

# OZONATION FOR DESTRUCTION OF ODORANTS IN ALUMINA REFINERY CONDENSATE

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## Abstract

The removal of odorants from alumina refinery condensate using ozonation is reported in this paper. The conditions present in refinery condensate (pH >10, temperature >80 °C) mean that many advanced oxidation processes (AOPs) such as UV/H<sub>2</sub>O<sub>2</sub> and Fenton systems are unlikely to perform satisfactorily. However, high pH ozonation could be a suitable technology provided the rate of ozone decomposition into hydroxyl radicals outweighs the increasingly poor solubility of ozone at higher temperatures. Bench scale ozonation tests have indicated that a 85% reduction in odour content of condensate could be achieved at a temperature of 40 °C to 60 °C, pH of 10 and ozonation dosage of 0.31g/L for 30 minutes. Changes in concentrations of selected odorous organics (aldehydes and ketones) present in condensate were observed, with significant reductions in concentrations obtained for some organics and increases in concentrations obtained for others, presumably due to their formation from oxidation of higher molecular weight organics. A decrease in pH from a desired 10.0 to 7.0 was observed after 30 minutes ozonation which suggested oxidation of organics had occurred to form organic acids. This change in pH would have reduced the efficiency of ozonation since the yield of hydroxyl radicals at the lower pH is significantly reduced. pH control was required to maintain high a yield of hydroxyl radicals during the dosing period.

The findings from this study suggest ozonation has significant potential to be an effective process for reduction in the odour associated with evaporation of condensates that could contribute to further reductions in fugitive odour emissions from alumina refineries.

## Keywords

Odour emission, alumina refinery condensate, volatile organic compounds, ozonation

## 1. Introduction

Odour emissions from Alumina plants can be highly pervasive and cause significant concern to workers and local residents (Coffey, 2002; Graham, *et al.*, 2002; Cox *et al.*, 2002; Coffey and Ioppolo-Armanios, 2004). Of particular concern is fugitive odour emitted from the handling and use of refinery condensate streams, particularly the digestion condensate. Digestion of humic substances from bauxite in the Bayer process leads to the formation of volatile low molecular weight organics which to a large extent report to the condensates obtained from the flash vapours. These condensates contain a large number of volatile substances including phenols, amines, pyrroles, ammonia, alcohols, aldehydes, ketones, sulfides and thiols, as well as low concentrations of less soluble VOCs such as toluene and C5-C7 hydrocarbons. Many of these substances have low odour thresholds which provide the characteristic odour obtained from evaporation of condensates. The flash vapours can also be contaminated with salts from carry-over of liquor in the flashing process that give rise to the relatively high pH observed in condensate.

In a previous review of advanced oxidation technologies and their applicability to the odour removal from condensate (Feitz *et al.*, 2005a), high pH ozonation appeared a promising option but little is known about the effectiveness at high temperatures. Conventional thinking would suggest that ozonation at high temperatures would be relatively ineffective as the ozone solubility decreases markedly with increasing temperature (Kosac-Channing and Helz, 1983). In fact it is often recommended by experts in water treatment not to use ozone above temperatures of 40°C due to

ozone solubility limitations. However, several studies have shown little dependence of degradation performance on temperature, especially at neutral to high pH (Oeller *et al.*, 1997). In one notable recent study, Bijan and Mohseni (2004) looked at the application of ozone for pulp and paper wastewater (COD = 1600mg/L) at pH 9, pH 11 and temperatures 20°C and 60°C and found no significant difference in extent of organics degradation. The result is surprising considering that ozone solubility decreased from 0.31mg/L of ozone in water per mg/L of ozone in air at 20°C to 0.093mg/L at 60°C. Ozone decomposes rapidly in the presence of hydroxide ions (*i.e.* at high pH) to form hydroxyl and superoxide radicals (Staehelin *et al.*, 1984; Bühler *et al.*, 1984) and together with the enhancement in oxidation kinetics due to the increased temperature, this is considered to counter the effect of lower concentration of ozone in solution due to lower solubility.

Previous work on the ozonation of benzoic acid, which was selected as a model compound to represent the organics in condensate, demonstrated significant degradation could be obtained at a relatively high temperature up to 80° C over a pH range from 7.5 -11 (Feitz, *et al.*, 2005b). In the work discussed in this paper, the tests have been extended to assess the impact of ozonation on an alumina refinery condensate, with measurements made on the residual odour and selected volatile aldehydes and ketones from condensate after ozone treatment for comparison with untreated condensate. Key variables tested in this work include the pH and temperature of the condensate, and the ozone dose rate.

## 2. Experiments

Experiments were conducted in a 90cm tall bubble column reaction vessel with a total sample volume of 3.5L. A large pyrex cylinder, connected to a water bath, acted as a water jacket for the reaction vessel for temperature control. Ozone was supplied using a Wedeco Ozomatic SWO 30 ozone generator equipped with a PSA oxygen generator. The gas flow rate was maintained at 0.14m<sup>3</sup>/h for all experiments and the ozone/oxygen mixture was sparged into the base of the reaction vessel. Residual ozone was destroyed by venting bubbling to potassium iodide solution and then venting to an activated carbon filter. An ozone detector was used to monitor possible ozone leaks (warning 0.1ppm; alarm 0.5ppm ozone).

Condensate samples were provided by an Australian alumina refinery. The pH of this condensate was approximately 10. A pH range of 9 -11 has been tested in this work to cover the range expected for typical digestion derived condensates. Condensates are typically recovered at temperatures of 90-95°C and it is desirable to maintain higher temperatures for applications such as washing of hydrate on filters and dilution at various stages of the refining process. However, lower temperatures are required for higher efficiencies in the ozonation process. A temperature range of 40-80°C was selected for this study as to establish the impact of temperature without exceeding the upper temperature limit for safe operation of the laboratory ozonation equipment. An ozone dosage of 0.31g/L was selected based on the findings from a preliminary study that suggested higher doses provided no additional reduction in odours.

Odour samples were prepared for olfactometry analysis using a method developed by The Odour Unit Pty Ltd for measurement of odour from condensates (Schulz, 2005). A volume of raw or treated condensate (200 µL) was injected into a Tedlar bag filled with 12 L of high purity nitrogen gas. The sample was equilibrated for at least 30 mins to ensure complete evaporation of the condensate (i.e. no visible liquid left in the bags) before the olfactometry test. The odour concentration of each prepared sample was determined by a dynamic olfactometer following the Australian and New Zealand standard (AS/NZS 4323.3: 2001).

The concentrations of 2 aldehydes (formaldehyde and acetaldehyde) and 2 ketones (acetone and methyl ethyl ketone) in raw and treated condensates were determined using a SPME GC-MS analysis method developed for this work.<sup>1</sup> These substances were considered to be significant contributors to the odour from condensates and if was of interest to examine the fate of these volatiles after ozonation. The analysis involves the derivatisation of the carbonyls to form the O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) derivatives then SPME extraction of the derivatives and GC-MS analysis of the volatile PFBHA derivatives.

## 3. Results and discussion

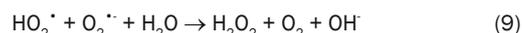
Ozone decomposes in water to generate hydroxyl radicals (OH·). The rate of ozone decomposition increases with pH because decomposition is initiated by the reaction of OH<sup>-</sup> with ozone (Eq. 1). This is followed by a chain of radical propagation reactions that cause further decomposition of ozone (Staehelin et al., 1984; Bühler et al., 1984):



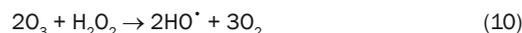
<sup>1</sup> SPME GC-MS = solid phase micro extraction gas chromatography mass spectrometry



The peroxy radicals undergo disproportionation to form hydrogen peroxide, i.e.



Hydrogen peroxide reacts with ozone and this is considered the major pathway for hydroxyl radicals:



Therefore high pH will help the formation of hydroxyl radicals and enhance odorants degradation.

The most significant changes in odour concentrations were observed for the ozonation of condensate at pH 10. In particular, treatment of condensate with ozone at temperatures of 40°C and 60°C resulted in reductions of 85% and 83%, respectively (Figure 1). An increase in the temperature to 80°C resulted in a lower reduction in concentration (49.5%) indicating that ozonation efficiency had decreased from the lower ozone solubility at the higher temperature. No significant differences in the residual odour concentrations were observed for reaction times of 30 and 60 minutes suggesting the oxidation reactions were essentially completed within 30 minutes.

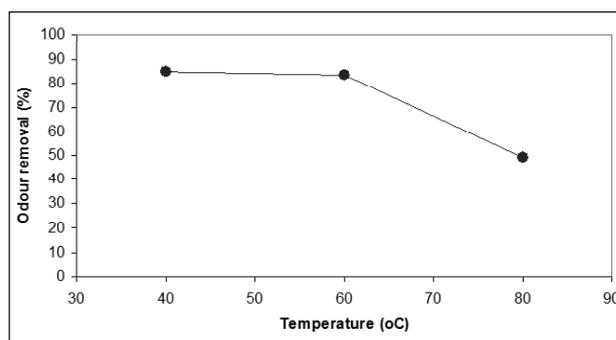


Figure 1. Odour removal by ozonation at pH 10 (ozone dosage 0.31g/L and reaction time 30 minutes)

In contrast, only a small reduction in odour (16.4%) was observed for condensate at pH 9 and 60°C while no removal occurred at 80°C, consistent with the low rate of hydroxyl radical formation expected under those conditions.

Insignificant reductions in odour concentrations were also obtained for condensates at pH 11. In particular, no change in odour concentration was observed at 60°C and a small reduction of 14% observed at 80°C.

A comparison of the odour removal efficiencies at different operating conditions is presented in Figure 2, which shows the highest efficiencies at pH 10 and the lower temperature.

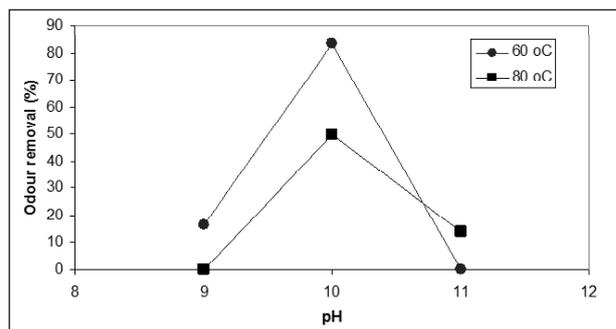


Figure 2. Odour removal by ozonation at different pH and temperature (ozone dosage 0.31g/L and reaction time 30 minutes)

Note that preliminary experiments had shown a decrease in pH from a starting pH of 10 to as low as pH 7 after 30 minutes ozonation, which suggested oxidation of organics had occurred to form organic acids. The production of hydroxyl radicals at pH 7 is greatly reduced compared with the higher pH conditions. As a consequence, pH control was required to maintain the target pH during the experiments and provide a relatively constant yield of hydroxyl radicals during the dosing period.

Blank tests were conducted where oxygen was bubbled through the condensate without operation of the ozone generator. These showed no significant change in odour had occurred (within the error in the olfactometry analysis). Ammonia concentrations were within 2.5% of the start value and pH varied by no more than 0.2 pH units after 30 mins.

Some apparently conflicting outcomes were observed from the analyses of aldehyde and ketone concentrations in the treated condensates from some of the experiments. For example, the concentrations of formaldehyde actually increased during ozonation with an increase in pH of the condensate (Figure 3), whereas fairly constant reductions in concentrations were observed for acetone and methyl ethyl ketone. Acetaldehyde was found to be unchanged after ozonation at pH 9 and 80 °C, but showed a small (~20%) decrease in concentration after ozonation at pH 11. The reductions in concentrations of acetone (~20%) and methyl ethyl ketone (~50%) were essentially constant with pH.

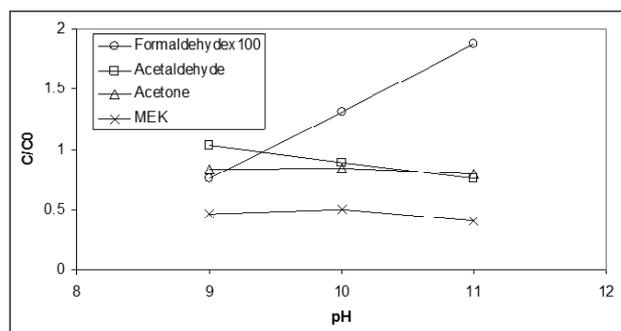


Figure 3. Odorous compound degradation by ozonation at 80 °C (ozone dosage 0.31g/L and reaction time 30 minutes)

Tests conducted at pH 10, which was found to be optimal for odour removal, showed higher concentrations of formaldehyde and acetaldehyde in the treated condensate at 40 and 60 °C compared with the raw condensate (Figure 4). At 80 °C, the concentration of formaldehyde continued to rise in treated condensate whereas the acetaldehyde levels began to decline to below those in the raw condensate. The reductions in concentrations of acetone and methyl ethyl ketone were essentially constant with temperature and of the same extent as observed for the pH experiment.

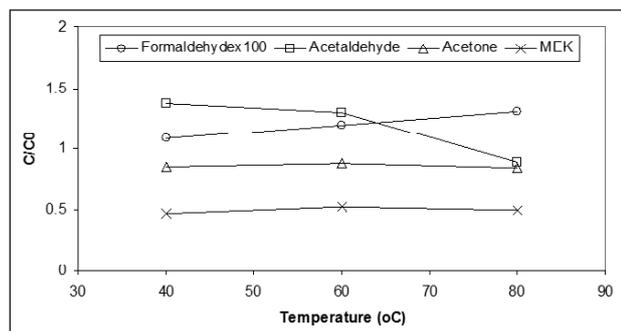


Figure 4. Odorous compound degradation by ozonation at pH 10 (ozone dosage 0.31g/L and reaction time 30 minutes)

However, blank tests indicated some change in concentrations of these substances also occurred from simply passing oxygen through the condensate (Figure 5). As observed in the ozonation test, the formaldehyde concentrations increased with pH in the blank tests, whereas reductions in acetaldehyde concentrations were observed (25% at pH 9, 35% at pH 10 and 20% at pH 11). Smaller reductions were observed in acetone (<10%) and methyl ethyl ketone (<15%) concentrations which are probably within measurement error.

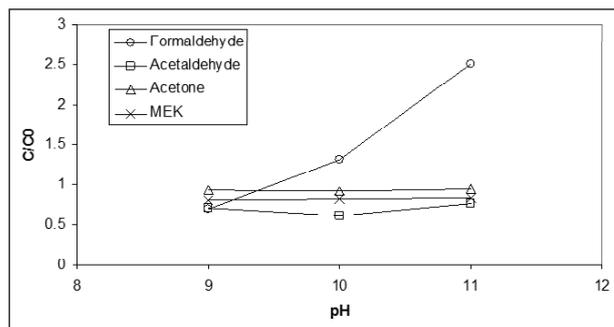


Figure 5. Odorous compound in blank experiment (bubbled with oxygen only and reaction time 30 minutes)

The results for the blank experiments confirm the reductions in acetone and methyl ethyl ketone concentrations from ozonation are significant. However, the changes in formaldehyde concentrations cannot be entirely attributed to the reactions with ozone, with similar increases observed from reaction with either oxygen or ozone. The acetaldehyde concentrations decreased in the blanks but increased in the ozone treated condensates. Presumably the increase in concentrations is a consequence of the oxidative breakdown of higher molecular weight (HMW) organics, which produces volatile organics. However it appears the ozone mediated oxidation was not sufficient to breakdown the formaldehyde produced. Clearly, a detailed analysis of all volatile organics concentrations is required to establish the rates of formation of volatile organics from the initial breakdown of the HMW organics compared with the degradation of those volatile organics and the native volatile organics present in raw condensate. An explanation for the lower efficiency of odour removal at pH 9 and 11 compared with pH 10 may then become apparent when details of the fate of all the substances that give rise to the odour are known.

Furthermore, the residual odour concentrations obtained after treatment were not always dependent on the concentration of the aldehydes and ketones detected in the treated condensate. Not surprisingly, these observations suggest that the odours associated with condensates are not entirely caused by these compounds, although acetone, acetaldehyde, formaldehyde and MEK were the dominant aldehydes and ketones (by concentration) in all analyses of the condensate used in these experiments. Condensates also contain phenols, pyrroles, dimethyl disulfide, ammonia and a large number of semi-volatiles, many of which have low odour thresholds and therefore will contribute to odour emissions. Although these substances were not measured in this study, the residual odour in ozone treated condensate will reflect the final concentrations of these substances after the respective formation and oxidation reactions have proceeded to completeness.

Although not quantified in this study, subjective assessments of the residual odour by the odour panellists suggested the character and hedonic tone (offensiveness) of the odour had changed in the treated condensates to a more acceptable character and less offensive odour. Further quantitative assessments of these parameters and the odour concentrations

would be required to establish the overall impact of the residual odour from evaporation of treated condensate.

It was found that increasing the pH of raw condensate from 10 to 11 caused the odour concentration to increase. In this case ammonia concentration did not increase although COD concentration was slightly higher at the higher pH. This could indicate that a higher pH caused some reactions of some organics to produce more odorous substances (as evident from the increased formaldehyde concentrations in the blanks at higher pH), or it may indicate that the pKa for some odorants is > 10. An example of the latter is the amines, which are highly odorous and have pKa values of 9-11. At lower pH, amines will primarily exist in solution as an alkyl ammonium ion which is not volatile. At higher pH, these ions will deprotonate to form the free amine which is volatile and available to contribute to the odour.

As a consequence, the olfactometry tests were conducted on condensates that were adjusted to pH 10 before preparation of the odour samples. This provides a compromise between deprotonation of amines and protonation of phenols that will increase the odour at high pH and lower pH, respectively.

#### 4. Conclusions

This study has indicated that ozonation can be applied to reduce the odour from refinery condensate. The optimum conditions established in this work for odour removal are summarised below.

pH	Temperature (° C)	Ozone dosage (g O <sub>3</sub> /L condensate)	Time (min)
10	60	0.31	30

These conditions provided an 83% reduction in odour concentrations. A similar reduction (85%) was observed for the lower temperature (40° C), whereas lower efficiencies were obtained for the higher temperature tested (80° C). The odour removal efficiencies were dependent on pH, with the optimal pH 10 identified in the study.

The measurements of selected aldehydes and ketones suggested other substances are significant contributors to the odour from condensate, with no obvious correlation observed from the changes in concentrations of these substances and the reductions in odour observed for some conditions assessed in this study. Although some conflicting results were obtained for aldehydes and ketones measured in this study, it appears that ozonation can produce more of the aldehydes than originally presented in untreated condensate even though the odour concentrations were significantly reduced.

Subjective assessments suggested the residual odour from treated condensate was less offensive than the raw condensate. These findings indicate the need for a quantitative assessment of hedonic tone of untreated and treated condensates to establish the true impact of the ozonation

Further work is required to optimise the odour removal efficiency and to study the fate of all significant odorous substances from ozonation of condensates to establish the full potential of this technology for odour mitigation.

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#### References

- Australian and New Zealand standard: Air Quality – Determination of odour concentration by dynamic olfactometry (AS/NZS 4323.3: 2001)
- Bijan, L and Mohseni, M (2004). 'Using ozone to reduce recalcitrant compounds and to enhance biodegradability of pulp and paper effluents', *Wat. Sci. Technol.* vol. 50, no. 3, pp. 173-182.
- Bühler R E, Staehelin J and Hoigné J (1984). 'Ozone decomposition in water studied by pulse radiolysis HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> and HO<sub>3</sub>/O<sub>3</sub><sup>-</sup> as intermediates', *J. Phys. Chem.*, vol. 88, no. 12, pp. 2560-2564.
- Coffey, P S (2002). 'Assessing odour impacts of an alumina refinery by source measurement, dispersion modeling and field odour surveying', Proc. 6<sup>th</sup> Int. Alumina Qual. Workshop, 8-13 September, Brisbane, CMS Australia.
- Coffey, P S and Ioppolo-Armanios, M (2004). 'Identification of the odour and chemical composition of alumina refinery air emissions', *Wat. Sci. Technol.*, vol. 50, no. 4, pp. 39-47.
- Cox, S J (2002). 'Odour emission reduction case study at Alcoa's Wagerup Alumina Refinery', Proc. 6<sup>th</sup> Int. Alumina Qual. Workshop, 8-13 September, Brisbane, CMS Australia.
- Graham, G, Capil, R and Davies, R (2002). 'Odour destruction for digestion vent gases', Proc. 6<sup>th</sup> Int. Alumina Qual. Workshop, 8-13 September, Brisbane, CMS Australia.
- Feitz, A J, Wang, X and Stuetz, R (2005a). 'Oxidation processes for destruction of odour from alumina refinery digestion condensate', Report no. 4.3, March 2005, Centre for Water and Waste Technology, University of New South Wales: Sydney.
- Feitz, A J, Guan, J and Wang, X (2005b). 'Assessment of ozonation for odour destruction in Bayer refinery digestion condensate. Stage 1', Report no. 2005/10, November 2005, Centre for Water and Waste Technology, University of New South Wales, Sydney.
- Hoigné J and Bader H (1976). 'The role of hydroxyl radical reactions in ozonation processes in aqueous solutions', *Water Res.*, vol. 10, no. 5, pp. 377-386.
- Kosac-Channing, L F and Helz, G R 1983, 'Solubility of ozone in aqueous solutions of 0 - 0.6M ionic strength at 5 - 30°C', *Environ. Sci. Technol.*, vol. 17, pp. 145-149.
- Oeller, H J, Demel, I and Winberger, G 1997, 'Reduction in residual COD in biologically treated paper mill effluents by means of combined ozone/UV reactor stages', *Wat. Sci. Technol.*, vol. 35, no. 2-3, pp. 269-276.
- Schulz, T, Bowden, N and Forster, P. (2005). 'A method for determining the odour release potential for odorous liquids evaporated to atmosphere'. Proc. 17<sup>th</sup> International Clean Air and Environment Conference, Clean Air Society of Australia and New Zealand, 3-6 May, Hobart, Australia.
- Staehelin J, Bühler R E and Hoigné J 1984. 'Ozone decomposition in water studied by pulse radiolysis 2. OH and HO<sub>4</sub> as chain intermediates', *J. Phys. Chem.*, vol. 88, no. 24, pp. 5999-6004.