Adsorbed Soda Investigations at Alunorte

Daniela Rossetto de Menezes[1] **and Robert LaMacchia**[2]
1. Researcher
2. Research Consultant
Hydro, Belém, Brazil
Corresponding author: daniela.menezes@hydro.com

Abstract

In an effort to better close the soda balance at Alunorte, it was noted that the losses via adsorption were not being recorded. To improve upon this, laboratory tests were conducted to determine the adsorption slope of Alunorte residue to enable quantification of this loss. A new experimental method, designed to enable adsorption slope determination somewhat easier than the conventional methodology is reported. Further to this methodology, it is shown that carbonate is leaching from the residue, and hypotheses are put forward to explain this phenomenon. Utilization of the predicted adsorption slope indicates the soda loss to be of the order of 2 kg NaOH/t, yet considerations are also presented regarding the need to consider kinetic impacts of adsorption, given the reduced residence time of residue washing achieved by press filter technology.

Keywords: bauxite residue, soda adsorption, soda loss minimization.

1. Introduction

Ideally, all the soda is recycled in the Bayer circuit; the losses through output streams must be minimized to achieve better cost curve positioning and reduced environmental footprint. A comprehensive evaluation of the main forms of soda loss is fundamental for process performance evaluation and improvement opportunity identification. Recent process management initiatives at Hydro Alunorte to elucidate unaccounted soda losses have led to the recognition that soda adsorbed on bauxite residue was lacking monitoring and control.

Soda adsorption parameters for bauxite residue were first obtained experimentally by Michael Thornber and David Binet [1]. They introduced the assumption of zero soda adsorption in residue in contact with liquor solutions at alkali concentration (TA) of 2 $g.L^{-1}$ and initially proposed an adapted Langmuir equation to describe the relationship between adsorption and liquor TA. This equation provided an overestimated number of adsorption sites for the actual surface area available indicating that DSP adsorbs/desorbs Na^+ both from the surface and from within the cages of its mineral structure [1] (see Figure 1 below [2]).

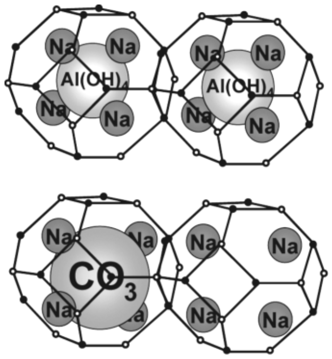

Figure 1. Model of DSP structure highlighting pores where sodium hydroxide may be able to adsorb/desorb [2].

The adsorption data obtained was thus applied to an empirical equation (Equation 1) and the slope S determined by linear regression [1].

$$Adsorption\ Na_2O = S\ (log_{10} c_{TA} - log_{10} 2) \tag{1}$$

where:

Adsorption Na_2O is the g of Na_2O adsorbed per 100 g of residue
c_{TA} is the equilibrium concentration of total alkali, in $g.L^{-1}$ Na_2CO_3

The level of soda adsorption affinity and saturation are thought to depend on mineral type, morphology and particulate surface area, as well as internal area in the case of minerals with zeolite structure like sodalite or cancrinite [1] [2]. Bauxite residue at Hydro Alunorte is composed mostly of the hematite and goethite, desilication product (DSP), and some anatase. Typical elemental composition is provided in Table 1. Process conditions of bauxite residue washing units also affect the degree of soda adsorption and desorption.

Table 1. Bauxite residue elemental composition at Hydro Alunorte (values in % m/m).

Fe_2O_3	Al_2O_3	SiO_2	Na_2O	LOI*	TiO_2	Others
32.6	23.1	17.1	9.8	9.1	5.6	0.3

*LOI stands for loss on ignition, the total mass of compounds volatilized at up to 1000°C.

Teemu Kinnarinen et al. [3] have reported differences on soda recovery from bauxite residue when submitted to press filtration at different temperatures and pressures, which was attributed to desorption and dissolution of Na^+. At Hydro Alunorte, drum and press filtration units operate with different washing residence times and solids concentrations (65 and 78 % solids, respectively).

Using plant-sourced or synthetic bauxite residue, the experiments of Thornber and Binet [1] consisted of a progressive desorption routine with multiple steps, involving: residue dilution into water, agitation for 30 minutes, centrifugation and removal of the supernatant liquor solution. All of the work was performed using 70 mL samples, constant temperature of 55 °C (including centrifuging), and an in-house liquor specific gravity correlation to assist with the mass balancing.

The samples were assumed to reach adsorption equilibrium at each dilution step, but no tests were presented to sustain this assumption. The study does not mention whether any differences existed between the experiments with different solids concentrations, suggesting that no difference was noted. Further, due to the significant amount of soluble soda removed in the early stages of washing, determining the adsorbed soda at the higher concentrations was particularly erroneous.

60 % solids samples	0.098	0.024
Combined data (40 % and 60 %)	0.144	0.010

Slope estimations with their respective standard errors for 60 % solids and 40 % solids concentrations, overlap at the 95 % level of confidence; so there is no indication in this data that the slopes are different for different solids loading.

The adsorption slope coefficient found for the complete data set was applied to the average plant data, so as to obtain an estimative for adsorbed soda loss. Given typical TCs at the output of bauxite residue, a residue/bauxite specific consumption of ~0.3 and overall alumina recovery of ~95 %, the slope would indicate ~2.0 kg of NaOH lost per tonne of alumina.

Comparing with results of other Fe-rich, Jamaican bauxite residues, the slope coefficient found for the overall experimental data is lower than values that correspond to high-hematite or high-goethite residues (0.314 ± 0.002 and 0.204 ± 0.003 g Na_2O/100 g, respectively) [10]. An intermediary slope value would be expected for this study, as the iron minerals present in the bauxite consumed at Alunorte are generally both hematite and goethite [11], which practically remain undissolved at low-temperature gibbsite digestion [12]. Further adsorption tests and residue characterization (in regard to mineralogy and particle size distribution) would be required to evaluate the contribution of DSP content to the adsorption slope and for more conclusive comparisons with the literature.

4. Conclusions

The soda adsorption on bauxite residue at Alunorte has been investigated through the development of an experimental method based on open literature techniques. The method has been applied to observe adsorption kinetics and adsorption equilibrium versus liquor composition. The results have shown that liquor TC/TA can decrease during the adsorption for high TC/TA start liquors, which perhaps corresponds to carbonate leaching from the DSP structure. Further, the test work has indicated that at 25 °C, the soda adsorption reaction has equilibrated after one-hour residence time. The reported slope, together with standard discharge liquor concentrations, suggests a soda loss on the order of 2 kg/t. It is essential that for this reporting, the TC (and not the TA) be used due to possible complications from carbonate leaching.

5. Acknowledgments

The authors acknowledge the R&D laboratory fellows Jaqueline Pinho, Danielle Gonçalves, Walter Santana and Roberta Bianca dos Santos for supporting the execution and improvement of the experimental activities, as well as the Technical Department Laboratory for providing access to additional equipment and instruments. Thanks are also extended to the Clarification Process engineers and Operations team for providing the plant-sourced sample materials. Finally, thanks to Hydro for enabling the development and publication of this work.

6. References

1. Michael Thornber and David Binet, Soda Adsorption in Bauxite Residue, *5th International Alumina Quality Workshop,* (1999), 99-105.
2. P. Smith, C. Wingate and L. D. Silva, Mobility of Occluded Soda in Sodalite, *8th International Alumina Quality Workshop,* (2008), 27-30.
3. T. Kinnarinen, M. Huhtanen, L. Holliday and A. Häkkinen, Challenges related to solute analysis of bauxite residue filter cakes, *Minerals Engineering,* Vol. 120, (2018), 1-6.

4. K. A. Powell, L. J. Kirwan, K. Hodnett, D. Lawson and A. Rijkeboer, Characterisation of Alumina and Soda Losses Associated with the Processing of Goethitic Rich Jamaican Bauxite, *Light Metals,* (2009), 151-156.
5. SysCAD, Alumina 3 Bayer Species Model, 18 May 2017. [Online]. Available: https://help.syscad.net/index.php/Alumina_3_Bayer_Species_Model. [Accessed August 2017].
6. G. E. P. Box, J. S. Hunter and W. G. Hunter, *Statistics for Experimenters,* New Jersey: Wiley-Interscience, 2005.
7. Harvard University, A Summary of Error Propagation, 2007. [Online]. Available: http://ipl.physics.harvard.edu/wp-uploads/2013/03/PS3_Error_Propagation_sp13.pdf. [Accessed June 2018].
8. C. Zaiontz, Real Statistics Using Excel, June 2018. [Online]. Available: www.real-statistics.com. [Accessed June 2018].
9. H. L. Watts and D. W. Utley, Volumetric Analysis of Sodium Aluminate Solutions, *Analytical Chemistry,* Vol. 25, No. 6, (1953), 864-867.
10. G. Gran, Determination of the equilvalence point in potentiometric titrations. Part II, *The Analyst,* Vol. 77, No. 920, (1952), 661-671.
11. R. LaMacchia, A. C. de Carvalho Jr, R. Gallais and A. Dagallier, A Novel Experimental Apparatus for Red Side Studies, in *Proceedings of 36th International ICSOBA Conference*, Belém, Brazil, 2018.
12. R. Neumann, A. N. Avelar and G. M. Costa, Refinement of the isomorphic substitutions in goethite and hematite by the Rietveld method, and relevance to bauxite characterisation and processing, *Minerals Engineering,* no. 55, (2014), 80-86.
13. P. Basu, G. A. Nitowski and P. J. The, Chemical Interactions of Iron Minerals During Bayer Digest and Clarification, in *Iron Control in Hydrometallurgy*, (1986), 223-244.