PerQuat® Technology: Enhanced Biocide and Biofilm Removal Agent for Cooling Water

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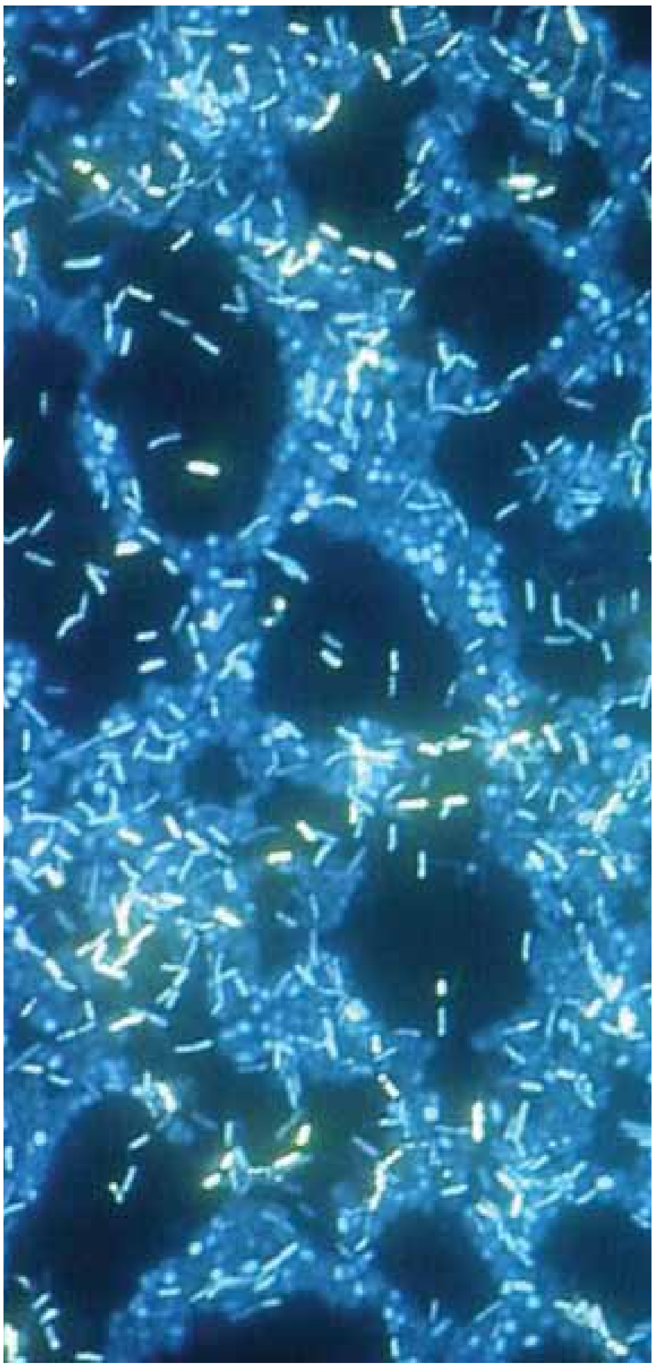


Abstract

PerQuat® technology consists of a proprietary hybrid biocide formulation characterized by the intimate ion pairing of the hydroperoxide anion (OOH^-) with a cationic phase transfer catalyst (HPI-PTC). The hydroperoxide/phase transfer technology can be classified as a hybrid biocide with oxidizing, non-oxidizing and dispersant mechanisms. Therefore, it has been hypothesized that it has the capability to eliminate the need for supplemental non-oxidizers and dispersants in many systems that use several biocides and dispersants on a rotation to prevent biofilm formation and control microbial growth.

The ability to use a single biocide to prevent and remove biofilm, provide broad-spectrum antimicrobial efficacy, and act as a highly effective algaecide offers both chemical and labor savings to water treaters. Another benefit of the HPI-PTC technology is that it provides the convenience of a "best practice" cleanup biocide on-site and is readily available in the event of an unexpected contamination in the system.

This article evaluates the use of the hybrid biocide in industrial cooling towers as a direct replacement for non-oxidizing biocide/dispersant programs at several end-use customer sites. The performance of the technology as compared to conventional non-oxidizing/dispersant programs was assessed at a range of recommended dosages and use frequencies using various forms of microbiological monitoring.

The case studies demonstrate that HPI-PTC technology can be used as a direct replacement for non-oxidizing biocides and dispersants in a wide variety of cooling tower applications and loading with enhanced efficacy at comparable economics.

Introduction

Background

Biocides are commonly added to cooling towers in an effort to control biological growth, fouling and slime, which can impede water flow and reduce heat transfer efficiency. In general, biocides are typically grouped into two categories based upon their primary mechanism of action: oxidizing biocides such as chlorine, bromine, chlorine dioxide, and other halogen releasers, and non-oxidizing biocides such as glutaraldehyde, isothiazolones, tetrakishydroxymethylphosphonium sulfate (THPS), and 2,2-dibromo-3-nitrilopropionamide (DBNPA).

Oxidizing biocides are often dosed on a low-level continuous basis with a primary goal of controlling bulk water microbiological counts. However, low-level dosages of oxidizing biocides are typically unable to control slime and sessile bacteria. While some water treaters have attempted to combat this limitation by introducing high levels of halogens, this can often result in incompatibilities with copper surfaces and organic treatment components with limited efficacy against sessile organism populations. To prevent this situation, water treaters have looked to use biocide combinations so that biological populations cannot adapt to resist one biocide mechanism of action. Increasingly, however, the presence of bacterial biofilm, the natural habitat for all microorganisms, has forced water treaters to re-evaluate how best to control biological growth, fouling and slime.

Continuous use of non-oxidizing biocides has been avoided in water treatment, partly due to the expense and environmental factors such as discharge limitations, but also due to the risk of selecting for organisms that are resistant to one particular biocide. Thus, dual alternating slug-fed biocide programs have become more common over the past decade.

Biofilm

Biofilms are communities of organisms that contain either bacteria or other higher organisms, "such as algae, that are held together by sticky extracellular (polymeric) matrix"[1] and are irreversibly associated with a surface.[2] The vast majority of a biofilm consists of extracellular polymeric substances (EPS). This negatively-charged polysaccharide-based structure protects biofilm bacteria from outside influences such as temperature, UV exposure, metal toxicity, acid exposure, dehydration and salinity, phagocytosis, antibiotics, and antimicrobial agents.[3] In fact, several studies have shown that the protective nature of the biofilm structure makes the bacteria embedded within them remarkably difficult to treat with antimicrobials; organisms living within biofilms are resistant to doses of antimicrobials 100- to 1000-fold over the minimum lethal dose for microbes outside of biofilms.[4] In addition to challenges associated with killing biofilm bacteria, the biofilm structure itself often appears as a macroscopic "slime" within cooling towers reducing heat transfer, clogging piping, and contributing to an overall unappealing appearance inside the tower and in the tower fill.

In the United States, under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) of 1947, biocides have been classified as pesticides and are regulated by the US EPA. While many technologies available today market themselves as "biofilm removal" or "biofilm prevention" agents, it is essential to ensure that the product used for this purpose be EPA registered and maintain a specific EPA registered claim for biofilm removal in water systems. According to the EPA in a letter published in 2004, "Biofilm is considered to be a pest by the Agency. Therefore, any claim to prevent, destroy, repel or mitigate biofilm is a pesticide claim which requires registration under FIFRA." The use of a biocide or other chemical agent without an EPA registered biofilm claim with the intent to remove or prevent biofilm is a violation of FIFRA. PerQuat® hydroperoxide ion-phase transfer catalyst technology (HPI-PTC) has biofilm efficacy data on file with the EPA and has been approved by the EPA to "penetrate and remove biofilm" in cooling towers.

PerQuat® Chemistry as Broad Spectrum Cooling Water Biocide and Biofilm Control Agent

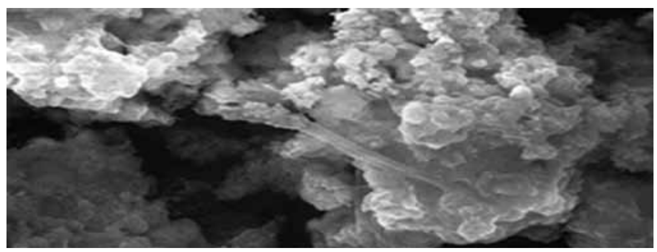
Background

PerQuat® hydroperoxide anion (OOH^-) phase transfer catalyst (HPI-PTC) chemistry is a patented hybrid biocide and biofilm removal agent characterized by a neutral ion pairing between the hydroperoxide anion (OOH^-) and a cationic phase transfer agent—most commonly an ADBAC quat. In an alkaline environment, hydrogen peroxide transforms into the hydroperoxide anion—a powerful negatively charged hydrolytic agent. Alone, however, this negatively charged anion is unable to penetrate biofilm, as it is insoluble in lipids and is repelled by the negative charge on the surface of the biofilm EPS. PerQuat® technology introduces a positively charged phase transfer catalyst that "grabs" hydroperoxide anions, transfers them into the biofilm, and enables them to lyse the biofilm and break down lipid-based soils. Once inside the biofilm, the anion of hydroperoxide reacts with acetyl esters to form peroxy-acids, which produces "strong hydroxyl radicals" that are very reactive and decompose cell material efficiently.[5] With broad efficacy against sessile organisms, the technology has the unique ability to dissolve the biofilm EPS matrix and physically clean the surface while simultaneously eliminating biofilm bacteria.

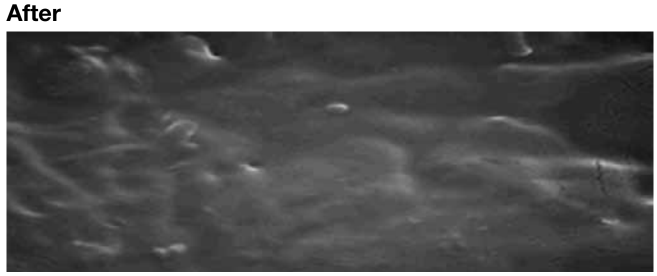
Figure 1 below illustrates a mature biofilm in a waterline treated with PerQuat® chemistry. Following the recommended treatment protocol, Figure 1 shows the before and after of the interior of the waterline free of biofilm deposits and organics.

Figure 1: Scanning electron micrograph before and after the use of PerQuat® chemistry in a waterline in the presence of biofilm

Before



After



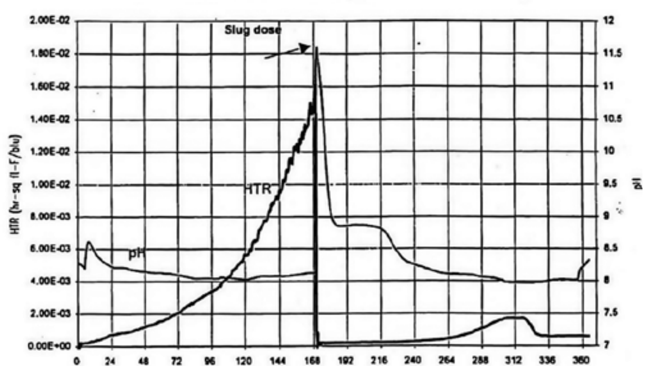
Remediation

Due to its biofilm removal capabilities, PerQuat® chemistry was at first utilized primarily as a remediation biocide and closed loop cleaner to eliminate slime and increase heat transfer efficiency in fouled systems. Slug doses of PerQuat® at shock concentrations are associated with rapid knock-down of bulk water counts, slime-forming and sulfate-reducing bacteria, as well as a quick spike in bulk water ATP followed by a reduction in ATP to negligible levels after several hours.

Figure 2 below measures heat transfer resistance across a heat exchanger in an experimental cooling tower rig as a function of time. After 168 hours into the operation of the tower, heat transfer resistance across the heat exchanger (measured as hr-ft^2 °F/BTU) reaches a peak level of 1.8 x 10^{-2}. A slug dose of PerQuat® chemistry at the 168-hour mark rapidly drops heat transfer resistance measurements to nearly undetectable levels, indicating removal of biofouling and the biofilm EPS matrix.

Figure 3 provides a photograph of a pipe used in transporting process supply and once through cooling water for a drywall manufacturing facility. The transfer piping shows the severity of the biofilm in the system that was leading to plugged feed lines and loss of heat transfer. A recirculation loop was established, and a 500 mg/L shock slug dose of PerQuat® chemistry (30 mg/L active) was used to remediate the biofilm deposits and restore heat transfer. The material in the bucket was biofilm removed during the remediation process that had accumulated in a 50 micron filter bag.

Figure 2: Rapid Reduction of Heat Transfer Resistance Following Slug Dose of PerQuat® Chemistry[7]



Dual-Action Non-Oxidizing Biocide and Biofilm Removal Agent

In addition to its remediation capabilities, it has been demonstrated that PerQuat® HPI-PTC technology would be a differentiated one-step, cost-effective replacement for conventional non-oxidizing biocide and biodispersant programs in cooling water systems. Formulated with an anti-foam agent, PerQuat® chemistry provides broad-spectrum bulk water kill, while providing sessile efficacy and biofilm removal in one technology. The use of this chemistry minimizes the amount of oxidizers needed to control bulk-water counts and prevent fouling, reducing the impact on carbon steel and copper corrosion and lowering the overall cost of the biocide program. In addition, PerQuat® chemistry, where quaternary phase transfer agents are paired with anionic perhydroxide compounds, has shown substantially increased compatibility with anionic scale inhibitors as compared to cationic-based biocidal technologies such as quaternary ammonium compounds alone.

Field studies were conducted to determine if PerQuat® chemistry could replace existing non-oxidizer programs and provide enhanced performance at economic equivalency. The field studies were conducted on HVAC towers at three locations over a several month time period.

Field Study #1

Background

A corporate center central utility plant HVAC system operates 365 days per year and uses partial reclaim water (excess RO permeate and air handler condensate) combined with city water as cooling tower makeup. The tower operates at an alkaline pH range of 9.0 - 9.3, and has a total system volume of 20,000 gallons.

Figure 3: Closed Loop Cleaning of Drywall Plant Process Water with PerQuat® Chemistry

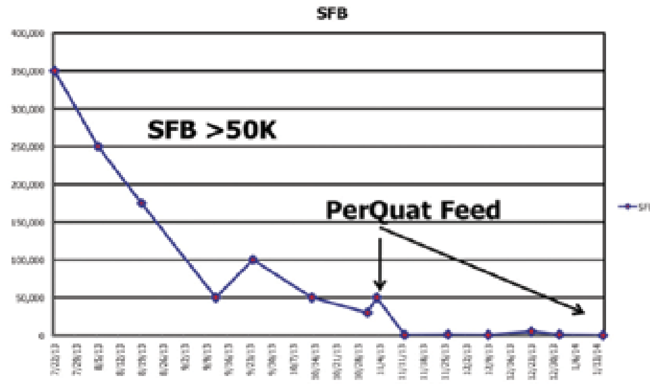
The microbial control program historically utilized BCDMH for the oxidizing biocide, which was slug fed on a daily basis. The BCDMH was supplemented with once-per-week slugs of isothiazoline. High bulk water, SFB, and SRB counts, the presence of thick foam on the tower sump, and the high system pH led to a change in biocides. The BCDMH was replaced with DBDMH, which was fed continuously to a target of 0.1 – 0.3 mg/L of free halogen utilizing ORP control. The weekly isothiazoline dosage was replaced with a 30 mg/L active dose (150 mg/L product) of THPS/surfactant combination. The result of the change in biocide programs was an improvement in bulk water counts, but not in the Slime Forming Bacteria (SFB) and Sulfate Reducing Bacteria (SRB) counts, nor in addressing the foam. (See Figure 4 for an example of the foam.)

Figure 4: Foamy sump at Field Study #1

While bulk water counts were acceptable at ≤ 10^4 CFU/mL, the SFB and SRB counts remained high. Figure 5 shows that the SFB counts remained above 50,000 CFU/ml. These high counts, along with the green foam visible on the sump, raised serious questions about the system's cleanliness.

PerQuat® Trial Usage

Figure 5: Slime-Forming Bacteria Counts for Field Trial #1



Beginning November 2, 2009, 150 mg/L of PerQuat® chemistry (9 mg/L active) directly replaced the once-per-week feed of 150 mg/L of the THPS product. There were no changes to the DBDMH feed, and the trial continued for two months. Immediately after the first feed on November 2, 2009, ATP counts in the bulk water temporarily jumped—an indication that biofilm and other organics are being lifted from the tower. During the course of the PerQuat® trial, bulk water counts remained in check ranging from 500 to 20,000 CFU/ml, and the SFB and SRB counts were dramatically reduced, with SFB counts mostly eliminated. The thick, green foam in the sump subsided after the first feed and did not reappear during the entire duration of the trial.

Results

The use of PerQuat® in lieu of THPS as the non-oxidizing biocide supplement to a continuous, low level feed of DBDMH resulted in a drastic reduction of SFB and SRB counts while maintaining low bulk water counts. Visual inspections demonstrated the elimination of green foam during the trial and a cleaner system as a whole. A 150 mg/L PerQuat® compared favorably on an economic basis to 120 mg/L THPS and provided enhanced performance. If a process in-leakage occurs or contaminant ever enters the system, the PerQuat® chemistry can be used to rapidly bring the system back under control. Table 1 shows the microbial data before, during and after the trial.

Field Study #2

Background

An injection mold facility has an internal HVAC tower that operates 365 days per year, with a system volume of 8,000 gallons, a hydraulic retention time of greater than six days, and operates at six cycles of concentration. The tower had an internal sump that all water drained, which contributed to the high retention time.

The microbial control program included daily slug doses (6X per week) of stabilized bromine as an oxidizing biocide to a control range of 0.8 – 1.2 mg/L free halogen. This was originally supplemented once per week with 90 mg/L of 45% glutaraldehyde (40 mg/L active). All microbial monitoring counts were above acceptable levels. To improve control, the glutaraldehyde was replaced with a THPS/surfactant product fed at 150 mg/L, or 30 mg/L active THPS. Bulk water counts in the tower had been inconsistent and averaged > 10^4 CFU/mL, SFB and SRB counts historically had been very high and visual inspections of the tower sump always revealed a thick green layer of foam on the surface, (see Figure 6 for an example) again suggesting an issue with biofilm in the tower.

Figure 6: Foamy Internal Sump Before Trial at Field Study #2 Tower

Table 1: Field Trial #1 Microbial Data Before/During/After Trial

Date	Treatment: Oxidizer	Treatment: Non-oxidizer Name/Dosage	Tester	Dip Slide: Aerobic (CFU/mL)	Dip Slide: Fungus (CFU/mL)	SRB (CFU/mL)	SFB (CFU/mL)	Foam (0-10)	ATP: Total RLU	ATP: Free RLU	ATP: MB RLU
3/6/09	DBDMH	THPS/150 ppm	Service Rep	1,000	0		66,500	5	76	2	74
4/28/09			Service Rep	500	0			5			
7/17/09			Service Rep	500	100	18,000		8			
7/21/09			Service Rep	500	0		350,000	8			
9/11/09			Service Rep	500	10,000		50,000	8			
9/23/09			Service Rep	500	5,000		100,000	10			
10/12/10	Cleaned Sump 10-08		Service Rep	500	100		50,000				
10/30/09			Service Rep	500	1,000		30,000	8	142	140	2
11/2/09	Pre-Feed		Service Rep	10,000	100	600	50,000	8	235	232	3
11/2/09	After 51 min feed	PerQuat/150 ppm	Service Rep						269	220	49
11/2/09	2 hours after feed		Service Rep						284	219	65
11/2/09	3.5 hrs after feed		Service Rep						335	305	30
11/6/09	6 Days Later - Pre 2nd		Service Rep					0	105	104	1
11/11/09		PerQuat/105 ppm	Service Rep	10,000	0	0	500	0	229	185	44
11/25/09		PerQuat/105 ppm	Service Rep	5,000	5,000	0	1,000	0	105	76	29
12/8/10		PerQuat/105 ppm	Service Rep	20,000	0	0	500	0	102	91	11
12/22/09		PerQuat/105 ppm	Service Rep	20,000	0	100	5,000	2			
12/31/09		PerQuat/150 ppm	Service Rep	10,000	0	0	1,000	2			
1/14/10	Last feed: 01-12-2010		Service Rep	10,000	0	0	0	0	180	148	32
1/19/10	1st re-feed	THPS/150 ppm	Service Rep								
1/27/10		THPS/150 ppm	Service Rep	20,000	0		66,500				

To address the high bulk water and sessile counts, the 6X per week slug dose of stabilized bromine was replaced with a continuous feed of DBDMH controlled to 0.1 – 0.3 mg/L of free halogen using ORP. THPS was still utilized as the supplemental biocide. This change resulted in improved bulk water counts to acceptable levels, but did not result in the desired reduction in sessile counts nor in the elimination of the foam. In late October and early November of 2009, remediation steps were initially taken with glutaraldehyde at 112 mg/L active dosage with little impact on SFB counts and foam reduction. That was followed the next week on November 6, 2009 by a 250 mg/L dosage of PerQuat® technology, which showed some very impressive results as measured with ATP. ATP numbers immediately shot up as biofilm was broken apart and sessile bacteria were knocked into the bulk water and killed. Within 3 hours, the microbial ATP dropped dramatically. From those results, a PerQuat® trial was planned.

PerQuat® Trial Usage

The two-month PerQuat® trial commenced on November 6, 2009. From the first week of the trial, bulk water counts immediately dropped and no green foam remained in the sump. The inspection report after the first slug dose noted that the "bulk water was so clean it looked like the Mediterranean Sea." Once the system was brought under control, the PerQuat® biocide was fed at 150 mg/L weekly and then fed at 140 mg/L weekly. Throughout the trial, there was not a single positive count for SRB (see Figure 7) and bulk water counts consistently were recorded at a much-improved 10^3 CFU/mL level. In addition, there was no evidence of any of the traditional green foam during visual inspections for the course of the trial.

Figure 7: Sulfate-Reducing Bacteria Counts for Field Trial #2

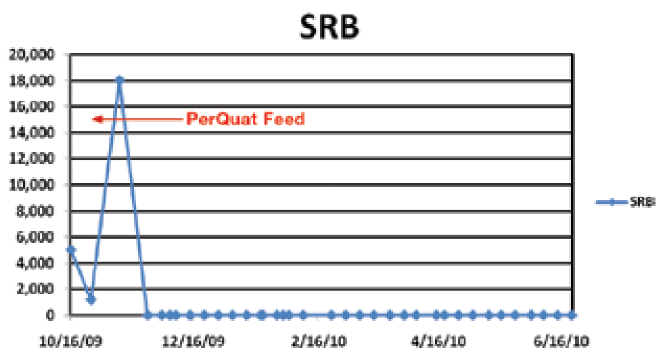


Table 2: Field Trial #2 Microbial Data Before/During/After Trial

Date	Treatment		Tester	Dip Slide*		SRB	SFB	Foam	ATP		
	Oxidizer	Non-oxidizer		Aerobic	Fungus				Total	Free	MB
		Name/Dosage		(CFU/mL)	(CFU/mL)	(CFU/mL)	(CFU/mL)	(0-10)	RLU	RLU	RLU
1/5/09	Stabilized Bromine	THPS-20/150 ppm	Operator	0							
1/12/09			Operator	0							
10/26/09		Glut/250 ppm	Service Rep	50,000		1,200					
11/2/09			Operator	5,000							
11/2/09		Glut/250 ppm	Service Rep	5,000			3" thick green	10	227	124	103
11/6/09		PerQuat/250 ppm	Service Rep						749	504	245
11/6/09		3 Hrs After	Service Rep					0	881	863	18
11/9/09			Operator	50,000							
11/9/09		THPS/250 ppm	Service Rep	50,000		18,000		8			
11/13/09			Service Rep	500	0			8			
11/16/09			Operator	1,000							
11/16/09			Service Rep	500							
11/19/09	DBDMH		Service Rep					8			
11/23/09			Operator	1,000							
11/23/09		PerQuat/150 ppm	Service Rep	500	100,000	0	0	8			
11/30/09			Operator	5,000							
11/30/09			Service Rep	5,000		0					
12/4/09			Service Rep	1,000		0	2,500	3			
12/7/09			Operator	1,000							
12/7/09			Service Rep	5,000	0	0	100	2	205	200	5
12/14/09			Operator	1,000							
12/14/09			Service Rep	500		0	0	0	143	138	5
12/19/09			Service Rep					0	248	171	77
12/21/09			Operator	5,000							
12/21/09			Service Rep	5,000		0	0	0			
12/21/09			3rd Part C.	1,000		0					
12/28/09			Operator	10,000							
12/28/09			Service Rep	10,000	0	0	500	0	133	89	44
1/4/10			Operator	20,000							
1/4/10			Service Rep	10,000	0	0	0	0	126	96	30
1/11/10			Operator	10,000							
1/11/10			Service Rep	500	0	0	500	0			
1/18/10			Operator	5,000							
1/18/10			Service Rep	5,000	0	0	0	0			
1/19/10			3rd Part C.	2,000							
1/25/10			Operator	10,000							
1/26/10			Service Rep	5,000	0	0	0	0			
1/29/10			Service Rep	5,000	0			0			
2/1/10			Operator	5,000							
2/1/10		Trial Rapped	Service Rep	500	0	0	500	0			
2/8/10		PerQuat application	Operator	5,000							
2/8/10		continues	Service Rep	500	0	0	0	0			
2/15/10			Service Rep	1,000				0			
2/22/10			Service Rep	500	0	0	0	0			
3/1/10			Service Rep	1,000	0			0			
3/8/10			Service Rep	1,000	0			0			
3/15/10			Service Rep	500	0			0			
3/23/10			Service Rep	500	0			0			
3/30/10			Service Rep	1,000	0			0			
4/5/10			Service Rep	10,000	0			0	No foam return since		
4/15/10			Service Rep	10,000	0			0	start of trial		
4/19/10			Service Rep	1,000	0			0			
4/26/10			Service Rep	1,000	0			0			
5/3/10			Service Rep	1,000	0			0			
5/11/10			Service Rep	1,000	0			0			
5/17/10			Service Rep	5,000	0			0			
5/24/10			Service Rep	5,000	0			0			
6/1/10			Service Rep	1,000	0			0			
6/7/10			Service Rep	1,000	0			0			
6/14/10			Service Rep	500	0			0			
6/21/10			Service Rep	500	0			0			

*Operator Dip Slide tesed on Friday and read every Monday
*Service Rep Dip Slide usually tested on Monday and read Wed/Thu.

Results

PerQuat® chemistry was used in this trial as both a remediation biocide as well as an ongoing, supplemental non-oxidizer replacement. Slugged at 250 mg/L, the PerQuat® chemistry was able to rapidly remove biofilm, knock down bulk water counts, and completely eliminate SRB counts. At a maintenance dose of 140 mg/L (8.4 mg/L active), the PerQuat® chemistry was more cost effective than the incumbent program and prevented fouling of the tower. If a process in-leakage occurs or contaminant ever enters the system, the PerQuat® chemistry can be used to rapidly bring the system back under control. Table 2 shows the microbial data before, during and after the trial.

Conclusions

The results of the two field trials confirm that PerQuat® chemistry is a novel, cost-effective biocide that can replace non-oxidizing biocide and dispersant programs. Bulk water counts were controlled during both trials and impressive sessile counts are consistent with biofilm removal. The product was easy to handle and apply, and no adverse interactions, corrosion, or incompatibility was noted.

In addition to lower bulk water, SRB, and SFB counts, PerQuat® technology differentiates itself from conventional biocides in its unique cleaning capabilities. In all of the trials described above, tower cleanliness, foam, and algae were additional concerns before the trial started. In all cases, microbiological foam was immediately eliminated and counts were drastically reduced. Additionally, a temporary spike in ATP readings typically immediately followed the first slug dose with PerQuat®. This spike is indicative of a true biofilm removal capability as attached organics are forced into the bulk water and sessile bacteria are killed by both the PerQuat® chemistry and oxidizing biocide residual.

PerQuat® technology has the capability to be a workhorse biocide for water treatment professionals. With broad, dual-active killing efficacy, algaecidal efficacy, and biofilm removal capabilities in one technology, PerQuat® chemistry offers a single biocide for remediation and maintenance biocide applications with cost-competitive economics. Although not explored in this study, with oxidizing, non-oxidizing, and dispersant activity, PerQuat® may also have the ability to replace entire biocide programs.

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