REMOVAL OF ODOROUS COMPOUNDS FROM ALUMINA REFINERY CONDENSATES

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Abstract

The aim of this project was to investigate the removal of odorous compounds from alumina refinery digestion condensates sourced from alumina refineries situated in Western Australia, Queensland and the Northern Territory. Odour reduction was investigated using commercially available oxidants (hydrogen peroxide, potassium permanganate, ozone, oxygen and sodium hypochlorite) and adsorbents (powdered activated carbon and smelting grade alumina) under different reaction conditions. The two processes that achieved the highest extent of odour reduction under the test conditions studied were potassium permanganate and powdered activated carbon. Both of these processes were capable of removing >70% of the condensate odour. Although powdered activated carbon and potassium permanganate are effective at removing odour from condensate there are a number of issues related to the use of these systems which would need to be resolved and / or significant improvements made before such systems could be implemented at an alumina refinery. These issues include removal of by-products (MnO_2) and disposal of waste (spent carbon, MnO_2).

1 Introduction

Alumina refinery digestion condensates contain a number of odorous compounds that restrict the re-use of this process water and contribute to the overall odour present at alumina refineries, hence processes that can remove / neutralise these compounds are of interest to the alumina industry. Based on a search of the literature, no openly published studies have investigated the removal / neutralisation of odorous compounds synonymous with digestion condensate or solutions of similar chemistry. As a result, an innovative approach was required. It was decided to investigate odour mitigation using commercially available processes that are capable of removing / converting (oxidising) organic compounds in other aqueous applications. The processes considered were ozonation; chemical oxidation (hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl) and potassium permanganate ($KMnO_4$); wet air oxidation and adsorption (activated carbon, smelter grade alumina). The selection of these processes was based on oxidising strength and the ability of these reagents to function under reaction conditions determined by the refinery operating environments (temp 50–90°C, pH 5–11).

2 Experimental

Screening tests were conducted to determine the most effective odour removal processes using condensate from Worsley Alumina's refinery in Western Australia. Odour removal tests were conducted using two batch test procedures (culture tubes rotating in a water bath and tests within a stirred autoclave) and a filtration procedure (activated carbon and smelting grade alumina). Odour was measured semi-quantitatively using a screening method specifically developed by The Odour Unit Pty Ltd. Assessment was based on a 1–10 scale where 10 equates to the odour from untreated condensate and 1 equates to the lowest detectable odour, that present in deionised water. Quantitative odour measurements were also conducted for selected samples by The Odour Unit Pty Ltd (Sydney Laboratory) using a recently developed method for the measurement of odours from aqueous liquids.

3 Results and discussion

Batch odour removal tests were conducted using each of the selected oxidants (excluding oxygen) under different reaction conditions (oxidant concentration, temperature, pH). The results of these tests are presented in Figures 1a, 1b and Table 1. From the results presented it can be seen that potassium permanganate was clearly the most effective oxidant for removing odour from Worsley Alumina condensate under the different reaction conditions. Sodium hypochlorite and ozone were also capable of significant odour removal, while hydrogen peroxide did not significantly remove odour. A small decrease in odour was observed when the pH of the condensate was adjusted from 10.6 to 5 (Figure 1b) using dilute sulphuric acid. This decrease was presumably mostly due to conversion of ammonia to ammonium ion, however it is possible that some of the odorous organic compounds in condensate could have been altered by the change in pH.

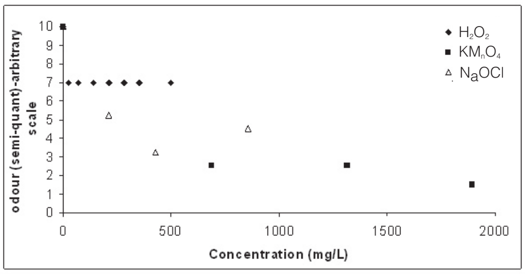

Figure 1a. Effect of oxidant concentration on odour removal. T= 90°C, pH = 10.6, t= 1h, tests conducted in culture tubes rotating in water bath.

*Note – in order to accurately compare the oxidants tested, the number of oxidation equivalents (OXE) per kg of oxidant must be taken into account (H_2O_2 = 58.8 OXE/kg, $KMnO_4$=19.2 OXE/kg, NaOCl = 26.9 OXE/kg, O_3 = 41.7 OXE/kg).

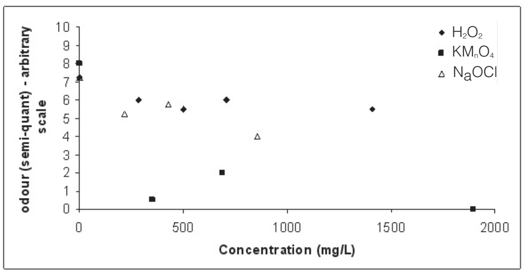

Figure 1b. Effect of oxidant concentration on odour removal. T= 90°C, pH = 5, t = 1h, tests conducted in culture tubes rotating in water bath.

Table 1. Ozone screening test results. 1h, tests conducted in Teflon-coated autoclave.

Temperature (°C)	pH	Dose (mg/L)*	Semi–quant Odour (/10)
50	10.6	200	5
50	10.6	400	4
90	10.6	200	8
90	10.6	400	5
90	5	400	4

*The amount of ozone needed to give the required concentration was bubbled through the condensate.

Based on the results of the initial screening tests it was decided to conduct kinetic tests using potassium permanganate, sodium hypochlorite, ozone and oxygen (wet air oxidation) to evaluate the rate of odour removal achieved by the aforementioned processes. Kinetic tests were not conducted with hydrogen peroxide due to the low degree of odour removal achieved by this oxidant. Some of the kinetic test results are presented in Figure 2. Of the oxidants investigated, potassium permanganate was the only oxidant capable of significantly reducing odour in a relatively short time period. There was very little difference in the amount and rate of odour removal achieved by the other oxidation processes.

The extent of odour removal brought about by the various oxidants did not correlate well with the relative oxidising strengths (under STP conditions) of the respective oxidants (ozone > hydrogen peroxide > sodium hypochlorite > potassium permanganate > oxygen). This poor agreement was most likely due to one or more of the following reasons:

- Ozone is only sparingly soluble at medium – high temperatures (<1 ppm in water @50ºC, using a 3% by wt feed) (Ozone properties, 2005).
- Reaction between hydrogen peroxide and the odorous compounds present in condensate is kinetically slow and / or hydrogen peroxide does not react selectively with the odorous compounds in condensate and is therefore consumed by other non-odorous compounds.
- Potassium permanganate is a more selective oxidant than the other oxidants tested. A significant proportion of the odorous compounds present in condensate react rapidly with potassium permanganate.

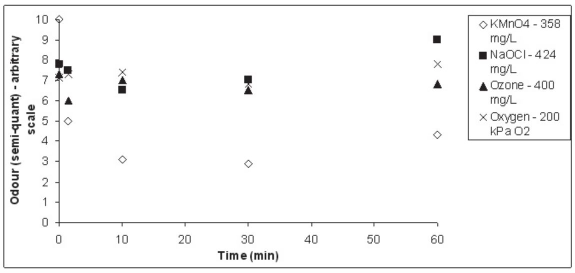

Figure 2. Kinetic test results (Worsley Alumina condensate). T= 90°C, pH = 10.6, stirring speed = 800 rpm. Note – ozone concentration based on quantity of ozone passed through condensate – amount of ozone dissolved in solution was considerably lower.

Odour removal was also investigated using two adsorbents, powdered activated carbon (a mixture of Norit AZO and Norit D10) and smelter grade alumina (supplied by Alcoa). The results of these tests are presented in Table 2. Of the two adsorbents tested, powdered activated carbon was the only one capable of removing significant odour under the test conditions.

Table 2. Odour removal from condensate (Worsley Alumina) using adsorbents (filtration procedure). T=90°C, pH = 10.6.

Adsorbent	Residence time (sec)	Bed volumes	Final odour / 10 (semi-quant)
Powdered activated carbon	14.7	10	2
Powdered activated carbon	58.0	2.5	1
Smelting grade alumina	150.6	2.5	7.5

Based on the results obtained using Worsley Alumina's condensate, odour removal was investigated for three other alumina refinery digestion condensates (Alcoa Kwinana, Alcan Gove and Queensland Alumina Ltd) using potassium permanganate and powdered activated carbon. Some of the results of these tests are given in Figures 3 and 4. Both of these processes significantly reduced the odour in each of the different refinery condensates.

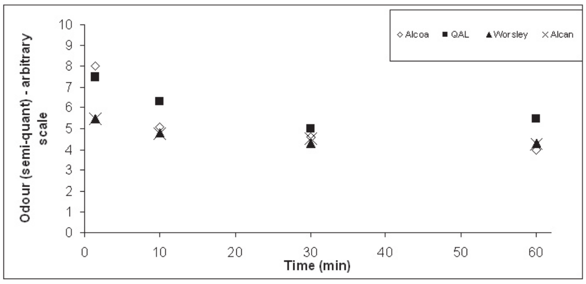

Figure 3. Removal of odour from different alumina refinery condensates using $KMnO_4$ oxidation. T= 90°C, pH = 10.6 ± 0.2, stirring speed = 800 rpm, $[KMnO_4]$ = 358 mg/L

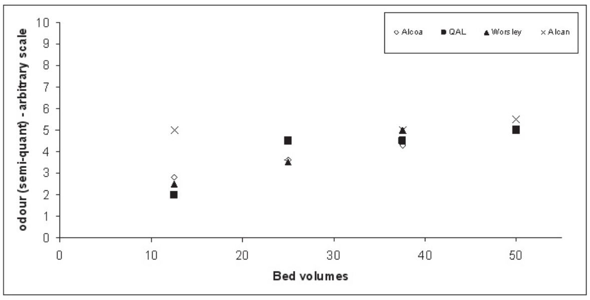

Figure 4. Removal of odour from different alumina refinery condensates using powdered activated carbon adsorption. T=90°C, residence times = 9.6 – 12.6 sec, pH = 10.6 ± 0.2.

4 Conclusions and recommendations

Potassium permanganate oxidation and powdered activated carbon adsorption are two processes capable of significantly reducing odour from a range of alumina refinery condensates. The powdered activated carbon process however, produces a significant amount of waste (this material cannot be regenerated) and therefore would not be suitable for use on a large scale. The potassium permanganate process imparts a dark colour on condensate and produces a fine solid by-product (MnO_2) which requires removal. It is recommended that odour removal using potassium permanganate in a supported form be investigated, as this would significantly reduce the degree of discolouration and the need for solid MnO_2 removal. It would also allow easier regeneration of potassium permanganate from MnO_2, which could be conducted on-site.

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