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Factors affecting activated carbon's bromate removal ability from concentrated, organic load rich cooling water, in the presence of residual bromine

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ABSTRACT

Bromination, in the form of hypobromous/hypobromite addition, is a broadly applied disinfection method used in cooling water treatment. One of bromination's most hazardous by-products is bromate, which results from hypobromous/hypobromite decomposition. Such decomposition is promoted by favorable conditions prevailing within a typical cooling circuit. In this work bromate removal from cooling water, using activated carbon, is studied. A number of commercial activated carbons are evaluated with respect to their ability to adsorb/reduce bromate from ultrapure water. Using sampled cooling water as reference matrix, isotherm curves are constructed under increasing pH values as well as applying 1:1, 1:2 and 1:3 mass ratios of polyacrylate/phosphonate anti-scaling agents, copper ion and residual bromine. The resulting curves fit the Freundlich model best. In terms of adsorption quality, as expressed by Freundlich model's K_F constant, pH is an important determinant of activated carbon's bromate removal ability, as it is also the case in drinking water. Appreciable copper ion presence, followed by polyacrylate/phosphonate and residual bromine, also has negative influence. Dubinin–Radushkevich model, which provides the second best fit, is used to evaluate activated carbon's maximum adsorption capacity. It is proven that all the above parameters significantly affect it.

Keywords: Cooling water treatment; Disinfection; Bromate; Hypobromous decomposition; Activated carbon

1. Introduction

Bromination is an effective treatment used for cooling water disinfection due to bromine's strong oxidative action [1–3]. Bromine's short degradation period and cost competitiveness make it in general more attractive than the use of synthetic biocides [4,5]. Chlorination, which is the most common disinfection technique, is less effective in alkaline pH [6–9], where most operators tend to adjust cooling water to render it less corrosive to the equipment. In most cases bromine in the form of hypobromous/hypobromite is produced in situ by mixing hypochlorite and sodium/potassium bromide solution as follows (Eq. (1)) [10]:

$$NaOCl + NaBr \rightarrow OBr^- + 2Na^+ + Cl^- \quad (1)$$

Bromine addition usually targets specific residuals. Cooling water's bromine demand can be estimated [11] and depends on operational characteristics such as concentration the water undergoes at the cooling tower and bromination period, as well as cooling water's organic load, pH and temperature. Bromate, a known carcinogen [12–14], is the product of hypobromous decomposition (Eq. (2)) [15,16], which is promoted in a cooling circuit by sunlight [17,18], residual free bromine [15], presence of copper oxide [19] as well as presence of other heavy metal species [20]. Materials of such kind are common in the construction of heat exchangers and piping.

$$3HOBr \rightarrow BrO_3^- + 3H^+ + 2Br^- \quad (2)$$

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Activated carbon is among the most widely used adsorbents in industry with proven abilities in bromate removal mainly from drinking water [21]. Due to its relatively low cost, ease of regeneration and various pollutants adsorption ability are the operators' first options to deal with bromate upon occurrence. Activated carbon's bromate removal capabilities have been reported, especially from drinking water, as well as the adsorption/reduction mechanism [22–28]. It involves a bridging ligand and is described in Eqs. (3) and (4):

$$\text{Adsorption: } {>}\text{acL}^+ + \text{BrO}_3^- \rightarrow {>}\text{acL}^+\text{BrO}_3^- \qquad (3)$$

$$\text{Reduction: } {>}\text{acLOBr} + \text{O}_2 \rightarrow \text{BrO}^- + {>}\text{acL}^+ \qquad (4)$$

where ac is activated carbon, and L the bridging ligand.

Further reduction on activated carbon's surface leads to Br^- formation. Cooling water poses serious additional challenges to activated carbon in comparison with drinking water [29]; it is far more concentrated (its electric conductivity can easily be found near 2,000 μS/cm) providing more competing constituents. It is substantially richer in organic load due to microbial growth promoted by sunlight and by nutrient abundance. Industrial cooling water treatment chemicals used for anti-scaling and anti-corrosion protection such as phosphonate and polyacrylate salts are also present. Depending on each operator's chosen disinfection scheme, strong presence of residual bromine (both in the form of hypobromous as well as of a variety of bromination by-products) is also expected. Finally, appreciable concentrations of heavy metals as by-products of equipment corrosion are commonly found. Copper in particular is commonly detected since it is a material broadly used in the construction of many cooling circuit parts.

Polyacrylate/phosphonate is chemical agents used for the protection of the cooling circuits against scale [30,31]. They act at the threshold of hard scale formation allowing the water to be supersaturated in scale forming salts. They become necessary with the increase of Langelier Saturation Index. They can be applied at doses as high as 50 mg/L or more, depending on water's concentration at the cooling tower.

In this work, activated carbon's ability to remove bromate from concentrated cooling water in the presence of all the above challenges is examined. For the purposes of this study, cooling water was sampled from a large metal-processing unit in the Greek territory. Different cooling water profiles, using the sampled water as base matrix, were prepared, varying the pH as well as the polyacrylate/phosphonate, the copper ion and the residual bromine content. All the adjustments were made at 1:1, 2:1 and 3:1 mass ratio in proportion to bromate concentration. Isotherm curves were constructed for each one of the synthetic matrices, and several isotherm models were tested for their ability to fit the experimental data.

2. Experimental setup

The basic chemical parameters of the sampled cooling water are shown in Table 1, in comparison with those of the drinking water of the city of Athens, Greece. The sampled cooling water was used as matrix subjected to additions and modifications corresponding to the various scenarios studied.

Table 1
Basic chemical parameters of the sampled concentrated cooling water in comparison with those of the city of Athens drinking water

	Sampled cooling water	City of Athens drinking water
Electric conductivity, μS/cm	1,920.0	270.0
pH	7.8	7.5
Total hardness (mg/L as $CaCO_3$)	1,021.0	130.0
Alkalinity (mg/L as $CaCO_3$)	415.0	112.0
Turbidity (NTU)	5.0	<1.0
Cl^- (mg/L)	220.7	5.0
SO_4^{2-} (mg/L)	94.3	20.0
NO_3^- (mg/L)	26.0	0.6
Ca^{2+} (mg/L)	364.4	45.0
Mg^{2+} (mg/L)	70.2	5.0
Cu^{2+} (mg/L)	0.2	0.09
Absorbance at 254 nm (indication of organic carbon content)	0.1	0.01
Langelier Saturation Index	1.58	0.17

2.1. Reagents and instrumentation

All reagents used were of analytical grade unless otherwise stated. Powder $KBrO_3$ and KBr (both 99.5% purity), humic acid sodium salt, NaOCl solution (10% of available chlorine), 1 N NaOH solution, [nitrilotris(methylene)] tris-phosphonic acid pentasodium salt, polyacrylic acid sodium salt, copper(II) sulfate pentahydrate and ethylenediamine (EDA – >99% purity) were all supplied by Sigma-Aldrich, USA (www.sigmaaldrich.com). Bromine solution was prepared by mixing 40% w/w potassium bromide and hypochlorite solutions. All activated carbon species used came from Cabot Corporation, US (www.cabotcorp.com).

All solutions' pH values were adjusted with the use of a Metrohm 716 DMS Titrino pH adjuster. The electric conductivity was measured with a Metrohm 660 Conductometer. All solutions' organic load was measured and adjusted using a Shimadzu TOC-VCSH E200V instrument. Bromate was measured with a BioLC ion chromatography system using a set of AS9-HC/AG9-HC columns (EPA Method 300.1). Residual bromine was determined with a DR 4000 Hach-Lange UV–Vis spectrophotometer using the DPD method (HACH Method 8016 with 30 μg/L detection limit at 530 nm wavelength). All dilutions were carried out with ultrapure water (18.2 MΩ resistance) coming from a Barnstead EASYpure device.

2.2. Activated carbon selection

A number of activated carbons, both in powder (PAC) and granular (GAC) form, were evaluated with respect to their bromate removal capabilities. All the activated carbons under study are presented in Table 2.

The evaluation method focused on the BrO_3^- percentage removal from ultrapure water. It included the preparation of 100 mL aliquots containing 1 mg/L bromate. 1 g of each activated carbon was dosed before each aliquot being intensely

Table 2
Physical properties of each activated carbon species under study

Activated carbon's commercial reference	ROW 0.8 SUPRA	830	830 W	PK 1-3	SA UF 8031-9	1,240 W	SA SUPER	W35
Activated carbon's nature	GAC	GAC	GAC	GAC	PAC	GAC	PAC	PAC
Activation method	Steam	Steam	Steam	Steam	Steam	Steam	Steam	Steam
Surface (BET) m^2/g	1,150	1,100	1,150	875	1,200	1,100	1,150	875
Apparent density, kg/m^3	390	500	485	290	225	485	250	425
Density after washing, kg/m^3	345	435	425	251		425		
Effective size D_{10}, mm	>0.6	1.0	0.9	1.2	0.005 (D_{50})	0.6–0.7	0.005 (D_{50})	0.015 (D_{50})
Uniformity coefficient		1.7	1.7	1.6		1.7		
Ash content, %	7	8	8	8	10	9	10	10
Percentage removal of BrO_3^- after 20 min contact time	52	76	63	22	20	78	25	24

Note: BET – Brunauer, Emmet and Teller.

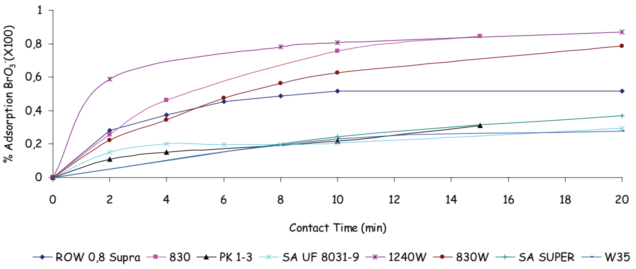

Fig. 1. Activated carbons evaluation with respect to their bromate removal ability from ultrapure water (initial BrO_3^- concentration 1 mg/L, activated carbon concentration 1 g/100 mL).

stirred under ambient conditions for 20 min. 1 mL samples were being withdrawn, filtered with the help of 0.45 μm membrane filters and measured. The results are presented in Fig. 1. Based on these results Norit GAC 1240 W was selected for further research.

2.3. Analytical procedure

The sampled cooling water was used as the background matrix throughout the experimental work. Different cooling water profiles prepared in the laboratory were examined. The parameters varied were the pH as well as the polyacrylate/phosphonate (PA/NMPA), the copper ion and the residual bromine concentration. The organic load was adjusted at 4 mg/L and was kept at constant concentration throughout. BrO_3^- concentration was maintained steady throughout the analytical work at 2 mg/L. All the prepared matrices are presented in Table 3. Additions were made at 1:1, 2:1 and 3:1 mass ratio with respect to BrO_3^- concentration.

Isotherm curves were constructed by adding 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 g of activated carbon to 100 mL aliquots of each matrix in 100 mL volumetric flasks. After intense stirring for 1 h the aliquots were left in tranquility, under ambient conditions and away from sunlight for 48 h. Each sample was filtered with the use of 0.45 μm pore size glass fiber filters. Ethylenediamine was added to the samples where bromine was initially added and bromate concentration was measured.

3. Results and discussion

Measurements on the base-case scenario (matrix #1) are shown in Fig. 2. Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm models were tested with respect to their ability to fit best to the experimental data. Each model's equation and R^2 value is presented in Table 4. The Freundlich equation gives the best fit with an R^2 value of 0.9697.

What is important to observe in Fig. 2 and Table 4 is the reduced ability of the Langmuir adsorption model to fit the data. The adsorption surface is becoming increasingly rough and inhomogeneous mainly due to cooling water's impurities, and especially organic content, which hinder GAC's adsorption/reduction ability.

As already reported, matrix #1 comprises the base-case scenario of this work. In all other matrices one specific parameter is varied while all others remain unchanged. That way, activated carbon's behavior to each change is evaluated. The criterion is the value of the Freundlich model's K_F constant. In Table 5 each K_F value is reported along with the R^2 value that articulates the quality of Freundlich's model fit. Special notice has to be paid to matrices #8 and #9. The existence of residual bromine implies that all the reducing constituents of cooling water have been oxidized. Cooling water's organic content (which is its main reducing constituent) is found in different form than in all other matrices. The identification of the species of oxidized organic matter, their respective properties and each one's individual influence on bromate removal are beyond the scope of this study.

From Table 5 can be inferred that pH is a critical parameter influencing bromate removal from cooling water. As pH rises (matrices #2 and #3 – Table 3), bromate removal efficiency diminishes. This has proven to be the case in other matrices, such as drinking and distilled water, as well. Copper ion presence (matrices #4 and #5) also inhibits bromate adsorption since both compete for GAC sites. As the pH of the cooling water becomes more alkaline, however, heavy metals in general tend to precipitate, reducing competition. Polyacrylate and phosphonate salts that are used to protect the cooling circuit against scale formation (matrices #6 and #7) as well as residual bromine (matrices #8 and #9)

Table 3
Matrices under study

	Matrix #1	Matrix #2	Matrix #3	Matrix #4	Matrix #5	Matrix #6	Matrix #7	Matrix #8	Matrix #9
pH	8.0	9.0	10.0	8.0	8.0	8.0	8.0	8.0	8.0
BrO_3^- (mg/L)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Cu^{2+} (mg/L)	2.0	2.0	2.0	4.0	6.0	2.0	2.0	2.0	2.0
PA/NMPA (mg/L)	2.0	2.0	2.0	2.0	2.0	4.0	6.0	2.0	2.0
Organic content (mg/L)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Residual Br_2 (mg/L)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	6.0

Note: Cu^{2+}, PA/NMPA and residual bromine concentration are varied proportionally to bromate concentration. pH values are adjusted at values normally measured in cooling water bodies.

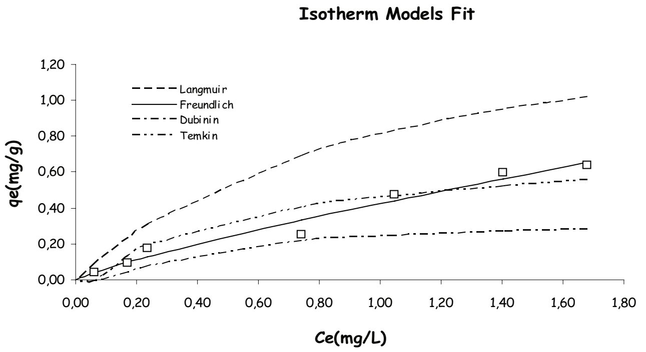

Fig. 2. Langmuir, Freundlich, Dubinin–Radushkevich and Temkin equations fit to the experimental findings (sampled cooling water spiked with 2.0 mg/L BrO_3^- and pH adjusted to 8.0 – matrix #1, Table 3)

Table 4
Equations and R^2 values of the isotherm models fitted to the experimental findings for Matrix #1

Isotherm model	Equation	R^2 value
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	0.4939
Freundlich	$q_e = K_F C_e^{1/n}$	0.9697
Dubinin–Radushkevich	$q_e = q_m \exp(-\beta\varepsilon^2)$	0.9094
Temkin	$q_e = \frac{RT}{b}\ln(AC_e)$	0.8728

Note: The Freundlich equation fits best with an R^2 value of 0.9697. C_e (mg/L) is bromate's concentration in solution after equilibrium is achieved; q_e is bromate mass adsorbed per g of activated carbon (mg/g); q_m (mg/g) is bromate maximum adsorbable mass per g of activated carbon; K_L (L/mg) is the Langmuir equation constant; K_F ($mg^{1-1/n}$ $L^{1/n}$/g) is the first Freundlich equation constant; n (dimensionless) is the second Freundlich equation constant; β (dimensionless) is the Dubinin–Radushkevich equation constant; $\varepsilon = RT\ \ln\left(1 + (1/C_e)\right)$, where R (J/mol K) is the ideal gas constant; T is the temperature (K); b (J/mol) is the Temkin equation constant that expresses the adsorption heat; and A (L/mg) is the Temkin equation adsorption constant.

also inhibit bromate removal. GAC's ability to remove bromate is less influenced by residual bromine than by copper or phosphonate/polyacrylate concentration appreciation.

In Figs. 3–6, BrO_3^- concentration is presented as a function of GAC's amount per 100 mL aliquot, for every matrix studied. In all matrices the initial bromate concentration was adjusted at 2 mg/L.

In Figs. 3–6, the way that GAC's ability to adsorb and reduce bromate is influenced by cooling water specific conditions can be seen. As the pH value ascends the ability of the GAC to adsorb/reduce bromate diminishes. That poses difficulties to operators since higher pH values are generally targeted to prevent corrosion of the cooling circuit metal parts. Furthermore, higher pH values are expected when water savings are a goal. Increased concentration at the cooling tower, as a result of reduced blow down, leads to pH values that challenge bromate removal.

Copper ion presence also inhibits the ability of GAC to remove bromate from cooling water. That highlights the importance of adequate protection against corrosion. Copper as well as iron, nickel, zinc and various alloys are common materials in the construction of heat exchangers, piping, valves and cooling tower internal parts. Copper in particular is sensitive to the presence of NH_4^+, a constituent fairly common in make-up waters coming from intensely cultivated areas.

PA/NMPA use is necessary with cooling waters containing high levels of hardness. This is normally the case when make-up water pre-treatment is absent. As the water's Langelier Saturation Index rises, higher levels of hardness are expected, and stronger presence of PA/NMPA is targeted to maintain cooling water supersaturated in scale forming salts. PA/NMPA polar molecules are competing with bromate for GAC sites.

Bromine in the form of hypobromous/hypobromite is bromate's predecessor. There is a variety of bromination schemes that are applied. Higher bromine residuals are sought after with more aggressive disinfection strategies especially in summer periods. Frequently disinfected circuits usually require lower bromine residuals. As it can be seen in Table 5 and Fig. 6, residual bromine poses relatively less stress to GAC when found in concentrations normally encountered in general practice. The Freundlich Model's K_F constant does not change as sharply as it does with appreciable concentrations of copper ion and PA/NMPA.

In order to estimate the maximum amount of bromate, the selected GAC can adsorb/reduce under all the different conditions; the Dubinin–Radushkevich equation is used since the Freundlich model does not provide such

Table 5
Freundlich's K_F constant along with the model's R^2 value for each one of the matrices investigated

	Matrix #1	Matrix #2	Matrix #3	Matrix #4	Matrix #5	Matrix #6	Matrix #7	Matrix #8	Matrix #9
K_F	0.4251	0.2068	0.1673	0.3611	0.2943	0.3830	0.2905	0.3774	0.3469
R^2	0.9697	0.9690	0.9372	0.9803	0.9848	0.9535	0.9255	0.9375	0.9418

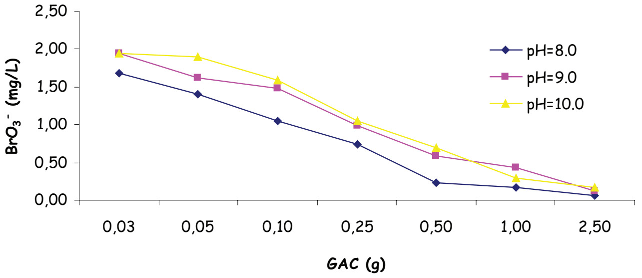

Fig. 3. BrO_3^- concentration with respect to GAC amount per 100 mL aliquot at various pH values (initial BrO_3^- concentration 2 mg/L, contact time 48 h).

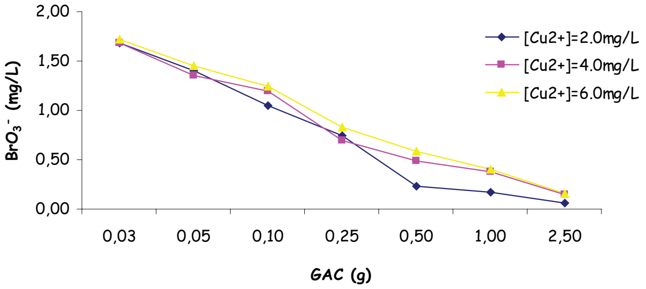

Fig. 4. BrO_3^- concentration with respect to GAC amount per 100 mL aliquot with different Cu^{2+} concentrations present (initial BrO_3^- concentration 2 mg/L, pH 8.0, contact time 48 h).

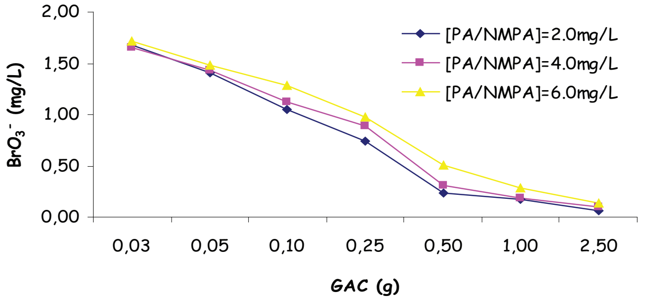

Fig. 5. BrO_3^- concentration with respect to GAC amount per 100 mL aliquot with different polyacrylate (PA) and phosphonate (NPMA) concentrations present (initial BrO_3^- concentration 2 mg/L, pH 8.0, contact time 48 h).

information. The Dubinin–Radushkevich equation features the second best, yet still acceptable fit to the data for the base-case scenario (R^2 = 0.9094). In Table 6 bromate's maximum adsorbable mass per g of activated carbon, q_m (mg/g GAC), is presented.

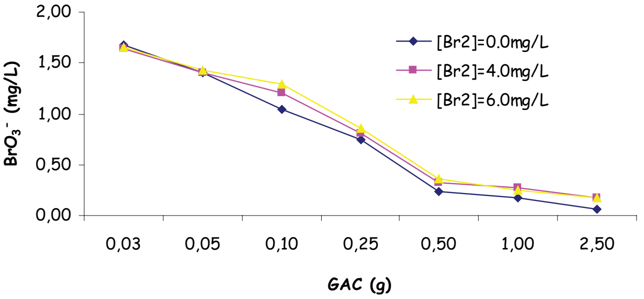

Fig. 6. BrO_3^- concentration with respect to GAC amount per 100 mL aliquot with different residual bromine (Br_2) concentrations present (initial BrO_3^- concentration 2 mg/L, pH 8.0, contact time 48 h).

From the results presented in Table 6 can be inferred that even though the rise of pH inhibits GAC's bromate removal capability, the total amount that can be adsorbed/reduced is not so gravely affected. pH rise is actually reducing GAC's capacity but not as heavily as the presence of anti-scaling treatment chemicals or copper ion. Residual bromine also plays a role in reducing GAC's capacity but again is not so influential as the other constituents. Maintaining corrosion-free circuits and limiting the use of anti-scalants are important goals to consider when aiming to optimize GAC's maximum adsorption/reduction capacity.

4. Conclusions

The scope of this work was to evaluate activated carbon's bromate removal performance from a challenging environment like cooling water body. Activated carbon, especially in its granular form, is one of the most common adsorbents in industry due to its low cost and ease of regeneration, with proven ability in BrO_3^- removal. It is therefore expected to be used for bromate removal as it is already used for other similar tasks such as dechlorination, removal of disinfection by-products etc. Cooling water is a matrix quite different than, for example, drinking water. It is highly concentrated, more alkaline and more heavily charged with organics and conditioning chemicals, and therefore, more demanding as far as bromate removal is concerned.

GAC's bromate removal performance, in terms of bromate adsorption/reduction ability and maximum adsorption capacity, from various cooling water profiles was studied. The results showed that increasing pH is a significant inhibitor of GAC's bromate removal ability. Other cooling water specific conditions such as strong presence of copper ion, polyacrylate/phosphonate-based anti-scalants and residual bromine also play important role. Regarding GAC's maximum capacity to adsorb/reduce bromate, the Dubinin–Radushkevich model implies that pH is less of a

Table 6
BrO_3^- maximum adsorbable mass per g of activated carbon as calculated by the Dubinin–Radushkevich equation

	Matrix #1	Matrix #2	Matrix #3	Matrix #4	Matrix #5	Matrix #6	Matrix #7	Matrix #8	Matrix #9
q_m (mg/g GAC)	0.7037	0.6399	0.6189	0.5233	0.4606	0.5127	0.4465	0.6227	0.5662

problem comparing with strong copper ion and scale-inhibiting chemicals presence.

All the above, highlight the complexity of the goal to mitigate the problem of bromate presence in cooling circuits. Special notice must be paid to the fact that bromate removal from cooling water has to take place in natural environments affected by conditions almost impossible to control such as weather, ambient temperature, sunlight etc. A general conclusion is that less concentrated, frequently disinfected and protected against scale and corrosion circuits with low targeted hypobromous/hypobromite residuals (a.k.a. the BrO_3^- precursors) are easier to apply bromate removal strategies that involve activated carbon.

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