

# Disinfection By-Products (DBP) Compliance through Pre-treatment for TOC Removal

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Over the last few years, utilities have adjusted their existing processes to reduce the formation of DBPs in order to comply with the Stage 1 DBP Rule. With Stage 2 looming in the near future, many utilities have nothing left to optimize in order to minimize DBP peaking in the distribution systems.

A non-chemical treatment process was developed in response to the need to remove greater amounts of TOC from water supplies to prevent problems associated with DBPs. The MIEX<sup>®</sup> System is an ion exchange pre-treatment process specifically targeted for removal of dissolved organic carbon (DOC) compounds, such as humic and fulvic acids, from drinking water supplies. These negatively-charged ions are removed from water by exchanging with a chloride ion on active sites on the resin surface. This resin has demonstrated the ability to remove the low molecular weight fraction of TOC that cannot be removed by coagulation; therefore allowing lower treated water TOC levels to be achieved.

Many downstream operational benefits are realized once organic matter is removed prior to coagulation such as:

- Reduced chemical doses to achieve turbidity removal, therefore less sludge production, and less pH adjusting chemicals.
- More stable, faster settling floc.
- Ability to continue using free chlorine for disinfection, while producing less DBPs.

This presentation will discuss the applicability of MIEX<sup>®</sup> pre-treatment for achieving DBP compliance without changing downstream processes. The results of testing on several waters in and around South Carolina are discussed.

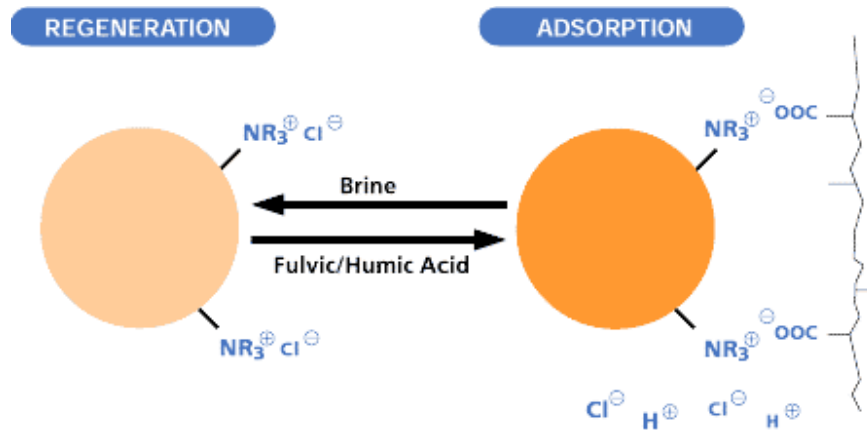
## Background

Within and around South Carolina many drinking water suppliers have managed to comply with the Stage 1 Disinfection By Product Rule (DBPR) by optimizing plant and distribution system performance at little cost. However, many water suppliers in the area have a growing concern as the Stage 2 Initial Distribution System Evaluation, or IDSE, monitoring schedule approaches, since their system will not comply with the locational running annual averages at high risk sites. For many organizations this means evaluating capital improvements for systemwide compliance.

A non-chemical treatment process was developed in response to the need to remove greater amounts of total organic carbon (TOC) from water supplies to prevent problems associated with DBPs. Based on the principle of ion exchange, the MIEX<sup>®</sup> System is a pre-treatment process specifically targeted at removal of dissolved organic carbon (DOC) compounds such as humic and fulvic acids from drinking water supplies. Negatively charged DOC ions are removed from water by exchanging with a chloride ion on active sites on the resin surface.

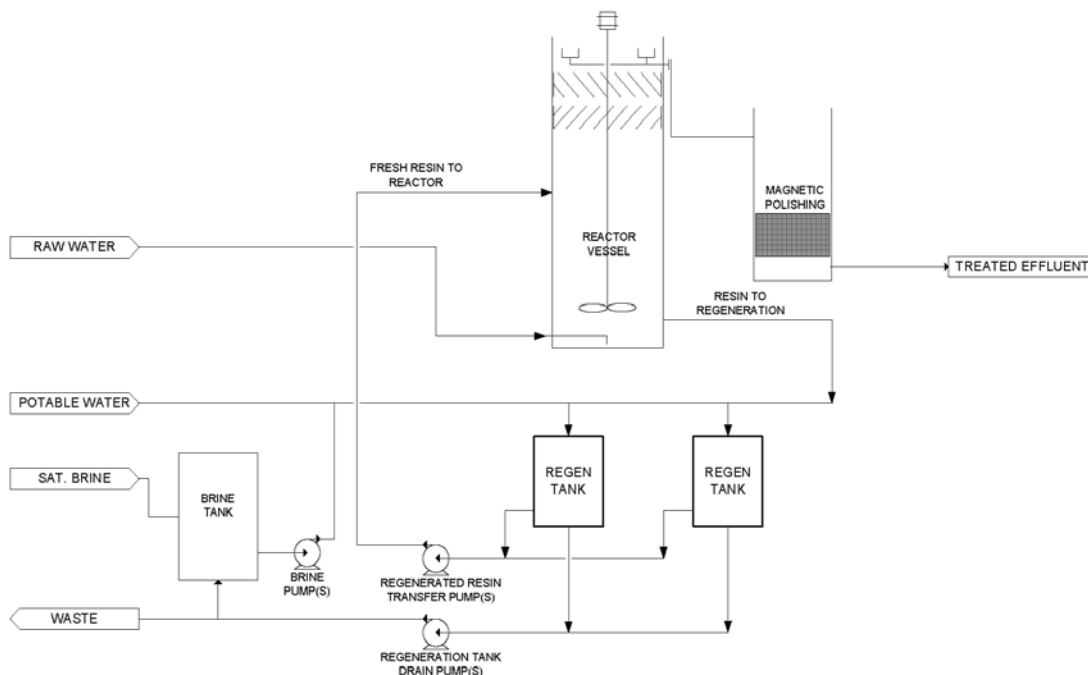
This resin has demonstrated the ability to remove a wide spectrum of polar DOC compounds across a wide range of molecular weight fractions, including the lower molecular weight fractions of DOC that cannot be removed by coagulation. By removing more of the naturally occurring organic matter, which can have a significant negative charge, ahead of coagulation reduces the source water's coagulant demand, while achieving lower treated water TOC levels.

The MIEX<sup>®</sup> DOC Resin is utilized in a continuous, dispersed bed ion exchange process rather than in a fixed bed. The 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. The resin beads are much smaller than conventional ion exchange beads, at around 180  $\mu\text{m}$  (80 mesh), to allow rapid DOC exchange in the contactor vessel. This combination of the uniformly mixed contactor and the small MIEX<sup>®</sup> DOC resin beads provides very efficient ion exchange, and allows relatively low resin concentrations to achieve excellent DOC removal. Figure 1 is an illustration of the DOC ion exchange process on the resin bead, using complex organic acids as the DOC structure.



**Figure 1: Resin Exchange Chemistry**

The MIEX<sup>®</sup> DOC Resin is not affected by suspended solids (i.e., turbidity); hence this process can be used as the first treatment stage in a water treatment plant (see Figure 2). DOC removal at the head of the plant provides significant benefits for downstream processes. It is recommended that this process be used as the first stage of a combined treatment process. This arrangement will likely result in a decreased coagulant dose to achieve the targeted water quality and, therefore, produce less chemical sludge.



**Figure 2: High Rate MIEX<sup>®</sup> Process Flow Diagram**

The process for DOC removal in a full-scale water treatment plant includes diversion of a percentage of the raw water influent (determined by treatment level), contacting resin with the water, resin separation and recycle, and resin regeneration.

A newer high-rate process differs from the traditional configuration of a mixed contactor followed by a gravity settler and recycle. The high-rate (HR) contactor provides 3-5 minutes detention time, during which the DOC is exchanged onto the resin. The suspended resin concentration in the HR contactor is typically around 200 mL/L (20% v/v). Magnetic attraction of individual resin beads is limited to very short separation distances; consequently, low energy inputs are required for maintaining the resin in suspension. The HR contactors may be sized such that the upward velocity of the water is enough to maintain full dispersal of the resin. At lower flow rates an agitator keeps the resin suspended, and helps to distribute the influent raw water evenly at the base of the contactor.

The magnetic attraction of the resin particles to one another, and the use of settling tubes at the top of the contactor vessel, allows the resin to be contained. A small volume of resin (typically 1 – 2 gal resin per MG treated) is carried out with the effluent. This volume consists mostly of smaller resin particles that have broken down due to mechanical attrition in the process.

For systems that may have multiple HR contactor vessels, a portion of the resin is conveyed to a transfer tank. The transfer tank is used to accumulate loaded resin for filling the resin regeneration vessels. For single HR contactor systems, loaded resin may be transferred directly to the regeneration vessels. A portion of the HR contactor resin volume is regenerated semi-continuously. The regenerant used is ~120 g/L NaCl or KCl solution. Upon completion of regeneration, fresh (regenerated) resin is transferred back to the contactor vessel for service. Waste from regeneration is typically in the range 200-300 gal/MG of treated water (for 1.0 gal/1,000 gal regeneration volume).

The MIEX<sup>®</sup> Process has been the object of many studies across the world, including a 2003 AWWARF project. Until lately it was only thought of as a large system process (e.g., >1 MGD), but new design materials and smaller packaging has proven the MagnaPak<sup>™</sup> HR system to be an affordable solution for many small rural water systems in the south.

In August 2004, small scale testing was completed at six South Carolina water treatment plants: North Augusta, Camden, Grand Strand, Santee Cooper, Georgetown, and Orangeburg. Georgetown raw water was also sent to an independent laboratory in November 2004 for comprehensive testing. In addition, the City of Louisburg completed a comprehensive MIEX<sup>®</sup> pilot in September 2003. The objectives of these tests were to pre-treat water with MIEX<sup>®</sup> resin to reduce TOC levels, thereby lowering the potential to form DBPs in the finished water. In turn, reductions in downstream chemical demand and formation of sludge were realized.

## **METHODOLOGY**

### **MIEX<sup>®</sup> Resin Tests**

MIEX<sup>®</sup> resin tests were performed by adding 15 mL/L of MIEX<sup>®</sup> resin to a 2-liter raw water sample and agitating at 140 rpm in a jar testing apparatus. One 2-liter jar with raw water was mixed for a control. Samples were withdrawn from the jars after 20 minutes. The samples were run through a 0.45-micron pore size filter then measured for either true color, ultraviolet absorbance at a wavelength of 254 nm (UVA), or DOC, depending on the laboratory equipment available at each site. True color and UVA were typically measured using a HACH DR4000U

Spectrophotometer. One liter of the raw water control and one liter of MIEX<sup>®</sup> Resin treated water were then each placed in a clean 2-liter jar for coagulation testing.

### **MIEX<sup>®</sup> Resin Pre-treatment Followed by Coagulation**

The raw water sample was dosed with the determined coagulant dose, simulating current plant treatment conditions as a control. The MIEX<sup>®</sup> pre-treated water was dosed with roughly one third of the current plant coagulant regimen. This method was chosen to better demonstrate the effect of MIEX<sup>®</sup> pre-treatment on downstream coagulant demand. A standard jar test procedure was typically used. At some locations, the jar testing procedure normally used at that particular plant was followed instead of the standard procedure, all of which included rapid mix, flocculation mix, and settling stages. After the jar test was performed, samples were then passed through a 0.45 µm filter and analyzed.

### **Laboratory Comprehensive MIEX<sup>®</sup> Resin Jar Testing**

The Cities of Bennetsville and Georgetown each sent 10 gallons of raw water to the WesTech Engineering Laboratory for a full range of MIEX<sup>®</sup> Resin tests. The first test was conducted using MIEX<sup>®</sup> Resin over a range of resin concentrations on the raw water sample. The second jar test was a coagulant control test. The jar test procedure currently being used at the Georgetown treatment facility was used in the coagulant control testing. These procedures were designed to simulate the organic removal observed at the plant. The final test was a combined treatment jar test. The water was first treated using the resin dose and mix time selected from Test #1. The MIEX<sup>®</sup> Resin treated water was then treated with selected aluminum sulfate and ferric chloride dosages to determine the lowest dosage that produced the greatest turbidity, UVA, and color reduction.

### **Pilot Plant Operation**

The MIEX<sup>®</sup> Process pilot plant was configured as shown in Fig. 1. Raw water was introduced to the Mixing Tanks at a measured flow rate. Since the volume of the Mixing Tanks was known, an average contact time was calculated. The Mixing Tanks contained a specified concentration of MIEX<sup>®</sup> resin previously determined in bench scale tests to be effective for the given water source. Mechanical mixers were used to suspend the MIEX<sup>®</sup> resin, and assure adequate contact between the resin and the raw water.

The slurry from the Mixing Tanks was distributed to the Resin Separation Tank where the MIEX<sup>®</sup> Resin quickly agglomerated and settled to the bottom of the vessel. The treated water flowed to a collection launder at the top of this tank, and was then available for testing. Using an underflow pump, the settled MIEX<sup>®</sup> resin was returned to the Mixing Tanks at a fixed rate to maintain the MIEX<sup>®</sup> resin concentration.

A small percentage of the underflow from the Resin Separation Tank was diverted to the Resin Regeneration Tank. An equivalent amount of fresh (regenerated) MIEX<sup>®</sup> resin was also added to the recirculation line to maintain the concentration of MIEX<sup>®</sup> resin in the Mixing Tanks. The percentage of withdrawn spent resin and reintroduced fresh resin is known as the *regeneration rate*. For example, if 5% of the underflow was sent to the regeneration tank and 95% of the underflow was recycled to the front of the process, the system was running with a 5% regeneration rate. Once there was a sufficient volume of MIEX<sup>®</sup> resin in the regeneration tank, the resin was regenerated using a 12% brine solution (120g/L NaCl). When the resin batch was regenerated, it was transferred to the Fresh Resin Feed tank to be reintroduced to the Mixing Tanks. A certain amount of brine containing concentrated organics is wasted periodically.

## **Pilot Plant Sampling and Analyses**

Once the system was operating under steady-state conditions, testing of the treated water commenced. Samples were collected from the following sources: Raw Water, MIEX<sup>®</sup> Resin treated water, Raw Water treated with the existing plant treatment regimen, MIEX<sup>®</sup> Resin treated water followed by treatment with the selected, reduced coagulant dose. The samples were analyzed for the following contaminants using the 20th Edition of *Standard Methods for Examination of Water and Wastewater* as a guide for all testing: TOC, DOC, true color, ultraviolet absorbance at a wavelength of 254 nm (UVA), DBPs.

The coagulant demand of water treated by the MIEX<sup>®</sup> Process was determined by measuring UVA on jar test samples with various levels of coagulant, and then selecting jar that the provided the largest benefit to water quality at the minimum dose (i.e., point of diminishing returns).

## **RESULTS**

### **North Augusta, SC**

These results show that MIEX<sup>®</sup> resin alone achieved a 75% reduction in UVA after 20 minutes of contact time, lowering the raw water UVA from 0.032 to 0.008. The plant control of 30 mg/L aluminum sulfate achieved a 28% reduction down to 0.023, and MIEX<sup>®</sup> resin followed by coagulation with 10 mg/L aluminum sulfate showed an 84% reduction down to 0.005.

The true color was reduced to 0 Pt-Co by MIEX<sup>®</sup> Treatment and by the coagulant control. The DOC was measured in the raw water and in the water treated with MIEX<sup>®</sup> resin followed by a reduced coagulant dose, the latter decreasing the DOC from 1.7 mg/L to 0.824 mg/L.

### **Camden, SC**

In Camden raw water MIEX<sup>®</sup> resin alone achieved an 83% reduction in UVA Absorbance after 20 minutes of contact time, lowering the raw water UVA from 0.127 to 0.022. The plant control of 30 mg/L aluminum sulfate achieved a 59% reduction down to 0.052, and MIEX<sup>®</sup> resin followed by coagulation with 10 mg/L aluminum sulfate showed a 90% reduction to 0.013. MIEX<sup>®</sup> Treatment followed by a reduced coagulant dose lowered the true color 95%, while the plant control reduced the true color 89%.

### **Grand Strand, SC**

Here MIEX<sup>®</sup> resin alone achieved an 80% reduction in UVA Absorbance after 20 minutes of contact time, lowering the raw water UVA from 0.799 to 0.099. The plant control of 140 mg/L aluminum sulfate achieved an 86% reduction to 0.088, and MIEX<sup>®</sup> resin followed by coagulation with 30 mg/L aluminum sulfate showed a 96% reduction to 0.017. Table 2 shows the DOC and color removal.

<b>Sample</b>	<b>DOC (mg/L)</b>
Raw Water	14
MIEX <sup>®</sup> resin alone	3.4
Plant Control	4.9
MIEX <sup>®</sup> resin + coagulant	1.9

### **Santee Cooper, SC**

These results show that MIEX<sup>®</sup> resin alone achieved an 87% reduction in UVA after 20 minutes of contact time, lowering the UVA to 0.027. The plant control of 21 mg/L aluminum sulfate and 0.5 mg/L polymer achieved a 60% reduction in UVA to 0.083, and MIEX<sup>®</sup> resin followed by coagulation with 5 mg/L aluminum sulfate showed an 88% reduction to 0.025.

### **Orangeburg, SC**

In North Edisto River water, MIEX<sup>®</sup> resin alone achieved a 70% reduction in UVA after 20 minutes of contact time, lowering the raw water UVA from 1.182 to 0.347. The plant control of 75 mg/L aluminum sulfate achieved an 82% reduction to 0.208, and MIEX<sup>®</sup> resin followed by coagulation with 30 mg/L aluminum sulfate showed a 99% reduction to 0.010. The true color was reduced to 1 color units (Pt-Co) by combined MIEX<sup>®</sup> treatment, while the plant control reduced the true color to 3 Pt-Co. The raw water true color was 109 color units.

### **Bennetsville, SC**

A MIEX<sup>®</sup> fresh resin dose of 20 mL/L and 10-minute batch mix time was selected. These operating conditions in full-scale application should reduce the UVA to 0.079, compared to 0.437 in the raw water - an 82% reduction. Additional mixing time did not significantly lower the UVA.

Testing aluminum sulfate demonstrated that, using alum as a coagulant at the plant dosage of 80 mg/L, would reduce the UVA from 0.437 to 0.085, a reduction of 80%. Bennetsville applies NaOH for pH adjustment.

The MIEX<sup>®</sup> resin pre-treated water was coagulated, with alum, at six dosages to determine the minimum amount necessary after MIEX<sup>®</sup> resin pre-treatment to achieve the lowest Turbidity, UVA, and True Color values. The alum dose selected was 5 mg/L, which achieved a reduced UVA to an undetectable level and required no application of NaOH. The combined treatment reduced the true color to 0 units (Pt-Co).

Samples of the raw water, plant control, MIEX<sup>®</sup> Resin treated, and the MIEX<sup>®</sup> /Coag were sent to the Georgetown WTP laboratory for DOC analysis. Current plant treatment reduced the DOC by 51%, while combined MIEX<sup>®</sup> Resin treatment reduced the DOC by 80% using 88% less coagulant.

### **Georgetown, SC**

A MIEX<sup>®</sup> fresh resin dose of 2 mL/L and 90-minute batch mix time was selected. This corresponds to a contactor concentration of 20 mL/L with a contact time of 27 minutes with a 10% regeneration rate in full-scale operation. These operating conditions should reduce the UVA to 0.163, compared to 0.413 in the raw water - a 61% reduction. Additional mixing time did not significantly lower the UVA.

Testing aluminum sulfate demonstrated that, using the alum as a coagulant at the plant dosage of 80 mg/L, would reduce the UVA from 0.413 to 0.091, a reduction of 78%. Ferric chloride at a dosage of 80 mg/L reduced the UVA from 0.413 to 0.077. Georgetown also requires the application of NaOH for pH adjustment.

The MIEX<sup>®</sup> resin pre-treated water was coagulated, with alum, at six dosages to determine the minimum amount necessary after MIEX<sup>®</sup> resin pre-treatment to achieve the lowest turbidity,

UVA, and true color values. The same was completed with ferric chloride. The alum dose selected was 10mg/L, which achieved a reduced UVA of 0.014 and required no application of NaOH. The ferric dose selected was 10mg/L, which achieved a reduced UVA of 0.015 and required no application of NaOH. Both coagulants reduced the true color to 0 units (Pt-Co).

Samples of the raw water, plant control, MIEX<sup>®</sup> resin-treated, and the MIEX<sup>®</sup>/Coag were sent to the Georgetown WTP laboratory for DOC analysis. Current plant treatment reduced the DOC by 57%, while combined MIEX<sup>®</sup> Resin treatment reduced the DOC by 83% using 94% less coagulant.

### Louisburg, NC

A trial of the MIEX<sup>®</sup> Process was conducted at the Louisburg Water Treatment Plant, where the results indicated an average DOC reduction from 13.1 mg/l in the raw water to 4.5 mg/l in water pre-treated by MIEX<sup>®</sup> resin followed by coagulation. This compares to DOC levels in the finished water from the current treatment plant of approximately 6.1 mg/l. By removing DOC from raw water, the coagulant demand was reduced on average from 101 mg/l to 41 mg/l PACl.

The Louisburg water plant had already established a correlation between DOC and DBPs. Due to the availability of this correlation and the resources required for DBP testing, the simpler surrogate tests of UVA and DOC were used to assess the performance of the MIEX<sup>®</sup> system. Additionally, Trihalomethane Formation Potential (THMFP) and Haloacetic Acid Formation Potential (HAAFP) analyses were performed in accordance with EPA methods 524.2 and 552.2. These results from the THMFP and HAAFP analyses showed that water pre-treated with MIEX<sup>®</sup> resin can lower TTHM and HAA5 levels in treated water by approximately 60% and 70%, respectively, over current treatment practices.

### DISCUSSION

The primary goal of the pilot plant study was to demonstrate that the MIEX<sup>®</sup> Process could achieve 50% or greater removal of organic carbon DBP pre-cursors. The results show that pre-treating water by the MIEX<sup>®</sup> Process provided a large margin of safety in meeting EPA standards. Although the average UVA organics removal by coagulation alone was 66%, this provides only a small safety margin for meeting the standards. The average removal using MIEX<sup>®</sup> pre-treatment was 91%. Table 3 shows the average organics removal for each location with and without MIEX<sup>®</sup> resin pre-treatment.

<b>Table 3: UVA Reduction</b>		
<b>Location</b>	<b>Reduction With MIEX<sup>®</sup> Resin Pre-Treatment</b>	<b>Reduction With Current Treatment Regimen</b>
North Augusta, SC	84%	24%
Camden, SC	90%	59%
Grand Strand, SC	96%	86%
Orangeburg, SC	99%	82%
Santee Cooper, SC	88%	60%
Bennetsville, SC	>99%	80%
Georgetown, SC	96%	81%
Louisburg, NC	73%	54%

*\*Louisburg percentages based on DOC Removal instead of UVA.*

The data also suggests that MIEX<sup>®</sup> Process pre-treatment can reduce coagulant demand by more than 50%. Table 4 shows the coagulant dosage used with and without MIEX<sup>®</sup> resin pre-treatment which should be associated with the reductions above in Table 3.

<b>Table 4: Coagulant Dosage</b>			
<b>Location</b>	<b>Dosage With Current Treatment Regimen</b>	<b>Dosage With MIEX<sup>®</sup> Resin Pre-Treatment</b>	<b>Percent Reduction</b>
North Augusta, SC	30 mg/L alum	10 mg/L alum	67%
Camden, SC	30 mg/L alum	10 mg/L alum	67%
Grand Strand, SC	140 mg/L alum	30 mg/L alum	79%
Orangeburg, SC	75 mg/L alum	30 mg/L alum	60%
Santee Cooper, SC	21 mg/L alum	5 mg/L alum	76%
Bennetsville, SC	80 mg/L alum	5 mg/L alum	94%
Georgetown, SC	80 mg/L ferric	10 mg/L ferric	88%
Louisburg, NC	101 mg/L PACl	41 mg/L PACl	59%

It should also be noted that pH correction employed by many facilities such as Georgetown, SC was not needed with the reduced coagulant dose.

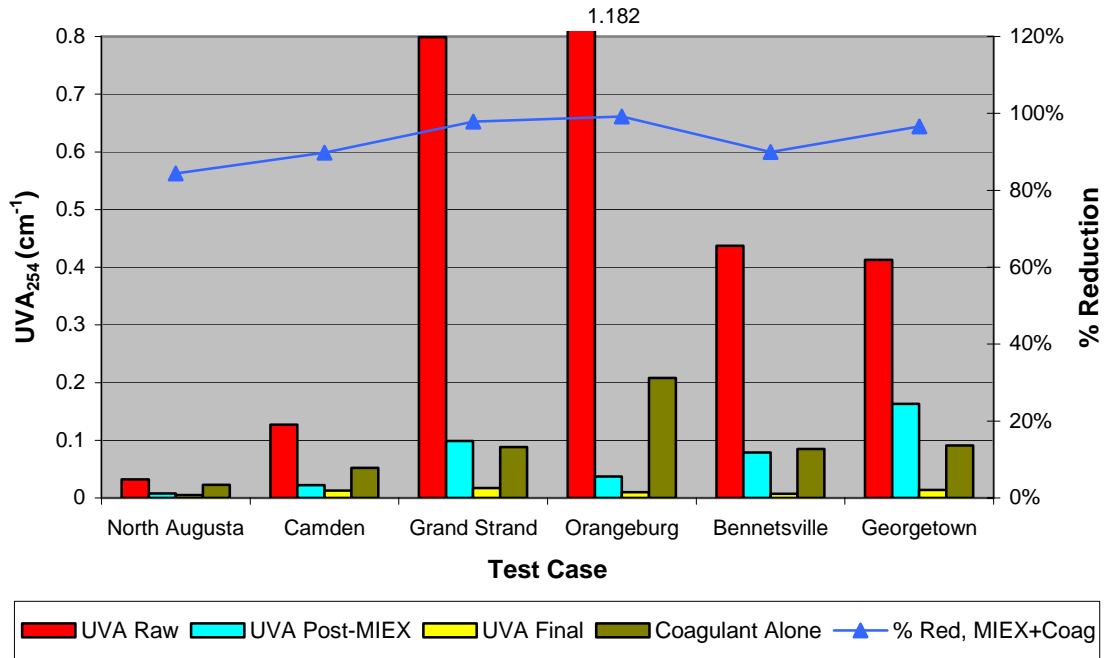
## **CONCLUSIONS**

These documented results show that MIEX<sup>®</sup> treatment combined with conventional coagulation was successful in reducing UVA by 73% to >99%. The coagulant demand was reduced by 59% to 88%. All of the results indicate that MIEX<sup>®</sup> Treatment is a viable option for improving TOC removal and therefore lowering DBP levels, while reducing overall chemical usage.

## **ACKNOWLEDGEMENTS**

We wish to thank North Augusta, Camden, Grand Strand, Orangeburg, Santee Cooper, Bennetsville, and Georgetown in South Carolina, and the City of Louisburg, North Carolina for their assistance in coordinating and executing these projects. We also wish to thank the staff of WesTech Engineering, Orica Watercare, and Interstate Utilities for providing the test equipment and resources necessary to complete this work.

### UVA<sub>254</sub> Reduction with MIEX<sup>(R)</sup>



### Coagulant Dose Reduction

