Thermal Denaturing and Study of Bauxite Organics

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Abstract

The distribution and removal of organic material within pisolitic bauxite, mined in Northern Queensland, Australia, has been studied in this research programme. Although bauxite organics as measured by Total Organic Carbon (TOC) content (< 0.30 %) may appear negligible, it increases oxalate formation disrupting the Bayer process. While previous studies have described the in-situ influence of decaying Bayer organics to increase oxalate production, the study and removal of bauxite organics prior to the Bayer process (pre-Bayer) have remained limited. The current research examined the nature and distribution of organics within pisolitic bauxite. LIBS/ToF SIMS indicate "younger" oxygenated organics evident on the outer perimeter of pisolites while within the pisolite, organics exhibit more of an aromatic character. Furthermore, bauxite organics tend to increase as the particle size distribution decreases and at shallower depths within the deposit. Additionally, the authors have previously investigated several techniques to reduce bauxite TOC (including dissolution, plasma, ultrasonics, abrasion and boric acid esterification). However, low-temperature thermal organics "denaturing" (275–350 °C) proved to have the largest impact on the Bayer process value chain and is reported. Low-temperature thermal organics denaturing reduces bauxite TOC by 42 % yet reduces oxalate formation by up to 86 %. A developing LCMS "fingerprint" programme provided a simple method to show the impact of thermal treatment on the molecular suite of Bayer organics. Bauxite QMID-TGA/DTA results indicate increased thermal stability of organics formed by thermal treatment partially explaining the noted compounding TOC/oxalate relationship. The research highlights the importance of understanding bauxite organics and shows that low-temperature thermal treatment can denature organics effectively, reducing oxalate formation with less energy compared to complete elimination.

Keywords: Bauxite organics, Thermal denaturing, Oxalate.

1. Introduction

Pisolitic bauxite mined in the Weipa region of north-east Queensland, Australia has been extensively studied by Taylor and Eggelton [1–4]. Bauxite grade (or quality) is typically defined by alumina and silica oxide equivalents from the sum of mineralogical composition [4]. One of the minor bauxite contaminants is organic carbon, which is primarily adsorbed on the outer perimeter of pisolitic bauxite particles through leaching of decaying humic matter, originating in the vegetative overburden. Total Organic Carbon (TOC) numerically defines the organic content of bauxite, which is typically below 0.3 % for most global deposits [5]. Bauxite organics are mostly insoluble in water (at a neutral pH). They comprise micro-organisms, cellulose, lignin, fulvic acid, humic acid and humins [7]. A portion of these organics are soluble within Bayer liquor (pH 12). As humic acids are the most abundant Bayer-soluble organics, their empirical chemical structure may be used as a reference biopolymer [7]. A humic acid molecule comprises several oxygenated molecular functions, primarily hydroxyl and carboxylic acids but additionally (in lesser concentration) esters, aldehydes and ketones. As such, most of these oxygenated organics are readily extracted into Bayer liquor and susceptible to caustic decay serving as molecular precursors producing stable low molecular weight (LMW) derivatives, including oxalate. Oxalate has limited Bayer solubility, precipitating as sodium oxalate ($Na_2C_2O_4$) at elevated concentration, disrupting the alumina refinery process. Although bauxite organics negatively influence the Bayer process in diverse modes [6–9], the primary focus of this research is the influence on oxalate production.

The impact of bauxite organics within alumina refineries has historically focused on fundamental studies of in-situ decaying organics (referencing model compounds) within Bayer liquor [7, 10, 11]. Subsequently, in-situ methodologies to remediate this impact have focused on Bayer liquor [26] and not pre-Bayer (bauxite pretreated to remove organics) processes. Apart from denoting the numerical TOC value, fundamental studies examining the nature of bauxite organics with the aim of developing pre-Bayer interventions to restrict refinery impact have been limited (as they are minor contaminants in pisolitic bauxite). The geological age of pisolitic bauxite in the Weipa region is estimated to be between 50 and 65 million years [2, 5]. On a molecular level (and over the bauxitization process), occluded humic material within the pisolitic core gradually transforms (decreasing H/C and O/C ratios), acquiring more of an aromatic character [12, 13] which hinders Bayer caustic decay in contrast with their "younger" humic counterparts deposited on the outer perimeter. Thus, the molecular character of organics within a pisolite core and those deposited on the outer perimeter of the cortex differ as would their individual impact within the Bayer process value chain. Increased caustic decay linked with "younger" humic acids is a function of organic oxygenate substitution (especially hydroxyls and carboxylic acids) which facilitate the decay mechanism through hydrogen transfer reactions [10, 14] within the Bayer process.

Bauxite activation examines the influence of thermal treatment (600 °C) on the dehydroxylation of gibbsitic and boehmitic alumina minerals forming amorphous alumina [15]. While this eliminates bauxite TOC (and thus oxalate production potential), it is only a secondary benefit. The primary driver for bauxite activation is to reduce refinery energy by operating a lower temperature Bayer circuit.

The current study aims to increase fundamental knowledge of pre-Bayer bauxite organics by examining their spatial distribution within pisolitic bauxite in conjunction with variance in chemical nature. These fundamental findings were used to explore potential pre-Bayer processes for bauxite TOC reduction. This internal research programme initially explored a diverse array of approaches including solvent dissolution, plasma, ultrasonics, boric acid esterification and abrasion. Low-temperature thermal treatment (275–350 °C) to "denature" bauxite organics was found to be effective and is discussed in this paper, along with its downstream impact within the Bayer process.

2. Experimental Methods

2.1 Bauxite Organics Characterisation

A Particle Size Distribution (PSD) was conducted using standard screens. PSD fractions that were isolated include > 9.5 mm, 2.0–9.5 mm, 0.6–2.0 mm and < 0.6 mm. The TOC of the fractions was established and is shown in Figure 2.

Two novel methodologies were used to characterize pisolitic bauxite organics:

- Laser-Induced Breakdown Spectroscopy (LIBS): Samples were analysed on a Elemission Coriosity LIBS utilising a pulsed high-energy laser (1064 nm) focused on the bauxite surface producing plasma emitting photons. The photons possess wavelengths specific to

research to provide a comprehensive scientific explanation of alternation to the nature of the organic content
- An overlay of rudimentary LCMS “fingerprint” traces provides a simple method to compare larger scale changes associated bauxite organics denaturing within the suite of Bayer organic intermediates

This research presents a practical approach to study and demonstrate the impact of denaturing bauxite organics through the Bayer value chain (from bauxite TOC to oxalate). As this research is relatively novel, it naturally invites further detailed investigation. Further work may include enhanced analytical methods to characterize bauxite TOC. This may be supplemented by further developing practical Bayer in-situ analysis techniques (for example FTIR and LCMS) to better understand denatured organics and the impact on caustic decay mechanisms. Future research should ultimately promote practical solutions to mitigate the impacts of organics within an alumina refinery.

4. References

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