# ORGANICS REMOVAL FROM ALUMINA INDUSTRIAL LIQUOR: APPLICATION OF THE CATALYTIC WET OXIDATION PROCESS TO NATURAL AND SYNTHETIC BAYER LIQUORS

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## Abstract

The removal of organic compounds from alumina industrial liquor was studied using the catalytic wet oxidation process at low temperature and conditions favourable to the industry. In the catalytic wet oxidation of organics in the Bayer liquor, high molecular weight organics were decomposed to low molecular weight organics, carbon dioxide and water. The catalytic wet oxidation process exhibited significant oxidation of organics present in the liquor.

Using the synthetic Bayer liquor, the wet oxidation of known model organic compounds was studied. The low temperature wet oxidation of low molecular weight organic compounds (sodium formate, acetate, malonate, and other organics) has been investigated in highly alkaline synthetic Bayer liquor. Only two of the compounds, sodium formate and sodium malonate, underwent appreciable wet oxidation in isolation under the reaction conditions such as temperature: 165ºC, Oxygen pressure: 500 kPa, concentration of sodium hydroxide 4.4–7.0 M NaOH, reaction period: 2 h.

## 1. Introduction

Following an intense era of industrialisation and competition, multi-billion dollar oil, chemical, alumina and pharmaceutical industries have recognised the importance of ensuring environmental sustainability for their operations. These industries are the main contributors to the economic growth of a country and the leaders of these industries endeavour to be good corporate citizens. As a consequence industrial research is becoming increasingly focussed on technologies that provide process improvements and can also be used for environmental applications (and vice versa).

Petroleum refinery wastes and paper and pulp wastes create colouration and toxicity problems for receiving water bodies due to the presence of phenolic and high molecular weight organics [1, 2]. Such streams often contain species such as carboxylic acids, phenols, ketones, aldehydes, amines, thiols, anilines, pyroles and pyridines. Within the alumina industry the presence of dissolved organic impurities (mainly carboxylic acids) causes major processing problems and production inefficiencies including: reduced aluminium hydroxide yield, impure and coloured aluminium hydroxide, interference with flocculation of iron oxide residues, foaming of process liquor, increased liquor viscosity.

The removal of organic compounds from industrial waste streams by complete or partial oxidation (wet oxidation) has received considerable attention over the last three decades [3]. To date few other technologies are available (within process limitations) for the removal of organic contaminants so this is of great interest to industries that have unwanted organic compounds in their waste or process streams.

The present investigation deals with the application of the catalytic wet oxidation method (CWO) for the removal of organics from alumina refinery process (Bayer) liquor under different conditions. Using synthetic Bayer Liquor, wet oxidation studies were performed on the low molecular weight organics, (which usually provide a barrier to achieving complete oxidation), in a simulated environment that is typically encountered in alumina refining.

## 2. Experimental

### 2.1 High Pressure Reaction System

The wet oxidation and catalytic wet oxidation experiments were carried out in a continuously stirred, 1.2L, nickel (Inconel) autoclave (Parr Autoclave, USA) which included attachments for gas addition into the liquid phase and sampling of the liquid phase. In the standard CWO reaction, the liquor (0.6L) and a certain known amount of catalyst (1–10g) were placed into the autoclave and the headspace area was evacuated to –0.95 bar. In the CWO experiments, catalyst prepared from various single and mixed transition metals and other f-block elements were tested. In the WO reaction, no catalyst was used. The vessel and contents were heated to the target temperature and a sample was collected from the autoclave after the run.

Oxygen was then introduced at a partial pressure ($P_{O2}$) of 500 kPa, which was maintained throughout the test. In the CWO and WO experiments, high purity oxygen (Linde) (with a minimum purity of 99.5%) was used. The autoclave set-up also included a Parr 4843 controller to allow temperature and stirrer speed to be maintained at predetermined values. Pressure readings were also obtained using the controller via a pressure transducer directly attached to the autoclave assembly. In the CWO study, different types of temperature and pressure were applied.

### 2.2 Bayer Liquor

Original Bayer liquor was supplied by Alcoa World Alumina, Kwinana, Western Australia. Since this liquor contains the organics originating from bauxite ore, we named the liquor Natural Bayer Liquor.

### 2.3 Synthetic Bayer liquor

The wet oxidation experiments of low molecular weight organics were conducted in a highly alkaline solution (>4 M). The highly alkaline solution is synthetic Bayer liquor, which was formulated to a similar chemical composition to the industrial Bayer liquor except for the organic contents. The chemicals used in preparation of synthetic Bayer liquor using Milli-Q water are as follows: Aluminium hydroxide, Al $(OH)_3$; sodium hydroxide,

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NaOH, (AR, BDH Chemicals); sodium carbonate, $Na_2CO_3$, (AR, BDH Chemicals); sodium sulfate, $Na_2SO_4$, (AR grade BDH Chemicals); sodium chloride, NaCl, (AR, BDH Chemicals); sodium phosphate, $Na_3PO_4$, (98, Ajax); and silicic acid (Sigma).

## 2.4 *Organic compounds*

The following organic compounds were used without further purification — formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid, succinic acid, and glutaric acid.

## 2.5 *Analysis Techniques*

The total organic carbon (TOC) and total inorganic carbon (TIC) concentrations were obtained using an O.I.Analytical Model 1010 (USA) total carbon analyser. The routine analysis techniques such as automated potentiometric titration system; Capillary Electrophoresis, ICP-AES, GC/MS and Gas Chromatography were used for analysing the inorganic and organic components, respectively [4–6]. The inorganic materials were characterized by elemental analysis, XRD, SEM, BET and XPS techniques. The details of characterisation techniques and instruments utilised for the chemical analysis and structure determination were reported earlier [7].

## 3.  Results and Discussion

### 3.1 *Wet oxidation and Catalytic wet oxidation*

The main aim of industrial scale wet oxidation (WO) and catalytic wet oxidation (CWO) is to decompose organic species to relatively harmless materials such as water and carbon dioxide or carbonate in alkaline systems [8–13]. In particular alkaline waste waters and process liquors are being targeted in order to meet environmental standards for discharge streams. Some industries, particularly the alumina industry has the dual interest of environmental targets and potential for process improvements. Many of these process streams contain the high molecular weight organics which further break down to smaller organic fragments or sodium salts of carboxylic acids. The literature on the behaviour of these species during the WO and CWO in highly alkaline solutions is scarce. The presence of organics in the Bayer liquor, and eventually accumulation in the liquor, not only creates environmental problems but also strongly affects the alumina yield, quality and production cost. Factors such as the organic or inorganic constituent content, their concentration, toxicity and environmental discharge standards govern the choice of treatment method for a particular effluent stream. For a number of years, wet oxidation (WO) technology has demonstrated its great potential for treating different varieties of waste streams pollutants [8–13].

In the WO process, the organic substances in aqueous streams are oxidised in the aqueous phase with peroxide/ozone/air/oxygen. The process can be carried out under different conditions of pressure/temperature/oxidant etc. The WO process is expensive when used to achieve complete oxidation of all organic material to carbon dioxide. Therefore it is integrated with the catalytic system. The oxidation of organics using oxygen over solid catalyst is an alternative to the WO process. The catalyst could be used either in the form of solids or liquid [10–13].

### 3.2 *Application of the Catalytic Wet Oxidation Process for organics removal in Natural Bayer Liquor*

CWO is an alternative technique for efficiently removing organics from the industrial liquor. CWO uses catalysts to obtain better oxidation rates at lower temperatures and pressures. The use of catalytic wet oxidation makes oxidation of

organic compounds more economically attractive as well as environmentally robust. The economic and environmental implications, which follow from removing the pollutants, are substantial. The organic impurities present in liquor significantly affects the processing cost, coloration of alumina, loss of caustic through reaction with organic acids, foaming, alumina yield, fine particles in ppt, pipeline blockage, and environmental pollution.

For more than six years, we have been continuously contributing towards the development of catalytic materials and catalytic wet oxidation technologies [6, 10, 12–14]. Our innovative application of the CWO technology to the alumina industry has resulted in significant organics removal from Bayer liquor. In CWO, use of the catalyst helped us to achieve higher oxidation rates and consequently to decrease the severity of reaction conditions to reduce COD/TOC to the same or larger degree as in the case of a non-catalytic process.

The success of CWO lies in selecting a proper Bayer liquor reaction system, evaluating the role of organic impurities, element and catalyst systems. In most of the alumina refineries, the process liquor contains millions of organics. The following is the incomplete list of organics present in the natural Bayer liquor, sodium salts of oxalate, succinate, formate, malonate, acetate, benzoic, nonanoic, dodecanoic, hexadecanoic, octanoic, propylbenzoic, butlybenzoic, ketomalonic and other undetected organics. The experimental set-up used for the CWO of organics removal and synthetic Bayer liquor studies is presented in Figure 1.

In the CWO of organics in the alumina liquor, the liquor itself imposes a number of restrictions against the favourable removal of organics. The restrictions are created by the complex nature of liquor (such as its highly alkaline nature, presence of metal impurities and multiple organic/inorganic reactants, hydrothermal conditions, seed poisons etc). These factors contribute to the degradation of the catalytic system.

A good catalytic material in the CWO process reduces the total organic carbon, increases the rate of organic destruction, maintains/slightly lowers the TC/TA ratio and undergoes minimal change. Using certain transition metal catalysts and low temperature (approx 165°C) and pressure, more than 30% of the total organic carbon removal was achieved.

The changes in the carbon content and intermediates formation during the wet partial oxidation [WPO] and catalytic wet partial oxidation [CWPO] of organic compound are presented in Figure 2.

In WPO, parent A compound decomposes fast but the intermediate formed or accumulated during the oxidation of a compound requires a long time to oxidise/or to form a desired product. In CWPO, decomposition/conversion of parent compound is extremely fast and it takes a few minutes to achieve the same results as WPO. In CWPO, the formation of intermediates is fast and total concentration of intermediates is lower than that of WPO (ie. lower yield). A high concentration of intermediates also appears in a very short duration.

A (parent) $\rightarrow$ [B+C] (intermediates) $\rightarrow$ D-H (low molecular weight compounds +)

Compared with WO, CWO yields higher conversions and consequently leads to more effective organics removal at the same WO operating conditions.

For evaluating the role of most common organic species in the Bayer liquor, further studies in oxidation of model organic compounds in synthetic Bayer liquor was undertaken. Investigations of model organic compounds in synthetic Bayer liquor helped in the understanding of reaction paths and the decomposition behaviour of organics.
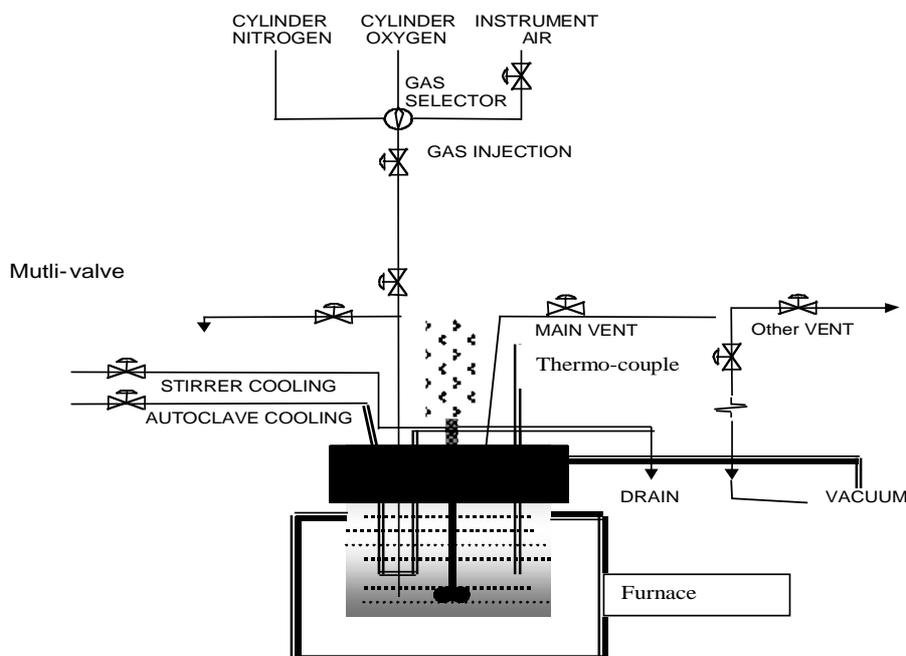
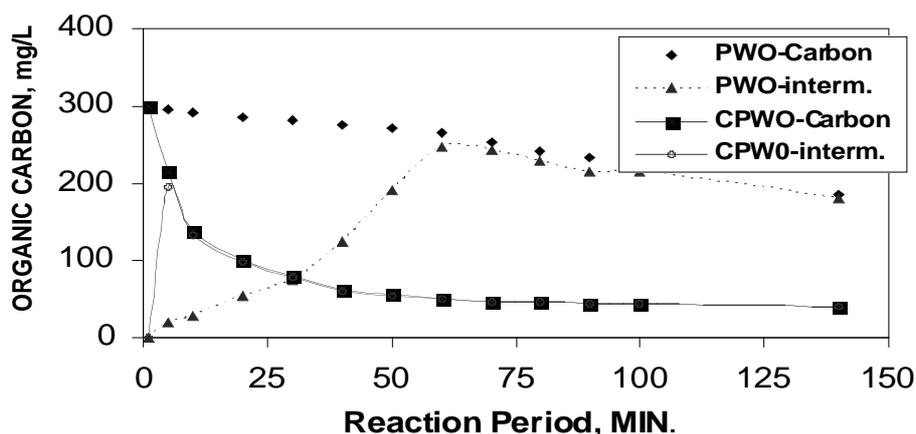Figure 1 — Sketch of the high-pressure inconel autoclave system used for the wet and catalytic wet oxidation.



Figure 2 — Partial wet and catalytic oxidation of a typical organic compound.

### 3.3 *Synthetic Bayer Liquor*

Low temperature wet oxidation (WO) and CWO of twelve different organic compounds (identified in Bayer liquor) was studied in synthetic Bayer liquor. None of the compounds studied were completely oxidised to carbonate under the WO reaction conditions. Of the 12 organic compounds studied, six underwent appreciable (>2%) overall conversion to carbonate and other low molecular weight compounds under the WO reaction conditions.

The WO of sodium formate, acetate, propionate, butyrate, oxalate, malonate, succinate and glutarate was investigated for each compound individually. Of the compounds studied only sodium formate and malonate underwent appreciable WO (to carbon dioxide and other low molecular weight compounds) under the given reaction conditions (Table 1). Sodium formate is oxidised relatively more than other organics to carbon dioxide. Two low molecular weight organic compounds were formed from the WO of sodium malonate in highly alkaline solution, sodium oxalate and sodium formate. A significant amount of sodium malonate was also converted to carbon dioxide

(carbonate) based on total organic carbon measurements. These results confirm the previously reported studies on the organics [16, 17]. Sodium formate and sodium malonate undergo wet oxidation due to the presence (comparatively) of more acidic non-carboxylic hydrogen atoms that could possibly react with sodium hydroxide.

Table 1 — Extent of overall compound removal and TOC removal of individual organic compounds.

| Compound | % TOC removal | % Compound removal |
|---|---|---|
| Sodium formate | 5.5 | 5.5 |
| Sodium acetate | <2 | <2 |
| Sodium propionate | <2 | <2 |
| Sodium butyrate | <2 | <2 |
| Sodium oxalate | <2 | <2 |
| Sodium malonate | 7.6 | 18.5 |
| Sodium succinate | <2 | <2 |
| Sodium glutarate | <2 | <2 |

Reaction Conditions: reaction time = 2 h; $T$ = 165°C; $P_{O2}$ = 500 kPa; 4.4 M NaOH synthetic Bayer liquor.

Investigation of the WO reaction mechanism(s) for these compounds revealed that one of the compounds was wet oxidised primarily via a free radical chain reaction mechanism, the other five compounds were found to be wet oxidised primarily via ionic reactions. The wet oxidation of sodium formate and sodium malonate was significantly affected by the concentration of NaOH with both compounds undergoing increased WO with increasing concentration of NaOH (Table 2). This result supports the hypothesis that these two compounds undergo WO via the abstraction of a slightly acidic hydrogen atom by NaOH. None of the other compounds investigated underwent appreciable wet oxidation.

Table 2 — Effect of NaOH concentration on WO of individual organic compounds.

| Compound | % Compound removal at varying [NaOH] | | |
|---|---|---|---|
| | 4.4 M NaOH | 5.7 M NaOH | 7.0 M NaOH |
| Sodium formate | 5.5 (5.5) | 8.5 (8.5) | 14.2 (14.2) |
| Sodium acetate | <2 | <2 | <2 |
| Sodium propionate | <2 | <2 | <2 |
| Sodium butyrate | <2 | <2 | <2 |
| Sodium oxalate | <2 | <2 | <2 |
| Sodium malonate | 18.5 (7.6) | 29.6 (12.7) | 39.5 (15.0) |
| Sodium succinate | <2 | <2 | <2 |
| Sodium glutarate | <2 | <2 | <2 |

Reaction Conditions: reaction time = 2 h; $T$ = 165°C;
$P_{O2}$ = 500 kPa; 4.4–7.0 M NaOH synthetic Bayer liquor.
% TOC removal in parentheses.

The ability of five transition metal oxides to catalyse the WO of the organic compounds was also investigated. Copper was clearly the most effective catalyst, catalysing the oxidation of five of the organic compounds studied. Investigation of the catalytic reaction mechanism occurring

during CWO revealed that the dissolved portion of copper catalyst was responsible for the observed activity. The catalyst functioning in highly alkaline solution is explained by two different reaction mechanisms (a) propagation of autoxidation and (b) initiation via complexation. The study provides significant support for the technology development applicable to Bayer process.

## 4. Conclusions

In a normal (WO) process, complete oxidation of all intermediate products is accomplished in a long time after a parent compound has disappeared. In the case of CWO: a shorter time is needed to convert parent compounds into intermediate products that are more amenable for catalytic treatment than those formed during WO. In the Bayer liquor, 10-30% organics could be easily removed at low temperature and pressure using the CWO process and a suitable transition metal catalyst system. The implementation of the CWO process by the alumina industry will be highly beneficial.

In synthetic Bayer liquor, sodium formate and sodium malonate compounds underwent appreciable WO in isolation, under the reaction conditions, as they contain comparatively more acidic non-carboxylic hydrogen atoms that react with NaOH at relatively low temperature (initiating WO). Sodium malonate and sodium formate undergoes appreciable WO in highly alkaline solution at relatively low temperature (165ºC). Both of these compounds undergo WO in highly alkaline solution as they contain slightly acidic non-carboxylic hydrogen atoms that can react with NaOH. The WO of sodium malonate occurs predominantly via a free radical chain reaction mechanism in highly alkaline solution. The WO of sodium formate also most likely occurs via a free radical reaction mechanism in highly alkaline solution.

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