The Pennsylvania State University
The Graduate School
The Department of Civil and Environmental Engineering

EVALUATION OF TAILORED GRANULAR ACTIVATED CARBON TO
REMOVE PERCHLORATE IN THE PRESENCE OF OXYANIONS

A Dissertation in
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by
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ABSTRACT

In this research, laboratory studies demonstrated that some anions greatly competed with perchlorate for adsorption sites, thus reducing the capacity of surfactant tailored granular activated carbon (GAC) to remove perchlorate.

It was observed that thiosulfate, an oxyanion and intermediate-valence sulfur species, competed with perchlorate for adsorption sites onto granular activated carbons that were tailored with quaternary ammonium surfactant. A reduced capacity of 50% of the surfactant tailored GAC was observed when Rapid Small Scale Column Tests (RSSCT) were employed. Rapid Small Scale Column Tests that employed Redlands, CA groundwater, with perchlorate of 30 µg/L, showed that 33,000 bed volumes of groundwater was processed through Arquad 2C-75 tailored GAC, before perchlorate was observed in the effluent at 6 µg/L. When the same water had 1000 µg/L of thiosulfate, 17,000 BV of Redlands, groundwater was processed through the surfactant tailored carbon before perchlorate was observed at 6 µg/L. It was determined that an implementation of a pretreatment step that utilized 2,500 µg/L of chlorine, diminished the effects of thiosulfate, by oxidizing the thiosulfate anion to sulfate and thus, returned the surfactant tailored GAC capacity to 90% of its capability. With this pre-treatment method, the surfactant tailored GAC technology can be a viable method in the removal of perchlorate from groundwater, in the presence of intermediate –valence sulfur species.
Nitrate, another oxyanion that is common in ground waters, was also observed to strongly compete with perchlorate for adsorption sites on activated carbon loaded with quaternary ammonium surfactant. It was observed that at 3 times the concentration of the initial nitrate of 30 mg/L in Fontana, CA groundwater, the surfactant tailored GAC capacity to adsorb perchlorate was reduced to 46%. Additional experiments demonstrated that surfactant tailored GAC works best at removing perchlorate from aqueous systems at low nitrate concentrations.

This research also evaluated the scaling technology that employed the RSSCT scaling equations for proportional diffusivity. The proportional diffusivity model was designed to predict the performance of pilot and field scale experiments by utilizing smaller fixed bed columns over a shorter test period. The proportional diffusivity model used an intra-particle coefficient of 1. A comparison of pilot scale tests and RSSCT indicated that the RSSCT design that employed the proportional diffusivity model, and used surfactant tailored GAC, over predicted the removal of perchlorate, by a ratio of 0.58. This result differs from activated carbon that was not tailored with surfactants, in that proportional diffusivity accurately predicts the performance of pilot scale tests. These results suggest that intra-particle diffusivity does not linearly correlates to particle radius when activated carbon was tailored with surfactants, as was demonstrated with non tailored activated carbon. An intra-particle diffusivity coefficient that is 0.5 less than the coefficient used for proportional diffusivity scale was evaluated. Results showed that
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1 CHAPTER 1 - INTRODUCTION

Chemicals that are released into our surface and subsurface waters are a pervasive environmental problem. Sources of chemical contamination range from incorrectly disposing of and treating chemical waste, to abandoned waste disposal sites, to leaking storage tanks that might contain hazardous chemicals. Remediation of these contaminations has been proven to be quite difficult.

Remediation efforts are frequently inhibited by an inability to extract contaminants from the environment due to the significant sorption of strongly hydrophobic compounds or due to physical and chemical properties that hinder them from being remediated from the environment.

Perchlorate is one of those contaminants that due to its kinetic and thermodynamic properties have made it quite difficult to remove from contaminated waters and soils (Urbansky and Brown, 2003; Urbansky, 2000, 1998). Because of this, perchlorate has become one of the most widespread contaminants found in the environment. Remediation of perchlorate includes technologies such as ion exchange, electrodialysis, and bioremediation (Gu and Coates, 2006; Gu et al., 2000). To date, the most successful of these is ion exchange. The ion exchange process employs cationic
surfactants that have quaternary ammonium or pyridinium groups attached to it (Gu and Coates, 2006). These surfactants have been loaded on to solid surfaces such as resins and clays. In this study, the surfactants were loaded on to bituminous granular activated carbon.

The perchlorate ion has exhibited a high affinity for the surfactant tailored solid surface. This characteristic has made it impractical to regenerate using the conventional chemical manner of brine solutions when using ion exchange resins (Gu and Coates, 2006; Gu et al., 2005; Gu and Brown, 2002, Gu et al., 2001). This led our group at Penn State to find a technology that utilized the same principle as the ion exchange, but reduced the need for highly concentrated brines. This technology has successfully used granular activated carbon, instead of resins as the solid media to load cationic surfactants on to. Results have shown that perchlorate had been removed to below 1µg/L for 30,000 to 35,000 bed volumes at the laboratory scale using Redlands, CA groundwater at perchlorate concentrations of 30 to 75 µg/L. Also instead of chemical regeneration, this tailored carbon can be thermally regenerated, thus removing the cost of having to treat and dispose of a regenerant.

Another complexity for remediating perchlorate using the ion exchange technology arises from adsorption of other anions. This is due to the affinity and concentration of anions that are present in aqueous systems. Even though perchlorate has a very strong affinity to cationic surfactants loaded on to solid surfaces, other anions compete with perchlorate for adsorption sites due to the parts per million concentrations
they are commonly found in. These translate to orders of magnitude greater than perchlorate concentration in the same system.

Another reason for perchlorate’s strong affinity to surfactant tailored solid surface, is its thermodynamic characteristic of having low hydration energy (Crittenden, 2005), which will be discussed in detailed in the upcoming chapter. So it is also expected that other anions that have low hydration energies will also compete with perchlorate for exchange sites. Nitrate is one example that is similar to perchlorate with certain thermodynamic properties that allows it to have a strong affinity as well to resins, and concentrations found in ground water are usually in the parts per million category. Perchlorate has a higher selectivity than nitrate, but the high concentration, in comparison to perchlorate, makes nitrate a strong competitor for ion exchange sites.

Other competition arises from divalent oxyanions that are present in groundwater at concentrations similar to that of perchlorate, but compete strongly with perchlorate for adsorption sites. These anions will utilize two adsorption sites instead of one. An example of this is intermediate-valence sulfur species such as thiosulfate. These competing anions will affect the capabilities of the ion exchange process to remove perchlorate and influence the overall water quality.

A disparity in the performance of the tailored granular activated carbon was observed at the field scale level. Perchlorate was observed in the effluent only after 17,000 bed volumes. It was hypothesized that this reduction in performance of the
tailored granular activated carbon could be attributed to reduced and intermediate-valence sulfur species. These can easily be transformed to other sulfur species that will not affect perchlorate adsorption to activated carbon tailored with surfactants. Peaks that could be attributable to reduced and intermediate sulfur species were observed in Redlands groundwater that was first received at Penn State.

The overall research objective of this study has been to evaluate the effects of intermediate-valence sulfur species and other oxyanions on the removal of perchlorate and to optimize the performance so as to demonstrate similar results that were observed at the laboratory scale.

Specific objectives have been to:

1. Evaluate the effects of intermediate-valence sulfur species on the adsorption of perchlorate to cationic surfactants that have been loaded unto granular activated carbon.
2. Demonstrate the removal or transformation of these species to more oxidized sulfur species that does not compete with perchlorate.
3. Evaluate common anions selectivity for exchange sites onto the tailored granular activated carbon.
4. Observe if proportional diffusivity is the proper intra-particle diffusion coefficient for scaling laboratory to field scale experiments.
This dissertation consists of 6 chapters that address the specific objectives and ultimately the overall goal. The organization of the dissertation is as follows:

Chapter 2 looks at past research on perchlorate, granular activated carbon, anions and ion exchange systems,

Chapter 3 evaluates the effects of intermediate-valence sulfur species and how to transform these species so as to make them less competitive,

Chapter 4 observes the effects of common anions found in groundwater to tailored GAC,

Chapter 5 investigates the intra-particle diffusion coefficient and to observe if proportional diffusivity is the correct scaling method, and

Chapter 6 suggests recommendations for future work that can be conducted as the surfactant tailored GAC is further explored.
### 2.1 Perchlorate

The perchlorate molecule is derived from salts such as ammonium, potassium and sodium perchlorate. The majority of perchlorate salts are in the form of ammonium perchlorate, which is a strong oxidant that is used in the rocket and missile engine as solid propellants. Perchlorate salts are also used in pyrotechnics, matches, munition, chemical analytical industries, lubricating oils, aluminum refineries, dyes and airbag inflators. Perchlorate salts are also found in fertilizer either through natural or manmade contamination.

In 1953, ammonium perchlorate production was 2,000 tons per year. By the mid 1980’s production peaked at 15,000 tons per year, and then declined to 4,000 tons per year in 1998 (Motzer, 2001). This decline was mainly due to its short shelf life, and because of this, periodic replacement was required of rockets and missiles, thus reducing the quantities that are used in rocket boosters or missiles (Damian and Pontius, 1999). To date there are 162 facilities in 36 states that either produce or use perchlorate compounds (www.ewg.com). Perchlorate also originates naturally from sources such as soils in hot dry climates, which are derived from ancient marine sea beds, for example in the country of Chile. Nitrate fertilizer from Chile is the largest known natural source of perchlorate (Sellers et al., 2006). According to Cox (2005), between 2002 and 2004, 75,000 tons of
Chilean nitrate fertilizer that contained 0.01% of natural perchlorate was imported to the United States, this would result in an approximate release of 15,000 pounds of perchlorate per year. Researchers have also detected perchlorate in similar arid climate that were formerly marine environments (Table 2-1).

Another source of naturally occurring perchlorate is in potassium ore deposits. These deposits originated from briny sea beds which are similar to that of the marine sea bed in arid areas. The concentration of perchlorate in these deposits ranges from 25-2,700 mg/kg of soil (Sellers et al., 2006).

Another source of perchlorate derives from the degradation of other compounds such as sodium hypochlorite. The Massachusetts Department of Environmental Protection (MassDEP) tested commercial grade hypochlorite solutions used in water and wastewater treatment plants and found perchlorate contamination of up to 4.6 mg/L. Mass DEP also subjected fresh sodium hypochlorite solution to different storage treatments and found that after 26 days, the perchlorate concentrations increase to as high as 6.8 mg/L. Perchlorate concentrations between 0.089 mg/L to 8 mg/L were also found in household bleach samples (MassDEP, 2005).
Table 2-1 List of areas in arid climates where perchlorate anions are found naturally.

<table>
<thead>
<tr>
<th>Locations</th>
<th>Perchlorate concentration detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bolivian Playa in Andean High Plains</td>
<td>500 mg/kg of soil</td>
</tr>
<tr>
<td>Portions of 60,000 sq.mi in West Texas</td>
<td>20-59 µg/L in public water supply</td>
</tr>
<tr>
<td>Portions of 6,800 sq. mi. in New Mexico</td>
<td>0.5-4 µg/L in public water supply</td>
</tr>
<tr>
<td>Mission Valley Formation – San Diego</td>
<td>-</td>
</tr>
</tbody>
</table>

Adapted from Sellers et al., 2006.

2.1.1 Fate and Transport of Perchlorate

Perchlorate salts are very soluble and will dissociate to form their corresponding cations and the perchlorate anion. The perchlorate anion is very mobile in aqueous systems and is relatively non reactive and very stable. This is because of the slow reduction in the central chlorine atom (Motzer, 2001; Clewell et al, 2000; Urbansky, 1998). It is these characteristics that make perchlorate a difficult anion to remove or decompose from aqueous systems.

Perchlorate can be released in the environment as a solid such as its salts or in the liquid such as perchloric acid or from perchlorate brines. It is the liquid release of perchlorate that mostly affects the ground and surface water bodies. The migration of perchlorate in water bodies is dependent on the migration flow of the water or the advection transport of dissolved perchlorate in solution. For example, water flowing through a saturated soil will have variable flow and flow paths, therefore a dilute
perchlorate plume with variable flow, will move at the same average velocity as the groundwater. Because it is inert in groundwater and surface water, the contamination of perchlorate can persist for long periods of time (Urbansky et al., 2003).

The tetrahedral symmetry of perchlorate coupled with the even charge distribution, allows the anion to have low affinity to soils and minerals (Urbansky et al., 2003). Perchlorate does not readily sorb to clays even though clay has some amount of cation exchange capacity (Sellers et al., 2006). According to Nzengung, et al. (1999), perchlorate sorption to soils is not significant and may take years to degrade. Studies conducted at the University of California showed that there was no adsorption of perchlorate to sterile soils, and that the soils that were saturated showed perchlorate transport similar to that of bromide which is an unreactive tracer (Tipton et al., 2003). The perchlorate anion also has a low hydration energy coupled with a small hydrated radius which allows it to bond strongly with large organic cations such as surfactants (Clewell et al., 2000).

Chemical reduction of perchlorate requires a large activation energy to be hurdled, and thus, this is not observed in subsurface environments under highly reducing conditions. Bliven, (1996) observed that lowering the energy of water to below -200mV did not produce any abiotic reduction in perchlorate.

The fate of perchlorate, if not remediated or treated, is dependent on hydrologic as well as biological factors (Urbansky et al., 2003). The biological transformation of
perchlorate has been widely studied (Attaway and Smith, 1993; Logan, 2001; Bruce et al., 1999). Microorganisms, specifically bacteria, that can transform perchlorate are very abundant in nature (Batista, 2003; Coates, 1999; Wu et al., 2001 and Logan, 2001). Microbial degradation of perchlorate in soil and water occurs mostly under anaerobic conditions, and can be affected by competing electron acceptors such as nitrate and chlorate as well as organic matter (Tan et al., 2005).

The perchlorate anion can also be absorbed to crops through a water source (Tan et al., 2005; van Aken et al., 2002). Plants such as bulrushes, crabgrass, goldenrod, and cupgrass have been shown to accumulate perchlorate in their leaves and stems. Smith et al., (2001), reported that crabgrass had perchlorate concentrations of 1,880 mg/kg in their seeds, and goldenrod had 1,030 mg/kg in their leaves. Plants, such as tobacco, that were grown on soil that used the Chilean nitrate fertilizer also accumulated perchlorate in their leaves (Ellington et al., 2001). Aquatic plants have also been shown to have perchlorate accumulated in their tissues and roots (Smith et al., 2001)

2.1.2 Contamination

Perchlorate salts are very soluble: solubility values of common perchlorate salts range from 15 g/L to 2000 g/L, which are orders of magnitude greater than drinking water (Sellers et al., 2006; Motzer, 2001). Once dissolved in water, the perchlorate anion is quite mobile in aqueous systems. Perchlorate is also very stable and non reactive, due to its high strength of the chlorine oxygen bonds (Motzer, 2001). Perchlorate does not
form complexes with metal cations, because of the even charge distribution that results in the tetrahedral symmetry of the perchlorate anion. The perchlorate anions can also form dense brines that can travel down the water column, pooling at the lower confining layer of aquifer systems. According to Flowers and Hunt (2000), it will take up to 100 years for perchlorate to naturally degrade and this is mostly by mass transfer and dilution. It is these characteristics that made perchlorate ubiquitous in surface and ground waters in many states.

Before 1997, the perchlorate anion could not be detected at concentrations below 100 µg/L. The California Department of Health developed an analytical method that could detect perchlorate at concentrations as low as 4 µg/L. It was after this method development that perchlorate detections were observed in water sources that were previously not suspected of being contaminated with perchlorate. In the state of Nevada, perchlorate contamination was observed at concentrations up to 37 g/L in the groundwater, which was traced back to two ammonium perchlorate manufacturing facilities. This resulted in perchlorate contamination of Lake Mead surface water, a significant water source for the Southwestern United states. The contamination affected 15-20 million people in Arizona, southern Nevada, and southern California (Hogue, 2003). La Puente, California also detected perchlorate in their domestic drinking water at a range of 40 -160 µg/L. The source of this contamination is said to be from facilities that used and disposed of perchlorate compounds miles from the city. Perchlorate contamination was also observed in groundwater and surface water up to 14.5 mg/L in the Longhorn Army Ammunition Plant in Karnack, Texas, near two former military
manufacturing facilities (USEPA, 1995). Also in Texas, at a former propellant mixing facility, perchlorate concentration ranged from 0.023 mg/kg to 1800 mg/kg in the soil and 5.6 mg/L in the tributary surface water at the facilities boundary. One mile from the tributary, the surface water contamination was 200 µg/L; and 3 miles downstream the tributary, perchlorate could still be detected at 56 µg/L. On the eastern part of the USA, perchlorate contamination was detected in the groundwater at the Indian Head Naval Surface Warfare Center in Maryland; concentration was as high as 43 g/L (USEPA, 2005). Perchlorate has also been detected at the Massachusetts Military Reservation in Cape Cod. Many of the sites that have been contaminated with perchlorate are associated with the manufacture of the compound or used in defense related facilities. Other contaminations are derived from the use of perchlorate in fire works, flares or blasting agents (Sellers et al., 2006).

2.1.3 Risk Assessment of Perchlorate

Due to perchlorate solubility in water and little to no sorption of perchlorate to soils, the primary exposure of perchlorate is through water. Exposure can also be through the consumption of vegetation, dairy products and breast milk. Perchlorate is rapidly absorbed once ingested and has a short retention time of 8 hours in humans. It is rapidly excreted unchanged in the urine. The major concern is the competition of perchlorate with iodine uptake by the thyroid gland for both humans and animals. The perchlorate anion blocks the protein that acts as an iodide pump to the thyroid glands. The inhibition is competitive and therefore is reversible, when the concentration of
perchlorate decreases (Sellers et al., 2006). Aquatic organisms may also be exposed to perchlorate through surface water.

### 2.1.4 Analytical Analysis of Perchlorate

Before 1997, the perchlorate anion was tested using a number of methods such as gravimetric, isotope dilution (Johannesson, 1964), potentiometric titration of perchlorate with tetr phenylarsonium chloride (Baczuk and Dubois, 1968), ion selective electrodes (Rohn and Guilbault, 1974), and spectrophotometric methods (Fritz et al., 1964; Trautwein and Guyon, 1968). The disadvantage for these methods for testing perchlorate is that they were for bulk analyses and at high concentrations. These methods were also limited by sensitivity and selectivity.

In 1997, California Department of Health Services (CDHS) published a method for testing perchlorate (CDHS, 1997). The protocol had a reporting limit of 4 µg/L. It was through this method that widespread contamination of perchlorate was observed at low limits. Two years later the USEPA published Method 314.0, this was similar to the CDHS protocol (USEPA, 1999). This is the technique that is most currently used today. The USEPA published a modification to Method 314.0, in 2005; this method uses a pre-concentration step. This modification allows for reporting limits as low as 0.14 µg/L (USEPA, 2005).
2.1.5 Remediation of Perchlorate

Treatment technologies that are used to remediate perchlorate are usually in the form of the separation and destruction process (Sellers et al., 2006). Typically, the separation treatment method is for the remediation of ground and surface water that is contaminated with perchlorate, while the destruction method is for soils. Many treatment technologies have been investigated for the removal of perchlorate (Tripp and Clifford, 2006). These include biological (Logan et al., 2001; Logan, 2001; Brown et al., 2005), chemical (Moore et al., 2003; Oh et al., 2006; Cao et al., 2005) and physical (Gu et al., 2000, 2005; Chen et al., 2005; Parette and Cannon, 2005; Parette et al., 2005; Tripp, 2001; Tripp and Clifford, 2003, 2006; Gu and Brown,). The most common and more successful being physical treatment in the form of ion exchange process (Gu and Coates, 2005). The success of the physical adsorption method over chemical and biological reduction processes is due to perchlorate’s kinetic and thermodynamic properties. It is also because of these properties that ground and surface water are more of a concern than soil remediation. Two types of ion exchange method are discussed below.

2.1.5.1 Ion Exchange Treatment

Ion exchange is a method of removing desired ions that are in the solution phase and exchanging them with ions that are associated with solid phase such as resins, granular activated carbon, and soils. This mechanism was carried out by way of electrostatic forces. These solid phases would have been tailored with functional groups that would enable the exchange of ions to occur. In the case of perchlorate, positively
charged functional groups such as quaternary ammonium compounds (a cationic surfactant) are loaded onto resins, which would then attract the negatively charge perchlorate anion in solution. The perchlorate would be exchanged for another anion, usually the Cl\(^-\) ion.

Resins are the more common form of solid phase that have been used in the treatment of perchlorate from contaminated water in ion exchange systems. These can be categorized as being selective or non selective base on their affinity to sorb perchlorate. Extensive studies have been conducted on the selectivity of resins for perchlorate anion (Tripp and Clifford, 2006, 2003; Tripp, 2001) and it was found that strong base ion exchange resins have been quite effective in removing the perchlorate from the aqueous phase (Batista et al., 2000). Tripp and Clifford, (2006) and Boodoo, (2003) observed that polyvinylpyridine resins were highly selective for perchlorate, followed by polystyrene resins, and the least selective were polyacrylic resins. In this case, the selectivity of the resin would be defined as resins that sorb perchlorate strongly in the presence of other competing anions that are typically found in aqueous systems at concentrations much greater than perchlorate, especially in dilute systems. There are also non selective resins that will sorb anions based on the charge and concentrations, example divalent anions would sorb more readily than monovalent anions (Venkatesh et al., 2000). A more detail discussion is presented in section 2.7

According to Gu and Brown (2006), strong base anion exchange resins, such as Type 1 polystyrenic, have the affinity for anions that have a poor hydration energy, such
as perchlorate, over Type II polyacrylic resins. This is because the Type-I resins are more hydrophobic than the Type-II resins. Increasing the length of the trialkyl group, found in the functional group of the cationic surfactants, from methyl to hexyl increases the hydrophobicity of the resins as well as the distance between charges. Therefore, as the chain lengths increase, the selectivity of perchlorate would increase, but a decrease in selectivity of hydrated and divalent anions such as sulfate. This is observed with polyvinylpyridine resins (Table 2-2).

Table 2-2 Effect of resin characteristics upon perchlorate separation factors (Tripp and Clifford, 2003)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Resin</th>
<th>Separation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Linking</td>
<td>IRA-400</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>IRA-402</td>
<td>100</td>
</tr>
<tr>
<td>Matrix</td>
<td>Polyvinylpyridine</td>
<td>275</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>Polyacrylic</td>
<td>6</td>
</tr>
<tr>
<td>Functional Group</td>
<td>Trimethyl</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>Triethyl</td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>

The regeneration of the resin is one aspect in the ion exchange process that is a problem. Selective resins are not usually regenerated because of their strong affinity to the particular anion as with the case of polyvinylpyridine. This strong affinity would require a high concentration of the brine solution to regenerate. Therefore, the alternative is to dispose of the resin after one use; this method has higher operational issues. Non selective resins can be regenerated. Regeneration of these resins is conducted frequently because of their non selectivity. This also incurs additional operational issues and produces large quantities of waste that have contamination (Chiang and Megonnell, 2005, Sellers et al., 2006) and therefore has to be treated as well.
2.1.5.2 Tailored Granular Activated Carbon

Granular Activated Carbon (GAC) has a long and successful history of use in drinking water treatment settings. For example, in 1977, GAC was reported to be used by several hundred municipalities as a substitute for powdered activated carbon due to its high organic removal efficiency (AWWA Committee, 1977). In the United States, GAC is generally used to combat taste and odor problems or to remove volatile organic compounds (VOCs) from groundwater, and as a filtration media. GAC was not historically known to remove perchlorate (Sellers et al., 2006). Patrick, (1995) observed that activated carbons are generally not a good method of removing high solubility contaminants and inorganic salts from aqueous systems. Studies have shown that GAC on its own is not a good treatment system. Parette and Cannon, (2005) observed that perchlorate broke through only after 1,100 bed volumes of perchlorate contaminated groundwater (70 µg/L) was processed through conventional activated carbon.

The technology developed at Penn State is used GAC, a solid phase, upon which a cationic surfactant with a quaternary ammonium functional group is loaded, to treat perchlorate contaminated waters. The cationic functional group would increase the positive charge sites on the activated carbon. This would make the GAC favorable to remove the inorganic ionic species such as perchlorate, which would not normally be highly adsorbed by GAC.
Significantly, the uncharged carbon surfaces are ideally suited to sorb surfactants. Surfactants consist of an uncharged tail (alkyl chain) and a charged head (in this case a quaternary ammonium or pyridinium). The uncharged alkyl tails are attracted to the uncharged carbon surface; while also aligning with each other as micelles. The hydrophilic heads face away from the carbon surface and away from the other alkyl tails, as shown in Figure 2-1. At high concentrations, that can occur within GAC pores, the surfactant micelles can congregate as hemimicelles or hexagonal liquid crystals that have charged heads that orient themselves toward the aqueous solution which can then bind perchlorate. Thus, by preloading the activated carbon with cationic surfactant that consists of alkyl quaternary amines or other active nitrogen groups, a non-charged surface is converted into a highly plus-charged matrix. This creates a unique rigid material, which offers properties that are well suited for capturing the perchlorate anion.

The sorption and binding of cationic surfactants have been studied onto graphite (Xu et al. 2002, Kiraly and Findenegg, 1998); cellulose, clay, quartz, titanium dioxide, zeolites, soils and membranes (Baillarger et al. 1994, Biswas and Chattoraj 1997 and 1997a, Churaev et al. 2000, Esumi et al. 1998, Gzara and Dhabhi 2001, Haggerty and Bowman 1994, Sheng et al. 1998, Wang et al. 1999). However, Penn State University is not aware of others who have explored pre-loading activated carbons with surfactants to enhance anion removal. To date, surfactants that have been successfully used as GAC tailoring agents for the removal of perchlorate from aqueous systems at the lab scale, pilot scale, and field scale level are tallowtrimethyl ammonium chloride (Arquad T-50), dicocodimethylammonium chloride (Arquad 2C-75), and cetylpyridinium chloride (CPC).
and cetyltrimethylammonium chloride (CTAC) (Parette, 2005; Parette et al., 2005; Parette and Cannon, 2005; and Parette, 2006).

Figure 2-1 Hypothesized Micelle Alkyl Quaternary Amine Configuration within Activated Carbon Pores: Planer, Spherical or Cylindrical; or Half-Cylinder on Carbon Surface

The surfactant arrangement offers distinct differences from conventional ion exchange resins, where functional groups rigidly reside in structured positions within the resin framework. Within surfactant tailored GACs, the perchlorate removal mechanism can behave in accordance with an electric double layer type phenomenon (Rosen, 1989), rather than the Langmuir-type bonding, that is observed with ion exchange resins. The surfactants are pre-loaded onto GAC by pumping a concentrated surfactant-water solution cyclically through a GAC bed. The solution cycles through the bed multiple times until the surfactant has been adsorbed to such a point that its water-phase concentration drops below a pre-selected threshold (approximately 0 to 10
milligrams/liter [mg/L]). The GAC bed is then rinsed several times to remove the water-phase surfactant residual and prepare the bed for water treatment service.

This technology is expected to be especially cost effective and suitable for applications where conventional GAC is already in use for taste and odor or organic contaminant removal.

Experiments conducted at Penn State University and during a field-pilot demonstration at Redlands CA, demonstrated that bituminous GAC pre-loaded with cationic surfactants dramatically increases its capacity to remove perchlorate. The cationic surfactants used in this project contained a quaternary ammonium or pyridinium functional group (Parette et al., 2005). These same functional groups have been shown to remove perchlorate in ion exchange resins (Clifford et al., 2004). These quaternary ammonium based cationic surfactants have a high $pK_a$ value and this characteristic renders their charge to be independent of pH in natural waters (Laughlin, 1991). Once the cationic surfactant is pre-loaded onto the GAC, it then acts as an exchange site where perchlorate can be adsorbed.

Other carbon sources have been tested for use in the manufacture of surfactant tailored GAC, such as coconut and wood. Of the three, the bituminous coal based carbons have shown overall the best performance of all of the carbons tested in this role. Coconut had a shorter run time due to less surfactant being loaded (Parette, 2005 and Parette, 2006). This is because coconut carbon predominantly has micropores. The wood
based carbons are mesoporous, and will load more surfactants, but will leach off more surfactants as well (Parette, 2004).

The selectivity of surfactant tailored GAC prepared with various tailoring agents against nitrate ($\text{ClO}_4^{-}/\text{NO}_3^{-}$) was measured (Parette, 2006). The values measured were 33.6 for CPC surfactant tailored GAC, 41.2 for Arquad T-50 surfactant tailored GAC, and 51.0 for Arquad 2C-75 surfactant tailored GAC. In comparison, the selectivity values for trimethylamine functionalized IX resin was 10, triethylamine IX resin was 40, tripropylamine IX resin was 70, and bifunctional IX was 100 (Parette, 2006).

### 2.2 Granular Activated Carbon

Activated carbon is created by hydrothermally treating carbon-based solids, such as bituminous coal, lignite coal, coconut shells, or wood. The pyrolysis step in hydrothermal treatment creates narrow fissures between the graphene plane; and the oxidation step facilitates the gasification of some of the graphene layers so as to create slightly wider spaces between the layers. The carbon layer surfaces are generally uncharged (hydrophobic), and they thus repel water and charged inorganic species such as perchlorate. However, the outer edges of the carbon layers (graphene planes) can carry a charge (Leon y Leon et al. 1994), which is why conventional activated carbons can adsorb a limited amount of perchlorate (Na and Cannon, Chen et al. 2005, 2005a, 2005b). Granular activated carbons have both physical and chemical properties that make it a good adsorbent. The porosity of the GAC, provides a high surface area, and thus makes it a good absorbent. There are 3 categories of pore size used to describe
GAC: microporous (< 2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm in diameter). The pore size can give a GAC a surface area greater than 1000 m$^2$/g, with micropores contributing the most area. Functional group is another property that plays an important role in the adsorptive nature of the GAC, as they provide the charge on the surface of the carbon. Major functional groups that provide a charge on the surface of the carbon are oxygenated groups, protonated amino groups, and graphene layers (Radovic, 1999). Functional groups can exist as acidic or basic groups.

Many studies have been conducted that investigated the treatment of the GAC to change its properties so as to better remove a particular contaminant. These treatments alter the pore structure or the surface chemistry. Heating conditions during pyrolysis can change the pore size of the carbon. Chemical treatments also affect the pore size. These include carbon dioxide, steam (Molina-Sabio et al., 1996), and aqueous oxidants such as HNO$_3$ (Mangun et al. 1999; Moreno-Castilla et al. 1998), hydrochloric acid, and hydrofluoric acid. The type of oxidation treatment will determine the oxygen functional groups that are produced on the surface. GAC can be treated to have basic or acidic functional groups (Mangun et al. 2001; Nowack et al. 2003; Menendez et al. 1996). It is these treatments that improve the ability of GAC to remove inorganics from aqueous systems.

There is much literature that demonstrates adsorption of perchlorate to GAC, but literature found on other anions adsorption will give us an idea of how well GAC works with anions adsorption. One anion that is somewhat similar to perchlorate is the chlorate
anion. It has been demonstrated that GAC can effectively remove chlorite and chlorate from water. Gonce and Voudrias, (1994), observed that chlorite was removed from synthetic water, which had a concentration of 5 mg/L chlorite, at pH 5 for 10,000 BV that translates to a removal of 100 mg chlorite/ g GAC. It was surmised that the method of chlorite removal using GAC was in the form of reduction to chloride. However, unlike chlorite, chlorate was not reduced by GAC, but instead adsorbed. The chlorate anion was observed in the effluent only after 7 hours of treatment, compared to 60 hours for chlorite. Gonce and Vondrias, (1994), found that 98.3% of chlorate was accounted for in a desorption process leading to the conclusion that adsorption was the main mechanism for removal.

Bromate is another anion that can be removed from water using GAC. The anion is adsorbed to GAC and then reduced to bromide. One thing to note is that the presence of other anions such as sulfate and chloride reduced the capacity of GAC to remove bromate (Mills et al. 1996). Kirisits et al. (2000) observed that natural organic matter also reduce the capacity of GAC to remove bromate, by blocking the pores. Other oxyanions that were effectively removed from water using GAC are arsenate (Rajakovic, 1992;), phosphate (Poonghazalli et al., 2001; Ferro-Garcia et al., 1990), dichromate (Aggarwal et al., 1999).

The performance of the GAC depends on pre-treatment, concentration of contaminant applied, presence of competing species, and hydraulic residence time. Spent GAC can be regenerated successfully for reused.
2.2.1 Regeneration of GAC

When activated carbons become exhausted, they can either be regenerated or replaced. Regeneration is usually the more cost effective of the two, and in conventional treatment, GAC can be regenerated to much of its original capacity. Usually GAC can be regenerated a number of times before the performance of the GAC has deteriorated to a point when it is no longer economical to do so.

There are a number of ways that GAC can be regenerated. The regeneration method that is used should be able to remove the adsorbents from the GAC and sufficiently restore its capacity. Regeneration methods of conventional GAC include: thermal, catalytic, supercritical fluids, surfactant enhanced, solvents, microbial, electrochemical, acid, and base treatments.

Thermal is the most common regeneration method for activated carbons. Suzuki et al. (1978) demonstrated three steps for regeneration of GAC. This includes drying the carbon at 105°C, followed by heating the carbon at 650-850°C. This step conducted in an inert gas environment pyrolzes the adsorbed material. Finally the pores are reopen, by removing the charred material at 700-900°C using either carbondioxide, steam or a combination. Accumulation of inorganics on to the GAC can cause some pore blockage, thus diminishing the capacity of GAC to remove the desired contaminant.
Thermal regeneration was shown to be a good method for removing perchlorate and restoring the GAC. Chen et al. (2005) observed a 90-100% restoration of the GAC tailored with NH₃ for perchlorate. Parette et al. (2005) observed a 25% reduction in capacity for perchlorate when GAC is regenerated and then tailored with quaternary ammonium compounds. Parette et al. (2005) contributed the low restoration capacity to not reopening of all the pores that were needed for perchlorate adsorption.

Chemical regeneration is most commonly used to regenerate ion exchange systems that are preloaded with quaternary ammonium compounds. Large volumes of high concentrations of sodium hydroxide are used because of the strong affinity of perchlorate to strong base anion exchange resins. With resins that are less selective for perchlorate, frequent regeneration would be needed. This would incur additional operational parameters to ensure proper treatment and disposal.

Gu et al. (2001) developed a method that uses a novel idea of tetrachloroferrate to displace the perchlorate on anion exchange resins. Gu et al. (2001) observed a 100% restoration of the ion exchange resins to remove perchlorate, with low bed volumes of the regenerant employed. This amounts to less brine solution being treated or disposed of.
2.3 Surfactants

Surfactants are surface active agents, and are characterized as compounds that can absorb to surface and interfaces. Surfactants are used in a wide variety of applications and in many industries such as paint, detergents, paper coatings, food, pharmacy, and water treatment systems. Surfactants are usually referred to as amphiphiles, meaning that the surfactants consist of two parts. In the case of the water environment, these parts are known as a hydrophobic tail and a hydrophilic head. The hydrophobic tail may be branched or linear in formation. The hydrophilic head maybe attached to the end of an alkyl chain that has carbon atoms ranging from 8-18. The type and length of the alkyl chain coupled with the position of the hydrophilic head are important parameters in determining physical and chemical properties of the surfactants. The hydrophilic head may also be classified as an ionic or a nonionic group, as well as cationic or anionic.

2.3.1 Types of Surfactants

Ionic surfactants are divided into three groups: anionic, cationic and zwitterionic as discuss below. Most ionic surfactants are monovalent, but there can also be divalent anionic surfactants as well.

2.3.1.1 Anionic Surfactants

Anionic surfactants are the most popular surfactant in the group. They are mostly used in the detergent industry (Porter, 2001) (Table 2-3). Carboxylate, sulfate and
phosphate are the hydrophilic head groups that are found in anionic surfactants with their counter ions being sodium, potassium, ammonium, calcium, and various protonated alkyls (Holmerg et al. 2003). Soap is the largest and most common single type of surfactant that is derived from animal or vegetable oil. Alkylbenzene sulfonates are the most used and the most popular synthetic surfactants. They are widely used in household detergent as well as a variety of industrial applications. As the name indicates, they are made from the sulfonation of alkylbenzenes (Figure 2-2) (Holmberg et al. 2003).

<table>
<thead>
<tr>
<th>Table 2-3 Important Facts about anionic surfactants (Holmberg et al. 2003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.  Largest surfactant class</td>
</tr>
<tr>
<td>2.  Not compatible with cationics</td>
</tr>
<tr>
<td>3.  Sensitive to hard water</td>
</tr>
<tr>
<td>4.  Sulfates are rapidly hydrolyzed by acids in an autocatalytic process</td>
</tr>
<tr>
<td>5.  Polyoxyethylene chain between the anionic and hydrocarbon group improves salt tolerance and solubility in organic solvents.</td>
</tr>
</tbody>
</table>

![Figure 2-2 A figure depicting alkylbenzene sulfonate, an anionic surfactant. (http://www.who.int/ipcs/publications/ehc/ehc_corrigenda_169.gif)](http://www.who.int/ipcs/publications/ehc/ehc_corrigenda_169.gif)
2.3.1.2 Cationic Surfactants

Cationic surfactants are surfactants that their hydrophilic head groups have a positive charge; this is usually the nitrogen atom (Holmerg et al. 2003; Myers, 1999). Quaternary ammonium (Figure 2-3) and amines are the most common, but others such as phosphonium, sulfonium, and sulfoxonium also exist. Amines only function at the protonated state, while quaternary ammonium is not pH dependent. Other cationic surfactants consist of non quaternary groups, these are also very pH sensitive (Porter, 1991). Quaternary ammonium compounds that do not have an ester group are produced from a fatty acid reacted with ammonia at high temperature.

![Figure 2-3 Schematic of a cetylpyridium chloride cationic surfactant.](http://www.chemblink.com/structures)

The prime uses of cationic surfactants are related to the tendency that they have, to adsorb to surfaces such as metals, minerals, plastics, and fibers, to name a few. They are useful for pigment dispersion and many of them have germicidal and fungicidal effects.

2.3.1.3 Zwitterionic Surfactants

Zwitterionic surfactants are compounds that have two charged groups of different charge, with the positive charge being an ammonium cation and the negative charge
being variable, with carboxyl group being the most common. Zwitterionic surfactants are compatible with any other classes of surfactants and are not sensitive to hard water. They are stable in acid and bases (Holmerg, et al. 2003).

2.3.2 Surfactant Adsorption to Solid Surfaces

In aqueous solutions (i.e. without GAC), at values below the critical micelle concentration (CMC), surfactants would appear as single molecules in solution, when CMC is reached, surfactants molecules can arrange themselves into micelles (Figure 2-). These micelles may be spherical in shape. Above CMC, the surfactant forms rod-like micelles (Nagarajan, 2003). Globular micelles can also be formed, when micelles cannot pack any closer in spheres, and if equilibrium conditions are not met for rod-like formations (Israelachvili et al., 1976). Error! Reference source not found. lists some common surfactants and their respective CMCs. A low CMC indicates that micelle formations occur at a low surfactant concentration. For example, a surfactant that has a longer hydrocarbon chain will have a low CMC. Another example, is a high degree of counter-ion binding results in a lower CMC. Extensive research has been directed in determining the physical and chemical properties that describe micelle formation (Gotz and Heckman, 1959; Reiss-Husson and Luzzati, 1964; Hoffman et al. 1982; Backlund et et al., 1982). Imae et al., (1985) showed that a concentration of 19.2 g/L of cationic surfactant changes the micelle shape from spherical to rod like, while only 450 mg/L is needed for spherical formation of micelles for CTAC (Velegol et al., 2000). The value of CMC is dependent on the nature of the hydrophilic part of the surfactant as well as the
length of the hydrocarbon chain (Nagarajan, 2003). The longer the hydrocarbon chain, the lower the CMC due to greater hydrophobic interactions. The intermicellar interaction energy is an important part in the aggregation process. The type of micelle is determined by the surface area. An increase in micelle concentration suppresses the intermicellar interaction energy and the system will then move to a more favorable type of micelle (Mikulski, 1993). Mikulski, (1993) showed that an increase in concentration, the interaction energy per molecule is increase until it finally reaches a level that rod-like micelles are formed and is the most stable. The formation of micelles is important as it affects many processes and properties of the surfactant, properties such as solubility, adsorption, wetting, and foaming. The existence of surfactant phases depend on its structure, the hydrophilic head group, concentration and the counter ion that is associated with the molecule. Mikulski, (1993) stated that with the absence of an additive, micelles appear spherical at a concentration that is close to the CMC and as the concentration increases rod-like micelles are formed.

Figure 2-4 Schematic diagrams of HDTMA (cationic surfactant) micelle formation in solution and on the zeolite surface. (http://www.ees.nmt.edu/bowman/research/SMZ/ZeoSurfInt.html)
Table 2-4 List of CMC values for some quaternary ammonium surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC (mol/Kg H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecylammonium chloride</td>
<td>1.47 x 10⁻²</td>
</tr>
<tr>
<td>Dodecyldimethylammonium chloride</td>
<td>2.03 x 10⁻²</td>
</tr>
<tr>
<td>Decyltrimethylammonium bromide</td>
<td>6.5 x 10⁻²</td>
</tr>
<tr>
<td>Dodecyldimethylammonium bromide</td>
<td>1.56 x 10⁻²</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium bromide</td>
<td>9.2 x 10⁻⁴</td>
</tr>
<tr>
<td>Dodecylpyridinium chloride</td>
<td>1.47 x 10⁻²</td>
</tr>
</tbody>
</table>

Adapted from Holmberg et al. 2003

Surfactant adsorption to solid phases can be divided into two categories: the type of surface (hydrophobic or hydrophilic) and the type of surfactant (nonionic and ionic). For this research, hydrophobic surfaces, as in the case of GAC and cationic surfactants were used. For hydrophobic surfaces, the adsorption of surfactants at low concentration is primarily due to the attraction of the hydrophobic tail to the surface. As the concentration of the surfactant increases, monolayer type or hemimicelles surfactants aggregates may be formed on the hydrophobic surface. As concentrations reach the CMC these hemimicelles may gradually transform into monolayer or surface micelles. It should be noted that the formation of the surfactant aggregates at the surface at different concentration is dependent of the properties of the surfactant as well as the surfactant-surface interactions.

The adsorption of a surfactant to a solid phase is controlled by three main factors: 1) the chemical make up of the surfactant; 2) the nature of the solid surface that would adsorbed the surfactant; and 3) the nature of the liquid environment (Chattoraj et al., 1996). Adsorption mechanisms include molecular interactions involving electrostatic
attractions, as well as van der Waals forces (Chattoraj et al., 1996). Research studies have indicated that the adsorption of cationic surfactants to solid surfaces occurs first by electrostatic interaction between the charged group and the anionic surface (Chattopadhyay and Mittal, 1996). Once the surface charge is neutralized, adsorption continues by way of the hydrophobic tails. The hydrophobic tail is directed toward the interior of the cluster and the hydrophilic head towards the solvent. This process is known as self assembly, and surfactants can assemble in many different structures (Chattoraj et al., 1996).

Adsorption of cationic surfactants to carbon surfaces was studied using an atomic force microscope (AFM). This method has been used to investigate the structure of the surfactant on many different solid phases such as graphite (Manne et al. 1994; Wanless et al, 1996; Liu and Ducker, 1999), mica (Lamont and Ducker, 1998), gold (Jaschke et al. 1997) and silica (Liu and Ducker, 1999; Grant et al. 1998). It has been found by AFM images that surfactants form cylindrical micelles at high concentrations or spherical micelle at low concentrations (Manne and Gaub, 1995). Figure 2-5 gives a proposed micelle formation of CPC, cationic surfactant, used in this research, on to GAC surface. It was also found that at low concentration, cationic surfactants form a flat monolayer on the surface of graphite.
Figure 2-5 Schematic diagram of CPC micelle formation in solution and on a GAC surface.

Parette, (2005) studied the structural formation of dodecyltrimethylammonium chloride (CTAC) in the pores of GAC. It was speculated that based on the loading of CTAC to the carbon and also the pore volume that has pores greater than 53 Å, half cylindrical micelles are formed on the GAC surfaces with rod micelles or hexagonal liquid crystals in between the pores that are above 53Å. This half cylindrical micelles structures formation were also observed in studies conducted by Manne and Gaub, (1995) and Kiraly and Findenegg, (1998), when they used CTAC.

The counter ions play a critical role in the adsorption mechanism. Counter ions bring stability to surfactant micelles by binding the micelle surface as well as screening the electrostatic repulsions between charged groups. This property of the counter ion increases the affinity to the anions based on the ion exchange constant.
The sorption of surfactants to solid surfaces has many uses one being in environmental applications by way of remediation of contaminated aqueous systems. Zhao and Vance, (1998) sorbed cationic surfactants on to clays to purify water; Brown and Burris, (1996) remediated contaminated groundwater and Jiang et al. (2002) treated industrial wastewater. Chromate removal by HDTMA modified zeolite was studied by Haggerty and Bowman, (1994).

2.4 Intermediate Valence Sulfur Species

Polythionates (S₈O₆²⁻), thiosulfate (S₂O₅²⁻), and polysulfides (Sₙ²⁻) are intermediate sulfur species that may be found in natural water environments. They can be produced during the bacterial degradation of metal sulfides such as pyrites or the oxidation of the reduced sulfur species hydrogen sulfide (H₂S). These species are often referred to as intermediate sulfur species because their oxidation states are between hydrogen sulfide, the most reduced (−2), and sulfate, the most oxidized (+6) (Table 2-5). These intermediate valence sulfur species play an important role in the oxidation of H₂S as well as redox transformations of other sulfur containing compounds in the environment (Druschel et al. 2003b,c). Based on kinetic and thermodynamic principles, the concentration of thiosulfate and polythionates should be less than 0.01% of the total sulfur concentration in an environment (Druschel et al., 2003a). However, research that has been conducted indicates that some of these intermediate valence sulfur species are abundant in different systems such as acid crater lakes (Veldeman et al., 1991) and gold
ore leaching (O’Reilly et al., 2002) for polythionates; hydrothermal waters in New Zealand (Webster, 1987), Bulgaria (Veldeman et al., 1991) and the Yellowstone National Park (Xu et al., 2000) for thiosulfate. Concentrations of these species range from 5 to a few hundred micro moles per liter. With this high concentration of intermediate sulfur species found in natural waters, it is speculated that these are formed from the slow and incomplete redox reactions of H\textsubscript{2}S and sulfate.

Determination of the kinetics of these species is important for a better understanding of their environmental processes, such as the formation of different sulfur compounds. Competition between disproportioning rates and complex formation rates will ultimately determine the speciation of intermediate sulfur complexes in the environment.

As was previously mentioned the key compound for the formation of these intermediate sulfur species is H\textsubscript{2}S. Hydrogen sulfide is a toxic, harmful compound that paralyzes the olfactory nerves at high concentration. The production of H\textsubscript{2}S in groundwater is brought about by the microbial processes in the sulfur cycle by degrading plants and animals in anaerobic, anoxic, and reduced environments. Equations 2-1 and 2-2 depict the processes that produce H\textsubscript{2}S.

\[
\text{SO}_4^{2-} + \text{Organic matter} \xrightarrow{\text{bacteria}} S^{2-} + H_2O + CO_2 \quad \text{Equation 2-1}
\]

\[
S^{2-} + 2H^- \rightarrow H_2S \quad \text{Equation 2-2}
\]
The presence of H$_2$S in the groundwater is highly dependent on pH (Haimour et al. 2005). As pH increases, concentration changes between bisulfide (HS$^-$), sulfide (S$^{2-}$), and H$_2$S in groundwater systems (Figure 2-4) (Thompson et al. 1995). At pH between 5.0 and 6.0 H$_2$S is the dominant species. According to Haimour et al. (2005), H$_2$S is volatile species that can be removed by aeration. Removal of H$_2$S by aeration at pH greater than 6.5 poses a problem because HS$^-$ is the dominant species and it is not very volatile. This allows for the formation of intermediate valence sulfur species (Table 2-5) such as polysulfides, polythionates, and thiosulfate in groundwater, which may lead to problems within treatment systems. In the following sections we will discuss these intermediate valence sulfur species as they relate to the removal of perchlorate using tailored activated carbon.

**Table 2-5 Species of sulfur based ions and their valence state**

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>FORMULA</th>
<th>S VALENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide, Bisulfide</td>
<td>H$_2$S, HS$^-$</td>
<td>-2</td>
</tr>
<tr>
<td>Elemental Sulfur</td>
<td>S</td>
<td>0</td>
</tr>
<tr>
<td>Hexathionate</td>
<td>S$_6$O$_6$</td>
<td>+1.67</td>
</tr>
<tr>
<td>Pentathionate</td>
<td>S$_5$O$_6$</td>
<td>+2</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>S$_2$O$_3$</td>
<td>+2</td>
</tr>
<tr>
<td>Tetrathionate</td>
<td>S$_4$O$_6$</td>
<td>+2.5</td>
</tr>
<tr>
<td>Trithionate</td>
<td>S$_3$O$_6$</td>
<td>+3.33</td>
</tr>
<tr>
<td>Sulfite</td>
<td>SO$_3$</td>
<td>+4</td>
</tr>
<tr>
<td>Dithionate (Hydrosulfite)</td>
<td>S$_2$O$_6$</td>
<td>+5</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SO$_4$</td>
<td>+6</td>
</tr>
</tbody>
</table>
2.4.1 Thiosulfates and Polythionates.

Polythionates are sulfur based molecules that are important intermediate species in the sulfur chemistry of many environments and also metabolic process of sulfur oxidizing and sulfur reducing microorganism. The formation of polythionates can occur through redox reactions or nucleophilic displacement and predominantly exist between pH 3 and 7 (Moses et al. 1987). Polythionates vary in chain length from 22 in bacteria sulfur excretions to 80 in sulfur sols (Druschel et al. 2003c; Steudel et al. 1987). Polythionates that have sulfur chains lengths between 3 and 6 (Table 2-5) are more dominant especially in aqueous systems (Druschel et al. 2003c). Hydrogen sulfide and SO\(_2\) are key compounds that form polythionates. The displacement reactions which lead to chain lengthening or shortening are governed by equation 2-3. These reactions usually occur at pH less than 7. Polythionates can also be formed through hydrolytic reactions (equation
2-4) and the through the oxidation processes of thiosulfate and metal oxides such as pyrite (Xu et al. 2000)

\[ S_xO_3^{2-} + S_2O_3^{2-} \rightarrow S_{x+1}O_3^{2-} + SO_3^{2-} \quad \text{Equation 2-3} \]

\[ 2S_xO_6^{2-} + H_2O \leftrightarrow S_{x-1}O_3^{2-} + SO_4^{2-} + 2H^+ \quad \text{Equation 2-4} \]

The formation of these intermediate sulfur species is very complex. They can react with themselves to form new sulfur species or react with the starting material that they were produced from to form other sulfur species. An example of this is the oxidation of thiosulfate to form tetrathionate. Tetrathionate can then react with the unreacted thiosulfate to form pentathionate and even higher polythionates.

Observations have shown that thiosulfate and polythionates oxidize from H₂S in circumneutral pH rather than at low pH (Elberling et al., 2000). Polythionates are not the predominant or stable form of sulfur in the oxygenated environment, but represent an important intermediate along the oxidation and reduction pathways between more reduced and intermediate sulfur species, and sulfate.

Thiosulfate is notably found in natural hydrothermal systems as well as in industrial wastewater systems; and has been recognized as an important intermediary species in the oxidation of sulfur compounds. Jorgensen, (1990) identified thiosulfate decomposition as an important process for coupling oxidative and reductive pathways in the sulfur cycle. Thiosulfate is also important in the transport of precious metals. For
example thiosulfate is beneficial in the gold ore industries as it complexes with metals making it easier to leach the metals (Abbruzzese et al., 1995; Aylmore et al., 2001; Breuer and Jeffery 2003a,b, 2002).

In natural environments where pH values are at 7 to 8.5, thiosulfate is formed from the gradual oxidation or the incomplete redox process of hydrogen sulfide en route to oxidizing to sulfite and sulfate. Thiosulfate can also be produced from the decomposition reactions of many polythionates with hydrogen sulfide as well as hydrolysis of these reduced species (Xu et al., 2000). Thiosulfates are also produced during the bacterial degradation of pyrite and other metal sulfides (Schippers et al., 1996). The decomposition of thiosulfate in natural aqueous systems is not fully understood. It has been found that thiosulfate formation occurs under low pH and at room temperature between bisulfite and sulfite and tends to accumulate in systems that have cations such as sodium (Na\(^+\)) and calcium (Ca\(^{2+}\)). Ueno (1976) studied the removal of sodium sulfide using various oxidants at temperatures ranging between 30 - 80 degrees C and at pH values between 10 and 12. Under these conditions thiosulfate and sulfate were produced with molar concentration ratio of 2:1. Hoffman and Lin (1979) also studied the oxidation of sodium sulfide with air at ambient temperature and pH values between 5.5 and 12.1. Thiosulfate, sulfite, sulfate and colloidal sulfur were observed; and the molal percent concentration for thiosulfate ranged from 11 to 51 percent. Sulfate was the only other compound that had a molal concentration percent greater than thiosulfate which ranged from 44-64 percent. Karchmer, (1970) found that passing H\(_2\)S intermittently through an acidic solution of sulfite produces thiosulfate.
The decomposition of thiosulfate is a very critical process in controlling its concentration, which has been the basis of many researches that have been conducted. It has been known that thiosulfate decomposes by a number of different pathways. The following are known pathways:

- To sulfite and elemental sulfur in weak acid
- To sulfate and sulfidic sulfur, S(-II), in strong acid or in neutral to alkaline solutions under the catalysis of certain bacteria or at elevated temperature;
- To hexathionate in the presence of sulfidic sulfur in strong acid
- To tetrathionate in the presence of oxidants such as iodine, Au (III), MnO$_4^{-}$, and Fe (III).

The next plausible step after thiosulfate production would be the reaction between sulfide and thiosulfate to form elemental sulfur. This step is slow and thus can lead to the accumulation of thiosulfate in the system. This was verified by Kundo et al. (1987), where it was shown that the reaction was dependent on the rate of change of gaseous H$_2$S to aqueous H$_2$S. With accumulation of thiosulfate in an aqueous system, polythionates are formed from the degradation of thiosulfate. An example of this is seen where metals such as copper (Cu$^{2+}$) can oxidize thiosulfate to form tetrathionate in the absence of oxygen. The reaction in the presence of oxygen is less likely to occur. According to O’Reilly et al. (2002), when tetrathionate is form, other polythionates can be form through various decomposition steps, as observed previously in this section. This depicts how important thiosulfate is, in the formation of other intermediate valence sulfur
species. It is for this reason that thiosulfate was chosen as the intermediate valence sulfur species that would be a representative for the other intermediate sulfur species in this study. Factors such as pH, temperature and ionic strength play a role in the formations of intermediate valence sulfur species. Xu, (1997) showed that the stability of thiosulfate is highly dependent on pH and temperature.

Thiosulfate has also been extensively used in industrial operations as a reducing agent specifically to dechlorinate systems (Bedner et al., 2004; MacCrehan et al., 2005) such as drinking water, cooling towers, or effluents from sewage systems; bleaching operations in textile mills and paper-pulping facilities; or cyanide destruction operations (Plaks and Fochtman, 1978; Tincher, 1978; White, 1978; Szal et al., 1991; Stewart et al., 1996).

Thiosulfate along with other intermediate valence sulfur species are not well understood or studied in the natural environments as it pertains to groundwater contamination from the formation processes described above. The formation and accumulation of these sulfur species ions in aqueous systems can compete strongly with other anions on exchange sites, thus lowering the effectiveness of treatment systems in removing the desired contaminants. For example, tetrathionate will compete with gold thiosulfate on ion-exchange resins therefore affecting the recovery of gold (O’Reilly et al., 2002). The characteristics of the environments where decompositions and oxidations processes occur are not fully understood.
Chun et al. (2000) looked at polythionates interaction with amminehalocobalt (III). It was found that when tetrathionate interacted with this compound, an unexpected cleavage occurs to form an S-S bond, which is followed by a disproportioning process to form the pentathionate ion that is attached to the amminehalocobalt. These observations can lead to the speculation of interactions between polythionates ions with each other through displacement or disproportionate processes when they are attached to cationic amine groups. If this analogy does occur, then treatment systems and other processes that have ion exchange sites will have great competition between other anionic compounds and these polythionates or intermediate sulfur species when present in the system. A case in point is the inhibition of perchlorate adsorption to the cationic sites of quaternary ammonium compounds that were tailored to granular activated carbon. With polythionates such as thiosulfate, trithionate and tetrathionate, occupying these sites, there would be limited sites left to adsorb the perchlorate anion, therefore decreasing the effectiveness of perchlorate removal from environmental natural systems by the tailored GAC.

2.4.2 Dithionite

The oxidation of alkaline sodium dithionite by molecular oxygen has been widely studied (Camacho et al., 1992; Rinker et al., 1960; Morello et al., 1964; Singh et al., 1978; Kawagoe and Robinson, 1981). Dithionite (S$_2$O$_4^{2-}$) with a sulfur valence of +3 is used in the textile industry, because of its high reducing power. Dithionite is also used in kinetic studies on oxygen transport in the hemoglobin. Dithionite will oxidize to sulfite
and eventually to sulfate, this reaction is very fast, especially in homogeneous solutions where the dithionite concentrations are great. Camacho et al., (1996) demonstrated that at a pH greater than 8, dithionate oxidizes to sulfite in the presence of molecular oxygen. These experiments were conducted at temperature between 20 and 45°C. This implies that $\text{S}_2\text{O}_6^{2-}$ can oxidize to sulfite under environmental conditions. Kawagoe and Robinson, (1981) observed an activation energy of 76 KJ/mol for the oxidation of dithionite by molecular oxygen, at pH greater than 8, and temperature ranging from 15-35°C. These experiments were conducted in heterogeneous conditions and dilute dithionite concentrations. With these observations, it can be concluded that dithionite may oxidized to sulfite in aqueous systems that represents the groundwater environment.

### 2.4.3 Dithionate

Dithionate ($\text{S}_2\text{O}_6^{2-}$), a sulfur-valence of +4, is a byproduct of oxidation reactions for some sulfur species, specifically sulfite. The dithionate ion is quite inert in aqueous solution at room temperature but it becomes more reactive as the temperature increases (Lente and Fabian, 2004). Studies have shown that dithionate formed in iron (III) – sulfite systems may accumulate (Lente and Fabian, 2004; Brandt and Eldik, 1997). According to Podkrajsek et al., (2002), the oxidation of dithionate by oxygen is uncertain. No observation of dithionate production was observed in the presence of oxygen, when sulfite oxides were used (Deister and Warneck, 1990; Fischer and Warneck, 1996). Lente and Fabian, (2004) observed no oxidation or disproportionation of dithionate in the presence of dissolved oxygen and other oxidizing agents. So this suggests that dithionate
could alter the overall reaction in a treatment system and potentially be a competitive species as well, if it is formed in the oxidation of reduced sulfur species, on its way to sulfate.

2.4.4 Polysulfides

Inorganic polysulfides and their protonated forms also play an important role in many fields of sulfur chemistry. They are readily obtained by oxidation of hydrogen sulfide solutions at basic pH, reaction of H\textsubscript{2}S and sulfur, or by the disproportionation of thiosulfate. Polysulfides are also found in anoxic as well as oxic aquatic environments, where even at low concentrations they play an important role in relevant processes. This is due to their redox reactivity and high nucleophilicity (Kamyshny et al. 2004). Studies on the rate of dissolution in aqueous HS\textsuperscript{−} solution show a first order reaction between elemental sulfur in the S\textsubscript{8} form, and HS\textsuperscript{−} with respect to H\textsubscript{2}S.

According to Boulegue and Michard (1978), it was observed that the transformation between tetrasulfide and higher polysulfides are most important in aquatic systems between pH levels of 7 and 12.5. Gun et al. (2000) and Licht and Davis, (1997) observed that, thermodynamically, aqueous polysulfide solutions are unstable and readily decomposed to thiosulfate and sulfite, in accordance with the observed net consumption of dissolved sulfur. This reaction is not reversible. So it can be suggested that this is one of the many ways to produce thiosulfate.
2.4.5 Analytical Processes for Intermediate Sulfur Species

The analytical determination has become very important as it relates to many processes in the chemistry environment. As previously noted, the chemistry of sulfur species in aqueous solution is quite complex, as they can take part redox processes as well as nucleophilic displacement. These are at least two reasons why accurate testing of sulfur species is difficult. The analysis of these intermediate sulfur species poses a problem as these intermediate species of sulfur are similar in chemical and physical properties. Some reduce sulfur species such as sulfite and sulfide will decompose in air, some more rapidly than others dependent on the environment that they are exposed to e.g. light. Some sulfur compounds may require pretreatment as in the case of sulfite that requires a stabilizing agent to accurately analyze for it (O’Reilly et al. 2001). With thiosulfate, tetrathionate and other polythionates, the decomposition of these species is dependent on the pH of the solution. Thiosulfate as discussed below will decompose to sulfite and elemental sulfur in acidic solutions at pH less than 5 and is stable in solutions that have a pH of 7 and greater, while other polythionates such as trithionate, tetra and pentathionate are unstable and will decompose to thiosulfate and other intermediate sulfur species.

Anion exchange and ion-interaction chromatographic have been the most extensively used methods for the detection of sulfur anions. Anion exchange is more suitable for sulfur species such as sulfide, thiosulfate, sulfate and sulfide (Miura and Watanabe, 2001; Miura and Kawai, 2000). Ion–interaction chromatographic methods
that use UV detection (Chapman and Beard, 1973; Weir et al. 1994), conductivity detection (Rabin and Stanbury, 1985) are methods that were proposed for polythionates detection. The late elution of hexathionate becomes a problem due to its strong retention on the separation column. Steudel and Holdt, (1986) separated thiosulfate and polythionates at a detection of 254 nm in wavelength. The author would like to point out that there is no one way of accurately storing aqueous phases of intermediate sulfur species for longer than several days.

The separation selectivity of sulfur species for anion exchange chromatography is $S_2 \leq SO_3^{2-} \leq SO_4^{2-} \leq S_2O_3^{2-} \leq S_2O_6^{2-} \leq S_nO_n^{2-}$ (O’Reilly et al. 2001). This selectivity for anions that were monitored was observed in our study using the DX 120 ion chromatograph from Dionex.

Other methods of testing for sulfur anions include capillary electrophoresis (Padarauskas et al. 2000; Jandik and Bonn, 1993; Salomon and Romano, 1992; Motellier and Descostes, 2001), planar chromatographic techniques (Blasius et al. 1968; Roy and Trudinger, 1970), ion exclusion chromatography (Wagner, 1995), reversed-phase liquid chromatography (Rethmeier et al. 1997; Steudel et al. 1990; Henshaw et al. 1997), gas chromatography, isotachophoresis (Janiczek, 1998), and capillary electrochromatography (Kitagawa et al. 1997).
2.5 Oxidation of Reduced Sulfur Compounds to Intermediate and Oxidized Sulfur species

Groundwater is a major source of drinking water in many communities across the country, and with the thermodynamic and kinetic nature of reduced and intermediate sulfur species, discussed in the previous section, it can be concluded that they can be found in abundance in groundwater systems. It has also been observed that reduced sulfur species, specifically $\text{H}_2\text{S}$ and $\text{HS}^-$, found in the groundwater can be problematic in water treatment systems as it relates to maintenance as well as treatment processes (Levine et al., 2004). At low concentrations, reduced sulfur species, specifically $\text{H}_2\text{S}$, have the odor of rotten eggs making it an environmental nuisance; and at very high concentrations these species can severely damage the olfactory nerves, which can result in death. $\text{H}_2\text{S}$ is a common contaminant in very reduced groundwaters, and in the progression of the reduced sulfur species in groundwater becoming oxidized ultimately to $\text{SO}_4^{2-}$; with intermediates that can persist for time frames of hours to days including $\text{S}_2\text{O}_3^{2-}$.

Some water treatment methods that have been used to mitigate the deleterious effects of sulfides include aeration or oxidation to $\text{SO}_4^{2-}$. Oxidants that effectively oxidize reduced sulfur species to $\text{SO}_4^{2-}$ include chlorine, ferrate, hydrogen peroxide, permanganate and ozone (Levine et al. 2004). Chemical requirements for complete oxidation depend on the pH and temperature of the solution. Table 2-6 gives an overview of the different oxidizing agents and their dose to oxidize 1 g of reduced species. Aeration and chlorination are discussed more in detail below.
Table 2-6 Comparison of oxidizing agents for the oxidation of Hydrogen sulfide*

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Dose (g/ g of H₂S)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acidic</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2.1</td>
<td>8.3</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>3.3</td>
<td>13.2</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>1.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Ozone</td>
<td>5.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Ferrate</td>
<td>2.7</td>
<td>4.4</td>
</tr>
</tbody>
</table>

*From Cadena and Peters, 1988 and Levine et al. 2004

2.5.1 Aeration

Aeration is one popular method of removing reduced sulfur species from water treatment systems. This reaction is pH dependent. In acidic environment, H₂S sulfide is the dominant species, and is oxidize to colloidal sulfur. In alkaline, HS⁻ is the dominant species, and is usually oxidize to sulfate. The demand of an oxidizer ultimately affects the oxidation process. Too little or two weak an oxidant will result in incomplete oxidation, but more oxidized forms of sulfur may not be produced, this allows for intermediate sulfur species to be present. When this occur, depending on the environment, and the thermodynamic and kinetics properties of these intermediate species, these compounds may be stable and the oxidant used may not be able to fully oxidize them to SO₄²⁻. Aeration is observed as an oxidant that cannot fully oxidize reduced and intermediate sulfur species specifically S₂O₃²⁻ and its intermediates to SO₄²⁻. Many researchers’ have observed the incomplete oxidation of intermediate sulfur species to SO₄²⁻. Zhang and Dreisinger (2002), Lam and Dreisinger (2003) and Breuer and Jeffrey (2003a, b) studied the kinetics of S₂O₃²⁻ and polythionate degradation in different
systems. They observed that aeration could not fully oxidize $S_2O_3^{2-}$ and its intermediates to $SO_4^{2-}$. Research by Senanayake (2004) reported that lower oxygen concentrations decrease the rate of $S_2O_3^{2-}$ oxidation and Rolla and Chakrabarti (1982) noted that air oxidation of $S_2O_3^{2-}$ under normal pressures and temperatures is a slow process. Rolla and Chakrabarti (1982) observed that oxidation of $S_2O_3^{2-}$ to $SO_4^{2-}$ was linear in solutions where the pH is greater than 7, at a range of 3-10 atm, and 125$^0$C. No reaction was observed in the absence of oxygen. Chu et al. (2003) showed that intensely oxygen sparging water that contained $S_2O_3^{2-}$ with 200 cm$^3$ O$_2$ per minute, the $S_2O_3^{2-}$ had decreased only by 10% after 10 minutes sparging and 40% after an hour of oxygen sparging. If such intense oxygen sparging were applied in water treatment applications (if even practical) it would mean that after an hour of oxygen sparging, most of the $S_2O_3^{2-}$ would still be present. This would leave $S_2O_3^{2-}$ to compete for exchange sites and this presence would decrease the ion exchange capacity to remove other anions. Millano et al., (1983) observed no significant decrease of $S_2O_3^{2-}$ in synthetic waters after 24 hrs of contact with air.

In many treatment plants, aeration is the first process implemented to remove H$_2$S from treatment systems, followed usually by a chemical treatment such as chlorine. This implies that a greater oxidizing power than oxygen is needed to oxidize these species to $SO_4^{2-}$.
2.5.2 Chlorination

Chlorine was discovered in 1744 in a laboratory in Sweden. A century and a half later, chlorine and chlorine-containing products were evaluated as a method to inactivate disease-producing organisms. The earliest use was recorded in Louisville, Kentucky in 1896 and England in 1897. Belgium was the first country that continuously uses chlorine for coagulation and for making the water biologically safe. This started in 1902. In 1908, Jersey City, NJ became the first city in North America to continuously use chlorine as a disinfection method (AWWA, 1973). Under specific conditions, chlorine can react with most elements, some very rapidly. It has a great affinity for hydrogen, so it will remove hydrogen from some compounds, one example is hydrogen sulfide (Equation 2-3). Chlorine is a strong oxidizing agent that reacts with water to form hypochlorite ions. It is the hypochlorite ion that oxidizes the sulfur species.

\[
\text{H}_2\text{S} + 4\text{Cl}_2 + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 8\text{HCl} \quad \text{Equation 2-3}
\]

Chlorination is commonly used in water treatment facilities and has been used for disinfection, oxidation, and also for taste and odor control (AWWA, 1973; Suidan et al. 1977). Chlorine has conventionally been the least expensive oxidant in a potable water treatment context; and it has been commonly used to oxidize hydrogen sulfide to \(\text{SO}_4^{2-}\). This reaction could be a two stage reaction in which intermediate sulfur species are first formed, followed by sulfate. The reaction rate is a function of pH and temperature.
Black and Goodson (1952) reported that 2.1 moles of chlorine was needed per mole of sulfide, while 8.33 moles is needed per mole of sulfate.

For this study it is not anticipated that formation of colloidal sulfur will occur, this is due to the reduced sulfur species that is investigated are more oxidized than elemental sulfur, but more reduced that sulfate, and also colloidal sulfur is produced only in an acidic environment. An acidic environment was not observed in this study, the average pH is 7.8. The oxidation of thiosulfate can proceed through a series of reactions, forming first tetrathionate, trithionates, sulfites and finally sulfates (Zhang and Dreisinger 2002; Lam and Dreisinger 2003 and Breuer and Jeffrey 2003a, b; Chu et al. 2003). These formations are pH dependent. In solutions that are typical for groundwater environment, the reaction normally proceeds to sulfates. It is expected that full oxidation to $\text{SO}_4^{2-}$ will occur in this study.

2.5.2.1 Chlorine and Activated Carbon

Activated carbon has been used to the dechlorinate waters and wastewater. Hassler, (1967) and Martin and Shackleton (1990) observed that activated carbon can dechlorinate water through a combination of adsorption and catalysis processes. The HOCl / OCl can cause oxidative degradation of the carbon, yielding oxygenated substituents (Snoeyink et al., 1981) such as carboxylics whose negative charge could repel the perchlorate anion. Also, chlorine could oxidize the reduced – N in the quaternary ammonium functionality, thus impairing the carbon surface of its adsorptive functions.
Sustituents such as acidic functional groups (Snoeyink et al. 1981) that are produced by chlorine oxidation on the surface of the carbon can occupy important adsorption sites that would be needed for (in this case) ClO$_4^-$ attachment. This will therefore lead to a decrease in the surfactant tailored GAC capacity to remove ClO$_4^-$ due to the surfactant tailored GAC becoming exhausted with chlorine atoms. Similar results were observed by Martin and Shackleton (1990) who reported that granular activated carbon (GAC) dechlorinates water. Martin and Shackleton (1990) recorded a 20% removal of chlorine after 160 minutes. Martin and Shackleton (1990) also showed that chlorine removal by carbon is more of a chemical reaction than physical adsorption.

Snoeyink et al., (1981) also observed no visible sign of chlorine in the effluent samples, when chlorine solution was pumped through activated carbon. These results were expected as Snoeyink et al. (1981) saw production of organic acid substituents by the chlorine carbon reaction at high chlorine dosage 2.5g /g carbon and high pH (11.5). According to Snoeyink et al. (1981) the kinetics of free chlorine-activated carbon reactions will affect the adsorptive properties of the carbon only when a large amount of chlorine is being used, or through prolonged exposure. In light of this literature, the Penn State team then decided only to use the stochiometric amount of chlorine needed to oxidize S$_2$O$_3^{2-}$, therefore eliminating any effects that residual chlorine may have on the GAC or quaternary ammonium functional group in a manner that could be detrimental to the adsorption of ClO$_4^-$. 
2.6 Why does Thiosulfate compete but not Sulfate?

The size of mesopores is an important factor in the application of tailoring GAC with cationic surfactants; this is due to pore size being a determining factor for the access of materials like surfactants to mesopores (Park et. al., 2008). Parette, (2004) assumed that the majority of surfactant loading occurs in the mesopores of the GAC. Spherical and rod like micelles could be formed in these mesopores, this type of micelle formation is dictated by concentration of the surfactant that is being used.

The surface area of Ultra Carb is 870 m$^2$/g, and a surfactant loading of 0.22 g of Arquad 2C-75/g GAC, the length of Arquad 2C-75 molecule was calculated to be 3 nm. The calculated available pore volume for mesopores with UltraCarb GAC is 0.24 ml/g. This calculates to a concentration of 1200 g/L within the pores. At these high concentrations it can be assumed that rod shaped micelles would form if they were in aqueous solution; and as a first approximation, we could anticipate a similar structure within the GAC mesopores, as adapted to GAC’s hydrophobic surface. Such rod shaped micelles could contain 700 – 800 Arquad 2C-75 molecules per layer, with each layer being 0.9 - 1 nm apart and have a diameter of 6 nm.

Divalent ions such as sulfate and thiosulfate need to have exchange sites that are closely spaced, this will satisfy the need for two charge sites. The spacing of the functional group affects the selectivity of divalent ions such as sulfate and thiosulfate (Clifford and Weber, 1983). In order for a divalent ion to attach itself to the positive sites
on surfactant loaded GAC, that are present in a rod shape format, the length of the ions would have to be at least the distance that is observe between two charged sites in the rod-like micelle. This would be the distance between each surfactant molecules. For Arquad 2C- 75 this would correlate to divalent ion such as sulfate and thiosulfate being at least 0.15 nm in length. Size exclusion studies that have been conducted showed that the size of sulfate anion is 0.149 nm (Nickless, 1968) this is less than the distance between the two positive sites that is needed by sulfate. This suggests that the sulfate cannot compete for adsorption sites because of the length of the anion. On the other hand it appears that the thiosulfate ion is large enough, with a length of 0.197 nm (Nickless, 1968; Senning, 1972), to occupy the two positive sites that they need to complete the adsorption process.

Another important factor is matrix. The electro-selectivity of multiple charge ions in dilute solutions is reduced by the steric hindrance of large functional groups and the probability of being properly spaced for divalent ion like sulfate and thiosulfate (Clifford and Weber 1983).

2.7 Anions Competition for Adsorptions Sites in Ion Exchange Processes

Anions selectivity, and thus anion competition, is an important factor in the design of ion exchange systems for the removal of a target contaminant from aqueous systems. This is because aqueous systems can be quite dilute, but contain many ionic
species. These ionic species may have a greater affinity for the ion exchange resins over that of the targeted contaminant. This affinity or preference to a given ion or ions is known as selectivity.

As discussed in previous section, ion exchange systems as in the case of this study consisted of cationic surfactant and a solid phase such as Type I and Type II resins, clays, graphites, zeolite, and granular activated carbon. Selectivity depends on the physical and chemical characteristics of the exchanging ion as well as the solid phase. Physical properties of the solid phase include the pore size and the type of functional groups that are found on the solid phase. Chemical properties include the valence of the ion, hydrated radius, and to some extent the atomic number (Crittenden et al. 2005). For example, in dilute solutions of an aqueous phase system, resins prefer counterions of higher valence such as sulfate, phosphate and chromate. This preference for multivalent ions is based on the spacing of the functional groups on the resins. According to Helfferich (1962), counterion selectivity increases with dilution of the solution, and is strongest with ion exchangers of high internal motility, which is also explained by the Donnan potential theory. Chmielewska, (2003) observed that the adsorption of chromate to a cationic surfactant-modified zeolite is preferred over nitrate and chloride. Gu et al. (2005), also observed a decreased in perchlorate adsorption in the presence of sulfate on to strong based anion resins with quaternary ammonium functional groups. These observations are not always the case as other factors play a role in ion competition. The reverse is also observed and will be discussed in the following sections.
It should be noted that these selectivity properties are for dilute aqueous systems that have a TDS of less than 1000 mg/L. As the TDS concentration increases the preference for multivalent ions over monovalent ions diminishes. The preference is reversed at high concentration and thus enhances regeneration. Table 2-7 gives the selectivity of anions to strong-based resins.

Table 2-7 Selectivity coefficients for strong based anion exchange resins for common anions.

<table>
<thead>
<tr>
<th>Anions</th>
<th>Selectivity (K_iC_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPO_4^{2-}</td>
<td>0.01</td>
</tr>
<tr>
<td>CO_3^{2-}</td>
<td>0.03</td>
</tr>
<tr>
<td>OH^-</td>
<td>0.06</td>
</tr>
<tr>
<td>F^-</td>
<td>0.1</td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>0.15</td>
</tr>
<tr>
<td>HCO_3^-</td>
<td>0.4</td>
</tr>
<tr>
<td>BrO_3^-</td>
<td>1</td>
</tr>
<tr>
<td>Cl^-</td>
<td>1</td>
</tr>
<tr>
<td>NO^-</td>
<td>1.3</td>
</tr>
<tr>
<td>HSO_4^-</td>
<td>1.6</td>
</tr>
<tr>
<td>Br^-</td>
<td>3</td>
</tr>
<tr>
<td>NO_3^-</td>
<td>4</td>
</tr>
<tr>
<td>I^-</td>
<td>8</td>
</tr>
<tr>
<td>ClO_4^-</td>
<td>10*</td>
</tr>
<tr>
<td>SeO_4^{2-}</td>
<td>17</td>
</tr>
<tr>
<td>CrO_4^{2-}</td>
<td>100</td>
</tr>
</tbody>
</table>

Adapted from Clifford, 1999; Crittenden et al. 2005
*Selectivity for trimethylamine resins, for triethylamine – 40; tripropylamine – 70 and bifunctional - 100

Hydrated radius plays a role in ion selectivity as well. It is closely related to free energy of hydration. Hydrated radius is defined as the group of water molecules that surrounds the ions. This allows for osmotic forces to be introduced to the solid phase. In the case of resins the crosslink bonds opposes this pressure and cause swelling (Crittenden et al. 2005), thus resins prefer ions that are low hydrated ions or have a low hydrated energy. These ions will reduce the swelling pressure and therefore bond more tightly to the resins. One example of this is the polystyrene resins and its strong affinity
for perchlorate. A list of common anions and their hydration energy is given in Table 2-8. Bors (1992) found that an addition of nitrate, bromide and chloride affects the adsorption of iodide to organobentonites tailored with cationic alkylammonium surfactants, while the addition of sulfate and phosphate had no effect. It should be noted that these divalent ions had higher hydration energies than the monovalent ions. Behsen and Riebe, (2008) also observed the preference of monovalent anions such as iodide, nitrate, and bromide over sulfate and selenate for adsorption sites on alkylammonium cationic surfactants tailored bentonites. Atkin et al. (2003) suggested that hydration could be a key factor in understanding adsorption of anions to alkylammonium compounds, seeing that this process results in the removal of the anion to the charged alkyl ammonium sites.

<table>
<thead>
<tr>
<th>Anions</th>
<th>Marcus, 1985</th>
<th>Sata, 1999</th>
<th>Moyer and Bonneses, 1997</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>306</td>
<td>270</td>
<td>300</td>
</tr>
<tr>
<td>Sulfate</td>
<td>-</td>
<td>1000</td>
<td>1080</td>
</tr>
<tr>
<td>Chloride</td>
<td>347</td>
<td>317</td>
<td>340</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>214</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The separation factor is another coefficient that plays an important role in the competition of anions. For monovalent ions, the separation factor is constant and is equal to the equilibrium constant. On the other hand, for multivalent ions, the separation factor is based on their concentration (Harland, 1994). These are for ion exchange systems that have a monovalent presaturation ion, which is also referred to as the reference ion. For
example the chloride anion is often used as the reference ion when appraising quaternary ammonium cationic surfactants.

The separation factor is affected by many factors such as size and charge of the exchangeable ion, functional group on the solid phase, and the matrix of the water.

Below is a list of anions and their separation factors (Table 2-9).

<table>
<thead>
<tr>
<th>Anions</th>
<th>Separation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO2(CO3)3^-</td>
<td>3200</td>
</tr>
<tr>
<td>ClO4^-</td>
<td>150*</td>
</tr>
<tr>
<td>CrO4^2-</td>
<td>100</td>
</tr>
<tr>
<td>SeO4^2-</td>
<td>17</td>
</tr>
<tr>
<td>SO4^2-</td>
<td>9.1</td>
</tr>
<tr>
<td>HAsO4^2-</td>
<td>4.5</td>
</tr>
<tr>
<td>HSO4^-</td>
<td>4.1</td>
</tr>
<tr>
<td>NO3^-</td>
<td>3.2</td>
</tr>
<tr>
<td>Br^-</td>
<td>2.3</td>
</tr>
<tr>
<td>SeO3^2-</td>
<td>1.3</td>
</tr>
<tr>
<td>HSO3^-</td>
<td>1.2</td>
</tr>
<tr>
<td>NO2^-</td>
<td>1.1</td>
</tr>
<tr>
<td>Cl^-</td>
<td>1.0</td>
</tr>
<tr>
<td>BrO3^-</td>
<td>0.9</td>
</tr>
<tr>
<td>HCO3^-</td>
<td>0.27</td>
</tr>
<tr>
<td>CH3COO^-</td>
<td>0.14</td>
</tr>
<tr>
<td>F^-</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Separation factor is for polystyrene SBA resin; for polyacrylic SBA resins the factor is 5

Adapted from Clifford, 1999

For multicomponent systems, the competitiveness of ions for ion exchange sites at equilibrium is a function of the total resin phase concentration and the aqueous phase concentration. Total concentrations are a function of the counterion and the presaturation ion for both the solid phase site and the aqueous solutions. If the ion concentration is
higher than the targeted ion to be removed, coupled with a greater preference for the functional group, then the equilibrium constant for the target ion or contaminant will be low (Crittenden et al., 2005).
2.8 References


Environmental working Group. www.ewg.org


Massachusetts Department of Environmental Protection. 2005. The Occurrence and Sources of Perchlorate in Massachusetts. www.mass.gov/dep


USEPA. 2005. Indian Head Naval Surface Warfare Center. www.epa.gov/reg3hwmd/npl/


CHAPTER 3 - Oxidation of Reduced sulfur species (Thiosulfate) by Free Chlorine to increase the bed life of Tailored GAC to remove Perchlorate.

3.1 Abstract

This research determined that the oxyanion thiosulfate ($S_2O_3^{2-}$) competed with perchlorate ($ClO_4^-$) for sorption onto activated carbons that had been pre-loaded with a quaternary ammonium surfactant. Thiosulfate is an anoxic sulfur species that served as a surrogate for a number of intermediate - valence sulfur oxyanions that could be present in groundwaters during the brief time frames of treatment processes. Specifically, $S_2O_3^{2-}$ hosts redox stability in time frame of days, rendering it as a candidate ion exchange competitor in anoxic groundwaters. When pre-chlorination oxidized this $S_2O_3^{2-}$ to sulfate ($SO_4^{2-}$), this competition was diminished. When Rapid Small Scale Column Test (RSCCT) employed Redlands, CA groundwater that contained a native 30 µg/L $ClO_4^-$, this exhibited a 6 µg/L $ClO_4^-$ breakthrough after 33,000 bed volumes (BV) when processed through bituminous- based GAC that had been preloaded with 0.24 g/ g Arquad 2C-75. When this same water was spiked with 1000 µg/L $S_2O_3^{2-}$, 6 µg/L of $ClO_4^-$ broke through at 17,000 BV. However, when $S_2O_3^{2-}$-spiked Redlands groundwater was also spiked with 2,500 µg/L chlorine, this reactant stoichiometrically oxidized the $S_2O_3^{2-}$ so as to diminish this competition, such that 6 µg/L $ClO_4^-$ broke through at 31,000 BV. Similar RSSCT trends were exhibited when using deionised distilled water that had been spiked with $ClO_4^-$, $S_2O_3^{2-}$, and chlorine.
3.2 Introduction

3.2.1 Sulfur Redox Species

Intermediate sulfur species can exist in anoxic waters that have a redox level between those of $\text{H}_2\text{S}$ and sulfates ($\text{SO}_4^{2-}$). These intermediate species could include polythionates, thiosulfate ($\text{S}_2\text{O}_3^{2-}$), and tetrathionate with sulfur valences of $+1.67$ and $+2.5$ (Table 3-1). Intermediate sulfur species can derive from reduced sulfur species such as sulfides, can occur naturally in reduced groundwaters and hydrothermal waters and aqueous systems where hydrogen sulfide ($\text{H}_2\text{S}$) and bisulfide ($\text{HS}^-$) are present (Druschell et al., 2003a,b; Jorgensen, 1990). Research indicates that thiosulfate ($\text{S}_2\text{O}_3^{2-}$) appears in hydrothermal waters (Webster, 1987; Barnes, 1979; Veldeman et al., 1991; Xu et al., 1998, 2000) and is an important intermediate in the sulfur cycle between $\text{H}_2\text{S}$ and $\text{SO}_4^{2-}$. Also, polythionates are abundant in many different systems such as acid carter lakes (Veldeman et al., 1991) and gold ore leaching solutions (O’Reilly et al., 2002). Schoonen 1989 stated that the concentrations of $\text{S}_2\text{O}_3^{2-}$ and other intermediate-valent sulfur species in natural waters should thermodynamically be less that 0.01% of the total dissolved sulfur. However concentrations have been observed considerably above this percentage (Boulegue, 1978; Webster, 1987, 1989; Veldeman, 1991). Concentration of $\text{S}_2\text{O}_3^{2-}$ in anoxic environments can range up to a few hundred micromoles per liter (Druschel et al. 2003a). Thiosulfate can constitute sixty-seven to seventy-five percent of the intermediate oxidation products from $\text{HS}^-$ (Jorgensen, 1990). Thus, $\text{S}_2\text{O}_3^{2-}$ has a kinetically dynamic relationship to $\text{H}_2\text{S}$ and $\text{HS}^-$ in anoxic environments, and $\text{S}_2\text{O}_3^{2-}$ is an important intermediate product of gradual oxidation reactions as $\text{H}_2\text{S}$ oxidizes to $\text{SO}_4^{2-}$. In the
aqueous environment, intermediate sulfur species are formed due to the gradual oxidation process of HS\(^{-}\) in the presence of low dissolved oxygen (DO). The oxidation of sulfides in a basic environment similar to that of groundwater has been postulated to yield intermediate products such as polysulfides, sulfites, and S\(_2\)O\(_3^{2-}\) as well as the oxidized species SO\(_4^{2-}\) (Lyn and Taylor, 1992; Siu and Jia, 1999; Thompson et al., 1995; Sharma et al., 1997). In a basic environment S\(_2\)O\(_3^{2-}\) is relatively stable when formed from the oxidation of sulfides (Siu and Jia, 1999). Allen and Day (1927, 1934, 1935) reported concentrations of S\(_2\)O\(_3^{2-}\) in alkaline hot springs water in the Yellowstone Natural Park and the geysers of California. Thiosulfate can also be formed from the fast oxidation of inorganic polysulfide that can be found in near-neutral and basic aqueous systems (Kamyshny et al., 2006). Thus, per redox reactions, S\(_2\)O\(_3^{2-}\) appears as an important intermediate – valence sulfur oxyanion in groundwaters.

**Table 3-1 Species of sulfur based ions and their valence state**

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>FORMULA</th>
<th>S VALENCE</th>
<th>Relative Stability/ Oxidation rate at near neutral pH in aqueous systems (in times of Days)</th>
<th>Observed IC (DX 12O) Peak time (mins)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>H(_2)S</td>
<td>-2</td>
<td>Unstable. Oxidized to form SO(_4^{2-}), S(_2)O(_3^{2-}), and other intermediate valence species. (Thompson et al., 1996; Senning, 1972)</td>
<td>3</td>
</tr>
<tr>
<td>Elemental Sulfur</td>
<td>S</td>
<td>0</td>
<td>Stable in the form of S8 ring. Slow oxidation (Steudel, 1996)</td>
<td>not tested herein</td>
</tr>
<tr>
<td>Hexathionate</td>
<td>S(_8)O(_6^{2-})</td>
<td>+1.67</td>
<td>Unstable. Oxidized in minutes to form S(_2)O(_3^{2-}). (Miura and Kawaoi, 200; Senning, 1972)</td>
<td>not tested herein</td>
</tr>
<tr>
<td>Pentathionate</td>
<td>S(_5)O(_6^{2-})</td>
<td>+2</td>
<td>Unstable. Fast oxidation to S(_2)O(_3^{2-}). (Miura and Kawaoi, 200; Senning, 1972)</td>
<td>not tested herein</td>
</tr>
</tbody>
</table>
Thiosulfate $\text{S}_2\text{O}_3^{2-}$ +2 Stable. Oxidize slowly to $\text{S}_4\text{O}_6^{2-}$, $\text{SO}_4^{2-}$ (Siu and Jia, 1999; Iguchi, 1958; Rolia and Chakrabarti, 1982; Senning, 1972) 7.4

Tetrathionate $\text{S}_4\text{O}_6^{2-}$ +2.5 Unstable. Decompose to form $\text{S}_2\text{O}_7^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ (Druschel, 2003; Rolia and Chakrabarti, 1982; Senning, 1972). not tested herein

Dithionate $\text{S}_2\text{O}_4^{2-}$ +3 Unstable. Oxidize in seconds to $\text{SO}_3^-$ radical, $\text{S}_2\text{O}_3^{2-}$ and $\text{HSO}_3^-$, in the presence of oxygen Not tested herein

Trithionate $\text{S}_3\text{O}_6^{2-}$ +3.33 Unstable. Decompose to $\text{S}_2\text{O}_3^{2-}$ (Druschel, 2003; Rolia and Chakrabarti, 1982) Not tested herein

Sulfite $\text{SO}_3^{2-}$ +4 Unstable, reacts with air to form $\text{SO}_4^{2-}$ (Senning, 1972) 6.2

Dithionate (Hydrosulfite) $\text{S}_2\text{O}_6^{2-}$ +5 Stable. Low oxidation rate with forced oxygen at room temperature. Oxidize to $\text{SO}_4^{2-}$, with strong oxidizing agents (Wang and Zhao, 2007; Senning, 1972) 3.9

Sulfate $\text{SO}_4^{2-}$ +6 Stable 5.4

* Peak times shown are for 1 IC run. Peaks times may vary due to eluent concentration, and age of column and ionic strength of water.

Sulfur intermediates can persist for times measured in hours and days and this constitutes significant durations, relative to the time that water resides within a water treatment facility. Amongst the sulfur intermediate shown in Table 3-1, $\text{S}_2\text{O}_3^{2-}$ is one that can persists for times measured in days when in the presence of incidental air contact (Senanayake, 2004; Rolia and Chakrabarti, 1982; Zhang and Dreisinger, 2002; Lam and Dresinger, 2003; Breuer and Jeffrey 2003a,b; Millano et al., 1983) Chu et al. (2003) showed that intensely oxygen sparging $\text{S}_2\text{O}_3^{2-}$ solution with 200 ml $\text{O}_2$ per min, the $\text{S}_2\text{O}_3^{2-}$...
had decreased only by 10% after 10 minutes sparging and 40% after an hour of oxygen sparging. Thus, even intense oxygen sparging would not offer a practically rapid means of transforming $S_2O_3^{2-}$ to $SO_4^{2-}$ in water treatment applications.

It can also be noted that when the oxidation rate of $HS^-$ to $S_2O_3^{2-}$ is higher than the oxidation rate of $S_2O_3^{2-}$ to $SO_4^{2-}$ in a system, then there will be an accumulation of these competitive intermediate species in a treatment system.

Several research papers have appraised the use of $S_2O_3^{2-}$ for leaching of gold (Byerley et al., 1973; Byerley et al., 1975; Breuer and Jeffrey, 2003; Chu et al., 2003). Intermediate products of $S_2O_3^{2-}$ oxidation during gold leaching can also affect the adsorption of anions to exchange sites (Senanayake, 2004; Nicol and O’Malley, 2001; 2002; Zipperan et al., 1988; Abbruzzese et al., 1995; Muir and Aylmore, 2004). It was observed by Chu et al., (2003) that disulfite, a polythionate formed in the oxidation of $S_2O_3^{2-}$ reduced the effect of gold leaching due to the competition of copper (II), $S_2O_3^{2-}$ and gold. Nicol and O’Malley (2002) showed that during the leaching of gold, the trithionate that is oxidized from $S_2O_3^{2-}$ will compete strongly with the gold - thiosulfate complex for exchange sites on ion exchange resins. Moreover, these species exhibited stabilities of several days duration when an aqueous solution contained 4,000 mg/L $S_2O_3^{2-}$ plus ammonia, a fifth of the $S_2O_3^{2-}$ had converted to trithionate after two days (Nicol and O’Malley, 2002). But tetrathionate was less stable.
3.2.2 Motivation for Hypothesis Regarding Intermediate-Sulfur Oxyanions

Our Penn State team has developed a water treatment technology where granular activated carbon (GAC) has been tailored with quaternary ammonium surfactants or ammonia to increase the bed life of the carbon for removing ClO$_4^-$ and other oxyanions (Parette and Cannon 2005a,b; Parette et al., 2005; Chen and Cannon, 2005; Chen et al., 2005a,b). The surfactant tailored GAC increased the carbon bed life 33 times when removing 70 µg/L of the ClO$_4^-$ from Redlands groundwater at the rapid small scale column test (RSSCT) level (Parette and Cannon 2005a,b; Parette et al., 2005).

Demonstration and pilot scale studies that were conducted at the Texas Street Water Treatment Plant depicted ClO$_4^-$ breakthrough earlier than in RSSCT trials that employed barrels of the Redlands water that had been stored in Penn State for a month or longer. However, when RSSCTs employed Redlands groundwater that was employed as soon as it reached Penn State, ClO$_4^-$ breakthrough occurred considerably sooner than when employing this same groundwater after it had been stored for a month. This led our team to suspect that the gradual oxidation of a competing oxyanion intermediate was playing a role. The authors also noticed that the Redlands groundwater that was tested at the source showed a negative redox value of -125 mV which inferred that this water was in a reduced form. In contrast, Redlands groundwater that had been shipped to our Penn State lab and stored for several months showed positive redox values ranging from +150 to 200 mV. These two redox probes may not have been normalized to the same redox solution; and some scientists question the quantitative value of any redox measurements. None the less these results together raised the intriguing hypothesis that the Redlands groundwater
contained a species that in its reduced form competed quite significantly with ClO$_4^-$, but in its oxidized form did not compete as prominently. Such could be the case with sulfur oxyanions which could represent transition species between the reduced sulfides and the oxidized sulfate. In time frames that would be significant relative to water treatment operations, the sulfur could appear as S$_2$O$_3^{2-}$, polythionate, or other intermediate sulfur oxyanions. We further hypothesized that these intermediate sulfur oxyanions (including S$_2$O$_3^{2-}$) competed with the adsorption of ClO$_4^-$ to the tailored GAC when fresh Redlands Water was employed. In concurrence with this hypothesis, background analysis of several fresh samples of Redlands water depicted an anion with the known retention time of S$_2$O$_3^{2-}$ and perhaps some other intermediate valence sulfur oxyanion via ion chromatography (see discussion of Figures 3-1 and 3-2 below). Thus, it was anticipated that S$_2$O$_3^{2-}$ specifically could be at least one of the intermediate sulfur species that competed with ClO$_4^-$ for adsorption sites. Also S$_2$O$_3^{2-}$ served as a surrogate for other anoxic / reduced sulfur based oxyanions that had a sulfur valence between that of H$_2$S and SO$_4^{2-}$.

### 3.2.3 Objective and Hypothesis

In light of this background, our specific objective was to test the hypothesis that S$_2$O$_3^{2-}$ competitively diminished ClO$_4^-$ sorption on GAC that had been preloaded with quaternary ammonium surfactant. Moreover we hypothesized that stoichiometrically designed chlorination could oxidize S$_2$O$_3^{2-}$ to SO$_4^{2-}$; and then the SO$_4^{2-}$ would not extensively diminish the bedlife for ClO$_4^-$ sorption.
3.2.4 Chlorine Oxidation of Intermediate-valence sulfur oxyanions

Oxidants that effectively oxidize reduced sulfur species to \( \text{SO}_4^{2-} \) include chlorine, ferrate, hydrogen peroxide, permanganate and ozone (Levine et al., 2004; Suidan et al., 1977). Chlorine is often the less expensive oxidant; and it has been commonly used to oxidize hydrogen sulfide to \( \text{SO}_4^{2-} \). However, we are aware of very few refereed journal papers that appraise the oxidation of other native intermediate valence sulfur oxyanions such as \( \text{S}_2\text{O}_3^{2-} \), tetrathionate, dithionate and polythionates. Also we are not aware of any other researchers who have appraised the competition of \( \text{S}_2\text{O}_3^{2-} \) with \( \text{ClO}_4^- \) or other oxyanions for adsorption sites onto media that employ quaternary ammonium functional groups.

This chapter appraises chlorine as an oxidant for converting \( \text{S}_2\text{O}_3^{2-} \) to \( \text{SO}_4^{2-} \) so the sulfur species incurs less sorption competition for \( \text{ClO}_4^- \). As background, the author conducted experiments with \( \text{SO}_4^{2-} \) (the most oxidized compound in the sulfur cycle), that showed that 250 mg/L \( \text{SO}_4^{2-} \) incurred only slight competition with \( \text{ClO}_4^- \) for adsorption sites.

Stoichiometrically, a molar ratio of 4 moles of chlorine to 1 mole of \( \text{S}_2\text{O}_3^{2-} \) will result in complete oxidation of \( \text{S}_2\text{O}_3^{2-} \) to \( \text{SO}_4^{2-} \) as per equation 3-1-3-3.

\[
\begin{align*}
4\text{Cl}_2 + 4\text{H}_2\text{O} & \rightarrow 4\text{HOCl} + 4\text{H}^+ + 4\text{Cl}^- \quad \text{Equation 3-1} \\
4\text{HOCl} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} & \rightarrow 2\text{SO}_4^{2-} + 4\text{Cl}^- + 6\text{H}^+ \quad \text{Equation 3-2} \\
4\text{Cl}_2 + \text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} & \rightarrow 2\text{SO}_4^{2-} + 8\text{Cl}^- + 10\text{H}^+ \quad \text{Equation 3-3}
\end{align*}
\]
With groundwater pH ranging between 7-8.5 and intermediate-valence sulfur oxyanions concentration in micromoles per liter, chlorination of these sulfur species will favor the formation of $\text{SO}_4^{2-}$ as opposed to elemental sulfur (Levine et al., 2004). And this outcome is desirable in water treatment systems.

Chlorination treatment processes are also influenced by activated carbon since the activated carbon as a redox surface will reduce the chlorine to chloride (Collivignarelli, et al., 2006; Dixon and Lee, 1991; Gonce and Voudrias, 1994; Hassler, 1967; Snoeyink et al., 1981; Hwang et al., 1989). Hassler, 1967 and Martin and Shackleton (1990) observed that activated carbon can dechlorinate water through a combination of adsorption and catalysis processes. Moreover, as unfavorable side effects incurred via excessive chlorination, the activated carbon surface can experience oxidative degradation, yielding oxygenated substituents (Snoeyink et al., 1981) such as carboxyls whose negative charge could repel the $\text{ClO}_4^-$ anion. Also, under the conditions herein, chlorine could oxidize the reduced – N in the quaternary ammonium functionality, of the preloaded surfactant thus impairing the carbon surface of its adsorptive functions.

3.3 Experimental

3.3.1 Materials

The granular activated carbon (GAC) that was used in these experiments was bituminous based UltraCarb unless otherwise identified. This activated carbon was
obtained from Siemens Water Technologies (formerly USFilter) of Los Angeles CA. One experiment employed activated carbon. This bituminous – based activated carbon was obtained from Superior Adsorbents Inc. of Emlenton, PA. The carbon was ground and sieved to a mesh size of US # 200 x 400, which was 38 x 75 µm.

Unless otherwise listed, the groundwater for these experiments originated Redlands California, Texas Street Well 31A. This native groundwater contained 30 µg/L ClO$_4^-$, 55 mg/L SO$_4^{2-}$, and 38 mg/L nitrate as NO$_3^-$ (Table 3-2). When fresh, this Redlands groundwater also contained some intermediate sulfur species, as discussed below. The Redlands water was stored in 55 gallons polyethylene barrel at ambient temperature and they were sealed with polyethylene caps that were not airtight.

Several initial experiments employed Redlands groundwater that was sampled earlier (identified as “earlier vintage” herein), and this contained 52 µg/L ClO$_4^-$ and 10 mg/L nitrate as NO$_3^-$. 

<table>
<thead>
<tr>
<th>Contaminants/ Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchlorate</td>
<td>30 µg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>55 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>14 mg/L</td>
</tr>
<tr>
<td>Nitrate as NO$_3^-$</td>
<td>38 mg/L</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>250 mg/L</td>
</tr>
<tr>
<td>Total Alkalinity</td>
<td>160 mg/L as CaCO$_3$</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>210 mg/L</td>
</tr>
</tbody>
</table>

*Some tests employed vintage Redlands groundwater that contained 52µ ClO$_4^-$ and 10 mg/L nitrate as NO$_3^-$. 

Table 3-2 Water Chemistry of Redlands Groundwater from Well 31A at the Texas Street Plant* used herein unless otherwise identified.
The cationic surfactant used was dicocoalkyldimethylammonium chloride (Arquad 2C-75). Arquad 2C-75 was chosen because its two long carbon chains facilitates low leaching of the surfactant from the carbon (Parette and Cannon, 2005, Parette et al. 2005). The $S_2O_3^{2-}$ source was sodium thiosulfate by Fisher Scientific. Arquad 2C-75 were prepared from analytical grade reagents that were dissolved in deionized distilled water.

3.3.2 Methods

3.3.2.1 Sodium Thiosulfate Solution Preparation

Thiosulfate spiking concentrations and analysis standards were prepared from 1g/L $S_2O_3^{2-}$ stock solution. To ensure that the correct concentration was used at all times, stock solutions and influent solutions were prepared every 3 days in a given RSSCT run period. All other solutions were prepared from analytical grade reagents and DI water.

To test the rate of thiosulfate degradation with incidental air contact, 1 mg/L of $S_2O_3^{2-}$ was mixed into 200 mL of DI or Redlands water and let stand without further agitation in capped bottles. Thiosulfate was tested at T=0 day and daily until 50% of $S_2O_3^{2-}$ remained in the solution.

3.3.2.2 Rapid Small Scale Column Tests

The rapid small scale column tests (RSSCTs) were designed for proportional diffusivity according to Parette and Cannon (2005a). The RSSCT columns were dry-
packed with UltraCarb; and glass wool was packed at both ends. 1.27 g of UltraCarb GAC was used and tailored with 33 bed volumes of 0.4% Arquad 2C-75 solution, and this protocol had been observed to pre-load 0.24 g Arquad 2C-75/ g GAC, which correspond to 0.56 meq of active N functionality / g GAC (Parette et al., 2005a).

The RSSCTs were conducted at ambient temperatures, which were measured at 20±2°C; and the flow rate was maintained at 2.5 mL/min through a 2.65 mL bed, giving a 1.1 minute empty bed contact time (EBCT) through the RSSCT. Per proportional diffusivity, this would simulate an EBCT of 10 minutes for the US# 12 x 40 mesh size GAC (0.55 mm x 0.75 mm) that could be used at the field scale level. Pumps (Waters models 501 and 510) were used to provide flow; and these had been disengaged from prior HPLC analytical instruments.

The quaternary ammonium surfactant tailoring process took approximately 3 days, during which the surfactant solution was pumped and recirculated at a rate of 2 mL per minute through the carbon media. Deionized distilled water was used to pre-load the surfactant onto the GAC. The surfactant tailored GAC was not washed before the introduction of the ClO₄⁻ contaminated influent water solution.

3.3.2.3 Chlorine Gas Preparation and Application

Because of the heightened security issues, US university labs cannot readily acquire chlorine gas directly. Thus, we produced chlorine gas by reacting 1.5 g of
potassium permanganate and 3.5 mL of concentrated HCl (Equation 3-4), then bubbled the resultant chlorine gas into a plastic polyethylene collapsible container that has DI water. This formed a mixture of HOCl and hydrochloric acid (Equation 3-5). Dilutions were carried out when necessary to get the correct concentrations that were needed stoichiometrically, to oxidize S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} but not more or less. HOCl solution was monitored daily to ensure the correct concentration of free chlorine was present to oxidize S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}.

$$6\text{HCl} + \text{KMNO}_4 + 2\text{H}^+ \rightarrow 3\text{Cl}_2 + 2\text{MnO}_4^- + 4\text{H}_2\text{O} + 2\text{K}^+ \quad \text{Equation 3-4}$$

$$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{HCl} \quad \text{Equation 3-5}$$

### 3.3.2.4 Operation of RSSCTs with concurrent perchlorate/thiosulfate spiking and chlorine oxidation

During RSSCT operations, one pump supplied water that was spiked with the ClO\textsubscript{4}^- and or S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} while the second pump supplied the HOCl solution separately when included (Figure 3-1). This was done to control the contact time between the free chlorine and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} solution. Collapsible plastic containers were used to store the solutions to ensure that the S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} did not oxidize before use and that the HOCl did not dissipitate before use. Also the S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} solution was replaced every 3 days, so as to maintain proper concentration. Both solutions were covered with a dark plastic to also ensure no reactions with light.

Various concentrations of chlorine, S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} and ClO\textsubscript{4}^- were appraised using DI water or Redlands, CA groundwater. Spiked concentration of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} included 40, 250, 500 and 1000 µg/L as S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}. The chlorine dose ranged from 0 – 3.5 mg/L as Cl\textsubscript{2} (Table
3-4); and was paced to offer either the stochiometric amount needed to oxidize the $S_2O_3^{2-}$ per equations 1-3 (in most cases), or to offer an excessive amount.

These experiments employed a mixing chamber when reacting the $S_2O_3^{2-}$ with HOCl. The chamber had a 5 minute detention time with a stir bar mixing at 250 rpm, and a velocity gradient $G$ of 348 sec$^{-1}$. Preliminary mixing test conducted showed that this achieved sufficient mixing to achieve $S_2O_3^{2-}$ oxidation before the water flow entered the column.
Water samples were collected 2 times per day from the RSSCT effluent until at least 50% of the ClO$_4^-$ concentration was observed in the effluent.

### 3.3.2.5 Monitoring Perchlorate, Thiosulfate Anion and Surfactants

Perchlorate and S$_2$O$_3^{2-}$ were monitored by use of Dionex 120 ion chromatograph system, which was equipped with an AS40 auto sampler, a 4 mm AS16 column, and a 4 mm AG16 guard column was used. The DS4 suppressor was set at 300 mA and a temperature of 35°C. Sodium hydroxide solution either at 25 mM or 30 mM was used as the eluent. Specifically the 1 mL sample loop allowed ClO$_4^-$ to be detected quantitatively at 1µg/L. Other anions were also monitored with Dionex 120 ion chromatograph system, while using the proper eluent concentration.

A colorimetric method was used to determine the concentrations of surfactants (Tsubouchi et al., 1957; Parette et al. 2005). This method has a detection limit of 0.1-0.2 mg/L.

Quality assurance analyses were conducted to discern the accuracy to which ClO$_4^-$ could be measured at Penn State. Experimental quality was conducted at all stages of the experiments and data handling protocols, which includes analyzing the samples, entering, verifying and reporting the data. A formal quality assurance program was practiced to ensure that the Penn State laboratory was operating according to the requirements of EPA method 314.0. Table 3-3 shows a list of our quality control checks and the acceptable
criterion that was met. The Minimum Detection Level (MDL) was also calculated and estimated to be 1µg/L for our instrument. The author noted that the chromatographic time for ClO$_4^-$, S$_2$O$_3^{2-}$ and other anions to elute will vary due to factors such as age of the column, eluent concentration and the type of water tested. It is observed that DI water has a shorter retention time than water that has an ionic strength. Also as the column gets older the retention time of anions will be longer. Eluent concentration affects elution time in that a higher concentration depicts shorter retention time.

Table 3-3 Quality control check criteria

<table>
<thead>
<tr>
<th>QC Check</th>
<th>Frequency</th>
<th>Acceptable Criterion</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Curve</td>
<td>1</td>
<td>R$^2$ ≥ 0.997</td>
<td>0.9995</td>
</tr>
<tr>
<td>Check Sample</td>
<td>1/10 samples</td>
<td>±15%</td>
<td>3%</td>
</tr>
<tr>
<td>Matrix conductivity</td>
<td>Each sample</td>
<td>&lt; 6400 µs/cm</td>
<td>Criterion met for all samples</td>
</tr>
<tr>
<td>Method Blank</td>
<td>2 per IC run</td>
<td>No trace</td>
<td>No trace</td>
</tr>
<tr>
<td>Replicate</td>
<td>1 per 10 samples</td>
<td>±20%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Matrix Spike/Duplicate</td>
<td>1/20 samples</td>
<td>80%-120%</td>
<td>111%</td>
</tr>
</tbody>
</table>

3.4 Experimental Results and Discussion

3.4.1 Initial Comparisons of Fresh versus Aged Redlands Water

In early work that compared various RSSCTs and field scale operations, the team had observed variations in bedlife performance. Specifically, when RSSCTs employed freshly received Redlands water within one week storage in a 55 gallon closed barrel, ClO$_4^-$ broke through sooner than when RSSCTs employed Redlands water that had been
aged (stored) for longer than a month. Likewise, when full-scale tests were demonstrated at Redlands with very fresh water, the initial ClO$_4^-$ breakthrough was sooner than when using Redlands water that had been aged for longer than a month (Figure 3-2). These initial RSSCTs and full-scale demonstrations used the earlier vintage Redlands water, with ClO$_4^-$ at 52 µg/L and nitrate at 10 mg/L as NO$_3^-$; and the surfactant tailoring agent was cetylpyridinium chloride (CPC). Some of these differences could be attributed to inherent distinctions between RSSCTs and full-scale operations, for example, others have observed that RSSCTs can often exhibit sharper breakthrough profiles than do full-scale beds when using conventional GAC; and that is the pattern observed here, where the full scale bed exhibited earlier initial breakthrough, but the same BV to half breakthrough as did the RSSCT. Also some compounds behave according to proportional diffusivity, while others do not (presented in Chapter 5). Also, the field scale GAC hosted slightly less surfactant loading by 10-15% than did the RSSCTs.
Nonetheless, the distinctions between the RSSCTs with fresh versus RSSCT with aged Redlands Water had to be attributed to something other than similitude considerations. The authors hypothesized that these distinctions were associated with competitive oxyanions whose concentrations were redox sensitive. For the work herein we particularly appraised suspected sulfur based oxyanions that were intermediate between sulfide and sulfates.

As a substantiation of this hypothesis, ion chromatograms of fresh Redlands water exhibited peaks that just preceded the ClO₄⁻ peak; and these peaks disappeared in the aged Redlands Water. For example, when the raw Redlands groundwater was sampled into a sealed vial and mailed overnight to Penn State, our team observed a distinct ion
chromatograph peak at 6.1 minutes (Figure 3-3), and for eluent and column conditions, this corresponded to the $S_2O_3^{2-}$ peak.

It is noteworthy that these peaks occur just before the $ClO_4^{-}$ peak. Since ion chromatogram resin media often employ quaternary ammonium functionality, this similar time to peak breakthrough behavior inferred that likewise in the tailored GACs that hosted quaternary ammonium functionality, these same intermediate sulfur species would likewise compete with $ClO_4^{-}$ relative to RSSCT bed life before breakthrough.

Figure 3-3 Conductivity Chromatogram for Redlands groundwater that was sampled on-site and shipped overnight to be tested, shows retention times of $ClO_4^{-}$ and an unknown peak that corresponds to when thiosulfate or other intermediate-valence sulfur oxyanions would elute using the DX 120 ion chromatogram instrument.
3.4.2 Stability of Sulfur Species in the Presence of Indicated Air Contact

In follow-up to this observation, the authors tested the stability that sulfides and intermediate sulfur oxyanions could have in a reduced groundwater when it becomes exposed to incidental air. To simulate this, the authors spiked 1 mg/L S$_2^-$ into deionized / distilled water that was exposed to incidental air contact. This water was held in a container that was closed but not air tight, or that was open to air on top with no lid—and these two configurations yielded the same results. Within an hour exposure to this incidental air contact, much of the S$_2^-$ oxidized to SO$_4^{2-}$. But ion chromatograph analyses revealed that some S$_2^-$ oxidized only partially to S$_2$O$_3^{2-}$ (Figure 3-4). These analyses employed 25 mM NaOH eluent, for which the IC thiosulfate peak appeared at 7.4 minutes. Additionally, the chromatogram showed two other peaks that exited the IC after the S$_2$O$_3^{2-}$ had; and these were taken to be other intermediate valence sulfur species. The chromatogram at 20 hours was essentially the same as the chromatogram at 1 hour.

Then, after 10 days, neither the S$_2^-$ nor the S$_2$O$_3^{2-}$ appeared; although a sulfur intermediate with a longer retention time still remained (Figure 3-4). It should be noted to the readers that intermediate valence sulfur compounds are very reactive and therefore unstable; as mentioned previously these compounds can react with each other and will undergo decomposition as was observed in Figure 3-4. As a consequence of this the analytical determination of intermediate sulfur species can be quite difficult.

The authors sought to discern how long the spiked S$_2$O$_3^{2-}$ would remain in a stock water supply. For this test, 1 mg/L sodium thiosulfate was spiked into distilled water,
which remained in a closed 5 gallon container that allowed for incidental surface contact with air, but no mixing. After 3 days the $\text{S}_2\text{O}_3^{2-}$ concentration in solution decreased by a mere 5% and after 5 days by 50% (Figure 3-5). When this experiment was repeated with Redlands groundwater, the same results occurred. There were no significant difference between Redlands groundwater and deionized distilled water.
Figure 3-4 Conductivity chromatogram showing sulfide oxidation by incidental contact with air, after 1 hour 20hr, 3 days and 10 days. Initial concentration is 1 mg/L of sulfide in DI water.
Figure 3-5 Rate of $S_2O_3^{2-}$ oxidation in DI and Redlands groundwater, when the water source experienced incidental surface contact with air but with no mixing. Initial $S_2O_3^{2-}$ is 1 mg/L.

3.4.3 Competition by Thiosulfate for Perchlorate Sorption and Chlorine Oxidation

Rapid Small Scale Column Tests (RSSCT) was conducted to test the hypothesis that intermediate valence sulfur species competed with $ClO_4^-$, for sorption onto GAC that had been preloaded with quaternary ammonium surfactants. In light of the literature, and the availability of operational and chromatographic protocols, the author chose to appraise $S_2O_3^{2-}$, served as a surrogate for both itself and other sulfur intermediates. To appraise such competition, the authors spiked either deionized distilled water or Redlands groundwater with various doses of $S_2O_3^{2-}$; and the RSSCT experiments that were conducted to test this hypothesis are listed in [Error! Reference source not found.]. Also the author sought to test the hypothesis that chlorine could diminish this competition by
oxidizing the $\text{S}_2\text{O}_3^{2-}$.

All these RSSCTs employed GAC that was tailored with Arquad 2C-75; and the Redlands groundwater source contained 30 µg/L ClO$_4^-$ and have 38 mg/L nitrate as NO$_3^-$. 

> Table 3-4 List of experiments conducted using both DI water and Redlands groundwater

<table>
<thead>
<tr>
<th>Water source</th>
<th>Experiments no.</th>
<th>ClO$_4^-$ Conc. (µg/L)</th>
<th>S$_2$O$_3^{2-}$ conc. (µg/L)</th>
<th>Free Chlorine dose (mg/L)</th>
<th>Bed Volumes to 6 µg/L ClO$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>1</td>
<td>1000</td>
<td>-</td>
<td>-</td>
<td>15,000</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1000</td>
<td>100</td>
<td>-</td>
<td>9,500</td>
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<tr>
<td></td>
<td>3</td>
<td>1000</td>
<td>1000</td>
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<td></td>
<td>4</td>
<td>1000</td>
<td>-</td>
<td>2.5</td>
<td>9,000</td>
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<tr>
<td></td>
<td>5</td>
<td>1000</td>
<td>100</td>
<td>0.25</td>
<td>13,000</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>500</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>7</td>
<td>500</td>
<td>500</td>
<td>-</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>500</td>
<td>500</td>
<td>3.5</td>
<td>16,000</td>
</tr>
<tr>
<td>Redlands Groundwater, 38 mg/L nitrate as NO$_3^-$</td>
<td>9 (Fresh)</td>
<td>52</td>
<td>-</td>
<td>-</td>
<td>22,000</td>
</tr>
<tr>
<td></td>
<td>10</td>
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<td>500</td>
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<td>17,000</td>
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<td>30</td>
<td>500</td>
<td>1.25</td>
<td>$&gt;28,000$</td>
</tr>
</tbody>
</table>

*Perchlorate did not breakthrough by 28,000 bed volumes, the duration of these tests

### 3.4.4 Treatment of Synthetic Deionized Distilled Waters

The first array of these RSSCTs discussed herein employed deionized distilled (DI) water that was spiked with 1000 µg/L ClO$_4^-$ plus various levels of S$_2$O$_3^{2-}$ (0 – 1000
µg/L) and free chlorine (0 – 3.5 mg/L), as presented in Table 3-4. When 1000 µg/L ClO₄⁻ alone was present in DI water, surfactant tailored granular activated carbon (TGAC) removed ClO₄⁻ to below 6 µg/L for 15,000 bed volumes (BVs). However, when the DI water contained 1000 µg/L S₂O₃²⁻, the TGAC removed ClO₄⁻ to below 6 µg/L for only 8,000 BVs (Figure 3-6). Thus S₂O₃²⁻ did indeed compete with ClO₄⁻ for adsorption sites.

![Figure 3-6 The effects of S₂O₃²⁻ on ClO₄⁻ adsorption to surfactant tailored GAC using DI water.](image)

Next we sought to discern the effects of adding 2,500 µg/L chlorine to DI water that contained 1,000 µg/L ClO₄⁻ but no S₂O₃²⁻. In this case, the chlorine diminished bed life to 9,000 BV, as shown in Figure 3-7. Thus the chlorine either oxidized the carbon surface to create negatively charged oxygenated substituent that hindered ClO₄⁻ diffusion
through the GAC grain; or the chlorine oxidized the quaternary ammonium active exchange site, or both. To test whether chlorine was oxidizing the quaternary ammonium surfactant, the authors conducted an experiment where chlorinated water - 2.2 g/L Cl₂ concentration in deionized distilled - was used as the tailoring solution instead of deionized distilled water. The surfactant loading was 0.25 g / g GAC and at 1000 µg/L ClO₄⁻, breakthrough of ClO₄⁻ occurred at 16,000 bed volumes. From these results the authors concluded that there was no significant difference between the experiments that used a tailoring solution that used chlorinated water and the solution that employed only deionized distilled. It was concluded from this result that chlorine does not affect the quaternary ammonium active exchange site for perchlorate.

The author notes that the conventional carbon surface offers little sorption capacity for perchlorate. Thus these results indicate that the chlorine was oxidizing the carbon surface in a manner that rendered it more negatively charge; and it was this negative charge that imposed a reverse Donnan effect (Jang et al., 2009) that precluded the perchlorate from penetrating the pores to where the resident surfactant quaternary ammonium could sorb it.
We next conducted three experiments with DI water where we included 1,000 µg/L ClO$_4^-$ for the control (spiked with only ClO$_4^-$), breakthrough occurred at 15,000 BV. However, when 100 µg/L of S$_2$O$_3^{2-}$ was also included, 6 µg/L breakthrough occurred at 9,500 BV (Figure 3-8). In contrast, when the stoichiometric amount of 0.25 mg/L chlorine was used to oxidize the S$_2$O$_3^{2-}$ to SO$_4^{2-}$, bed life reverted to 13,000 BV. Thus, this prechlorination process reverted the capacity of GAC to remove ClO$_4^-$ when the spiked S$_2$O$_3^{2-}$ was oxidized by chlorine. It is noted that SO$_4^{2-}$ competed far less than did S$_2$O$_3^{2-}$ with ClO$_4^-$ in this surfactant tailored GAC, even when the SO$_4^{2-}$ concentration was as high as 250 mg/L.
Similarly we conducted three experiments with DI water that was spiked with 500 µg/L ClO$_4^-$
. The control exhibited breakthrough at 20,000 BV. Then when 500 µg/L S$_2$O$_3^{2-}$ was also added, bed life dropped to 10,000 BV. When pretreated with 3.5 mg/L chlorine the bed life reverted to 16,000 BV (Figure 3-9). With this result it can be observed that the chlorine usefully oxidized S$_2$O$_3^{2-}$ and extended the bed life of the GAC. These results using DI water showed that there was an affect for ClO$_4^-$ adsorption when S$_2$O$_3^{2-}$ was present, and properly mixed pre chlorination oxidized this species, thus restoring to some degree the bed life of the surfactant tailored GAC. Next, the author tested strategy using groundwater from Redlands, California.
3.4.5 Redlands Groundwater

The first of these Redlands experiments involved validating the fresh versus aged distinctions in RSSCT performance that was discussed above relative to figure 3-2, while using the most recent Redlands water source that contained 38 mg/L nitrate as NO$_3^-$ and 30 µg/L ClO$_4^-$

As shown in Figure 3-10, this fresh Redlands groundwater exhibited 6 µg/L ClO$_4^-$ breakthrough at 24,000 BV. In contrast, this water after aging (by storage in barrels for more than a month) exhibited breakthrough at 33,000 BV. This result was quite similar to Figure 3-12 trends discussed above. Next, the author sought to mimic the hypothesized effect of sulfur intermediate by adding 1000 µg/L S$_2$O$_3^{2-}$ to aged Redlands water. As observed in Figure 3-10, 6 µg/L ClO$_4^-$ breakthrough occurred at 25,000 BV,
virtually the same as when fresh Redlands groundwater had been used. This result concurs with the notion that when the Redlands groundwater was fresh, it contained sulfur oxyanion intermediates species that exerted the same level of competition as 1,000 µg/L of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}.

The aged Redlands water was spiked with other levels of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}, including 40, 250, 500 and 1,000 µg/L of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} (Figure 3-11). As shown, even 250 µg/L S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} exerted competition.

The author noted that the competition of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} and other intermediate sulfur valence oxyanions may have eluded prior appraisal in the literature, because the
relatively short lives of these species dictate the need for real time analytical protocols to discern their presence. As a further complication when using granular activated carbon as the structural matrix for hosting these quaternary ammonium surfactants, the GAC surface itself can serve as a redox reactant. In all these RSSCTs the authors never observed $S_2O_3^{2-}$ presence in the tailored GAC effluent.

![Graph showing perchlorate concentration vs. bed volumes](image)

Figure 3-11 The effects of ClO$_4^-$ adsorption to tailored GAC when spiked with 40, 250 and 1000 µg/L of $S_2O_3^{2-}$, when using Redlands water where the native ClO$_4^-$ influent is 30 µg/L.

With an understanding of the effects of $S_2O_3^{2-}$ on ClO$_4^-$ adsorption onto tailored GAC when using this native groundwater, the author next looked at whether $S_2O_3^{2-}$ could be oxidized with chlorine, so as to diminish its competition with ClO$_4^-$ sorption. These RSSCTs were all conducted with aged Redlands groundwater that contained 38 mg/L nitrate as NO$_3^-$. Figure 3-12 depicts the effects of chlorination on the oxidation of $S_2O_3^{2-}$.
to $\text{SO}_4^{2-}$. With no pre-chlorination, the bed volumes to ClO$_4^-$ breakthrough was 33,000 BV. The capacity was furthered reduce by 30% when 1,000 µg/L of $\text{S}_2\text{O}_3^{2-}$ was spiked into the groundwater. However, when the stochiometric amount of 2.5 mg/L chlorine (needed to oxidize $\text{S}_2\text{O}_3^{2-}$) was mixed in the BV to 6 µg/L ClO$_4^-$ breakthrough increased to 31,000 BV. Thus the chlorine again diminished the $\text{S}_2\text{O}_3^{2-}$ competition by oxidation.

![Figure 3-12 The effects of $\text{S}_2\text{O}_3^{2-}$ and chlorine on the adsorption of ClO$_4^-$ to surfactant tailored GAC when using Redlands water. Native influent ClO$_4^-$ 30 µg/L spiking with 1000 µg/L $\text{S}_2\text{O}_3^{2-}$.](image)

Similar favorable results were observed when 500 µg/L of $\text{S}_2\text{O}_3^{2-}$ was oxidized by completely mixing with 1.25 mg/L chlorine, (Figure 3-13). Whereas mere spiking with 500 µg/L $\text{S}_2\text{O}_3^{2-}$, diminished the capacity of TGAC to remove ClO$_4^-$, pre chlorinated restored that capacity for the duration that these runs proceeded.
The author would like to briefly point out that the mixing of chlorine with the water source is important. Contact time was increased from 5 minutes to 10 minutes to evaluate the effect of contact time on ClO$_4^-$ adsorption. It was observed that ClO$_4^-$ breakthrough at 6,500 BV at a 5 minute residence time versus 7,800 at a 10 minute residence time. This compared to 15,000 BV observed when no S$_2$O$_3^{2-}$ is present (Figure 3-14). It was observed that there was no improvement in the surfactant tailored GAC performance to remove ClO$_4^-$ when pseudo concentrations of chlorine were not induced (Figure 3-15). This indicated that chlorine – thiosulfate redox reaction required proper mixing and contact time between the two species for the full redox reaction to occur. It is
suggested that when chlorine is present but does not completely react with S$_2$O$_3^{2-}$, the chlorine can actually oxidize the GAC which can impact the results in an unfavorable manner.

Figure 3-14 The effects of S$_2$O$_3^{2-}$, chlorine and retention time on the adsorption of ClO$_4^-$ to tailored GAC when using D1 water. ClO$_4^-$ influent is 1000µg/L and Influent S$_2$O$_3^{2-}$ is 1000µg/L. Control contact time is 5 minutes
Figure 3-15 The effects of $S_2O_3^{2-}$ and chlorine on the adsorption of $\text{ClO}_4^-$ to tailored GAC when using D1 water. Stochiometric amount (2.5 mg/L) and pseudo amount (7 mg/L) of chlorine was used. $\text{ClO}_4^-$ influent is 1000 µg/L and Influent $S_2O_3^{2-}$ is 1000 µg/L.

3.5 Summary and Conclusions

It was shown in RSSCT experiments with GAC that had been pre-loaded with quaternary ammonium surfactants (TGAC) that thiosulfate greatly diminished the effectiveness of TGAC to remove $\text{ClO}_4^-$ from a DI water source, and also from Redlands groundwater at high concentrations. Also when thiosulfate concentration equaled 1,000 µg/L for both cases, the extent of $\text{ClO}_4^-$ interference was comparable to the diminished $\text{ClO}_4^-$ bed life that has been observed with fresh Redlands groundwater in RSSCTs. It can also be concluded that chlorine oxidation of the thiosulfate, increased the bed life of the carbon to adsorb $\text{ClO}_4^-$ when the chlorination was conducted in the proper
stochiometric proportion and with complete mixing. However, when the chlorine was added in an unbalanced and incompletely mixed manner such that HOCl or OCl\(^-\) entered the GAC vessel, this chlorine could react with the carbon surface and/or cationic surfactant in an unfavorable manner. With these results, it can be seen that stoichiometrically applied chlorination with proper mixing offers a technically useful means of oxidizing thiosulfate and other intermediate –valent sulfur species that it mimics so that these species would not compete as extensively with ClO\(_4\)^- for adsorption to surfactant tailored granular activated carbon.
3.6 Reference


Webster, J.G.1989. An analytical scheme for the determination of sulfide, polysulfide, thiosulfate, sulfite, and polythionate concentrations. DSIR, Petone, NZ.


4 CHAPTER 4 - Competition of common anions with Perchlorate for Adsorption sites on Cationic Surfactant Tailored GAC

4.1 Abstract

The competitive effects of anions found in aqueous environment with respect to perchlorate (ClO$_4^-$) adsorption were studied. Oxyanions nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$) and thiosulfate (S$_2$O$_3^{2-}$) competed with ClO$_4^-$ for adsorption sites on to granular activated carbon that had been tailored with cetylpyridinium chloride (CPC). It was observed overall, that NO$_3^-$ had the greatest competition at concentrations that were two times that of the native NO$_3^-$ concentration found in Fontana, CA groundwater. Using Rapid Small Scale Column Test (RSSCT) with Fontana, CA groundwater that had an influent nitrate of 32 mg/L as NO$_3^-$ and ClO$_4^-$ of 7 µg/L, ClO$_4^-$ breakthrough at 25,000 bed volumes, while when the same groundwater was spiked to three times the native nitrate concentration, ClO$_4^-$ breakthrough occurred at 12,000 bed volumes. This nitrate competition was greater than exhibited by sulfate. Thiosulfate, at far lower concentrations also exhibited competition. At the same spiked concentrations of 100 mg/L nitrate, for both RSSCT and pilot scale test, RSSCT experiments showed a greater competition than pilot scale test. With CPC tailored GAC the sequence of anions competition observed with perchlorate was NO$_3^->$ S$_2$O$_3^{2-} > $ SO$_4^{2-}$.
4.2 Introduction

Perchlorate has often originated from ammonia perchlorate salts, which have been used for rocket fuels. Perchlorate is a very soluble and mobile species in aqueous system, and these characteristics have made it a constant fixture in surface and ground waters in states such as Arizona, California and Nevada (Motzer, 2001). At relatively high concentrations, the perchlorate oxyanion may inhibit the uptake of iodide by the thyroid gland. Moreover, the uptake of large doses of perchlorate has been linked to anemia and brain damage (Li et al., 2001).

The removal of ClO$_4^-$ from aqueous systems has been challenging due to its kinetic properties. Thermodynamically, the +7 valence of chloride in the perchlorate renders this species very unstable at ambient redox levels. However, dissolved perchlorate reacts very slowly at ambient temperatures, because of the high energy barriers (Motzer, 2001; Urbansky 1998), thus it persists for long times in aquifers. Perchlorate does not precipitate with cations that can be filtered out (Brown and Gu, 2005; Horanyi and Vertes, 1975). Also, perchlorate does not significantly sorb to the typical sediments minerals and soils to an extent that impedes its migration through aquifers (Urbansky and Brown, 2003; Brown and Gu, 2005). These properties have made the ClO$_4^-$ anion a significant contaminant in surface and groundwater. Perchlorate possesses other characteristics such as low hydration energy and a small hydrated radius, and because of this it has been shown that it has a remarkable affinity for ion exchange media. Many studies conducted on treatment of ClO$_4^-$ showed that the adsorption process
is considered generally better among treatment technologies for ClO$_4^-$ (Gu and Coates, 2005; Urbansky, 2005; Motzer, 200).

A number of research teams have appraised the removal of perchlorate by ion exchange resins that include quaternary ammonium functional groups (Gu et al., 2001; Tripp and Clifford, 2000, 2006; Batista et al., 2000; Tripp et al., 2003). Gu et al., (2000) and (2002), used a selective bifunctional anion-exchange resin, that hosted trialkylammonium functional groups; and showed that this reached perchlorate breakthrough after processing 100,000 bed volumes of groundwater that contained 50 µg/L perchlorate. Both Gu and Brown, (2005) and Tripp and Clifford (2000) further observed that perchlorate adsorption increase with an increased in hydrophobicity of the resins (refer to Table 4-1). Resins with pyridine as the functional group showed a higher affinity for perchlorate over quaternary amine functional groups even when competing anions were present (Tripp and Clifford, 2006; Sata et al., 1997). Sata et al., (1997) studied the properties of ion exchange resins when pyridine and pyridine derivatives were the functional groups on Type 1 resins. They observed that the placement of hydrophilic groups increase the selectivity of anions.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Separation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylpyridine</td>
<td>275</td>
</tr>
<tr>
<td>Trimethyl</td>
<td>125</td>
</tr>
<tr>
<td>Triethyl</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Tripropyl</td>
<td>&gt;1500</td>
</tr>
</tbody>
</table>
Ion exchange systems are being used because it is simple, can facilitate high capacity as well as functioning at high flow rates (Gu et al., 2007). However, ion exchange media are often regenerated with concentrated salts; and the disposal issues pertaining to this may pose unfavorably with municipalities. In light of these issues, our Penn state team sought to develop an alternative method that would be effective in removing perchlorate while avoiding some of these unfavorable issues.

The work at Penn State consisted of preloading GAC with cationic surfactants that hosted quaternary ammonium or pyridinium functional groups, so that these functional groups could exchange the perchlorate (Parette and Cannon, 2005; Parette et al., 2005; Patterson et al., 2009). When considering overall media costs, performance offered the potential results that this could be a viable method relatively to ion exchange for removing perchlorate from aqueous systems. At high concentrations, cationic surfactants form a monolayer, or monolayer type aggregate with hydrophobic tail group and the GAC surface; this increased the exchange sites needed for perchlorate adsorption. These exchange sites are the positively charge heads that are hydrophilic in nature. This technology is similar to ion exchange resins that were mentioned above. Pore size and volume of the GAC also play a role in the formation of surfactant micelles on its surface thus will affect the exchange capacities of the GAC. Larger pore volume will result in more surfactant being adsorbed thus potentially having more exchange sites. In the work conducted by Parette and Cannon, (2005), it was observed that there was minimal leaching of the quaternary ammonium and pyridinium functional groups off of the GAC (Parette and Cannon 2005).
Selectivity is an important factor for the exchange of the perchlorate. Selectivity is expressed through a separation factor and through a selectivity coefficient. A ClO$_4^-$ selective surfactant tailored GAC, can be defined as one when conducting RSSCTs or pilot scale test using groundwater that is contaminated with ClO$_4^-$ retains ClO$_4^-$ as the last anion to breakthrough. The selectivity of a system can be affected by the sorbate – sorbent interactions, sorbate-solvent interactions (Xiong et al., 2007) as well as by the functional groups and matrix. The selectivity of perchlorate on surfactant tailored GAC with cetylpyridinium chloride in respect to nitrate is 33.6 (Parette, 2006), compared to a selectivity of 10 for trimethyl ion exchange resin. Table 4-2 gives a list of selectivity factors for both cationic surfactants with GAC and ion exchange systems.

<table>
<thead>
<tr>
<th>Ion Exchange System</th>
<th>Cationic Surfactants</th>
<th>Selectivity (ClO$_4^-$ / NO$_3^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>Cetylpyridinium chloride</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>Tallowalkyltrimethylammonium chloride</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>Dicocoalkyldimethylammonium chloride</td>
<td>51.0</td>
</tr>
<tr>
<td>Resins</td>
<td>Trimethylamine</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Triethylamine</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Tripropylamine</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Bifunctional</td>
<td>100</td>
</tr>
</tbody>
</table>

The adsorption of a specific anion is strongly influenced by the presence of competitive anions and other agents (Inglezakis et al., 2005). The capacity of ion exchange systems are dependent on the composition of the influent that is to be treated. According to Helfferich (1995), ion exchange systems are greatly affected by the
complex formation of the various mobile species with one another, which can cause poor removal of their specific ion due to the formation of highly stabilized complexes on the surface. Najm et al., (1999) found that the efficiency of ion exchange systems to remove ClO₄⁻ decreased in the presence of SO₄²⁻ and NO₃⁻. These concentrations were orders of magnitude greater than the ClO₄⁻ ion. Roach and Tush, (2008), showed that the retention of ClO₄⁻ on the quaternary ammonium functional group decreased when competing ions, specifically chloride and SO₄²⁻ were present in the poly (diallyldimethylammonium) chloride solution. Zhang et al. (2007) also observed that the sorption of perchlorate decrease in the presence of competing anions specifically NO₃⁻, when using cationic surfactant modified zeolite. It was observed that NO₃⁻ significantly affects the sorption of ClO₄⁻ on quaternary ammonium modified zeolite when concentrations were 2.5 to 10 times the concentration of ClO₄⁻, where ClO₄⁻ concentrations ranged from 100- 400 mg/L. It was also observed that the competitive effects were greater at 100 mg/L ClO₄⁻ than at 400 mg/L ClO₄⁻. Zhang et al. (2007) also demonstrated the competitiveness of NO₃⁻, by using 31g/L of NO₃⁻ to desorb ClO₄⁻ that was previously sorbed to the surfactant modified media. They showed that approximately 40% of ClO₄⁻ was displaced by NO₃⁻. This shows that NO₃⁻ will displace the ClO₄⁻ that was already attached to the ion exchange site. This also suggests that at high concentrations, NO₃⁻ will compete with ClO₄⁻ for adsorption sites on solid surfaces that utilize cationic surfactants, for example GAC. This makes anion selectivity an important factor especially in the case of GAC adsorption systems design for the removal of ClO₄⁻.
Hydration energies also play a role in the adsorption of anions to ion exchange sites. Sata et al., (1997) studied hydration energy properties and reported that hydration energy rather than ionic size plays an important role in the ion exchange process. Ions that have lower hydration energies tend to have a greater affinity to the exchange site more so than ions that have higher hydration energies. Behnsen and Riebe, (2008) also observed anions selectivity when they used surfactant modified bentonite clay and correlated it with hydration energy. Anions that were more selective had low hydration energy than anions that had high hydration energy.

The competitive effects of NO$_3^-$, Cl$^-$, and SO$_4^{2-}$ anions in ion exchange processes has been studied extensively. But to the author’s knowledge, there has not been any published article on the effects of these anions on the ability for GAC that has been preloaded with quaternary ammonium or pyridinium functional groups to remove ClO$_4^-$.

In the present study the effects of NO$_3^-$, SO$_4^{2-}$, and S$_2$O$_3^{2-}$ on the adsorption of ClO$_4^-$ to surfactant tailored GAC was examined. The aim of this study was to observe the specific effects of these anions competition on ClO$_4^-$ adsorption to exchange sites on surfactant tailored GAC at both the laboratory scale and pilot scale.
4.3 Experimental

4.3.1 Materials

The laboratory columns were designed according to Parette and Cannon, 2005. Unless otherwise noted all experiments used acid washed AquaCarb, an anthracite carbon supplied by Siemens Technology. For RSSCT experiments, 1.64g acid washed AquaCarb was used for all test. This corresponded to 0.48 g/mL bed density and a surfactant loading of 0.30 g of CPC/g of GAC. In all experiments, the GAC used was ground and sieved to a size range of US Mesh #200 x 400 mesh (75 x 35 um). The pilot scale system contained approximately 375 gallons of CPC tailored 20 x 50 acid wash AquaCarb in each vessel. The pilot scale loading was 0.30 g CPC/g of GAC.

The study used ground water obtained from Fontana, CA. The groundwater contained 7 µg/L ClO₄⁻; nitrate 32 mg/L as NO₃⁻; sulfate 5 mg/L; Cl⁻ 12 mg/L; TDS 250 mg/L and a pH of 7.5.

4.3.2 Methods

4.3.2.1 Rapid Small Scale Tests

For the tailoring of the carbon with surfactant, a column was filled with approximately 1.27 g of GAC and tailored with 33 BV of 0.4 % surfactant solution. The tailoring process took approximately 2 days, during which surfactant solution was
pumped and recirculated at 2 mL per minute through the activated carbon. Deionised water was used to pre-load the surfactant on the GAC. After the tailoring process, groundwater from Fontana CA was pumped into the tailored carbon at flow rates of 2.5 ml/min, which provided a 1 minute empty bed contact time (EBCT). This simulated a 10 minute EBCT at the field scale level for a #20 x 50 mesh GAC. Samples were collected two times per day until there was total breakthrough of the ClO$_4^-$.

For the first 10,000 bed volumes, each sample collected was tested for cationic surfactant using the colorimetric method (Parette and Cannon, 2005; Parette et al., 2005), which could detect the cationic surfactants at concentrations above 0.2 mg/L. The length of the RSSCTs ranged from 5-20 days until there was breakthrough of ClO$_4^-$. The bedlife was influenced by the extent of competition by other anions.

### 4.3.2.2 Pilot Scale Tests

The pilot scale system consisted of three vessels in series. Two of the vessels were stratified with conventional surfactant tailored GAC, which overlayed conventional GAC in the same chamber. These contained 1.5-2.2 cubic feet of surfactant tailored GAC in the lead chamber (on top), and 0.8-1.5 cubic feet of conventional GAC in the second chamber (on bottom) (Figure 1). These vessels were designed to operate at a 10 EBCT for the surfactant tailored GAC portion of a bed, plus another 5 minute EBCT for conventional GAC. This corresponds to a flow rate of approximately 2.3 gpm.
The influent water for the pilot-scale tests was pre-filtered to remove particulates using 10 micron cartridge filters. This pre-filtration reduces particulate accumulation that could have otherwise lead to excessive pressure drop across the surfactant tailored GAC/conventional GAC beds. Flow meters monitored influent flows; and mechanical totalizers monitored effluent processed.

![Figure 4-1 – Schematic of the pilot scale surfactant tailored GAC system. * TGAC – surfactant tailored GAC](image)

### 4.3.2.3 Stock Solutions

For the RSSCT experiments, spiking and standard concentrations for the anions were made from 10 g/L stock solutions. The stock solutions were prepared from reagent grade chemicals and deionized distilled (DI) water. Sodium salts of NO$_3^-$, SO$_4^{2-}$ and chloride were used. These salts were obtained from J.T. Baker. Table 4-3 and 4-4 show all the experiments that were conducted and the concentrations of anions that were employed for the RSSCT and pilot scale experiments. Standards were prepared and refrigerated. Standards were analyzed each time anion analyses were conducted.
Table 4-2 Pilot scale and RSSCT experiments conducted with Fontana groundwater

<table>
<thead>
<tr>
<th>Anions</th>
<th>Spiked Concentration of Anions (mg/L)</th>
<th>RSSCT</th>
<th>Pilot Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>30, 70</td>
<td>361</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>250</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>1, 10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>50, 250</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

1 The total amount of anions that were present in the spiked test waters.

Table 4-3 - Summary of Spiking Levels and EBCT in Pilot-Scale Test

<table>
<thead>
<tr>
<th>Train Name</th>
<th>Compound Spiked</th>
<th>Mean EBCT</th>
<th>Mean influent conc. (mg/L)</th>
<th>Mean spiked influent conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>none</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrate Spiked</td>
<td>Sodium Nitrate</td>
<td>11.6</td>
<td>41</td>
<td>61</td>
</tr>
<tr>
<td>Sulfate Spiked</td>
<td>Magnesium sulfate</td>
<td>13.2</td>
<td>274</td>
<td>995</td>
</tr>
</tbody>
</table>

4.3.2.4 Anions Analysis

All anions measurements were analyzed with the use of Dionex DX-120 ion chromatography. This was equipped with an AS40 autosampler, 4 mm AS16 column, a 4 mm AG16 guard column, a 4 mm self-regenerating suppressor and DS4 detection stabilizer. The stabilizer used a current of 300 mA and a temperature of 35°C. Elluent concentration used was 25 mM. The sample loop for the ClO₄⁻ anion was 1000µL, while for other anions was 25µL.
4.4 Experimental Results and Discussion

4.4.1 Rapid Small Scale Column Tests

4.4.1.1 Nitrate

The results of column experiments for anion competition with ClO$_4^-$ using Fontana groundwater are presented here. Figure 4-2 shows the results of experiments that were conducted using an array of NO$_3^-$ concentrations on ClO$_4^-$ adsorption. Throughout this paper, nitrate is reported as NO$_3^-$. A decrease in surfactant tailored GAC’s capacity for ClO$_4^-$ was observed at varying nitrate spiked concentrations. There was a 24% and 50% decrease in the capacity for the surfactant tailored GAC to adsorb ClO$_4^-$ when the NO$_3^-$ concentrations were two and three times the amount that was observed in the native groundwater. With native groundwater, ClO$_4^-$ at 6 µg/L broke through at 25,000 BV. While, when the same water was spiked to a total NO$_3^-$ concentration of 60 mg/L, ClO$_4^-$ breakthrough at 19,000 BV, and 12,000 BV when the nitrate concentration increased to 100 mg/L as NO$_3^-$. 
Figure 4-2 The effects of ClO$_4^-$ adsorption to surfactant tailored GAC when two different concentration of NO$_3^-$ was used in RSSCT experiments using Fontana groundwater. Shown are the total concentrations of NO$_3^-$ in each experiment. Control had a background concentration of 32 mg/L NO$_3^-$. 

4.4.1.2 Sulfate and Thiosulfate

In RSSCTs, Fontana groundwater that contained a native sulfate concentration of 5 mg/L, was spiked with additional sulfate to concentration of 50 mg/L and 250 mg/L. The latter corresponds to the maximum secondary contaminant level set by the USEPA. For each of these cases, 6 µg/L ClO$_4^-$ breakthrough occurred at 25,000 bed volumes (Figure 4-3). Thus, these levels of sulfate competition posed little change in the performance of the tailored carbon to remove ClO$_4^-$ when SO$_4^{2-}$ concentration was increased.
Figure 4-3 The effects of ClO$_4^-$ adsorption to surfactant tailored GAC when various concentration of SO$_4^{2-}$ were added to the Fontana groundwater in RSSCT experiments. Shown were the total spiked concentrations of SO$_4^{2-}$ (50mg/L and 250 mg/L) in each experiment. Control had a background concentration of 5 mg/L SO$_4^{2-}$.

Thiosulfate, an intermediate-valence sulfur species, at 1 mg/L and 10 mg/L concentration was also added to native Fontana groundwater, so as to appraise its competitive effect in this water, to observe any effects on the removal of ClO$_4^-$ by the surfactant tailored carbon (Figure 4-4). As indicated above, thiosulfate or other intermediate-valence sulfur species were not noticeably present in Fontana groundwater; and this groundwater hosted a positive oxidation potential at the well head. The 6 µg/L ClO$_4^-$ breakthrough occurred at 22,000 with 1 mg/L S$_2$O$_3^{2-}$ and at 20,000 bed volumes with 10 mg/L S$_2$O$_3^{2-}$. These bed lifes represented a 12% and 20% decrease respectively, in the performance of the surfactant tailored carbon to remove ClO$_4^-$. 
4.4.2 Pilot Scale

In conjunction with column tests, pilot scale experiments were also conducted so that a direct comparison could be made between laboratory scale and pilot scale experiments. The pilot scale study also focused on anion competition for perchlorate adsorption to surfactant tailored GAC.

Results from the pilot scale showed that nitrate affects the adsorption of perchlorate to surfactant tailored GAC. Perchlorate was tested out of both the first stratified bed (Effluent 1) and out of the second (Effluent 2). For native Fontana
groundwater, perchlorate broke through from the Effluent 1 at 16,000 BV and from Effluent 2 at 32,000 BV (Figures 4-5 and 4-6). With the treatment train that was spiked with 61 mg/L nitrate (to a total nitrate concentration of 100 mg/L of nitrate), perchlorate breakthrough at 12,000 BV for Effluent 1 and 21,000 from Effluent 2. It should be noted that BV in this case was calculated as water treated through the first vessel/bed which is Effluent 1. This was a 25% reduction in the surfactant tailored GAC to remove perchlorate from Effluent 1 and 34% from Effluent 2. In comparison to the RSSCT tests, the RSSCT showed a greater competition with nitrate at 100 mg/L versus the pilot scale experiments.

The effect of sulfate was also studied (Figure 4-5 and 4-6). Perchlorate breakthrough at 16,000 BV from Effluent 1 with the treatment that spiked 1000 mg/L \( \text{SO}_4^{2-} \) and 21,000 BV from Effluent 2. There was no competition for adsorption sites by the sulfate anion with perchlorate at Effluent 1 in the pilot scale test. This was also depicted at the RSSCT level. Competition however, was observed at Effluent 2, where the surfactant tailored GAC capacity to remove perchlorate decreased by 34%. This was similar to the competition of nitrate at Effluent 2 port. It could be seen that at sulfate concentrations 10 times that of nitrate, there was no competition at Effluent 1 and the same percent competition at Effluent 2. From this it could be concluded that nitrate had a greater competitive nature than sulfate when pyridinium functional group is the exchange site.
Figure 4-5 – The effects of ClO$_4^-$ adsorption to surfactant tailored GAC when different concentration of NO$_3^-$ and SO$_4^{2-}$ is used in the pilot scale test, out of the first GAC bed in series. Shown are the total concentrations of NO$_3^-$ and SO$_4^{2-}$ (100 mg/L and 1000 mg/L) in each experiment. Control has a background concentration of 32 mg/L NO$_3^-$ as NO$_3^-$ and 5 mg/L SO$_4^{2-}$. 
Figure 4-6 - The effects of ClO$_4^-$ adsorption to surfactant tailored GAC when different concentration of NO$_3^-$ and SO$_4^{2-}$ is used in the pilot scale test, Effluent 1. Shown are the total concentrations of NO$_3^-$ and SO$_4^{2-}$ (100 mg/L and 1000 mg/L) in each experiment. Control has a background concentration of 32 mg/L NO$_3^-$ as NO$_3^-$ and 5 mg/L SO$_4^{2-}$.

It was demonstrated through this study that NO$_3^-$ gave the greatest competition of all the anions followed by S$_2$O$_3^{2-}$ and then SO$_4^{2-}$. From the results presented above, the authors sought to understand why NO$_3^-$ was more competitive than both S$_2$O$_3^{2-}$ and SO$_4^{2-}$ and also why S$_2$O$_3^{2-}$, a sulfur species and a divalent anion was more competitive than SO$_4^{2-}$ which is also a divalent anion.

One possible explanation that may explain NO$_3^-$ competitiveness with ClO$_4^-$ for adsorption sites on solid surfaces that are tailored with cationic surfactants can be related to hydration energy (Table 4-6); Perchlorate and NO$_3^-$ anion have low hydration energies, so therefore it may depict the similar characteristics for ion exchange sites. While on the
other hand, SO$_4^{2-}$ has a high hydration energy, therefore would have little to no competition with ClO$_4^-$ for adsorption sites on surfactant tailored GAC.

From the data given in Table 4-4, for anions used in this study, it would appear that hydration energy can be one way to explain the order of competition that was observed in this study. It was observed that the selectivity sequence of the pyridinium tailored GAC was ClO$_4^-$, NO$_3^-$, SO$_4^{2-}$, from this observation it could be speculated that the order of selectivity could be based on the hydration energies, because the order correlates to the increasing order of the hydration energies for the anions.

<table>
<thead>
<tr>
<th>Anions</th>
<th>Hydration Energy (-ΔG (KJ/mol))</th>
<th>Marcus, 1985</th>
<th>Sata, 1999</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchlorate</td>
<td>214</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>306</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>347</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>-</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

From ion activity table (Table 4-5), for quaternary ammonium ion exchange media, the SO$_4^{2-}$ anion would have been more competitive than NO$_3^-$ anion for adsorption sites at low ionic strength (Clifford and Weber, 1983), but the opposite was also observed with ion exchange media that have quaternary ammonium functional groups, demonstrated an affinity sequence of NO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ at high ionic strength (Smith and Woodburn, 1978). Clifford and Weber, (1983) showed that the functionality of the ion exchange process plays an important role on ion selectivity. They observed that size and steric hindrance produced by the functional groups are the determining factors for ion
adsorption. Large functional groups such as quaternary ammonium may prevent the required proximity needed by nitrogen atoms. For similar steric hindrance reasons, a number of research teams have noted that divalent sulfate competes less with monovalent nitrate, perchlorate etc. when employing resins that have triethyl or tributyl quaternary ammonium substituents than when employing resins that have trimethyl quaternary ammoniums (Clifford, 1999; Gu et al., 2000; Tripp and Clifford, 2000). This concurs with the findings of Sata et al. (1997) and Behnsen and Riebe (2008), who observed that anions with low hydration energy were more selectively exchanged than anions with high hydration energy. In particular relative to the micellar structure herein, this trend would be emphasized in that $\text{SO}_4^{2-}$.

### Table 4-5 - Separation Factor for strong base anion exchange resins

<table>
<thead>
<tr>
<th>Anions</th>
<th>Separation Factor ($\alpha_{\text{Cl}^-}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$(CO$_3$)$_3^{4-}$</td>
<td>3200</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>150*</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>100</td>
</tr>
<tr>
<td>SeO$_4^{2-}$</td>
<td>17</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>9.1</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$</td>
<td>4.5</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>4.1</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>3.2</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>2.3</td>
</tr>
<tr>
<td>SeO$_3^{2-}$</td>
<td>1.3</td>
</tr>
<tr>
<td>HSO$_3^-$</td>
<td>1.2</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>1.1</td>
</tr>
<tr>
<td>CI$^-$</td>
<td>1.0</td>
</tr>
<tr>
<td>BrO$_3^-$</td>
<td>0.9</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.27</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>0.14</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Adapted from Clifford, 1999

* Separation factor is for polystyrene strong based anion resin; for polyacrylic strong based anion resin resins the factor is 5
From the order of anion selectively observed for CPC tailored GAC, stated above, coupled with experiments conducted at low ionic strength; the sequence that was observed when pyridinium is the ClO$_4^-$-exchanging functional group on GAC, is opposite of what is observed when quaternary ammonium compounds were the functional groups with low ionic strength waters. With this observation, the authors hypothesized that the non competitiveness of the SO$_4^{2-}$ anion might be due to the inability of the SO$_4^{2-}$ anion to simultaneously access two charged sites on the surfactant tailored GAC. Ions size and the spacing of the surfactant micelles on to the GAC surface play a significant role in the adsorption of ions, specifically divalent ions. It is assumed by the author that spherical and rod-like micelles are formed at CPC concentration that is loaded on to the GAC. The radius of the sphere is usually the length of the surfactant molecule. The length of a CPC molecule is 19.4 Å or 1.94 nm (Yei et al., 2005) and consists of 80 CPC molecules in the sphere (Singh et al., 2005; Kalyanasundaram, 1987). This translates to a spacing of 0.152 nm between charged sites in the spherical or rod-like micelles, when the “flat” sides of the pyridinium groups are aligning with one another. With this observation of the distance between charged sites, the author speculate that SO$_4^{2-}$, a divalent tetrahedral compound, that has a bond length of 0.148 nm (Nickless, 1968), cannot access the two charged sites on the surfactant tailored GAC that it needs to form ion pairs. So instead of adsorption of the SO$_4^{2-}$ anion to the CPC charge sites on the GAC, the SO$_4^{2-}$ anion would pass through the column. Thus, not hindering ClO$_4^-$ adsorption to the charged sites on the CPC tailored GAC. This process was somewhat observed by Sata, (1999). They reported that SO$_4^{2-}$ had a low transport number as the distance between exchange sites increases.
On the other hand, thiosulfate, also a divalent ion, with a bond length of 0.197 nm (Nickless, 1968), would access the two charge sites on the CPC tailored GAC, that it needs to form ion pairs. This will occupy charged sites that ClO$_4^-$ needs, thus competing with ClO$_4^-$ for adsorption sites. It is with these observations that the author speculates as to why S$_2$O$_3^{2-}$ and not SO$_4^{2-}$, competes with ClO$_4^-$ for adsorption sites, even though they are both divalent sulfur species.

The author also sought to understand the difference in competition observed based on concentration of the anions. From the results presented above, it could be seen that 10 mg/L S$_2$O$_3^{2-}$ had also the same competitive effects as 60 mg/L NO$_3^-$. The author speculates that a single CPC monomer can be adsorbed to the GAC at pore size that is equal to or greater than 2 Å; this would form a monolayer, rather than a sphere or rod shaped micelle, of the CPC surfactant on the surface of the GAC. This monolayer would represent a single charged site. The surface area of the GAC that has a pore size ranging from 2-10 Å is greater than the pore size between 10-50 Å (which is more favorable for divalent anions due to ion size and charge spacing). Therefore greater concentrations of nitrate can be adsorbed, due to only needing one charged size, rather than divalent anions such as thiosulfate, that is a larger anion and needs two charged CPC sites.
4.5 Conclusions

The present study shows that anions such as nitrate and thiosulfate compete with ClO$_4^-$ for adsorption sites, while sulfate does not. The sequence of competition suggests that hydration energy of the anions is a key factor in adsorption to N-surfactant tailored GAC, and also the formation of surfactant aggregates and surfactant micelle size may also play a significant role as well. The observation that thiosulfate and not sulfate competes with ClO$_4^-$ also suggest that spacing between exchange sites as well as the size of the anions plays a role in the adsorption process, this is especially for divalent ions.
4.6 References


5 CHAPTER 5 – Evaluation of Proportional Diffusivity as a Scaling Model for Cationic Surfactant-tailored GAC.

5.1 Abstract

Results for Rapid Small Scale Column tests (RSSCTs) and pilot scale tests for the removal of perchlorate from groundwater, using surfactant tailored activated carbon, were compared to determine the accuracy of scale – up. Results demonstrated that RSSCT designed on the basis of proportional diffusivity, a diffusion coefficient of 1, over predicted the adsorptive capacity of the pilot scale by 58 percent. This result was observed both with anthracite and bituminous-based carbons. This suggested that intra-particle diffusivity and particle radius were not linearly related when surfactant tailored GAC was used. However, results from RSSCT, that was designed with a coefficient of 0.5, under predicts the model for perchlorate adsorption to surfactant tailored GAC when compared to pilot scale columns. This experiment gave a ratio of 0.38.

5.2 Introduction

The scaling of this technology has employed the RSSCT scaling equations for proportional diffusivity by Crittenden et al. (1991). When proportional diffusivity model holds true then a properly designed RSSCT will accurately predict field scale performance. This model works even though the test period is dramatically shorter since RSSCT uses a smaller particle size and its performance is governed by the same
adsorption capacity and kinetics factors that govern larger scale performance (Crittenden 1991, 1986). In this study both demonstration-scale tests and RSSCT’s were conducted with the same water source, as in this case Fontana groundwater, Redlands groundwater and Penn State University Tap water, so as to appraise whether the proportional diffusivity model fits for perchlorate sorption here. Penn State has demonstrated with conventional GAC that proportional diffusivity is indeed the proper model. However, when employing tailored GAC, there are some possible distinctions; the proportional diffusivity model addresses how to scale-up diffusion effects in small grains that are simulating full-sized grains. However, similitude with regard to the redox level of the water may be difficult to achieve in RSSCT’s.

The Rapid Small Scale column tests (RSSCTs) were developed to reduce the time and cost that is associated with conducting pilot scale studies. RSSCT are a smaller scaled down fixed bed column that can actually utilize the same raw water that needs to be treated. The scaling model uses the dispersed-flow pore and surface diffusion model pioneered by Crittenden and company (1986 and 1991). This model can be a good predictor for the full scale experiments. The idea behind using RSSCT to predict full scale performance is to maintain perfect similarity between the two. This is done by setting the dimensionless group for the RSSCT to equal that of the large scale column. Similarity is maintained when proper particle size, empty bed contact time and hydraulic loading are considered. An RSSCT column uses a smaller grain size carbon to produce identical breakthrough columns if the dimensionless principle holds true. It should be noted that in order for the RSSCT to correctly predict the full scale column, changes in
adsorptive capacity and kinetics when there is a change in particle size needs to be considered. Intra-particle diffusion also plays an important role in the scaling of full scale to RSSCT.

5.3 Scaling Model

The scaling model that was designed by Crittenden et al. (1991) found that if scaling parameters such as void fractions, bulk densities, and capacities are identical for the GAC used in both the RSSCT and full-scale process, then the scaling of the EBCT can be determined from intra-particle mass transfer resistances (Equation 5-1).

\[
\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^{2-X} = \frac{t_{SC}}{t_{LC}}
\]

Equation 5-1

Where: SC = Small Column, LC = Large Column

\( d_p \) = adsorbent particle size [cm]
\( t \) = elapsed time in the respective column test [min]
\( X \) = the dependence of the intra-particle diffusion coefficient on particle size

The intra-particle diffusion coefficient, denoted as \( X \) in equation 5-1, is important in the scaling model as this determines the rate of adsorption. Intra-particle diffusion is affected by the compounds that are present in the water. It was observed that water that
has DOC and other organic chemicals can affect the adsorptive capacity of the particle size and this will introduce a difference between full scale and RSSCT. When the intra-particle diffusion coefficients were assumed not to be depend on particle size, X = 0, this is referred to as constant diffusivity. Constant diffusivity is defined as when the amount of spreading in the breakthrough curve is identical to the column length. RSSCT and full scale experiments are identical when their Reynolds numbers are set the same.

When the intra-particle diffusivity is a linear function of particle size then is referred to as proportional diffusivity, where X = 1. For hydraulic loading, or superficial velocity \( v \), the equation that ensures proportional diffusivity, is given by (Crittenden et al, 1991):

\[
\frac{v_{SC}}{v_{LC}} = \left[ \frac{d_{p,LC}}{d_{p,SC}} \right] \ast \frac{Re_{SC, min}}{Re_{LC}} \quad \text{Equation 5-2}
\]

\( Re_{SC, min} \) is the minimum Reynolds number that guarantees the effects of dispersion and external mass transfer in the small column do not exceed those of the large column. The Reynold’s number is defined as (Droste, 1997):

\[
Re = \left[ \frac{\rho v \psi d_{p}}{u} \right] \quad \text{Equation 5-3}
\]

Where:
- \( \rho \) = density of water [g cm\(^{-3}\)]
- \( v \) = superficial velocity [cm s\(^{-1}\)]
- \( u \) = viscosity of water [g cm\(^{-1}\) s\(^{-1}\)]
- \( d_p \) = media grain diameter [cm]
\[ \psi = \text{sphericity of filter media [unitless]} \]

These scaling equations allow the RSSCT results to design a full-scale system. The EBCT for the full-scale system is found by using equation 1, which is needed to size the system \( V_{LC} \) using equation 5-2. The time to breakthrough from the RSSCT results is recorded, annotated in equation 1 as \( t_{bk} \).

### 5.4 Motivation for this Experiment

As a follow-up to the RSSCTs, pilot-scale tests were conducted in Redlands, California. Redlands groundwater contained 50-70 \( \mu \)g/L of perchlorate and moderate nitrate levels. The bed volumes to initial breakthrough was 17,000 bed volumes for the pilot scale system; and this compared to 30,000-35,000 bed volumes to initial breakthrough in RSSCT using Arquad 2C-75 as the functional group. This depiction of an earlier perchlorate breakthrough for the pilot scale test than the RSSCT, led the author to suspect that the diffusion model used may not be appropriate for surfactant tailored GAC.

### 5.5 Objectives

The objective of this study is to observe if proportional diffusivity is a good similitude for the scaling of RSSCT to pilot scale and thus ultimately full scale when tailored GAC is used. This study will compare RSSCTs and pilot scale tests for three
types of water that differs in water chemistry in some way. If proportional diffusivity does not hold then RSSCTs will be conducted to explore intra-particle diffusion (X) coefficient best fit this model for tailored GAC will best describe the scaling model for RSSCT and pilot scale tests as it relates to tailored GAC.

5.6 Experimental

Three pilot scale systems were compared with their RSSCT to observed perchlorate breakthrough. This consisted of Redlands groundwater, Fontana Groundwater and Penn State Tap water. Each system design parameters are described individually in the coming sections. The same raw water was used for each set of experiment i.e. the same water for both pilot scale and RSSCT, such as Fontana.

5.6.1 Pilot Scale Column Tests

5.6.1.1 Fontana Groundwater

The 37 gpm system comprised three vessels operating in series Figure 5.1. The treatment train included a lead and lag tailored GAC vessel and a third conventional GAC vessel for tailoring agent polishing. AquaCarb, an anthracite carbon, was used in these experiments and was tailored with cetylpyridinium chloride surfactant. All three vessels contained approximately 375 gallons of media (either TGAC or conventional GAC). This system was designed to treat water at a flow rate of approximately 37.5 GPM, which corresponds to a 10 minute empty bed contact time EBCT in each vessel (total EBCT of
20 minutes for TGAC and 10 minutes for the conventional GAC). Each of the three beds was designed to be 4 feet in diameter, with a 4 foot depth of GAC media.

![Diagram](image)

**Figure 5-1 Schematic of the pilot scale set of Tailored GAC treating Fontana Groundwater**
*TGAC- tailored GAC

### 5.6.1.2 Redlands Groundwater

This pilot scale study operated at 60 gpm with a 12 min EBCT through each of the three 2,000 pounds tailored carbon beds in series. The bed was 4 feet deep and 4 feet in diameter. The first two beds were tailored with cetylpyridinium chloride (CPC) and the third a non-tailored polishing bed. This pilot study employed a dual bed system, which means that \( \frac{2}{3} \) of the beds was CPC tailored GAC and bottom third was conventional GAC. This applies to 2 out of the 3 beds in series. The third bed was packed with
conventional GAC only. All three GAC beds used Ultracarb, a bituminous-based GAC at full-scale GAC grains of US #12 x 40.

5.6.1.3 Penn State Tap Water

The Penn State system consisted of 1 tailored bed with 2 Kg of carbon. The system was designed to treat water at a flow rate is 385 ml/min (0.1 gpm) at a 10 minute EBCT. The bed depth is equivalent to 4 feet with an internal diameter of 3.5 inches. Penn state Tap water has not had any perchlorate present, so perchlorate was spiked into the influent concentration at either to 50 ppb or 500 ppb. AquaCarb, an anthracite carbon, was used in these experiments and was tailored with cetylpyridinium chloride surfactant.

5.6.2 Rapid Small Scale Column Tests

For all RSSCTs, a column is filled with approximately 1.40 g of GAC and tailored with the surfactant in 87 mL of water. The tailoring process took approximately 2 days where the surfactant solution was pumped and recirculated at 2 mL per minute through the carbon. In all experiments, the GAC was ground and sieved to a size range of US Mesh #200 x 400 mesh (74 x 37 µm). The laboratory columns used were manufactured to withstand the high pressures that are required with the use of the small GAC grains. After the tailoring process, water from the individual source was pumped into the tailored carbon at a flow rate that simulated each pilot scale. Table 5-1 list experiment criteria for each water source.
Perchlorate measurements were conducted with the use of Dionex DX-120 ion chromatograph in accordance with the methodology presented in Chapter 3. The length of each RSSCT experiment is dependent on column design and is depicted in Table 5-1.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Parameters</th>
<th>Surfactant</th>
<th>EBCT (minutes)</th>
<th>Length of Column</th>
<th>Bed Volumes (mL)</th>
<th>Perchlorate concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redlands Groundwater</td>
<td>GAC</td>
<td>UltraCarb</td>
<td>0.975</td>
<td>13.5</td>
<td>2.65</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(bituminous)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fontana Groundwater</td>
<td>GAC</td>
<td>Acid wash</td>
<td>0.975</td>
<td>13.5</td>
<td>2.65</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AquaCarb (anthracite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penn State Tap Water</td>
<td>GAC</td>
<td>Acid wash</td>
<td>0.975</td>
<td>13.5</td>
<td>2.65</td>
<td>50 and 500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AquaCarb (anthracite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penn State Tap Water</td>
<td>GAC</td>
<td>Acid wash</td>
<td>0.309</td>
<td>4</td>
<td>0.77</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AquaCarb (anthracite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Samples were taken twice daily until breakthrough was more than 50% of influent perchlorate concentration.

5.7 Results and Discussion

The tailored GAC capacity to adsorb perchlorate at the RSSCT level should agree with the adsorption capacity at the pilot scale level. When this occurs, it would be
interpreted as the scaling model being a good fit. Two type of intra-particle diffusion
coefficient was tested: X=1 which is proportional diffusivity and X= 0.5 which indicates
somewhere between that of proportional diffusivity and constant diffusivity. This was
chosen to observe if the intra-particle diffusion coefficient was dependent on particle
size, but the relationship somehow was not linear. Table 5-2 presents a summary of the
results for this study.

Table 5-2 Summary of pilot and laboratory experiments conducted and their corresponding
ratios, for each water source.

<table>
<thead>
<tr>
<th>Water Source</th>
<th>Influent ClO$_4^-$ (µg/L)</th>
<th>Bed Volumes to 6 µg/L ClO$_4^-$ breakthrough</th>
<th>Ratio (RSSCT: Pilot Scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pilot Scale</td>
<td>RSSCT</td>
</tr>
<tr>
<td>Fontana</td>
<td>7</td>
<td>16,000</td>
<td>25,000</td>
</tr>
<tr>
<td>Redlands</td>
<td>55</td>
<td>19,000</td>
<td>32,000</td>
</tr>
<tr>
<td>Penn State</td>
<td>50</td>
<td>27,000</td>
<td>50,000</td>
</tr>
<tr>
<td>Penn State</td>
<td>500</td>
<td>8,000</td>
<td>15,000</td>
</tr>
<tr>
<td>Penn State*</td>
<td>500</td>
<td>8,000</td>
<td>3,000</td>
</tr>
</tbody>
</table>

* This experiment was conducted using an intra-particle diffusion coefficient (X) = 0.5

It was observed from the results that perchlorate had earlier bed volumes to
breakthrough for pilot scale than RSSCT for all proportional diffusivity experiments that
utilized an intra-particle coefficient of X = 1 (Figures 5-2 -5-5). An RSSCT to pilot scale
ratio was observed that averaged 0.58. This translates to the RSSCT predicting
perchlorate bed life to be 50% longer than the pilot scale experiments. This suggests that
diffusivities were not linearly dependent on particle radius, and this over-prediction of
RSSCT might be due to external mass transfer coefficients.
It is observed by Crittenden et al. (1989), that pilot scale experiments have a higher external mass transfer coefficient than that of the RSSCT. According to Crittenden et al. (1989), RSSCT cannot be good predictors of GAC performance and capacity unless the intra-particle diffusivity of the substances that causes GAC reduced capacity is dependent on the particle size in the same way that target contaminant does. Seeing that proportional diffusivity was a very good predictor for GAC that was not tailored with an organic cationic surfactant, but not good with the organic tailored GAC, then it can be concluded that organic cationic surfactants affect the intra-particle diffusion and thus the adsorption rate of the contaminant to the tailored GAC. It could be speculated that the adsorption rate was much greater at the RSSCT than at the pilot scale.

With these results, the author then sought to use an intra-particle diffusion coefficient that was between that of constant diffusivity and proportional diffusivity. A value of $X= 0.5$ was used. Results observed from this experiment showed that perchlorate breakthrough earlier than the pilot scale experiments, and gave a ratio of 0.38 (Figure 5-5 and Table 5-2). This showed that the difference between RSSCT and pilot scale was less than what was observed when proportional diffusivity ($X = 1$) was employed. This further demonstrated that intra-particle diffusion and particle size play a significant role in RSSCT scale parameters, but these parameters are not linearly related, as well as not being independent of each other. This experiment suggest that if intra-particle diffusion and particle size are important parameters of mass transfer, then the diffusivity coefficient could be between $X= 0.5$ and $X =1$. 
The author also speculated that the reduction observed with intra-particle kinetics may be due to the tailoring of the GAC with cationic surfactant. The cationic surfactant might have reduced or eliminated surface diffusion, thus pore diffusion was controlling the mass transfer rate. This may have occurred because the cationic surfactant was already adsorbed to the surface of the GAC, thus transforming the surface area and the pore volume. With this transformation, the scale-up model that was used for GAC that was not tailored with cationic surfactants, cannot be used for the tailored GAC.

Figure 5-2 Comparison of RSSCT and Pilot scale experiments on perchlorate adsorption to TGAC using Fontana groundwater. Influent Perchlorate is 7 µg/L.
Figure 5-3 Comparison of RSSCT and pilot scale experiment for Perchlorate adsorption on TGAC using Redlands groundwater. Influent Perchlorate is 70 µg/L.

Figure 5-4. Comparison of RSSCT and pilot scale experiment for Perchlorate adsorption on TGAC using Penn State University tap water spiked with 50 µg/L perchlorate.
Figure 5-5. Comparison of RSSCT and pilot scale experiment for Perchlorate adsorption on TGAC using Penn State University tap water spiked with 500 µg/L perchlorate, using different intraparticle diffusion coefficient. PD is denotes that proportional diffusivity (X=1) was employed, while NPD denotes an X value of 0.5

5.8 Conclusions

This study demonstrated that intra-particle diffusivity is an important parameter in the scaling of tailored GAC at the small scale versus the large scale. It also demonstrated that an intra-particle diffusion coefficient of 1 was not the proper similitude to use for RSSCT to predict the adsorptive rate at the pilot scale. It can also be concluded that the tailoring of the GAC with cationic surfactant affects the relationship between the diffusion coefficient and particle radius.
5.9 References


A powerful oxidant, used to power rocket engines and used extensively in many industries, perchlorate has added to its list of accolades as being a persistent contaminant that now garners attention from top environmental institutions and agencies. To date, it is estimated that 36 states and 11 million people are affected by perchlorate contamination.

Fresh water supply is becoming very limited, and the presence of contaminants compound the issue. Now many states are faced with the challenge of providing contaminant free water, as well as to meet the water demands of its citizens in the future. Up to this point, many measures have been implemented to improve the water supply reliability, and most if not all requires waters that are not impaired. This makes water quality more important. Many states have limited water supply for their citizens; and they seek inexpensive options to treat contaminated water.

The kinetic and thermodynamic properties of perchlorate have made remediation and treatment a challenging task. The most commonly used technologies for perchlorate remediation are ion exchange and bioremediation. These are the two most developed technologies. Other treatment technologies are either cost prohibitive or still in the development stage. Surfactant tailored Granular Activated Carbon (GAC) is still in the development stage. Penn State has developed this technology, and as with other treatment technologies, many experiments have to be conducted with different types of water to
develop its flexibility to be used in many environments. There is no one perfect treatment technology for contaminant removal, and considerations of geochemical and hydrological environments should be noted.

The development of this technology continues, as the goal of this project has been to evaluate and optimize the opportunity of employing surfactant tailored GAC to remove perchlorate from aqueous systems.

The author contributed to science and engineering through this research, by demonstrating that reduced and intermediate valence sulfur species affects the adsorption of perchlorate to tailored granular activated carbon. It is to the author’s knowledge that no one has studied the removal of these intermediate sulfur species, specifically thiosulfate, by surfactant tailored GAC. The author has also demonstrated through this research, the competition of anions for adsorption sites on activated carbon that is tailored with cationic surfactants. It was suggested from the results of this research, that a divalent, multivalent or organic species might be affecting the adsorption of perchlorate. These two areas of contribution demonstrated that with proper pre-treatment and low ionic strength for ground waters that have intermediate sulfur species, then surfactant tailored GAC can be a viable solution in the treatment of perchlorate.
6.1 Recommendations for Future Work

With the goal of continued improvement in this technology, more research needs to be conducted to better evaluate and improve each component of the technology. Consideration should be given to the following areas for future research:

1. Oxidation of Intermediate – Valence Sulfur Species – Evaluate other methods of oxidation, such as the use of hydrogen peroxide and ozonation, for reduced and intermediate sulfur species transformation; identifying the most cost effective method that will demonstrate the same results as chlorine, but will minimize or mitigate the possibility of disinfection by-products.

2. Ionic Strength – Investigate the effects of ionic strength on the adsorption of perchlorate on to cationic surfactants from GAC. It was observed that ionic strength played a role in the adsorption of perchlorate. Batch experiments can be conducted that may identify the ionic strength that tailored GAC is optimal in the removal of perchlorate.

3. Diffusion Model – Proportional diffusivity was observed not to be an accurate similitude for tailored GAC. More studies should be conducted to demonstrate the appropriate intra-particle diffusion co-efficient for predicting the proper scaling model.
This could be conducted using mathematical methods such as homogenous – surface diffusion model (HSDM) or through batch experiments. These methods could accurately predict breakthrough curves for tailored GAC and thus answer questions such as:

1. What is the rate of adsorption?
2. What is the method of diffusion, and
3. Is surface or solid diffusion, the mode of intra-particle mass transport?
Appendix A

Technical Report-Perchlorate Removal from Redlands, CA Groundwater

September 30, 2006
By: Judodine Patterson, Bob Parette, Fred S. Cannon, Pennsylvania State University

Collaborators:
Doug Headrick, Dave Commons, Greg Gage, Rebecca Schwartz, City of Redlands,
Jim Graham, US-Filter; Bob Simpson, Lockheed-Martin

ABSTRACT

Cationic surfactants were tailored on to granular activated carbon (GAC) to increase its capabilities for the removal of perchlorate from drinking water systems. Virgin GAC removes perchlorate for up to 1000 bed volumes (BV) before breakthrough. By pre-loading the GAC with cationic surfactants, perchlorate was effectively removed for up to 17 times longer for the demonstration scale tests and 30 times longer for rapid small scale column test (RSSCT). With cationic surfactants such as dicocodimethylammonium (Arquad 2C-75), tallowtrimethyl ammonium (Arquad T-50) and cetylpyridinium chloride (CPC), 50 ppb perchlorate was removed for 17,000 – 34,000 BV before there were breakthroughs of perchlorate above 1ppb. Groundwater was used that also contains other anions such as sulfate and nitrate.

For demonstration scale testing, we have been processing water through beds in series: The first bed is tailored with cationic surfactants such as CPC, and the next bed is non-tailored bituminous GAC. Breakthrough of perchlorate from the first tailored bed occurred at around 11,000 bed volumes for phase 1, 15,000 bed volumes for phase 2 and 17,000 bed volumes for
phase 3 field scale projects (with an average of 23% pre-loading of the surfactants on the GAC). This compared to RSSCTs which showed breakthrough should occur at approximately 33,000 bed volumes (with 29% loading of the CPC on the GAC).

INTRODUCTION

Pennsylvania State University has developed a technology that uses a cationic surfactant to tailor the carbon which will cost effectively remove perchlorate from water at concentrations below 1ppb (Parette and Cannon, 2005). This tailoring of GAC with cationic surfactants extends its bed life for adsorbing perchlorate up to 34 times that of virgin GAC when treating Redlands CA water (50-70 perchlorate) in Rapid small scale column test (RSSCTs). This technology has not been permitted for use in drinking water system and it has also not been commercialized.

It is expected that the cationic surfactant will act similar to that of quaternary ammonium group that are used in strong based ion exchange media. The loading of the surfactants produces positively charged groups of the surfactant micelle can act as an ion exchange site where perchlorate can be adsorbed.

The purpose of this study was to evaluate the use of GAC that was tailored with cationic surfactants for the removal of perchlorate from groundwater in Redlands California. It is shown that virgin GAC was ineffective in the removal of perchlorate for concentration averaging 50ppb, as breakthrough was detected at 1100 BV of water treated. By tailoring with cationic surfactants, positively charged groups are now used as exchange sites for the adsorption of perchlorate as well as other anions.
Demonstration scale tests as well as RSSCTs were conducted to evaluate the efficiency of the GAC pre-loaded with cationic surfactants. These demonstration tests describe the procedures for an evaluation of a tailored GAC treatment process for perchlorate treatment in drinking. Groundwater was processed through vessels in series. Each phase is described in full in the following sections.

**Phase 1**

Phase 1 was the first demonstration scale test implemented to evaluate the technology of tailored GAC at a field scale level. For this phase there were two beds in series. Each bed was half-filled with 10,000lbs of GAC of which the first bed is tailored with Arquad 2C-75 and the second bed contained virgin GAC to remove residual tailoring agent. The phase utilized a number 8 x 30 mesh size grains (full-scale size) and an empty bed contact time (EBCT) of 7.5 minutes. They were problems with tailoring the GAC as well as backwashing in the system. We monitored for perchlorate, nitrate and N-nitrosodimethylamine (NDMA).

**Phase 2**

Phases 2 followed the same processes as Phase 1, but with knowledge gathered from phase 1 problems of backwashing and tailoring were better handled. For this phase instead of using Arquad 2C-75, Arquad T-50 was used instead. This phase also utilized a # 8 x 30 mesh grain size but this time the EBCT was 11 minutes. Perchlorate, nitrate and NDMA were also monitored for.

**Phase 3**

As follow-up to the Phase 1 and 2 demonstration scale testing, we have progressed to Phase 3. The Phase 3 testing involves three GAC beds in series; each bed uses full-scale GAC
grains (#12 x 40). The first two beds are tailored with cetylpyridinium chloride (CPC) and the third a non-tailored polishing bed. All three GAC beds used Ultracarb (Siemens Water Technology), a bituminous-based GAC. Each of these three beds is four feet in diameter by four feet tall.

The overall objectives for demonstration scale tests have been:

1. Enable the Texas Street plant to supply water to customers of the City of Redlands and others.
2. Evaluate the performance of tailored carbon with full-scale GAC grains.
3. Demonstrate that the tailoring of GAC does not cause significant secondary water quality issues.
4. Gather results from the full scale demonstration so that we can apply for and receive certification from the National Sanitation Foundation (NSF) and the California Department of Health Services (DHS).
5. Gather results that will enable collaborators to calculate the capital and operating costs for full scale operation of the tailored activated carbon.

Collaborative efforts between Penn State, City of Redlands and Siemens Water Technology have monitored the operation. Penn State and subcontractors have monitored NDMA, pH, perchlorate, radioactivity, and the organic monomers. The tailoring of the GAC, along with installation, has been done by Siemens. Sample collection and monitoring of nitrate, nitrite, TCE, and DBCP have been facilitated by the City of Redlands.

Alongside the full scale demonstration tests, Penn State has conducted RSSCT experiments that have been aimed at better understanding the process and improving the protocol of reliability and performance.
METHODS

The three demonstration-scale projects operated at a 7.5, 11 and 12 minute EBCT for phase 1, 2 and 3 respectively. For phase 1 and 2, two beds were operated in series where the first beds were tailored and the other is the polishing bed that additionally removes any surfactant that would leach from the first bed. These beds were half-filled with 10,000 pounds #8 x 30 mesh sized Ultracarb carbon. Arquad 2C-75 and Arquad T-50 were the surfactants used to tailored the carbon for phase 1 and 2 respectively. Phase 3 had three beds in series consisting of 2,000 of (# 12 x 40) pounds of carbon tailored with CPC surfactant. From this it can be seen that the Phase 1 and 2 project was operating at half the scale of the full scale. The tailoring of GAC for the demonstration scale was carried out by Siemens Water Technologies.

For the Phase 3 demonstration scale test ten different parameters have been tested, some of which were subcontracted to different labs. Table 1 shows the sampling procedure and the labs and company that have coordinated this testing. All ten parameters were sampled for at the beginning of the demonstration to give us an idea of the water characteristics. It should be noted that at the Texas street plant, the influent concentration of perchlorate is between 50-70 ppb and the nitrate is 3-4 ppm as N. This report herein includes the data of some of parameters. For phase 1 and 2 only 4 parameters were tested, with the data also included in this report.

In the RSSCT’s, a column is filled with approximately 1.45 g of GAC and tailored with 33 BV of 0.4 % surfactant solution. The tailoring process took approximately 2 days where the surfactant solution was pumped and recirculated at 2 mL per minute through the carbon. For phase 1 and 2 deionised water was used to pre-load the surfactant on the GAC. On the other hand for Phase 3, three different sources of water were used to make the surfactant solution. They were (i) perchlorate free Redlands water (Texas Street, Redlands water that had been processed
through a tailored and polishing bed of GAC during Phase 2 testing) (ii) the softened water from Siemens Water Technologies and (iii) deionised distilled water. This was to evaluate the performance of different water sources on the tailoring process and how does this affect the longevity of the carbon with respect to perchlorate breakthrough and bed life. The carbon grains used were #200x 400 mesh (0.074 x 0.037 mm). The laboratory columns used were design to withstand high pressures that is associated with the small grain size used. The columns were 0.5cm in diameter and 13.5 cm in length. HPLC pumps (Waters Model 501 and 510) were used to provide flow. After the tailoring process, water from the Texas street plant was pumped into the tailored carbon at 5 mL per minute which produced a 0.5 minute EBCT; this was simulated to a 9 minute EBCT at full scale. Samples were taken every 15 minutes for the first hour after start up and then two times per day until there was total breakthrough of the perchlorate. For the first 10,000 bed volumes, each sample collected was tested for organic monomer using the colorimetric method. The RSSCTs took about 13-15 days until there was full breakthrough of perchlorate. Perchlorate measurements were conducted utilizing a Dionex 120 ion chromatograph.

RESULTS

Phase 1

Perchlorate breakthrough for the first demonstration scale test was at approximately 7,000 bed volumes for the tailored bed and 11,000 bed volumes for the polishing bed (Figure 1). It was speculated that this early breakthrough of perchlorate was cause by the system short-circuiting due to flow rate being greater through some of the drains. This increased the EBCT therefore affecting the rate at which perchlorate passed through the system. Results of the concentration of Arquad 2C-75 leached from tailored and polishing bed are shown in Figure 2. Initially they were 3.5mg/L Arquad 2C-75, 0.5mg/L by 1000 BV and non-detect at 4500 BV for
the tailored bed. For the polishing bed 0.2 mg/L initially and non-detect at 1500 BV (i.e. < 0.2 mg/L per titration method)

For the demonstration scale nitrogen breakthrough was also monitored (Figure 3). It can be seen that within the first 20 hours there was breakthrough of nitrogen for the tailored bed. Full breakthrough of nitrogen was observed after 150 hours. There was no apparent evidence that there was nitrogen rollover in the system.

Additional analyses were conducted to determine if N-nitrosodimethylamine (NDMA) and/or N-nitrodiethylamine (NDEA) as well as other nitrosamine in the treated water. Two part per trillion was detected in the influent while effluent was non-detect.

Lab scale experiments conducted using Arquad 2C-75 and SAI carbon showed that breakthrough occurred at approximately 23,300 bed volumes (Figure 4). Sixty-six percent more bed volumes were treated by this tailored GAC than the demonstration scale test.

**Phase 2**

Initial perchlorate breakthrough occurred at 15,000 bed volumes through the tailored bed, and at 16,000 bed volumes through the polishing bed. The bed volumes given are as measured through the first bed.

It can be seen that perchlorate breakthrough is approximately 7,000 bed volumes greater than phase 1 field scale demonstration (Figure 5). The Phase 2 demonstration employed preloading with Arquad T-50, whereas the Phase 1 demonstration employed preloading with Arquad 2C-75. It is noted that for the Phase 2 demonstration, Redlands tap water was used to
preload the surfactant. Figure 6 showed no detection of the Arquad T-50 for the tailored or polishing bed with the titration method.

RSSCT tests were also conducted in conjunction with the Phase 2 project. Figure 7 shows perchlorate breakthrough comparisons of the field scale Phase 2 project (with 23.5% Arquad T50 preloading) and for four RSSCT experiments, in which 27.3% Arquad T-50 was preloaded onto the GAC’s, while diluting this surfactant in either Redlands water or deionized water. The Redlands water, here, was Phase 2 effluent water that was collected while there was no perchlorate breakthrough. Also, the RSSCT GAC used was either Ultracarb or SAI (Superior Adsorbents, Inc.).

When preloading Arquad T-50 with Redlands water, RSSCT perchlorate breakthrough occurred at 18,000 bed volumes in one case and at 31,000 bed volumes in another case. The reasons for these distinctions are being investigated in on-going work, in light of the redox hypothesis that are posed and discussed below.

In Figure 8, the breakthrough curves are all normalized to the expected performance if the preloading had uniformly been 27.3%. In such case, the Phase 2 breakthrough could have been expected at 16,000 BV.

**Phase Three**

In the Phase 3 demonstration-scale testing, the CPC was diluted in deionized water for the first loading cycle, and then it was diluted in Siemens Water Technologies softened water during a second loading program. Concentration of CPC sorbed to the carbon was 23%, by the time the testing commenced. Results of the amount of CPC leached from each effluent in Figure
9 showed 14 mg/L CPC initially, 5mg/L after 500 bed volumes, and non-detect (i.e. <0.2 mg/L per titration method) by 4000 bed volumes. There was no CPC detection in the non-tailored polishing bed, as determined by the titration colorimetric method. On the other hand results from the Gas Chromatography Mass Spectrophotometry (GCMS) (Figure 10) showed that unlike the colorimetric method 190 Ng/L and 151 Ng/L CPC were detected for the first 20,000 bed volumes for tailored bed A and B respectively. This method also showed 16 Ng/L of CPC detected after 92 bed volumes and non-detect after 4,000 bed volumes (i.e. <10 Ng/L per GSMS method) for the polishing bed.

Nitrate was also monitored for the phase 3 demonstration scale tests. Figure 11 shows that there was breakthrough of nitrate as nitrogen at 200, 400 and 600 bed volumes for Effluent A, B and C respectively. There were no signs of nitrate rollover up to 4000 bed volumes.

Also there was no detection for N-nitrosodimethylamine (NDMA) at the reporting limit of 1.07ng/L.

In the Phase 3 demonstration, there has been complete breakthrough of perchlorate for both the tailored (Effluent A and B) and polishing bed (effluent C) (Figure 12). There has been perchlorate breakthrough after the first tailored GAC bed (i.e. effluent A) at 17,000 bed volumes. Breakthrough as also occurred at 18,000 bed volumes for the second tailored and 20,000 for the polishing bed. Perchlorate samples were also sent to a certified lab to validate the results that we have been getting here at the PSU lab. So far the results verify the lab’s results.

Based on results that compared Phase 2 demonstration-scale results to RSSCTs, we hypothesized that the water source that was used to pre-load the surfactant may have impacted the
bed volumes to breakthrough. To test this hypothesis we conducted RSSCT’s with several water sources. For each of these tests, we preloaded 29.0% CPC onto Ultracarb GAC; which was preloaded in the presence of (a) deionised water, (b) ion-exchange softened water or (c) perchlorate free Redlands well water from Texas Street (i.e. Redlands water that had passed through a tailored GAC bed during previous RSSCT’s).

From Figure 13 it could be seen that there was little difference between the perchlorate-free Redlands water and deionized (DI) distilled water (~ 33,000 BV) to initial breakthrough. Moreover with the softened water, performance was nearly as good (29,000 BV to initial breakthrough). Figure 14 further shows a comparison between the field scale test for Phase 3 (with 23% CPC loading) and the RSSCT for perchlorate breakthrough for the monomer using perchlorate free Redlands water for tailoring (with 29% CPC loading). It can be seen that perchlorate breakthrough for the field scale test was approximately 13,000 bed volumes sooner than what would have been predicted by the RSSCT’s results.

As indicated, the field-scale GAC beds had been pre-loaded with 23% CPC, whereas these RSSCT’s had been preloaded with 29% CPC. To make a good comparison, the full-scale data has been normalized to what results we could have expected if we had preloaded with 29% CPC, and this normalized response (eg. 17,000 x 29.0/23) is compared to the RSSCT results (at 29% CPC loading) in Figure 15. If 29% CPC had been loaded on the full-scale GAC bed, then we could have expected breakthrough at 21,000 BV. This is less than the 30,000-33,000 BV that we observed in the RSSCT experiments, and thus there must be yet another distinction between full-scale performance and bench-scale simulation.
We hypothesize that there could be three possible distinctions that cause this disparity:

(1) In the full-scale testing, we are using Texas Street water that has a low redox level, whereas this water becomes oxidized by the time of its use in the Penn State labs. This could particularly affect sulfur species, which may compete with perchlorate. (2) the surfactant has not been loaded as thoroughly with full-scale grains as it was in the smaller RSSCT grains, or (3) whereas proportional diffusivity properly characterized the relation between full-scale grains and RSSCT grains when using non-tailored GAC, for some reason, this similitude does not properly characterize this relationship for surfactant-tailored grains.

We are currently pursuing the first of these hypotheses, namely that the distinctions in redox level are the factors that are causing this disparity. Specifically, we hypothesize that a reduced sulfur species (perhaps thiosulfate- \( \text{S}_2\text{O}_3^{2-} \)) is appearing within the full-scale GAC bed, and these species are competing for adsorption sites with the perchlorate more than the oxidized sulfate (\( \text{SO}_4^{2-} \)) does. This hypothesis stems from our earlier work where we effectively removed perchlorate from spent conventional GAC by regenerating with thiosulfate. Moreover, in some of our early work with thiosulfate regeneration, we observed the presence of some reduced sulfur species that eluted through our ion chromatography column at about the same time as perchlorate. This means this species could also “elute” through the tailored GAC bed at the same time as perchlorate, and thus prematurely displace the perchlorate from the GAC bed.

An experiment was carried out using deionized distilled water that had been spiked with 1 mg/L perchlorate, where we looked at the competition of thiosulfate with perchlorate at different thiosulfate concentrations ranging from 10 mg/L to 10 µg/L. Figure 16 showed that thiosulfate did indeed incur a competition effect. The control experiment, which had 1 mg/L of perchlorate but no thiosulfate showed breakthrough starting at 15,300 bed volumes. In contrast,
when this water was also spiked with 1 mg/L thiosulfate (the same concentration as perchlorate), perchlorate breakthrough commenced at 12,000 bed volumes. At 10 mg/L, 100 µg/L and 10 µg/L, respectively, breakthrough commenced at 4,000, 12,000 and 14,000 bed volumes respectively. Thus, these experiments reveal that indeed thiosulfate will compete with perchlorate for adsorption sites; and when the thiosulfate concentration equals the perchlorate concentration, the dampening of bed volumes is of about the same magnitude as we had observed in the earlier demonstration-scale versus RSSCT comparison at this other site. Figure 15 also showed the competition of sulfate at the same equimolar concentration of sulfur as 1 mg/L of thiosulfate. Breakthrough occurred at 14,000 bed volumes. Sulfate data further proves that reduced sulfur species competes with perchlorate. Yet more experiments are on going, and further tests needs to be conducted to further evaluate this hypothesis.
Table 1: Revised Sample Procedure and time Line for Phase 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Destination</th>
<th>Times for Collecting Sample</th>
<th>Sample container</th>
<th>Beds to Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchlorate</td>
<td>Redlands</td>
<td>weekly</td>
<td>plastic, 250 - no headspace</td>
<td>All</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>PSU</td>
<td>weekly</td>
<td>plastic, 250 - no headspace</td>
<td>All</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>Babcock</td>
<td>monthly</td>
<td>plastic, 250 - no headspace</td>
<td>All</td>
</tr>
<tr>
<td>Nitrate, Nitrite</td>
<td>Redlands</td>
<td>2 times per month</td>
<td>plastic, 250</td>
<td>All</td>
</tr>
<tr>
<td>TCE</td>
<td>Redlands (Babcock)</td>
<td>once every two months</td>
<td>100 ml glass, no headspace, teflon-lined cap</td>
<td>Influent and Effluent C (polishing bed)</td>
</tr>
<tr>
<td>DBCP</td>
<td>Redlands (Babcock)</td>
<td>once every two months</td>
<td>100 ml glass, no headspace, teflon-lined cap</td>
<td>Influent and Effluent C</td>
</tr>
<tr>
<td>NDMA</td>
<td>CH2M -Hill</td>
<td>once every two months</td>
<td>Amber glass container. No head space, wrap bottles in bubble wrap and pack in ice and cooler, ship overnight</td>
<td>ALL</td>
</tr>
<tr>
<td>TOC</td>
<td>Redlands</td>
<td>once per month</td>
<td>VWR Trace Clean vials (40ml). No head space, wrap bottles in bubble wrap and pack in ice and cooler, ship overnight</td>
<td>ALL</td>
</tr>
<tr>
<td>Organic Monomer</td>
<td>Shane Synder</td>
<td>once every two months</td>
<td></td>
<td>Effluent B and C</td>
</tr>
<tr>
<td>Radioactivity in water</td>
<td>PSU</td>
<td>once every three months</td>
<td>2- 1 liter bottles full to capacity no head space</td>
<td>polishing bed</td>
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Table 2: Species of sulfur-based ions and the sulfur valence state

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>FORMULA</th>
<th>S VALENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>H₂S</td>
<td>-2</td>
</tr>
<tr>
<td>Elemental Sulfur</td>
<td>S</td>
<td>0</td>
</tr>
<tr>
<td>Polythionate</td>
<td>S₆O₆⁻</td>
<td>+1.67</td>
</tr>
<tr>
<td>Polythionate</td>
<td>S₅O₆⁻</td>
<td>+2</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>S₂O₃⁻</td>
<td>+2</td>
</tr>
<tr>
<td></td>
<td>Chemical</td>
<td>Reduction</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Tetrathionate</td>
<td>$\text{S}_4\text{O}_6^-$</td>
<td>+2.5</td>
</tr>
<tr>
<td>Dithionate (hydrosulfite)</td>
<td>$\text{S}_2\text{O}_4^-$</td>
<td>+3</td>
</tr>
<tr>
<td>Sulfite</td>
<td>$\text{SO}_3^-$</td>
<td>+4</td>
</tr>
<tr>
<td>Sulfate</td>
<td>$\text{SO}_4^-$</td>
<td>+6</td>
</tr>
</tbody>
</table>

Figure 1 - Perchlorate breakthrough for Phase 1 demonstration field scale test
Figure 2 – Concentration of Arquad 2C-75 leached off tailored and polishing bed for the Phase 1 project.

Figure 3 – Nitrate Data for Influent, Tailored and polishing bed for phase 1.
Figure 4 – Comparison of Perchlorate Breakthrough at the Field Scale (phase 1) and the RSSCT with Arquad 2C-75

Figure 5 - Perchlorate Breakthrough from the Phase 2 demonstration project; preloading with Arquad T-50.
Figure 6 – Arquad T-50 leached off Tailored and polishing bed for Phase 2 using the colorimetric method.

Figure 7 - Comparison of Perchlorate Breakthrough at the field scale (phase 2) and the RSSCT with Arquad T-50 loading using different water sources.
Comparison between field scale and RSSCT Normalised for Bed Volumes.

Figure 8 - Comparison of Perchlorate Breakthrough at the field scale (phase 2) and the RSSCT with Arquad T-50 loading with perchlorate free redlands normalized for percent loading and apparent density.

CPC leached from Effluent A and B from Phase 3

Figure 9 - Concentration of CPC leached off of first tailored bed (Effluent A), the second tailored bed (Effluent B) during Phase 3 field-scale test. CPC off the polishing bed (Effluent C) was all non-detect.
Figure 10 - Concentration of CPC leached for Effluent A, B and Polishing bed for the Phase 3 field scale using the GC/MS method.

Figure 11 - Nitrate breakthrough for Phase 3 demonstration scale test.
Figure 12 - Perchlorate Breakthrough from the Phase 3 field scale project (12 minute EBCT)

Figure 13 - Perchlorate Breakthrough of tailored carbon: Preload CPC with different water sources (47,000 BV=15 days RSSCT) Ultracarb GAC.
Comparison of Perchlorate breakthrough between the RSSCT and Phase 3

Figure 14 - Comparison of perchlorate breakthrough between the RSSCT and field scale (Phase 3) test

Phase 3 Field Scale Normalized to the RSSCT Percent Loading

Figure 15 - Comparison of perchlorate breakthrough between the RSSCTs and field scale (Phase 3) test normalized by percent loading.
Figure 16 – Perchlorate and Thiosulfate competition with deionized water at different orders of magnitude for thiosulfate. Perchlorate concentration kept constant at 1mg/L.
References

Appendix B - Tailored Granular Activated Carbon Treatment of Perchlorate in Drinking Water

Environmental Security Technology Certification Program (ESTCP) Project ER-0546
Contract W 912HQ-06-C-005

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It should be noted to the readers that this report is a small portion of the full report. This part of the report only demonstrates the work that Penn State University was involved in. This includes monitoring of perchlorate and cetyl pyridinium chloride from the pilot scale systems as well as conducting laboratory scale experiments that mimics the fullscale.
Abstract

This final report describes the results of an Environmental Security Technology Certification Program (ESTCP) Environmental Restoration project evaluating the use of tailored granular activated carbon (TGAC) in wellhead treatment of perchlorate in drinking water. Two field test installations were implemented and evaluated along with bench scale experiments. The first installation consisted of three vessels in series treating 37 gallons per minute (GPM) (0.14 m$^3$/minute), and the second installation consisted of six smaller scale treatment trains treating 1.5 GPM (0.0057 m$^3$/minute). For the larger scale treatment train, approximately 38 GPM (0.14 m$^3$/minute) of water was processed. The 38 GPM (0.14 m$^3$/minute) passed through three demonstration vessels connected in series. Six smaller scale treatment trains were operated to permit the determination of TGAC performance under different groundwater chemistry conditions. For both demonstration systems, perchlorate breakthrough earlier than what was predicted and observed at the laboratory scale. However when comparing both the 38 gpm system and the 1.5 gpm system, perchlorate results were comparable within experimental error.

Introduction

Recognizing a need to improve the removal of perchlorate in GAC systems, Penn State started looking at cationic surfactants as a tailoring agent, first starting with a polymer known as polyDADMAC. These surfactants were selected for initial testing because they were already used in treatment facilities as well as being NSF approved. Results using Redlands water and polyDADMAC tailored SAI carbon showed perchlorate breakthrough at 4,200 bed volumes which is 3.5 times more than virgin carbon. It was noted that tailoring with low molecular weight blends of polyDADMAC led to greater perchlorate capacity in GAC than with their high molecular weight counterparts (Parette, 2004). After these initial results PSU worked to improve the tailoring process of the carbon as well as to find as smaller molecule cationic surfactants. Thus tailoring with quaternary ammonium monomer species was investigated. These alkyl monomers contain the same functional group as polyDADMAC. However due to their small size (molecular weight of a few hundred Daltons vs. in the tens of thousands for polyDADMAC), the monomers should have access to the micropores of the GAC, whereas the polymer was only expected to enter the meso and macropores. The micropores contain the majority of surface area for the GAC (Bansal 1988). A number of quaternary ammonium and pyridium monomers were used and the adsorption capacity for GAC after they were pre-loaded with any one of these
monomers were as great as 34,000 bed volumes (33 times that of virgin carbon) when using Redlands CA groundwater. After this discovery more studies were conducted and these were reported by Parette, 2004, 2005, 2005a and 2005b. A comparison of the various tailoring agents used by Penn State University is given in Table 1:
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant</th>
<th>MW</th>
<th># of long alkyl chains</th>
<th># of carbon atoms in chain</th>
<th>Applications for Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>decyltrimethylammonium bromide</td>
<td>DTAB</td>
<td>280.3</td>
<td>1</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>myristyltrimethylammonium bromide</td>
<td>MTAB</td>
<td>336.4</td>
<td>1</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>tributylheptylammonium bromide</td>
<td>THAB</td>
<td>364.5</td>
<td>1</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>cetyltrimethylammonium chloride</td>
<td>CTAC</td>
<td>320</td>
<td>1</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>tallowtrimethylammonium chloride</td>
<td>T-50</td>
<td>350</td>
<td>1</td>
<td>16-18</td>
<td>-</td>
</tr>
<tr>
<td>dicocodimethylammonium chloride</td>
<td>2C-75</td>
<td>450</td>
<td>2</td>
<td>12-14</td>
<td>-</td>
</tr>
<tr>
<td>cetylpyridinium chloride</td>
<td>CPC</td>
<td>358</td>
<td>1</td>
<td>16</td>
<td>Antiseptic in mouth wash</td>
</tr>
<tr>
<td>Poly(Dimethyldiallylammonium Chloride)</td>
<td>polyDadmac</td>
<td>Varies</td>
<td>2 per monomer</td>
<td>3</td>
<td>Coagulant, flocculant in waste water and water treatment technologies</td>
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</tbody>
</table>
The experimental design associated with this project was intended to transition the TGAC technology from laboratory testing to field implementation. During this project, a series of TGAC experiments were implemented with sufficient performance monitoring to delineate the functional lifetime of the media and generate data for the California regulatory approval process. From an experimental design prospective, the demonstration consisted of three main experimental components discussed in detail below. The output from these three experimental components was then coupled to a predictive model that will expedite the screening of future sites for the practicality and economics of TGAC implementation.

The demonstration study experimental design focused on consistently conducting analyses aimed at delineating TGAC performance over the long time period of operation typically seen for adsorptive technologies in drinking water service. Accordingly, this demonstration had an eighteen month duration. The project team also designed the project to gather data on the scalability of the system. The scaling of this technology employed the RSSCT scaling equations for proportional diffusivity by Crittenden et al. (1991). Additional information used in the experimental design and pertaining to scaling relationships for adsorption technologies is provided in Weber (1975 and 1983).

A 37 GPM scale field pilot system was a major component of the TGAC demonstration designed to evaluate TGAC performance over an extended demonstration interval. With greater than fifty samples of influent water conducted over the demonstration interval, an accurate assessment of the perchlorate influent flux and other general groundwater chemistry parameters such as nitrate was developed. The long operational interval permitted the project team to evaluate the system’s ability to accommodate temporal variation in groundwater chemistry found in Fontana production wells Fontana Water Company (FWC) #17B and FWC #17C. Groundwater chemistry varied modestly over the demonstration interval with some variability in nitrate concentration likely associated with repositioning of well packers within well 17C which was conducted by FWC during the demonstration interval. In addition, operation at 37 gpm was utilized to better understand and document TGAC’s reliability and operations and maintenance requirements. Lastly, the effectiveness of TGAC treatment and its longevity in service were documented.
An additional component of the experimental design for this demonstration project was PSU evaluation of water quality parameter affects on TGAC performance through the application of RSSCT tests. PSU conducted RSSCTs with groundwater that has been spiked to an array of concentrations of perchlorate, nitrate, sulfate, chloride, thiosulfate, bicarbonate and adjusted to more acidic and basic conditions. This RSSCT data provides information on how the technology’s critical design and operating factors vary with differing influent concentrations. The RSSCT procedure is fully described in Crittenden (1986 and 1991). The effect of the influent water quality on the perchlorate treatment performance has been mathematically modeled by AFIT. The results of the RSSCTs and Field Sensitivity tests have been intercompared and used to support AFIT’s model development. The intent of varying each water quality parameter during RSSCT is briefly documented below:

- Perchlorate was varied to demonstrate the effect on TGAC performance and longevity so that performance at sites with higher perchlorate influent concentrations could be projected
- Nitrate is known to compete with perchlorate for sorption sites on TGAC. Therefore, variation of nitrate concentrations during RSSCT permits the project team to predict performance over a range of nitrate concentrations.
- Sulfate content in groundwater varies widely across the western geography where perchlorate groundwater contamination is widespread. Sulfate RSSCT analysis was conducted to document that sulfate does not compete with perchlorate for TGAC sorption sites.
- Increases in total dissolved solids through the addition of chloride and bicarbonate ions were studied to document TGAC performance in the presence of variable dissolved solids concentrations.
- Thiosulfate was studied during RSSCT testing as potential detrimental to TGAC sorption capacity.
- Acidic and basic groundwater pH values were investigated during RSSCT to generate a more complete understanding of TGAC response to pH variation and to provide insight into the sorption mechanisms behind TGAC functionality.
Six additional smaller-scale field column tests were performed in addition to the 37 GPM TGAC field pilot demonstration in order to confirm the system response to variations of selected groundwater chemistry parameters. These sensitivity tests were included so as to identify the overall performance impacts of changes in influent TDS, TCE, perchlorate, nitrate, and residual chlorine. An additional baseline test (Small Scale Treatment Train 5 – stratified bed control) was performed to provide a direct comparison of elevated concentrations of these components and to provide a direct comparison to the field pilot.

Compilation and analysis of the data resulting from the 37 GPM system, the RSSCT results, and the small-scale field pilot tests in this report document TGAC performance and reliability over a broad range of contaminant concentrations and realistic groundwater chemistries. The resulting data contained in this report can be used for future evaluations of TGAC performance and economic feasibility over a broad range of groundwater chemistries.

Lastly, the results of this demonstration at Fontana have compared to the results of previous TGAC demonstrations at Redlands and the Massachusetts site tests previously described. This will provide further insight into how the technology’s critical design and operating factors vary with differing combination of general influent chemistry.

The overall goal of this project was to evaluate the technical and economic performance of the TGAC technology for wellhead treatment of groundwater supplies. Specifically, the technical objectives for this project included:

- Demonstrate that the TGAC technology is a cost-effective treatment method for removing perchlorate from drinking water to effluent concentrations of 6 micrograms per liter (µg/L) or less.
- Demonstrate that the TGAC technology does not cause significant secondary water quality issues. Specifically, the potential for interactions between disinfection processes and the adsorption system will be assessed.
- Demonstrate that the TGAC technology requires low capital, operating, and energy costs.
- Develop treatment costs for a range of water chemistry conditions determining performance after varying total dissolved solids, nitrate, perchlorate in the small scale field pilot treatment trains and the presence and absence of TCE.
- Demonstrate that the TGAC technology’s operation and maintenance requirements are simple.
• Demonstrate that the TGAC technology minimizes residual waste streams for the host municipalities.
• Obtain performance data for water that contains varying concentrations of TCE during RSSCT studies at Penn State University and in the small scale field pilot treatment train.
• Demonstrate that the performance of the TGAC technology is predictable so that monitoring can be minimized

Experimental

This demonstration project was conducted on groundwater that was pumped from a perchlorate-impacted aquifer that is contaminated on a regional-scale (see section 4.2). The perchlorate plume is a very large plume that affects the region where the demonstration was conducted and the production wells have a high yield, thus the local demonstration site cannot be feasibly characterized using the same tools as a remediation project. In the previous section however, the physical elements of the demonstration site were described—two groundwater extraction wells, perchlorate treatment system, distribution reservoir—as well as the location of the site. The demonstration site can be described as a “typical” example of a site where a water supply perchlorate treatment system might be located in that the baseline prechlorate concentration only modestly exceeds the 6 μg/L standard. The chemistry of the groundwater that was used in the demonstration is typical of groundwater that is treated in the California Inland Empire, however, the average perchlorate concentration is slightly lower, and the nitrate concentration is slightly higher than at other perchlorate treatment systems in the area.

For the purposes of this project baseline was thus defined as the untreated water as pumped during routine operation from wells 17B and/or 17C. Which wells were operated at which times were controlled by the needs of the Fontana Water Company. It was observed that there is some variability in the levels of nitrate and perchlorate in these wells, which is likely a function of regional hydrogeology and the pumping rate and depth adjustments made to these supply wells. A statistical analysis of the influent concentration during the demonstration is presented in Table 2
Table 2: Influent Perchlorate concentration Statistical Analysis.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>8.3</td>
</tr>
<tr>
<td>Standard Error</td>
<td>0.2</td>
</tr>
<tr>
<td>Median</td>
<td>8.3</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.7</td>
</tr>
<tr>
<td>Minimum</td>
<td>5.1</td>
</tr>
<tr>
<td>Maximum</td>
<td>12.6</td>
</tr>
<tr>
<td>Count</td>
<td>58</td>
</tr>
</tbody>
</table>

During the demonstration itself, influent water quality was consistently monitored using the same methods used for effluent quality.

Pilot Scale Columns

37 GPM systems

The 37 gpm system comprised three vessels operating in series Figure 1. The treatment train included a lead and lag TGAC vessel and a third conventional GAC vessel for tailoring agent polishing. All three vessels contained approximately 375 gallons (1.4 m$^3$) of media (either TGAC or conventional GAC). This system was designed to treat water at a flow rate of approximately 37.5 GPM (0.14 m$^3$/min), which corresponds to a 10 minute empty bed contact time EBCT in each vessel (total EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC). Each of the three beds was designed to be 4 feet (1.22 m) in diameter, with a 4 foot depth (1.22 m) of GAC media.

1.5 GPM systems

The second major element of the field test program consisted of six sets of three vessels operating in series as shown in Figure 2 and 3. The first two vessels in each set were stratified with conventional TGAC overlying conventional GAC in the same chamber. They contained 1.5-2.2 cubic feet of TGAC in the lead chamber (on top), and 0.8-1.5 cubic feet of conventional GAC in the second chamber (on bottom) to remove residual TCE (from spiking) and/or tailoring agent, if present. These smaller vessels were designed to operate at a 10 minute TGAC empty bed contact time (EBCT) and 5 minute activated carbon EBCT, which corresponds to a flow rate of approximately 2.3 gpm. These were implemented to test varying arrays of common competitive species such as nitrate, sulfate and TCE. Table 3 gives the spiking levels for each treatment.
The influent water for the pilot-scale tests was pre-filtered to remove particulates using 10 micron cartridge filters. This pre-filtration reduces particulate accumulation that can lead to excessive pressure drop across the TGAC/GAC beds. Battery-powered flow meters were installed in the influent piping to each of the six trains, and mechanical totalizers were installed in the effluent piping of each treatment train.

Table 3: Summary of Spiking Levels in Six Condition Pilot Scale Test

<table>
<thead>
<tr>
<th>Train</th>
<th>Mean Concentration Unspiked Influent</th>
<th>Standard Deviation Unspiked Influent</th>
<th>Mean Concentration Spiked Train Influent</th>
<th>Standard Deviation Spiked Train Influent</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>&lt;0.5 µg/L</td>
<td>NA</td>
<td>35.7 µg/L</td>
<td>16.2</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>8.0 µg/L</td>
<td>1.7</td>
<td>314.7 µg/L</td>
<td>134.9</td>
</tr>
<tr>
<td>Nitrate</td>
<td>40.5 mg/L</td>
<td>3.3</td>
<td>60.9 mg/L</td>
<td>12.1</td>
</tr>
<tr>
<td>Disinfectant (chlorine)</td>
<td>NA</td>
<td>NA</td>
<td>0.28 mg/L</td>
<td>0.33</td>
</tr>
<tr>
<td>TDS</td>
<td>274.3 mg/L</td>
<td>30.6</td>
<td>995.0 mg/L</td>
<td>511.7</td>
</tr>
</tbody>
</table>

Figure 1- Bed Ordering/Operational Diagram of 38 gpm Systems at Fontana, California
1. TDS/Chloride
2. TCE
3. Increased Perchlorate
4. Nitrate
5. Stratified Beds
6. Disinfectant/Oxidant

Figure 2 - Flow Path Schematic for Six Small-Scale TGAC Treatment Trains

Figure 3. Cross Section of a Single Small-Scale TGAC Treatment Train Illustrating the Stratified Bed Approach
Results

Bench Scale

In parallel with the field scale work, the Penn State team conducted a number of rapid small scale column tests (RSSCTs). These focused on how other anions compete with perchlorate in a manner that diminishes the capacity of the cationic surfactant-tailored GAC for removing perchlorate. The anions appraised include nitrate, sulfate, chloride, and bicarbonate. In addition, they conducted extensive work regarding the competition of thiosulfate for perchlorate removal; and whether this thiosulfate competition can be diminished by prechlorinating the groundwater. Additionally, they have appraised whether the cationic surfactant tailoring has impacted TCE removal, as appraised by bench-scale isotherms.

The scaling of this technology employs the RSSCT scaling equations for proportional diffusivity by Crittenden et al. (1991). If this proportional diffusivity model holds then a properly designed RSSCT will accurately predict field scale performance. This approach is effective even though the test period is dramatically shorter since RSSCT uses a smaller particle size and its performance is governed by the same adsorption capacity and kinetics factors that govern larger scale performance (Crittenden 1991, 1986) Both demonstration-scale and rapid small scale column tests (RSSCT’s) were conducted with the same Fontana water so as to appraise whether the proportional diffusity model is appropriate for perchlorate sorption here. A discussion of the critical scaling parameters and how they relate to scale-up of larger columns will be included in the final technical report. When employing virgin GAC, PSU has demonstrated that that proportional diffusivity is indeed the proper model. However, when employing TGAC, there was some possible distinction; and we want to address what might cause such a distinction as part of the activity in this ESTCP. Significant modeling differences between virgin GAC and TGAC will also be discussed in the final technical report. As per its name, the proportional diffusivity model addresses how to scale-up diffusion effects in small grains that are simulating full-sized grains. However, since the RSSCT’s reach breakthrough in time scales of weeks, they are not perceived to achieve well-developed microbial populations. Moreover, similitude with regard to the redox level of the water may be difficult to achieve in RSSCT’s.

There were several problems with running RSSCTs with TCE and perchlorate concurrently defined during this work. The largest problem was that an RSSCT designed for
perchlorate works on proportional diffusivity, while an RSSCT designed for TCE works on constant diffusivity. This means that an RSSCT cannot be compatibly run on both at the same time. Thus we chose to evaluate the effects of the concurrent operation using the field scale 1.5 gpm beds and the isotherm information.

Seventeen rapid small scale column tests (RSSCT) were conducted with groundwater from Fontana, California under different operational variables and water chemistry solutions. Results show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment was 50% greater than neutral pH, and 75% greater than at an alkali pH. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration reduced the removal of perchlorate by 17%; and a tripling of nitrate concentration reduced removal by 53%. Sulfate, thiosulfate, chloride and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to the maximum contaminant level. Also the bench scale experiments showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7. A full report is given in Appendix C.

38 GPM

Results for perchlorate for the 38 gpm systems are shown in Figure 4 and 5. Figure 4 shows just the primary perchlorate dataset. Figure 5 compares PSU results to those of certified laboratories. Figure 6 shows individual bed breakthrough curves. Perchlorate breakthrough was observed at 12,000 bed volumes for bed A which was used in the lead position. Breakthrough was observed at 20,000 bed volumes for bed B which was the initial lag bed. Saturation was observed at approximately 16,000 BVs for bed A (measured through one bed) and 27,000 BVs for Bed B (measured through one bed).

Bed D was placed in service at 18,000 bed volumes as the new lag bed while bed B became the lead bed. A low level of perchlorate breakthrough from Bed D was observed between 21,000 and 26,000 bed volumes into the demonstration before the concentration reverted to nondetect. Breakthrough clearly occurred at 35,000 bed volumes and saturation was reached by 40,000 bed volumes.
Bed C was not tailored, and thus was intended only to treat any CPC that leached from the tailored beds, not to provide significant perchlorate treatment. As expected bed C breaks through soon after Bed D. This is consistent with the low capacity of untailored GAC for perchlorate that has been shown in other experiments.

During the later periods of operations beds B, C and D all reached effluent concentrations that exceeded the influent. Thus they showed some evidence of a chromatographic roll-over effect.

Perchlorate results were also confirmed by splitting samples with outside laboratory. Figure 5 shows that results both from Penn State and Weck Lab were generally similar.

**CPC Results, 38 GPM**

CPC leaching was also monitored from beds A, B, C and D (Figure 7). The lead bed showed substantial leaching of CPC immediately after being placed in service, which rapidly declined. The maximum concentration observed from any bed was observed from the lab bed at 4,600 ug/l. CPC was never detected in the effluent of the final polishing bed C, suggesting that the provision of a polishing bed was an adequate precaution against the release of the tailoring agent to the treated water.

The CPC concentration for backwash water showed 1.3mg/L for the colorimetric method and 5.8mg/L for the GCMS method.
Figure 4 - Breakthrough Curves for All Beds in 38 gpm system. Bed volumes are calculated cumulatively for the entire demonstration. Primary PSU analytical dataset only. Bed volumes are as measured through the first bed.

Figure 5 – Comparison of results from Penn State with certified laboratories, 38 GPM bed data. Bed volumes are as measured through the first bed.
Figure 6- Perchlorate breakthrough curves from individual beds. Bed volumes are as measured through the first bed.

Figure 7 – CPC Leaching, Including Data from Two Laboratories - Penn State and Exygen. Bed volumes are as measured through the first bed.
Perchlorate Results, Six Condition Pilot Scale System

Table 4 lists the bed volumes to breakthrough for perchlorate in each of the 6 conditions. The breakthrough curves for each condition are shown as figures 8 (Effluent port 1) and 9 (Effluent port 2).

In the effluent 1 results the perchlorate spike had the most dramatic effect on performance, followed by TDS, Nitrate and TCE. The prechlorinated train also performed more poorly than the control. All of the trains except the TCE spiked train display substantial evidence of a chromatographic roll over effect.

When perchlorate concentration was 40 times that of the control, a 39% reduction in the TGAC capacity to absorbed perchlorate was observed for effluent 1. Overall, for perchlorate parameter there was a 30% reduction in the TGAC capacity when there is an increased in perchlorate concentration of 40 times. This was also observed in the bench scale experiments and at the effluent 2 port (31% reduction, Table 3).

The magnitude of the nitrate effect at the effluent 1 port was about a 22% reduction in breakthrough volume when influent nitrate increased from 41 to 61 mg/l. This is consistent with the bench scale data and with the behavior at the effluent 2 port (Table 3).

Substantial problems were experienced with the initial design of the TCE spiking system. Therefore our analysis of the effect of TCE in the influent water will focus on the data collected from that train with the second spiking system – after May 22nd, 2008. In figure 11 that data is compared to the behavior of the lead bed of the control stratified bed train. That figure shows that the range and variance of the perchlorate influent concentration were similar in the two
periods of operation. Breakthrough and saturation both occurred much sooner with the TCE spiked system than with the control system.

Comparing the effluent 2 dataset to the effluent 1 data set, the greatest inconsistency in terms of tabulated breakthrough time was seen with the prechlorinated system, which reduced performance 15% at Effluent 1 and 40% at effluent 2. However a close examination of figure 9 will show that while prechlorination had a substantial effect on the time of initial breakthrough at effluent 2 it had much less of an effect on the overall shape of the breakthrough curve. Another possible explanation for this difference in behavior is that the prechlorinated train and control train were operated more rapidly for the second half of their operational period than the first.

The average influent concentration during the six column operational period was calculated to be 8.15 µg/L; with most of the data in the range of 6 µg/L and 10µg/L (Figure 10).

### Table 4: Bedvolumes to Breakthrough In Six Condition Pilot Scale Test

<table>
<thead>
<tr>
<th>Train</th>
<th>Bed Volumes to Breakthrough</th>
<th>Difference from Control (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Effluent 1</td>
<td>Effluent 2</td>
</tr>
<tr>
<td>Control (Stratified)</td>
<td>12,794</td>
<td>23,191</td>
</tr>
<tr>
<td>TCE Spiked</td>
<td>9,9421</td>
<td>21,266</td>
</tr>
<tr>
<td>TDS Spiked</td>
<td>9,145</td>
<td>19,940</td>
</tr>
<tr>
<td>Nitrate Spiked</td>
<td>9,966</td>
<td>17,986</td>
</tr>
<tr>
<td>Perchlorate Spiked</td>
<td>7,767</td>
<td>15,894</td>
</tr>
<tr>
<td>Pre Chlorinated</td>
<td>10,881</td>
<td>13,863</td>
</tr>
</tbody>
</table>

1 The data for the TCE spiked train at effluent 1 should be viewed cautiously since as discussed in section 5.5 there were difficulties in the spiking system during the period the first bed was being used.
Figure 8 - The effects on perchlorate breakthrough from effluent port #1 of different water chemistries in Six condition Pilot scale test. Y axis is effluent concentration over influent concentration. Bed volumes are as measured through the first bed.

Figure 9 – The effects on perchlorate breakthrough from effluent port #2 of different water chemistries in Six Condition Pilot Scale test. Y axis is effluent concentration over influent concentration. Bed volumes are as measured through the first bed.
Conclusion

The experience at bench scale and Redlands, Fontana at field scale indicates that the surfactant-tailored GAC will be most suitable for removing perchlorate when the nitrate levels are
low. The dual surfactant tailored/ conventional GAC combination is likely to be the more economical when removing both perchlorate and volatile organic compounds. This technology has potential applications both to drinking water treatment and groundwater remediation.

Comparing the data for the stratified beds between the 1.5 and 38 gpm systems, it can be conclude that semi quantitatively they agree reasonably with each other. Since the influent concentrations varied somewhat and the two tests were not conducted simultaneously a more in-depth comparison was not made.

Unexpectedly, the RSSCT did not accurately predict the full scale performance in this study. However the comparison between the two field scales tested does suggest that full scale performance can be predicted from small pilot tests. However these small-scale pilot tests would have the disadvantage of requiring a time equivalent to the full scale EBCT for performance.

The experience at Fontana and at other locations where this approach to perchlorate removal has been applied indicate that the surfactant-tailored GAC will be most suitable for removing perchlorate when the nitrate levels are low; and the dual surfactant / conventional GAC combination will be the more economical when removing both perchlorate and volatile organic compounds. The TGAC system is less selective vs. nitrate as interference than the most advanced IX systems currently in use. Therefore in retrospect although the Fontana demonstration site provides a useful test of the system, it is not an ideal location for the TGAC technology to be cost competitive.
Reference


Appendix C - Final Report, Perchlorate Removal From Fontana, CA.

Groundwater

June 13, 2008

Judodine Patterson, Bob Parette, Fred S. Cannon,
The Pennsylvania State University, University Park, PA

Abstract

The adsorption of perchlorate to tailored granular activated carbon (TGAC) was studied in this research. Seventeen rapid small scale column tests (RSSCT) were conducted with groundwater from Fontana, California under different operational variables and water chemistry solutions. Results show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment was 50% greater than neutral pH, and 75% greater than at an alkali pH. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration reduced the removal of perchlorate by 17%; and a tripling of nitrate concentration reduced removal by 53%. Sulfate, thiosulfate, chloride and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to the maximum contaminant level.

Introduction

Perchlorate (ClO$_4^-$) is a compound that is used in the rocket fuel industry as a propellant, due to its strong oxidizing capabilities. This has led to contamination of drinking water that could otherwise have been available to several million people across the United States (Gullick et al., 2001). Perchlorate is thermodynamically favorable but kinetically inert at low concentrations (Gullick et al., 2001) and it is these two properties that lead to the dominant presence of perchlorate in groundwater and surface water. Perchlorate is also very soluble in water and offers
scant complexing capability; and these traits cause perchlorate to be a very persistent and mobile compound in groundwater.

Perchlorate inhibits the uptake of iodine by the thyroid glands and in large doses has been shown to cause anemia and fetal brain damage (Li et al., 2001). With these health concerns, several states, including Massachusetts, Texas, and California, have established statewide action levels for perchlorate as low as 1-6 parts per billion (Renner, 2001).

Virgin GAC has only been conditionally effective in removing perchlorate from water (Parette et al., 2005). However, our Penn State team has hypothesized that virgin carbon could be pre-loaded with cationic surfactants so as to increase the GAC capacity for removing perchlorate from water. The cationic surfactants used in this project contain a quaternary ammonium functional group (Parette et al., 2005). These same functional groups have been shown to remove perchlorate in ion exchange resins technology (Clifford et al., 2004). These quaternary ammonium based cationic surfactants have a high pKₐ value and this characteristic renders their charge to be independent of pH in natural waters (Laughlin, 1991). Once the cationic surfactant is pre-loaded onto the GAC, it then acts as an exchange site where perchlorate can be adsorbed.

The Pennsylvania State University has developed a technology that uses a cationic surfactant to tailor activated carbon. This has been shown to efficiently remove perchlorate from water at concentrations below 1 ppb (Parette and Cannon, 2005). This tailoring of GAC with cationic surfactants extends its bed life for adsorbing perchlorate up to 34 times that of virgin GAC when testing Redlands CA water (50-75 ppb) in rapid small scale column tests (RSSCTs). This technology has not been permitted for use in drinking water systems; and it has also not been commercialized yet, although we are actively pursuing this.

This earlier work by Parette et al. (2005) also showed that the pyridinium cationic surfactant will also efficiently remove perchlorate from water. The loading of the quaternary ammonium or pyridinium (as a subset of quaternary ammonium) surfactants produces positively charged groups that act as ion exchange sites where perchlorate can be adsorbed.

Although ion exchange and microbial methods have been shown to be effective technologies to treat perchlorate contaminated water, the use of tailored GAC to treat microgram
per liter concentration of perchlorate has some advantages over these methods. If full-scale performance were to conform to RSSCT results with Redlands, CA groundwater, then Siemens Water Technology has predicted that the tailored GAC would be a cheaper method for removing perchlorate plus organic species than the ion exchange method. Such cost estimates are predicated on the costs for various components of these tailored GACs, and also of ion exchange media; and these costs have changed markedly in recent years. One inherent reason for the favorability of the tailored GAC is that it can be thermally reactivated, while ion exchange systems cannot. In order for ion exchange systems to be regenerated, a brine solution has to be used which will have to be handled and dispose of later on.

In comparison, microbial treatment processes are less favorable for processing low-concentrations of perchlorate, as another stable food supply must be added to the water such that perchlorate can be a secondary substrate. Also, a number of utilities are not comfortable with using microbial methods for treating drinking water.

The purpose of the study herein has been to evaluate the use of GAC that was tailored with a cationic surfactant (cetylpyridinium chloride) for the removal of perchlorate, under different water chemistry parameters, from groundwater. Previous work has shown that virgin GAC was ineffective in the removal of perchlorate for concentration ranging between 50 - 75 ppb, as breakthrough was detected at 1100 BV of water treated. By tailoring with cationic surfactants, positively charged groups can be used as exchange sites for the adsorption of perchlorate as well as other anions.

**Experimental**

In all experiments, the GAC was ground and sieved to a size range of US Mesh #200 x 400 mesh (0.074 x 0.037 mm). The laboratory columns used were manufactured to withstand high pressure that is required with the use of the small GAC grains. The columns were designed according to the RSSCT (Figure 1) proportional diffusivity equations; and the columns measured 0.5 cm in diameter and 13.5 cm in length (Figure 2). Therefore 1 bed volume (BV) was equal to 2.65 mL. HPLC pumps (Waters models 501 and 510) were used to provide flow in the experiments (Figure 3). The flow rates of the RSSCTs were 2.5 ml/min which was simulated from a 10 minute empty bed contact time (EBCT) at the field scale level; this corresponds to a
#20 x 50 mesh GAC. Perchlorate measurements were conducted with the use of Dionex DX-120 ion chromatograph.

The stock solutions used in these experiments were prepared using reagent grade chemicals as well as deionized distilled water.

Table 1 shows all the experiments that were conducted and the concentrations of perchlorate and anions that were employed. With the exception of experiment 1 all other experiments were conducted using tailored carbon. The concentration of perchlorate in the Fontana groundwater was 7 µg/L and with the exception of experiment 3 and 5, all other experiments were conducted using that concentration. Fontana groundwater was also monitored for other background species such as nitrate, sulfate and chloride concentration.

**Results**

For the virgin carbon test, 1.27 grams of AquaCarb 2050AW (by Siemens Water Technologies) was placed in the column; and this corresponded to a bed density of approximately 0.48 g/mL. Perchlorate breakthrough in this column was observed at 1100 to 1150 BV. The result shown in Figure 4 compares favorably to RSSCT results obtained with bituminous GAC in the January 2003 study with Fontana groundwater prior to the development of cationic surfactant tailored GAC.

**Table 1. List and Description of Rapid Small Scale Column Tests (RSSCTs) conducted with Fontana water.**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Virgin Carbon</td>
</tr>
<tr>
<td>2</td>
<td>Tailored carbon by Siemens</td>
</tr>
<tr>
<td>3</td>
<td>Water spiked to 50 ppb perchlorate</td>
</tr>
<tr>
<td>4</td>
<td>Carbon Tailored by Penn State</td>
</tr>
<tr>
<td>5</td>
<td>Water spiked to 500 µg/L of perchlorate</td>
</tr>
<tr>
<td>6</td>
<td>Nitrate concentration increased to 100 mg/L</td>
</tr>
<tr>
<td>7</td>
<td>Sulfate concentration increased to 50 mg/L</td>
</tr>
</tbody>
</table>
Sulfate concentration increased to 250 mg/L
Carbon tailored with Arquad 2C-75
Nitrate concentration increased to 60 mg/L
Water spiked with 1 mg/L thiosulfate
Chloride concentration increased to 250 mg/L
Water spiked with 10 mg/L Thiosulfate
Bicarbonate concentration increased to 500 mg/L
Flow rate decreased to 0.25 mL/min
pH lowered to 4.2
pH increased to 10

The time to perchlorate breakthrough was 18,700 bed volumes for tailored carbon. Two sources of origin for tailored carbons were used in these experiments: both those prepared by Penn State, and that prepared by Siemens Water Technologies. This was done to compare the breakthrough for both carbons. Figure 5 shows that there were no differences in performance between the carbon that was tailored at Penn State and the carbon that was tailored by Siemens Water Technologies. The loading was 0.30 g CPC/g GAC for the carbon tailored at Penn State tailored carbons; and 0.29 g CPC / g GAC for the carbon tailored by Siemens.

Experiments were also conducted where perchlorate concentration was spiked to 50 µg/L and 500 µg/L which were approximately one and two orders of magnitude greater than the concentration found in the native Fontana ground water. Breakthrough occurred at 16,000 for 50 µg/L-spiked water and at 10,000 bed volumes for the 500 µg/L-spiked water (Figure 6 and 7). This showed that there would be about a 14% decrease in the tailored carbon performance to remove perchlorate from the groundwater if the concentration was an order of magnitude higher; and this result highlights that it was the background competing anions that dictated breakthrough performance, more than the level of perchlorate present (see further discussion as follows).

Activated carbon that was loaded with dicocoalkyl Notre ammonium chloride (Arquad 2C-75) was also tested to observe if there would be a difference in perchlorate adsorption. Arquad 2C-75 was chosen since it has two long chains instead of one as in the case of CPC. This property of the Arquad 2C-75, facilitated lower leaching of the surfactant off of the carbon. The loading for Arquad 2C-75 was 0.245 g/g GAC compared to 0.30 g/g GAC for CPC. It can be seen from
Figure 8, that even though CPC had a greater concentration loading, there were no significant
difference for bed volumes to break through between the Arquad 2C-75 and CPC. Breakthrough
of perchlorate when using Arquad 2C-75 as the surfactant occurred at 19,500 bed volumes while
for CPC, it was 18,500 bed volumes.

Figure 9 shows the results of experiments that were conducted using an array of
concentrations for nitrate, sulfate, and thiosulfate. When the nitrate concentration was 100 mg/L
as nitrate, which is three times the concentration of nitrate found in Fontana groundwater, the
breakthrough for perchlorate occurred at 8,500 bed volumes. While when the nitrate
concentration was two times (60 mg/L as nitrate) the initial concentration, breakthrough for
perchlorate occurred at 15,600 bed volumes. It could be seen from the graph that nitrate was the
one anion that greatly diminished the effectiveness of the tailored carbon to remove perchlorate
from Fontana groundwater when using CPC as the surfactant.

Sulfate concentration was increased to (a) 50 mg/L, which is 10 times the initial
concentration of Fontana water, and (b) 250 mg/L, which corresponds to the maximum
contaminant level (250 mg/L). For each of these cases, perchlorate breakthrough was unaffected,
and occurred at 20,000 bed volumes. This showed that there was no change in the performance of
the tailored carbon to remove perchlorate when sulfate concentration is increased.

Thiosulfate at 1 mg/L and 10 mg/L concentration was also added to Fontana water to
observe any effects on the removal of perchlorate by the tailored carbon. Breakthrough of
perchlorate occurred at 16,700 and 14,500 bed volumes respectively, which is a 10 and 19 percent
decrease in the performance of the carbon to remove perchlorate from the groundwater when
thiosulfate is added.

From ion activity tables for quaternary ammonium ion exchange media, the sulfate anion
would have been more competitive than nitrate anion for adsorption sites if the CPC tailored
carbon followed the same pattern as the quaternary ammonium does. The results show the
opposite of this statement when pyridinium is the perchlorate-exchanging functional group; and
from this it can be hypothesized that the sulfate anion cannot simultaneously access two charged
pyridinium sites. Sulfate is a tetrahedral compound and only has a covalent diameter of
approximately 0.500 nm so based on this analogy it appears that the sulfate anion cannot access
both charged sites that it needs to attach to. So instead of adsorption of sulfate anion to the charge sites on the carbon, it could pass through the column, therefore not affecting perchlorate removal. Nitrate on the other hand only needs one charge site so the spacing arrangement does not matter for it.

The effect of pH (Figure 10), bicarbonate and chloride (Figure 11) was also evaluated to observe the effects of perchlorate adsorption on CPC-tailored GAC. Fontana groundwater was spiked with sodium bicarbonate to the amount equivalent to 550 mg/L as bicarbonate.

In another run, hydrochloric acid was added to lower the pH of Fontana groundwater to approximately 4.2; and in yet another run, the pH was increased to approximately 10 by adding sodium hydroxide.

Lowering the pH to approximately 4.2 increased the bed life of CPC-tailored GAC to remove perchlorate from Fontana groundwater, to where initial perchlorate breakthrough occurred at 30,000 bed volumes. This was a 42% increase in bed life of the CPC-tailored GAC. Figure 10 also depicts that when the Fontana water contained 3 μg/L perchlorate, the bed life was 20,000 bed volumes to initial perchlorate breakthrough. When the pH of this water was lowered to roughly 4.2, its bed life was 34,000 bed volumes. This shows that perchlorate breakthrough is more gradual in an acidic environment compared to an environment that depicts groundwater characteristics. Increasing the pH to 10 showed results opposite of what was observed when the pH was lowered. Breakthrough for perchlorate was observed at 8,500 bed volumes. This indicated that a higher pH will diminish the capacity of the TGAC to adsorb perchlorate. There was a 54% reduction in CPC-tailored GAC capacity to adsorb perchlorate at pH 10 than for Fontana groundwater at its natural pH. The background pH for Fontana groundwater ranges from 7-8.

From Figure 11 it can be seen that a bicarbonate concentration that is almost twice the secondary standard set by the state does not affect the adsorption of perchlorate to granular activated carbon tailored with CPC. Breakthrough of perchlorate occurred at 24,000 bed volumes. This is approximately 5,000 bed volumes more or approximately 25% more than Fontana groundwater that is not spiked with sodium bicarbonate. The Fontana groundwater already has a background bicarbonate concentration of 330 mg/L. We are speculating that the bicarbonate does
not directly increase the adsorption capacity of the CPC, but rather that the increased concentration of bicarbonate might have changed the equilibrium of the experiment by affecting the electrical potential of the system. It is however, unclear as to why breakthrough occurred later when the bicarbonate concentration almost doubled.

The mass of sorbed perchlorate and the percent of surfactant sites occupied by perchlorate were also calculated, as shown in Table 2 for each experiment. It was estimated that 10% of the CPC and 1% of Arquad 2C-75 desorbed. With native perchlorate levels, the mass of perchlorate adsorbed per gram of carbon ranged from 0.16 to 0.502 mg / g GAC; with high nitrate concentration incurring the lowest perchlorate loading; and the acidic environment facilitating the highest. On the other hand the percent of CPC sites occupied with perchlorate ranged from 0.0002 to 0.6580 for experiment 17 and 16 respectively.

**Conclusion**

Activated carbon tailored with cationic surfactants has a greater capability to remove perchlorate from Fontana groundwater than activated carbon not tailored with cationic surfactants. Nitrate was the only anion tested that greatly diminished the CPC-tailored GAC to remove perchlorate from Fontana groundwater; and thiosulfate diminished capacity slightly. It was also observed that at alkaline pH, the CPC-tailored GAC capacity was diminished, while at pH 4.2, the capacity is increased. It can be concluded that activated carbon tailored with CPC can significantly remove perchlorate concentration ranging from 7-50 µg/L. Also the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7.
### Table 2 – Mass of perchlorate adsorbed and percent CPC sites occupied for each experiment.

<table>
<thead>
<tr>
<th>EXP. #</th>
<th>Condition</th>
<th>Bed Volumes*</th>
<th>Total Mass of ClO₄⁻ (mg)</th>
<th>mgClO₄⁻ /gGAC</th>
<th>% of CPC sites occupied by ClO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Virgin Carbon</td>
<td>640</td>
<td>0.0258</td>
<td>0.0204</td>
<td>0.0266</td>
</tr>
<tr>
<td>2</td>
<td>Tailored carbon by Siemens</td>
<td>17,700</td>
<td>0.403</td>
<td>0.318</td>
<td>0.4157</td>
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<tr>
<td>3</td>
<td>Water spiked to 50 µg/L perchlorate</td>
<td>15,200</td>
<td>2.65</td>
<td>2.08</td>
<td>2.7332</td>
</tr>
<tr>
<td>4</td>
<td>Carbon Tailored by Penn State</td>
<td>16,500</td>
<td>0.422</td>
<td>0.33</td>
<td>0.4353</td>
</tr>
<tr>
<td>5</td>
<td>Water spiked to 500 µg/L perchlorate</td>
<td>9,200</td>
<td>14.5</td>
<td>11.4</td>
<td>14.9554</td>
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<tr>
<td>6</td>
<td>Nitrate concentration increased to 100 mg/L</td>
<td>7,900</td>
<td>0.204</td>
<td>0.16</td>
<td>0.2104</td>
</tr>
<tr>
<td>7</td>
<td>Sulfate concentration increased to 50 mg/L</td>
<td>18,800</td>
<td>0.436</td>
<td>0.34</td>
<td>0.4497</td>
</tr>
<tr>
<td>8</td>
<td>Sulfate concentration increased to 250 mg/L</td>
<td>19,000</td>
<td>0.45</td>
<td>0.358</td>
<td>0.4641</td>
</tr>
<tr>
<td>9</td>
<td>Carbon tailored with Arquad 2C-75</td>
<td>19,000</td>
<td>0.429</td>
<td>0.338</td>
<td>0.6713&quot;</td>
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<tr>
<td>10</td>
<td>Nitrate concentration increased to 60 mg/L</td>
<td>15,200</td>
<td>0.251</td>
<td>0.198</td>
<td>0.2589</td>
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<td>11</td>
<td>Water spiked with 1 mg/L thiosulfate</td>
<td>15,800</td>
<td>0.359</td>
<td>0.283</td>
<td>0.3703</td>
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<tr>
<td>12</td>
<td>Chloride concentration increased to 250 mg/L</td>
<td>22,500</td>
<td>0.473</td>
<td>0.372</td>
<td>0.4879</td>
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<tr>
<td>13</td>
<td>Water spiked with 10 mg/L thiosulfate</td>
<td>13,700</td>
<td>0.378</td>
<td>0.298</td>
<td>0.3899</td>
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<tr>
<td>14</td>
<td>Bicarbonate concentration increased to 500 mg/L</td>
<td>23,300</td>
<td>565</td>
<td>445</td>
<td>0.5827</td>
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<tr>
<td>15</td>
<td>Flow rate decreased to 0.25 ml/min</td>
<td>10,800</td>
<td>0.275</td>
<td>0.217</td>
<td>0.2836</td>
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<tr>
<td>16</td>
<td>pH Lowered to 4.2</td>
<td>28,700</td>
<td>638</td>
<td>502</td>
<td>0.6580</td>
</tr>
<tr>
<td>17</td>
<td>pH Increased to 10</td>
<td>5,500</td>
<td>315</td>
<td>248</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

*Bed Volumes is defined here as the last undetectable perchlorate before Breakthrough.

#Arquad 2c-75 was used instead of CPC to calculate the percent sites occupied by perchlorate.
Figure 1 – Rapid Small Scale Column Tests in the Laboratory

Figure 2 - Picture showing 13.5cm x 0.5cm columns
Figure 3- High Pressure Liquid Chromatography pumps used in RSSCT experiments

Figure 4 - Graph shows perchlorate adsorption to activated carbon that is not tailored.
Figure 5 - Graph showing perchlorate breakthrough for carbon that was tailored by Penn State and Siemens Technology.

Figure 6 - Graph showing perchlorate breakthrough when Fontana water had a 50 ppb concentration of perchlorate.
Figure 7 – Perchlorate breakthrough when Fontana water is spiked to 500 ppb perchlorate.

Figure 8 – Graph showing perchlorate adsorption results with different tailoring agents.
Figure 9 – Graph showing the effects of increased concentration of anions on perchlorate removal. Notations: NO3 –nitrate, SO4-sulfate, S2O3-thiosulfate.

Figure 10 – The effects of pH on perchlorate adsorption to TGAC.
Figure 11 – Graph depicting the effects of total dissolved solids on perchlorate adsorption to TGAC. Notation: - Cl- Chloride, HCO3- Bicarbonate.
References


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Publications

“Oxidation of Reduced Sulfur species (Thiosulfate) by free chlorine to Increase the Bed-Life of tailored GAC to remove Perchlorate. Judodine Patterson, Robert Parette and Fred Cannon. 2008. In the conference Proceedings of Water Quality Technology Conference, AWWA.


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Available upon request