Z. Lei, S. Pavia (2025) Proc. of the CEES Construction, Energy, Environment and Sustainability. Vol. 1.
In Book Series: Lecture Notes in Civil Eng. (LNCE, vol 743). Berardi et al Eds. SPRINGER. eBook ISBN 978-981-95-1822-7

Potential of bauxite refining residue (BR) as CEM II replacement to produce low carbon cement

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Abstract. Europe's largest alumina refinery is located in Ireland, with an annual output of approximately 1,900 kilotons. Despite their high efficiency and advanced residue management facilities, they generate significant residue: approximately one tonne of residue per tonne of alumina. This creates a considerable waste management challenge. This study uses Irish bauxite refining residue (BR) in combination with CEM II and ground granulated blast-furnace slag (GGBS) to produce cements with a lower carbon footprint than clinker cements. The Irish BR is characterized by a high iron content and relatively low aluminium and silicon contents which influence the resulting cement performance. Replacing CEM II with BR led to a significant reduction in mechanical strength and flowability. A 20% replacement of CEM II with BR resulted in an 18.33% decrease in compressive strength, while replacements of 40% and 60% caused strength losses of 26.46% and 54.6%, respectively. In contrast, BR demonstrated a good synergy with GGBS. The BR´s high alkalinity served as an activator for the GGBS, promoting gel formation and enhancing mechanical strength development. A combination of 20% BR and 20% GGBS produced mortar with mechanical strength comparable to 100% CEM II mortar. However, the incorporation of BR did not significantly affect the hydration products. Due to the crystalline nature of the BR, inert phases, such as hematite, remained largely unchanged within the hydrated cement matrix.

Keywords: Bauxite refining residue, Portland cement, Clinker cement, Low-carbon cement, reactive waste, circular economy.

1 Introduction

Aluminium is the most abundant metallic element in the Earth's crust. Due to its high chemical reactivity, pure aluminium does not occur naturally [1]. In the mid-19th century, the price of aluminium exceeded that of gold, as it could only be produced in small quantities by reducing aluminium-containing compounds with alkali metals such as sodium or potassium [2]. The casting of a 2.85 kg aluminium block placed atop the Washington Monument in 1884 marked the pinnacle of technological advancement at the time [3].

By the late 19th century, the development of the Hall-Héroult and, especially, the Bayer processes significantly reduced the cost of aluminium production, transforming it from a luxury item into a common metal [4]. Today, approximately 97% of alumina is produced via the Bayer process [5]. This involves high-temperature, high-pressure digestion of bauxite in concentrated caustic soda, followed by the precipitation of aluminium hydroxide at lower temperatures [5]. The precipitated hydroxide is subsequently calcined to yield alumina, which serves as the feedstock for aluminium smelting. During this process, clarification and filtration are employed to remove residual solids, referred to as red mud (RM) or bauxite refining residue (BR).

The generation of BR is unavoidable; even the most advanced refineries produce nearly one tonne of BR per tonne of alumina. According to Swain et al. [6], global BR generation reached 120 million tonnes annually, with a recovery rate below 15%, resulting in an accumulated stockpile of approximately 4.17 billion tonnes by 2019.

The largest alumina refinery in Europe is in Aughinish, Limerick, Ireland. In 2019, the facility produced 1.893 million tonnes of alumina, alongside 1.400 million tonnes of BR [7]. The BR is stored as a solid, non-hazardous material in a safe and stable storage facility. The method of storage is called dry stacking, which is considered the best available technology. It is aligned with world-class standards and independently audited and verified by various international firms. However, despite the effort, the management of the waste constitutes an important management and economic burden. Furthermore, as reported in its 2023 environmental statement, only 8.66% of BR has been recovered to date [8]. The BR is a valuable resource, and its continued accumulation constitutes a waste.

Recycling BR into construction materials presents a promising pathway for large-scale BR utilization. The construction industry is currently under increasing pressure to transition toward more sustainable and low-carbon practices. Portland cement (PC), the primary binder in concrete, is responsible for 6-8% of global anthropogenic CO_2 emissions [9]. Reducing PC content in concrete fabrication is therefore an effective strategy for lowering emissions. The partial replacement of PC with industrial by-products and natural minerals is a well-established approach. European standard EN 197-1 permits the incorporation of materials such as ground granulated blast-furnace slag, silica fume, natural and calcined pozzolana, siliceous and calcareous fly ash, burnt shale, and limestone for the production of cement ranging from CEM II to CEM V [10].

The incorporation of BR into PC-based materials has been explored for decades. However, inconsistent results, stemming from variations in BR composition, have hindered consensus and broader adoption. Romano et al. [11] investigated Brazilian BR, which contained 21.4% Al_2O_3, 35.9% Fe_2O_3 and 15.9% SiO_2, with hematite and sodalite identified as the main crystalline phases. Their study found that BR addition did not affect the setting time of PC and appeared to enhance hydration, despite BR being considered inert. Viyasun et al.[12] studied Indian BR (18.1%-21% Al_2O_3, 35-37% Fe_2O_3 and 6-

6.5% SiO_2), reporting that replacing 20% of PC improved both compressive and flexural strengths. In contrast, Ghalehnovi et al.[13] observed that increasing BR content consistently reduced compressive strength at all ages.

These conflicting findings have limited the practical use of BR in PC systems. To support the valorisation of local BR, Irish BR was collected and characterised. The mechanical properties and hydration products of PC-based composites with varying BR replacement levels were evaluated. Furthermore, to better reflect real-world applications, the synergistic effects of BR and ground granulated blast-furnace slag (GGBS) within PC systems were also investigated.

2 Materials and methods

2.1 Materials

The BR used in this study was sourced from the Aughinish Alumina Refinery. It was received as a wet sludge with a moisture content of 22.98%. The material was oven-dried at 105 °C to a constant weight and subsequently ground for two hours to obtain a fine powder. Ground granulated blast-furnace slag (GGBS) was supplied by Ecocem Ireland Ltd. The Portland cement (PC) used is a CEM II-A/L cement, compliant with EN 197-1, provided by Irish Cement.

2.2 Mix design

BR and GGBS were used to replace CEM II-A/L at replacement levels ranging from 0% to 80% in 20% increments. The detailed mix proportions are presented in Table 1. All solid components were dry-mixed for 2 minutes, after which the full amount of water was added and mixed for an additional 8 minutes using a mechanical mixer. The resulting fresh slurry was cast into prism moulds measuring 160 × 40 × 40 mm and covered with polyethylene sheets to minimize moisture loss. Specimens were demoulded after 24 hours and cured at 20 ± 3 °C for 28 days.

Table 1. Mix design for BR-GGBS-PC mortars.

Notation	BR	GGBS	CEM II-A/L	Sand: binder ratio	water: binder ratio
100PC	0%	0%	100%	3:1	0.6
20BR80PC	20%	0%	80%		
20BR20G60PC		20%	60%		
20BR40G40PC		40%	40%		
20BR60G20PC		60%	20%		
40BR60PC	40%	0%	60%		
40BR20G40PC		20%	40%		
40BR40G20PC		40%	20%		
60BR40PC	60%	0%	40%		
60BR20G20PC		20%	20%		
80BR20PC	80%	0%	20%		

Pastes with the proportions in Table 1 were also produced for XRD/FTIR analyses. The mineralogy of the resulting cement was analysed with a Bruker XRD D5000 apparatus with a 2.2 kW Cu long fine focus from 5° to 70 ° 2θ. The chemical bonds in the geopolymer were analysed with Fourier-transform infrared spectroscopy (FTIR), carried out using a PerkinElmer Spectrum 100 FTIR apparatus. The spectra were acquired within the wavenumber range of 4000 to 400 cm^{-1}, employing a spectral resolution of 4 cm^{-1}, and an averaging of 32 scans for each measurement.

3 Results and discussion

3.1 Characterization of Irish BR

The chemical composition of the Irish BR is presented in Table 2. Fe_2O_3 was identified as the predominant component, accounting for 50.50% of the total composition. This iron content is significantly higher than that reported for BR elsewhere [14–17]. In contrast, the SiO_2 and Al_2O_3 contents were 7.18% and 15.20%, respectively, slightly lower than those typically observed in BR from other sources. Given that silicon and aluminium are the primary contributors to pozzolanic activity, the relatively low Si and Al content suggests that the reactivity of Irish BR may be limited.

Table 2 Chemical composition of BR determined by X-ray fluorescence (wt%).

Oxide (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	TiO_2	MnO	P_2O_5	SrO	BaO	LOI
BR	7.18	15.20	50.50	4.16	0.10	3.82	0.04	0.16	6.46	0.05	0.32	0.01	0.01	6.34

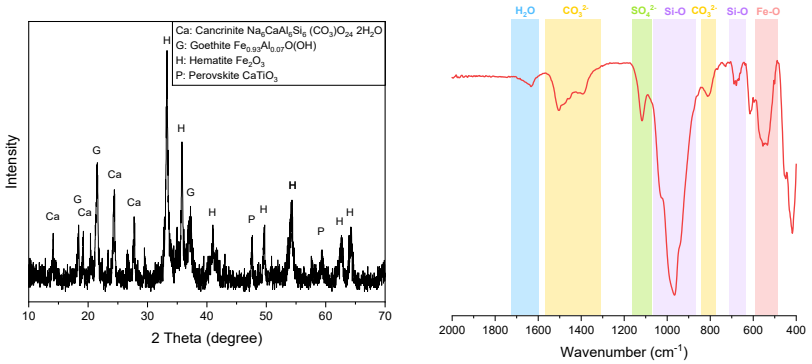

Fig. 1 (a) Mineral composition and (b) chemical bonds in Irish BR.

The mineral composition and chemical bonds in the BR are shown in Fig. 1. Consistent with the high iron content reported in Table 1, hematite was identified as the primary crystalline phase in the Irish BR. Cancrinite, a common phase in BR characterized by Si-O and CO_3^{2-} functional groups in the FTIR spectra, was also detected. In

addition, minor phases of goethite and perovskite were observed. Notably, the presence of goethite, which contains a significant amount of hydroxyl (-OH) groups, is expected to increase both the water demand and adsorption capacity of the BR.

3.2 Properties of the BR-GGBS-PC system

The flowability and compressive strength of the BR-GGBS-PC ternary mortars are presented in Fig. 2(a). In general, the incorporation of BR reduced flowability, as reflected by the decreased initial flow diameter. This reduction is attributed to the hydroxyl groups present in BR, which tend to form hydrogen bonds with water molecules, thereby limiting the movement of the slurry. Conversely, the addition of GGBS improved flowability. The combined use of BR and GGBS within the PC system demonstrated a synergistic effect, enabling increased BR incorporation without severely compromising workability.

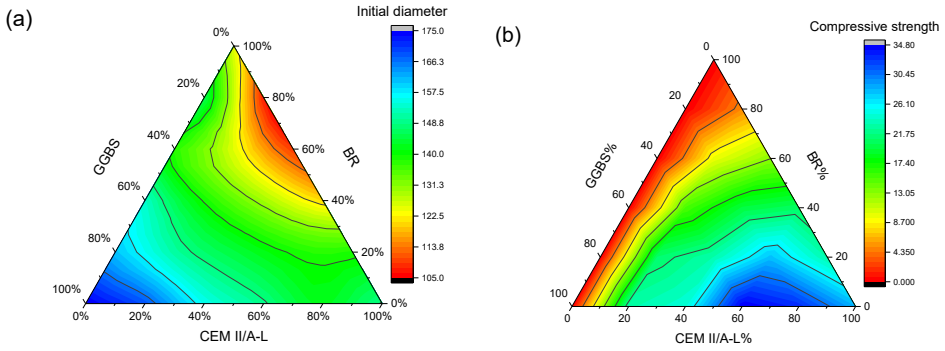

Fig. 2 (a) Flowability and (b) strength of BR-GGBS-PC ternary mortar.

The compressive strength of the BR-GGBS-PC mortars is presented in Fig. 2(b). As expected, CEM II/A-L was the primary contributor to strength development. Increasing the dosage of BR had a detrimental effect on compressive strength, consistent with the previously noted low reactivity of Irish BR. A 20% replacement of CEM II with BR resulted in an 18.33% decrease in compressive strength, while replacements of 40% and 60% caused strength losses of 26.46% and 54.6%, respectively. The addition of BR reduced the overall cementitious content, thereby limiting strength development. However, GGBS exhibited a strong synergistic effect with BR. Notably, even with a high replacement level, containing only 20% CEM II/A-L, the mortar achieved a compressive strength of 21.08 MPa, demonstrating the potential of combining BR with GGBS to partially replace PC in binder systems.

3.3 Microstructure of BR-GGBS-PC cements

To better understand the role of BR in the PC system, the reaction products of both the BR-PC and BR-GGBS-PC systems were investigated. Fig. 3(a) illustrates the mineralogical composition of hydrated PC with varying BR replacement levels. Portlandite and calcite were identified as the primary crystalline reaction products in hydrated CEM

II. As the BR replacement increased, the intensity of portlandite and calcite peaks declined, while peaks corresponding to inert BR phases such as hematite and goethite became more pronounced. This shift indicates that the low reactivity of BR reduces the formation of cementitious phases, thereby hindering strength development in the BR-PC system.

Fig. 3(b) presents the evolution of chemical bonding in the BR-PC system with increasing BR content. In the control PC specimens, Si-related bonds dominated the cementitious matrix. With higher BR replacement, Fe-related bonds, such as Fe-O in hematite and Fe-OH in goethite, became increasingly prominent. Additionally, a notable increase in Si-O bonds was observed in specimens with high BR content. These Si-O bonds are primarily associated with cancrinite, a feldspathoid mineral formed during the Bayer process through the reaction between bauxite and NaOH. Cancrinite is low pozzolanic [14]. However, its increased Si-O bond does not seem to contribute to early strength development. This agrees with the generally accepted pozzolan kinetics contributing to late strength.

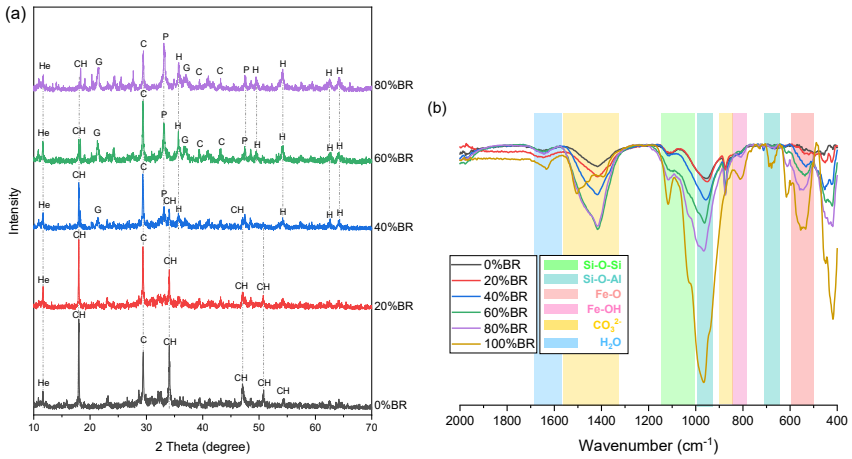

Fig. 3. Mineral composition (a) and chemical bonds (b) of the BR-PC specimens.

(CH: Portlandite, $Ca(OH)_2$; C: Calcite, $CaCO_3$; P: Perovskite, $CaTiO_3$; H: Hematite, Fe_2O_3; He: Calcium aluminum carbonate hydroxide hydrate, $Ca_4Al_2(CO_3)(OH)_{12}(H_2O)_5$)

Fig.4 presents the mineral composition of the BR-GGBS-PC system. At a constant BR replacement level of 20%, increasing the proportion of GGBS replacing PC led to a transformation in the microstructure from crystalline to semi-amorphous. The XRD pattern of the high-content GGBS specimens shows an amorphous characteristic comparable to other geopolymers previously investigated [18].

The production of semi-amorphous cementing hydrates is likely due to the reaction of the portlandite with the BR alkalis. This reaction transfers the BR-GGBS-PC cement system investigated from a merely PC system to an alkali-activation (geopolymer)

system. The formation of additional cementitious gels contributes to mechanical strength development. Therefore, the BR and GGBS demonstrate a good synergy effect.

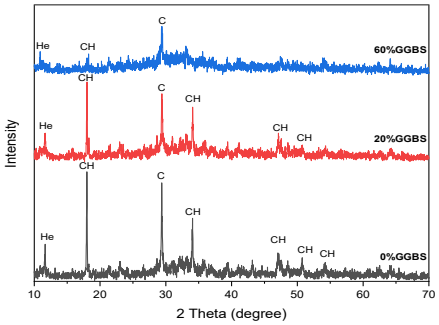

Fig. 4 Mineral composition of the BR-GGBS-PC specimens.

(CH: Portlandite, $Ca(OH)_2$; C: Calcite, $CaCO_3$; He: Calcium aluminum carbonate hydroxide hydrate, $Ca_4Al_2(CO_3)(OH)_{12}(H_2O)_5$)

4 Conclusion

In this study, the mechanical performance and microstructural characteristics of the BR-GGBS-PC ternary system were investigated. The following conclusions can be drawn:

- The Irish BR is characterized by high Fe and low Si and Al contents. Hematite, goethite, and cancrinite were identified as the main crystalline phases. The low levels of reactive Si and Al, along with high crystallinity, indicate limited pozzolanic reactivity.
- The incorporation of BR negatively affected both the flowability and mechanical performance of the BR-PC system. The high hydroxyl content increased water demand, while the limited reactivity of BR reduced strength development. However, a synergistic effect was observed when BR was combined with GGBS, mitigating some of the negative impacts.
- Increasing BR content led to a reduction in cementing hydrates. As BR replacement increased, the presence of inert phases such as hematite and goethite became more prominent, while the quantity of cementing hydrates decreased, leading to poor mechanical performance.
- The incorporation of GGBS consumed portlandite and, in combination with the alkalis in BR, facilitated the formation of additional cementing gels through alkali activation. As a result, the mineralogy of the matrix shifted toward a semi-amorphous structure, showing similar properties to alkali-activated slag.

Reference

1. Davis, J.R.: Aluminum and Aluminum Alloys. ASM International (1993)
2. Venetski, S.: “Silver” from clay. Metallurgist. 13, 451–453 (1969). https://doi.org/10.1007/BF00741130
3. Binczewski, G.J.: The point of a monument: A history of the aluminum cap of the Washington Monument. JOM. 47, 20–25 (1995). https://doi.org/10.1007/BF03221302
4. Tarcy, G.P., Kvande, H., Tabereaux, A.: Advancing the industrial aluminum process: 20th century breakthrough inventions and developments. JOM. 63, 101–108 (2011). https://doi.org/10.1007/s11837-011-0120-4
5. Habashi, F.: A Hundred Years of the Bayer Process for Alumina Production. In: Donaldson, D. and Raahauge, B.E. (eds.) Essential Readings in Light Metals: Volume 1 Alumina and Bauxite. pp. 85–93. Springer International Publishing, Cham (2016)
6. Swain, B., Lee, C.G., Park, J.R.: Assessment of bauxite residue as secondary resource for rare earth metal and valorization challenges: A perspective. Resour. Conserv. Recycl. Adv. 14, 200078 (2022). https://doi.org/10.1016/j.rcradv.2022.200078
7. Aughinish Alumina Ltd.: Aughinish Alumina Ltd. Annual Environmental Report 2019. Aughinish Alumina Ltd., Limerick, Ireland (2020)
8. Aughinish Alumina Limited: Aughinish Alumina Limited Annual Environmental Report (AER) 2023. , Limerick, Ireland (2024)
9. Fennell, P., Driver, J., Bataille, C., Davis, S.J.: Cement and steel — nine steps to net zero. Nature. 603, 574–577 (2022). https://doi.org/10.1038/d41586-022-00758-4
10. EN: 197-1. Cement–Part 1: Composition, specifications and conformity criteria for common cements. Lond. Eur. Comm. Stand. (2011)
11. Romano, R.C.O., Bernardo, H.M., Maciel, M.H., Pileggi, R.G., Cincotto, M.A.: Hydration of Portland cement with red mud as mineral addition. J. Therm. Anal. Calorim. 131, 2477–2490 (2018). https://doi.org/10.1007/s10973-017-6794-2
12. Viyasun, K., Anuradha, R., Thangapandi, K., Santhosh Kumar, D., Sivakrishna, A., Gobinath, R.: Investigation on performance of red mud based concrete. Mater. Today Proc. 39, 796–799 (2021). https://doi.org/10.1016/j.matpr.2020.09.637
13. Ghalehnovi, M., Roshan, N., Hakak, E., Shamsabadi, E.A., de Brito, J.: Effect of red mud (bauxite residue) as cement replacement on the properties of self-compacting concrete incorporating various fillers. J. Clean. Prod. 240, 118213 (2019). https://doi.org/10.1016/j.jclepro.2019.118213
14. Alelweet, O., Pavia, S., Lei, Z.: Pozzolanic and Cementing Activity of Raw and Pyro-Processed Saudi Arabian Red Mud (RM) Waste. Recent Prog. Mater. 3, 1–1 (2021). https://doi.org/10.21926/rpm.2104047
15. Anirudh, M., Rekha, K.S., Venkatesh, C., Nerella, R.: Characterization of red mud based cement mortar; mechanical and microstructure studies. Mater. Today Proc. 43, 1587–1591 (2021). https://doi.org/10.1016/j.matpr.2020.09.504
16. Li, X., Zhang, Q., Mao, S.: Investigation of the bond strength and microstructure of the interfacial transition zone between cement paste and aggregate modified by Bayer red mud. J. Hazard. Mater. 403, 123482 (2021). https://doi.org/10.1016/j.jhazmat.2020.123482
17. Liu, Y., Zhuge, Y., Chen, X., Duan, W., Fan, R., Outhred, L., Wang, L.: Micro-chemo-mechanical properties of red mud binder and its effect on concrete. Compos. Part B Eng. 258, 110688 (2023). https://doi.org/10.1016/j.compositesb.2023.110688
18. Lei, Z., Pavia, S., Wang, X.: Biomass ash waste from agricultural residues: Characterisation, reactivity and potential to develop one-part geopolymer cement. Constr. Build. Mater. 431, 136544 (2024). https://doi.org/10.1016/j.conbuildmat.2024.136544