Citric, Ascorbic and Acetic Acids for Bauxite Residue pH Neutralization and their Effects on the Sodalite Phase

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Abstract

Bayer sodalite is the main desilication product (DSP) formed during the refining of alumina in the low temperature Bayer process and can represent 16 - 24 % of the bauxite residue (BR) composition. BR's sodicity and alkalinity, mainly due to soluble sodium salts and solid sodalite contents, can limit its use as a raw material for other applications (e.g. agriculture, building materials, and steel industry). Chemical, physical, and biological approaches have been developed to mitigate BR´s sodicity and alkalinity. Among them, treatment with organic acids, from chemical or biological sources, demonstrates great potential. However, more research is needed to understand the effects on sodalite dissolution and its impact on pH and other parameters over time. In this context, batch tests were carried out using citric, ascorbic, and acetic acids for the treatment of a Brazilian BR. The BR sample (20 % w/v) was mixed with organic acid solutions at different concentrations (50, 100, 200, and 400 mmol) and stirred at 100 rpm, at 28 °C. XRD, SEM, EC, and pH were evaluated up to the equilibrium factor $F \leq 0.5$. At 400 mmol, the equilibrium pH was lower using ascorbic and citric acids (pH ~ 7) than using acetic acid (pH ~ 8). SEM analysis showed small aggregates (< 5 µm), typical of sodalite mineral in the BRs treated with acetic and ascorbic acids. In the treatments with citric acid, these aggregates were less frequently seen. XRD peak intensities indicated a reduction in sodalite phase only at higher citric acid concentrations (> 200 mM). The result suggests that citric acid (≥ 200 mmol) is more effective in reducing BR pH and sodicity, indicating this as a promising pre-treatment for BR processing before use in other applications.

Keywords: Sodalite dissolution, Bauxite residue, Mineral biotechnology, Green mining.

1. Introduction

Bauxite residue (BR) is generated as a by-product of alumina production from bauxite by the Bayer process. BR alkalinity and sodicity result from bauxite ore digestion in a sodium hydroxide (NaOH) solution, at around 145 °C. The mineral phases in BR are mainly the primary bauxite minerals (e.g. hematite, quartz, anatase, rutile, boehmite), as well as secondary phases formed during the process, such as sodalite, cancrinite, hydrogarnet (generally referred as desilication products or 'DSP's), re-precipitated gibbsite, calcite, tricalcium aluminate and others [1].

Despite filtering and washing to reduce the soluble caustic and sodium in the solids, at discharge from the refinery BR still contains residual dissolved, and leachable sodium hydroxide, sodium carbonate, sodium aluminate, and other soluble substances. BR´s sodium content and alkalinity is mainly as soluble sodium salts and DSPs, where the latter can represent 16 – 24 % of the BR composition [2]. The DSPs, Bayer sodalite and Bayer cancrinite, have a common chemical formula $Na_6[Al_6Si_6O_{24}].2NaX.6H_2O$, where X represents OH^-, Cl^-, NO_3^-, ½ CO_3^{2-}, or ½ SO_4^{2-}, their crystal structures however, are different. Sodalite is cubic while cancrinite is hexagonal, and if calcium is present in the liquor, it can replace Na_2X in the cancrinite formula. Sodalite is formed in Bayer circuits designed for gibbsitic bauxite digestion at temperatures around 145 ºC, while cancrinite is formed at the higher reaction temperatures (> 220 ºC) used for boehmitic and diasporic bauxite digestion [3].

Due to the large and increasing annual global production, and BR´s large worldwide inventory [4], residue application research has increased in the last decade. Studies have reported potential BR application in waste-water and waste-gas treatment (for phosphorus adsorption and purification of acidic waste gases), as building materials, catalysts, as a secondary source of metal and rare earth elements, and in agriculture as a soil conditioner [5-8]. However, its physico-chemical characteristics limit wide application, and a dealkalization and sodium reduction step would facilitate its broader use [1-2]. Physical and biological approaches to mitigate BR´s alkalinity and sodium content, such as salt ion precipitation or displacement, pyrometallurgy and hydrometallurgy, acid neutralization, and microbial-driven remediation have been investigated [9-11].

BR transformation by mineral (hydrochloric and sulfuric) and organic (citric) acids at low concentrations, with and without gypsum amendment has also been studied [10]. All treatments were successful in decreasing total alkalinity and pH to some degree in experiments using cancrinite-rich bauxite residue. Citric acid reacts with cancrinite, promoting macro-aggregate formation, improving BR's physical properties [10]. Cancrinite was also leached using high concentrations of citric acid [11]. It is important to note that while inorganic acid leaching can neutralize and remove sodium from BR, it can also dissolve undesirable metals, making the option of organic acid treatment more interesting. Silica gel formation has also been described during sulfuric acid hydrometallurgical processing at pH < 7.0 [12].

Organic acid pretreatment (either from chemical or biological sources) offers the potential to boost BR use [13-14], further closing the aluminum circular economy loop. However, more research is needed to understand the effects over time on sodalite dissolution and on BR pH and other parameters. In this context, the present work reports batch tests carried out using citric, ascorbic, and acetic acids at different concentrations (50, 100, 200, and 400 mmol) for the treatment of a Brazilian BR, to determine their effects in reducing alkalinity and on sodalite dissolution. The study's results will contribute to a better understanding of the potential use of organic acids as a pre-processing step before BR use in various applications.

2. Experimental

The study was conducted at the SENAI Innovation Institute for Mineral Technologies (ISI-TM), in Brazil using a press-filtered BR sample obtained from an alumina refinery located in the state of Pará, Brazil. The BR´s chemical and physical characterization has been previously reported [15].

The experiment was carried out in batches (three replicates) using ACS grade acetic ($C_2H_4O_2$), citric ($C_6H_8O_7$), and L-ascorbic ($C_6H_8O_6$) acids, at concentrations of 50, 100, 200, and 400 mmol, according to an adapted methodology [14]. BR samples at 20 % (w/v) concentration were added into 60 mL clear capped polypropylene bottles and filled with the acid solutions to a final volume sodium (XRF) and sodalite (XRD/SEM) removal capacity was observed compared with citric acid treatments. In conclusion, the results of this study indicates that citric acid, under the tested conditions, is effective as a BR treatment to reduce alkalinity and sodicity prior to BR's use in other applications which require lower pH and sodicity, and represents a promising route for pre-processing before large-scale commercial utilization.

5. References

1. M. Gräfe, G. Power and C. Klauber, Bauxite residue issues: III. Alkalinity and associated chemistry, *Hydromettallurgy*. Vol. 108 (2011), 60-79.
2. Fei Lyu et al., Dealkalization processes of bauxite residue: a comprehensive review. *Journal of Hazardous Materials*, Vol. 403, (2021), 123671.
3. Bingan Xu et al., The effect of calcium and temperature on the transformation of sodalite to cancrinite in Bayer digestion, *Hydrometallurgy*, Vol. 105, (2010), 75-81.
4. Sheng-guo Xue et al., Industrial wastes applications for alkalinity regulation in bauxite residue: A comprehensive review, *Journal of Central South University*,Vol. 26 (2019), 268-288.
5. Chenna Rao Borra et al., Recovery of rare earths and major metals from bauxite residue (red mud) by alkali roasting, smelting and leaching, *Journal of Sustainable Metallurgy*, Vol. 3, (2016), 393-404.
6. Paula de Freitas. et al. (2020) Bayer Process Towards the Circular Economy—Metal Recovery from Bauxite Residue. In: Tomsett A. (eds) Light Metals 2020. The Minerals, Metals & Materials Series. Springer, Cham. https://doi.org/10.1007/978-3-030-36408-3_14.
7. Roseanne Holanda. et al. (2020) Bayer Process Towards the Circular Economy—Soil Conditioners from Bauxite Residue. In: Tomsett A. (eds) Light Metals 2020. The Minerals, Metals & Materials Series. Springer, Cham. https://doi.org/10.1007/978-3-030-36408-3_15.
8. Paula de Freitas. et al. (2021) Gravity Methods Applied to Bauxite Residue for Mineral Pre-concentration. In: Perander L. (eds) Light Metals 2021. The Minerals, Metals & Materials Series. Springer, Cham. https://doi.org/10.1007/978-3-030-65396-5_11.
9. M. Gräfe and Craig Klauber. Bauxite residue issues: IV. Old obstacles and new pathways for in situ residue bioremediation. *Hydrometallurgy*. Vol. 108, (2011), 46-59.
10. Xiangfeng Kong et al., Acid transformation of bauxite residue: conversion of its alkaline characteristics, *Journal of Hazardous Materials*, Vol. 324, (2017), 382-390.
11. W. Li, X. Zhu and S. Tang, Selective separation of sodium from red mud with citric acid leaching. *Separation Science and Technology*, Vol. 52, (2017), 1876-1884.
12. Gözde Alkan et al., Novel approach for enhanced scandium and titanium leaching efficiency from bauxite residue with suppressed silica gel formation. *Scientific Reports, (2018),* DOI:10.1038/s41598-018-24077-9
13. Manas C. Mishra et al., Potencial of citric acid for treatment of extremely alkaline bauxite residue: effect on geotechnical and geoenvironmental properties. Journal of Hazard, Toxic, and Radioactive Waste, Vol. 24, No.4, (2020).
14. Sicheng Wang et al., On the mechanism of sodic removal from bauxite residue and bauxite desilication products (BDP) using acetic acid. *Jom*, Vol. 72, No.1, (2020), 309-318.
15. Patricia M.P. Silva et al., Bauxite residue neutralization potential using biogenic sulfuric and citric acids, *Light Metals* 2021, 52-61.
16. H. Peng, T. Kim and J. Vaughan, Acid leaching of desilication products: implications for acid neutralization of bauxite residue, *Industrial & Engineering Chemistry Research*, (2020) https://dx.doi.org/10.1021/acs.iecr.0c00423.