Comparison of Non-calcined and Calcined Red Muds from Different Sources as Potential Supplementary Cementitious Material

Shaoliang Chen[1] and Abdul Ghani Razaqpur[1,2]

[1]Sino-Canada Joint R&D Center on Water and Environmental Safety, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, PR China,
chenshaoliang@mail.nankai.edu.cn (Shaoliang Chen), Grazaqpur@nankai.edu.cn (Abdul Ghani Razaqpur, Corresponding author)

[2]Department of Civil Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada,
razaqpu@mcmaster.ca (Abdul Ghani Razaqpur)

Abstract. *Red mud (RM) is a hazardous by-product of alumina refining processes. Due to its high alkalinity, large specific surface area, and complex and variable composition, RM is hard to treat or utilize on a large scale. To date, more than 4 billion tons of RM have been stockpiled globally and is still growing by more than 120 million tons annually. Many investigations have focused on the large-scale utilization of RM as a construction material, either in its virgin form or after heat treatment. However, the huge differences among the chemical/mineralogical compositions of RMs due to differences among bauxite ores from different sources and/or different refining processes, it is difficult to prescribe a unique process for activating RM cementitious/pozzolanic properties. The present study aims to identify the key chemical and process-dependent factors that influence the cementitious/pozzolanic properties of RM. Two types of RM from different sources are investigated to determine the effects of the chemical/mineralogical composition, the alumina refining process, and calcination on the mineralogical phases and compressive strength of mortar cubes made with ordinary Portland cement (OPC)- RM blended cement. Mortar made with 15 wt.% OPC replaced by one type of virgin RM produced by the Bayer's process was found to have better strength than a control mortar made with 15% OPC replaced by sand, which indicates that this RM had cementitious/pozzolanic property without requiring heat treatment. On the other hand, the RM produced by the bauxite calcination method needed heat treatment to improve its pozzolanicity, but, despite the improvement, mortar made with its optimally treated form had lower 91-day compressive strength than the companion control mortar made with extra sand as RM replacement. The compressive strength of mortars made with calcined RM was not only affected by the phase changes of the virgin RM properties brought about by calcination but also by changes to its physical.*

Keywords: *Cementitious Material; Compressive Strength; Mortar; Red Mud; Thermal Activation*

1 Introduction

Red Mud (RM) is a by-product generated by the alumina refining process, which could not be directly used due to its complex composition, and high alkalinity (Liu et al., 2014). At the same time, the cement industry is striving to find less energy intensive and CO_2 emitting alternative materials to ordinary Portland cement (OPC). To reduce/eliminate the negative effects of RM on water and soil safety, air pollution, and other aspects of the environment (Xue et al., 2019) (Hyeok-Jung et al., 2018), RM has been extensively studied for its potential as a supplementary cementitious material (SCM) in concrete and other cement products.

The similarity of the chemical composition of RM to that of OPC and its high alkalinity are

expected to contribute to the formation of cementitious and/or pozzolanic products in hydrated cement. The high alumina content of RM would promote the formation of $3CaO \cdot Al_2O_3$ (C_3A), which could accelerate the hydration process of cement. Some studies (Ribeiro et al., 2012) have indicated that the addition of RM can improve the durability of concrete by increasing its resistance to chloride penetration and carbonation due to hydrated cement pore refinement. However, it has been reported that RM in its virgin form has very limited pozzolanicity or cementitious activity as its addition to concrete decreases the concrete compressive strength and any concrete made with such product could be only used in non-structural applications(Ribeiro et al., 2011, Song et al., 2022).

On the other hand, it has been also reported (Liu et al., 2011, Zhang & Pan, 2005) that heat treatment or calcination is a necessary, technically and economically feasible, and direct way for industrially activating the pozzolanicity of RM. Its microstructure, crystallinity, and mineralogical composition can be altered by calcination, which could contribute to its pozzolanicity. However, RM is the generic name of bauxite residue generated by the alumina refining process, but RMs from different bauxite sources and generated by different refining processes have hugely different properties. There is no standard for RM classification or its calcination, so every RM need to be tested on an ad hoc basis together with the companion cement that will form the blend to gauge its cementitious/pozzolanic reactivity.

To corroborate the veracity of the last statement, the current research investigates the calcination effects on two red RMs from different sources and demonstrates the widely different effects of calcination temperature on the investigated RMs pozzolanicity.

2 Materials and Methods

2.1 Materials

In the current work, two types of RM are investigated, one generated by Bayer's process (BP) and the other by the Bayer's-calcination method (BCM), designated as RMA (from Binzhou, China) and RMB (from Jiaozuo, China), respectively. For consistency. and uniformity, both were first oven-dried and grounded into particle sizes smaller than 150 μm. The calcination was carried out in a muffle furnace for 2 hours at 600℃, 800℃, and 1000℃, with heating and cooling rate of 5 ℃/min. The OPC was obtained from a cement manufacturer in Tai'an, China, and it met the requirements of Type I cement in ASTM C150/C150M-22(ASTM International, 2022). The chemical composition of OPC, RMA, and RMB are listed in Table 1. The fine aggregate used in the mortar mix is standard sand (from Tianjin, China), meeting the requirements of EN 196-1(BS-EN Standard, 2016). All mixes were made with tap water.

For easy reference, calcined RMs are designated as RMX-CT, where X denotes A for RMA and B for RMB, C denotes calcination and T represents the calcination temperature in 100℃. The virgin or non-calcined form of the RMs is designated as RMX-OD. The mortars made with RMX-OD or RMX-CT are designated as MRMA-OD or MRMB-CT, and the blended paste made with RMX-OD or RMX-CT is termed BPRMX-OD or BPRMX-CT. The pure cement paste used as control is termed CP and the associated mortars are denoted as CM. To investigate whether RM served as a filler like sand, another re control mortar was made with 15 wt. % extra sand and 85 wt% of OPC (compared to CM) and is designated as CM-ES.

Table 1. Chemical composition of RM and OPC by XRF analysis.

Name	Chemical Composition (wt.%)							
	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	TiO_2	CaO	SO_3	K_2O
RMA	53.59	21.06	7.92	5.85	8.15	1.81	0.58	0.06
RMB	9.62	7.74	18.83	3.70	4.80	51.98	0.06	0.88
OPC	3.75	4.06	15.94	0.36	0.52	69.29	2.56	0.68

Note, with reference to Table 1, although the two RMs and OPC are composed of the same basic oxides, the oxide proportions are vastly different among them.

2.2 Methods

The mix design and the compressive strength tests of 50 mm mortar cubes followed ASTM C109/C109M-21 (International, 2021a). All the mortar cubes had a water-to-binder ratio (W/B) of 0.485 and a binder-to-sand ratio of 1:2.75. The CM was made with pure OPC as binder. In the other mixes, except CM-ES, the binder was composed of 15 wt.% RM and 85 wt.% OPC.

To understand the mechanism of hydration and investigate the existing phases of hydration products, Φ10 mm* 10 mm blended cement paste discs were prepared by using 15 wt.% of RM and 85 wt.% of OPC with a W/B ratio of 0.40. The curing conditions and specimen-making process followed ASTM C511-21(International, 2021b). One day after casting, all the specimens were demolded and cured in storage tanks filled with saturated lime water at 20℃. For each mix six repeat specimens were tested at the ages of 3, 7, 14, 28, 56, and 91 days.

The chemical composition of OPC and RM before and after calcination were determined by XRF Spectrometer. The pH value of the solution made with 1 g RM and 10 g of water was determined by an automatic titrator. The mean particle size, specific gravity, and BET-specific surface of RMs were determined by laser particle size analyzer, automatic gas displacement true density instrument, and surface area and pore analyzer, respectively. The crystal phases of RM and the hydration products of blended pastes were determined by X-Ray Diffraction (XRD).

3 Property changes of RMs due to calcination

3.1 Chemical composition and pH value

The chemical composition and pH value of each RM before and after calcination at different temperatures are listed in Table 2. RMA-OD has high iron and aluminum content but low calcium and silica content. In contrast, RMB-OD, with its main compounds of calcium and silica has a relatively high pH and low alkalinity. Calcination did not alter the basic oxide composition of the RMs, but the pH of RMA-C10 dropped significantly compared to the virgin and other calcined forms of RMA.

Table 2. Chemical composition of two types of RM before and after calcination at different temperatures.

Name	Chemical composition (wt. %)								
	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	TiO_2	CaO	SO_3	K_2O	pH
RMA-OD	53.59	21.06	7.92	5.85	8.15	1.81	0.58	0.06	10.37
RMA-C6	55.05	20.30	7.47	4.20	9.36	2.00	0.46	0.07	10.43
RMA-C8	54.86	20.53	7.34	4.31	9.32	2.05	0.48	0.05	10.52
RMA-C10	55.98	20.59	6.64	4.07	9.11	1.99	0.46	0.11	9.00
RMB-OD	9.62	7.74	18.83	3.70	4.80	51.98	0.88	0.83	12.10
RMB-C6	10.34	7.92	18.00	2.98	5.05	52.39	1.02	0.90	11.64
RMB-C8	10.48	7.46	17.80	2.68	4.97	53.67	0.77	0.80	11.69
RMB-C10	10.58	7.52	17.19	2.87	5.46	53.22	0.79	0.83	11.89

3.2 Physical properties

The specific gravity, mean particle size, and specific surface of the two types of RM before and after calcination at different temperatures are listed in Table 3. Compared with RMB-OD, RMA-OD has a larger specific gravity and specific surface, but a smaller mean particle size. After calcination, with increased temperature, the specific gravity of both two types of RMs increased, but their specific surfaces decreased, except for RMA-60, whose specific surface increased by calcination at 600°C but subsequently decreased under higher temperature. Also, the specific surface of RMA was found to be larger than that of RMB. Notice, the specific surface of RMB decreased dramatically as the calcination temperature exceeded 600°C.

The particle size changes of neither RM show any correlation with its corresponding specific surface. In general, calcination did not change the particle size significantly, except in the case of RMB, where calcination at 1000°C reduced its mean particle size nearly 40% compared to its size in the virgin form. The above change in specific surface may be caused by changes in crystallinity rather than the change in particle size.

Table 3. Physical properties of two types of RM before and after calcination at different temperatures.

Name	Specific Gravity (g/cm^3) (Normalized Specific Gravity%)	Mean Particle Size (μm) (Normalized Mean Particle Size%)	Specific Surface (m²/g) (Normalized Specific Surface%)
RMA-OD	3.37 (100.0)	24.1 (100.0)	25.94 (100.0)
RMA-C6	3.70 (109.8)	26.2 (108.9)	36.21 (139.6)
RMA-C8	3.70 (109.8)	25.2 (104.4)	20.58 (79.3)
RMA-C10	4.03 (119.8)	26.6 (110.6)	15.42 (59.5)
RMB-OD	2.82 (100.0)	32.4 (100.0)	8.26 (100.0)
RMB-C6	2.91 (103.4)	30.2 (93.0)	8.11 (98.3)
RMB-C8	3.05 (108.1)	34.5 (106.3)	2.99 (36.2)
RMB-C10	3.09 (109.8)	20.3 (62.7)	1.07 (13.0)

3.3 Mineralogical composition

The existing crystal phases of the two types of RM before and after calcination are listed in Table. 4. The phases in the two are rather different, which is reflective of their different bauxite sources. In RMA, at 600°C, the phases of Goethite and Boehmite were decomposed while, per

XRD analysis, the $Na_8(Si_6Al_6O_{24})(OH)_2(H_2O)_2$, Quartz, Anatase, and Rutile phases were newly formed. At 800°C, the Calcite phase disappeared but no new phases formed. At 1000°C, the $Na_8(Si_6Al_6O_{24})(OH)_2(H_2O)_2$ phase also disappeared, and the new phases of Corundum, Larnite, and Sodium silicate appeared.

In RMB, at 600°C, Portlandite disappeared but no new phases formed. At 800°C, Calcite also disappeared., but the new phases of Gehlenite and Magnetite appeared. At 1000°C, Magnetite was s transformed into Magnesioferrite.

Table 4. Existing phases of two types of RM before and after calcination at different temperatures.

RM Types	Existing phases
RMA-OD	Hematite, Goethite, Boehmite,Calcite
RMA-C6	Hematite, $Na_8(Si_6Al_6O_{24})(OH)_2(H_2O)_2$, Quartz, Calcite, Rutile, Anatase
RMA-C8	Hematite, $Na_8(Si_6Al_6O_{24})(OH)_2(H_2O)_2$, Quartz, Rutile, Anatase
RMA-C10	Hematite, Corundum, Quartz,, Larnite,, Rutile, Anatase, Sodium Silicate
RMB-OD	Calcite, Portlandite, Larnite, Dicalcium silicate-alpha, Perovskite
RMB-C6	Calcite, Larnite, Dicalcium silicate-alpha, Perovskite
RMB-C8	Magnetite, Gehlenite, Larnite, Dicalcium silicate-alpha, Perovskite
RMB-C10	Magnesioferrite, Gehlenite, Larnite, Dicalcium silicate -alpha, Perovskite

Despite the many and diverse phase changes, some general observations can be made. The hydrated minerals like Goethite and Boehmite, which mainly relates to the iron and alumina phases, easily decomposed at somewhat lower than 600°C (Pera et al., 1997, Sglavo et al., 2000) while the Calcite in both RMA and RMB decomposed at lower than 800°C, which contributed to the decrease of specific surface and will negatively affect the cementitious activity and pozzolanicity of the RMs (Luo et al., 2019). The phases Corundum and Larnite formed in RMA at 1000°C are known to have low reactivity (Sglavo et al., 2000).

4 Compressive strength of mortar cubes made with the RMs

The compressive strength of mortar cubes made with 15 wt. % RM and 85 wt. % of OPC is shown in Figure 1. At the ages of 28 and 91 days, all the mortars made with blended RM had lower compressive strength than CM. The best performing mortars made with RM are MRMA-OD and MRMB-C6, which could achieve 94.1% and 82.7%, respectively, of the CM strength at 91 days. MRMA-OD had higher strength compared to CM-ES, which means that RMA-OD did not simply serve as filler like the sand in CM-ES but contributed to the mortar strength. Besides, the rate of strength development of MRMA-OD between the ages of 56 and 91 days was three times faster than that of the companion CM during the same period. In fact, the strength development of MRM-OD seems better than some mortars/concrete made with similarly proportioned OPC-fly ash blended cement (Neville, 2011). The above strength development can be attributed to the RMA-OD pozzolanicity. On the other hand, MRMB-OD had low strength and a decelerating strength development, which indicates the lack of its cementitious reactivity and/or pozzolanicity.

As for the mortars made with calcined RM, the compressive strength of MRMA-C6, MRMA-C8, and MRMA-C10 were lower than MRMA-OD. The MRMA-C6 had relatively

high strength at the curing age of 3 days, but its strength development decelerated with time. The MRMA-C10 had low strength up to the age of 28 days, but its strength development accelerated thereafter. If it continued with its strength development rate between 56 and 91 days beyond 91 days, it could reach or even surpass the strength of CM at a later age. So, calcination of RMA at 1000°C appears to have delayed the initiation of its pozzolanic activity but did not eradicate it. This could be due to the 40% reduction in the specific surface of RMA caused by the 1000°C calcination and not due to mineralogical changes because the newly formed phases of Larnite and Corundum in RMA-C10 are relatively inert.
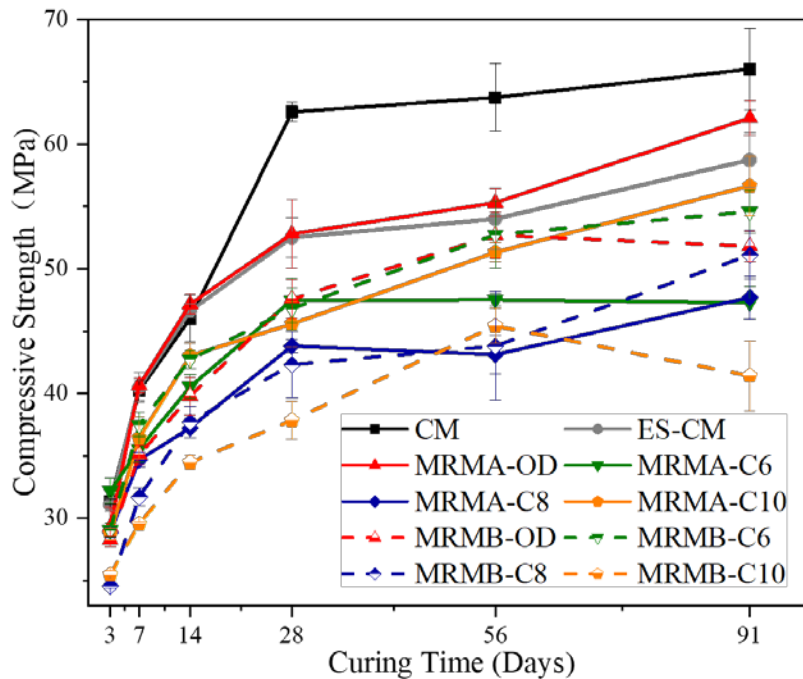

Figure 1. Compressive strength of mortars made with RMs before and after calcination at different temperatures.

With regard to the RMB mortars, MRMB-C6 had higher strength than MRMB-OD at all times except 28 days, but its strength was always lower than both CM and CM-ES. On the other hand, between the ages of 56 and 91 days, its strength development was improved than MRMB-OD but still very slow. Mortars MRMB-C8 and MRMB-C10 had relatively low compressive strength. As Liu et al. (2011) reported, the absence of Calcite and the formation of Gehlenite would decrease the compressive strength, which is corroborated by the lower compressive strength of the last two mortars in the current study.

Besides the phase change effects, the effect of the changes on some of the physical properties of RM caused by calcination should be also considered. Generally, the particle size change in the investigated RMs did not correlate the corresponding specific surface change. RM with large specific surface could absorb more free water during the mixing of fresh mortar and adversely impact the cement dilution effect and the mix consistency. The MRMA-C6 relatively high strength at the age of 3 days but subsequent poor strength development may be due to its high specific surface. Even though both RMB-C8 and RMB-C10 have low specific surface, the compressive strength of mortars made with them are quite different. To understand the

influence of calcination on the pozzolancity of RMs, the phase changes and changes in physical properties of RM induced by calcination need be considered simultaneously.

5 Hydration products of blended pastes

The before and after calcination crystal phases in the blended cement pastes made with the two types of RM are listed in Table 5. Due to the high iron and aluminum content of RMA, the new phases of Calcium Aluminum Oxide Hydrates, Hydrocalumite, and Srebrodolskite were formed during hydration. Portlandite, which occupies a large part of the volume of the matrix, but has very limited contribution to the compressive strength, existed in all the blended pastes, except BPRMA-OD. The Portlandite in BPRMA-OD was likely consumed by the pozzolanic reaction of RMA-OD. Note, the phases found in BPRMB-OD and BPRMB-C6 are very similar. The Calcite, Peroskite, Kuzelite, and $3CaO \cdot SiO_2$ phases disappeared in BPRMB-C8 and BPRMB-C10, which may be the reason for the lower strength of their companion mortars.

Table 5. Existing crystal phases in the blended cement pastes made with RMA and RMB

Name	Existing Phases
Pure cement paste	$2CaO \cdot SiO_2$, C-S-H, Katoite, Rustumite, Calcite, Prehnite, Ettringite
RMA-OD	$2CaO \cdot SiO_2$, C-S-H, Katoite, Rustumite, Calcite, $3CaO \cdot SiO_2$, Srebrodolskite
RMA-C6	$2CaO \cdot SiO_2$, C-S-H, Katoite, Calcium Aluminum Oxide Hydrate, Hydrocalumite, $3CaO \cdot SiO_2$, Srebrodolskite, Gypsum, Portlandite
RMA-C8	$2CaO \cdot SiO_2$, C-S-H, Katoite, Calcium Aluminum Oxide Hydrate, Hydrocalumite, $3CaO \cdot SiO_2$, Srebrodolskite, Portlandite
RMA-C10	$2CaO \cdot SiO_2$, Katoite, Portlandite, Calcium Aluminum Oxide Hydrate, Brownmillerite, $3CaO \cdot SiO_2$, Srebrodolskite
RMB-OD	$2CaO \cdot SiO_2$, Calcite, Portlandite, Perovskite, Kuzelite, $3CaO \cdot SiO_2$
RMB-C6	$2CaO \cdot SiO_2$, Calcite, Portlandite, Perovskite, Kuzelite, $3CaO \cdot SiO_2$
RMB-C8	$2CaO \cdot SiO_2$, C-S-H, Katoite, Prehnite, Portlandite
RMB-C10	$2CaO \cdot SiO_2$, C-S-H, Katoite, Portlandite

6 Conclusions

This study investigated the changes in the pozzolanic/cementitious activity of two types of RM produced by refining of bauxite from two sources using different refining processes. Within the scope of the study, the findings support the following conclusions:

− Red mud A could be used directly, without any calcination, to replace up to 15% of Portland cement when making mortar and possibly concrete. The MRMA-OD had high compressive strength and favorable strength development up to the age of 91 days.

− Red mud B could not be used directly as partial cement replacement in making cement products, the strength of mortars made with RMB was much smaller the strength of the companion CM or CM-ES. But when calcined at 600ºC, MRMB-C6 exhibited better strength development between the ages of 56 and 91 days than MRMB-OD, which proved the improvement of pozzolanicity. To demonstrate its significant pozzolanicity, more research is needed to investigate its strength development for six months or even a year.

− Calcination not only will not render all RMs pozzolanic, but it could diminish or eliminate

the pozzolanicity of some of them. When investigating the effect of calcination on a red mud pozzolanicity, the mineralogical and physical property changes brought about by calcination must be considered simultaneously.

– Due to the huge differences among the mineralogical composition of red muds from different sources and the effect of the refining processes on their minerology and physical properties, each one must be investigated on ad hoc basis, together with the cement with which it will be blended, to determine its pozzolanicity and whether or how calcination can render it more cementitious and/or pozzolanic.

Acknowledgments

References

Hyeok-Jung, K., Kang, S.-P., & Choe, G.-C. (2018). Effect of Red Mud Content on Strength and Efflorescence in Pavement using Alkali-Activated Slag Cement. *International Journal of Concrete Structures and Materials*, *12*(1).

International, ASTM. (2021a). Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50 mm] Cube Specimens). In (Vol. ASTM C109/C109M-21 pp. 12).

International, ASTM. (2021b). Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes. In (Vol. ASTM C511-21, pp. 3).

International, ASTM. (2022). Standard Specification for Portland Cement. In (Vol. ASTM C150/C150M-22).

Liu, W., Chen, X., Li, W., Yu, Y., & Yan, K. (2014). Environmental assessment, management and utilization of red mud in China. *Journal of Cleaner Production*, *84*(dec.1), 606-610.

Liu, X., Zhang, N., Sun, H., Zhang, J., & Li, L. (2011). Structural investigation relating to the cementitious activity of bauxite residue — Red mud. *Cement and Concrete Research*, *41*(8), 847-853.

Luo, S., Liu, M., Yang, L., Chang, J., Yang, W., Yan, X., Yu, H., & Shen, Y. (2019). Utilization of waste from alumina industry to produce sustainable cement-based materials. *Construction and Building Materials*, *229*.

Neville, A. M. (2011). *Properties of Concrete*. Pearson.

Pera, J., Boumaza, R., & Ambroise, J. (1997). Development of a pozzolanic pigment from red mud. *Cement and Concrete Research*, *27*(10), 1513-1522.

Ribeiro, D., Labrincha, J. A., & Morelli, M. (2011). Potential Use of Natural Red Mud as Pozzolan for Portland Cement. *Materials Research*, *14*, 60-66.

Ribeiro, D. V., Labrincha, J. A., & Morelli, M. R. (2012). Effect of the addition of red mud on the corrosion parameters of reinforced concrete. *Cement and Concrete Research*, *42*(1), 124-133.

Sglavo, V. M., Campostrini, R., Maurina, S., Carturan, G., Monagheddu, M., Budroni, G., & Cocco, G. (2000). Bauxite 'red mud' in the ceramic industry. Part 1: thermal behaviour. *Journal of the European Ceramic Society*, *20*(3), 235-244.

Song, Y., Dong, M., Wang, Z., Qian, X., Yan, D., Shen, S., Zhang, L., Sun, G., Lai, J., & Ruan, S. (2022). Effects of red mud on workability and mechanical properties of autoclaved aerated concrete (AAC). Journal of *Building Engineering*, *61*, 105238.

Standard, BS-EN. (2016). Methods of testing cement - Part 1: Determination of strength. In (Vol. EN 196-1-2016).

Xue, S., Wu, Y., Li, Y., Kong, X., Zhu, F., William, H., Li, X., & Ye, Y. (2019). Industrial wastes applications for alkalinity regulation in bauxite residue: A comprehensive review[J]. *Journal of Central South University*, *26*(2), 268-288.

Zhang, Y., & Pan, Z. (2005). Characterization of Red Mud Thermally Treated at Different Temperatures. *Journal of Jinan University (Sci & Tech)*, *19*(4), 293-297.