

**USE OF A MAGNETIC ION EXCHANGE RESIN FOR THE REMOVAL OF  
DISSOLVED ORGANIC CARBON TO ALLOW COMPLIANCE WITH THE EPA'S  
D/DBP RULE AT THE NETMWD WTP**

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**ABSTRACT**

Tightening EPA standards for disinfection by-products (DBPs) will make it necessary for many utilities to remove a larger fraction of dissolved organic carbon (DOC) from their water supplies prior to disinfection. Raw water treated in NETMWD's Mims Water Treatment plant (WTP) is drawn from the Lake of the Pines and has total organic carbon (TOC) levels generally in the range of 5 to 8 mg/L (most of which is in the form of DOC). The alkalinity of this water is low at 5 to 20mg/L as CaCO<sub>3</sub> and therefore based on the EPA Stage 1 DBP Rule, up to 50% TOC removal is required through the WTP. For at least 6 months of the year, it is not possible to achieve the required TOC removal using the existing coagulation treatment process at the Mims WTP although during this period, the treated water is still in compliance with the EPA's secondary SUVA standard. If a water treatment plant cannot meet the TOC standard, the plant must then meet a SUVA (ratio of UV Absorbance at 254nm and TOC) standard. As part of NETMWD's investigation of treatment options to allow compliance with the EPA Stage 1 DBP Rule, a trial of a magnetic ion exchange resin (MIEX<sup>®</sup>) was conducted from July 14-25, 2003.

The trial conducted at the Mims WTP showed that MIEX<sup>®</sup> resin pretreatment followed by alum coagulation could consistently remove at least 60% and as high as 90% of the raw water TOC, easily achieving the EPA Stage 1 DBP Rule requirement of 45-50% removal. This compares with an average TOC removal achieved by the plant of around 41% during the trial. This paper will discuss the results of laboratory and pilot testing to remove TOC from raw water at the NETMWD's Mims WTP including operating costs of a MIEX<sup>®</sup> pretreatment system.

**KEYWORDS**

Magnetic ion exchange, disinfection byproducts, total organic carbon, MIEX

## INTRODUCTION

A continuous ion exchange process utilizing a magnetized ion exchange resin (MIEX<sup>®</sup>) was developed in Australia in response to the need to remove greater amounts of DOC from Australian water supplies to prevent problems associated with DBPs, bacterial regrowth in the distribution system and tastes and odors. Several full-scale plants are now in operation in Australia, the largest with a capacity of 30 MGD. The first two US installations are currently under construction in Florida and will be commissioned by mid-2004.

Unlike conventional ion exchange processes, the MIEX<sup>®</sup> resin has been developed to enable removal of DOC to occur in a stirred contactor, much like a flash mixer in a conventional water treatment plant. Under mixing conditions, the resin beads are uniformly dispersed in water to maximize the kinetics of DOC exchange. This reduces the resin inventory in contact with water to only a fraction of that normally associated with conventional ion exchange processes.

A magnetic component is built into the resin particle structure so that when mixing is removed, the fine resin beads rapidly agglomerate into larger, fast settling particles. This enables conventional up-flow settlers to be used for resin-water separation. While the treated water overflows from the settler, the resin is recovered as a concentrated underflow stream. The efficiency of resin recovery exceeds 99.95% at very high settler loading rates (6 gpm/ft<sup>2</sup>). A small amount of recycled resin is continuously removed for regeneration and replaced with regenerated resin. A schematic of the process is shown below in Figure 1.

The majority of DOC present in drinking water supplies is in the form of negatively charged humic and fulvic acids. The MIEX<sup>®</sup> resin removes these negatively charged ions from water by exchanging with a chloride ion on active sites on the resin surface. Research conducted in Australia has shown that MIEX<sup>®</sup> resin, used in a continuous ion exchange process, is highly effective at removing low and medium molecular weight TOC and can achieve greater removals of TOC than enhanced coagulation<sup>1</sup>. Coagulants are effective at removing the high molecular weight fraction of TOC but remove very little of the lower molecular weight fraction. This has been demonstrated on a 30 MGD MIEX<sup>®</sup> groundwater treatment plant at Wanneroo in Perth, Western Australia (Figure 2)<sup>2</sup>.

There are many water sources, particularly in the South East and Mid Atlantic regions of the US, where coagulants cannot achieve the TOC removal required by the EPA Stage 1 DBP Rule due to the characteristics of the TOC. This is the case at the Mims WTP where for up to 6 months of the year, enhanced coagulation cannot achieve the EPA's TOC removal requirement.

Figure 1: Schematic of the MIEX<sup>®</sup> continuous ion exchange process

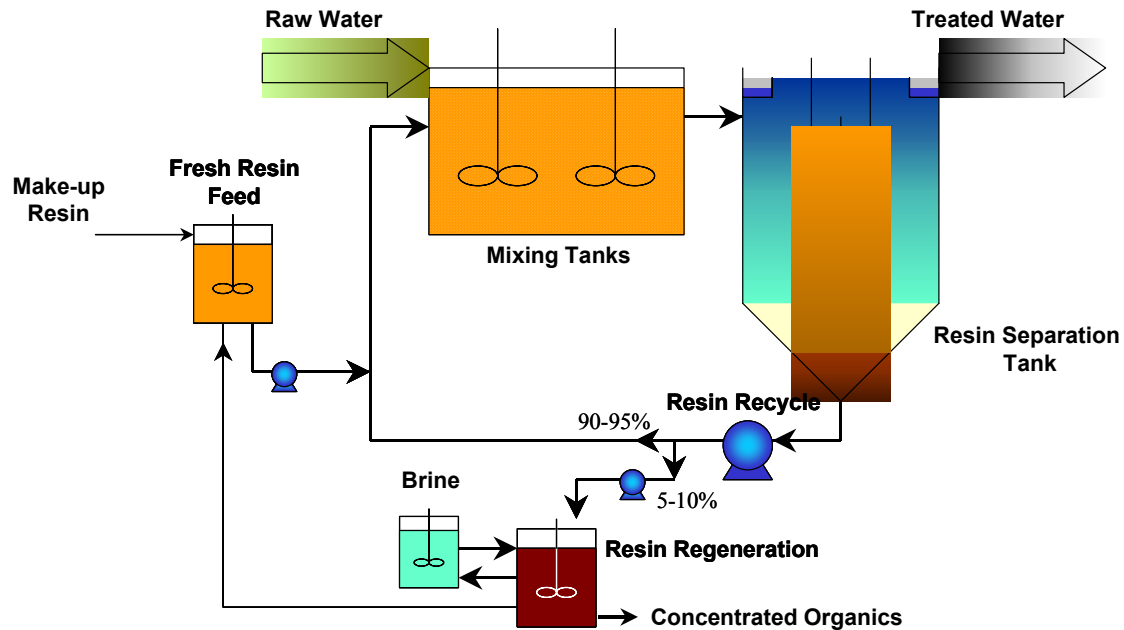
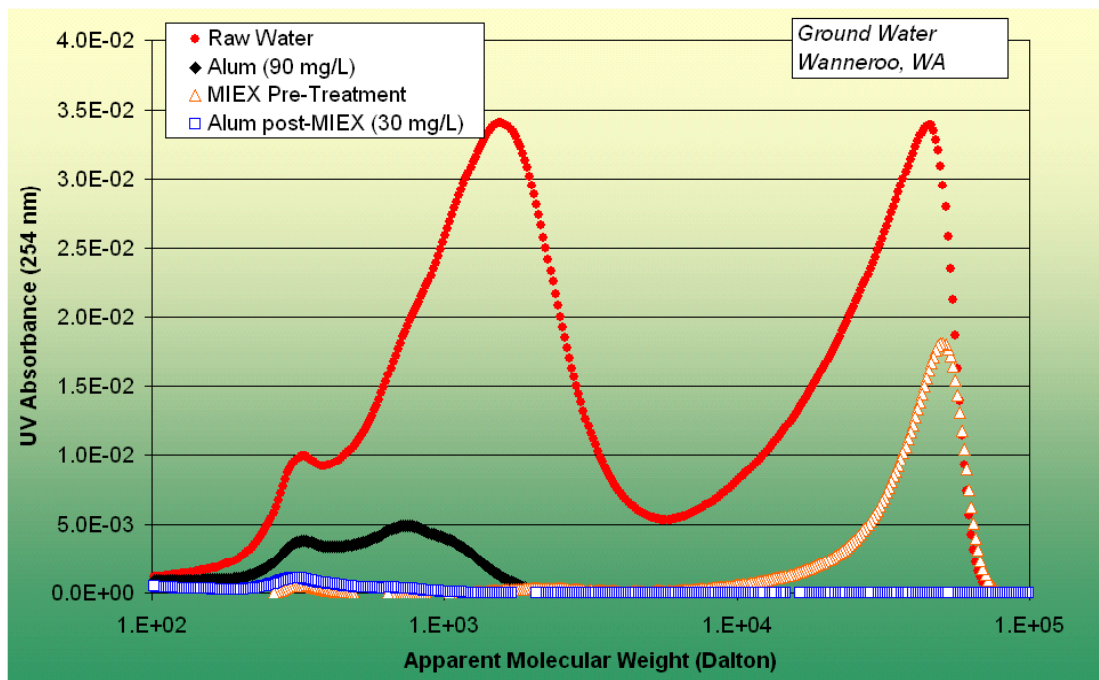


Figure 2: Characteristics of TOC removed with MIEX<sup>®</sup> resin and Alum on Wanneroo ground water, Western Australia.



Laboratory jar tests initially conducted on raw water that supplies the Mims WTP demonstrated that the MIEX<sup>®</sup> resin removed a greater amount of TOC than the current coagulation process,

while significantly reducing downstream alum doses required for turbidity removal. A pilot plant trial was therefore conducted during July 2003 to demonstrate that the laboratory test results could be achieved on a continuous process and to provide operating costs estimates for a full scale MIEX<sup>®</sup> system.

## METHODOLOGY

The MIEX<sup>®</sup> trial was conducted at the Mims WTP using a continuously operating 2gpm pilot plant (Figure 3) to treat raw water sourced from the Lake of the Pines in North East Texas.

The major trial objective was set at achieving a 60% reduction in raw water TOC after MIEX<sup>®</sup> resin treatment followed by alum coagulation.

Secondary objectives were as follows:

- Determine how much the alum dose could be reduced after MIEX<sup>®</sup> resin pretreatment in order to reduce downstream chemical usage and sludge disposal costs.
- Evaluate the potential for partial treatment of the WTP throughput to minimize capital and operating costs and waste quantities.

**Figure 3: MIEX<sup>®</sup> Pilot Plant at the Mims WTP**



During the trial the raw water characteristics were as follows:

**Table 1: Raw Water Characteristics During Trial**

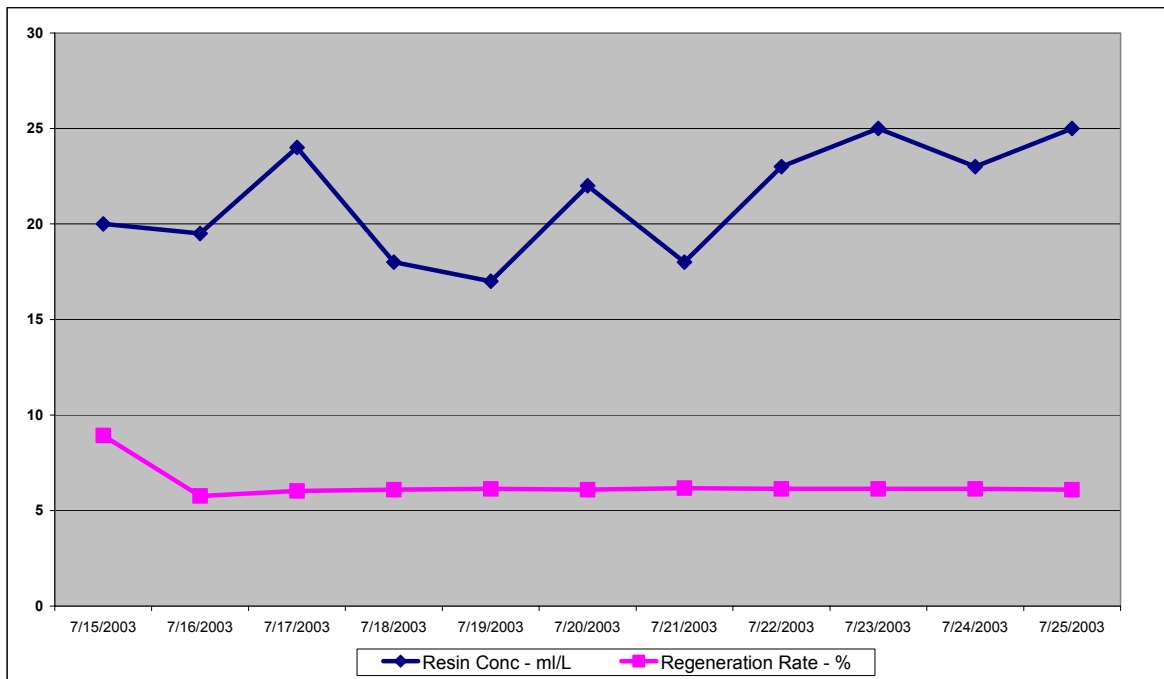
| Parameter                             | Analysis (range) |
|---------------------------------------|------------------|
| pH                                    | 6.16 – 6.85      |
| Alkalinity, mg/L as CaCO <sub>3</sub> | 8-14             |
| True Color, Pt Co Units               | 1-17             |
| Apparent Color, Pt Co Units           | 102-1300         |
| Turbidity, NTU                        | 4.8-118          |
| Iron, mg/L                            | 0.21-1.14        |
| Manganese, mg/L                       | 0.087-0.890      |
| Sulfate, mg/L                         | 23.8-25.3        |
| Total Organic Carbon, mg/L            | 7.24 –8.68       |

The main MIEX<sup>®</sup> process operating parameters from the trial are summarized below in Table 2 and Figure 4:

**Table 2: Summary of MIEX<sup>®</sup> Process Operating Parameters**

| Parameter                    | Value   |
|------------------------------|---------|
| Total Water Treated (gal)    | 19,000  |
| Actual Flow Rate (gpm)       | 1.2     |
| Resin Concentration (mL/L)   | 20-26   |
| Actual Regeneration Rate (%) | 6.1-8.9 |
| Contact Time (min)           | 15-17   |

**Figure 4: Process Operating Variables for MIEX<sup>®</sup> Pilot Plant**



## RESULTS

### TOC Removal

During the trial, samples of raw water, MIEX<sup>®</sup> resin treated water and MIEX<sup>®</sup>/alum treated water were collected to determine the TOC removal achieved in each step of the MIEX<sup>®</sup>/Alum treatment regime. These results were compared with the current Mims WTP performance by analyzing samples of finished plant water. The overall TOC removal objective was to achieve the removal rates specified in the EPA Stage 1 Rule where there is a requirement for “enhanced coagulation.” Enhanced coagulation is the practice of using a coagulant dose in excess of what is normally required for turbidity removal to achieve a specific reduction in the concentration of total organic carbon (TOC). The enhanced coagulation requirements mandate reductions in TOC concentrations based on the TOC and alkalinity of the source water as shown in Table 3.

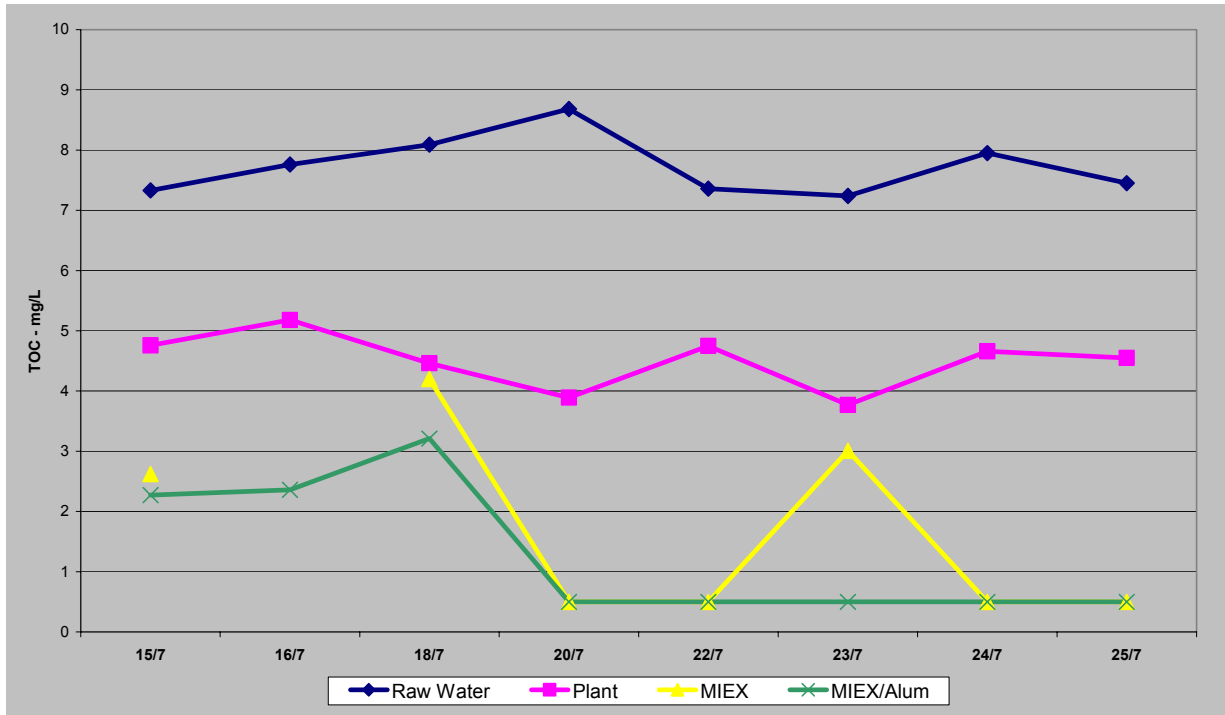
Table 3: Stage 1 TOC Removal Requirements of the D/DBP Rule (USEPA, 1998)

| TOC Concentration, mg/L | Alkalinity, mg/L as CaCO <sub>3</sub> |           |           |
|-------------------------|---------------------------------------|-----------|-----------|
|                         | 0-60                                  | >60-120   | >120      |
| <2.0                    | no action                             | no action | no action |
| 2.0-4.0                 | 35%                                   | 25%       | 15%       |
| >4.0-8.0                | 45%                                   | 35%       | 25%       |
| >8.0                    | 50%                                   | 40%       | 30%       |

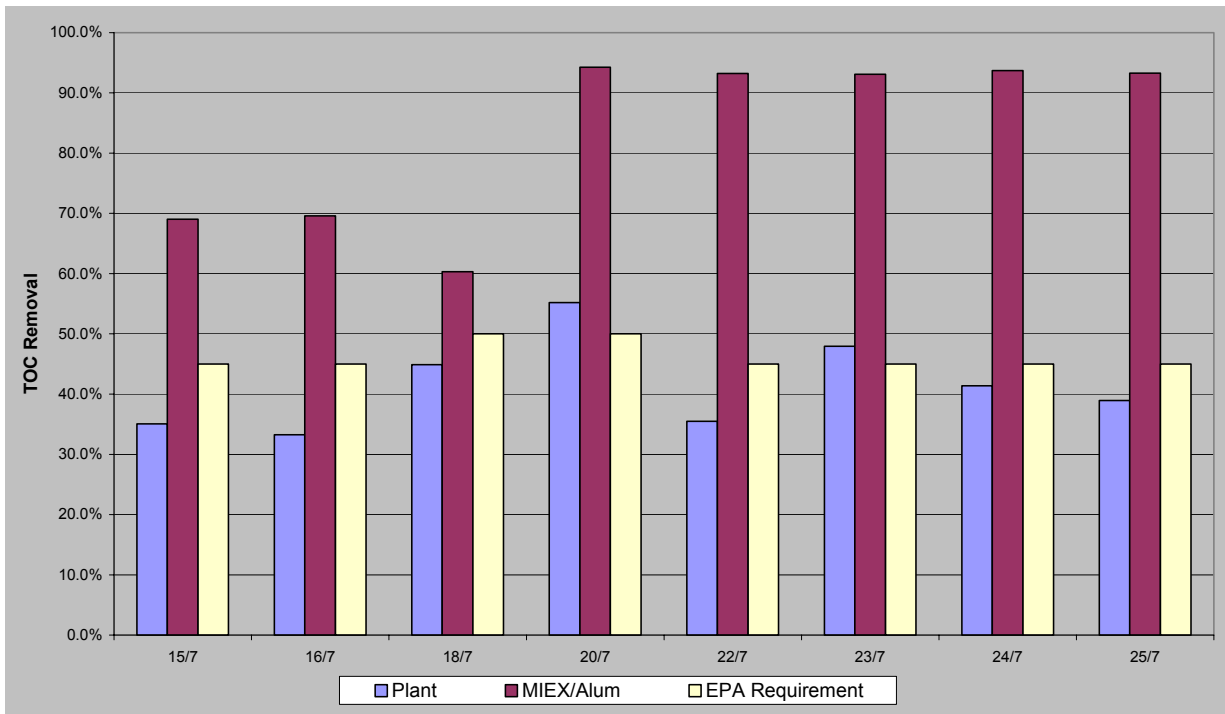
The TOC removals achieved during the trial are shown in Figures 5 and 6. These results show that the current plant did not achieve the required TOC removal for six of the 8 samples taken over the trial period while MIEX<sup>®</sup>/Alum treatment easily achieved the EPA requirement for all samples taken (Figure 6). TOC levels after 7/20 for all MIEX<sup>®</sup>/Alum treated samples and all but one MIEX<sup>®</sup> only treated sample were below the detection limit of 0.5mg/L.

Raw water TOC levels ranged between 7 and 8 mg/L during the trial period, which is typical for summer. TOC levels can be as high as 12 mg/L during spring and fall. A MIEX<sup>®</sup> treatment system has the flexibility to increase the resin concentration or regeneration rate to provide greater TOC removal to accommodate raw water fluctuations. The water demand from the plant will also be lower in spring and fall, which will allow a greater proportion of the raw water to be passed through a MIEX<sup>®</sup> plant (if MIEX<sup>®</sup> is implemented to only treat a portion of the plant capacity).

**Figure 5: TOC Removal Results**



**Figure 6: Comparison of TOC Removal Results with EPA Requirements**



It should also be noted that alum doses used on MIEX<sup>®</sup> resin treated samples were only 5 to 10 mg/L. At these doses the flocs formed were significantly larger than those formed on the plant at a dose of around 40 mg/L. While a small amount of sodium hydroxide was still required to maintain a coagulation pH of 6.2-6.5, at the lower alum doses of 5 to 10 mg/L, significantly less NaOH will be used for pH correction and the treated water alkalinity should also be higher, resulting in less corrosion in the distribution system.

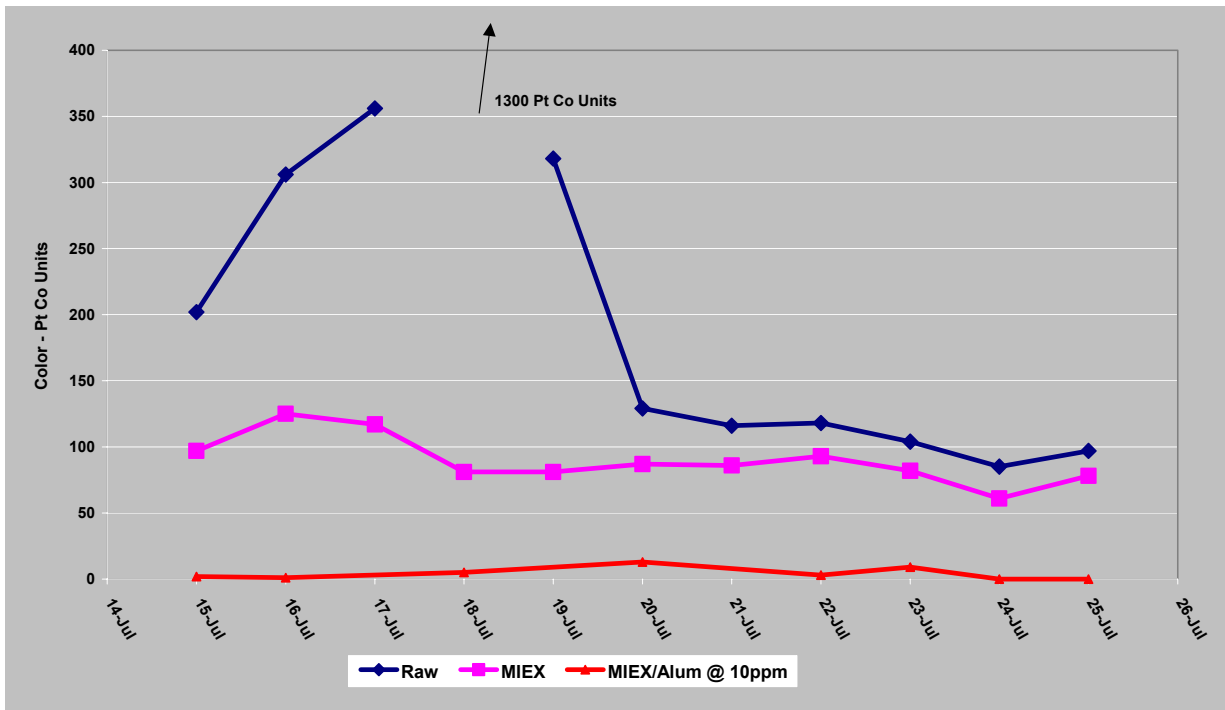
When coagulation conditions were optimized, the settled water turbidity after 5 minutes settling was in the range of 0.4 to 0.7 NTU on MIEX<sup>®</sup>/alum treated samples. Turbidity was used to select the optimum coagulant dose rather than simulate the WTP clarifiers, as it was not possible on the bench scale to simulate the impact of the clarifer feedwell and detention times.

In summary, the TOC results show that MIEX<sup>®</sup> /Alum treatment can consistently reduce the raw water TOC by at least 60% and easily achieve the maximum EPA removal requirement of 50%. Parallel tests conducted on the full-scale plant effluent showed that the EPA removal requirements of 45-50% could only be achieved on 25% of samples taken.

### Color Removal

After MIEX<sup>®</sup> resin pretreatment, subsequent alum doses for turbidity and color removal were reduced from 40 to 10mg/L. Figure 7 shows that following MIEX<sup>®</sup> resin pretreatment and an alum dose of 10 mg/L, the unfiltered color was consistently reduced to at least 5 Pt Co Units. In most cases this was equal to or better than the filtered plant output. All filtered MIEX<sup>®</sup> resin treated samples had all color removed (i.e. were at 0 Pt Co Units).

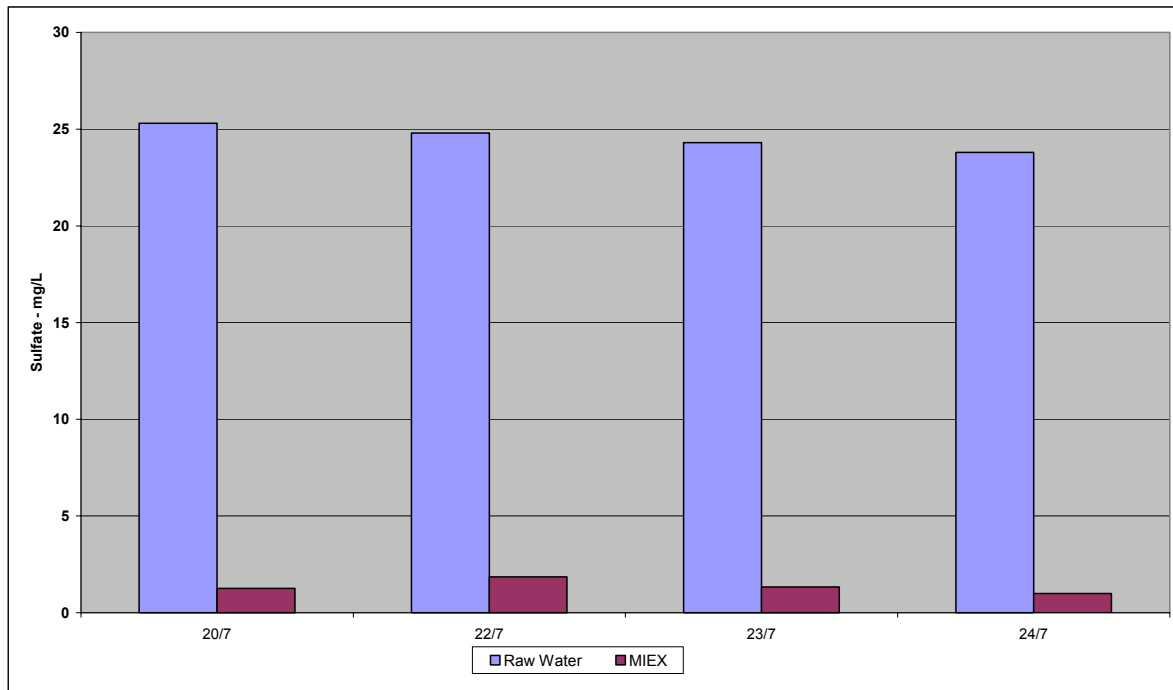
**Figure 7: Color Removal Results**



## Sulfate Removal

Figure 8 shows that a significant amount of sulfate was removed after MIEX<sup>®</sup> resin treatment. A buildup of sulfate in the regeneration brine will have a slight impact on the amount of waste brine generated.

**Figure 8: Sulfate Removal Results**



## Iron & Manganese Removal

Iron and manganese data indicated significant removals after MIEX<sup>®</sup> resin treatment when raw water levels were high (see shading), but negligible removal when raw water levels were low. The MIEX<sup>®</sup> resin is not designed to remove Fe and Mn, which are cations (MIEX<sup>®</sup> resin removes anions), so the high raw water values may have been due to experimental error.

**Table 6: Iron and Manganese Data**

| Date  | Fe - mg/L |           | Mn - mg/L |           |
|-------|-----------|-----------|-----------|-----------|
|       | Raw       | Post MIEX | Raw       | Post MIEX |
| 16/07 | 0.73      | 0.28      | 0.268     | 0.139     |
| 18/07 | 1.14      | 0.22      | 0.631     | 0.104     |
| 20/07 | 0.25      | 0.23      | 0.190     | 0.115     |
| 22/07 | 0.25      | 0.21      | 0.129     | 0.113     |
| 23/07 | 0.21      | 0.21      | 0.097     | 0.097     |
| 24/07 | 0.21      | 0.15      | 0.890     | 0.086     |
| 25/07 | 0.29      | 0.24      | 0.087     | 0.076     |

## CONCLUSIONS

Based on the results of the MIEX<sup>®</sup> trial conducted from 7/14/03 to 7/25/03 the following conclusions can be made:

- MIEX<sup>®</sup> resin pretreatment followed by alum coagulation will allow the final treated water TOC to be lowered by at least 60% and by as much as 90%, comfortably in excess of the highest EPA Stage 1 DBP Rule requirement of 50%. In comparison, parallel analyses conducted on filter effluent from the Mims WTP showed an average of 41.5% TOC removal (range of 33.2 to 55.2%) and only 2 of the 8 samples taken met the EPA requirement.
- After MIEX<sup>®</sup> resin pretreatment the alum dose was reduced from 40mg/l on the full-scale plant to 10mg/L, a 75% reduction. MIEX<sup>®</sup> resin pretreatment will therefore significantly reduce costs for coagulant, pH correction chemicals and downstream sludge disposal.
- The incremental operating cost increase of a MIEX<sup>®</sup> system will be in the range of 5.3 to 10.7 cents per 1000 gallons of water treated.
- Assuming waste brine is coagulated to minimize the volume of liquid waste generated, the waste generated from a MIEX<sup>®</sup> system treating 100% of the plant throughput will consist of approximately 200lb/MG of coagulation sludge and 10 gal/MG of brine waste. There will be a large net reduction in waste sludge produced at the Mims WTP due to a 75% reduction of the alum dose after MIEX<sup>®</sup> resin pretreatment.

In summary, the trial results showed that a MIEX<sup>®</sup> resin pretreatment step can improve TOC removal at the Mims WTP to at least 60% and reliably meet the maximum EPA removal requirement of 50%. If the worst TOC data point is ignored (and this was significantly different from the other points) the data shows that at least 69% removal will be possible with MIEX<sup>®</sup>/Alum treatment. Assuming all of the raw water is treated through a MIEX<sup>®</sup> system, the cost of MIEX<sup>®</sup> treatment will be approximately 10.7 cents/1000 gals treated, but against this cost there will be savings in sodium hydroxide usage and sludge disposal costs. If MIEX<sup>®</sup> resin treatment is only required for 6 months of the year when the existing treatment plant cannot achieve the target TOC removal, the annualized treatment cost will be halved to around 5.3 cents/1000 gals. The MIEX<sup>®</sup> system operating cost could be reduced further if it was not necessary to pretreat the entire plant throughput through a MIEX<sup>®</sup> system to meet the EPA TOC removal requirement. The trial results indicate that because MIEX<sup>®</sup>/Alum treatment will remove TOC well in excess of the EPA requirement, it may only be necessary to treat 75% of the raw water in a MIEX<sup>®</sup> system.

It is probably prudent to install MIEX<sup>®</sup> treatment capacity to treat the whole raw water flow allowing for future tightening of EPA standards, while allowing some of the raw water to be bypassed around the MIEX<sup>®</sup> plant to reduce operating costs to as low as 4 cents per 1000 gals (treating 75% of the flow for 6 months of the year).

## ACKNOWLEDGEMENTS

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## REFERENCES

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