



ISSN (PRINT) : 2320 -1967  
ISSN (ONLINE) : 2320 -1975



## ORIGINAL ARTICLE

*CHEMXPRESS 8(3), 208-213, (2015)*

# Effect of lime causticization on silica, calcium, oxalate and organic carbon levels in Bayer process washer overflow liquor

Max A. Wellington

Department of Biology, Chemistry & Environmental Science, Northern Caribbean University,  
Mandeville, Jamaica W.I., (USA)

School of Science and Engineering, Atlantic International University, Hawaii, 96813, (USA)

E-mail: max.wellington@ncu.edu.jm

**Abstract :** Inductively coupled plasma (ICP) and Spectrometric analysis of washer overflow liquor (Stage 1-3) from a high temperature Jamaican Alumina refinery revealed significant reductions in liquor calcium (>75%) and Silica (~90%) respectively after causticization using lime (CaO). Reductions were also observed in liquor sulfate (7-14%), fluoride (5-14%), oxalate (2-7%), chloride (6-13%) and Organic Carbon (4-5%) concentrations after

causticization. Analysis of the causticization sludge by X-Ray Fluorescence (XRF) and Infra-red thermal analysis confirmed the removal of silica, calcium, phosphorus and organic carbon respectively from the Bayer process liquor.

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**Keywords :** Lime; Causticization; Bayer process; Alumina; Silica; Calcium; Organic carbon.

## INTRODUCTION

Lime has been often described as the “aspirin” of the Bayer process due to its importance in reducing the levels of a number of impurities which impact the productivity of the process as well as the quality of alumina produced<sup>[1,2,3]</sup>. An important use of lime in Bayer process operations is in the re-causticization of Bayer process side streams such as overflow liquor in the mud washing circuit to concomitantly reduce carbonate levels and increase caustic levels<sup>[2,4,5,6]</sup>. Many of the research papers ex-

amined in this area focused largely elucidating the thermodynamics or on improving the efficiency of the causticization reaction but there seem to be a paucity of research publications looking at the impact of causticization on liquor purity which can affect the quality and efficiency of smelter grade alumina produced in the Bayer Process. In this study we examined the impact of the causticization of mud washer overflow liquor on the resulting levels of silica, calcium, oxalate and organics which are important liquor impurities that can significantly impact the quality of alumina produced by the Bayer

process<sup>[7-18]</sup>. The study was conducted using liquor from a high temperature alumina refinery that processes a blend of both gibbsitic ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) and boehmitic ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) bauxites at digestion temperatures of about  $250^\circ\text{C}$ .

## EXPERIMENTAL

### Determination of % CaO by titration

Triplicate samples of 0.5 grams of dried, finely grounded lime sample was analyzed by titration to determine %CaO according to the method described in reference<sup>[19]</sup>.

### XDB phase analysis of lime

Triplicate samples of a 5 g subsample of the lime sample used in this study was placed in a spex cap and pressed into a pellet at 20, 000 psi using a briquetting sample press. The pellet was then analyzed by x-ray fluorescence (Phillips) and X-ray diffraction (Phillips) and the resulting spectra were then integrated using XDB (or X-ray Database) software to yield the XDB phase spectra using mass balances to refine the final phase composition as described in reference<sup>[20]</sup>.

### Alumina, caustic and soda analysis

Analyses were done in triplicate by the Worsely/Metrohm titration method as described in references<sup>[6, 21]</sup>.

### Causticization test

Causticization reactions were conducted as described in reference<sup>[6,23]</sup>. Samples for analysis for Alumina, Caustic, Soda, Fluoride, Sulfate, Oxalate and Chloride were withdrawn from the batch reactor periodically or at the end of the reaction period as required using a syringe fitted with a 0.45 micron

filter.

At the end of the reaction the solids were collected and oven dried for 1 hour at  $100^\circ\text{C}$  for analysis for  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$  by XRF; Organic Carbon using the Leco SC144DR Analyzer and LOI using the Leco TGA 601 Thermogravimetric Analyzer as described in reference<sup>[6, 21]</sup>.

### Ion chromatography

Determination of Fluoride, Chloride, Oxalate and Sulfate was done using a Dionex 6000 Ion Chromatogram in isocratic mode as described in references<sup>[6, 21]</sup>.

### Determination of calcium and silica in Bayer liquors

Calcium concentrations of Bayer process liquor were assayed using a Perkin-Elmer Optima 4300 DV ICP spectrometer (OES) previously calibrated for calcium determination and equipped with an auto-sampler and argon furnace according to the method described in reference<sup>[21]</sup>. Silica concentration in the liquor was determined spectrophotometrically according to the method described in reference<sup>[21]</sup>.

## RESULTS AND DISCUSSION

TABLE 1. shows the results of XDB phase and titimetric analysis of the industrially prepared lime sample used during the study. The results show an approximate concentration of 96% CaO with small amount of Sulfate (0.2%) and carbonate (1.2%) impurities and particle size of  $3\mu\text{m}$ . This compares well with purified lime which ranges from 95-97% CaO and 2-5 $\mu\text{m}$  particle size.

TABLE 2. shows the results of lime causticization of washer over flow liquor from stages 1-3 of the Bayer process mud circuit from a high temperature

TABLE 1 : XDB phase and titration analysis of lime

	XDB	Titration
CaO%	96.9 ± 0.2%	95.6± 0.3%
CaSO <sub>4</sub> (%)	0.2%	-
CaCO <sub>3</sub> (%)	1.2%	-
H <sub>2</sub> O (%)	1.7 %	-
LOI (%)	2.8 %	-
Particle Size (μm)	3	-

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**TABLE 2 : Batch causticization of Bayer plant washer overflow liquor (stages 1-3) for 2 hours at 99°C at varying lime stoichiometries (target C/S = 0.920)**

Stage	Initial Soda (g/L)	Initial C/S	Final C/S		
			Lime Factor: 1.0*	1.2	1.5
1.	177.18	0.761	0.837	0.848	0.848
2.	129.46	0.766	0.866	0.890	0.907
3.	95.4	0.772	0.869	0.893	0.943
Mean	(Weighted)	0.765	0.854	0.872	0.890
Mean	Caustic (g/L)	307.6	343.3	350.9	357.8

\*Stoichiometric lime dosage

**TABLE 3 : % Reduction in analytes present in washer overflow (WOF) stages 1-3 liquor before and after causticization for 2 hours at 99°C. (lime charge = 1.5)**

	WOF 1		WOF 2		WOF 3	
	Before	After	Before	After	Before	After
Fluoride (g/L)	1.12 ± 0.17	0.96 ± 0.14	0.82 ± 0.12	0.77 ± 0.11	0.57 ± 0.09	0.56 ± 0.08
Chloride (g/L)	3.56 ± 0.53	3.09 ± 0.46	2.75 ± 0.41	2.55 ± 0.38	2.01 ± 0.30	1.89 ± 0.28
Sulfate (g/L)	10.00 ± 1.50	8.57 ± 1.30	7.98 ± 1.20	7.37 ± 1.11	5.85 ± 0.88	5.45 ± 0.82
Oxalate (g/L)	1.43 ± 0.22	1.36 ± 0.20	1.39 ± 0.21	1.36 ± 0.20	1.32 ± 0.20	1.23 ± 0.18
Org. Carbon(%)	9.4 ± 0.5	8.9 ± 0.4	8.2 ± 0.4	7.9 ± 0.4	6.4 ± 0.3	6.1 ± 0.3

alumina refinery in Jamaica. The aim of the causticization reaction is to convert sodium carbonate (soda) in the liquor to sodium hydroxide (caustic) thereby increasing the liquor causticity or C/S (caustic/soda) ratio. Carbonation or conversion of Bayer caustic (NaOH) to carbonate ( $\text{Na}_2\text{CO}_3$ ) occurs largely as a result of the limestone ( $\text{CaCO}_3$ ) and to a lesser extent from the organic content of the bauxite utilized as well as from flocculants, crystal growth modifiers and anti-foaming agents<sup>[8,17,21]</sup>.

Jamaican bauxites have been shown to contain up to 2.5% calcite and 0.2% organic carbon<sup>[20]</sup>. The optimum C/S ratio for Bayer process refineries is 0.8 and above and it has been shown that a 0.06 drop in C/S could reduce alumina yield by 2.1 g/L of pregnant Bayer liquor<sup>[22]</sup>. From the results in TABLE 2, the highest C/S ratios were obtained using the lime charge factor of 1.5 and so this lime charge was used for the subsequent studies in this paper.

TABLE 3. shows the impact of causticization on the levels of fluoride, chloride, sulfate, oxalate and Total Organic Carbon (TOC) of the Bayer process liquor. The concentration of these Bayer impurities were highest in Stage 1 WOF liquor and lowest in

Stage 3 WOF liquor. In all cases there was a reduction in these Bayer impurities in the liquor after lime causticization with the greatest percent reductions being observed after the causticization of Stage 1 Washer overflow liquor (WOF 1) followed by stages 2 and 3 respectively. It can be suggested that the reduction in these impurities is due to the formation of calcium salts which form part of the sludge in the causticization vessel.

Fluorine is present in bauxites at reported concentrations between 0.01- 0.30% and dissolves into the liquor during digestion forming a relatively minor portion of the liquor anionic impurities<sup>[23]</sup>. Fluoride and aluminum are known to form stable compounds with calcium ( $\text{CaF}_2$ ) and has also been shown to interact with sulfate in Bayer liquors to form the sparingly soluble double salt Kogarkoite ( $\text{NaF} \cdot \text{Na}_2\text{SO}_4$ ). Formation of these sparingly soluble salts could account for the reduction in liquor fluoride after lime causticization. It is surmised that chloride enters the Bayer liquor via the bauxite feed and is reduced after causticization due to its adsorption or association with the desilication products (DSP) sodalite and cancrinite. DSP products are also capable of sequestering carbonate and sulfate anions

from the liquor<sup>[12,24]</sup>. The relatively high levels of sulfate observed in the liquor (Supporting Information) is due largely to the addition of sodium sulfide for the control of zinc which is relatively high in Jamaican bauxites<sup>[25]</sup>. Due to the oxidizing nature of the Bayer process, the sulfide is eventually oxidized to sulfate which account for in excess of one-half the total sulfate in the liquor the balance emanating from the bauxite feed<sup>[26]</sup>. Sulfate removal from the liquor could be due to the formation of sulfate bearing hydrocalumite and possibly the sparingly soluble calcium sulfate salt ( $\text{CaSO}_4$ ) during the causticization reaction<sup>[27]</sup>.

The organic component of Bayer liquors emanate largely from the bauxite feed in the form of humates, lignin, cellulose, proteins as well as additives to the process such as acrylics, flocculants, crystal growth modifiers<sup>[15,28]</sup>. The exposure to high temperature and pressures and strong sodium hydroxide concentrations degrade these complex organic species to benzene-carboxylic acids, hydroxyl-benzene-carboxylic acids, succinate, acetate and formate and a plethora of other compounds<sup>[6,15,29-32]</sup>. The ultimate degradation products however, because of the recycling of the liquor are sodium oxalate and sodium carbonate<sup>[33]</sup>. The decrease of oxalate from the liquor observed during causticization is most likely due to reaction with lime to form the relatively insoluble calcium oxalate which subsequently deposits with the sludge in the reactor. The use of lime for oxalate removal in the Bayer process is a well established technology in the alumina industry where it is added to seed wash liquor after precipitation of alumina<sup>[34]</sup>.

The reduction (~5%) in organics could be due in part to formation of some insoluble calcium salts with organic acids present in the liquor as well as by adsorption of some liquor organics to various

components of the causticization sludge<sup>[2]</sup>. Many Bayer plant problems originate from organics contamination of the Bayer liquor and as such their removal usually augurs well for the process<sup>[13]</sup>. Some of the difficulties caused by organic impurities include: reduced alumina yield; generation of excessive fine alumina particles; increased density, viscosity, specific heat and boiling point of the Bayer liquor; increased impurity content in the alumina; colored alumina; lower red mud settling rates; loss of caustic due to formation of sodium organic salts; increase scale formation; excessive foam in the liquor process; co-precipitation of sodium oxalate with the product hydrate and increase in scale formation<sup>[13]</sup>.

TABLE 4. shows the calcium and silica levels in the Bayer liquor before and after causticization with lime (calcite). Calcite has been shown to have low solubility in Bayer liquors and under mud washing conditions was found to have solubility of less than 5ppm<sup>[35]</sup>. Studies demonstrated that temperature, carbonate levels and organic carbon concentration of Bayer liquors affected calcium solubility<sup>[35, 36]</sup>. Calcium oxide solubility was shown to decrease with increased temperature, increased carbonate and decreased organics<sup>[35, 36]</sup>. From our study both the pre and post-causticization calcium levels were highest in stage 1 washer overflow and lowest in washer overflow stage 3. This observation could be due in part to the higher organic and carbonate levels in the Stage 1 overflow liquor compared to stages 2 and 3 respectively.

The decrease in silica levels to nil in all the liquors could be due largely to formation of Desilication Product (DSP). Between temperatures of 60 and 140°C silica will co-precipitate with sodium aluminate as sodium aluminum silicate (sodalite or cancrinite)<sup>[12, 37]</sup>. These DSP compounds are in-

TABLE 4 : Washer overflow (WOF) liquor  $\text{SiO}_2$  and calcium levels before and after causticization

	Before		After	
	$\text{SiO}_2$ (g/L)	CaO (ppm)	$\text{SiO}_2$ (g/L)	CaO (ppm)
WOF1	0.36 ± 0.05	6.0 ± 0.3	0.04±0.01	1.5 ± 0.1
WOF2	0.22 ± 0.03	4.0± 0.2	0.02 ±0.004	0.80 ±0.04
WOF 3	0.16 ±0.02	2.5± 0.1	0.01± 0.002	0.04 ± 0.01

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soluble and therefore form a part of the causticization sludge (Supporting Information).

Due to the cyclical nature of the Bayer process impurities can build up to untenable levels if they are not removed in a timely fashion. As a result of this many processes and technologies have been developed to control the levels of impurities in order to maintain the efficiency and productivity of Bayer process operations as well as the quality of the alumina produced as substantiated by a number of patents to this effect<sup>[13]</sup>. This paper highlights the potential uses of lime causticization in the removal of several important impurities from the Bayer process.

## ACKNOWLEDGMENTS

The author would like to thank Alumina Partners of Jamaica for their support of this research; Mr. Robert Finlayson, Senior Chemist, Alumina Partner of Jamaica for assistance with the XRF/XDB analysis and Mr. Alpha Boubacar Barry, Senior Process Engineer, Alumina Partners of Jamaica for technical advice.

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