Methodology for a Safe and Low-Cost Large-Scale Application for Bauxite Residue in association with Portland Cement in Compositions Applied in Civil Construction

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Abstract

Using bauxite residue (BR) in association with Portland cement (PC) presents an opportunity to address challenges facing the aluminium and cement industries: the roadmap of the International Aluminium Institute identifies this application as one of the most impactful uses for BR in large-scale. The route developed in this study, with support from the Alcoa Foundation, focuses on developing a large-scale and low-cost application for the BR without the requirement for additional treatment of the residue, such as energy intensive calcination or additives addition. This study has investigated the properties and compositional variability of BR collected from two different alumina refineries, and the synergistic interactions of the BR with different Portland cements. The chemical reactions and formation of hydrated products were monitored during the development of eco-friendly compositions, with the performance and durability of the components produced being a key output of this study. This methodology has facilitated the production of components at a pilot-scale, without a negative impact on the development of microstructure.The material was easily molded, demonstrated high performance, and was environmentally safe. This paper presents the methodology, and illustrates the overall strategic approach and challenges faced relating to the production of large-scale cement components exposed to environmental conditions.

Keywords: Bauxite residue, Portland cement, Chemical reaction, Rheology, Performance, and methodology of development.

1. Global Bauxite Residue Overview

Over 95% of the alumina produced globally is through the Bayer process. On average, for every ton of alumina produced, approximately 1 to 1.5 tonnes of BR are produced. Annual production of alumina in 2021 was over 138 million tonnes, resulting in the generation of over 180 million tonnes of BR [4]. The BR is deposited and stored in specially engineered facilities commonly called impoundments [1]. These impoundments securely contain the tailings to avoid BR contact with surface or underground water [2,3] and otherwise serve to store BR safely and efficiently.

The aluminium industry is actively investigating options to reduce the quantity of BR produced and the land area required for storage. An important enabler to this is identifying and developing opportunities for value adding uses of BR [5]. Presently, the main applications evaluated for BR include element recovery (heavy metals, rare earth elements, and other critical minerals), synthesis of zeolites, landfill capping, soil amelioration, production of Portland cement clinker, manufacture of building materials, concretes and cementitious components, tiles and bricks, road construction (sub-base and sub-grade), geopolymers, water treatment, production of red ceramics, selective filters for SO_2 or H_2S, and others [3,6–26]. The main challenges relating to BR reuse are high alkalinity and the presence of heavy and alkaline metals. This explains, in part, the reason for why less than 4Mt of BR produced annually is being utilized [17].

The physical properties of BR vary significantly between alumina refineries due to the bauxite mineralogy and processing conditions [27]. For example, the specific surface area (SSA) reported by [28] ranged from 64 - 187 m²/g, according to the BET method [29], highlighting the difference between BR generated from a Bayer process versus a sintering process. In a separate study, the average SSA of BR was ~ 35 m²/g for BR generated in the Bayer process, with a range of 15 and 55 m²/g. Generally BR contains a large proportion of fine particles, varying from 100 nm - 200 µm [5,17,27,28,30], with a d_{90} <75 µm.

Similarly, BR chemical composition potentially changes with time when stockpiled. Typical BR chemical compositions reported in the literature are presented in Table 1, separated by country and the results for Brazil highlighted.

Table 1. Survey of the range of chemical composition of bauxite residue in different countries.

Country	Fe_2O_3	Al_2O_3	TiO_2	SiO_2	Na_2O	CaO	K_2O	LOI	References
Australia	24-44	15-40	3-10	9-32	0.4-9	2-4.5	-	-	[22,31]
Brazil	**20-49**	**10-25**	**3-10**	**3-50**	**2-12**	**1-4.8**	**0.1-2**	**9-14**	[18,25,31–34]
China	5-47.5	6.5-26	0.7-7.3	15-25.9	5.2-12.2	2.6-47	0.1-0.77	7-16.3	[35]
Germany	25-35	22-28	8-24	6-16	4-9	0.5-4	-	-	[31]
Greece	41-47	15-26	5.3-5.5	6.8-7.5	~2.9	~10	-	~9.2	[31,36]
Hungary	38-51	14-15	4.5-8	10-13	5-8	>3.5	-	-	[22,31]
India	33-53	14-27	3-23	5-9	4-6	2.7-3.3	-	-	[22,31]
Italy	4-35	10-20	0.5-9	11-37	1.9-7.5	6.5-22	2	7-19	[26,37]
Jamaica	~50	~15	~6.7	1.5-3.4	1-3.2	7	-	-	[22,31]
Japan	39-45	17-20	2.5-4	14-16	7-9	-	-	-	[31]
Russia	~23	~29	~4	~17	~11	~1			[31]
Suriname	24-33	19-24	3.5-12	12-16	8-9	~5			[22,31]
Taiwan	~41	~20	~3	~18	~4				[22]
Turkey	~36	~23	~4	~12	~7	~3	~0.3	~9	[38]
USA	10-60	5-29	3.5-11	4-23	2-8	5-47	-	-	[22,31]
IAI	24-45	10-22	4-20	5-30	2-8	0-14	-	-	[36]
Liu and Wu[2]	6-28	9-17.7	3.2-7.3	8.3-22.7	2.9-4	20-41	0.05-0.4	11.8-17	[28]
Evans	5-60	5-30	0.3-15	3-50	1-10	2-14	-	5-20	[17]

The main mineralogical phases of BR are presented in Table 2. These predominantly consists of oxides and hydroxides of iron, aluminium, silica, calcium and titanium [2,5,39,40].

[2] Considering both process of bauxite residue generation, Bayer and sintering.

Leaching of sodium and aluminates, and consequent efflorescence, was higher with increasing BR additions, but it was possible to fix a considerable proportion of these soluble ions by associating the BR with slag and selecting the most suitable Portland cement.

The monitoring of alkali-silica reaction by the Brazilian standard accelerated method, indicates that at up to 20% of BR addition the trend is similar to that observed by the reference material. However, using a larger amount of BR replacement resulted in a lower reaction compared to the reference, possibly caused by clinker dilution or by the higher availability of soluble aluminate ions that may impart a mitigating effect.

Finally, we produced some cementitious components using the best conditions evaluated for the fresh and hardened state properties, chemical reaction, and leaching. The components were evaluated and exposed to the environment. The results indicated that it is possible to produce safe, large-scale applications for BR by using appropriate criteria for particle properties, choice of raw materials, and the development of compositions with correct proportioning to guarantee the performance in the fresh and hardened state, with good durability and environmental performance with respect to leaching.

4. References

1. Impoundment, *Alcoa*, https://www.alcoa.com/sustainability/en/improving-our-footprint/impoundment-management/ (accessed on 4 August 2022).
2. Power G., Gräfe M. and Klauber C., 2011, Bauxite residue issues: I. Current management, disposal and storage practices, *Hydrometallurgy*, 108, 33–45.
3. Wang S., Ang H. M. and Tadé M. O., 2008, Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes, *Chemosphere*, 72, 1621–35.
4. Statistics of Alumina Production, *International Aluminium org*, https://international-aluminium.org/statistics/alumina-production/ (accessed on 4 August 2022).
5. Romano R C. de O., 2020, Propriedades químicas, reológicas e estado endurecido de composições de cimento Portland e diferentes materiais cimentícios suplementares.
6. A. N. B., G.V. K. M., K. K. and K. R., 2018, Removal of fluoride from water using H2O2-treated fine red mud doped in Zn-alginate beads as adsorbent, *Journal of Environmental Chemical Engineering*, 6, 906–16.
7. Agrawal S., Rayapudi V. and Dhawan N., 2018, Extraction of Iron values from Red mud, *Materials Today: Proceedings*, 5, 17064–72.
8. Agrawal S., Rayapudi V. and Dhawan N., 2019, Comparison of microwave and conventional carbothermal reduction of red mud for recovery of iron values, *Minerals Engineering*, 132, 202–10.
9. Akinci A. and Artir R., 2008, Characterization of trace elements and radionuclides and their risk assessment in red mud, *Materials Characterization*, 59, 417–21.
10. Alam S., Das S. K. and Rao B. H., 2017, Characterization of coarse fraction of red mud as a civil engineering construction material, *Journal of Cleaner Production*, 168, 679–91.
11. Altundoğan H. S., Altundoğan S, Tümen F. and Bildik M., 2002, Arsenic adsorption from aqueous solutions by activated red mud, *Waste Management*, 22, 357–63.
12. Ascensão G., Seabra M. P., Aguiar J. B. and Labrincha J. A., 2017, Red mud-based geopolymers with tailored alkali diffusion properties and pH buffering ability, *Journal of Cleaner Production*, 148, 23–30.
13. Bădănoiu A. I., Abood Al-Saadi T. H. and Voicu G., 2015, Synthesis and properties of new materials produced by alkaline activation of glass cullet and red mud ,*International Journal of Mineral Processing*, 135, 1–10,
14. Borra C. R., Pontikes Y., Binnemans K. and Van Gerven T., 2015, Leaching of rare earths from bauxite residue (red mud), *Minerals Engineering* ,76, 20–7.

15. Cengeloglu Y., Kir E., Ersoz M., Buyukerkek T. and Gezgin S., 2003, Recovery and concentration of metals from red mud by Donnan dialysis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 223, 95–101.
16. Das N. and Das D., 2013, Recovery of rare earth metals through biosorption: An overview, *Journal of Rare Earths,* 31, 933–43.
17. Evans K., 2016, The History, Challenges, and New Developments in the Management and Use of Bauxite Residue, *J. Sustain. Metall.*, 2, 316–31.
18. Fujii A. L., dos Reis Torres D., de Oliveira Romano R. C., Cincotto M. A. and Pileggi R. G., 2015, Impact of superplasticizer on the hardening of slag Portland cement blended with red mud, *Construction and Building Materials,* 101, 432–9.
19. Li X., Xiao W., Liu W., Liu G., Peng Z., Zhou Q. and Qi T., 2009, Recovery of alumina and ferric oxide from Bayer red mud rich in iron by reduction sintering, *Transactions of Nonferrous Metals Society of China,* 19,1342–7.
20. Liu Y. and Naidu R., 2014, Hidden values in bauxite residue (red mud): Recovery of metals, *Waste Management,* 34, 2662–73.
21. Nguyen-Huy C. and Shin E. W., 2016, Amelioration of catalytic activity in steam catalytic cracking of vacuum residue with ZrO 2 -impregnated macro–mesoporous red mud, *Fuel,* 179, 17–24.
22. Paramguru R. K., Rath P. C. and Misra V. N., 2004, Trends in Red Mud Utilization – a Review, *Mineral Processing and Extractive Metallurgy Review,* 26, 1–29.
23. Pontikes Y. and Angelopoulos G. N., 2013, Bauxite residue in cement and cementitious applications: Current status and a possible way forward, *Resources, Conservation and Recycling,* 73,53–63.
24. Qu Y., Lian B., Mo B. and Liu C., 2013, Bioleaching of heavy metals from red mud using Aspergillus niger, *Hydrometallurgy,* 136, 71–7.

25 Romano R. C. O., Bernardo H. M., Mesquita J. A. F. S., Niza D. A., Cincotto M. A. and Pileggi R. G., 2018, Evaluation of the hardened state properties of zero-cement mortars produced using bauxite residue as an activator to ground blast furnace slag vol 1 (Athens: KU Leuven), pp 293–300.

26 Sglavo V. M., Campostrini R., Maurina S., Carturan G., Monagheddu M., Budroni G. and Cocco G., 2000, Bauxite ‘red mud’ in the ceramic industry. Part 1: thermal behaviour, *Journal of the European Ceramic Society,* 20, 235–44.

27 Reeves H. J., Wealthall G. and Younger P. L., 2011, *Advisory visit to the bauxite processing tailings dam near Ajka, Vesprém County, western Hungary* (Keyworth, UK: British Geological Survey).

28 Liu D-Y. and Wu C-S., 2012, Stockpiling and Comprehensive Utilization of Red Mud Research Progress, *Materials,* 5 ,1232–46.

29 Sinha P., Datar A., Jeong C., Deng X., Chung Y. G. and Lin L-C., 2019, Surface Area Determination of Porous Materials Using the Brunauer–Emmett–Teller (BET) Method: Limitations and Improvements, *J. Phys. Chem. C*, 15.

30 Antunes M. L. P., Couperthwaite S. J., da Conceição F. T., Costa de Jesus C. P., Kiyohara P .K., Coelho A. C. V. and Frost R. L., 2012, Red Mud from Brazil: Thermal Behavior and Physical Properties, *Ind. Eng. Chem. Res*,. 51,775–9.

31 Garcia M. C. S., 2012, *Modificação do residuo de bauxita gerado no Processo Bayer por tratamento térmico,* Disseertação (Mestrado) (Universidade de São Paulo).

32 Liberato C. C., Romano R. C. de O., Montini M., Gallo J. B., Gouvea D. and Pileggi R. G., 2012, Efeito da calcinação do resíduo de bauxita nas características reológicas e no estado endurecido de suspensões com cimento Portland *Ambient. constr.*, 12, 53–61.

33 Romano R., Liberato C., Montini M., Gallo J., Cincotto M. and Pileggi R., 2013, Evaluation of transition from fluid to elastic solid of cementitious pastes with bauxite residue using oscillation rheometry and isothermal calorimetry, *Applied Rheology*, 23.

34 Romano R.C. O., Bernardo H. M., Maciel M. H., Pileggi R. G. and Cincotto M. A., 2018, Hydration of Portland cement with red mud as mineral addition, *J Therm Anal Calorim,* 131, 2477–90.

35 Liu W., Yang J. and Xiao B., 2009, Review on treatment and utilization of bauxite residues in China, *International Journal of Mineral Processing,* 93, 220–31.

36 World Aluminium, 2015, *Bauxite residue management: Best practice.*

37 Sglavo V. M., Maurina S., Conci A., Salviati A., Carturan G. and Cocco G., 2000, Bauxite 'red mud' in the ceramic industry. Part 2: production of clay-based ceramics, *Journal of the European Ceramic Society,* 20 ,245–52.

38 Yalçın N. and Sevinç V., 2000, Utilization of bauxite waste in ceramic glazes, *Ceramics International,* 26, 485–93.

39 Gräfe M., Power G. and Klauber C., 2011, Bauxite residue issues: III. Alkalinity and associated chemistry, *Hydrometallurgy,* 108 ,60–79.

40 Reddy P. S., Reddy N. G., Serjun V. Z., Mohanty B., Das S. K., Reddy K. R. and Rao B. H., 2021, Properties and Assessment of Applications of Red Mud (Bauxite Residue): Current Status and Research Needs, *Waste Biomass Valor,* 12, 1185–217.

41 Quarcioni V. A., Chotoli F. F., Coelho A. C. V. and Cincotto M. A., 2015, Indirect and direct Chapelle's methods for the determination of lime consumption in pozzolanic materials, *Rev. IBRACON Estrut. Mater.,* 8 ,1–7.

42 Thornber M. R. and Binet D., 1999 ,Caustic soda adsorption on Bayer residues.

43 Rebmann M. S., 2017, *Robustez de concretos com baixo consumo de cimento Portland: desvios no proporcionamento e variabilidade granulométrica e morfológica dos agregados.,* Doutorado em Engenharia de Construção Civil e Urbana (São Paulo: Universidade de São Paulo).

44 Romano R. C. O., Rebmann M. S., Bernardo H. M., Raucci J., Massucato C. and Pileggi R. G., 2017, Impact of particle packing on the rheological properties of cementitious pastes dispersed with polycarboxylate vol 25 (Kopenhagen), pp 397–404.

45 Maciel M. H., Soares G. S., Romano R C. de O. and Cincotto M. A., 2019, Monitoring of Portland cement chemical reaction and quantification of the hydrated products by XRD and TG in function of the stoppage hydration technique, *J Therm Anal Calorim,* 136, 1269–84.

46 Ahmadah O., Bessaies-Bey H., Yahia A. and Roussel N., 2022, A new mix design method for low-environmental-impact blended cementitious materials: Optimization of the physical characteristics of powders for better rheological and mechanical properties, *Cement and Concrete Composites,* 128, 104437.

47 Oliveira I. R. de, 2000, *Dispersão e empacotamento de partículas: princípios e aplicações em processamento cerâmico* (São Paulo: Fazendo Arte).

48 Barra Bizinotto M., Faleschini F., Jiménez Fernández C. G. and Aponte Hernández D. F., 2017, Effects of chemical admixtures on the rheology of fresh recycled aggregate concretes, *Construction and Building Materials,* 151, 353–62.

49 Berodier E., Gibson L. R., Burns E., Roberts L. and Cheung J., 2019, Robust production of sustainable concrete through the use of admixtures and in-transit concrete management systems, *Cement and Concrete Composites,* 101, 52–66.

50. Rashad A. M., Bai Y., Basheer P. A. M., Milestone N. B. and Collier N. C., 2013 ,Hydration and properties of sodium sulfate activated slag ,*Cement and Concrete Composites,* 37, 20–9.

51. Shafaatian S. M. H., 2013, How does fly ash mitigate alkali–silica reaction (ASR) in accelerated mortar bar test (ASTM C1567), 11.

52. Lothenbach B., Scrivener K. and Hooton R. D., 2011, Supplementary cementitious materials ,*Cement and Concrete Research* ,41, 1244–56.

53. Scrivener K. L., Füllmann T., Gallucci E., Walenta G. and Bermejo E., 2004, Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods, *Cement and Concrete Research,* 34, 1541–7.

54. Snellings R., 2016, Assessing, Understanding and Unlocking Supplementary Cementitious Materials, *RILEM Tech Lett*, 1, 50.
55. Nicoleau L. and Nonat A., 2016 , A new view on the kinetics of tricalcium silicate hydration *Cement and Concrete Research*, 86, 1–11.
56. Guo S., Zhang Y., Wang K., Bu Y., Wang C., Ma C. and Liu H., 2019, Delaying the hydration of Portland cement by sodium silicate: Setting time and retarding mechanism *Construction and Building Materials,* 205, 543–8.
57. Romano R. C. de O., Bernardo H. M., Maciel M. H., Pileggi R. G. and Cincotto M. A., 2019, Using isothermal calorimetry, X-ray diffraction, thermogravimetry and FTIR to monitor the hydration reaction of Portland cements associated with red mud as a supplementary material, *J Therm Anal Calorim*, 137 ,1877–90.
58. Bentz D., Garboczi E. J., Haecker C. and Jensen O., 1999, Effects of Cement Particle Size Distribution on Performance Properties of Portland Cement-Based Materials, *Cement and Concrete Research*, 29, 1663–71.
59. Alam S., Das S. K. and Rao B. H., 2017, Characterization of coarse fraction of red mud as a civil engineering construction material, *Journal of Cleaner Production,* 168, 679–91.
60. Romano R. C. de O., Mesquita J. A. F. S. de, Bernardo H. M., Niza D. A., Maciel M. H., Cincotto M. A. and Pileggi R. G., 2021, Combined evaluation of oscillatory rheometry and isothermal calorimetry for the monitoring of hardening stage of Portland cement compositions blended with bauxite residue from Bayer process generated in different sites in Brazil , *Rev. IBRACON Estrut. Mater.*, 14 ,e14211.
61. Alam S., Das S. K. and Rao B. H., 2019, Strength and durability characteristic of alkali activated GGBS stabilized red mud as geo-material, *Construction and Building Materials,* 211, 932–42.
62. Güneyisi E., Gesoğlu M., Karaoğlu S. and Mermerdaş K., 2012 ,Strength, permeability and shrinkage cracking of silica fume and metakaolin concretes, *Construction and Building Materials,* 34, 120–30.
63. Tang W. C., Wang Z., Donne S. W., Forghani M. and Liu Y., 2019, Influence of red mud on mechanical and durability performance of self-compacting concrete, *Journal of Hazardous Materials,* 379, 120802.
64. Zajac M., 2018, Impact of microstructure on the performance of composite cements_ Why higher total porosity can result in higher strength, *Cement and Concrete Composites,* 15.
65. Agarwal S. K., Masood I. and Malhotra S. K., 2000 ,Compatibility of superplasticizers with different cements, *Construction and Building Materials* ,14, 253–9.
66. Marques P. F., Chastre C. and Nunes Â., 2013, Carbonation service life modelling of RC structures for concrete with Portland and blended cements, *Cement and Concrete Composites,* 37, 171–84.
67. Scrivener K. L., John V. M. and Gartner E. M., 2018, Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry, *Cement and Concrete Research,* 114, 2–26.
68. Kang S-P. and Kwon S-J., 2017, Effects of red mud and Alkali-Activated Slag Cement on efflorescence in cement mortar,, *Construction and Building Materials,* 133, 459–67.
69, Liu S., Hu Q., Zhao F. and Chu X., 2014, Utilization of steel slag, iron tailings and fly ash as aggregates to prepare a polymer-modified waterproof mortar with a core–shell styrene–acrylic copolymer as the modifier, *Construction and Building Materials,* 72, 15–22.
70. Qu Y., Li H., Tian W., Wang X., Wang X., Jia X., Shi B., Song G. and Tang Y., 2015, Leaching of valuable metals from red mud via batch and continuous processes by using fungi, *Minerals Engineering,* 81, 1–4.
71. Romano R. C. O., 2018, *Chemical, rheological and hardened state properties of Portland cement and calcined bauxite residue compositions* (São Paulo - Brasil: University of São Paulo).