



Evaluation of blends bauxite-calcination-method red mud with other industrial wastes as a cementitious material: Properties and hydration characteristics

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ABSTRACT

Red mud is generated from alumina production, and its disposal is currently a worldwide problem. In China, large quantities of red mud derived from bauxite calcination method are being discharged annually, and its utilization has been an urgent topic. This experimental research was to evaluate the feasibility of blends red mud derived from bauxite calcination method with other industrial wastes for use as a cementitious material. The developed cementitious material containing 30% of the bauxite-calcination-method red mud possessed compressive strength properties at a level similar to normal Portland cement, in the range of 45.3–49.5 MPa. Best compressive strength values were demonstrated by the specimen RSFC2 containing 30% bauxite-calcination-method red mud, 21% blast-furnace slag, 10% fly ash, 30% clinker, 8% gypsum and 1% compound agent. The mechanical and physical properties confirm the usefulness of RSFC2. The hydration characteristics of RSFC2 were characterized by XRD, FTIR, ²⁷Al MAS-NMR and SEM. As predominant hydration products, ettringite and amorphous C–S–H gel are principally responsible for the strength development of RSFC2. Comparing with the traditional production for ordinary Portland cement, this green technology is easier to be implemented and energy saving. This paper provides a key solution to effectively utilize bauxite-calcination-method red mud.

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1. Introduction

Red mud is an industrial waste obtained from alumina production. Generally, 0.8–1.5 tons of red mud is generated from per ton of alumina production. With the quick development of alumina industry all over the world, the disposal of red mud has caused serious environmental problems mainly due to its large quantities and strong alkalinity (pH 10.0–12.5). As a corrosively hazardous material, the comprehensive utilization of red mud has attracted more and more researchers' attention. It was estimated that over 66 million tons of red mud is impounded annually in the world [1,2], with 7 million tons in China [3]. As it is mainly composed of Fe₂O₃, Al₂O₃, TiO₂, SiO₂, CaO and Na₂O, it is thought that using red mud as a cement admixture is an effective way to consume such a large quantity of alkaline waste.

There are three processes for producing alumina, which are Bayer process, bauxite calcination method, combined Bayer process and bauxite calcination method [4], and thus, the generated

red mud widely differs in chemical and mineralogical properties. It is known that the Bayer process is the principal method for alumina production in the world. Red mud obtained from the Bayer process contains high amount of Fe₂O₃ (>30%) and Al₂O₃ (>15%), and many papers were written about this kind of Bayer-process red mud used for preparation of cement [1,2,5–7]. However, in China, there are over 7 million tons of red mud are being discharged annually but only about 10% of the red mud is derived from pure Bayer process [8]. Most of the local bauxite ores in China possess low grade and contain a high proportion of silicon, and therefore, bauxite calcination method or combined Bayer process and bauxite calcination method is more frequently used for alumina production. The red mud derived from these two methods can be viewed as bauxite-calcination-method red mud, and it is mainly composed of CaO, SiO₂, Fe₂O₃, Al₂O₃, TiO₂ and Na₂O. Besides, it contains small quantities of MgO, K₂O and SO₃, and trace amounts of minor/trace elements such as Zr, P, Sr, Cr, Ba, Mn, Nb, Y and Ni. Concerning the bauxite-calcination-method red mud, Pan et al. [9,10] developed a new kind of alkali-slag-red mud cementitious material through the application of composite solid alkali activator into slag-red mud mixture system. Nevertheless, the comprehensive utilization ratio of red mud in China is still less than 15%.

Many efforts have been made to find effective ways to utilize bauxite-calcination-method red mud in our research group. We

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Table 1
Chemical composition and physical properties of raw materials.

Oxides (%)	Red mud	Slag	Fly ash	Clinker
SiO ₂	18	33.59	51.22	21.94
Al ₂ O ₃	6.31	14.37	36.4	5.27
CaO	35.09	38.32	2.64	66.09
Fe ₂ O ₃	12.38	1.11	3.65	2.96
Na ₂ O	2.71	0.18	0.13	0.3
K ₂ O	0.45	0.11	0.82	0.7
MgO	1.13	8.43	0.42	0.88
TiO ₂	3.32	0.85	1.62	–
SO ₃	0.54	2.26	0.31	0.31
Cr ₂ O ₃	0.11	0.05	0.05	0.07
LOI	20.07	0.44	2.03	0.67
Specific gravity	2.81	2.78	2.4	3.16
Specific surface, Blaine (m ² /kg)	425	405	500	400

have carried out some investigations on the thermal activation technics of red mud from bauxite calcination method showing that the red mud sintered at 600 °C for 3 h had the best cementitious properties [11,12]. As bauxite-calcination-method red mud usually contains some quantities of amorphous aluminosilicate materials and gibbsite, they can be transformed into reactive silica and alumina during the calcination process, resulting in some pozzolanic behaviours. Thus, the bauxite-calcination-method red mud sintered at 600 °C for 3 h was used as a main material to produce composite cements in this study.

Countless papers were written on the use of ground-granulated blast furnace slag and fly ash as extenders in Portland cement or to be alkaline-activated for the production of geopolymers [13–21]. However, there are still few literatures focusing on the use of bauxite-calcination-method red mud as an extender in blended cement system, although we have conducted an experiment on using bauxite-calcination-method red mud, coal gangue, blast furnace slag, clinker and gypsum to produce cementitious material, and demonstrated that the developed red mud-coal gangue based cementitious material had good mechanical properties comparable with 32.5 ordinary Portland cement [22]. In order to further improve the utilization ratio of bauxite-calcination-method red mud in cement industry, the bauxite-calcination-method red mud was blended with other industrial wastes such as blast furnace slag and fly ash as main compositions to produce cementitious material, including evaluation of properties and characterization of its hydration products by means of XRD, FTIR, ²⁷Al MAS-NMR and SEM.

2. Experimental

2.1. Materials

Red mud was obtained from Shandong alumina refining plant, the process of which is bauxite calcination method. Granulated blast furnace slag was supplied by Tangshan steel refining plant, and fly ash was provided by Beijing Shijingshan power plant. A sample of clinker from Beijing Xingang was employed for this investigation. The chemical composition (analyzed using X-ray fluorescence technique) and physical properties of these materials are presented in Table 1. The mineralogical phases of granulated blast furnace slag, fly ash and clinker are shown in Fig. 1.

2.2. Experimental procedure

Red mud was sintered at 600 °C for 3 h in a programmable electrical furnace, and then removed from the furnace and allowed to cool spontaneously to room temperature in air. The mineralogical phases of the raw red mud and sintered red mud (600 °C, 3 h) are presented in Fig. 2. The sintered red mud (600 °C, 3 h) was blended with granulated blast furnace slag, fly ash, clinker, gyp-

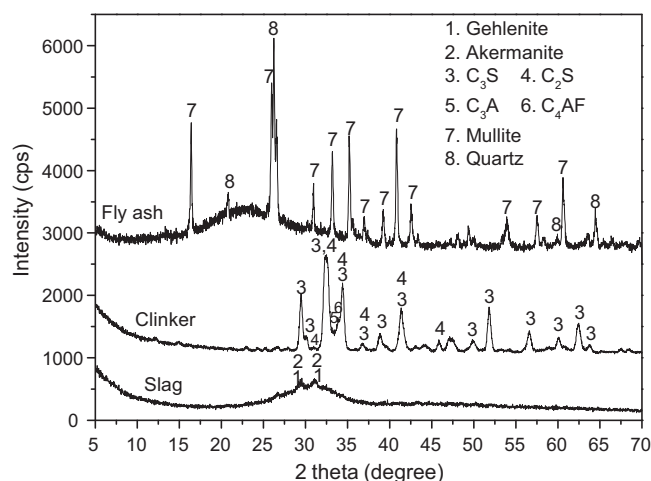


Fig. 1. Mineralogical phases of granulated blast furnace slag, fly ash and clinker.

sum and compound agent, in appropriate proportions to produce red mud-slag-fly ash blended cements, abbreviated as RSFC. The gypsum used was of industrial origin (CaSO₄·2H₂O, 40% SO₃, w/w). The compound agent was comprised of Na₂SO₄ and NaCl at a ratio of 7:3 to improve the mechanical properties of the produced cementitious material. Six batches were prepared for the mechanical test with attempt to find the best mix proportion of RSFC. The batch NPC was used as a reference Portland cement in the mechanical test. The designed proportions are listed in Table 2, and the chemical analysis (by X-ray fluorescence technique) corresponding to each mixture is shown in Table 3.

Mechanical tests were carried out according to Chinese Standard GB/T17671-1999 [23], with a water/cement ratio of 0.50 and cement/sand ratio of 1:3. Mortar specimens in size of 40 mm × 40 mm × 160 mm were cured in a moist cabinet at 95% humidity and 20 °C for 24 h, and then demoulded and placed in the isothermal curing cabinet at the previously mentioned humidity and temperature until the desired testing ages of 1, 3, 7 and 28 days.

Water requirement of normal consistency and setting time of RSFC paste were determined by Vicat probe and Vicat needle apparatus according to Chinese Standard GB/T 1346-2001 [24].

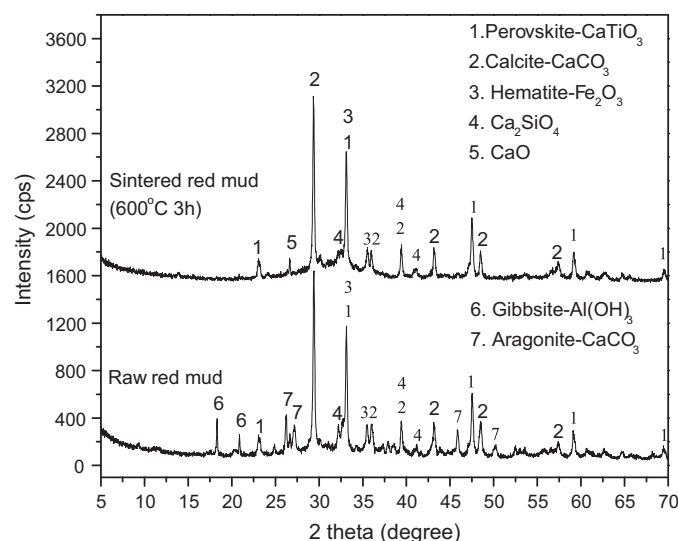


Fig. 2. Mineralogical phases of the raw red mud and sintered red mud (600 °C, 3 h).

Table 2
Designed proportions of blended cementitious materials (%).

Symbol	Red mud (600 °C, 3 h)	Slag	Fly ash	Clinker	Gypsum	Compound agent
NPC	0	0	0	95	5	0
RSC	30	31	0	30	8	1
RSFC1	30	31	10	20	8	1
RSFC2	30	21	10	30	8	1
RSFC3	30	11	20	30	8	1
RSFC4	40	21	10	20	8	1

Table 3
Chemical composition of blended cementitious materials (%).

Oxides	NPC	RSC	RSFC1	RSFC2	RSFC3	RSFC4
SiO ₂	21.70	24.85	27.78	26.65	28.45	26.66
Al ₂ O ₃	5.46	8.98	12.07	11.19	13.39	11.49
CaO	62.96	44.92	38.74	41.44	37.96	38.75
Fe ₂ O ₃	3.51	7.39	7.40	7.67	7.94	9.27
MgO	2.13	4.11	3.94	3.24	2.38	3.18
Na ₂ O	0.24	1.24	1.23	1.23	1.23	1.57
K ₂ O	0.71	0.46	0.47	0.53	0.60	0.50
TiO ₂	–	1.82	1.98	1.88	1.94	2.38
SO ₃	2.49	4.17	4.14	3.98	3.78	3.96

The RSFC pastes with water to solid ratio of 0.35 were prepared and molded in 20 mm × 20 mm × 20 mm test cubes that were cured in a moist cabinet at 95% humidity and 20 °C. After 1 day of hydration, the pastes were demoulded and transferred to isothermal curing cabinet at the previously mentioned humidity and temperature. The hydration of the pulverized and sieved specimens were terminated by alcohol drenching at the desired testing ages, and then dried at 60 °C in a vacuum oven for 24 h for further characterization.

XRD analysis was conducted on Rigaku D/max-RB X-ray diffractometer with CuK α radiation, voltage 40 kV, current 200 mA and 2 θ scanning, ranging between 5° and 70°. Infrared spectra of hydrated RSFC pastes were recorded on a Spectrum GX Perkin-Elmer Fourier transform infrared (FTIR) spectrometer using the KBr pellet technique. ²⁷Al solid-state MAS-NMR spectroscopy was carried out using a BRUKER-AM300 spectrometer (Germany) operating at 78.20 MHz for the ²⁷Al resonance frequency. SEM observations were performed on 28-day RSFC pastes using JSM-6460LV scanning electron microscope.

3. Results and discussion

3.1. Chemical and mineralogical characteristics of the bauxite-calcination-method red mud

As shown in Table 1, the main oxides of the bauxite-calcination-method red mud used are CaO, SiO₂, Fe₂O₃ and Al₂O₃. Besides, it has high content of Na₂O (2.71%). Comparing with Bayer-process red mud containing higher amount of Fe₂O₃ and Al₂O₃, the red mud used contains higher amount of CaO and SiO₂. It can be seen from Fig. 2 that the major mineralogical phases present in the raw red mud used in this study are calcite (CaCO₃), aragonite (CaCO₃), Ca₂SiO₄, perovskite (CaTiO₃), hematite (Fe₂O₃), and gibbsite (Al(OH)₃). After sintering at 600 °C, the peaks of aragonite and gibbsite disappeared, suggesting the decomposition of aragonite into CaO and dehydroxylation of gibbsite into reactive Al₂O₃, respectively. In bauxite calcination method, bauxite ores are often mixed with limestone and sodium carbonate, and the mixtures are calcined under high temperature (above 1200 °C) [4]. In China, most of the local bauxite ores contain a high portion of silicon and therefore, Ca₂SiO₄ can be formed in the high-temperature calcining process, and subsequently present in the red mud used here. Ca₂SiO₄ phase, which can take part in the cement hydration

to form hydrated calcium silicate, is present in both the raw and sintered red mud as seen in Fig. 2. In addition, it should be noted that the peaks of Ca₂SiO₄ declined and became obscure at 600 °C, suggesting poorly-crystallized Ca₂SiO₄ occurring in the red mud sintered at 600 °C. It is thought that this poorly-crystallized Ca₂SiO₄ can provide good cementitious property when used for blended cement.

3.2. Mechanical and physical properties of blended cements

The compressive strength results of RSFC and NPC mortars are presented in Fig. 3. The best 28-day compressive strength value of 49.5 MPa was obtained by RSFC2 sample. All the compressive strength values of RSFC2 at 1, 3, 7 and 28 days were about 1.98, 6.59, 3.88 and 9.03% higher than those of the reference NPC, respectively. The mortars of RSC, RSFC1 and RSFC3 reached a 28-day compressive strength in the range of 45.3–46.8 MPa, which is close to the strength of reference NPC (45.4 MPa). However, the sample of RSFC4 showed strength values at 1, 3, 7 and 28 days that were about 50.50, 18.32, 18.01 and 7.93% lower than those of the reference NPC. It is observed that a delay occurred in the strength development of RSFC1 and RSFC4 at 1 day, e.g., 19.80 and 50.50% lower than the 1-day compressive strength of NPC, respectively.

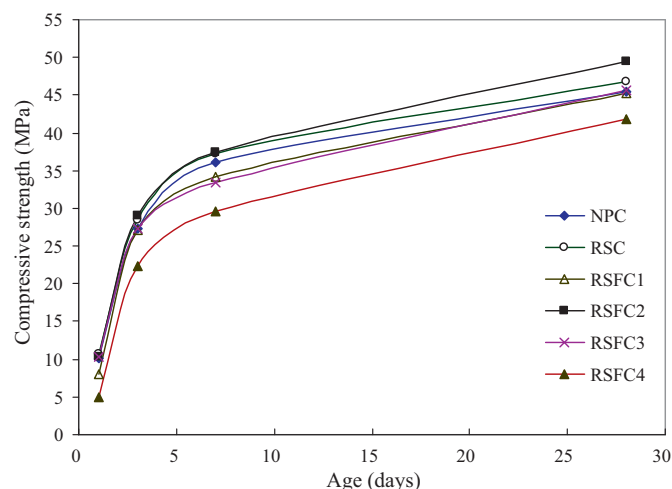


Fig. 3. Compressive strength of RSFC and NPC mortars.

Table 4
Physical properties of RSFC2.

Sample	Specific gravity	Specific surface Blaine (m ² /kg)	Setting time (min)		Water of normal consistency (%)	Soundness	Compressive strength (MPa)	
			Initial	Final			3 days	28 days
RSFC2	2.88	423	145	243	31.3	Good	29.1	49.5

This can be explained by the low clinker content (20%) in these blended cementitious materials.

According to the compressive strength results, the proper mix ratio for RSFC was determined. Specimen RSFC2 containing 30% sintered red mud (600 °C, 3 h), 21% blast furnace slag, 10% fly ash, 30% clinker, 8% gypsum and 1% compound agent, had better mechanical properties compared with the specimens using other mix ratios. Therefore, characterization of the hydrated RSFC2 pastes was further carried out in the following analyses.

The general physical and mechanical properties of RSFC2 are reported in Table 4. It is noted that the setting time of RSFC2 can satisfy the requirement in Chinese Standard GB175-1999 for ordinary Portland cement (initial setting time ≥ 45 min; final setting time ≤ 600 min). The water demand for standard consistency of RSFC2 was higher than that of Portland cement, which is normally in a range of 25–28% [25–27]. Although the content of gypsum used in RSFC2 was up to 8%, the soundness obtained was still good with expansion of 1.9 mm determined by the Le Chatelier method.

The mechanical and physical properties confirm the usefulness of RSFC2, which indicates that it is feasible to use the bauxite-calcination-method red mud blended with blast furnace slag and fly ash to replace up to 61% of the raw materials to produce cementitious material. This produced red mud-slag-fly ash cementitious material can be utilized in various applications such as building materials and stabilization/solidification materials. Furthermore, possessing important environmental and economic significances, the developed red mud-slag-fly ash blended cement can not only help to mitigate environmental pollution, but also save a lot of natural resources for the cement clinker (as limestone and iron source in particular) and finally decrease the production cost of cement.

3.3. Hydration characteristics

3.3.1. XRD analysis

The XRD patterns of RSFC2 pastes hydrated at 3, 7 and 28 days are presented in Fig. 4. It can be seen that all specimens are mainly amorphous in view of the broad diffuse halo in the background between 26° and $37^\circ 2\theta$, assigned to C–S–H gel. Besides, all the XRD patterns show some diffraction peaks corresponding to ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$), portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3), larnite (Ca_2SiO_4), hematite (Fe_2O_3) and perovskite (CaTiO_3). It is known that portlandite is the primary crystalline product of clinker hydration, whereas minor amounts of $\text{Ca}(\text{OH})_2$ were contained in the hydrated RSFC2 specimens, which can be obtained from the weak XRD signals for $\text{Ca}(\text{OH})_2$. Moreover, it is noted that the amount of $\text{Ca}(\text{OH})_2$ tends to decline with the increase of curing time due to both the pozzolanic reactions of sintered red mud, slag and fly ash, and carbonation (as the intensity of XRD signals for calcite grow with curing time). Calcite can be assigned to two parts: one part is from the sintered red mud (600 °C, 3 h) as seen in Fig. 2, and the other part results from the carbonation of $\text{Ca}(\text{OH})_2$. Strong peaks of larnite can still be detected after the hydration of 28 days. As inert phases, hematite and perovskite are obtained from the bauxite-calcination-method red mud. Thus, it is thought that, as the predominant hydration products, crystal ettringite and amorphous C–S–H gel are principally responsible for the strength development of RSFC2 in early hydration process.

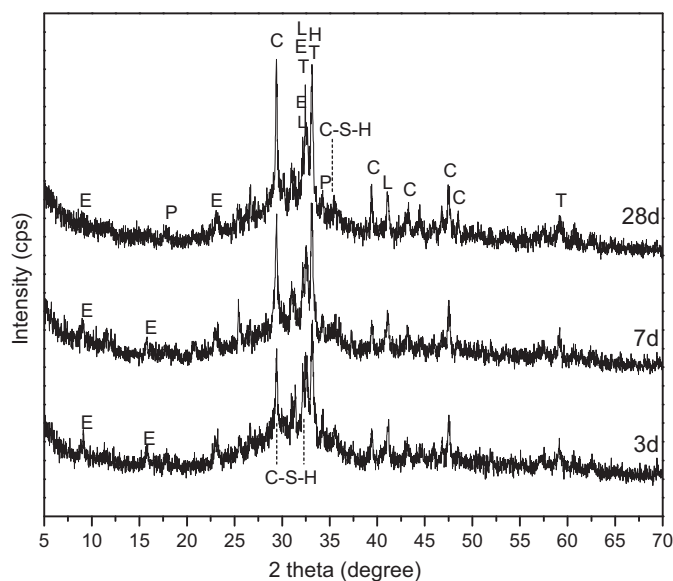


Fig. 4. XRD patterns of RSFC2 pastes hydrated at 3, 7 and 28 days [E = ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$); P = portlandite ($\text{Ca}(\text{OH})_2$); C = calcite (CaCO_3); L = larnite (Ca_2SiO_4); H = hematite (Fe_2O_3); T = perovskite (CaTiO_3)].

3.3.2. FTIR analysis

Fig. 5 displays the FTIR absorption spectra of RSFC2 pastes hydrated at 3 and 28 days, respectively. These two spectra are rather similar, presenting analogous absorption bands. All show bands at 602 , 670 and 875 cm^{-1} , respectively, related to symmetric stretching, bending vibration and asymmetric stretching vibrations of Al–OH bands in the $\text{Al}(\text{OH})_6$ octahedra of ettringite [28]. The

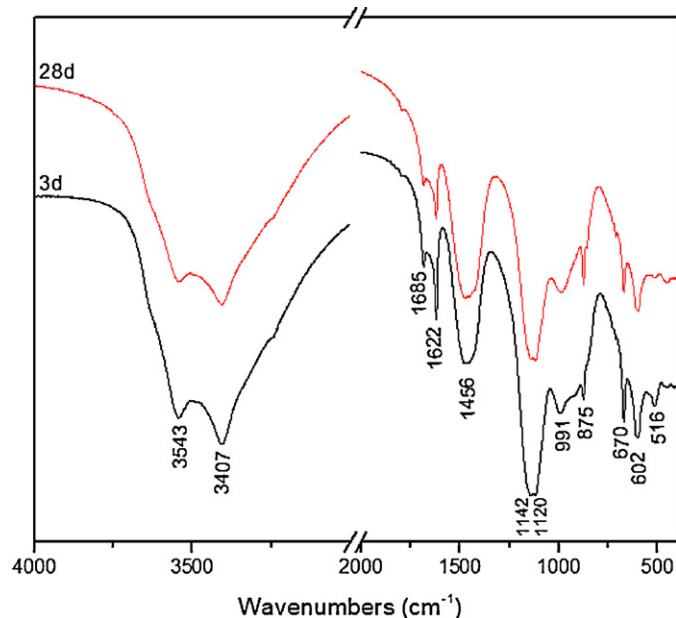


Fig. 5. FTIR spectra of RSFC2 pastes hydrated at 3 and 28 days.

bands at 1120 and 1142 cm^{-1} can be attributed to S–O₄ stretching mode (ν_3), suggesting the presence of ettringite in the specimens hydrated at 3 and 28 days. The band at 1622 cm^{-1} is a well-defined H–O–H deformation band corresponding to the H–O–H vibration of interlayer water, whereas the wide bands around 3407 and 3543 cm^{-1} are associated with the vibrations of OH⁻ ions in structure water. Both samples contain carbonate species pointed out by the presence of the large absorption band at 1456 cm^{-1} , corresponding to anti-symmetric stretching (ν_3) modes of CO₃²⁻ ions [29,30].

It should be noted that the band at 991 cm^{-1} in both spectra, due to anti-symmetric Si–O(Al) stretching vibrations (ν_3) in SiO₄ tetrahedra [29], is indicative of the presence of C–S–H gel. C–S–H gels formed in Portland cement generally have a typical band around 960–970 cm^{-1} [20,29], whereas the peak of C–S–H gel here formed in the hydrated RSFC2 has a higher frequency of 991 cm^{-1} , indicative of a more polymerized structure. As the Si–O stretching modes for the SiQⁿ units display infrared absorption bands located around 850, 900, 950, 1100 and 1200 cm^{-1} for $n=0, 1, 2, 3$ and 4, respectively [29,31], the band at 991 cm^{-1} indicates a distribution of the SiQⁿ units centered around SiQ² and SiQ³ units for the hydrated RSFC2 samples at 3 and 28 days. The position of this band suggests that the C–S–H gel formed is similar to the gel-type aluminosilicate found in the alkali-activated systems [20,29,32,33]. It is thus believed that the C–S–H gel formed in the hydrated RSFC2 has high polymerization of SiO₄ tetrahedra with a part of silicon substituted by aluminium.

In the infrared spectrum of the hydrated RSFC2 at 3 days, the small band at 516 cm^{-1} is ascribed to out-of-plane O–Si–O bending modes (ν_4) in SiO₄ tetrahedra of Ca₂SiO₄ [34]. However, this band disappeared at 28 days, suggesting the hydration of Ca₂SiO₄ into C–S–H gel.

3.3.3. ²⁷Al MAS-NMR analysis

²⁷Al MAS-NMR technique was used to probe structure features of hydrated RSFC2 pastes, and to determine the aluminium coordination number with oxygen. Figs. 6 and 7 display the ²⁷Al MAS-NMR spectra of RSFC2 pastes hydrated at 3 and 28 days, respectively. It can be seen that both spectra show a very large band centered approximately at 64–65 ppm, associated with tetrahedrally coordinated Al [29,35] incorporated in the C–S–H gel. This resonance could be assigned to AlQ²(2Si) or AlQ³(3Si) structural units [29],

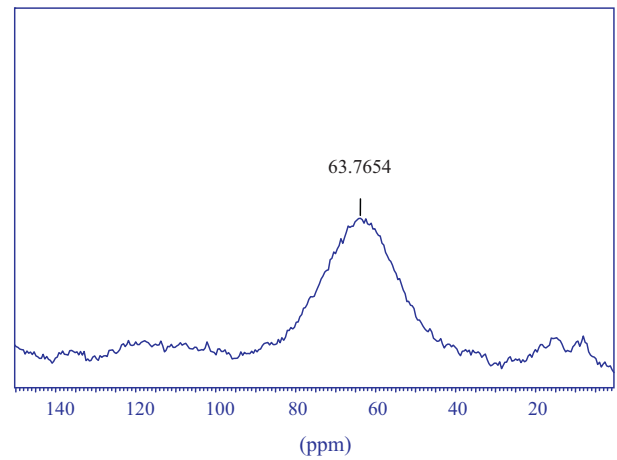


Fig. 6. ²⁷Al MAS-NMR spectrum of RSFC2 paste hydrated at 3 days.

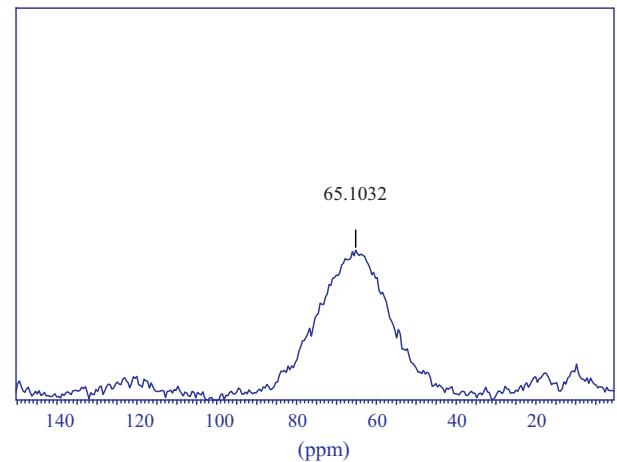


Fig. 7. ²⁷Al MAS-NMR spectrum of RSFC2 paste hydrated at 28 days.

which concurs with the structural analysis of the C–S–H gel in the above FTIR results.

It can be deduced that the C–S–H gel formed in RSFC2 sample has highly polymerized structure with Al substitution for Si, and may

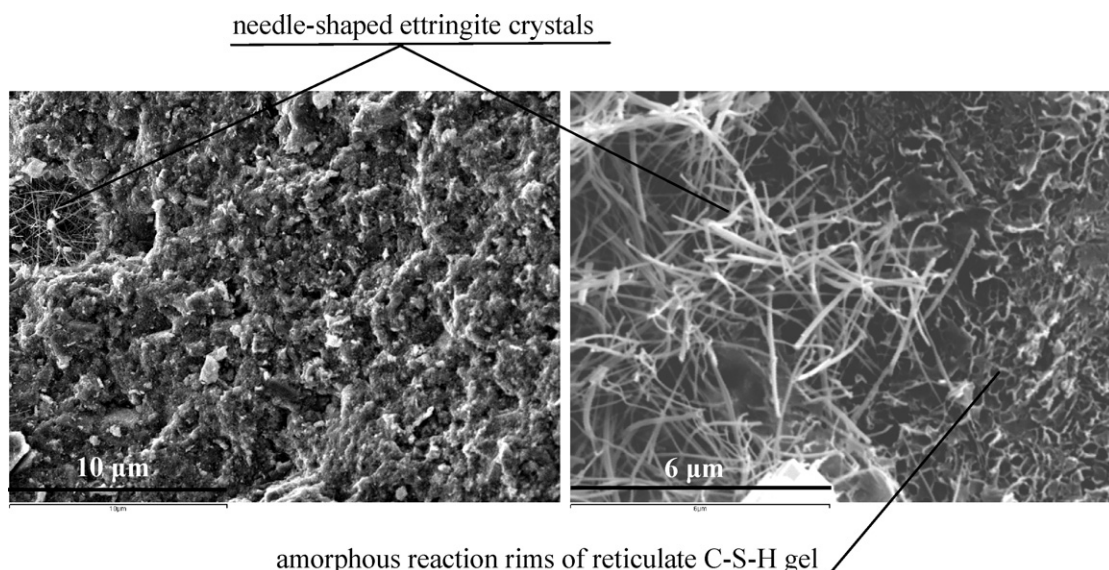


Fig. 8. Microstructure of RSFC2 pastes hydrated at 28 days.

be similar to the gel-type aluminosilicate found in alkali-activated binders such as geopolymers or alkali-activated slag cement. However, it should be noted that the developed RSFC2 in the current work is quite different from the traditional alkali-activated binders. Alkali activators such as sodium hydroxide, potassium hydroxide or water glass, are usually used to activate aluminosilicate-based materials, such as metakaolin, blast furnace slag or fly ash. On the contrary, no alkali metal hydroxides were used in RSFC2. It is known that the red mud sintered at 600 °C contains the phase of poorly-crystallized Ca_2SiO_4 which can take part in the hydration to form C–S–H. Besides, as an alkaline material containing about 3% $\text{Na}_2\text{O} + \text{K}_2\text{O}$, red mud could provide a proper alkaline environment combining with clinker to activate the slag and fly ash, resulting in the formation of C–S–H gel with cross-linked structures which are responsible for the strength development of the produced composite cement.

3.3.4. SEM analysis

Fig. 8 shows the microstructure of RSFC2 pastes hydrated at 28 days. It is noted that particles of various shapes and sizes are well connected to a cementitious matrix and coated by a layer of amorphous gel, resulting in a compacted structure with lower porosity (Fig. 8, left). The amorphous gel is assigned to C–S–H gel with reaction rims of reticulate morphology (as shown in Fig. 8, right). Needle-shaped ettringite crystals dispersed through the paste can be observed, while few layer $\text{Ca}(\text{OH})_2$ crystals can be found in the hydrated RSFC2 sample at 28 days. Although 30% of clinker contained in RSFC2, it is thought that $\text{Ca}(\text{OH})_2$ formed in the hydration of clinker was depleted quickly at the early age primarily due to the pozzolanic reactions of sintered red mud, blast-furnace slag and fly ash. It is confirmed again from the SEM observation that the dominant hydration products of ettringite crystals and amorphous C–S–H gel play an important role in the strength development of RSFC2, which agrees well with the XRD results.

4. Conclusions

The developed red mud-slag-fly ash cementitious material containing 30% of the bauxite-calcination-method red mud possessed compressive strength properties at a level similar to normal Portland cement, in the range of 45.3–49.5 MPa. Best compressive strength values were demonstrated by the specimen RSFC2 containing 30% bauxite-calcination-method red mud, 21% blast-furnace slag, 10% fly ash, 30% clinker, 8% gypsum and 1% compound agent. The mechanical and physical properties confirm the usefulness of RSFC2, which indicates that it is feasible to use the red mud derived from bauxite-calcination-method blended with blast-furnace slag and fly ash to replace up to 61% of the raw materials to produce composite cement. Comparing with traditional production for ordinary Portland cement, this green technology is easier to be implemented and energy saving. The produced composite cement can be utilized in various applications such as building materials and stabilization/solidification materials. Furthermore, possessing important environmental and economic significances, the developed red mud-slag-fly ash cementitious material can not only save a lot of natural resources for the cement clinker, but also help to mitigate environmental pollution caused by the industrial wastes. The hydration products of red mud-slag-fly ash cementitious material are essentially ettringite and amorphous C–S–H gel, which are principally responsible for the strength development of this composite cement. The C–S–H gel formed has a highly polymerized structure in SiQ^2 and SiQ^3 units with a part of silicon substituted by tetrahedrally coordinated aluminium. The present study provides a practical solution to effectively utilize bauxite-calcination-method red mud.

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References

- [1] P.E. Tsakiridis, S. Agatzini-Leonardou, P. Oustadakis, Red mud addition in the raw meal for the production of Portland cement clinker, *J. Hazard. Mater.* B116 (2004) 103–110.
- [2] M. Singh, S.N. Upadhyay, P.M. Prasad, Preparation of special cements from red mud, *Waste Manage.* 16 (1996) 665–670.
- [3] D. Ren, Y. Mao, Comprehensive utilization of red mud, *China Nonferr. Metals Ind.* 5 (2002) 57–58 (in Chinese).
- [4] Y. Liu, C. Lin, Y. Wu, Characterization of red mud derived from a combined Bayer process and bauxite calcination method, *J. Hazard. Mater.* 146 (2007) 255–261.
- [5] J.N. Gordon, W.R. Pinnock, M.M. Moore, A preliminary investigation of strength development in Jamaican red mud composites, *Cem. Concr. Compos.* 18 (1996) 371–379.
- [6] M. Singh, S.N. Upadhyay, P.M. Prasad, Preparation of iron rich cements using red mud, *Cem. Concr. Res.* 27 (1997) 1037–1046.
- [7] J. Pera, R. Boumazza, J. Ambrose, Development of a pozzolanic pigment from red mud, *Cem. Concr. Res.* 27 (1997) 1513–1522.
- [8] P. Zhang, Y. Yang, G. Li, Utilization of red mud as hot metal pretreatment flux, *Exp. Inf. Min. Ind.* 3 (2005) 26–30.
- [9] Z. Pan, L. Cheng, Y. Lu, N. Yang, Hydration products of alkali-activated slag-red mud cementitious material, *Cem. Concr. Res.* 32 (2002) 357–362.
- [10] Z. Pan, D. Li, J. Yu, N. Yang, Properties and microstructure of the hardened alkali-activated red mud-slag cementitious material, *Cem. Concr. Res.* 33 (2003) 1437–1441.
- [11] H. Chen, H. Sun, H. Li, Effect of heat treatment temperature on cementitious activity of red mud, *Light Metals* (2006) 22–25 (in Chinese).
- [12] X. Liu, H. Sun, X. Feng, N. Zhang, X. Bai, Study on the thermal activation technics of red mud, *Rare Metal Mater. Eng.* 36 (2007) 983–986.
- [13] I.G. Richardson, G.W. Groves, Microstructure and microanalysis of hardened cement pastes involving ground granulated blast-furnace slag, *J. Mater. Sci.* 27 (1992) 6204–6212.
- [14] J.-I. Escalante-Garcia, J.H. Sharp, The chemical composition and microstructure of hydration products in blended cements, *Cem. Concr. Compos.* 26 (2004) 967–976.
- [15] I. Pane, W. Hansen, Investigation of blended cement hydration by isothermal calorimetry and thermal analysis, *Cem. Concr. Res.* 35 (2005) 1155–1164.
- [16] K. Luke, E. Lachowski, Internal composition of 20-year-old fly ash and slag-blended ordinary Portland cement pastes, *J. Am. Ceram. Soc.* 91 (2008) 4084–4092.
- [17] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes: a cement for the future, *Cem. Concr. Res.* 29 (1999) 1323–1329.
- [18] A. Fernandez-Jimenez, A. Palomo, M. Criado, Microstructure development of alkali-activated fly ash cement: a descriptive model, *Cem. Concr. Res.* 35 (2005) 1204–1209.
- [19] A. Fernandez-Jimenez, A. Palomo, Composition and microstructure of alkali activated fly ash binder: effects of the activator, *Cem. Concr. Res.* 35 (2005) 1984–1992.
- [20] A. Palomo, A. Fernandez-Jimenez, G. Kovalchuk, L.M. Ordóñez, M.C. Naranjo, Opc-fly ash cementitious systems: study of gel binders produced during alkaline hydration, *J. Mater. Sci.* 42 (2007) 2958–2966.
- [21] X. Guo, H. Shi, L. Chen, W.A. Dick, Alkali-activated complex binders from class C fly ash and Ca-containing admixtures, *J. Hazard. Mater.* 173 (2010) 480–486.
- [22] N. Zhang, H. Sun, X. Liu, J. Zhang, Early-age characteristics of red mud-coal gangue cementitious material, *J. Hazard. Mater.* 167 (2009) 927–932.
- [23] GB/T 17671-1999, Test method for cements – determination of strength, 1999.
- [24] GB/T 1346-2001, Standard test method for water requirement of normal consistency, setting time and soundness of the Portland cement, 2001.
- [25] Y. Abali, S.U. Bayca, S. Targan, Evaluation of blends tincal waste, volcanic tuff, bentonite and fly ash for use as a cement admixture, *J. Hazard. Mater.* B131 (2006) 126–130.
- [26] Z. Li, Z. Ding, Property improvement of Portland cement by incorporating with metakaolin and slag, *Cem. Concr. Res.* 33 (2003) 579–584.
- [27] J. Paya, M.V. Borrachero, J. Monzo, M. Bonilla, Properties of Portland cement mortars incorporating high amounts of oil-fuel ashes, *Waste Manage.* 19 (1999) 1–7.
- [28] G. Qian, Y. Cao, P. Chui, J. Tay, Utilization of MSWI fly ash for stabilization/solidification of industrial waste sludge, *J. Hazard. Mater.* B129 (2006) 274–281.
- [29] I. Lecomte, C. Henrist, M. Liegeois, F. Maseri, A. Rulmont, R. Cloots, (Micro)-structure comparison between geopolymers, alkali-activated slag cement and Portland cement, *J. Eur. Ceram. Soc.* 26 (2006) 3789–3797.
- [30] P. Yu, R.J. Kirkpatrick, B. Poe, P.F. McMillan, X. Cong, Structure of calcium silicate hydrate (C–S–H): near-, mid-, and far-infrared spectroscopy, *J. Am. Ceram. Soc.* 82 (1999) 742–748.

- [31] N.J. Clayden, S. Esposito, A. Aronne, P. Pernice, Solid state ^{27}Al NMR and FTIR study of lanthanum aluminosilicate glasses, *J. Non-Cryst. Solids* 258 (1999) 11–19.
- [32] A. Fernandez-Jimenez, F. Puertas, Structure of calcium silicate hydrates formed in alkaline-activated slag: Influence of the type of alkaline activator, *J. Am. Ceram. Soc.* (2003) 1389–1394.
- [33] A. Fernandez-Jimenez, A. Palomo, T. Vazquez, R. Vallepu, T. Terai, K. Ikeda, Alkaline activation of blends of metakaolin and calcium aluminate cement. Part I. Strength and microstructural development, *J. Am. Ceram. Soc.* (2007) 1–6.
- [34] J. Besnsted, S.P. Varma, Some application of infra-red and Raman spectroscopy in cement chemistry. Part 1. Examination of dicalcium silicate, *Cement Technol.* 5 (1–2) (1974) 256–261.
- [35] X. Liu, H. Sun, X. Feng, N. Zhang, Relationship between the microstructure and reaction performance of aluminosilicate, *Int. J. Miner. Metall. Mater.* 17 (2010) 108–115.