–15]. The relevant interest lies in the use of red mud as a road base material (RBM) because this practice is expected to consume a large amount of red mud and mitigate issues related to its safe disposal [16]. However, roads undergo surface and structural deterioration under the influence of traffic load and weathering and the damage corresponds to the types of material used for its construction [17]. Thus, long-term durability is an important criterion to be considered in designing a road base [18]. More importantly, an investigation of durability against wetting–drying (W–D) and freezing–thawing (F–T) processes of RBM made of different wastes is also critical to facilitate the incorporation of wastes in geotechnical engineering projects [19]. For in-
stance, Zhang and Li [20] investigated the durability of a RBM containing 70wt% red mud, 7.5wt% lime, and 22.5wt% fly ash and cured for 28 d. After F–T cycles, the compressive strength slightly decreased from 3.4 to 3.2 MPa, which represents a strength loss of 5.88%; this loss is substantially lower than the maximum of 30% allowed by the Chinese standard. Liu et al. [21] also studied the strength and durability of a RBM made of 75wt% red mud–coal gangue and 5wt% blast furnace slag (BFS) and cured for 28 d. Their findings showed that the compressive strength decreased from 9.97 to 5.98 MPa after 20 W–D cycles and to 6.89 MPa after 5 F–T cycles, representing a strength loss of 30.89%. However, the microstructure evolution and deterioration mechanism of the solid-waste-based RBM during W–D and F–T exposures has not been evaluated. Therefore, a better understanding of these conditions on the RBM is required for further improvement of the red mud utilization rate in road base construction.

In this paper, we investigate the effect of weathering on a RBM composed mainly red mud and flue gas desulfurization fly ash (FGDFA) in terms of W–D and F–T exposures, exploring the mechanism of resistance to weathering as well as the mechanism of deterioration of the RBM due to weathering.

2. Experimental

2.1. Raw materials

Red mud was obtained from the Zunyi aluminum plant, and FGDFA was acquired from the Zunyi coal power plant in Guizhou province in China; blast furnace slag (BFS) was also obtained from Guizhou. The chemical composition of red mud, FGDFA, and BFS were analyzed by X-ray fluorescence (XRF, model XRF-1800, Shimadzu, Japan); the results are presented in Table 1.

The aggregates used in this study were crushed rocks from Guizhou Province. Guizhou is located in southwest China and is part of the Qiangtang–Yangtze–South China landmass. It is one of the regions in China with the most completely developed sedimentary stratum. Cambrian strata are the most widely distributed, with dolomite being the main lithology [22].

The mineralogy of raw materials was analyzed by X-ray diffraction (XRD) on a diffractometer (Bruker D8 ADVANCE) equipped with a Cu Ka radiation source operated at 40 kV and 200 mA; samples were scanned over the 2θ range from 10° to 90°, as shown in Fig. 1. The main chemical composition was Al(OH), CaSO₄, and Ca₃SiO₅ in the red mud and CaSO₄·2H₂O in the FGDFA.

2.2. Procedures

2.2.1. Specimen preparation

Three proportions of road base materials (RBMs) were designed with different contents of the binder BFS and corresponding specimens with the size of 50 mm × 50 mm were prepared as per standard T 0841-2009 for testing the unconfined compressive strength and its change during the W–D and F–T cycles and for conducting the leaching test. Table 2 shows the composition of the designed RBMs.

### Table 1. Chemical composition of raw materials wt%

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red mud</td>
<td>19.484</td>
<td>22.45</td>
<td>19.55</td>
<td>8.83</td>
<td>13.26</td>
<td>3.905</td>
<td>1.14</td>
<td>0.832</td>
<td>2.16</td>
<td>7.22</td>
</tr>
<tr>
<td>FGDFA</td>
<td>25.72</td>
<td>17.25</td>
<td>8.42</td>
<td>1.54</td>
<td>20.36</td>
<td>1.86</td>
<td>11.42</td>
<td>0.62</td>
<td>0.98</td>
<td>11.41</td>
</tr>
<tr>
<td>BFS</td>
<td>30.28</td>
<td>15.57</td>
<td>0.29</td>
<td>0.38</td>
<td>39.7</td>
<td>0.66</td>
<td>2.92</td>
<td>8.44</td>
<td>0.42</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Note: LOI—loss on ignition.

![Fig. 1. Mineralogical phases of raw materials. FGDFA represents flue gas desulfurization fly ash; BFS represents blast furnace slag.](image)

### Table 2. Composition of road base materials wt%

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Red mud</th>
<th>Aggregate</th>
<th>FGDFA</th>
<th>BFS</th>
<th>Admixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBM1</td>
<td>35</td>
<td>44</td>
<td>20</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>RBM2</td>
<td>35</td>
<td>44</td>
<td>18</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>RBM3</td>
<td>35</td>
<td>44</td>
<td>16</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

Note: FGDFA represents flue gas desulfurization fly ash; BFS represents blast furnace slag.

To prepare specimens, raw materials were hand mixed to uniformity, water was added according to the optimum water content, and the mixture was stored in an airtight and wa-
terproof bag for 18–24 h to attain a uniform distribution of the moisture throughout the whole mixing process prior to making the test specimens. Then, the uniform mixture was compacted to achieve maximum dry density, as determined in preliminary experiments, and the specimens were demoulded, sealed in plastic bags and cured at 20°C by maintaining 95% humidity for 7 d or 28 d.

2.2.2. Testing conditions

The unconfined compressive strength test was conducted as per the Chinese testing method T 0805-1994 for materials stabilized with inorganic binders for highway engineering.

To simulate the effect of weathering on the durability of the red mud-based RBM, RBM specimens were subjected to W–D and F–T cycles. The effect of W–D exposure was evaluated by subjecting RBM specimens to 0, 4, 8, 12, 16, and 20 W–D cycles after curing for 7 or 28 d. A complete W–D cycle consisted of submerging samples in water for 5 h and then oven drying them at 71°C for 42 h. After completion of every four cycles, the strength was measured. The effect of F–T on the durability of RBM was evaluated as per T 0858-2009 in JTG E51-2009. RBM specimens were subjected to 5 F–T cycles after curing for 28 d as required by the standard. A complete F–T cycle consisted of freezing specimens at –18°C for 16 h and then thawing them for 8 h at 20°C. The mass change was determined after each cycle, whereas the compressive strength was measured after 5 cycles; the strength ratio after F–T was then calculated using the formula

$$\text{BDR} = \frac{R_{\text{Dc}}}{R_{\text{C}}} \times 100\%$$

where BDR is the compressive strength ratio after freezing and thawing, $R_{\text{Dc}}$ is the compressive strength measured after 5 F–T cycles, and $R_{\text{C}}$ is the compressive strength measured before freezing and thawing. The material was considered resistant to the F–T process if the strength loss was less than or equal to 30%, i.e., $\text{BDR} \geq 70\%$.

To qualitatively investigate the mechanism for the durability development for RBMs during W–D and F–T cycles, RBM specimens were analyzed by XRD, Fourier transform infrared (FTIR) spectroscopy, mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM) and aluminum magic-angle spinning nuclear magnetic resonance ($^{27}$Al MAS NMR) before and after W–D and F–T exposures. Specimens were immersed in ethyl alcohol (CH$_3$CH$_2$OH) for 24 h to stop the hydration reaction and then oven-dried at 60°C for 24 h.

For SEM analysis, a small portion of the specimen was coated with gold and the microstructure was observed using a Hitachi SU8020 scanning electron microscope. The FTIR and XRD analyses were performed on fine powders obtained after grinding and sieving dried specimens to 0.074 mm. The XRD data were recorded using a Bruker D8 AD-VANCE (Cu Kα radiation, 40 kV, 200 mA, 10° ≤ 2θ ≤ 90°). The FTIR spectra were recorded in the range 4000–500 cm$^{-1}$ on a Nicolet iS10 FTIR spectrometer. For MIP analysis, the pore size distribution was measured using an AutoPore IV 9500 automatic mercury intrusion meter; the maximum pressure was 228 MPa, and the aperture measurement range was 5–100 nm.

The leaching characteristics of both raw materials and RBM specimens were evaluated as per Chinese standard HJ/T 300-2007. Specimens were immersed in polytetrafluoroethylene (PTFE) bottles containing acidic buffer solution with PH = 2.64 at a solid-to-liquid ratio of 1:20 and then extracted in a rotatory extracting machine spinning at 30 ± 2 r/min for 18 h. Thereafter, the leachate was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce). The obtained results were compared with limits specified in Chinese drinking water standards GB 5749-2006 given the possibility of hazardous compounds leaching from the RBM into groundwater used mainly for drinking purposes.

3. Results and discussion

3.1. Compressive strength of cured RBM

The unconfined compressive strength of RBMs cured at 20°C by maintaining 95% humidity for 7 and 28 d is shown in Fig. 2. The unconfined compressive strength of the RBMs made by different formulas all exceeded 3–5 MPa required in Chinese standards.

![Fig. 2. Compressive strength of cured RBMs made by different formulas.](image)

When cured for same time, the compressive strength of RBM increases with increasing BFS, in the order of RBM1, RBM2, and RBM3. Rao et al. [23] reported that increasing the BFS content promotes the formation of bonds between silicates and aluminates present in red mud and BFS, which
results in the formation of more hydration products that fill voids and refine the pore structure [24] within the RBM and enhance the microstructure densification, which increases the load-bearing capacity and then improves the compressive strength. To deeply understand the densification behavior in RBM as an important phenomenon for the change in load-bearing capacity and strength, the pore size distribution of cured RBM1, RBM2, and RBM3 specimens was explored.

The pore structure properties are summarized in Table 3, and the cumulative pore size distribution and differential pore size distribution of cured RBMs are shown in Fig. 3. The pore size distribution classification scheme was adapted from that of Dong et al. [25]. Pores were divided into four categories: gel pores (<10 nm), medium capillary pores (10–50 nm), large capillary pores (50 nm–1 μm), and macropores (>1 μm).

### Table 3. Pore structure properties of cured road base materials

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Average pore diameter / nm</th>
<th>Pore size distribution / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&lt;10 nm</td>
</tr>
<tr>
<td>RBM1 (7 d)</td>
<td>71.4</td>
<td>2.05</td>
</tr>
<tr>
<td>RBM2 (7 d)</td>
<td>70.9</td>
<td>2.66</td>
</tr>
<tr>
<td>RBM3 (7 d)</td>
<td>60.7</td>
<td>3.12</td>
</tr>
<tr>
<td>RBM3 (28 d)</td>
<td>61.9</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Fig. 3 shows that cured RBM1, RBM2, and RBM3 exhibit a unimodal distribution of pores, where only one maximum peak is observed. The critical pore diameter $d_c$ (determined by the highest point of log differential intrusion curve) for RBM1, RBM2, and RBM3 cured for 7 d, is 363, 351, and 283 nm, respectively. As reported by Fernández–Jiménez et al. [26], the lower the critical pore diameter, the finer the microstructure, which implies that microstructure is refined from RBM1 to RBM3 as a result of the addition of BFS. The critical pore diameter $d_c$ for RBM3 after hydration for 7 and 28 d was 283 and 122 nm respectively, which also indicates that the microstructure becomes finer with age. At early ages, the pores were slightly larger; however, during aging, the maximum volume shifted toward smaller pores. This shift of mean pore size can be explained by the gradual filling of larger pores by the formed hydration products as the hydration proceeds.

The results in Table 3 also show that, in all cured RBMs, large capillary pores (50 nm–1 μm) are predominant, followed by medium capillary pores 10–50 nm, macropores (>1 μm), and gel pores (<10 nm). For the same cured time, the fractions of gel pores (<10 nm) in RBM increase in the order of RBM1, RBM2, and RBM3 with increasing BFS. The reason for this order may also be the increasing of bonds between silicates, aluminates present in red mud and BFS [23], which enhances the formation of hydration products that refine the microstructure and form a denser and more compact microstructure. This explanation is consistent with the strength trend in Fig. 2. We also observed from Table 3 that the fraction of macro pores (>1 μm) decreased with increasing hydration time, which indicates that the formation of hydration products and the pore-filling effect also increased with increasing hydration time, which explains why the compressive strength increased with curing time.

### 3.2. Durability behavior of road base materials

#### 3.2.1. Effect of W–D process on the strength of RBM

The effect of W–D cycles was evaluated on RBM1, RBM2, and RBM3 specimens cured for 7 d as well as RBM3 specimens cured for 28 d. Figs. 4 and 5 show the
variation of strength and the mass loss, respectively, as the functions of the number of W–D cycles. The strength after 20 W–D cycles for RBM1, RBM2, and RBM3 specimens cured for 7 d and RBM3 cured for 28 d is 5.21, 5.75, 6.90, and 7.40, respectively.

![Image](image.jpg)

**Fig. 4.** Variation of compressive strength with the number of wetting–drying (W–D) cycles for different road base materials.

The strength for all specimens showed high durability by withstanding 20 W–D cycles; the compressive strength measured after 20 cycles was higher than that required in Chinese road base compressive strength standard (3–5 MPa). The increasing order of resistance against W–D condition (RBM1 < RBM2 < RBM3) is the same as the order of microstructure densification (according to pore structure in Table 3) because of the increasing hydration degree with increasing BFS [23], which suggests that a denser RBM structure leads to greater resistance to repeated W–D exposure. In addition, Fig. 4 shows that the compressive strength first increased and then decreased with increasing number of W–D cycles, consistent with results reported by Uchaipichat [27]. In the first four cycles, the supplied temperature accelerated pozzolanic reactions and more hydration products were formed [28], which increased the strength. Beyond four cycles, the strength decreased because repeated W–D cycles formed more cracks in the specimen’s microstructure and intensified the heterogeneity of particles, which results in reduced load-carrying capacity and reduced compressive strength [29]. In addition, sudden cooling in water upon termination of heating while the interior of the specimen was still hot may have caused thermal cracking that increased the looseness of particles in the RBM structure, reducing its compressive strength.

### 3.2.2. Effect of F–T process on the strength of RBM

The effect of F–T cycles was evaluated on RBM1, RBM2, and RBM3 specimens cured for 28 d. The strength loss was calculated after 5 cycles, and the results are presented in Fig. 5 together with the compressive strength for specimens before F–T process.

![Image](image.jpg)

**Fig. 5.** Variation of compressive strength before and after freezing–thawing (F–T) exposure for different road base materials.

Fig. 5 shows that all of the RBMs cured for 28 d exhibited high resistance to and survived the F–T process, as revealed by the strength recorded after 5 cycles their strength still meeting the required for RBMs in Chinese standards (3–5 MPa). This resistance against exposure to F–T condition is due to the formation of hydration products that filled voids within specimens, thereby forming a more densified, crack-resistant microstructure. It also explains why the observed order of increasing resistance against F–T (decreasing strength loss) is RBM, RBM2, and RBM3. RBM3, with the densest microstructure or more refined microstructure (fewer voids), suffered the lowest deterioration rate.

Also, the measured compressive strength decreased with F–T condition compared with that of specimens before F–T process. The recorded strength losses of 25.6%, 17.9%, and 12.3% for RBM1 (28 d), RBM2 (28 d), and RBM3 (28 d), respectively, after 5 cycles are less than the 30% maximum allowed under Chinese standards, indicating that the RBMs made in this study exhibit acceptable durability against F–T condition. The observed decrease in strength with F–T exposure is caused by water within the pores of the specimens freezing and expending when changing from the liquid to the solid state. The expansion alters the material’s pore structure, and the repeated F–T process further enlarges pores within the specimen, resulting in cracking and deterioration of the material, which then results in low strength [30].

### 3.3. Microstructure evolution of RBM during W–D and F–T exposures

#### 3.3.1. MIP analysis

The pore structure of RBM1 and RBM2 specimens cured...
for 7 d, RBM3 cured for 28 d was analyzed to investigate the microstructure change in the RBM subjected to W–D condition while that of RBM3 specimen cured for 28 d was also analyzed to evaluate the effect of F–T condition. The obtained data are presented in Table 4.

To better understand the change in pore structure due to W–D and F–T exposures, we compare the data from Tables 3 and 4 for RBM specimens before and after W–D and F–T exposures, respectively. The amount of gel pores (<10 nm) increased by 1.44% and 3.36% for RBM1 (7 d) and RBM2 (7 d), respectively, after 12 W–D cycles and increased by 2.06% and 2.57% for RBM3 (28 d) after 20 W–D cycles and after 5 F–T cycles, respectively. These results are attributed to the high temperature [28] in the case of W–D and to the specimens being immersed in water [31], which accelerated pozzolanic reactions and led to the formation of more hydration products at the early stage. However, the number of macropores (>1 μm) increased from 18.98% to 27.54% when the number of W–D cycles (Fig. 4).

The XRD patterns of RBM1, RBM2, and RBM3 cured for 7 d are presented in Fig. 7. All of the diffraction patterns show similar patterns, with some differences in peak intensity. The main hydration products of the RBMs are calcium silicate hydrate (C–S–H), ettringite- and zeolite-like minerals such as calcium aluminum silicate hydrate (C–A–S–H), sodium aluminum silicate hydrate (N–A–S–H), and a mixture of unreacted phases such as AlO(OH), CaSO₄, Ca₂SiO₄, and Ca₃SiO₅ from the raw materials. Numerous other minor peaks are present but not sufficiently well defined to be identified with certainty.

The damaging effects of F–T and W–D exposures were compared from the data in Table 4. In the case of the pore structure of RBM3 (28 d) after 20 W–D cycles and 5 F–T cycles, the fraction of macropores (>1 μm) increased by 11.29% and 21.52%, respectively; these results clearly indicate that more damage was induced by pore enlargement during F–T than during W–D exposure. The large deleterious effects of F–T condition compared with W–D condition were even visually observed from the appearance of the specimens as shown in Fig. 6. The surface of RBM3 (28 d) after 20 W–D cycles remained almost the same as that before the process except for small bumps and lumps of the materials were peeled off; by contrast, obvious cracks were observed in the RBM3 (28 d) specimen subjected to 5 F–T cycles.

### Table 4. Pore structure properties of RBM hardened pastes after W–D and F–T exposures

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Average pore diameter / nm</th>
<th>Pore size distribution / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&lt;10 nm</td>
</tr>
<tr>
<td>RBM1 (7 d, 12 W–D cycles)</td>
<td>62.2</td>
<td>3.49</td>
</tr>
<tr>
<td>RBM2 (7 d, 12 W–D cycles)</td>
<td>46.9</td>
<td>6.02</td>
</tr>
<tr>
<td>RBM2 (7d, 16 W–D cycles)</td>
<td>53.9</td>
<td>5.48</td>
</tr>
<tr>
<td>RBM3 (28 d, 20 W–D cycles)</td>
<td>42.1</td>
<td>5.07</td>
</tr>
<tr>
<td>RBM3 (28 d, 5 F–T cycles)</td>
<td>51.8</td>
<td>5.58</td>
</tr>
</tbody>
</table>

3.3.2. XRD analysis

The peaks at approximately 60° and 72° for Ca(OH)₂, 57° for Ca₂SiO₄, and 68° for AlO(OH) from the raw materials decreased from RBM1 to RBM3, indicating that raw materials were consumed increasingly in this order (RBM1 to RBM3) during pozzolanic reactions to form hydration products. Therefore, the formation of hydration products increased in the order of RBM1, RBM2, and RBM3, which is the same order observed for both the increase in compressive strength and the resistance against W–D and F–T exposures, as observed in Figs. 2, 4, and 5. Therefore, the formed
hydration products are responsible for the strength and durability in road base material. The formed hydration products fill the voids and increase the dense packing of the RBM microstructure, which in turn increases the load-bearing capacity and, thus, the compressive strength. The main hydration products of the RBM were formed during pozzolanic reactions as follows: $\text{Ca}_2\text{SiO}_4$ and $\text{Ca}_3\text{SiO}_5$ from red mud (Fig. 1) are hydrated to form C–S–H according to the Eqs. (1) and (2).

$$\text{Ca}_2\text{SiO}_4 + \text{H}_2\text{O} \rightarrow \text{C–S–H} + \text{Ca(OH)}_2$$  \hspace{1cm} (1)

$$\text{Ca}_3\text{SiO}_5 + \text{H}_2\text{O} \rightarrow \text{C–S–H} + \text{Ca(OH)}_2$$  \hspace{1cm} (2)

Reactive aluminous and siliceous substances from red mud react with Ca(OH)$_2$ produced via Eqs. (1) and (2) to

![Fig. 6. RBM3 (28 d) specimens exposed for (a) 5 F–T cycles and (b) 20 W–D cycles.](image_url)

![Fig. 7. XRD patterns of different road base materials cured for 7 d.](image_url)
form C–A–S–H and N–A–S–H gels according to Eqs. (3)–(7).

\[ \text{SiO}_2 + \text{OH}^- + \text{H}_2\text{O} \rightarrow [\text{H}_3\text{SiO}_4]^-(3) \]

\[ \text{AlO}_2^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow [\text{H}_3\text{AlO}_4]^2-(4) \]

\[ [\text{H}_3\text{SiO}_4]^- + [\text{H}_3\text{AlO}_4]^2^- + \text{Ca}^2+ \rightarrow \text{C–A–S–H} (5) \]

\[ [\text{H}_3\text{SiO}_4]^- + [\text{H}_3\text{AlO}_4]^2^- + \text{Na}^+ \rightarrow \text{N–A–S–H} (6) \]

\[ \text{AlO}_2^- + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow [\text{Al(OH)}_6]^{3-} (7) \]

The formed \([\text{Al(OH)}_3]^–\) reacts with \(\text{Ca}^{2+}\) and \(\text{SO}_4^{2–}\) dissolved from raw materials to form ettringite:

\[ 2[\text{Al(OH)}_6]^{3–} + 6\text{Ca}^{2+} + 3\text{SO}_4^{2–} + 26\text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} (8) \]

Notably, the presence of unreacted phases specifically, \(\text{Ca}_3\text{SiO}_4\), \(\text{Ca}_3\text{SiO}_3\), \(\text{Al(OH)}_3\), and \(\text{CaSO}_4\) in Fig. 7 implies the continuous formation of hydration products even beyond 28 d; as a result, the strength will also increase.

The XRD diffractograms of RBM3 cured for 28 d before and after exposed to W–D and F–T cycles are presented in Figs. 8 and 9, respectively. The unreacted phases from raw materials are not marked in Figs. 8 and 9 to avoid excessive marks that may obscure the peaks of the hydration products.

In Fig. 8, the diffractograms for RBM3 (28 d) before and after 12 W–D cycles show the same trends but with different peak intensities. All of the hydration products in the diffractograms of RBM3 (28 d) before the W–D process also appeared in the diffractogram after 12 W–D cycles, with the exception of ettringite (Ca$_6$Al$_2$SO$_4$(OH)$_{12}$·26H$_2$O). The absence of ettringite in the diffractogram of RBM3 (28 d) after 12 W–D cycles indicates that it was decomposed at the high temperature (71°C) used in this process. Jiménez and Prieto [32] have reported that ettringite decomposes at temperatures greater than 70°C, losing its hydroxyls and water molecules and thereby forming a product that is amorphous to X-rays.

Fig. 8 also shows that the intensity of the peaks at ~34.4° and ~50.4°, which are associated with Na$_2$Al$_2$SiO$_5$·2H$_2$O and Ca$_3$SiO$_4$·0.5H$_2$O, increased in the diffraction pattern of the specimen subjected to W–D cycles. This phenomenon can be explained by the fact that the immersion of specimens in water during wetting accelerates the hydration process [31]. In addition, the use of elevated temperature (71°C) during the drying process accelerates pozzolanic reactions and enhanced the rate of formation of hydration products at early age, which increases the compressive strength at early age [33]. This high rate of formation of hydration products during the W–D process is possibly the reason why the compressive strength in specimens exposed to W–D condition is higher than in the strength of nonexposed specimens (see Fig. 2). Also, the increase in the intensity of peaks at 34.4° and 56° of CaCO$_3$ in the W–D diffraction pattern is a clear indication of the carbonation of RBM materials during the W–D process, which negatively affects the compressive strength. This observation can be explained by the fact that
the W–D process occurred in presence of atmospheric air and that part of the Ca(OH)$_2$ produced during pozzolanic reactions (Eqs. (1) and (2)) reacted with CO$_2$ from atmospheric air to form CaCO$_3$.

In Fig. 9, the two patterns are similar in trend and the main hydration products detected in the two patterns are the same, with some small differences in peak intensities. Peaks observed to decrease in intensity are also associated with phases from the raw materials (Fig. 7), and the observed decrease in intensity may be due to their consumption during pozzolanic reactions to form hydration products even during F–T exposure, especially during the thawing process (soaking specimens in water). Moreover, a new peak of Na$_2$Al$_3$Si$_3$O$_{10}$·2H$_2$O appeared at ~21° in the patterns of the F–T specimens. Also, the intensities of peaks at ~10.5° for Na$_2$Al$_3$Si$_3$O$_{10.6}$, ~14.6° for CaAl$_2$Si$_2$O$_6$·6H$_2$O, Na$_2$Al$_3$Si$_3$O$_{10}$·2H$_2$O, and CaAl$_2$SiO$_4$·4H$_2$O, ~16.5° for Na$_2$Al$_3$Si$_3$O$_{10.6}$ and Na$_2$Ca$_2$Al$_3$Si$_3$O$_{10}$·2H$_2$O, ~30° for CaSiO$_3$·0.5H$_2$O, and ~31° for CaAl$_2$SiO$_4$·4H$_2$O and CaSiO$_3$·0.5H$_2$O increased in the patterns of the F–T specimens compared with their intensities in the pattern of the nonfrozen specimens. This phenomenon of increasing formation of hydration products during the F–T process can be explained by the observation that the immersion of specimens in water during thawing accelerated the hydration process of cementitious materials [31], thereby forming more hydration products. This explanation indicates that freezing condition did not affect the hydration process.

Normally, the formation of more hydration products during the F–T process would increase the compressive strength of the RBM material; however, the results in Fig. 5 show that the compressive strength decreased. Therefore, the RBM deterioration mechanism is likely caused by the development of cracks in the RBM matrix.

3.3.3. FTIR analysis

The FTIR spectra for RBM1, RBM2, and RBM3 cured for 7 d as well as RBM3 cured for 28 d were detected in the wavenumber region between 4000 and 400 cm$^{-1}$; the results are presented in Fig. 10. The FTIR spectra of RBM3 cured for 28 d before and after W–D, as well as those before and after F–T exposure, are presented in Fig. 11. All FTIR results of specimens show bands at 3341, 1630, 1470, 1114, 999, 683, 622, 550, and 460 cm$^{-1}$; while the band at 875 cm$^{-1}$ appeared in other spectra except in RBM3 (28 d) and the band at 1430 cm$^{-1}$ only appeared in the spectrum of RBM3 (7 d and 28 d).

In Fig. 10, the broad absorption band at 3441 cm$^{-1}$ is assigned to an Al–OH stretching vibration in the octahedral structure of ettringite. The band at 1630 cm$^{-1}$ is related to the bending vibration of the H–O–H band for interlayer water. This peak decreases with increasing hydration time because free water was involved in the hydration process and transformed into crystal water [34–35]. The absorption bands at 1470 and 875 cm$^{-1}$ associated with vibrations of CO$_2$ in carbonate indicate the occurrence of carbonation in the RBM. In the spectrum of RBM3 (28 d), the peak at 1470 cm$^{-1}$ de-
increased substantially in intensity and shifted to 1491 cm\(^{-1}\), whereas that at 875 cm\(^{-1}\) disappeared, possibly indicating a lesser degree of carbonation of RBM in the RBM3 (28 d). The carbonation reaction adversely affects strength development, which suggests that its decrease also contributed to the increase in compressive strength from RBM1 to RBM3 observed in Fig. 2. The new spectral band at 1430 cm\(^{-1}\), which is characteristics of C–S–H, appeared in the spectrum of RBM3 before and after W–D and F–T cycles was also evaluated; the corresponding FTIR analysis results are shown in Fig. 11.

In Fig. 11, the band at 1430 cm\(^{-1}\) in the spectrum of RBM3, which is characteristic of C–S–H gel, increased in intensity after 12 W–D and 5 F–T cycles, indicating that the amount of C–S–H increased after W–D and F–T exposures and also consistent with the XRD findings. The reason for this behavior is that the immersion of RBMs in water during wetting in W–D and thawing in F–T accelerated the hydration process and then formed more hydration products. The absorption peak at ~876 cm\(^{-1}\) corresponding to C–O bending vibration in carbonate became stronger during W–D and F–T exposures, which suggests a large extent of carbonation in RBMs with W–D and F–T exposures, consistent with the XRD findings. We speculated that part of the Ca(OH)\(_2\) produced via the reactions shown in Eqs. (1) and (2) reacted with CO\(_2\) from the atmosphere to form CaCO\(_3\).

### 3.3.4. Al NMR analysis

The \(^{27}\)Al MAS NMR was used to further investigate the change in the hydration process of RBM3 before and after W–D and F–T exposures; the corresponding spectra are shown in Fig. 12. All of the spectra show two very sharp peaks at approximately 61 ppm for tetrahedrally coordinated Aluminium [AlO\(_4\)] noted as (Al\(^{IV}\)) and between 7 and 10 ppm for octahedrally coordinated Aluminium [AlO\(_6\)] noted as (Al\(^{VI}\)). The two peaks are identical in all of the spectra; the only difference lies in their relative contents. The results obtained by deconvolution of the \(^{27}\)Al MAS NMR spectra using the MestReNova program are presented in Table 5.

The results in Table 5 show that the amount of [AlO\(_4\)] species in RBM3 (28 d) specimen decreased after exposed to F–T and W–D conditions. According to the dreierkettten chain structure, possible positions for [AlO\(_4\)] are Q\(_1\) (dimer), Q\(_2\) (where it may be either a bridging (Q\(_{3b}\)) group or pairing (Q\(_{2p}\)) group), and Q\(_{3}\) (where [AlO\(_4\)] can be a branching site) [36]. However, [AlO\(_4\)] cannot easily occupy the Q\(_1\) (Al–O–Al) position, suggesting that it occupies Q\(_2\) and Q\(_{3}\). According to the results of the XRD (Figs. 7–9) and FTIR (Figs. 10–11) analysis, the C–A–S–H increased with increasing hydration time, implying that more [AlO\(_4\)] combines with [SiO\(_4\)] to form more C–A–S–H. Therefore, this combination of [AlO\(_4\)] with [SiO\(_4\)] suggests that the likely position for
corresponding to the signal at approximately 61 ppm is the bridging site (Q$_{2B}$). This deduction is consistent with the findings of Wang et al. [37], who also speculated that the [AlO$_4$] with a signal 63.5 ppm occupied a Q$_{2B}$ bridging site.

Table 5 shows that the relative content at 61 ppm for [AlO$_4$] in RBM3 (28 d) decreased during exposed to W–D and F–T, which implies that more C–A–S–H was continuously formed during RBM3 (28 d) exposed to W–D and F–T conditions, which agrees well with the XRD observations (Figs. 7–9), which also confirms that harsh conditions in W–D and F–T did not inhibit the formation of hydration products. We also observed that the relative content of [AlO$_4$] increased in F–T and W–D compared with nonexposed RBM3, which indicates that more [AlO$_4$] was converted into [AlO$_6$] during F–T and W–D exposures, which continuously reacted with Ca$^{2+}$ and SO$_4^{2−}$ from unreacted materials to form ettringite. However, the ettringite, which is stable at 50°C, was decomposed at the higher temperature applied in the W–D process, thereby losing its hydroxyl groups and water molecules and forming an X-ray-amorphous product [32].

Table 5. Deconvolution results of $^{27}$Al MAS NMR spectra for RBM3 (28 d) before and after F–T and W–D processes

<table>
<thead>
<tr>
<th>Condition</th>
<th>Peak information</th>
<th>Al$^{IV}$</th>
<th>Al$^{VI}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W–D exposure</td>
<td>Peak position (ppm)</td>
<td>61.04</td>
<td>10.76</td>
</tr>
<tr>
<td></td>
<td>Relative peak area</td>
<td>0.475</td>
<td>0.161</td>
</tr>
<tr>
<td></td>
<td>Relative content / %</td>
<td>74.68</td>
<td>25.31</td>
</tr>
<tr>
<td>F–T exposure</td>
<td>Peak position (ppm)</td>
<td>61.17</td>
<td>9.43</td>
</tr>
<tr>
<td></td>
<td>Relative peak area</td>
<td>0.599</td>
<td>1.097</td>
</tr>
<tr>
<td></td>
<td>Relative content / %</td>
<td>35.32</td>
<td>64.68</td>
</tr>
<tr>
<td>Non-exposure</td>
<td>Peak position (ppm)</td>
<td>61.16</td>
<td>7.92</td>
</tr>
<tr>
<td></td>
<td>Relative peak area</td>
<td>3.595</td>
<td>0.624</td>
</tr>
<tr>
<td></td>
<td>Relative content / %</td>
<td>85.20</td>
<td>14.79</td>
</tr>
</tbody>
</table>

3.3.5. SEM analysis

The SEM micrographs of RBM1 cured for 7 d, RBM3 cured for 28 d, and RBM3 cured for 28 d and exposed to W–D and F–T conditions are shown in Fig. 10.

Hydration products such as needle-shaped/rod-shaped-like ettringite were formed, surrounded by the gel matrix of C–S–H, C–A–S–H, and N–A–S–H in reference to the XRD findings, except in Fig. 13(d), where no ettringite is observed. In Fig. 13(a) and 13(b), ettringite crystallites formed in RBM1 (7 d) are thin, whereas thick rod-shaped structures are observed in RBM3 (28 d). This phenomenon is attributed to the greater degree of hydration in RBM3(28 d), which resulted in the formation of more ettringite in RBM3 (28 d) than in RBM1 (7 d) and RBM2 (7 d), as previously explained in the discussion of the XRD results.

The effect of F–T process on the RBM3 (28 d) is observed in Fig. 13(b) and 13(c); rod-shaped ettringite crystallites are thinner in Fig. 13(c) for RBM3 (28 d) after F–T exposure than in Fig. 13(b) for nonfrozen RBM3. However, the reason for this phenomenon is not very clear and further investigations of this matter are needed. No ettringite crystallites is observed in Fig. 13(d) for RBM3 (28 d) after exposing to 12 W–D cycles because the process was conducted at 71°C, which is substantially greater than the ettringite decomposition temperature of 50°C reported by Jiménez and Prieto [32]. Thus, the absence of ettringite suggests that it decomposed.

3.4. Leaching characteristics of road base materials

The presence of hazardous substances hinders the sustainable recycling and reuse of industrial solid wastes; their...
solidification to a minimum level that complies with discharge and/or drinking standards is the only way forward but very challenging. In this study, the leaching behavior of raw materials and RBM cured for 7 d was evaluated; the results are presented in Table 6.

From Table 6, it can be seen that all of the tested parameters for RBM1, RBM2, and RBM3 were below the Chinese drinking water standard limits specified in GB 5749-2006, which indicates that the RBM has excellent solidification ability. Therefore, the mixture of red mud and FGD-FA can be used as an alternative to natural materials in road base construction.

Table 6. Leaching characteristics of raw materials and road base materials

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Hg</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red mud</td>
<td>1183.40</td>
<td>0.0052</td>
<td>0.0133</td>
<td>0.0355</td>
<td>0.0268</td>
<td>0.0222</td>
<td>0.0044</td>
<td>0.3041</td>
</tr>
<tr>
<td>FG DFA</td>
<td>7.83</td>
<td>0.0040</td>
<td>0.0191</td>
<td>0.0335</td>
<td>0.1790</td>
<td>0.0205</td>
<td>0.0018</td>
<td>0.0077</td>
</tr>
<tr>
<td>RBM1 (7 d)</td>
<td>216.55</td>
<td>0.0010</td>
<td>0.0084</td>
<td>0.0056</td>
<td>0.0089</td>
<td>0.00054</td>
<td>0.00081</td>
<td>0.0051</td>
</tr>
<tr>
<td>RBM2 (7 d)</td>
<td>189.09</td>
<td>0.0007</td>
<td>0.0010</td>
<td>0.0060</td>
<td>0.0108</td>
<td>0.0010</td>
<td>0.00074</td>
<td>0.0087</td>
</tr>
<tr>
<td>RBM3 (7 d)</td>
<td>177.75</td>
<td>0.00095</td>
<td>0.0128</td>
<td>0.0119</td>
<td>0.0772</td>
<td>0.0074</td>
<td>0.00141</td>
<td>0.0066</td>
</tr>
<tr>
<td>GB 5749-2006 limits</td>
<td>200</td>
<td>≤0.002</td>
<td>≤0.02</td>
<td>≤1</td>
<td>≤1</td>
<td>≤0.01</td>
<td>≤0.005</td>
<td>≤0.05</td>
</tr>
</tbody>
</table>

4. Conclusions

This study investigated the durability and deterioration mechanism of the RBM prepared by partial replacement of aggregates with red mud and FGDFA. On the basis of the findings, the following conclusions were made.

(1) The RBMs prepared by red mud and FGDFA showed excellent durability in terms of resistance against F–T and W–D processes, which implies that the designed materials can be used in both extremely hot and cold environments. The resistance against F–T and W–D exposures increases in the same order as the increasing order of hydration degree (RBM1 < RBM2 < RBM3), which suggests that the formed hydration products are responsible for the resistance of RBM against F–T and W–D conditions.

(2) The W–D and F–T exposures did not affect the hydration process because hydration products continuously formed even during W–D and F–T. The only major difference was a substantial increase in macropores (>1 μm) observed in RBM specimens after F–T and W–D exposures, which indicates that the mechanism for RBM deterioration is pore enlargement due to cracks developed inside the materi-
al matrix. The cracks cause particle disjunction, which results in reduced load-carrying capacity and failure when stress is applied.

3) The F–T condition exerted a greater negative effect on the road base durability than the W–D condition. Thus, the design of solid wastes-based RBMs for application in extremely cold regions must be undertaken with great care.

4) The RBM prepared by red mud and FGDFA showed excellent eco-friendly performance and good heavy metal solidification ability, which makes it the best option as a natural materials replacement in road base construction.

Acknowledgements

This word was financially supported by the National Natural Science Foundation of China (Nos. 51574024 and U1760112) and Fundamental Research Funds for the Central Universities of China (FRF-AT-19-007).

References


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