OUTCOMES OF THE AUSTRALIAN OZONE/CERAMIC MEMBRANE TRIAL ON SECONDARY EFFLUENT

Performance results from a trial using ozone combined with ceramic membranes to treat secondary effluent at Eastern Treatment Plant in Melbourne

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ABSTRACT
This paper presents the performance results from a trial using ozone combined with ceramic membranes to treat secondary effluent at Eastern Treatment Plant (ETP), Melbourne. The ceramic membrane employed was a 25m² Metawater (Japan) microfiltration element, installed in the CeraMac system provided by PWN Technologies (The Netherlands).

The overall objective of the project, funded primarily by the Australian Water Recycling Centre of Excellence (AWRCE), was to demonstrate the performance and cost benefits of ceramic membranes to treat water containing high organic matter typical of secondary effluent.

Operating with raw feed water (no ozone or coagulation), a water flux of 50 L/m².h was achieved within an acceptable clean-in-place frequency of 90 days. When 3 mg/L of polyaluminium chloride (PACl) coagulant was dosed immediately prior to the membrane, a sustainable flux of 100 L/m².h was achieved. The addition of ozone (no coagulant) also enhanced flux to 75L/m².h. However, combining ozone and coagulant resulted in a sustainable flux of 182L/m².h where the equipment became limiting. Thus, higher fluxes may be achievable but were not found.

Ozone reduced trans-membrane pressure (TMP) rise rate between backwashes, while coagulant improved TMP reversibility. Their combination led to higher sustainable fluxes. The main chemical consumed was coagulant (when used), then hypochlorite solution. Long-term TMP profiles demonstrated a reduced need for cleaning chemicals when operating at low or moderate flux. Therefore, flux can be traded for reduced chemical use. The decision of which aspect to favour would, therefore, depend on the application.

Pathogen removal work found an LRV (virus) of 4.0 attributed to the membrane process alone, while an LRV (bacteria) >2.3 was measured over the entire process. E. coli was not detected in the product water under any operation condition. Enhanced disinfection of the reject stream was confirmed with an LRV of 0.6 when reject is not employed, which is expected for the process operating at 93% water recovery.

The ozone and ceramic membrane hybrid process, therefore, has unique performance virtues that could be of value for water recycling in Australia.

INTRODUCTION
Membrane technologies are now widely adopted in water treatment, with most installed membranes using polymeric materials. All membrane processes undergo some degree of fouling as a consequence of their operation, resulting in a loss of performance, and thus need to be routinely cleaned. Membranes generally require regular chemically enhanced backwashing (CEB) to maintain production rates, while more intensive chemical Clean-in-Place (CIP) routines are used to remove more strongly bound fouling compounds, especially when more ‘challenging’ waters are being filtered.

Degradation of polymeric membranes from chemical attack as a direct consequence of this cleaning weakens their structure over time. Eventually membrane elements fail, compromising water quality, and ultimately complete replacement is needed after five to 10 years. The cost associated with membrane degradation can be significant for secondary effluent filtration, as cleaning and membrane replacement costs are responsible for about 60% of the total operating costs (Bartels et al., 2004). Therefore, exploration of more robust membrane materials is gaining interest, especially in the areas of challenging waters.

One group of membrane materials that resists cleaning-chemical attack is ceramics, which have recently emerged as a viable water treatment technology (Karnik et al., 2005; Lehman and Liu, 2009). Ceramic membranes are largely chemically inert and installations dating from 1998 have reported no replacement, no membrane breakage, and no loss of flux. The application of ceramic membranes is attracting increased interest, with Japan installing many plants, mostly for decentralised treatment (Clement et al., 2009). Currently, there are 117 plants operating or under construction with pressurised ceramic membranes in Japan, with a total capacity of 547ML/day. There are very few plants operating on wastewater, so opportunities for water recycling are still emerging. Based on the experience from surface water treatment, ceramic membranes offer longer life, more robust operation and lower failure rates than polymeric membranes.

In turning to ceramic membranes for water treatment, new concepts have emerged. One area of interest is the ability to pair ceramic membrane filtration with direct ozone addition. The combination of ozone and ceramic membranes is an innovative step for water recycling for a number of reasons. Ceramic membranes do not degrade in the presence of ozone, but instead assist...
Technical Features

in the oxidation reactions. Dissolved ozone in contact with the ceramic surface accelerates the formation of highly reactive free radicals that break down organic matter and disinfect the water. This can improve ozonation efficiency over conventional ozone treatment and potentially reduce ozone demand.

This leads to the second innovative step where the ozone works as a continuous membrane cleaner (Clement et al., 2009; Karnik et al., 2005; Lehman and Liu, 2009; Zhu et al., 2011). This gives the unique opportunity of a potential "low cleaning chemical" operation. Ceramic membranes are reported to operate at higher flux and/or water recoveries, and are commercially available, with installation costs reducing as markets grow. Due to their chemical robustness, improved efficiency with ozone, reduced residuals for disposal and longer life, ceramic membranes combined with ozonation may offer cheaper operation (on a $/m^3 water-treated basis). This project seeks to test this hypothesis and investigate the combined ozone/ceramic membrane advantage in the context of recycling of secondary effluent.

Uniquely in this project, disinfection performance of the ozone/membrane system was investigated. The purpose of this was to estimate the pathogen rejection and inactivation capability of the new process. Of particular interest is the ability of the membrane/ozone system to catch viable organisms on the membrane within a stream of flowing ozonated water. This in theory would enhance disinfection by means of much longer contact times. Effective disinfection of both permeate and reject streams is now possible, which potentially expands the options where the reject water can be disposed. The robustness of the process to real wastewater, potential for reduced chemical use and disinfection performance are key tasks for this project, with results presented in this paper.

EXPERIMENTAL METHODS

Pilot trials were carried out using a 2.5m³/h nominal capacity (based on flux of 100L/m².h) ceramic microfiltration membrane process, operated with ozonation at Melbourne Water’s Eastern Treatment Plant, treating secondary effluent to a quality suitable for reuse applications. The CeraMac pilot plant (as shown in Figure 1) provided by PWN Technologies was constructed by RWB Water Services (the Netherlands). The simplified flow diagram is shown in Figure 2 and consists of a single Metawater, 2,000 channel, 25m² ceramic element (0.18m diameter x 1.5m long, as shown in Figure 3) of 0.1 µm pore size configured in dead-end mode.

Ozone addition was performed through a Statiflo static mixer with the dose determined by ensuring residual ozone concentrations of >0.8mg/L at the membrane surface (sample point 3). In-line coagulation was performed using polyaluminium chloride (PACl – 23% as Al₂O₃) dosed into the ozonated effluent directly after the pilot plant’s feed pump, and immediately before the membrane. To determine the minimum dose of PACl, a ‘jar test’ was conducted to identify an appropriate level of coagulant dosing. For the secondary effluent at ETP, this amount was 3 mg(as Al³+)/L. To confirm the validity of the jar test, the PACl was dosed into the pilot plant in-line and a grab sample taken immediately prior to the membrane. Pin floc was observed in a similar fashion to the jar test, confirming the minimum dose required for the plant.

The ETP effluent contains approximately 10–15mg/L dissolved organic carbon (DOC), and is moderately coloured (true colour approx. 80 PtCo units). The high organic content presents a reasonably high fouling potential for
polymeric membranes and represents the type of wastewater where ceramic membranes may find application.

The ceramic plant was operated under the following pre-treatment modes:

- Direct feed (un-pre-treated);
- Coagulant pre-treated;
- Ozone pre-treated; and
- Ozone plus coagulant pre-treated.

In each test, the plant was operated at three or more steps of increasing permeate flux with all other operational parameters fixed. The goal of the stepped test was to establish the highest flux for each pre-treatment condition that was determined to operate sustainably over the long term. Each step treated approximately 360 m³ of water unless gross fouling stopped the run early. This attempt to filter the same volume at each step was to expose the membrane to similar fouling loads. At fluxes above 150 L/m².h volumes of 360 m³ are reached within seven days, so operation was maintained for at least a week to account for incoming water variations. Chemically enhanced backwashing (CEB) using 100 mg/L sodium hypochlorite was carried out after every five regular backwashes. An acid CEB using HCl at pH 2 was performed after seven hypochlorite CEBs.

Prior to each experiment, the membrane was cleaned using a prescribed CIP method featuring a soak in hypochlorite (1,000 mg/L as free Cl₂) for one hour, then acid solution (HCl at pH 2) for 20 minutes. The effectiveness of the cleaning procedure was confirmed by performing a clean water test at 100 L/m².h for a minimum of one hour, and achieving a TMP of < 0.4 bar.

Virus and bacteria log reduction value (LRV) capability was explored in the process. For viruses, the common surrogate MS2 coliphage was used in a challenge test. While this study was not a validation, challenge tests were guided by the US EPA Membrane Filtration Guidance Manual. The test was performed in clean water to avoid fouling layer rejection effects, and without the influence of ozone, thereby providing a conservative estimate for virus LRV. A high flux, 200 L/m².h, was used with feed water spiked with MS2 in the order of 10⁷ PFU/100 mL.

For the bacterial test particle, naturally occurring E. coli in the feed was typically in the order of 10⁵ orgs/100 mL. An additional test feature was to assess the novel concept for enhanced inactivation when ozonated water flows continuously over pathogens caught on the membrane. Natural E. coli was also used to explore this concept by quantifying their numbers in the backwash water. Coliphage were enumerated by Australian Laboratory Services (ALS) using fRNA double and single agar layer methods. E. coli was measured by ALS using the Colilert method.

RESULTS AND DISCUSSION

The results from the different pre-treatment modes are shown as TMP vs. volume filtered, presented in Figures 4 to 7. Examples of the full TMP profile over the entire test period for the nominal flux of 100 L/m².h for un-pre-treated and coagulation only, and ozone plus coagulant runs at 162 L/m².h are shown in Figure 10.

MAXIMUM FLUX – DIRECT FEED TO MEMBRANE

The results in Figure 4 show a graph of initial TMP (i.e. the TMP after backwash at the start of each filtration cycle) as a function of volume filtered. This shows that the complete run of over 300 m² of filtered water was captured with negligible rise in initial TMP. However, when flux was increased to 75 L/m².h, TMP rise was rapid, and the run was terminated as TMP hit the maximum limit of 3 bar. Therefore, the maximum sustainable flux of effluent without pre-treatment was between 50 L/m².h and 75 L/m².h.

MAXIMUM FLUX – WITH OZONE

Ozone was injected into the raw feed water until >0.8 mg/L was detected at the membrane (sample point 3 in Figure 2). Residual ozone was measured using the indigo method (Standard Methods, APHA, 2005). Results of the fouling rate of a maximum flux test with ozone pre-treatment are shown in Figure 6. The effect of ozone provided more stability to the TMP as compared to the un-pre-treated feed (Figure 4) at 50 L/m².h. At the increased flux of 75 L/m².h, stable TMP was also observed, which provides evidence that ozone on its own can assist with cleaning the membrane.
MAXIMUM FLUX – OZONE PLUS COAGULATION

Figure 7 shows the results of the maximum flux test with both in-line coagulation and ozone injection. We see that the benefits of each pre-treatment combined to yield even higher fluxes achieved without severe fouling in the course of the run. Flux up to 182 L/m²·h was achieved, but could not be exceeded due to the limit of the water supply and ozone injection system. Higher fluxes may, therefore, be possible.

Overlaying TMP profiles of the four combinations is shown in Figure 8. This plot reveals a more detailed explanation of the observed performance benefits. The TMP curves are between the CEBs (TMP recovery at each hydraulic backwashes are visible). Compared to effluent without pre-treatment, ozone pre-treatment uniquely prevented TMP rise between backwash cycles, indicating ozone reduces the fouling nature of the influent. This could be due to ozone reacting with the organics, which prevents their build-up on the membrane, either because they are physically smaller, or because of their altered chemistry.

This was observed in previous studies of this group, thus confirming the effect on the pilot trial (Zhu et al., 2011). On the other hand, the TMP profile of coagulant pre-treated effluent reveals similar TMP rise per cycle to the raw feed, but returns closer to the initial value after backwash, indicating improved filter cake structure.

The combination of coagulation and ozonation appears to combine these individual effects, resulting in an unnoticeable TMP rise. The ozonated organics are potentially more amenable to coagulation, resulting in greatly improved filtration characteristics. Therefore, the two pre-treatments appear to work together to allow much higher fluxes. However, further investigation into this combined ozonation/coagulation effect is needed as there are other possible explanations.

These results imply that ozone can potentially reduce the need for hydraulic backwash (leading to improved water recovery) and/or reduced coagulant use. Furthermore, in combination there appear to be synergistic effects that may enable reduction of hypochlorite CEB frequency and, therefore, chemical costs and associated disposal. Thus the use of ozone as a water treatment barrier can also offset membrane cleaning chemicals, demonstrating one of the objectives of chemical reduction proposed in this project.

Figure 8. TMP rises as a function of time for a period between CEB. Results show un-pre-treated profile, coagulant only, ozone only, and ozone plus coagulant addition. Flux = 50 L/m²·h.

CHEMICAL USE

The chemicals required for normal operation of the plant, as delivered in concentrated form, are presented in Table 2. PACI solution, when used, had the highest consumption based on the dose rate of 3 mg (as Al³⁺)/L. Next was hypochlorite solution, but about three times lower by volume compared to PACI. Acid use was lower again, although initial acid consumption was reduced due to a revised acid CEB frequency. It was observed acid CEBs were having little improvement on TMP. As shown in Figure 8, when coagulant is used and operating at low flux, there does not appear to be any need for CEB (i.e. no TMP rise observed). This is the basis to support the notion that reduced chemical consumption operation is possible.

PATHOGEN REDUCTION POTENTIAL

Table 3 lists the results of the virus removal test carried out at 200 L/m²·h. Samples were taken before and after the membrane at five minutes and 10 minutes into two filtration cycles. The overall LRV was found to be 4.0, which indicates the virus rejection potential of this ceramic membrane. By comparison, a pilot study on a 0.4 µm polymeric MBR membrane showed an LRV of 3 for coliphage (DeCarolis and Adham, 2007), while a lab scale study on a 0.1 µm PVDF hollow fibre membrane found an LRV of 2 to 3 for MS2 coliphage (Huang et al., 2012).
To assess the LRV potential for bacteria, *E. coli* naturally present in the secondary effluent was utilised as the challenge particle. The results displayed in Table 4 show the LRV of *E. coli* between the feed and the pre-treatment (when used) and membrane permeate. All permeate samples were found to contain no *E. coli*, indicating the naturally occurring population was insufficient to calculate actual LRV. Based on the incoming *E. coli* count, LRV at any condition was >2.3.

Also shown in Table 4 is viable *E. coli* measured in the backwash water, expressed as a negative LRV with respect to feed *E. coli* count. The negative value indicates a concentrating effect of bacteria, which is to be expected considering all particles caught by the membrane can only leave the system via the backwash (a 14-fold concentration of solids is expected with a water recovery of 93%). However, this swings to positive LRV values of 0.5 to 0.7 when ozone is used. This indicates ozone reactivity with chromophore-containing compounds, but the organic matter was not mineralised.

**CONCLUSIONS**

These results represent key performance outcomes of the PWNT CeraMac ceramic membrane/ozone trial on secondary effluent. Raw secondary effluent applied to the process achieved a sustainable flux of 50L/m².h. The addition of coagulant led to enhanced sustainable fluxes, which reached up to 100L/m².h. Using ozone resulted in sustainable fluxes up to 75L/m².h. Ozonation and coagulation led to sustainable fluxes of at least 182L/m².h. But as the ozone injection equipment on the site reached its limit at this flux, higher fluxes appear to be likely.

The functions of coagulant and ozone appeared synergistic in terms of enabling the improved membrane performance. Coagulant assisted TMP reversibility during backwash, while ozone reduced the TMP rate between backwashes. Together, these effects yielded the

### Table 1: Estimation of run time before CIP for various pre-treatment options.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Max. flux (L/m².h)</th>
<th>TMP rise (kPa/h)</th>
<th>Days to CIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>50</td>
<td>none</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Coag</td>
<td>100</td>
<td>0.031</td>
<td>172</td>
</tr>
<tr>
<td>Ozone</td>
<td>75</td>
<td>none</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Coag + Ozone</td>
<td>182</td>
<td>0.268</td>
<td>NC*</td>
</tr>
</tbody>
</table>

*NC = Not confirmed

### Table 2. Summary of approximate chemical use in L of solution (as delivered) per ML water treated.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>PACI 23% (L/ML)</th>
<th>Hypo 13% (L/ML)</th>
<th>HCl 32% (L/ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>8</td>
<td>2.2</td>
</tr>
<tr>
<td>Coag only</td>
<td>22</td>
<td>8</td>
<td>0.6</td>
</tr>
<tr>
<td>Ozone only</td>
<td>-</td>
<td>8</td>
<td>0.6</td>
</tr>
<tr>
<td>Ozone + Coag.</td>
<td>22</td>
<td>8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### Table 3. LRV results of MS2 coliphage, flux 200L/m².h, clean water (no ozone or coagulant).

<table>
<thead>
<tr>
<th>Test</th>
<th>Sampling Time (min)</th>
<th>Feed phage (pfu/100ml)</th>
<th>Perm phage (pfu/100ml)</th>
<th>LRV (Lowest feed – highest perm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>6.7 x 10^6</td>
<td>200</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>6.9 x 10^6</td>
<td>700</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.4 x 10^6</td>
<td>400</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.6 x 10^6</td>
<td>&lt;100</td>
<td>4.0</td>
</tr>
<tr>
<td>LRV overall</td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
</tr>
</tbody>
</table>

### Table 4. LRV determinations using *E. coli* in feedwater, flux 150L/m².h, with various pre-treatments.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>LRV – feed to pre-treatment</th>
<th>LRV – feed to permeate</th>
<th>LRV – feed to BW</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>&gt;2.4</td>
<td>-1.2*</td>
</tr>
<tr>
<td>Coagulant</td>
<td>0</td>
<td>&gt;2.3</td>
<td>-1.3*</td>
</tr>
<tr>
<td>Ozone</td>
<td>1.4</td>
<td>&gt;2.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Ozone + coag.</td>
<td>1.4</td>
<td>&gt;2.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*Negative LRV indicates increasing concentration of *E. coli* in backwash (BW) water.

**WATER QUALITY**

Figure 9 shows water quality indicators (true colour, UV_{254} absorbance and DOC) measured in terms of % reduction to the influent at a flux of 50L/m².h. The results show that little reduction of organic matter related indicators was observed until ozone was used. This was to be expected as the MF membrane has little rejection of dissolved organic compounds. The addition of ozone showed an expected reduction in colour measurements and some reduction in UV absorbance, but resulted in little DOC removal. This indicates ozone reactivity with chromophore-containing compounds, but the organic matter was not mineralised.

![% reduction of water quality indicator with different pretreatments](image-url)
higher fluxes achieved. It was observed that use of cleaning chemicals, and even coagulant, could potentially be reduced. It appeared reductions in CEB frequency (i.e. chemical use) is possible when operating at moderate or low flux, but generally not when high flux is sought.

Pathogen removal testing found an LRV (virus) of 4.0 attributed to the membrane process alone. The absolute bacterial LRV was determined to be >2.3 as no E. coli could be found in the product permeate. The concept of enhanced pathogen inactivation in the reject stream was confirmed with an LRV of 0.6 between feedwater and reject water. This contrasts with a 1.3-log increase in the reject stream when ozone was not employed. While the challenge testing indicated expected performance across MF membranes, it is the enhanced backwash pathogen disinfection that is unique to this ozone/ceramic membrane hybrid process. This has benefits to operations where disinfected reject water would be useful with respect to the disposal strategy.

This work therefore supports the performance benefits proposed by ceramic membranes in conjunction with ozone. High fluxes, and/or reduced chemical usage and enhanced total disinfection, are unique features that would have benefits for wastewater recycling. A costing study is due to be completed by late 2013 to quantify these benefits for water recycling in Australia.

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REFERENCES


