DBNPA AS AN ALTERNATIVE METHOD FOR MICROBIAL CONTROL IN RECYCLED WATER DUAL MEMBRANE PLANTS

Paper Presented by:

Kevin He

Authors:

Kevin He, Carlota Rodriguez, Mohammad Helmy,
City West Water

Daniel Palm, Dow Chemical Australia

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Kevin He, Carlota Rodriguez, Mohammad Helmy, City West Water
Daniel Palm, Dow Chemical Australia, Melbourne

ABSTRACT

Industry practices have varied in the control of microbial growth and biofouling of membrane filtration systems in recycled water applications. Some of the strategies utilised include chlorination/dechlorination, chloramination, Sodium Bisulphite and Biocide dosing in Feedwater. Each strategy has its advantages and disadvantages; as well as associated operational risks including risk of oxidation of RO membranes. It is well documented that any free chlorine can damage polyamide RO membranes which is further oxidised in presence of transition metals. RO performance deterioration is typically characterised by reduction in salt rejection and permeate flow.

Altona Salt Reduction Plant (ASRP) is an UF and RO (two pass) recycled water plant, owned and operated by City West Water (CWW). It receives tertiary treated effluent from its wastewater treatment plant. This paper summarises ASRP's experiences with a non-oxidising and biodegradable biocide, DBNPA and provides insights into alternative methods to manage biofouling in membrane filtration systems. The paper will also compare operating cost of using Chlorine/dechlorination Chloramination and DBNPA dosing.

1.0 INTRODUCTION

DB2,2-Dibromo-3-nitrilopropionamide (DBNPA CAS#10222-01-2) is a non-oxidising biocide used to reduce microbial and biological fouling in Reverse Osmosis (RO) systems for industrial water production, off-line cleaning of RO membranes producing potable and municipal water, ultra-filtration, nano-filtration and microfiltration systems and a wide range of other industrial and water treatment applications.

DBNPA has been used at ASRP during its operational history, dosed in varying concentration and at different injection points. The experiences and analysis from previous operational periods proved there were opportunities to optimise the microbial control and performance of the plant.

ASRP was offline between 2013 and 2015 and upon recommencement, various strategies were discussed for microbial control as part of an options analysis. Feasible options include chlorination with sodium bisulphite quenching and chloramination but consideration was given to continue with DBNPA. In consultation with DOW Chemical Australia, a control strategy was selected for a daily shock dose of DBNPA for 60 minutes and at 20 ppm into the feedwater prior to the UF strainers which has increased lifespan of RO elements and overall plant capacity.

2.0 DISCUSSION

2.1 Plant Hygiene Audit Analysis

Plant microbial audits designed to assess plant hygiene, equipment design and raw material quality by analysis of swab and liquid samples at ASRP has been intermittently conducted at ASRP.

The bacteria colony counts from the hygiene assessments quantify the severity of biofouling and effectiveness of the microbial strategy. The rating scale in Table 1 is used to quantify the extent of bacterial growth of plated samples taken from each location; higher the score, the greater bacteria count.

Table 1: ***Hygiene report bacteria score***

Plating Results	Score	~ cfu/ml
No detectable survival	0	$<1\times10^1$
1 – 9 colonies	1	1×10^1 - 9×10^1
10 – 99 colonies	2	$1\times10^2 – 9.9\times10^2$
100 – 300 colonies	3	$1\times10^3 – 3\times10^3$
> 300 colonies	4	$> 3\times10^3$

The applications of DBNPA in earlier operational periods varied from using it as a CIP chemical, continuous dose at 1ppm into the RO cartridge filters and intermittent shock dose via RO displacement tanks. Without any pre-treatment of the feedwater prior to the RO system, there were many areas for bacteria to spawn and populate thus higher bacteria counts were detected throughout the system.

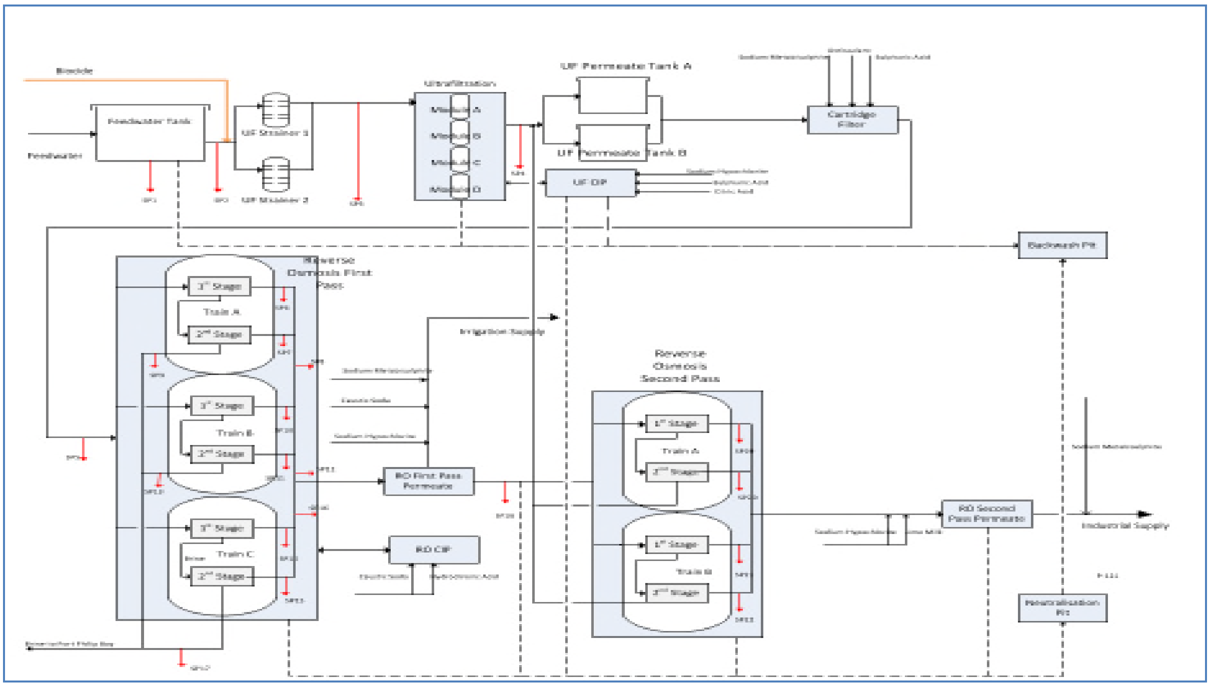

Figure 1: ***Schematic of Altona Salt Reduction Plant (22 Sampling locations denoted by SP)***

The hygiene audits conducted at the 11 equivalent sampling locations across the plant between different operational periods shows a significant reduction in the total bacteria score. The results emphasize the importance of sterilisation of the feedwater as early upstream as possible, particularly if DBNPA is used alone as pre-treatment for microbial and biofouling control. By treating the piping system upstream of the RO membranes, the DBNPA is attacking any potential source areas for bacteria to spawn and proliferate. The average total bacteria score during periods where DBNPA dosage was focused only on the RO system either as continuous or shock dose, returned an average score of 15 (out of a maximum 44) across the 11 SPs.

When the DBNPA dosage was moved to the feedwater stream, a 63% reduction in bacteria score was realised across the same11 SPs; average total bacteria score was 5.6. The biocide was able to sterilise previously missed process areas upstream of the RO system including RO cartridge filters, UF System, UF storage tanks and UF strainers. As a result, less fouling was observed on the RO cartridge filters and the performance of the RO membranes improved; there is a direct correlation between bacteria counts and frequency of RO CIP cleans.

Table 2: ***Comparison of total bacteria score between periods of different DBNPA application***

	2011-13	**2015-16**
Location of DBNPA Application	RO Cartridge Filter/CIP Tank/RO Displacement Tank	Feedwater
No. of Reports	3	8
Average Total Bacteria Score (lower score is better)	15	5.6
% Improvement	63%	

A comprehensive set of hygiene audits over 22 sampling locations (Refer to Figure 1) across ASRP were conducted on a fortnightly basis (by DOW Chemical) to quantify effectiveness of the current DBNPA regime. SP1, SP2 and SP18 were locations of concern due to the absence of DBNPA because they are located either before the dosing point or after where it has exited the system. Anecdotal evidence supports almost all of the DBNPA is rejected in the RO concentrate. At a shock dose of 20 ppm, residual DBNPA was detected through the biocide testing kit between SP3 and SP17 for up to 4 hours from time of dosage. Future works include a secondary biocide dosing point post 1st Pass RO permeate. However, ASRP has not seen any deterioration in Second Pass RO performance.

Table 3: ***Average bacteria score across 22 SPs of current DBNPA application***

	SP1	**SP2**	**SP18**	**SP3-SP17**
Sampling Description	Feedwater Tank	Pre-UF Strainer	RO 2nd Pass Feed	All Other Process Areas
Average Bacteria Score	2.12	2.63	3	1.03

SP18 returned the highest average bacteria score of 3, best explained with microbial growth in areas without DBNPA. The other 19 SPs have shown good results with a Bacteria Score ranging from 0 – 1.

2.2 RO Cleaning-in-Place Frequency

The ASRP RO membranes are subjected to fouling of foreign materials that are present in feed water. Typically, organic and biological matters are the primary contributors to fouling in 1st Pass RO membranes. Metal oxides and inorganic metal precipitates are controlled by pre-treatment, recovery control, feed pH correction and Antiscalant dosing systems. Fouling reduces performance of membranes which is represented by reduction in permeate flow, increased salt passage and a higher pressure drop. A Clean-in-Place chemical cleaning process is required to remove the fouling on membranes and recover the performance of the RO system. Excessive fouling leads to frequent CIPs, decreased plant capacity and increased chemical costs.

Greater biological fouling on the RO membranes occurred during periods when DBNPA application was targeted only at the RO process areas. Characteristics in the Feedwater into ASRP such as pH, alkalinity and metal concentration has not varied significantly between different periods of DBNPA application to suggest the primary fouling was other than biological based. Autopsies of the RO cartridge filter show a slimy brown foulant indicative of organic or biological matter rather than scaling precipitates.

During periods where the feedwater was not treated by DBNPA, a combination of influent nutrients and bacteria colonies potentially encourage biological growth in un-sterilised areas prior to the RO membranes. This leads to rapid fouling on the RO cartridge filters and subsequently RO membranes trigger set points for CIPs. CIPs reduce plant capacity as a RO train needs to be taken offline and is a costly exercise due to chemical consumption. Most typically, the RO membranes at ASRP undergo a Caustic Soda followed by a Hydrochloric Acid clean for each CIP.

The frequency of CIP cleans significantly reduced when DBNPA was used as pre-treatment to the feedwater, directly relating to reduced RO membrane fouling. Pre-treatment aims to prevent microbial outbreaks upstream thus relating to reduced chances of rapid fouling. For example, a CIP was required on average once every 60 days compared to 105 days in 2nd Pass RO Trains between the two different DBNPA operations.

Table 4: ***Average time since last CIP (days)***

		2011-13	**2016**
Location of DBNPA Application	No. of Trains	RO Cartridge Filter/CIP Tank/RO Displacement Tank	Feedwater
1st Pass RO	3	46	86
2nd Pass RO	2	60	105

3.0 DBNPA PROPERTIES

DBNPA is a fast-acting biocide that demonstrates a broad spectrum of activity, at low concentration, against bacteria, fungi, yeast, cyanobacteria (also referred to as blue green algae) and true algae. It is completely miscible with water and begins to function immediately upon addition into the feed water and antimicrobial control is rapidly achieved if properly dosed. Recommended dosage rates for DBNPA are between 1 – 200ppm dependent on the system and degree of fouling and the addition of sodium bisulphite or other reducing agents must be suspended at least 15 minutes prior to addition of the product to prevent neutralisation and deactivation. When added to an RO system, DBNPA is rejected by the thin-film composite membrane layer, and at use dilution, shows excellent compatibility with all materials of construction of the RO membrane module.

DBNPA offers an advantageous combination of quick kill properties followed by fast chemical degradation, including hydrolysis. The dominant degradation pathway at use conditions involves reactions with nucleophilic substances or organic material invariably found in water. Nucleophilic degradation forms cyanoacetamide. When the disposal/storage of concentrate involves exposure to UV-radiation additional degradation will occur.

When sufficiently diluted, DBNPA and its degradation products become biodegradable. The ultimate degradation products formed from both chemical and biodegradation processes of DBNPA include ammonia, carbon dioxide, and bromide ions.

4.0 COMPARISON COST WITH OTHER ALTERNATIVES

Below is a brief introduction to different strategies utilised to control of microbial growth and biofouling of membrane filtration systems in recycled water applications and its target doses.

Table 5: ***Chemical consumption and cost analysis***

Pre-Treatment Strategy	Chemical	Target Concentration (ppm)	Usage/day (L/day)	Cost/day (AUD/day)	Cost/ year (AUD/year)	Total Cost/year (AUD/year)
Chloramination	Aqua Ammonium Hydroxide[3] (25% w/v as Ammonia)	2 (as NH_3)	124	187	68,135	**$ 153,755**
	Sodium Hypochlorite[4] (13% w/v as Chlorine)	9 (as Cl_2)[2]	920	235	85,620	
Chlorination / Dechlorination	Sodium Hypochlorite[4] (13% w/v as Chlorine)	15 (as Cl_2)	742	390	142,350	**$ 534,895**
	Sodium Metabisulphite[5] (31% w/v)	22.5[1]	1,533	1,075	392,545	
Biocide continuous	DBNPA[3] (20% w/w)	5	280	1,830	667,950	**$ 667,950**
Biocide (shock dosing)	DBNPA[3] (20% w/w)	20	47	300	109,500	**$ 109,500**

[1]Based on 1.5:1 SBS to Chlorine ratio; [2]Based on 4.5:1 Chlorine to Ammonia ratio; [3]Chemical delivered in a 1,000L IBC; [4]Chemical delivered into 2 x 20,000L tanks, [5] Chemical delivered into 1 x 2,000L tank

- ***Chloramines:*** can be used as a disinfectant and can be effective in control of biofilms. Chloramine can last longer than chlorine in water and produces fewer disinfection by-products (EPA 2015). Monochloramine is the most effective Chloramine disinfectant. Chloramines are usually formed by adding anhydrous or aqueous ammonia to water containing free chlorine (HClO). The process of chloramination depends on pH and concentration, pH levels below 7.5 or chlorine to ammonia ratios exceeding 5:1 increase the formation of dichloramine (NHCl2) and nitrogen trichloride (NCl3) which are undesirable by-products (Water Quality Association 2013).

- ***Chlorination/dechlorination:*** Chlorine is a highly effective method of disinfection however, chlorine attack will irreversibly damage the FILMTEC™ RO membranes. Dechlorination upstream of the membranes is required to protect the membranes from oxidation. In theory, 1.34 mg of sodium metabisulfite will remove 1.0 mg of free chlorine (DOW n.d. a).

- ***Biocide:*** Biocide can be dose continuously like chlorine, monochloramines or can be slug dosed.

20ppm for slug dose and 5 to 10ppm for continuous dose (DOW n.d. b). Fouling microorganisms can build up a resistance to biocide over time, slug dosing biocide minimises the likelihood of this happening.

The daily and annual cost associated to each strategy has been estimated based on the recommended chemical doses of each strategy, the ASRP daily flows treated (14MLD), chemical concentrations, specific gravity of the chemicals as currently provided by supplier and its costs based on the contract with chemical supplier currently in place.

5.0 CONCLUSION

ASRP has improved its plant performance with no additional pre-treatment for biofouling such as chlorination or chloramination. The sole DBNPA application at head of the plant at 20 ppm and for 60 minutes a day, has helped to optimise ASRP operations by reducing frequency of CIP cleans, extending life of process assets and lowered bacteria colony counts throughout the plant.

The items for future implementation include:

1. Infrequent Chlorine Disinfection of the Feedwater Tank (SP1), upstream of the DBNPA dosing point to attack biological species which have shown to be immune to DBNPA, followed by Sodium Bisulphite quenching

2. Secondary DBNPA dosing point post RO 1st Pass Permeate Tank for sterilization between 1st Pass RO and 2nd Pass RO due to DBNPA being rejected in the 1st Pass RO concentrate.

The future works aim to prevent microbial outbreak in potential ASRP's process areas, specifically at the feedwater Tank into the plant, as well as expanding the control to all biological species. Preliminary investigations have shown a once a month Sodium Hypochlorite shock dose followed by DBNPA is a very effective control measure.

6.0 REFERENCES

DOW Water & Process Solutions n.d. a, *Section* 2.6.3 Chlorination / Dechlorination *of FILMTEC™ Reverse Osmosis Membranes, Technical Manual*, DOW Water & Process Solutions n.d, viewed 29 June 2016, <http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0039 /0901b80380039060.pdf?filepath=liquidseps/pdfs/noreg/609-02034.pdf&fromPage=GetDoc>

DOW Water & Process Solutions n.d. b, *Section 2.6.5 DBNPA of FILMTEC™ Reverse Osmosis Membranes, Technical Manual*, DOW Water & Process Solutions n.d., viewed 29 June 2016, <http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0039/0901b80380039060.pdf?filepath=liquidseps/pdfs/noreg/609-02034.pdf&fromPage=GetDoc>

EPA 2015, *Public Water Systems, Disinfection By-products, and the Use of Monochloramine*, EPA, viewed 29 June 2016, <https://www.epa.gov/dwreginfo/public-water-systems-disinfection-byproducts-and-use-monochloramine>

Water Quality Association 2013, *Chloramine Fact Sheet*, WQA Organization, viewed 29 June