Effect of Combination of Fly Ash and Bauxite Residue on the Fresh and Hardened States Properties of Cement Compositions

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Abstract



The investigation of the use of bauxite residue from the Bayer process in association with Portland cement has grown substantially in recent years, but there are still uncertainties regarding aspects related to environmental issues and pathologies after the hardening of the cementitious component. The high alkali content and salinity, resulting from the bauxite digestion with NaOH, can leave free and soluble ions in the material, that if not fixed by association with cement, can culminate in efflorescence, leaching, and alkali-silica reaction. The positive effect of the addition of supplementary cementitious materials in cementitious products with the residue has already been observed, with improvement of some properties in the ternary system. In addition to technical issues, logistics must also be considered when choosing raw materials, as the high cost of long-distance transport can be an impediment to the large-scale use of the residue. Therefore, in this work fly ash generated in an alumina plant was chosen to combine with its bauxite residue in compositions formulated with Portland cement from the region, making the aspects related to the transport economically viable. This work aims to investigate the impact on the fresh and hardened state properties of pastes with different levels of additions. The results show that fly ash has a positive effect on pastes, resulting in better mechanical and microstructural properties of ternary systems in relation to the binary of cement with the residue. The addition of fly ash improves the flow of the pastes and delays the gain of consistency and agglomeration of particles. In this way, the combination of these materials can make the cementitious system more ecoefficient, durable and reduce environmental risk, allocating two industrial residues for large-scale application, in addition to reducing the consumption of cement in the compositions.

Keywords: Bauxite residue, Red mud, Fly ash, Synergistic effect, Ternary cementitious mixtures.

1. Introduction

Only about 3 % of the bauxite residue generated from the Bayer process (here called only as BR, to simplify) is successfully used on an industrial scale, most of which in civil construction [1]. According to the International Aluminum Institute [2], BR generation is equivalent to 4 % of cement production, and due to its chemical and mineralogical characteristics, has potential to be applied in association to the cement during the production of clinker Portland or in the compositions of cement components, contributing with the development of a large-scale application.

Several studies in recent years have shown the possibility of obtaining products suitable for use in civil construction, with improved microstructural, mechanical, and hygroscopic properties [3,4]. *Pontikes and Angelopoulos* [5] presented a review of some applications of bauxite residue in association with Portland cement, providing a critical point of view on the research conducted in the last 40 years, pointing out that the main barrier for the transition from the laboratory scale to the industry is the economic aspect. *Ribeiro, Labrincha and Morelli* [6] identified that the use

of BR in cementitious compositions can be beneficial in the corrosion resistance of reinforcement concrete, due to its high alkalinity and presence of aluminosilicates. *Viyasun et al.* [7] observed an increase in compressive, tensile and bending strengths in compositions with 20 and 30 % replacement of cement by BR. *Romano et al.* [8], showed that bauxite residue can be used as an alkaline activator to ground blast furnace slag, producing compositions with zero-Portland cement. In chemical reaction, *Fujii et al.* [9] and *Romano et al.* [10] observed a delay in the cement reaction, with an increase in the induction and acceleration periods, reducing the formation of the main hydrated products and increasing the formation of ettringite. *Dodoo-Arhin et al.* [11] indicated that up to 5 % of substitution of Portland cement by the BR in compositions of pavements did not affect the mechanical strength or water absorption. *Romano et al.* [12] showed the impact of using BR in microconcrete of Portland cement and did a comparison with other kinds of ordinary supplementary cementitious materials, concluding that this practice is technically viable.

Consequently, the use of BR in this sector has the potential to contribute to reducing the energy spent in the related processes, the use of natural resources, the storage of BR and CO_2 emissions [2]. However, the use of BR in cementitious compositions is complex and many other characteristics still need to be investigated to scale-up its production. The high alkali content and the high salinity, resulting from the treatment of bauxite with NaOH, can leave free and soluble ions in the formed material. If they are not treated to try to mitigate these effects, fixing the free ions, pathological manifestations can occur in the materials in which the residue is reused, such as efflorescence, leaching and alkali-silica reaction (ASR) [13,14].

The addition of supplementary cementitious materials (SCM) in concrete mixtures is widely recognized as the most practical way to diminish ASR in cementitious compositions, acting as mitigating agent to sequester free ions [15]. The most used SCMs are limestone, ground granulated blast furnace slag and natural pozzolans. Fly ash (FA) can also be used as SCM, being collected from coal furnace filters of thermoelectric power plants, rich in reactive silica and alumina, containing little or no CaO. When combining SCM and/or inert material with Portland cement, it is possible to have a synergistic effect in the binary or ternary systems, with superposition of physical and chemical effects in the mixture, resulting in better mechanical and microstructural properties [16].

In addition to technical concerns after hardening of the cementitious component, logistical issues must also be considered when combining different raw materials. The high cost of transport over long distances can be an impediment to the large-scale use of the residue [1,2]. Thus, it is important to evaluate the use of BR in local synergies, making its transport economically viable.

This work aims to investigate the impact of the addition of BR and FA in cement pastes in the fresh and hardened states. Both additions combined are generated from the same alumina plant, in the northeast region of Brazil, and the cement is also from the same region. Isothermal conduction calorimetry in addition to rotational and oscillatory rheometry were used to analyze the fresh properties and the transition from fluid to solid state; and total porosity, splitting tensile strength and dynamic modulus of elasticity were employed for the hardened state evaluations at 28 days of curing.

2. Materials

The pastes were formulated with bauxite residue (BR) and fly-ash (FA) from the aluminum plant in São Luís, Maranhão, northeastern Brazil, dried at 105 °C for 24 h. The BR was ground and sieved through a 106 μ m mesh opening and the FA was sieved through the same mesh. All tests presented here were made with the materials with this preparation. The cement was a Brazilian Portland cement named according to the national standard [17] as CPIV, commonly found in agglomeration is increased. As the BR has more fine particles than the cement, while the FA has coarser, the first dominated the effects in the ternary systems.

For the hardened state properties, there was a tendency of decreasing the splitting tensile strength and modulus of elasticity with the increase in the replacement level of cement. The combination of FA had a positive effect on cementitious compositions, improving the mechanical strength and reducing the total porosity of the compositions of ternary systems in relation to the binary of cement and BR.

The inclusion of materials with different specific surface areas and particle sizes, enabled the formation of a more packed matrix when more cement was replaced, resulting in better mechanical and microstructural properties. Therefore, when FA was added to the system with BR and CPIV, the different granulometry enable a pore refinement in the matrix, improving the properties, as the voids were better filled and reduced.

6. References

- K. Evans, The History, Challenges, and New Developments in the Management and Use of Bauxite Residue, J. Sustain. Metall. 2 (2016) 316–331. https://doi.org/10.1007/s40831-016-0060-x.
- [2] IAI, Technology Roadmap: Maximising the use of bauxite residue in cement, International Aluminium Institute, 2020.
- [3] E.P. Manfroi, M. Cheriaf, J.C. Rocha, Microstructure, mineralogy and environmental evaluation of cementitious composites produced with red mud waste, Construction and Building Materials. 67 (2014) 29–36. https://doi.org/10.1016/j.conbuildmat.2013.10.031.
- [4] R.C.O. Romano, A.L. Fujii, R.B. Souza, M.S. Takeashi, R.G. Pileggi, M.A. Cincotto, Acompanhamento da hidratação de cimento Portland simples com resíduo de bauxita, Cerâmica. 62 (2016) 215–223. https://doi.org/10.1590/0366-69132016623632039.
- [5] Y. Pontikes, G.N. Angelopoulos, Bauxite residue in cement and cementitious applications: Current status and a possible way forward, Resources, Conservation and Recycling. 73 (2013) 53–63. https://doi.org/10.1016/j.resconrec.2013.01.005.
- [6] D.V. Ribeiro, J.A. Labrincha, M.R. Morelli, Effect of the addition of red mud on the corrosion parameters of reinforced concrete, Cement and Concrete Research. 42 (2012) 124–133. https://doi.org/10.1016/j.cemconres.2011.09.002.
- [7] K. Viyasun, R. Anuradha, K. Thangapandi, D. Santhosh Kumar, A. Sivakrishna, R. Gobinath, Investigation on performance of red mud based concrete, Materials Today: Proceedings. 39 (2021) 796–799. https://doi.org/10.1016/j.matpr.2020.09.637.
- [8] R.C.O. Romano, H.M. Bernardo, J.A.F.S. Mesquita, D.A. Niza, M.A. Cincotto, R.G. Pileggi, Evaluation of the hardened state properties of zero-cement mortars produced using bauxite residue as an activator to ground blast furnace slag, in: KU Leuven, Athens, 2018: pp. 293–300.
- [9] A.L. Fujii, D. dos Reis Torres, R.C. de Oliveira Romano, M.A. Cincotto, R.G. Pileggi, Impact of superplasticizer on the hardening of slag Portland cement blended with red mud, Construction and Building Materials. 101 (2015) 432–439. https://doi.org/10.1016/j.conbuildmat.2015.10.057.
- [10] R. Romano, H. Montefusco, M. Hark Maciel, R. Pileggi, M. Cincotto, 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, Journal of Thermal Analysis and Calorimetry. (2019). https://doi.org/10.1007/s10973-019-08095x.
- [11] D. Dodoo-Arhin, R.A. Nuamah, B. Agyei-Tuffour, D.O. Obada, A. Yaya, Awaso bauxite red mud-cement based composites: Characterisation for pavement applications, Case

 Studies
 in
 Construction
 Materials.
 7
 (2017)
 45–55.

 https://doi.org/10.1016/j.cscm.2017.05.003.
 7
 (2017)
 45–55.

- [12] R.C. de O. Romano, J.A.F.S. Mesquita, H.B. Montefusco, G.P. Brasileiro, G.H.U. Muniz, M.A. Cincotto, R.G. Pileggi, Impact of Using Bauxite Residue in Microconcrete and Comparison with Other Kind of Supplementary Cementitious Material, in: 35th Conference and Exhibition ICSOBA, Hamburgo, 2017: pp. 505–518.
- [13] C.C. Liberato, R.C. de O. Romano, M. Montini, J.B. Gallo, D. Gouvea, R.G. Pileggi, Efeito da calcinação do resíduo de bauxita nas características reológicas e no estado endurecido de suspensões com cimento Portland, Ambient. constr. 12 (2012) 53–61. https://doi.org/10.1590/S1678-86212012000400005.
- [14] S.-P. Kang, S.-J. Kwon, Effects of red mud and Alkali-Activated Slag Cement on efflorescence in cement mortar, Construction and Building Materials. 133 (2017) 459–467. https://doi.org/10.1016/j.conbuildmat.2016.12.123.
- [15] M.J. Tapas, L. Sofia, K. Vessalas, P. Thomas, V. Sirivivatnanon, K. Scrivener, Efficacy of SCMs to mitigate ASR in systems with higher alkali contents assessed by pore solution method, Cement and Concrete Research. 142 (2021) 106353. https://doi.org/10.1016/j.cemconres.2021.106353.
- [16] C.S. Feltrin, G.C. Isaia, A. Lübeck, Synergic effects between mineral admixtures on strength and microstructure of concretes, Rev. IBRACON Estrut. Mater. 13 (2020) e13604. https://doi.org/10.1590/s1983-41952020000600004.
- [17] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 16697 Cimento Portland Requisitos, (2018).
- [18] ASTM International, ASTM C114-18 Standard Test Method for Chemical Analysis of Hidraulic Cement, (2018).
- [19] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 13810 Água Determinação de metais – Método de espectrometria de absorção atômica por chama, (1997).
- [20] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 15895 Materiais pozolânicos – Determinação do teor de hidróxido de cálcio fixado – Método Chapelle modificado, (2010).
- [21] J.S. Raucci, R.T. Cecel, R.C.O. Romano, R.G. Pileggi, V.M. John, Effect of mixing method on the mini-slump spread of Portland cement pastes, Rev. IBRACON Estrut. Mater. 11 (2018) 410–431. https://doi.org/10.1590/s1983-41952018000200010.
- [22] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 7222 Concreto e argamassa Determinação da resistência à tração por compressão diametral de corpos de prova cilíndricos, (2011).
- [23] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 15630 Argamassa para assentamento e revestimento de paredes e tetos – Determinação do módulo de elasticidade dinâmico através da propagação da onda ultrassônica, (2008).
- [24] R.C.O. Romano, H.M. Bernardo, M.H. Maciel, R.G. Pileggi, M.A. Cincotto, Hydration of Portland cement with red mud as mineral addition, J Therm Anal Calorim. 131 (2018) 2477–2490. https://doi.org/10.1007/s10973-017-6794-2.
- [25] K.L. Scrivener, P. Juilland, P.J.M. Monteiro, Advances in understanding hydration of Portland cement, Cement and Concrete Research. 78 (2015) 38–56. https://doi.org/10.1016/j.cemconres.2015.05.025.
- [26] S. Goñi, F. Puertas, M.S. Hernández, M. Palacios, A. Guerrero, J.S. Dolado, B. Zanga, F. Baroni, Quantitative study of hydration of C3S and C2S by thermal analysis: Evolution and composition of C–S–H gels formed, J Therm Anal Calorim. 102 (2010) 965–973. https://doi.org/10.1007/s10973-010-0816-7.
- [27] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, Cement and Concrete Research. 41 (2011) 1244–1256. https://doi.org/10.1016/j.cemconres.2010.12.001.

- [28] F. Deschner, F. Winnefeld, B. Lothenbach, S. Seufert, P. Schwesig, S. Dittrich, F. Goetz-Neunhoeffer, J. Neubauer, Hydration of Portland cement with high replacement by siliceous fly ash, Cement and Concrete Research. 42 (2012) 1389–1400. https://doi.org/10.1016/j.cemconres.2012.06.009.
- [29] R.C. de O. Romano, J.A.F.S. de Mesquita, H.M. Bernardo, D.A. Niza, M.H. Maciel, M.A. Cincotto, R.G. Pileggi, 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 (2021) e14211. https://doi.org/10.1590/s1983-41952021000200011.
- [30] D. Hou, D. Wu, X. Wang, S. Gao, R. Yu, M. Li, P. Wang, Y. Wang, Sustainable use of red mud in ultra-high performance concrete (UHPC): Design and performance evaluation, Cement and Concrete Composites. 115 (2021) 103862. https://doi.org/10.1016/j.cemconcomp.2020.103862.
- [31] 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, (n.d.) 14.
- [32] M. Ghalehnovi, E. Asadi Shamsabadi, A. Khodabakhshian, F. Sourmeh, J. de Brito, Selfcompacting architectural concrete production using red mud, Construction and Building Materials. 226 (2019) 418–427. https://doi.org/10.1016/j.conbuildmat.2019.07.248.
- [33] R.-X. Liu, C.-S. Poon, Utilization of red mud derived from bauxite in self-compacting concrete, Journal of Cleaner Production. 112 (2016) 384–391. https://doi.org/10.1016/j.jclepro.2015.09.049.
- [34] W.C. Tang, Z. Wang, Y. Liu, H.Z. Cui, Influence of red mud on fresh and hardened properties of self-compacting concrete, Construction and Building Materials. 178 (2018) 288–300. https://doi.org/10.1016/j.conbuildmat.2018.05.171.
- [35] W.C. Tang, Z. Wang, S.W. Donne, M. Forghani, Y. Liu, Influence of red mud on mechanical and durability performance of self-compacting concrete, Journal of Hazardous Materials. 379 (2019) 120802. https://doi.org/10.1016/j.jhazmat.2019.120802.
- [36] Y. Yao, Y. Li, X. Liu, S. Jiang, C. Feng, E. Rafanan, Characterization on a cementitious material composed of red mud and coal industry byproducts, Construction and Building Materials. 47 (2013) 496–501. https://doi.org/10.1016/j.conbuildmat.2013.05.030.
- [37] R.C.O. Romano, R.G. Pileggi, Use of rheological models for the evaluation of cement pastes with airentraining agent in different temperatures, in: Nordic Rheology Society, Copenhagen, n.d.
- [38] L. Senff, D. Hotza, J.A. Labrincha, Effect of red mud addition on the rheological behaviour and on hardened state characteristics of cement mortars, Construction and Building Materials. 25 (2011) 163–170. https://doi.org/10.1016/j.conbuildmat.2010.06.043.
- [39] R. Romano, C. Liberato, M. Montini, J. Gallo, M. Cincotto, R. Pileggi, Evaluation of transition from fluid to elastic solid of cementitious pastes with bauxite residue using oscillation rheometry and isothermal calorimetry, Applied Rheology. 23 (2013). https://doi.org/10.3933/ApplRheol-23-23830.
- [40] P.F.G. Banfill, RHEOLOGY OF FRESH CEMENT AND CONCRETE, (n.d.) 70.
- [41] P. Chindaprasirt, S. Rukzon, Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar, Construction and Building Materials. 22 (2008) 1601–1606. https://doi.org/10.1016/j.conbuildmat.2007.06.010.