The Pennsylvania State University

The Graduate School

College of Engineering

TAILORING AND REGENERATION OF GRANULAR ACTIVATED CARBON FOR
PERCHLORATE REMOVAL

A Thesis in
Environmental Engineering

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2005
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ABSTRACT

TAILORING AND REGENERATION OF GRANULAR ACTIVATED CARBON FOR PERCHLORATE REMOVAL

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Perchlorate contaminates waters in 15 US states that 15 million American could otherwise drink. Although, conventional granular activated carbon (GAC) has a very limited capacity for removing perchlorate, it was found that ammonia thermal tailoring could enhance its bed life.

For carbon tailoring, first, a commercially available bituminous GAC was subjected to thermal treatment with ammonia at temperatures of 500-800°C. Elemental analysis results showed that nitrogen was incorporated into the carbon matrix during the thermal treatment. The ammonia treatment caused an increase in positive surface charge density, reflected in a higher pH_{pzc} and pH_{IEP}. This was attributed to the more basic nature of the carbon surface after its treatment in ammonia. Ammonia-tailored carbon achieved as much as a 4-fold improvement in bed life for adsorbing perchlorate as determined by rapid small-scale column tests (RSSCT) using groundwater from City of Redlands with perchlorate concentration 70-78 ppb. The RSSCTs simulated full-scale operation with high reproducibility between runs. Increased perchlorate adsorption corresponded to increased positive surface charges. Ammonia-tailored activated carbons also exhibited an increase in TOC removal.

Activated carbon could also be tailored electrochemically while using ethylene diamine as the reagent. Results indicate that electrochemical treatment effectively incorporated nitrogen-containing groups onto carbon surface without damaging the carbon’s surface area and pore volume. The resultant carbons had two times the adsorption capacity for perchlorate as compared with its non-tailored counterpart.
An essential factor in applying activated carbon to water treatment is regeneration after exhaustion. The author also tested chemical regenerations by both calcium thiosulfate and a base/acid method in small-scale for perchlorate-exhausted conventional carbon. RSSCT results indicate that base/acid regeneration was an effective way to restore the adsorption capacity of carbon. Full-scale regeneration with base/acid did not restore as much capacity as has bench-scale RSSCTs. It was believed that short-circuiting and carbon damage by the base solution would have been this distinction.

Another frequently used regeneration method is thermal regeneration. Thermal regeneration was focused on ammonia-tailored carbon. To address this, the author tested whether ammonia-tailored GAC could be regenerated after the tailored GAC had adsorbed perchlorate. Thermal regeneration tests indicated that reactivations by CO$_2$ and NH$_3$ at 600-800°C for 10-20 minutes restored the perchlorate adsorption capacity of the tailored carbon. In comparison, steam regeneration at temperature >700 appears to be too harsh and reduction in carbon bed life was observed. As indicated by proximate analysis, the steam reaction removed the nitrogen that the ammonia tailoring had affixed, and this destroyed the surface chemistry characteristics that had been created during the ammonia tailoring process. It was these characteristics that are improving perchlorate adsorption.
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Acknowledgements

There are many people who have helped to complete this work, and I owe thanks to all of them. First and foremost, I wish to express my appreciation to Dr. Fred S. Cannon, whose knowledge and insight guided me throughout this study. It has been a pleasure working for him.

I would like to thank Dr. Bruce E. Logan, Dr. Tze-Chiang Chung, and Dr. John M. Regan for their willingness to serve on my doctoral committee.

Thanks also to the graduate students I came to know during my time at Penn State. Special thanks to Robert Parette, Jose R. Rangel-Mendez, Kirk O. Nowack, Adam Redding, Wang Yujue and Jiying Zou

This research has been funded through the American Water Works Association Research Foundation, and the Department of Energy. The AWWARF funds originated from the US EPA; and this funding was prompted in part by the proactive activity of the East Valley Water District and Congressperson Jerry Lewis. The authors’ frequent interaction with US Filter and The City of Redlands is acknowledged.
CHAPTER 1
INTRODUCTION

Perchlorate in the environment originates as a contaminant from the solid salts of ammonium, potassium or sodium perchlorate mainly used as propellant for rocket, missiles and fireworks. It now contaminates the water supplies that serve millions of people in US. With regard to human health, the targets of perchlorate include the thyroid gland, bone marrow, and muscle tissue at high concentrations (Urbansky 1998). In 1997, California established an action level of 18 ppb for perchlorate in public water supplies. The action level was updated to 4 ppb in 2002; this has become a public health goal of 6 ppb in 2004.

Although perchlorate is thermodynamically reactive, it is kinetically stable in groundwater at low concentration. Practice with conventional granular activated carbon (GAC), air stripping and advanced oxidation had limited or no effect on low perchlorate concentration water (Brown et al. 2000, Wallace et al. 1998).

This research aimed to devise a means to remove low levels of perchlorate from groundwater in a cost effective manner. Activated carbon has been widely used in the water treatment industry. Therefore, one of the advantages in applying GAC to remove perchlorate is that several of the water utilities that must deal with perchlorate-contaminated water already have installed GAC beds to remove trace organic compounds. Experience has shown that GAC is able to adsorb perchlorate and leave no detectable levels in the treated water. However, its adsorption capacity for perchlorate is very limited, amounting to only about 6 weeks’ of operation according to the experience from Texas Street Water Treatment Plant, City of Redlands, CA (Na et al. 2002). To place this in perspective, it corresponds to only 10% of the life for organic contaminants. If carbon has to be regenerated or replaced at so short an interval, the cost for the operation will be prohibitive. Two of the remedies are to regenerate the carbon on the spot or extend the adsorption capacity to a duration that is comparable to that for organics. The research herein contains both in-situ chemical regeneration and activated carbon tailoring by chemical or electrochemical method. The GAC has to be thermally reactivated once the capacity for organics had been reached. Therefore, thermal
reactivation also offers an important opportunity for restoring a carbon’s adsorption capacity for perchlorate.

Activated carbon is a complex and heterogeneous material with unique adsorption characteristics. The main features that give the material these characteristics are its porous structure, surface area and surface properties (Puri, B. 1970). It has long been recognized that both physical and chemical characteristics of carbon will have great effect on the adsorption capacity for an adsorbate. High specific surface area and large micropore volume (especially micropores with widths that are one to ten times the dimensions of the adsorbate) have long been proven to be helpful for adsorption. On the other hand, more work still needs to be done to understand the surface chemistry effects on carbon performance. The difficulty with the research on carbon is that its behavior is closely related to not only its own characteristics but also the status of the adsorbate and solvent. This means that one must be cautious when extending conclusions drawn from one research study to another.

Numerous studies have found that adsorption by GAC of both inorganics and organics is highly dependent on the surface functional groups, solution pH and so on. The advance in new technologies makes possible detailed research on the surface chemistry of carbon. Modification of carbon by chemical or electrochemical methods has been widely reported in application of carbon for removal of metal (Cu, Cr, Cd et al.) and trace organics (phenol, TCE, benzene et al.) in both gas and liquid phases. Various materials have been utilized for tailoring purposes, and the most suitable approach has depended on the specific situation of each case. The most commonly used processes for altering surface chemistry have included oxidizing agents such as H$_2$O$_2$, O$_3$, nitric acid or reducing agent such as NH$_3$ gas and thiosulfite. Studies indicated that thermal treatment of carbon by NH$_3$ could effectively add basic functional groups onto the carbon surface at elevated temperatures (Menendez et al. 1996; Mangun et al. 2001; Xie et al. 2001).

The research herein aimed to explore the effects of both chemical and electrochemical methods for carbon tailoring so as to enhance perchlorate removal. The authors also conducted carbon characterization of both the physical and chemical properties so as to take advantage of the recent advances in our technical capabilities. It was expected that armed with a relatively full understanding of the factors affecting
For granular activated carbon, a high initial cost mandates regeneration. The most common regeneration technique is thermal regeneration, in which adsorbates are desorbed by means of volatilization and oxidation at high temperature. Chemical regeneration is an alternative to thermal regeneration. It has a number of significant advantages: (1) it can be done in-situ; (2) the loss of carbon from thermal desorption is eliminated; (3) recovery of valuable of adsorbate or reuse of regenerant is possible. Compared with thermal regeneration, chemical regeneration is more suitable in the case where frequent regeneration is required or where recovery of the adsorbate if preferable.

**Research Objectives**

The objectives of this research were:

1. To extend the bed life of activated carbon for perchlorate adsorption.
2. To test the hypothesis that perchlorate adsorption is more related to the surface chemistry of activated carbon than the physical properties (surface area, pore volume).
3. To test the hypothesis that by incorporating nitrogen-containing surface functional groups onto activated carbon surface, the resultant carbon would be more effective in perchlorate adsorption. Thermal tailoring by NH$_3$ and electrochemical tailoring by nitrogen–containing organic compounds have been chosen to be two of the directions explored in detail in this research.
4. To test the hypothesis that carbons with basic features are more effective in adsorbing perchlorate by exhibiting a more positively charged surface at natural water pHs.
5. To characterize the tailored carbons so as to obtain a better understanding of the factors that are most beneficial for perchlorate removal.
6. To discern the optimal way to regenerate the carbon by preserving beneficial chemical and physical characteristics.
7. To test the hypothesis that thermal reactivation could restore the adsorption capacity of exhausted carbon and at the same time eliminate the perchlorate adsorbed, thus the carbon can be recycled.
CHAPTER 2
LITERATURE REVIEW

2.1 PERCHLORATE

2.1.1 Background

Perchlorate (ClO$_4^-$, Figure 2.1) contamination in both ground and surface water mainly originates from facilities that manufacture or use perchlorate salts such as ammonium, potassium or sodium for various purposes. Perchlorate products are mainly used for rocket propellant (about 90%) though it can also be found in other products such as explosive, automobile air bags et al. (Gullick et al. 2001). When used as propellant, it has to be replaced periodically via a high-pressure water jet due to its limited shelf life. The resultant perchlorate-containing water was released non-cautiously onto soils and ultimately made its way into the groundwater (Gullick et al. 2001). Perchlorate has been detected in at least fifteen states including California, Arizona, Nevada, Iowa, Texas and others, and it affects water supplies that approximately 15 million people could otherwise drink (US EPA 1999-2).

In California, perchlorate has been reported in about 300 water supply wells. The majority of the contaminated areas are related to the twelve facilities that have manufactured or tested solid rocket fuels for the Department of Defense or the National Aeronautics and Space Administration (US EPA 1999). Perchlorate was detected in Riverside County drinking water wells (up to 29 µg/L) and in some San Bernardino County drinking water wells (up to 325 µg/L). In those areas, perchlorate contamination was in a trichloroethylene (TCE) plume associated with past operation of the Lockheed Propulsion Company (California Department of Health Service 1998).

In Arizona, the Environmental Protection Agency has been conducting perchlorate concentration analysis along the Colorado River with results ranging from non-detectable to 9 µg/L (Arizona Department of Environmental Quality 2000).
In Nevada, the state with the largest perchloate concentration identified to date, perchlorate contamination is related to two ammonium perchlorate manufacturing facilities. Water samples collected 300 meters from the former Pacific Engineering & Production Company of Nevada (PEPCON) site, a rocket fuel plant, contain perchlorate concentration as high as 630 mg/L (Urbansky, 1998).

There are indications that perchlorate may occur naturally in the environment. Investigations have shown that there was occurrence of perchlorate in natural nitrate deposits in Chile (Schilt 1979; Susarla et al. 1999). Susarla et al. (1999) also investigated the presence of perchlorate in some other compounds. Lengbenite, the single most important source of potassium sulfate for all major manufacturers, has shown perchlorate amounts up to 1.86%.

2.1.2 Toxicology

Perchlorate was once used to treat Graves’ disease, a form of hyperthyroidism. Therefore, its health effect at high doses is relatively well known. Perchlorate dose in the milligrams per day range have been shown to inhibit the uptake of iodide by the thyroid, which caused hypothyroidism (Li et al. 2001).

The toxicity of perchlorate has been the focus of much research, with the primary concern being potential effect of perchlorate on hindering the synthesis of thyroid hormones and/or subsequent consequences resulting from decreases in thyroid hormones as perchlorate competes with the iodine ion. No short-term detrimental effects were found in rats in a 90-day study with perchlorate exposure below 1 mg/kg (body weight)/day while its prolonged effects are yet to be determined (Siglin et al. 2000).

There are still plenty of gaps to fill before a complete estimation on the potential health effect of perchlorate is possible. Based on an EPA reference dose (RfD) range of 0.001 to 0.005 mg/kg-day, as revised in 2002, and applying standard defaults relative to body weights and water consumption levels, several agencies have proposed that the drinking water standard should be 4 to 18 part per billion (ppb).

In addition, there have been a few papers concerning the potential for toxicological effect of perchlorate on terrestrial and aquatic species (York et al. 2001;
Smith et al. 2001; Manzon and Youson 1997). However, much more research is necessary to evaluate the potential ecological effects of this contaminant. Thus the environmental and human health effects resulting from long-term exposure to low levels of perchlorate remain largely unknown.

2.1.3 Regulatory

There is currently no federal National Primary Drinking Water Regulation for perchlorate. But perchlorate is on the EPA’s Safe Drinking Water Act’s Contaminant Candidate List. Further information concerning occurrence, health effects, treatment technologies, and analytical methods are continuing as the EPA and others seek to discern the most appropriate primary drinking water standard for perchlorate.

In 1997, California established an action level of 18 ppb for perchlorate in public water supplies. This was based on the provisional reference dose for perchlorate of 0.14 mg/kg/day determined by EPA at the same year. In 2002, the EPA further reduced its estimated No Observable Adverse Effect Level (NOAEL) to 0.001 mg/kg/day. It caused the California Department of Health Service (2002) to change its perchlorate action level to 4 ppb. In 2004, California DHS has a Public Health Goal of 6 ppb perchlorate.

2.1.4 Treatment Technologies

Since the time perchlorate was discovered in water supplies in California, Nevada, and Arizona, much progress has been made in developing treatment methods capable of removing perchlorate from water. It is important to know the characteristics of a specific contaminant before any treatment technologies can be successful. Perchlorate salts are highly soluble (e.g. ammonium perchlorate is soluble to 200 g/L) and dissociate completely. The resulting perchlorate anion is nonvolatile, highly mobile, and chemically stable in aqueous systems under normal conditions present in groundwater and surface water. As a result, in areas where substantial quantities of perchlorate salts have been disposed, large groundwater plumes of perchlorate are often observed. Because of its physical characteristics (i.e. low reactivity, low volatility, high solubility), water
treatment technologies including air stripping and advanced oxidation are not effective options for perchlorate removal from groundwater (Damina and Pontius 1999; USEPA 2001a).

The feature of perchlorate that makes it useful in rocket fuel is its high reduction potential. The perchlorate ion (ClO$_4^-$) is the most oxidized form of chlorine that exists in water, and thus perchlorate is a strong oxidizing agent. When reduced to chloride in acidic solution, perchlorate has a standard reduction potential of 1.29V (equation 2-1), making it a stronger oxidant than oxygen (Bard et al. 1985; Emsley 1989).

\[
\text{ClO}_4^- + 8e^- + 8H^+ \rightarrow \text{Cl}^- + 4H_2O \quad E^0 = 1.29V
\]  

(2-1)

However, the reduction rate of pure aqueous perchlorate under normal conditions (i.e. neutral pH, low concentration and ambient temperature) is immeasurably slow. As perchlorate does not exhibit its oxidizing properties under the conditions found in contaminated raw and treated waters, it cannot be reduced in groundwater at ambient temperatures with common agents, such as thiosulfate (S$_2$O$_3^{2-}$), sulfite (SO$_3^{2-}$) or elemental metals (e.g. Fe, Zn, Cu).

Current technologies under most investigation for perchlorate removal include biological treatment, ion exchange, electrochemical treatment, membrane filtration and tailored activated carbon adsorption and others.

2.1.4.1 Biological Treatment

Results reported up to now about biological treatment processes appear to be quite promising at least in small or pilot-scale. Thermodynamically, perchlorate is a strong oxidant and could readily accept electrons. Several species of microorganisms are found to be capable of using perchlorate as an oxidant (electron acceptor) for metabolism (Logan 1998; Urbansky 1998; Achenbach et al. 2001; Coates et al. 1999). Rikken et al. (1996) reported that perchlorate and chlorate were reduced to chloride by Proteobacteria with acetate as a nutrient (reductant) at near-neutral pH. Those bacteria grow through anaerobic respiration. During the process, the bacteria require an organic or inorganic electron donor (e.g. ethanol, acetate, hydrogen gas) for growth, and they utilize the perchlorate molecule as a terminal electron acceptor. A (per)chlorate reductase enzyme
appears to catalyze an initial two-step reduction of perchlorate (ClO$_4^-$) to chlorate (ClO$_3^-$) and then chlorite (ClO$_2^-$) (Kengen et al. 1999). The chlorite is then further reduced to chloride.

Several types of bioreactor systems have been evaluated for perchlorate treatment. Packed bed systems with a variety of media and nutrients were reported to show sustained perchlorate removal.

Kim and Logan (2000) demonstrated that bioreactors packed with sand (detention time 18 min) could reduce perchlorate concentration from 20 mg/L to below detection (<4 µg/L) while adding 30 mg/L acetate (8.8 mg/L as carbon). However, perchlorate removal efficiency was significantly diminished after the filter was backwashed. Using a biologically active carbon (BAC) filter operated at a 25-min empty bed contact time (EBCT), Brown et al. (2002) removed 50 µg/L influent perchlorate to below detection and the removal was sustained by adding an electron donor mixture (acetate, lactate and pyruvate at a total concentration of 1.7 mg/L as carbon).

Min et al. (2004) used fixed bed bioreactors packed with sand or plastic media to remove perchlorate (77 µg/L) from a groundwater. Perchlorate was completely removed (< 4 µg/L) in the sand medium bioreactor at flow rates of 0.063-0.126 L/s and in the plastic medium reactor at flow rate < 0.063 L/s.

Microbial perchlorate removal processes that use hydrogen as the electron donor have also been investigated. Nerenberg and Rittmann (2001) observed the reduction of 6, 50 and 100 µg/L influent perchlorate concentrations to between 2 and 4.5 µg/L in a hollow fiber membrane biofilm reactor. The process used a hydrogen pressure of 2.5 psi and a detention time of 44 min. Miller and Logan (2000) showed a sustained perchlorate removal of 38±9% in a gas-phase, packed-bed bioreactor (detention time 1.1-1.3 min) with hydrogen and carbon dioxide gas flow rates of 43 and 7.5 mL/min, respectively. The influent perchlorate concentration was 740 µg/L.

Besides packed bed systems, fluidized bed reactors (FBR) have also been tested for perchlorate removal. Hatzinger et al. (2002) developed a fluidized bed reactor system to remove perchlorate from groundwater in California using ethanol as the electron donor and activated carbon as the media. With average influent nitrate and perchlorate
concentrations of 33.2 mg/L and 770 µg/L, the system was able to reduce both contaminants to below detection throughout the 52-day treatment period.

Although microbes have been shown to reduce perchloate to chloride, microorganisms cause disease and/or prefer oxygen. A large amount of reductant (food) may be consumed by the organism without any reduction of perchlorate when incoming water contains a significant concentration of dissolved oxygen. Moreover, municipality staff will want to exclude any organisms known or found to be pathogenic.

Municipalities are reluctant to accept biological treatment technology for drinking water in spite of the fact that bioreactors appear to work efficiently when removing low perchlorate concentrations from drinking water supplies. This is because one of the primary missions of water treatment is to eliminate microorganism, rather than propagate them. Moreover, these biological systems require high maintenance, organic chemical feed (such as acetic acid etc.), and they can be easily perturbed out of favorable operational conditions. In addition, biological reduction of perchlorate occurs under anoxic conditions, and production of sulfide and other reduced compounds could be problematic.

One feasible application of biological treatment is for perchlorate removal of waters with high salinity, such as wastes from ion exchange regeneration after perchlorate removal. Okeke et al. (2002) reported to have successfully isolated a species of bacterium, Citrobacter sp., which could substantially reduce perchlorate in 0-5% NaCl and maximally at 30°C and pH 7.5. In simulated brines with 100 mg/L ClO₄⁻, the Citrobacter sp. significantly reduced both perchlorate and nitrate with 34.9 and 15.6% reduction, respectively.

2.1.4.2 Ion Exchange

Ion exchange technology has been widely used for water treatment for years (Bastial et al. 2000; Brown et al. 2000; Gu et al. 2000a). The technology is based on the interchange between an innocuous ion, which is attached to the ion exchange resin, with the contaminant ion present in the solution that needs treatment. In home and business, ion exchange processes have been used for water softening for many decades (US EPA
1998). Ion exchange can also be a natural phenomenon that occurs in soil, humus, cellulose, activated carbon, coal, living cells, minerals and tissues of plant and animals. In the modern civilization, Way and Thompson (1850) were the two first scientists that independently recognized and examined the ion exchange phenomenon in soils. But it was two English chemists, Adams and Homes (Samuelson, 1963), who first developed synthetic ion exchange resins. Synthetic ion exchange resins are insoluble polymers formed by a system of hydrocarbon radicals to which ionic functional groups are attached. The toughness and insolubility of the resin is due to its three-dimensional matrix in which the hydrocarbon molecules are cross-linked.

Ion exchange resins are classified as anionic and cationic based on the charge of the ion bound to the functional group (counter-ion). The counter ions are the ions replaced in the ion exchange process and the functional groups remain fixed to matrix. Ion exchange resins are further classified as strong or weak, and basic or acidic as determined by their functional groups. Functional groups derived from strong acids (e.g. \( \text{H}_2\text{SO}_4 \)) form strong acid resins. Functional groups derived from weak acids (e.g. \( \text{HCO}_3^- \)) form weak-acid resins. Ion exchange resins that have amino or substituted amino as functional groups are called weak-base resins, and resins with quaternary ammonium as functional groups are called strong-base resins. Ion exchange resins can also be classified as styrenic and acrylic based on the resin structure. Styrenic resins have an aromatic polymer structure while acrylic resins have an aliphatic structure.

Since perchlorate is anion in water, research on perchlorate removal is focused on anionic, strong or weak-base ion exchange resins. The exchangeable counter-ions for a basic anion resin may be chloride, hydroxide or other monovalent anions. When these counter-ions have been exchanged to the extent that the targeted ion starts to breakthrough, the regeneration of the ion exchange material is required to reestablish its exchange capacity. The regeneration process is conventionally performed with a strong (approximately 2-12% by weight) solution of exchangeable counter-ion.

A variety of studies have been conducted for perchlorate removal by ion exchange resins. In 1998, field trials for perchlorate removal conducted by Calgon Carbon Corporation in California demonstrated that the perchlorate concentration could be
reduced from 75 µg/L to below the action level of 18 µg/L by a continuous ion exchange system.

Vieira (2000) evaluated several commercially available strong and weak-base ion exchange resins for their perchlorate removal capacities. Column tests with synthetic perchlorate-containing (40 mg ClO₄⁻/L) water indicate that strong-base styrenic type resins were very effective in removing perchlorate from water. Column utilization to breakthrough reached 100%. Column utilization to breakthrough was defined in this study as the amount of contaminant that exchanged with the resins from time zero to the time immediately before breakthrough divided by the theoretical amount of contaminant that would exchange with the resin and given by the resin exchange capacity. On the other hand, the strong-base acrylic resin had column utilization to breakthrough ranged from 50-70%. Regeneration of both strong-base styrenic and acrylic resins by 12% NaCl revealed that acrylic resins regenerate better than their styrenic counterparts. 100% of the loaded perchlorate could be regenerated by 12% NaCl from acrylic resins while regeneration efficiency was only 20-40% for styrenic resins. This may be because that perchlorate attached more strongly to styrenic resins than to acrylic ones. Perchlorate removal by Vieira (2000) using weak-base ion exchange, however, showed very low column utilization for both styrenic and acrylic resins. The poor performance of weak-base ion exchange resins is related to the pH value of the perchlorate containing water.

Wachinski and Etzel (1997) stated that weak base anion exchange resins perform poorly at pH above 6, whereas, strong base resins can operate over a wide range of pH conditions. In Vieira’s research, the pH of the solution was between 6.0 and 9.5.

Vieira (2000) also conducted column tests for perchlorate removal by the same strong and weak-base resins with natural water. Results demonstrated that ion exchange was significantly affected by other anions and TOC in water. The natural water was a groundwater from Las Vegas Valley, which contained about 80 mg ClO₄⁻/L, 50 mg NO₃⁻/L, about 1900 mg SO₄²⁻/L and 50 mg TOC/L. Column utilization dropped to 30-50% for strong-base styrenic resins as compared to 100% when applying synthetic perchlorate solution. The column utilization for weak-base resin was only about 15% when treating natural water. There was strong evidence that humic acid substances were irreversibly sorbed by ion exchange resin.
It’s understandable that the effectiveness of the ion exchange is highly dependent on the presence of other anions. Najm and co-workers (1991) also found that the efficiency of perchlorate removal by ion exchange decreased in the presence of sulfate or nitrate.

To improve perchlorate removal, an optimum ion exchange resin would be one that could selectively remove perchlorate and at the same time limit the unnecessary removal of other ions that are typically present in higher concentrations than perchlorate (e.g. chloride, sulfate, nitrate, bicarbonate). Gu et al. (2000a) investigated the use of a highly selective anion exchange resin for the treatment of perchlorate-contaminated groundwater. The resin in question is a bi-functional anion exchange resin and was developed by the Oak Ridge National Laboratory, NJ. The bifunctional group is trihexylamine/triethylamine. It has high selectivity for large poorly hydrated anions such as perchlorate. In the bi-functional resin, the triethylamine group has the objective of improving the exchange kinetics while the trihexylamine is required for selectivity purpose. Resin exchange kinetics is a very important factor to be considered. It does not matter how high the selectivity of the resin is for perchlorate. If the rate of exchange is too slow, the resin will not be effective. Gu et al. (2000a) stated that no pretreatment of organic or inorganic components in the groundwater was needed for the application of the bifunctional resin for perchlorate removal. Small-scale field trials showed that the breakthrough did not occur until about 11,000 bed volumes of water were treated. The small scale tested was carried out with a flow rate of 200 mL/min (2 bed volume/min), and influent perchlorate concentration 50 µg/L. In related research, Gu et al. (2001) developed a regeneration method for the above-mentioned bifunctional resins. By applying a solution containing 1 M FeCl₃ and 4 M HCl, nearly 100% of loaded perchlorate was desorbed after 5 bed volumes of regenerant. It’s assumed that tetrachloroferrate (FeCl₄⁻) was the dominant species in the regeneration solution. Since FeCl₄⁻ has a similar structure to ClO₄⁻. It was surmised that ClO₄⁻ was easily displaced from the ion exchange resin by FeCl₄⁻. The small amount of regenerant necessary (5 bed volumes) to achieve the regeneration means that less amount of brine waste was produced. No significant loss of perchlorate capacity was observed following several regeneration cycles.
Perchlorate is only separated but not destroyed during the ion exchange process, thus subsequent disposal of both the perchlorate and any waste products are needed. Gu et al. (2003) developed a method to completely destroy perchlorate in FeCl₃-HCl solution by solid-phase ferrous Fe(II) (as FeCl₂·2H₂O). Perchlorate was found to decompose into non-hazardous Cl⁻ and water under certain catalytic conditions and a complete reaction occurs within a few hours to one day with an initial perchlorate concentration 87 to 91 mmol/L. Batch kinetic tests indicated that the rate constant of perchlorate decomposition increased with the increase of temperature. The rate constant for the pseudo-first-order reaction increased nearly three orders of magnitude when the temperature was increase from 110 to 195°C, and a complete reduction of perchlorate occurred in less than 1 hour at 195°C. This method was applied to regenerating waste from ion exchange resins. The destruction process does not alter properties of the regeneration solution; so it could be reused.

2.1.4.3 Electrochemical Reduction

Due to its kinetic barrier, perchlorate cannot be readily reduced by common reducing agents such as thiosulfate or elemental Fe et al., when cold or dilute. A variety of studies have been focused on overcoming this kinetic activation barrier. With the right catalyst, perchlorate may be reduced to either chlorate or chloride depending on the reductants. Cotton and Wilkinson (1988) stated that ruthenium (II) reduces perchlorate to chlorate, whereas, vanadium (II), vanadium (III), molybdenum (III), chromium (II), dimolybdenum (III) and titanium (III) all reduce perchlorate to chloride. The problems with chemical reductants include: (1) they tend to suffer from oxidation by atmospheric oxygen; and (2) they are too slow under normal conditions (i.e. pH and concentration).

The mechanism of electrochemical reduction is well understood. Perchlorate is reduced to chloride at a cathode when an electric current is applied to the water. The electrochemical reduction of perchlorate ion has been reported for a wide variety of cathodes, including platinum (Horanyi and Vertes, 1975), aluminum (Kiss et al., 1973), titanium (Mathieu and Landolt, 1978; Mathieu et al., 1978). Brown (1986) showed that chlorate and perchlorate may be reduced successfully to chloride by active titanium, and
he also discussed the possibility of passivation of the titanium electrode as titanium (IV) forms, presumably from the deposition of titanium.

The major problem with electrochemical reduction pertains to mass transfer issues. It may take a long time to get ions to the electrode surface from the bulk water as well as for them to associate with the surface, and these limitations make the process unrealistic in application. Moreover, technological difficulties that could arise from possible electrode corrosion, surface passivation and natural organic matter adsorption may well obstruct the electrochemical reduction application at large scale.

2.1.4.4 Reverse Osmosis and Nanofiltration

Membrane-based processes had long been applied to remove ions such as magnesium and calcium before it was investigated for perchlorate removal. The processes included are reverse osmosis (RO) and nanofiltration. By adjusting the permeability of the membrane in manufacture, perchlorate would be rejected and stay in the concentrate, and it would be separated from the final water product. Pilot-scale test by Roquubert et al. (2000) showed that nanofiltration process could reduce perchlorate concentration from 18 µg/L to less than detectable level of 4 µg/L. Yoon et al. (2000) evaluated two nanofiltration membranes on their perchlorate removal ability. The two membranes are ESNA and MX07 with molecular mass cut off (MMCO) 200 and 400 respectively. It was observed that perchlorate rejection was inversely related to zeta-potential. Perchlorate rejection increased as the zeta potential became more negative. Zeta potential of surface is closely related to the solution pH. Zeta-potential became more negative with the increase of pH. Therefore, perchlorate rejection increased with the increase of solution pH. ENSA was able to reject 70% of the perchlorate at pH 4. The number increased to 75% at pH 6 and 88% at pH 8. It was 93% at pH 10. The influent perchlorate concentration in the test was 100 µg/L. At the same pH values, 4, 6, 8, and 10, membrane MX 07 was able to reject 40, 49, 60, and 70% perchlorate respectively. Results from membrane pore size analysis (by polyethylene glycols rejection test) and contact angle measure (by goniometer) suggested that perchlorate was dominantly
rejected by electrostatic exclusion for charged nanofiltration and ultrafiltration membrane.

Yoon (2003) tried to modify membrane surface by anionic and cationic surfactants to increase their perchlorate rejection rates. A commercially available ultrafiltration membrane made of polyethersulfone coated with polyimide was employed for perchlorate rejection test. The cationic surfactant was tetradecyl trimethyl ammonium bromide (TTAB) and the anionic surfactant was sodium dodecyl sulfate (SDS). For cationic surfactant modified membrane, perchlorate rejection caused by electrostatic exclusion decreased due to a decrease in membrane negative surface charge. But a desired amount of the perchlorate was excluded by steric exclusion. The steric exclusion was a result of decrease in membrane pore size caused by adsorption of the cationic surfactant. In the case of modification by anionic surfactant, perchlorate rejection was surprisingly not enhanced by electrostatic exclusion because anionic surfactant showed little effect on the membrane surface charge. A limitation in the use of cationic surfactant to modify membrane is that a significant flux decrease occurred.

Membrane-based techniques can be effective, but they suffer from several drawbacks. The possibility of membrane fouling by alkaline earth, transition metal compounds, NOM or certain microbiota may shorten the lifetime of membrane or even damage it. Treated water may have to be remineralized to prevent degradation of the distribution system and to make water palatable since deionized water generally is considered to have an unpleasant taste.

2.1.4.5 Electrodialysis

Electrodialysis (ED) or Electrodialysis reversal (EDR) is one of the membrane processes that have been used mostly in drinking water treatment. Electrodialysis has been proven to be capable of removing small charged contaminant ions. Electrodialysis differs from other membrane separation processes such as reverse osmosis, ultrafiltration because it is driven by electric potential instead of driven by pressure. In a pressure-driven process, such as reverse osmosis, water is removed from a process stream. In electrodialysis, ions are removed from a process stream. Basically, negatively charged
ions (anions) are drawn toward the positively charged electrode, or an anode, and positively charged ions (cations) are drawn toward the negatively charged electrode, or cathode. Consequently, ED or EDR can only remove ionic contaminant and are ineffective for pathogen and organic compounds. The drawbacks for the ED process include polarization and scaling on the membrane surface and competition with other anions. EDR improved the performance of ED by reversing module polarity every 15 to 20 min during application. Compared to ED, EDR has the advantage of reducing scaling potential, breaking up fresh scale, reducing microbiological growth on membrane surfaces.

Roquebert (2000) reported a pilot-scale test on perchlorate removal by EDR. Perchlorate-free groundwater from a well in Salt Lake County, Utah was spiked with perchlorate to concentrations of 130, 60 and 15 µg/L. The EDR was run at 7.4 gpm. The system was operated continuously for more than four months. 87% of perchlorate was removed at the beginning of the operation with an influent perchlorate concentration of 130 µg/L. It stabilized in the low 70s during the 3-week operation with this concentration. Changing the influent concentration from 130 to 60 and 15 µg/L had little impact on its removal rate. The high removal rate of 87% at the beginning was likely caused by adsorption to the ion exchange membrane. As the ion exchange capacity exhausted, the removal rate stabilized at around 70%. Overall, removal efficiencies for TDS, sulfate, chlorate and perchlorate were 75, 84, 81 and 71% respectively. The authors also estimated the overall production cost for a variety of EDR system configurations. For example, the overall production cost was estimated to be $1.10-1.50/kgal for a two-stage EDR system. The evaluation provided a comparison with other treatment processes.

2.1.4.6 Activated Carbon Adsorption

Na et al. (2002) have shown that conventional GAC can adsorb perchlorate while leaving no detectable perchlorate levels in the treated water. But the capacity of conventional GAC is very limited. It is presumed that the adsorbed perchlorate could later be destroyed in a thermal regeneration process after carbon reaches exhaustion. Perchlorate removal capacity by GAC could be improved by 25% through GAC
modification by iron preloading. However, the improved adsorption capacity was still small compared with that for organic compounds such as TCE. Column tests by Na et al. (2002) revealed that there was no detectable perchlorate for about 1200 bed volumes using a bituminous GAC from Superior Adsorbents Inc. (Emlenton, PA). This was increased to 1500 bed volumes after modification by iron-preloading. Water used in this test was groundwater from the City of Redlands, CA with a perchlorate concentration of approximately 75 ppb. 1200-1500 bed volumes represented about four to six weeks of operation when the EBCT (empty bed contact time) was 20 min at full scale. In contrast, the same GAC bed at the treatment plant was able to last 18 months for TCE removal before thermal reactivation.

An important issue related to perchlorate removal by activated carbon is its low concentration compared with other commonly found inorganic anions or organics, and these other anions could occupy sites that perchlorate could otherwise adsorb to. As shown in both small and full scale tests of conventional GAC, the bed volumes of water treated before breakthrough for perchlorate is only about 10% of that for such volatile organic species such as trichloroethylene (TCE) (Na et al. 2002).

Two of the remedies are to regenerate the carbon in situ or to extend the adsorption capacity to what is comparable for organics. One of the advantages of activated carbon is that many water utilities already have carbon beds installed for other purposes. If ways could be found that can develop carbons that have capacity comparable to that for organics, or can develop inexpensive in-situ regeneration methods, then municipalities would welcome such a method.

2.1.4.7 Other Methods

**Precipitation.** Perchlorate has a highly delocalized and sterically blocked monovalent anionic charge and large volume. The low charge density reduces its affinity for cations and its extent of aquation. This low association with cations is responsible for the extremely high solubilities of perchlorate salts in aqueous and nonaqueous media. However, some insoluble or sparingly soluble perchlorate compounds are known, for example, nitron. Gravimetry with nitron was reported to quantitate perchlorate by Harris...
Nitron takes its name from its ability to precipitate the nitrate anion. It includes 4,5-dihydro-2,4-diphenyl-5-(phenyl-imino)-1H-1,2,4-triazolium hydroxide, inner salts; mesoionic didehydroderivative; 1,4-diphenyl-3,5-endaniolodihydrotriazol, and 3,5,6-triphenyl-2,3,5,6-tetraaza-bicyclo[2,2,1]hex-1-ene (Harris, 1991). The solubility of HNitClO$_4$ was reported to be 0.08 g/L, while that for HNitNO$_3$, HNitI are 0.099 and 0.17 g/L respectively. It may be possible to exploit this low solubility for purpose of remediation. However, nitron has only the potential to remediate those sites with very high perchlorate concentrations unless it can be synthesized more cheaply. At present, nitron is about 50 times more expensive than an equal mass of reagent-grade sodium chloride. Nitron also precipitates BF$_4^-$, WO$_4^{2-}$, ReO$_4^-$ and NO$_3^-$. In addition, precipitation also presents the problem of waste disposal like other physical separation processes.

Phytoremediation. Phytoremediation encompasses a range of processes and may be best described as a plant-assisted remediation. Salt cedars in Las Vegas have been found to be capable of accumulating perchlorate from water (Urbansky, 2000). Nzengung et al. (1999) showed that willow tree roots have the ability to reduce perchlorate to chloride. 11% of the initial perchlorate was converted to chloride after 26 days by roots placed in a solution containing 100 mg/L perchlorate. The mechanism of perchlorate removal by plants may include uptake, volatilizing it to the atmosphere, degradation of the contaminant with the plant, and biodegradation by the microbes associated with the roots (Nzengung et al. 1999). Similarly, Susarla et al. (2000) have described the capacities of six plant species, including two tree species (Liquidambar styraciflua, S. nigra), two herbaceous wetland species (Allenrolfea occidentalis, Polygonum punctatum), and two herbaceous aquatic species (Nymphaea odorata, Spirodela polyhyza), to take up and to partially reduce perchlorate inside the plant tissue. Van Aken and Schnoor (2002) studied the transformation of perchlorate in plant tissues using poplar tree cutting and tissue cultures under sterile conditions. Using $^{36}$Cl radio-labeled perchlorate, the authors were able to track reduced metabolite. The trees were shown to reduce perchlorate continuously to around 52% of the initial 25 mg/L. Chemical speciation of radioactive $^{36}$Cl in plant tissues revealed stepwise reduction and subsequent detoxification of perchlorate since large proportions of reduced metabolite (i.e. ClO$_3^-$,
ClO$_2^-$ and Cl$^-$) were recovered not only from the leaves but also from the other parts of the plant.

Unlike microbial (per)chlorate-reducing enzymes, plant biocatalysts tolerate oxygen since they are located in photosynthetic tissues where oxygen is produced in situ.

### 2.1.5 Perchlorate Analysis Techniques

Perchlorate analysis techniques have experienced remarkable development since perchlorate became an environmental concern.

#### 2.1.5.1 Ion Chromatography

Ion chromatography (IC) is the state-of-the-art method for perchlorate in water. All chromatographic methods share the same basic principles and mode of operation. In every case, a sample of the mixture to be analyzed (the analyte) is applied to some stationary fixed material (the adsorbent) and then a second material (the eluent) is passed through or over the stationary phase. The compounds contained in the analyte are then partitioned between the stationary adsorbent and the moving eluent. The success of the method depends on the fact that different materials adhere to the adsorbent with different forces. Some adhere to the adsorbent more strongly than others and are therefore moved through the adsorbent more slowly as the eluent flows over them. Other components of the analyte are less strongly adsorbed on the stationary phase and are moved along more quickly by the moving eluent. So, as the eluent flows through the column, the components of the analyte will move down the column at different speeds and therefore separate from one another.

The eluent type and concentration used in ion chromatography are important factors that influence the effectiveness of separation among anions. Daignault et al. (1990) used 1.7 mM NaHCO$_3$-1.8 mM Na$_2$CO$_3$ eluent for high perchlorate concentration. Jandik et al. (1990) used acetonitrile to modify the eluent dielectric constant and a solid phase reagent to obtain retention time under 20 min. Biesaga et al. (1997) showed that phthalate can be used, but retention time was long (40 min) and some degradation of peak
shape was observed. In 1997, the California Department of Health Service established an IC method that used p-cyanophenoxide to displace perchlorate from the resin. Wirt et al. (1998) reported a new IC method using only NaOH as the eluent with a retention time less than 10 min. At present, US EPA method 314.0 has been widely accepted for the measurement of perchlorate in drinking water. The method can measure perchlorate concentration as low as 1-2 ppb (US EPA 1999).

2.1.5.2 Capillary Electrophoresis

Capillary electrophoresis, or CE, describes a family of techniques used to separate a variety of compounds. These analyses, all driven by an electric field, are performed in narrow tubes and can result in the rapid separation of many hundreds of different compounds. The versatility and number of ways that CE can be used means that almost all molecules and even whole organisms can be separated using the powerful methods. The advantages of capillary electrophoresis are that it: (1) has very high efficiencies, meaning hundreds of components can be separated at the same time; (2) requires minute amounts of sample; (3) is easily automated (4) can be used quantitatively; (5) consumes limited amounts of reagents. Avdalovic et al. (1993) showed that perchlorate can be eluted by CE at 10 min; meanwhile, bromide, chloride and iodide all take more than 15 min. The major drawback of the CE method is that it can only detect perchlorate concentration higher than 400 ppb (Giblin and Frankenberger, 2000).

2.1.5.3 Gravimetry

Perchlorate analysis by gravimetry is base on the low solubility of HNitClO₄, or AsPh₄ClO₄. Nit here represents Nitron, and AsPh₄ represents tetraphenylarsonium. As might be expected, Nitron and AsPh₄ also quantitatively precipitate BF₄⁻, WO₄²⁻, ReO₄⁻ and NO₃⁻ and interference from those anions presents the main problem of this technique. Practically, NO₃⁻ can always be expected to be present in groundwater that contains perchlorate.
2.1.5.4 Potentiometry and Ion-selective Electrodes (ISE)

One technique that holds excellent promise as a routine monitoring device is potentiometric measurement via an ion-selective electrode. Perchlorate, along with other anions, has been determined using flow injection analysis with a carbon electrode and bis(diphenylphosphion)propane-copper complex as an ion exchanger (Wang and Kamata, 1992). A liquid-membrane ISE has been shown to have nearly Nernstian response to perchlorate in the range of $10^{-5}$ to $10^{-2}$ M with a lower limit of detection ~$10^{-6}$ M (Hassan and Elsaied, 1986). The perchlorate ISE has already established itself as a research tool, and it has been used to monitor perchlorate concentration in a variety of investigations (Akegret et al. 1986; Silber and Zhang 1991; Jain et al. 1987). Based on the significant advances in perchlorate ISEs, the time is ripe for exploration of perchlorate ISEs as a technique in the field or for continuous monitoring within a treatment facility.

2.2 ACTIVATED CARBON

2.2.1 Production

The term activated carbon defines a group of materials with highly developed internal surface area and porosity and hence a large capacity for adsorbing chemicals from gases or liquid (Patrick, 1995). Activated carbon has been used for purification purposes and in chemical production for centuries. It is produced from a tremendous variety of carbonaceous starting materials including bituminous coal, lignite coal, coconut shells, peach pits, sawdust, wood char, lignin, petroleum coke, peat, carbon black etc. The following criteria are considered when choosing a carbonaceous raw material: (1) potential for obtaining high-quality activated carbon; (2) presence of minimum inorganics; (3) volume or cost of the raw material; (4) storage life of the raw material and (5) workability of the raw material.

The first step in activated carbon production is carbonization. Carbonization is conducted at 600-650°C in an inert atmosphere. Between 400 and 600°C most organic
solids undergo reactions leading to the loss of hydrogen and formation of free radicals, which condense to form a rigid cross-linked solid char. The carbonization process causes some increase in porosity and modifies the pore structure inherent to the precursor.

The subsequent activation step helps to develop pore structure by selective gasification of carbon at 850-950°C in steam or CO₂ or a mixture of these. The removal of carbon atom increases the average size of already existing pores and opens up closed porosity. Following activation, there is final screening and a de-dusting operation.

Chemical activation is another way to increase porosity. Compounds such as ZnCl₂ and H₃PO₄ are added to parent feed stock prior to carbonization. The reaction usually is carried out at temperature in the range of 500-900°C. The precursors are usually cellulosic materials such as wood. It is believed that chemicals attack the cellulosic structures in the precursor. Water is eliminated and cross-linking and increased aromatization are promoted during the carbonization. Chemically activated carbons from wood have high pore volume, high surface area and low bulk density (~0.27 g/cm³) (Patrick 1995).

Activated carbons are classified on the basis of their particle size and particle shapes into powdered, granular, spherical or pelleted activated carbon (Bansal et al. 1988). The most widely used among them in the water industry are powdered and granular activated carbon. Powdered activated carbons are by definition less than 100 µm with average diameters of 15 and 25 µm. Thus they present a large grain surface and a small diffusion distance. Powdered activated carbons are preferably used for adsorption from solution phase because of their low diffusion rates. Granular activated carbons have a relatively larger size of carbon particles than carbon powders. Diffusion of the adsorbate is an important factor in granular activated carbon application.

### 2.2.2 Liquid-Phase Application

Activated carbon has been broadly used in water/wastewater treatment, air pollution control, solvent recovery, food processing, chemical and pharmaceutical industries and medicinal uses such as the treatment of ailment of the digestive system by the adsorption of bacterial toxins (Bansal et al., 1988).
Nearly 80% of the activated carbon produced every year is used for liquid-phase application (Patrick 1995). Most of the aqueous-based applications are for removing contaminants in water treatment, metal recoveries and decolorizing in industries.

2.2.2.1 Water Treatment

Powdered activated carbons have been used for more than 50 years to treat public water supplies for the removal of compounds that adversely affect taste and odor. There has been a growing interest in granular activated carbon (GAC) because of the increase in use of chlorine in water treatment. GAC is found to be effective for removing disinfection by-products (DBP) such as halogenated organics. If the usage is high, GAC can be regenerated and reused (Clark and Lykins 1989; Moore et al. 2000). GAC treatment is a feasible technique for the removal of low-solubility constituents such as trihalomethanes (THM), detergents, pesticides, herbicides, trace metal and polyaromatic hydrocarbons and is effective for improving taste and odor (Patrick 1995). Extensive investigation has been conducted on adsorption of trace metal such as cadmium, mercury, chromium and vanadium from water (Bansal et al. 1988). Studies have also shown that activated carbon can feasibly remove many of the impurities with various dimensions from water. Small organic molecules with low solubility have sizes in the range of 0.6-0.8 nm and can be adsorbed in micropores; color bodies and humic acids have dimensions (1.5-3.0 nm) that will favor their adsorption in mesopores while bacteria have diameters of 500-2000 nm and can be accommodated in the macropores and also in the interstices between carbon particles (Jagtoyen et al. 1992).

GAC has also been used in both industrial and municipal wastewater treatment. There are examples of many successful applications of GAC in advanced wastewater treatment plant. Industrially, activated carbon can be used to purify industrial process water, cooling water and water to run turbines. Demineralized water is used to these applications to prevent damage to equipment from scale formation. The ion exchangers used to demineralize are extremely sensitive to organic compounds and are protected by pretreating the water with activated carbon (Clark and Lykins 1989).
Important properties of a granular activated carbon for water treatment are its adsorption capacity and selectivity, ability to withstand thermal reactivation, and resistance to attrition losses during transport and handling.

2.2.2.2 Metal Recovery

One of the most important activated carbon applications for metal recovery is the recovery of gold or silver from their ores. The process involves the treatment of finely ground ore with a very dilute solution of sodium cyanide and oxygen. In gold recovery, the gold is oxidized to Au(I), which is obtained in solution as aurocyanide anion \([\text{Au(CN)}_2^-]\) by complexation with cyanide ions. The gold is recovered from the liquid by adsorption onto activated carbon, which can add directly to the cyanide pulp. After screening, the gold-loaded carbon is treated to recover gold and then recycled after some regeneration steps. Gold is recovered by elution using either solutions of metals salts, such as \(\text{K}_2\text{CO}_3\)-\(\text{KOH}\), or organic solvent, such as mixture of acetone, methanol and ethanol (Bansal 1988).

2.2.2.3 Decolorizing

Activated carbon has proved to be effective in the removal of color from sugar and food. In the sugar industry, activated carbons are mainly used to remove coloring matters from syrup, thus giving the sugar a better appearance and also improving markedly its processing properties. Treatment with activated carbon helps in removing surface-active agents and colloidal substances, raising their surface tension and decreasing their viscosity. This leads to higher rates of sugar crystallization and improved separation of syrups from crystals by centrifugation (Bansal et al. 1988).

2.2.3 Activated Carbon Adsorption Isotherm

The adsorption capacity of activated carbon for specific chemicals depends on the chemical and porous structures of the carbon as well as on the chemical and physical
characteristics of the adsorbate. The determination of a correct model for adsorption on activated carbon with complex chemical structure is, therefore, a complicated problem. One of the most important ways to characterize adsorbent like activated carbon is the quantity of adsorbate it can accumulate. The constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent \( q_e \) and its equilibrium solution \( C_e \) is called the adsorption isotherm. The most common equations for single-solution adsorption are the Freundlich and Langmuir equations.

The Freundlich has the form:

\[
q_e = K C_e^{1/n}
\]  

(2-2)

It can be linearized to:

\[
\log q_e = \log K + \frac{1}{n} \log C_e
\]  

(2-3)

\( q_e \): mass or mole adsorbate/mass adsorbent

\( C_e \): mass or mole/volume

\( K, 1/n \): constant

\( K \) in Freundlich equation is related to the capacity of the adsorbent for the adsorbate, and \( 1/n \) is a function of the strength of adsorption. The larger the value of \( K \), the larger is the capacity when \( C_e \) and \( 1/n \) are fixed. The smaller the value of \( 1/n \), the stronger is the adsorption bond when \( C_e \) and \( K \) are fixed.

The Langmuir equation has the form:

\[
q_e = \frac{q_{max} b C_e}{1 + b C_e}
\]  

(2-4)

Where \( b \) and \( q_{max} \) are constant and \( q_e \) and \( C_e \) are the same as in Freundlich equation. The \( q_{max} \) corresponds to the surface concentration at monolayer coverage and is the maximum value of \( q_e \) that can be achieved as \( C_e \) increases. \( b \) is related to the energy of adsorption and increases as the strength of the adsorption bond increases. The Langmuir equation assumes that: (1) only monolayer adsorption can occur; (2) adsorption is localized, with no adsorbate-adsorbate interactions; (3) the heat of adsorption is independent of surface coverage and (4) the adsorbent has a homogeneous surface.

Characteristics that affect isotherms include adsorbent surface area, pore size distribution, and surface chemistry.
2.2.4 Properties that Affect Activated Carbon Adsorption

The activated carbon surface has a unique character. It has a porous structure which determines its adsorption capacity. It has a chemical structure which influences its interaction with polar and non-polar adsorbates, and it has active sites in the form of edges, dislocations and discontinuities which determine the chemical reaction of its surface with other heteroatoms. It has long been recognized that the carbon efficiency for removing a given pollutant depends on its physical characteristic (surface area, pore distribution) and its surface chemistry. Thus the adsorption behavior of an activated carbon cannot be interpreted on the basis of surface area and pore size distribution alone. Carbons having equal surface area but prepared by different methods or given different activation treatments show markedly different adsorption characteristics. In general, a carbon containing numerous pores in the size range of the pollutant is expected to be efficient due to the enhancement of the adsorption potential for such condition (Everett et al. 1976). At the same time, significant progress has also been achieved on the understanding of the effect of carbon surface chemistry on adsorption.

2.2.4.1 Physical Characteristics

The most important physical characteristics of activated carbon include surface area and pore size distribution. The maximum amount of adsorption has also been proposed to be proportional to the amount of surface area within pores that is accessible to the adsorbate (Snoeyink and Summers, 1999). Subsequent research has shown more correlation to pore volume for many species (Nowack et al. 2004).

Both surface area and porosity are usually characterized from information contained within the adsorption isotherm. The adsorption of nitrogen at 77 K, the determination of the isotherm and its interpretation by the Brunauer, Emmett and Teller (BET) equation to give monolayer coverage is often assumed and quoted as being the preferred method to determine surface area of activated carbon. However, BET surface area by nitrogen adsorption is not beyond dispute. It only describes the response of the activated carbon to this particular adsorbate and is no better or no worse than any other
adsorbates. The surface areas of activated carbons can range from a few hundred to more than 1500 m$^2$/g. Not all of the carbon’s area that is accessible to nitrogen is also accessible to the adsorbate under investigation.

The International union of pure and applied chemistry (IUPAC) classifies porosity into micropore (width less than 20 Å), mesopores (width between 20 and 500 Å) and macropores (width greater than 500 Å). Micropores are further divided as ultra- (width <5 Å) and super- (10-20 Å) micropores (Patrick, 1995). At least 90% of the total surface area of an activated carbon can correspond to surface area within micropores. The main techniques used for the characterization of microporous carbons are based on the adsorption of gases and vapors and the immersion calorimetry.

Pore size distribution is important because it determines the fraction of the total pore volume that can be accessed by an adsorbate of a given size. Using a series of molecular dyes as probes and microporous carbons, Kasaoka et al. (1989a) found that when micropores are present, adsorption occurred only when the average micropore diameter increased to about 1.7 times the molecule’s second widest dimension. Ebie et al. (1995) conducted single solute adsorption experiments with small halogenated organic compound and showed that these molecules adsorbed in pores of width less than 15 Å, while NOM is best adsorbed in pores of size 30-100 Å. Nowack et al. (2002) found that MIB adsorption was closely related to carbon’s pore size distribution. MIB uptake mainly occurred in pores less than 63 Å in width. It is not difficult, therefore, to understand that competitive adsorption may happen if adsorbates with similar molecular structure coexist in target waters.

Another pore distribution-related phenomenon is pore blockage. NOM is larger than most trace organic pollutants, and it adsorbs in larger pores. Pore blockage occurred when adsorbed NOM molecules block the access of micropollutants to primary micropores thus affected its adsorption. Li et al. (2003) preloaded powdered activated carbon with NOM and found that the pore blockage effect caused a reduction of up to more than two orders of magnitude in the surface diffusion rate of atrazine when compared to simultaneous adsorption of atrazine and NOM. Large micropores and mesopores were found to play an important role in alleviating the effect of pore blockage. A powdered activated carbon with a relatively large fraction of large micropores and
mesopores was shown to suffer much less from the pore blockage effect. Therefore, it is important to select activated carbon with the right pore distribution in practice based on the unique characteristics of the specific target water.

2.2.4.2 Surface Chemistry

Solid carbons consist of mainly carbon atoms arranged into graphene planes, which can extend from a few rings to thousands of them. In either case, the individual layers are likely to contain imperfections (e.g. twists, non-aromatic links and carbon vacancies). These structure arrangements are responsible for some remarkable chemical, electronic, and electrical properties of activated carbons (Leon y Leon and Radovic 1994). In water treatment, the effect of the adsorbent surface chemistry is very important, since adsorption proceeds via the displacement of the existing water-covered surface by the dissolved pollutant molecules. The chemical groups found on an activated carbon surface are directly attributed to (a) the activated carbon precursors; (b) the method of activation; and (c) any additional treatment conditions.

The precursor of activated carbon and its production procedure played an important role in surface chemistry. Carbons made from coal, lignite or polymer precursors usually have higher amounts of nitrogen and higher basicity, while those made from wood-based precursors (often with phosphoric acid) are more likely to have higher acidity (Laszlo et al. 2001). Ferro-Garcia et al. (1989) studied the removal of orthophosphate using a range of well-characterized activated carbon at initial pH 7.0. They attributed the lower uptake of the olive-stone-derived carbons to its lower basicity. Low basicity indicates a pH<7 and a negatively charged surface at neutral pH. This negatively charged surface initiated an electrostatic repulsion between surface and phosphate anions. The results were in agreement with the fact that adsorption of anions is favored at pH<pHpzc.

As dictated by the extent of the oxidizing reaction, two forms of activated carbon can be produced (Corapcioglu and Huang 1987). The H-type activated carbons assume a positive charge upon introduction into water, and can adsorb strong acids and are hydrophobic. The L-type are obtained at high temperature (as high as 1200°C) under
vacuum or in a CO\textsubscript{2} atmosphere, and then exposed to air at room temperature. This type of carbon assumes a negative charge in water, and can neutralize strong base and are hydrophilic. Cookson et al. (1998) studied the distribution of surface acid groups of an L-carbon (Nuchar C-190) and an H-carbon (Filtrasorb 200). It was found that Nuchar carbon has significantly more carboxyl groups than Filtrasorb carbon, whereas its phenolic groups are less than the Filtrasorb carbon.

As far as additional treatment is concerned, all carbons can chemisorb oxygen even on mere exposure to air. The oxygen is fixed firmly and comes off only as oxides of carbon on high-temperature evacuation (Zawadeki 1981). Similarly, it is well known that all activated carbons have chemically bonded hydrogen, and the amount of this depends on the history of their formation. The hydrogen is bonded so strongly that it is not given off completely even on outgassing at 1000°C. Carbons can also bind nitrogen on treatment with ammonia, sulfur on treatment hydrogen sulfide, carbon sulfide or sulfur, and halogens on treatment with halogen in gaseous or solution phase. These treatments give rise to carbon-nitrogen, carbon-sulfur and carbon-halogen surface compounds.

Activated carbons generally contain appreciable amounts of various heteroatoms such as oxygen, hydrogen, nitrogen, phosphorous and sulfur, exist on the carbon surface. These heteroatoms are either derived from the starting material or from additional treatments. They can also be chemically bonded to the carbon surface during the treatment process. X-ray examination has shown that those heteroatoms are bonded to the carbon atoms at the edges of the giant molecules forming the aromatic sheet (Pradhan and Sandle 1999). Since these edges constitute the main adsorbing surface, there is little wonder that the bonded oxygen and hydrogen exercise a profound influence on the surface characteristics of carbons, such as surface acidity or basicity, ion exchange capacity and adsorption of polar and non-polar gases and vapor. The direct effect of these surface groups is that they give the carbon surface an acid-base character.

It has long been recognized that a carbon surface can display both acidic and basic characters. In general, acidic reactions have been associated with an oxygenated structure. These can arise from chemisorbed oxygen that can be found on all surfaces, which have been exposed to air or other oxidizing media. The existence of surface functional groups such as carboxyls, phenols, lactones, and acid anhydrides has been
postulated as constituting the sources of surface acidity. The basic properties of the carbon surface are not well understood. In one model, the presence of Chromene (benzpyran)-type structures was postulated to account for acid uptake (Leon y Leon et al. 1992). According to this model, chromene-type groups and free radical sites were assumed to generate resonance stabilized carbonium ions via oxidation/reduction reactions in solution. The other concept claims that carbon basicity comes from Lewis basicity. Lewis bases were thought to be present on the carbon surface, as they exist on polycondensed aromatic hydrocarbon molecules (Prui, 1970). Leon y Leon et al. (1992) studied the surface basicity of carbons by HCl adsorption, stepped temperature-programmed desorption, electrophoresis and mass titration. Carbon surfaces acquire a basic character upon high-temperature (>700°C) heat treatment, provided that any subsequent exposure to air falls outside the range of 200-700°C. Four types of interactions have been invoked to account for the nature of carbon basic sites: electrochemical, physical (electrostatic, polarization), chemical (anion exchange, functional groups protonation) and coordination. Results indicate that basic sites arise from two types of interaction: (1) electron donor-acceptor complex formation predominates in carbons of low oxygen content; (2) pyrone-type group contribution prevails in carbons of high oxygen content.

Attempts have been made to identify and estimate the surface functional groups using several physical, chemical and physicochemical techniques which include neutralization of bases, desorption of the oxide layer, potentiometric, thermometric, and radiometric titration, direct analysis by specific chemical reaction, polarography, infrared (IR) spectroscopy and X-ray photoelectron spectroscopy. Among various surface function groups, oxygen-containing structures are the best understood by now. As a result of these investigations, the existence of such functional groups as carboxyls, phenols, lactone, aldehyde, ketone, quinine, hydroquinones, anhydrides, and ethereal structures have been postulated.

Numerous studies have been conducted on the effect of surface chemistry on the adsorption capacity of activated carbon. Many of these appraised the effect of oxygen-containing surface groups. In an adsorption study of methanol-benzene solutions, Bansal et al. (1988) showed how carbons containing more carbon-oxygen structures adsorbed
more methanol and less benzene relative to less-oxidized carbons. Considine et al. (2001) tested a series of carbons with a range of oxygen-content, and appraised the effect of oxygen content on adsorption capacity of 2-methylisoborneol (MIB) from water. The results showed that the increasing surface oxygen content at a constant pore volume leads to a decrease in both the amount adsorbed and the enthalpy of adsorption.

The pH of the target water is an important factor affecting the surface chemistry of carbon. Solution pH affects the status of surface functional groups and the adsorbates (e.g. protonated or not), and it thus affects the interaction between those groups and the adsorbate. Ramos et al. (2002) conducted research on the adsorption of zinc(II) from aqueous solution onto activated carbon. They concluded that the adsorption of zinc(II) was highly dependent on solution pH. At pH below 2, there was almost no adsorption. The adsorption increased as the pH increased from 3 to 7. They explained the results by claiming that the surface charge of the carbon particle depended on solution pH. The surface is positively charged when the solution pH is below the isoelectric point (IEP), and it is negatively charged at pH above the IEP. At pH lower than the IEP, the positively charged surface of carbon causes a mutual repulsion between Zn$^{2+}$ and the carbon. If adsorption occurs at all, it is not due to an electrostatic attraction, but to a chemical interaction with sufficient energy to overcome the surface ion repulsion. When the solution pH is above the IEP, Zn$^{2+}$ is attracted to the negatively charged carbon surface.

A full understanding of the effect of carbon properties on adsorption could help select the most suitable materials for adsorption. When necessary, the knowledge can also be used to produce materials with optimum surface chemical, electrochemical and physical properties for selected application.

2.2.5 Activated Carbon Tailoring

In general, the ability of activated carbon to adsorb pollutants is often estimated experimentally without anticipating a relationship between the chemical structure and adsorption capacity. Adsorption tests are commonly used to characterize a given activated carbon. However, knowledge of the activated carbon structure is necessary if we wish to adapt the product for adsorption of a specific pollutant. The nature of the
surface functional groups can be modified through physical, chemical and electrochemical treatment. For example, carbon modification can be done by means of liquid phase treatments, using oxidizing agents such as HNO₃ or H₂O₂ at different temperatures, concentrations and/or contact. Modification can be also achieved by gas phase oxidation with O₂ or N₂O at different temperatures, pressures, concentrations and/or contact times, and by heat treatment at different temperatures, gas atmosphere. These procedures change the physicochemical structure of activated carbon, i.e. the specific surface area, porosity and surface functional groups. With recent advances in surface chemistry and physics, tools are now available to identify the carbon properties that most strongly influence adsorbate-adsorbent interactions, and to modify these properties so as to maximize activated carbon performance (Radovic, 1999).

Although no referred papers on modifying carbon to enhance perchlorate removal were found (other than Na, et al. 2002), efforts have been made on tailoring of carbon for adsorption of both organics and inorganics.

2.2.5.1 Activated Carbon Oxidation

Carbons are always associated with varying amount of chemisorbed oxygen unless special care is taken to eliminate it. Therefore, surface oxygen-groups are the most common type of functional groups found on activated carbon surfaces. In fact this combined oxygen has often been found to be the source of the property by which a carbon becomes useful or effective for some roles, and less useful for others.

Oxidation is one of the processes, which can effectively change the oxygen content of the carbon and thus the properties of a carbonaceous material, specifically its affinity toward polar adsorbate (Leon y Leon et al. 1994; Bansal et al. 1988). Figure 2.2 is the oxygen-containing functional groups and their possible decomposition products by temperature programmed desorption (TPD) (Figueiredo et al. 1999). Oxidizing agents have been used to oxidize carbons, either as a liquid phase or as a gas phase reaction. It was found that the type of surface structures formed and the extent of formation depend on the oxidizing agent, the concentration and the pH of the oxidizing solution (Ramos et al.1993). HNO₃, H₂SO₄, HClO₄, H₂O₂, KMnO₄, ClO₂ and KIO₃ oxidizing solution have
been proven to be effective for the formation of surface carbonyl structures (C=O) (Ramos et al. 1993).

Among the methods leading to the formation of surface oxygen complexes, two main categories can be distinguished: reaction in oxidizing solutions and utilizing oxidizing gases such as oxygen and ozone. Oxidation in some cases also changes the physical structure of carbon. Mangun et al. (1999) oxidized activated carbon fibers (ACF) with concentrated HNO₃/H₂SO₄, 30% H₂O₂ and air at 400°C. It was found that as much as 29 wt % oxygen could be incorporated onto the pore surface in the form of phenolic hydroxyl, quinone and carboxylic acid groups. The average micropore size was typically affected very little by aqueous oxidation while the micropore volume and surface area decreased with such a treatment. In contrast, the micropore size and volume both increased with oxidation in air. Oxidation of ACFs produced surface chemistries in the pores that provide for enhanced adsorption of basic (ammonia) and polar (acetone) molecules at ambient and non-ambient temperatures. The adsorption capacity of the oxidized fibers for acetone was modestly better than the untreated ACFs while the adsorption capacity for ammonia increased up to 30 times compared to untreated ACFs.

Pradhan et al. (1999) used elemental analysis, selective neutralization, FTIR (Fourier transformed infrared spectroscopy) and X-ray diffraction (XRD) to characterize surface chemical and physical natures. Their results revealed that carboxyl, lactone, aryl carboxylic acid, β-diketone, keto-enol, ketene, alcoholic, phenolic and ethereal groups were detected after oxidation with 1 N HNO₃, 30 % H₂O₂ and saturated (NH₄)₂S₃O₈ solutions. Figueiredo et al. (1999) studied in detail the effect of different treatments on carbon surface. They employed techniques such as N₂ adsorption, XPS (X-ray photoelectron spectroscopy), TPD (temperature programmed desorption) and DRIFTS (diffusion reflectance FTIR) to characterize carbon surface properties obtained from gas/liquid oxidation and heat treatment in N₂. XPS and TPD results indicate that liquid phase oxidation (5 N nitric acid or 10 M H₂O₂) increase carboxylic groups which evolves mostly as CO₂ at heat treatment, while gas phase oxidation (5% O₂) increase anhydride, lactone, phenol and carbonyl/quinone groups, which evolves as CO at high temperature by TPD. Also, liquid phase oxidation has almost no effect on pore structure. Gas phase
oxidation increases pore width and volume. Heat treatment up to 600°C removes carboxylic anhydrides and most of lactone, some of phenol groups.

Oxidation increases carbon’s acidity by creating acidic surface functional groups (carboxylic, phenolic groups et al.), and carbon surface becomes more hydrophilic. The most obvious effect of oxidation is decrease in pHpzc (pH of point of zero charge). Decrease in pHpzc means that oxidized carbon has a net negative surface charge at lower solution pH than untreated ones. The phenomenon is helpful for the adsorption of positively charged species while detrimental to anions or most organic compounds.

Chlorine can also react with GAC and bring about change in surface properties. Chlorine was found to be adsorbed to carbon surface and produce non-oxygen acidity. Puri and Bansal (1984) carried out systematic investigations into the formation and properties of carbon-chlorine surface compounds formed on sugar and coconut charcoal associated with varying amount of oxygen and hydrogen in the temperature range 35-600°C. Their results showed that the fixation of chlorine occurred partly by addition at the unsaturated sites vacated by oxygen and partly in exchange (substitution) for hydrogen. Evans et al. (1998) found that GAC treated with chlorine had a reduced adsorption capacity for water vapor. Hall and Holmes (1992) proposed the possible replacement of the oxygen-containing functional groups by chlorine to be the reason for a reduction in the polar water adsorption sites. The research is of significance when chlorination was employed ahead of GAC treatment like in some water treatment plant.

Oxidized activated carbons have found applications in a variety of fields, most of them in metal adsorption. Rivera-Utrilla and Sanchez-Polo (2003) investigated the adsorption of Cr (III) by a series of activated carbon oxidized by ozone. The adsorption capacity and affinity of the adsorbent for Cr(III) increased with the increase in oxygenated acid groups on the surface of the activated carbons. The improvement in Cr(III) adsorption is due to the formation of surface oxygen groups, through their ionization, increase the attractive electrostatic interaction between the surface of the activated carbon and the metallic cations present. In another try, Rangel-Mendez et al. (2002) utilized novel electrochemical techniques to oxidize the surface of a wood-based activated carbon and found that this technique enhanced cadmium uptake in batch adsorption test.
On the other hand, oxidized carbons are less effective in adsorption of organic compounds. Considine et al. (2001) found that increasing surface oxygen at a constant pore volume lead to a decrease in both the amount of 2-methylisoborneol (MIB) adsorbed and the enthalpy of adsorption. Pendleton et al. (1997) demonstrated that there is a fairly convincing correlation between MIB adsorption and the concentration of hydrophilic (acidic) sites on carbon surface. As the relative concentration of hydrophilic sites increased, MIB uptake decreased. This trend has been widely observed for other organic compounds, particularly phenol (Mazet et al. 1994; Leng and Pinto 1997). Karanfil et al. (1999) also concluded that oxidation of the carbon surface significantly decreased the uptake of natural organic matter from water. Therefore, for adsorption of organic compounds or anions, carbon with less oxygen-containing groups is preferred.

2.2.5.2 Heat Treatment

As is well recognized, heating is a direct way to remove carbon-oxygen structures from a carbon (Laine et al. 1963; Boehm 1966, Bansal et al. 1988; Otake and Jenkins 1991; Menendez et al. 1996a; Deadekar et al. 1998; Figueiredo et al. 1999). Carbon dioxide, carbon monoxide, water and hydrogen are the main products evolved during heating. As a matter of fact, temperature programmed desorption (TPD) has been considered to be an effective way to distinguish surface functional groups, and its operation is based on the stability of those groups under heat treatment. Using helium as carrier gas, the temperature was programmed to rise from room temperature to around 1000°C at certain rate. CO and CO$_2$ evolved from the activated carbon were monitored by mass spectrometer. It was surmised that CO$_2$ peak results from carboxylic acids at low temperatures (100 to 400°C), or lactone at higher temperatures; carboxylic anhydrides originate both a CO and a CO$_2$ peak; phenol, ethers and carbonyls (and quinone) originate a CO peak. Heating up to 600°C removes carboxylic anhydrides, most of the lactones, and some phenol groups. Based on this, it’s possible to remove certain groups by temperature control in heat treatment.

An important consequence of CO and CO$_2$ evolution in heat treatment is the creation of highly reactive sites. These highly reactive sites readily adsorb O$_2$ and causes
re-formation of oxygen-containing groups. Nowack et al. (2004) and Menendez et al. (2005) used \( \text{H}_2 \) in heat treatment. This treatment produced a stable basic carbon surface when compared with heat treatment by \( \text{N}_2 \). Hydrogen-treated (1025°C) carbon processed about 110% more bed volumes than untreated carbon in MIB removal (Nowack et al. 2003). Bansal et al. (1974) suggested that \( \text{H}_2 \) chemisorption forms stable C-H bonds at the edges of graphene layers, thus minimizing \( \text{O}_2 \) adsorption.

Tests by Ogino et al. (1992), Asakawa et al. (1988) and Kaneko et al. (1988) also concluded that high-temperature surface treatment with hydrogen could remove acidic surface functional groups, thereby enhancing the adsorption capacity of traces organics (TCE, benzene) in aqueous solution.

Heat treatment by ammonia can give GAC a basic nature. Economy et al. (1992) reported that activated carbon fibers (ACF) could be nitrided with \( \text{NH}_3 \) at elevated temperature to obtain a product with basic characteristic and showed that such fibers were effective in adsorbing acidic materials such as \( \text{HCl} \) and \( \text{SO}_2 \).

2.2.5.3 Thermochemical Treatment by \( \text{NH}_3 \)

The focus of this research is on surface modification of carbon to improve its adsorption for perchlorate. The study of anion adsorption on activated carbons is less advanced compared with adsorption of cations on activated carbons (Kaneko et al. 1991). Some of the studies of anion adsorption include removal of bromate (Asami 1999; Bao et al. 1999; Kirisits and Snoeyink 1999; Mills et al. 1996; Siddiqui et al. 1996), chromate (Han et al. 2000; Selomulya et al. 1999; Bautistatoledo et al. 1994; Jayson et al. 1993), nitrate (Kaneko et al. 1991), arsenite and arsenate (Huang and Liu 1997; Huang and Vane 1989), \( \text{HgCl}_4^{2-} \) (Carrott et al. 1998), and cyanide (Adams 1994; Guo et al. 1993). Study on perchlorate removal by activated carbon has indicated that the adsorption capacity of carbon is very limited. They also showed that surface chemistry of carbon has a great effect on the adsorption of perchlorate. A metal-preloading method improved the capacity about 25% (Na et al., 2002).

Though efforts have been made on the removal of perchlorate since it was first found in groundwater several years ago, there rarely have been any study on tailoring of
activated carbon for the purpose of perchlorate removal. While building on others’ understanding of the effect of physical and chemical characteristics on carbon adsorption for both organic and inorganic pollutants, we have derived several hypotheses about how to treat carbon so as to make it adsorb perchlorate better. First, since perchlorate exists as an anion in the whole pH range of natural water encountered, it stands to reason that a carbon that exhibits more positive charges in the near-natural pH range (carbon with basic surface groups) will help increase the adsorption capacity. Secondly, modification of carbon has been proven to change both the physical and chemical characteristics of carbon. Our goal is to take into consideration all aspects of carbon tailoring so that the surfaces could be modified to selectively adsorb anions, and particularly perchlorate. By comparing the factors that affect the performance of carbon, we expect to find an optimal way to modify the carbon for perchlorate removal.

The preparation of carbons with basic surface properties is of great interest in a variety of applications. It has been reported that the adsorption affinity of phenolic compounds increased with increasing basicity of the carbon surface and with increasing electron-withdrawing ability of the substitute on the aromatic rings (Radovic et al. 1996; Tamon et al. 1993). The presence of basic surface groups on carbon has also been found to increase the \( \text{SO}_2 \) adsorption capacity of activated carbons (Davini 1990). Even though basic character on carbon surface has been associated with the presence of some oxygen-containing surface groups at edges of carbon crystallites (e.g. chromene and pyrone-type structures), the main contribution to surface basicity is from oxygen-free Lewis base sites on the basal plane (Papirer et al. 1987; Boehm et al. 1970; Abotsi et al. 1990; Leon y Leon et al. 1992). In other words, carbon basicity is associated with the absence of oxygen-containing groups which are predominantly of acidic nature. For this reason, most of the treatments proposed to obtain carbon surface with basic properties consist in heating the carbon in different gases in order to remove the oxygen-containing groups. Carbons are known to acquire a basic character upon high-temperature heat treatment in an inert atmosphere and subsequent exposure to air below 200°C (Kinoshita 1988). Treatment with ammonia has been also shown to be effective for a wide variety of application. The treatment, performed typically at 400-900°C, removes the acidic oxygen-containing functional groups and it may also introduce nitrogen-containing (e.g.
amine) onto the carbon surface. Economy et al. (1992) found that basic nitrogen groups could be introduced into activated carbon fibers (ACFs) by treatment with ammonia at 800°C.

Using mass spectroscopy technology, Boehm et al. (1984) were able to recommend the reactions that were supposed to occur when carbon was treated by ammonia at elevated temperatures (around 400°C and above). These authors proposed that NH₃ would decompose to H, NH and NH₂ radicals which would react with carbon to produce methane (CH₄), hydrogen cyanide (HCN) and cyanogens (CN)₂ as indicated in equation (2)-(5).

\[
\begin{align*}
H + H & \rightarrow H₂ (g) \quad (2-2) \\
C + 2H₂ & \rightarrow CH₄(g) \quad (2-3) \\
C + NH & \rightarrow HCN (g) \quad (2-4) \\
C + 2NH₂ & \rightarrow (CN)₂ + 2H₂ (g) \quad (2-5)
\end{align*}
\]

A decrease in sulfur and oxygen content was observed after ammonia treatment. The research did not clarify the nitrogen groups that were possibly created at the surface due to a limitation in the technology at the time. However, the nitrided samples did show more than 1.1 unit increase in pHpzC after the treatment.

With the help of recent technology developments, a variety of techniques have been employed in research to clarify the structures of nitrogen-containing groups that could be created on carbon surface by ammonia treatment. Changes in physical properties (pore distribution, surface area) were also closely monitored to provide a clear picture of ammonia treatment.

It was found that surface groups created by ammonia treatment were closely related to treatment temperature and time. Stohr et al. (1991) employed XPS to study the surface groups after carbons were treated with ammonia at 600-900°C for 4 hours. XPS showed two N 1s signals for ammonia treated carbon with binding energy of 401-400ev and 399-398ev, which they assigned to be amine groups and nitrile and/or pyridine-like nitrogen respectively. Heat treatment in N₂ and H₂ at 700 and 900°C decreased the nitrogen content. The carbon is gasified in the reaction with NH₃ at 900°C leading to an increase of the pore volume in micropore range. They suggested reactions as shown in Figure 2.3 at elevated temperatures (600-900°C) between carbon surface and NH₃.
Carboxylic, hydroxyl and Ether-like oxygen react with NH₃ leading to amide, nitrile, amine and pyridine- or acridine-like nitrogen created on the carbon surface.

Mangun et al. (2001) studied a series of ACFs and ammonia-treated ACFs. An apparent increase in N-content was observed after ACFs were treated in ammonia for 10-60 min at 500 to 800°C. The increase in nitrogen is due to addition of groups at the carbon edge sites where they can directly affect adsorption properties. The types of groups present were analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). They suggested that 500°C treatment yields amide, aromatic amine and nitrile groups while higher temperatures result in formation of aromatic amines and pyridine.

Xie et al. (2000) conducted a study on the microcalorimetry of acid and ammonia-pretreated activated carbon as a probe of acid/base on carbon surfaces. Combined with techniques such as Boehm titration, point of zero charge (PZC) and temperature programmed desorption (TPD), they concluded that the largest amount of ammonia was incorporated to the carbon at 400°C while the corresponding PZC values increase monotonically with the temperature of treatment. An interesting phenomenon observed in their research was that the sample treated at 400°C had higher population of acid groups, including carboxylic and phenolic compared with that of higher temperature. This was considered to be because of air exposure after the ammonia treatment and more acid sites were formed for carbon treated at 400°C. It was further pointed out that at high temperature, ammonia treatment was able to remove oxygen groups and in the process increase unsaturated edge sites. But if the temperature was too high, the previously created active carbon edge was gasified. It’s well known that the active sites are responsible for the formation of oxygen-containing surface groups during air exposure. The test also showed an increase in the basic groups of carbon after the ammonia treatment and Xie et al. attributed the basicity to the existence of unpaired electrons at edge sites rather than to surface oxygen-containing groups.

Instead of pure NH₃ gas, NH₃ mixture was employed in some research for as an ammonia treatment method. Jansen and Bekkum (1994) studied amination and ammonoxidation on activated carbons. Carbons were subjected to ammonia (amination) and ammonia/oxygen (ammonoxidation) gas at temperatures between 200 and 420°C. For
amination, carbon was first oxidized by nitric acid. Amination is expected to take place at carboxylic sites formed by nitric acid oxidation. Pore structure was unchanged by amination or ammoxidation at the temperatures studied in the research. Heat treatment of ammonia treated samples under N\textsubscript{2} caused increase in BET surface area. Pores are possibly enlarged by removal of functional groups from inside of pores or pores become accessible to N\textsubscript{2} by surface groups removal. Heat treatment indicates that N groups are more strongly bonded to the carbon surface than are O groups. Amination leads to a higher N-content than ammoxidation. TPD of aminated and ammoxidated carbons show HCN desorption at around 600 and 900°C. Amides are supposed to decompose at around 650°C. Amination created more groups in ring system (imides and lactam). Groups created by amination and ammoxidation (amides, imides and lactam) are different from those by thermally ammonia treatment at 600-900°C, which creates pyridine-like groups. FTIR results also show removal of oxygen groups (carbonyl) by amination at T<600°C.

Another way to create nitrogen-containing groups was chemical vapor deposition (CVD). Yang et al. (2001) tried to characterize nitrogen-alloyed activated carbon fiber (ACF) by elemental analysis, scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) for nitrogen-containing surface functional groups. N-alloyed ACFs were prepared by chemical vapor deposition of pyridine at 700-1000°C for 30-120 min. They observed remarkable increase in nitrogen content after the chemical vapor deposition, from zero to 4.4 wt% for ACF treated at 1123 for 60 min. The main species of nitrogen functionality detected by XPS is pyridinic and quaternary nitrogen, and the fraction of quaternary nitrogen increased from 60% to 91% by high-temperature heating from 750 (2% N) to 1000°C (2% N) for 60 min. The fraction of two nitrogen structures of N-alloyed ACF treated at the same temperature was almost constant regardless of the CVD times, suggesting that nitrogen structure produced by the CVD is governed by temperature. Pore structure analysis also showed that CVD treatment decreased the surface area and pore volume while the average micropore width was not significantly changed. The pyridine deposition at 1000°C was the best preparation method of nitrogen-deposited ACF with high microporosity and positively charged surface nitrogen atoms.

Ammonia treatment and chemical vapor deposition both affect the surface charge distribution. Abotsi and Scaroni (1990) examined the influence of the ammonia reaction
on the surface electrical properties of carbons with the aid of electrophoretic mobility and adsorption experiments. Ambersorb XE-348 carbon was nitrided at 600°C for 1.5 h. Elemental analysis shows that the nitrogen content of the carbons increased substantially with heat treatment from 0.38 % wt for the parent carbon to 3.74% wt. The nitrogen incorporation was accompanied by a 4.7% gasification. The electrophoretic mobility results reveal that the original carbon is negatively charged over the pH range 2-12 while its ammonia-treated derivative is negatively charged above pH 6.0. Besides the protonation of surface carboxyl and hydroxyl groups to form positively charged sites, it has been postulated that carbon surface posses pyrone-type or chromene structures which are capable of creating positively charged surfaces through the formation of carbenium ions. On the other hand, nitrogen-containing groups are protonated to form positively charged surface sites such as RNH$_3^+$. In summary, a carbon surface became more positively charged as a result of reaction in ammonia. This treatment enhanced the adsorption and possibly the dispersion of thiomolydate anion.

Nitrogen functional groups were also found to show transformation under treatment at different temperatures. Stanczyk et al. (1995) studied the influence of carbonization temperature on chars containing nitrogen groups, such as pyrrole, pyridine, amino and cyano groups. Carbonization was carried out in a fixed bed reactor in an argon flow at 460, 600 and 800°C respectively. Amount of N carbonized at 460°C depends on precursor and it decrease as the carbonization temperature increase. N/C is similar for 460°C and 600°C and is higher than that from 800°C. The transformation of nitrogen functionalities is complicated. At low temperature, pyridine and pyrrole structure transform into each other depends on the precursor while they transform into more stable quaternary N at higher (800°C) temperature. XPS studies on nitrogen functionalities in coals indicate that pyrrolic and pyridinic groups are the main constituents. There are also quaternary and nitro/nitroso groups present. The exact structure of quaternary may be protonated pyridinic-N as described by some researchers. When coals were subjected to pyrolysis, nitrogen functionality distribution changed with the severity of pyrolysis. Under severe pyrolysis, the final distribution is not relevant to the original material. Pyrrolic-N was found stable at T as high as 600°C. Above that, it converts gradually into pyridinic-N or quaternary-N. Under higher temperature, longer time pyrolysis, it
converts completely, that is, only N in six-member ring structure exists. Conversion of pyridinic-N to quaternary-N starts at relative low temperature (<450°C). Exposure to air after pyrolysis may cause formation of pyridinic-N-oxide or pyridone structure. Overall, it appears that pyridinic-N or quaternary N was the most stable groups at high temperatures (>600°C). It is also possible that ammonia treated carbon will undergo changes in nitrogen-containing groups after it was exposed to air.

Ammonia tailored carbons have been studied on their adsorption for acidic gas (HCl), H₂S or SO₂ from flue gas, or their catalytic activities.

Mangun et al. (2001) treated a series of ACFs with ammonia to yield basic surface. Micropore size (determined by nitrogen adsorption experiments) showed that micropore volume increased with increase of treatment time and temperature. The adsorption of HCl gas was greatly enhanced by treating the fibers with ammonia to create a basic surface. The adsorption of HCl was dominated by the amount of nitrogen present since it is a gas with a very low boiling point and not adsorbed well by untreated carbons. In their efforts to elucidate the role of pore size, pore volume and surface chemistry on adsorption of SO₂, Mangun et al. (2001) also compared several ACFs and their ammonia-treated counterparts on their abilities to remove SO₂ from flue gas. ACFs were treated in ammonia for 10-60 min at 500 to 800°C. It was found that the SO₂ adsorption energy increased with the increase of nitrogen content. Before ammonia treatment, ACF with the highest microporosity shows the highest SO₂ adsorption due to its higher adsorption energy. Ammonia treatment results in a competition between increasing the chemical interaction from increased nitrogen versus decreasing the physical interaction because micropores were widened. The ACF with the right combination of nitrogen content and pore volume shows the best result. The larger pore ACFs which do not provide as much overlap in adsorption potentials has a significant increase in the amount of SO₂ as the nitrogen content is increased.

Boudou et al. (2003) investigated how ammonia treatment of the surface can influence the activity of viscose-based activated carbon cloth (ACC) for the oxidative retention of H₂S and SO₂. The ACC was subjected to an ammonia/steam (28% NH₃ solution, carrying gas 100mL/min) treatment at 800°C or to two types of ammoxidation treatment with ammonia/air (NH₃, air 3.0l/h each) at 300°C. X-ray photoelectron
spectroscopy showed nitrogen groups such as pyridine, pyrrole, quaternary N and N-oxide being introduced to carbon surface by ammonia treatment. Pyridinic N was dominant in ACC treated by ammonia/steam process, which is much lower for carbon samples produced by ammoxidation. Ammonia/steam treatment also created more surface area and micropores in the sample. Temperature programmed desorption indicate that ammonia treatment increased evolution rate of CO above 1250 K, which is ascribed to basic groups (pyrone-type oxygen). The distribution of nitrogen and oxygen functional groups is influenced by the type of ammonia treatment, but the mechanism of that is not very clear. Fixed bed sulfur removal tests showed that an enhancement of the sulfur removal ability by ammonia/steam treatment. The improvement was attributed to three combined factors: increase in micropore volume, increase in nitrogen content and removal of surface acidic groups.

Stohr et al. (1991) observed considerable increase in their catalytic activity after carbons were treated with ammonia. The catalytic activities of the carbons were measured in the oxidation of dilute sulfurous acid.

Not many studies on adsorption of perchlorate or other anions by ammonia treated carbon from aqueous solution were found in the literature review. Godfried et al. (1990) investigated the effect of surface charge of ammonia treated carbon on molybdenum adsorption. Molybdate anion (MoO$_3$)$^{2-}$ and polyanion (Mo$_7$O$_{24}$)$^{6-}$ were found to be the dominant species in acidic media from an ammonium heptamolybdate solution. Results showed that the parent carbon was negatively charged over the pH range 3-12, and had an isoelectric point (IEP) of 2.0. Treatment in ammonia raised the IEP to pH 5.7. The carbon was positively charged below this value. The higher positive charge density on the ammonia-treated carbon enhanced its molybdenum adsorption capacity. The same may be possible for perchlorate adsorption. By increase the positive charge density of activated carbon, it is possible that more perchlorate could be adsorbed by activated carbon.
2.2.5.4 Electrochemical Treatment

There are only a few studies related to electrochemical treatment of carbon with nitrogen-containing compounds to enrich the nitrogen functional groups.

In an effort to improve the toughness of carbon-epoxy composite, Barbier and Pinson (1990) tried to graft diamine to establish a continuous succession of covalent bonds from the carbon surface to the epoxy resin. Electrochemical oxidation in an acetonitrile (CHN) solution was reported to achieve an increase in the nitrogen content in the carbon surface.

Gonzales et al. (2001) reported that electrochemical treatment of activated carbon fiber in amine solution was able to greatly increase the density of positive charge on the carbon surface without changing much the surface area and pore volume distribution of the carbon. Acetonitrile was selected to be the solvent and LiClO₄ as supporting electrolyte in the test. The activated carbon fiber was attached to the anode. A shift to basic in pH_{IEP} was observed.

Park and Kim (1999) tried to treat GAC with an anode to increase the number of functional groups, especially basic functional groups, on the surface of the activated carbon, without changing the surface area or pore sizes appreciably. Coconut shell GAC supplied by Dong-Yang Carbon Co. was subjected to treatment with a 35% sodium hydroxide (NaOH) electrolyte for 60 seconds with current varying between 0 and 3 A. The virgin GAC contained 123 meq/g of acidic groups, 227 meq/g of basic groups, and had a pH_{pzc} of 7.8. Treatment with 3 A of current increased the acidic groups to 164 meq/g, the basic groups increased to 383 meq/g, and the pH_{pzc} increased to 8.5.

Compared with thermal treatment by ammonia, electrochemical treatment does not require high temperature and the treatment time ranges from seconds to minutes at most. The advantage of energy consumption is obvious. However, the disadvantage of electrochemical treatment is that it may need solvents or reagents that are not environment-friendly. Disposal of wastes may pose another problem to the environment.
2.2.5.5 Carbon Tailoring by Surface Impregnation

Besides the above-mentioned methods for carbon tailoring, efforts have also been made to explore other ways for carbon modification such as modification by loading of certain compounds without drastic thermal or chemical reactions. The impregnation of carbons brings to mind the impregnation by metals, a subject that has been widely studied in heterogeneous catalysis. Metals and their oxides, dispersed as small particles on high surface area carbons and other supports, are being used as catalysts for various industrial applications. The impregnation of metals in carbonaceous materials modifies the gasification characteristics and varies the porous structure of the carbon product. For example, loading of iron(III) was explored by Na et al. (2002) to change the surface chemistry of activated carbon. The theory behind this is that the carbon surface is more positively charged by the iron loading. As result, Na et al. (2002) saw a 25% increase in perchlorate removal capacity for a bituminous activated carbon. Activated carbon impregnated with Cu$^{2+}$, Ag$^+$, Cr$^{6+}$ were found to create efficient adsorbents for arsenate, hydrogen cyanide and cynogen chloride (Barnir and Aharoni 1995).

Besides metals, other inorganic and organic chemical have also been used in carbon impregnation. Activated carbons impregnated with potassium iodide and similar compounds and with amines including several pyridines have been widely used in the nuclear industry for the retention of radioactive iodine compound from coolant release and ventilation system (Billings et al. 1984). Baker and Poziomek (1974) tried to modify adsorptive properties of coal-based activated carbon by impregnating them with pyridine, 4-vinylpyridien, 4-aminopyridine, 4-cynopyridine and 4-n-propyl-pyridine. The carbons were impregnated by volatile impregnants in a rotary evaporator and the amounts impregnated determined by the difference between the initial and the final weight of the carbon. The nonvolatile impregnants were adsorbed on the carbon surface from alcohol solutions. The adsorption capacity of the impregnated activated carbons was compared for methyl iodide. The adsorption of methyl iodide increased with the increase in the amount of impregnant. The effect of different impregnants followed the order:

Pyridine > 4-vinylpyridine > 4-aminopyridine > 4-cynopyridine > 4-n-propylpyridine
Ferro-Garcia (1998) reported that adsorption of gallic, tannic and humic acid on activated carbon brings about both pore blockage and an increase in the negative surface charge of the carbon. At low acid concentration, the pore blockage effect dominates which resulted in a decrease in Cr (III) adsorption. When the acid concentration increases, the Cr (III) uptake increases due to interaction of Cr (III) cations with the negatively charged unbound functional groups of the adsorbed acid. Moore et al. (2003) observed that NOM adsorption likewise brings about pore blockage and increases negative surface charge of the carbon.

Although no drastic thermal or chemical reaction is present during carbon tailoring by impregnation, impregnation is able to change the physical or chemical characteristics of carbon. For example, Baker and Poziomek suggested that polymerization occurred between impregnated species such as 4-vinylpyridine and adsorbate (methyl iodide) thus resulted in the improvement of methyl iodide adsorption.

2.2.6 Activated Carbon Regeneration

2.2.6.1 Thermal Regeneration

The process of thermal regeneration involves drying, pyrolysis and oxidation. The drying stage includes loss of highly volatile adsorbates, at temperatures of up to 200°C and elimination of the approximately 50% water (by weight) associated with GAC. The pyrolytic stage occurs when the spent carbon is exposed to temperatures up to 800°C under inert conditions. When the adsorbate contains organic materials, this eliminates any volatile compounds adsorbed in the carbon porosity, including residual moisture, and it thermally decomposes other less-volatile compounds. A residue of carbonized char is formed from the adsorbed compounds, which occupies some of the carbon porosity. The oxidative stage involves the controlled gasification of the pyrolysed carbon at temperatures usually around 800°C in the presence of a mildly oxidizing atmosphere, usually steam or carbon dioxide or a mixture of both. This results in the elimination of the charred residue and the exposure of the original carbon-type structure (Waer et al., 1992).
The reaction of carbon with steam and carbon dioxide are as follows:

\[
C + H_2O \rightarrow CO + H_2 \quad (2-6)
\]

\[
C + CO_2 \rightarrow 2CO \quad (2-7)
\]

\[
C + CO_2 \rightarrow C\bullet(O) + CO \quad (2-8)
\]

\[
C\bullet(O) \rightarrow C\bullet + CO \quad (2-9)
\]

C\• represents a radical and/or a reactive site and (O) is a chemisorbed oxygen. If steam were not used, equation 2-6 would not apply. When steam is used, all 4 equations could apply. Steam is preferred over CO\_2 as the activation gas. The water molecule is smaller than a CO\_2 molecule, allowing for faster diffusion into the pore network, allowing easier access to micropores, and also facilitating a faster reaction rate (Patrick 1995).

Traditional thermal regeneration has been conducted in multiple hearth furnaces or rotary kilns while fluidized bed regenerators, and electric belt furnaces have been introduced more recently for the same purpose.

The characteristics of the regenerated GAC are primarily determined by the conditions employed during the oxidation stage. The amount of char that is formed from the organic adsorbate establishes the amount of material that needs to be adjusted in order to control the extent of carbon gasification. The application of too mild conditions will not achieve the complete elimination of accumulated carbonized char and recovery of the carbon characteristics will not be maximized. However, the use of too severe conditions will result in damage to the original carbon structure and reduced yields (Juhola, 1970). The thermal regeneration of GAC exhausted with different organic species has been investigated by various researchers (Moore et al. 2002; Moreno-Castilla et al. 1995; Ferrero-Garcia et al., 1993; Waer et al., 1992). Results reported show that surface areas and adsorption characteristics could easily be restored or even improved, when regeneration conditions were optimized. Cairo et al. (1992) compared thermal regeneration of activated carbon that was laden with organics from industrial and municipal wastewater with carbon used in drinking water treatment. They found that the conventional manner of regeneration for carbon used for wastewater, temperature as high as 950°C was too harsh for carbon used in drinking water. The 950°C regeneration severely fractured the micropores needed for adsorption of volatile organics and also
weaken the macroporous structure thus producing higher carbon loss. Lower temperature (850°C) with longer retention time in the furnace may be a good compromise condition. Therefore, it is important to choose the right combination of regeneration conditions (temperature, oxidation gas and retention time) to achieve the best results.

In addition to organic matter, activated carbons accumulate substantial amount of inorganic species. Metal concentrations in spent carbons depend essentially on the quality of the pre-treated water and also on the design of the water treatment line. In this respect, high aluminium and iron loadings have been found in GAC used in filter beds situated just after coagulation-flocculation systems (Pilar et al., 1995; Cannon et al., 1994). Reports have shown that the accumulation of metals affects the process of thermal regeneration by catalyzing the reaction between solid carbon and the oxidizing agent (Cannon et al. 1997; Knappe et al. 1992; Kapteijn et al., 1986). Minerals accumulated, especially calcium, can act as catalyst during thermal regeneration, which leads to the deterioration of the micropore structure. Cannon et al. (1994) recommended acid washing as an effective way to avoid calcium catalysis. After washed with hydrochloric acid prior to traditional thermal regeneration, GAC was able to maintain its virgin pore volume distribution.

Besides inorganic and organic adsorbates that could affect the GAC regeneration, the type of material used to produce the base GAC is also an important factor. Junjgen (1976) observed that the reactivity of GAC made from wood was much higher than of GAC made from hard coal, and that, in general, the reaction rate during regeneration was an important function of the raw material type. The differences in reactivity of base material should be taken into account when deciding regeneration conditions.

Thermal regeneration has been in application in full-scale for decades. Technology in the field is quite mature at present stage. It has been successfully employed in full-scale applications worldwide for decades. San Miguel et al. (2001) investigated the development of porosity and adsorption capacity of field-spent carbon during the process of thermal regeneration. It was observed that spent carbons were able to recover most of their adsorption characteristics when heated to 800°C under inert conditions. They also found that gasification in the range of 5-10 wt% burn-off had some positive effects on the characteristics of the spent carbon. In related research, Moore et al.
(2002) observed that the NOM adsorption capacity of activated carbon could be fully restored through multiple reactivations.

A number of parameters were used to monitor the effectiveness of the regeneration process: volume loss, adsorption capacity and apparent density (AD). Few data are available that show the dependence of volume loss on furnace type, operation procedures, or any other variable. The loss of adsorption capacity can have a dramatic effect on the run length of the GAC adsorber. Several researchers (Randtke et al. 1983; Carrott et al. 1988; Sontheimer et al. 1988; Adam et al. 1989) have shown that the time and temperature of regeneration can be varied to control capacity. Apparent density is the mass of GAC per unit of non-stratified, packed-bed volume. AD is the value most often used to determine whether a GAC has been properly regenerated. The optimum time of regeneration is usually defined as the time necessary to maximize adsorption capacity without decreasing the adsorption capacity below that of virgin GAC. Other parameters like iodine number or adsorption capacity for certain compounds have also used as indicated by the application of carbon.

The cost of regeneration can be broken down into three major categories: capital costs for the regeneration system and transportation equipment, operation and maintenance costs for the furnace and the cost of the makeup GAC to replace the GAC that was lost. Makeup GAC was frequently found to be the single most expensive item in regeneration cost.

The drawbacks of thermal regeneration include high energy demand, carbon loss (5-10%) from attrition during transportation and from burnoff and attrition during regeneration. Also, micropore volume and surface area loss are common after thermal regeneration (Leng and Pinto, 1996). Surface area declined by almost 50% after 10 regenerations as reported by Hutchins (1973). However, surface area, pore volume and TOC adsorption could be maintained through 13 cycles of regeneration at the City of Cincinnati water treatment plant (Moore, 2002).
2.2.6.2 Chemical Regeneration

The high initial cost of granular activated carbon (GAC) makes it necessary that spent carbon be regenerated. Thermal regeneration of GAC is the most widely used technique in which adsorbates are desorbed by means of volatilization and oxidation at high temperature. It is known that about 5-10% of the carbon is usually lost by attrition, excessive burnoff and washout during each cycle (Guymont, 1980). It was estimated that the cost of carbon regeneration is around 75% of the operation and maintenance cost of using GAC (EPA, 1989). Therefore, it is highly recommended that an alternative way of regeneration be found especially in situations where transportation is a problem, or frequent regeneration is necessary.

It was perceived that the advantages of chemical regeneration include first that it can be done in situ, thus there was no problem with unloading, transporting and repacking of carbon. Secondly, there was almost no loss of carbon during regeneration. Thirdly, it was possible that the regenerant could be reused, thus further reducing the cost for regeneration. Finally, it was also possible that the adsorbate could be recovered for subsequent applications.

Chiang and Wu (1989) compared the effect of chemical and thermal regeneration of activated carbon that are saturated with aromatic compounds. The regenerants used included methanol, ethanol and sodium hypochloride. They reported that the regeneration efficiency ranged from 15.15 to 96.8%, depending highly on the adsorbate. The efficiency for thermal regeneration ranged from 75-86%, and it was independent on the characteristics of the adsorbate.

In most cases, two categories of substances are considered to be possible candidates as regenerant: organics with solubilizing features (solvent regeneration) or inorganics with oxidizing powers. It has been found that organic regenerants with solubilizing powers are more effective than inorganic regenerants with oxidizing powers.

Martin and Ng (1984) evaluated a wide range of regenerants, inorganic and organic, as regenerants for carbons that were exhausted with mono-substituted benzene compounds. Inorganic chemical regenerants with oxidizing power (10% KMnO₄, 10% K₂Cr₂O₇ and 0.35% NaOCl) were generally ineffective (regeneration efficiency from
negative to 60% at the extreme). It’s likely that poor results are a consequence of steric hindrance arising from the effect of oxidizing agent on the activated carbon and from the reactions between the oxidizing agent and the adsorbate.

Organic chemical regenerants with solubilising powers were found to be generally more effective (regeneration efficiency more than 90%) in some cases. The regeneration efficiency was affected by solubility of regenerant. The use of water soluble organic regenerants in water was found to be less effective. It’s possible that bonding between these organic regenerants (such as carboxylic acids and alcohols) and water hinders the regeneration. When there is reaction between regenerant and adsorbate, the degree of regeneration depends on the properties of reaction products. Regeneration was based on physical displacement when reactions are unlikely. Regeneration efficiency was found to depend highly on the relationship between the molecular weight of the adsorbate and that of the regenerant. It’s desirable to use a regenerant of molecular weight smaller than that of the adsorbate.

In the same study, it was found that the success of inorganic regenerants (HCl or NaOH) used to induce high or low pH conditions was dependent on the nature of the adsorbate. The pH will have impact on the dissociation of the adsorbate and surface charge distribution. Therefore, carbon was regenerated by direct replacement of adsorbate by OH\(^-\) or H\(^+\) by base or acid regeneration. Or base or acid used was able to create an electrostatic repulsion force between the carbon surface and the adsorbate. For example, at high pH (base regeneration), the carbon surface will be more negatively charged and it can act to repel negatively charged adsorbates. Besides replacement and electrostatic repulsion, there is also the possibility of chemical reaction between adsorbate and regenerant. For example, when NaOH solution was used to regenerate phenol-exhausted carbon, the formation of water-soluble salt sodium phenate, C\(_6\)H\(_5\)O\(^-\)Na\(^+\), meant that desorption was facilitated.

Sodium hydroxide is one of the most commonly used inorganic regenerants. Newcombe and Drikas (1993) applied a regeneration procedure that employed a base solution (1 M NaOH) followed by an acid (0.01 M HCl) wash to remove organics from carbons that have been in use for 2 years in North Richmond Treatment Works, Sydney, Australia. The procedure was able to restore up to 90% of the original capacity.
Overall, efficiency of chemical regeneration depends heavily on the selection of regenerant. Regenerants with solubilizing power is relatively more effective when carbon was exhausted with organic compounds. To regenerate carbon exhausted with inorganics, a regenerant with a high affinity for the carbon surface is always an advantage if the regenerant still subsequently readily comes off.

As far as perchlorate-exhausted carbon is concerned, in a small-scale regeneration by sodium borohydride (NaBH₄) solution, Na et al. (2000) were able to achieve a 75-100% desorption of previously adsorbed perchlorate by passing about 150 BV of 100 mg/L of this regenerant through the GAC bed. In addition, no chemical reduction of perchlorate was observed during this regeneration.

Chemical regeneration of perchlorate-activated carbon can also draw inspiration from other fields. Tetrachloroferrate (FeCl₄⁻) anions was used by Gu et al. (2001) to regenerate a perchlorate-exhausted ion exchange resins.

It still is to be seen if the same technology that was used in ion exchange resin would be effective on activated carbon.

2.2.6.3 Microwave Regeneration

Microwaves are used in various technological and scientific fields in order to heat dielectric materials (Zlotorzynski, 1995). The main difference between conventional methods of heating and microwave heating is the way in which heat is generated. In the conventional approaches, the heat source is located outside the carbon bed, and the bed is heated by conduction and/or convection. A temperature gradient is established in the material until conditions of steady state are reached. In the microwave method, microwaves supply energy to the carbon particles. This energy is converted by dipole rotation and ionic conduction into heat inside the particles themselves.

Menendez et al. (1999) compared the textural and chemical properties of two commercial activated carbons that were subjected to thermal treatment in N₂ using a microwave multimode resonant cavity and a conventional electric tube furnace. Treatments in the electrical furnace were carried out in a 100 mL/min N₂ gas flow for 3 h at 950°C. Microwave treatments were carried out in a microwave cavity with input
power of 1000 W and microwave frequency of 2,450 MHz for 5 min under the same gas flow. Results indicate that when similar treatment temperatures were used, both techniques produced similar changes in the textual and chemical properties. Oxygen-containing functionalities were removed from carbon surface and the resulted carbons were more hydrophobic and basic. Compared with conventional heating, microwave treatment was much less time-consuming.

Regeneration by microwave offers certain advantages, including rapid and precise temperature control, small space requirements and greater efficiency in intermittent use (Balbaa et al., 1991; Haque, et al., 1993; Strack et al., 1995; Bradshaw et al., 1997). Strack et al. (1995) reported that microwave regeneration reduced carbon loss by half and improved material hardness while the activity of regenerated materials was still comparable to that by conventional regeneration. They used a 30 kW 915 MHz microwave unit in their test and found that the operating cost could be cut by 1/3 when comparing between a conventional kiln processing 120 Kg/h and the microwave system. Van Wyk et al. (1998) conducted regeneration on carbons used in gold recovery by steam using microwave heating. Judged by parameters such as loading capacity, abrasion resistance factor and dimensionless activity, the authors found that 5 minutes at 750°C was enough to regenerate carbon to acceptable levels while optimum conditions in terms of activity and loading capacity is 850°C for 20 minutes.

Microwave regeneration of carbon loaded with organics was found to be able to convert the organics to non-hazardous compounds without causing damage to the carbon properties. Tai and Jou (1999) used GAC to adsorb phenol in a packed bed system. The carbons were loaded with phenol by passing solutions containing 5 and 50 mg/L phenol for 48 h respectively before they were subjected to microwave treatment (1000 Watts, 2,450 MHz). No phenol was detected after only 240 seconds treatment for carbon loaded with phenol of initial concentration 50 mg/L and it took only 150 seconds when the phenol initial concentration was 5 mg/L. Phenol in exhaust gas was monitored by gas chromatography. A serious “Arcing” phenomenon was observed among GAC particle after 50-100 seconds in microwave. GAC temperature reached as high as 1200°C during microwave treatment. Phenol was converted to simple and nontoxic H₂O and CO₂ in the process.
Coss and Cha (2000) investigated regeneration by microwave of activated carbon that was used to remove solvents from vented air. Their experiment used methyl ethyl ketone (MEK) as the representative solvent. And the carbon was loaded with the solvent by bubbling MEK through a carbon bed by N\textsubscript{2} gas. The saturated carbon was regenerated in the microwave reactor for 30 min at 200 W incident power. More than 80 % of the MEK adsorbed was desorbed during the first 10 min of regeneration. Surface area measurements and adsorption capacity tests indicated that microwave regeneration was able to successfully restore the carbon to its original status even after 20 cycles of saturation and regeneration.

Adsorbents other than activated carbon were also studied. Weissenberger and Schmidt (1994) found that microwave regeneration of activated alumina on molecular sieves was able to reduce regeneration time by 240% compared with conventional regeneration. Price and Schmidt (1997) conducted research on microwave regeneration to effect recovery of volatile organic compounds (VOCs) from molecular sieves adsorbents. Their results showed that microwave regeneration was able to enhance the mass transfer rates and resulted in a quasi-equilibrium process in the bed with vacuum purge. Desorption increased with temperature and decreasing system pressure and is not rate-limited by mass transfer resistance.

2.2.6.4 Supercritical Fluid Regeneration

A supercritical fluid is a material that can be either liquid or gas, used in a state above the critical temperature and critical pressure where gases and liquids can coexist. It shows unique properties that are different from those of either gases or liquids under standard conditions. A supercritical fluid has both the gaseous property of being able to penetrate anything, and the liquid property of being able to dissolve materials into their components. In addition, it offers the advantage of being able to change density to a great extent in a continuous manner. On this account, use of carbon dioxide or water in the form of a supercritical fluid offers a substitute for an organic solvent in the fields of the food industry and medical supplies (Taylor 1996). Furthermore, it is attracting wide attention as a new technology which is user-friendly to both human beings and the
environment. Supercritical CO$_2$ regeneration is one of the possibilities for spent carbon regeneration loaded with organics.

The first treatment of supercritical regeneration appears to be the research of de Modell et al. (1979) and Filippi et al. (1980). Modell et al. (1979) examined cyclic regeneration of phenol by using supercritical CO$_2$ (146-186 atm). The phenol was adsorbed onto carbon surface from an aqueous solution. It was reported that 70% (55°C) and 86% (120°C) of phenol were desorbed.

Chihara (1997) employed supercritical CO$_2$ to regenerate activated carbons that were loaded with organic adsorbates (benzene, toluene, m-xylene, o-xylene, p-xylene, phenol). The results showed that desorption of organic compounds is closely related to CO$_2$ density and the compounds’ boiling point. Desorption increases with the increase of CO$_2$ density and decreases with increase of boiling point. Rough estimation of energy consumption for steam regeneration and supercritical CO$_2$ regeneration indicates that the utility for supercritical fluid regeneration is ten times cheaper than that for steam regeneration. The calculation was based on the assumption that 1 g of steam or CO$_2$ would be necessary to regeneration 1 g of carbon.

Compared with thermal regeneration, supercritical fluid regeneration is less energy intensive since it was carried out in much lower temperature. It also makes recovery of adsorbate very easy. Simply return the waste regenerant to ambient temperature and pressure. Adsorbate could be easily separated from CO$_2$ gas and leaves no serious environmental problem. In addition, there will be little loss of carbon, and no pore volume and surface area change as caused by gasification in thermal regeneration. The disadvantage of the process is that supercritical fluid regeneration may have special demand on the equipment.

2.2.6.5 Biological Regeneration

Activated carbon adsorption and biological degradation are two important methods used in the treatment of industrial wastewater. Biological treatment is relatively inexpensive but, because of the sensitivity of biological systems to environmental conditions, is subject to system upsets. Research in the area of simultaneous activated
carbon adsorption and biological degradation has been directed primarily toward the study of biological activated carbon (BAC) (Miller et al. 1980; Rice and Robson 1982) and the application of powered activated carbon (PAC) to activated sludge systems (Wu and Mahmud 1980; Janeczek and Lamb 1982). Very little attention has been directed toward the development of biological regeneration as an alternative to traditional methods of activated carbon regeneration.

Hutchinson and Robinson (1990) investigated biological regeneration of activated carbon exhausted with phenol. The carbons were regenerated using a mono-culture of *Pseudoomonas putida*. The performance of bioregenerated activated carbon was evaluated on the basis of the breakthrough of phenol in a continuous flow bed. The research compared two regeneration methods. One was direct contact bioregeneration where fermentation broth was pumped directly through the activated carbon adsorber. The second was filtered broth regeneration in which the activated carbon was regeneration using cell-free filtrate. The broth was passed through a cross-flow filtration unit, and only the cell-free permeate was used for regeneration.

An accumulation of biomass, especially on the bottom on the carbon column was observed for direct contact regeneration. The fouling of column increased with each regeneration cycle, which resulted in significant deterioration of bioregeneration efficiency with each cycle. Fresh carbon could treat water with 205 mg/L phenol up to 6 hours without phenol breakthrough, while there is 20 mg/l phenol in effluent immediately after start for carbon bioregenerated once. The phenol concentration in effluent increased to 80 mg/L for carbon undergoing second cycle of regeneration.

The activated carbon regenerated using cell-free permeate performed much better than the activated carbon regenerated with the unfiltered broth. A gradual increase in effluent phenol levels was observed rather than the immediate breakthrough during the direct contact regeneration. There is no phenol breakthrough for 5 hours after first cycle of bioregeneration as compared with 6 hours with fresh carbon. The improvement in the breakthrough performance with cell-free permeate demonstrated that microbial fouling was responsible for the poor performance observed with direct contact regeneration. Still, the regeneration efficiency deteriorated after each cycle of regeneration. The operation time to breakthrough was 2 hours for carbon after 2\textsuperscript{nd}, 3\textsuperscript{rd} and 4\textsuperscript{th} regeneration cycle.
Overall, the bioregeneration did not completely restore the adsorption capacity of the activated carbon with the bacterium tested. Hutchinson and Robinson (1990) suggested that bioregeneration might not be appropriate for regenerating activated carbon used in tertiary waste treatment. However, it may be appropriate for use in combination with other secondary treatment process.
Figure 2.1: Structure of the perchlorate ion
Figure 2.2: Functional groups on the surface of GAC (Figueiredo et al. Carbon (37), 1999)
Figure 2.3: Conversion of oxygen-containing surface functional groups into nitrogen-containing groups by reaction with ammonia (Stohr et al. Carbon (29), 1991)
3.1 MATERIALS

3.1.1 Granular Activated Carbon

Bituminous granular activated carbon (GAC) manufactured by Superior Adsorbents Inc. (Emlenton, PA) was used in carbon tailoring study, designated SAI carbon hereafter. Other bituminous carbons used as comparison include Filtrasorb 300, Filtrasorb 400, Filtrasorb 600 and Centaur from Calgon Carbon Corporation (Pittsburgh, PA). All carbons were acid-washed by 1 M HCl to reduce ash content to less than 0.3% before conducting any experiment or treatment. GACs were ground and sieved to US mesh 60×80 (250-180 µm). They were then washed with deionized-distilled water to remove fines, and dried at 105°C overnight to remove moisture. The carbon samples were stored in a vacuumed desiccator until use.

3.1.2 Groundwater from the City of Redlands, CA

The perchlorate-containing groundwater was obtained from well that feeds the Texas Street Water Treatment Plant, City of Redlands, CA. It contained around 50-80 ppb of perchlorate. The concentration of perchlorate was observed to fluctuate slightly from season to season. Aside from perchlorate, four other anions were prominent in the Redlands groundwater. These anions were chloride (7-8 mg/L), sulfate (30-35 mg/L), nitrate (5-7 mg/L as N), and bicarbonate (145-155 mg/L). The conductivity of water was measured to be 330 µS and it contained 2.4-2.6 mg/L TOC. This water has been identified as Redlands water hereafter.

The water was shipped to the Pennsylvania State University right after it was pumped out of the Redlands well in 55-gallon barrels (galvanized steel or plastic-coated steel). At Penn State, the water was transferred into chemical-resistant plastic containers,
which contained 6½ gallons of water each. No growth of microorganism and deterioration of perchlorate were observed during the storage process.

3.1.3 Chemicals

Nitric acid solution was made from concentrated nitric acid (68-70% by weight) from VWR (West Chester, PA). In chemical regeneration tests, calcium thiosulfate (from Ag Formulators, Inc.) with concentration 30% (w/w) was tested as regenerant. For the base/acid method, NaOH was obtained from a VWR 50% (w/w) solution. Hydrochloric acid was obtained from EM Science (36.5–38% by weight). Ethylene diamine was from J.T. Baker, and anhydrous sodium perchlorate from EM was used to make perchlorate standards.

3.2 METHODS

3.2.1 Rapid Small-Scale Column Test (RSSCT)

Column tests were conducted to evaluate GAC’s perchlorate adsorption capacity and regeneration efficiency, as that would occur in a full-scale bed. The similarity of RSSCT simulation and full-scale performance was appraised by comparing the breakthrough curves that were obtained via the RSSCT column, with available full-scale data from the operating cycle of GAC beds at the Texas Street Water Treatment Plant, City of Redlands, CA.

The rapid small-scale column test (RSSCT) can be considered as a small physical simulation of full-scale GAC columns. Mass transfer models have been developed to scale down the full-scale adsorber to a small column that contains GAC grains of smaller particle size. Two different design approaches have been presented, and the proper design depends on whether internal diffusion does not change with particle size (i.e. constant diffusivity occurs) or is linearly dependent on particle size (i.e. proportional diffusivity occurs). The following equations have been developed for simulations.
• **EBCTs:**
  
  − For the constant diffusivity:
    
    \[ \frac{EBCT_{SC}}{EBCT_{LC}} = \left( \frac{D_{SC}}{D_{LC}} \right)^2 \]
    
    − For the proportional diffusivity:
      
      \[ \frac{EBCT_{SC}}{EBCT_{LC}} = \frac{D_{SC}}{D_{LC}} \]

• **Flow Rates:**
  
  \[ \frac{\nu_{SC}}{\nu_{LC}} = \frac{D_{LC}}{D_{SC}} \cdot \frac{Re_{SC,min}}{Re_{LC}} \]

• **The RSSCT Column Length:**
  
  \[ L_{SC} = EBCT_{SC} \times \nu_{SC} \]

• **The Carbon Mass:**
  
  \[ m_{SC} = \rho_{LC} \times V_{SC} \]

where \( EBCT \) = empty bed contact time

\( SC = \) small column

\( LC = \) large column

\( D = \) carbon grain diameter

\( \nu = \) flow rate or velocity

\( Re = \) Reynolds number

\( L = \) column length

\( m = \) carbon mass

\( \rho = \) apparent density

\( V = \) carbon volume
Re_{SC,min} is the minimum Reynolds number in the small column. According to previous work with column tests in Penn State University, RSSCT columns that can best simulate the full-scale test are based on the proportional diffusivity assumption when adsorbing perchlorate onto activated carbon (Na et al. 2000). Re_{SC,min} equals to 0.13 for a molecule the size of perchlorate exhibiting proportional diffusivity.

Table 3.1 is the configuration of full-scale activated bed in Texas Street Water Treatment and small-scale column based on proportional diffusivity. For carbon samples with particle size US mesh 60×80 (250-180 µm), the columns used were approximately 23 cm in length and had an inner diameter of 1.3 cm on the basis of these similitude equations. Each test employed about 9.8 g of GAC that was held in place by glass wool. The actual EBCT of these columns were about 3.65 min to simulate a full-scale EBCT of 20 min. RSSCT with carbon particle size 60×80 was used only in tests for carbons by chemical regeneration. The rest of the RSSCT used carbon particle size 200×400. For carbon sample with particle size US mesh 200×400 (38-15 µm), the columns used were 15 cm long and 0.5 cm in diameter. Each test needed 1.67 g carbon with a EBCT 0.75 min.

During RSSCT operation, initial breakthrough corresponding to when there was consistently detectable perchlorate in the effluent. Since the DX-120 method detection limit was 4 ppb, the bed volume to initial breakthrough of the column test has been defined as the bed volume before perchlorate concentration in the effluent first reaches 4 ppb.

<table>
<thead>
<tr>
<th>Diffusivity Model</th>
<th>EBCT (min)</th>
<th>Column length (cm)</th>
<th>Column diameter (cm)</th>
<th>Particle size (US mesh)</th>
<th>Carbon mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-scale</td>
<td>20</td>
<td>5500</td>
<td>304.8</td>
<td>12×40 (1700-425 µm)</td>
<td>9,080,000</td>
</tr>
<tr>
<td>Small-scale (proportional)</td>
<td>3.65</td>
<td>23</td>
<td>1.3</td>
<td>60×80 (250-180 µm)</td>
<td>9.8</td>
</tr>
<tr>
<td>Small-scale (Proportional)</td>
<td>0.75</td>
<td>15</td>
<td>0.5</td>
<td>200×400 (38-15 µm)</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Table 3.1

Configuration of full and small-scale carbon column
3.2.2 Quantitative Analysis of Perchlorate

Perchlorate was analyzed by ion chromatography. The analytic system was a DX-120 Ion Chromatograph (Dionex Corp., Sunnyvale, CA) at Penn State University while a DX-600 was used at the Redlands Wastewater Treatment Plant during the full-scale regeneration demonstration in 2001.

For Dionex DX-120, the system setup is as follows: AS40 autosampler, 1000 µL sample loop for ppb level perchlorate, Dionex AG16 (4 mm) guard column and AS16 (4 mm) ion exchange column, ASRS ULTRA suppressor (4mm) and Dionex CD 20 suppressed conductivity detector. Fifty mM NaOH was used as eluent and eluent flow was set at 1.0 mL/min. Typical system backpressure was 1900-2200 psi. The suppressor used external water regeneration mode, 300 mA current, and a temperature of 35°C. Background conductivity was from 2-3 µS. Method total analysis time was 15 min and analyte (perchlorate) retention time was 10.1±0.2 min.

For Dionex DX-600, the system setup is as follows: AS40 autosampler, 750 µL sample loop for ppb level perchlorate, Dionex AG16 (4 mm) guard column and Ionpac AS16 (4 mm) ion exchange column, Dionex CD 25 conductivity detector, DS3 detection stabilizer and LC20 chromatography enclosure. Fifty mM KOH was used as eluent. The suppressor was external water regeneration mode, 300 mA current, and a temperature of 35°C. Method total analysis time was 12 min and perchlorate retention time was 7.8±0.2 min.

Perchlorate standards of 2.5, 5, 10, 25, 50, 100, 250, 500, 1000, 2000, 3000 were prepared with sodium perchlorate (EM Science, ACS grade) and deionized-distilled water. Standards were kept in refrigerator. Standard samples were run each time samples were analyzed.
3.2.3 Activated Carbon Tailoring

3.2.3.1 Oxidation by Nitric Acid

Carbon oxidation was conducted by mixing 20 g of the SAI carbon with 200 mL of nitric acid solution. The concentration of nitric acid solution ranged from 0.01 to 6 N. The carbon and nitric acid mixture was held and constantly stirred for 3 h at room temperature. The oxidized activated carbon samples were washed until the pH of the filtrate reached almost neutral. It was dried at 105°C overnight and stored in a vacuum desiccator. The carbon samples were denoted by SOX plus the nitric acid concentration. For example, SOX0.01 means SAI carbon oxidized by 0.01 N nitric acid solution.

3.2.3.2 Pyrolysis by \( \text{N}_2 \)

Pyrolysis in \( \text{N}_2 \) was carried out in a thermogravimetric analyzer (TGA-Cahn Instruments, Inc., Cerritos, CA). \( \text{N}_2 \) flow rate was set at 70 mL/min. The sample was heated at 50°C/min to predetermined temperature and held at this temperature for 1 h. It was then cooled to room temperature under the same flow of nitrogen. The samples were washed with deionized-distilled water and dried overnight at 105°C. The dried samples were stored in vacuum desiccator. The carbon samples were coded by N plus the temperature. For example, N1000 means SAI carbon pyrolyzed in \( \text{N}_2 \) at 1000°C.

3.2.3.3 Thermochemical Treatment by \( \text{NH}_3 \)

The tailoring of the SAI carbon by \( \text{NH}_3 \) was carried out in TGA. About 1 g of carbon sample was placed in the center of the TGA furnace. The furnace was heated to a desired temperature in a nitrogen atmosphere before the gas was switched to undiluted ammonia (anhydrous, min. purity 99.99%). Both the \( \text{N}_2 \) and \( \text{NH}_3 \) flow rate were set at 70 mL/min. The sample was treated in ammonia for a predetermined time at constant temperature and then was cooled to room temperature under a nitrogen atmosphere.
Changes in mass, temperature and operation time were monitored continuously and data recorded automatically. The nomenclature for the tailored samples has been denoted on the basis of carbon type, treatment temperature and time. For example, SAI-500-60 is a carbon sample treated by NH$_3$ at 500$^\circ$C for 60 minutes. Tailored samples were washed thoroughly by deionized-distilled water until the effluent pH was neutral. The samples were then dried overnight at 105$^\circ$C and stored in a vacuumed desiccator.

3.2.3.4 Electrochemical Treatment

Electrochemical tailoring was carried out in an electrochemical cell with platinum-coated stainless steel sheet as cathode and a stainless steel basket as anode. A solution containing 0.1M of supporting electrolyte, LiClO$_4$, and 0.05-0.1M reactant, ethylene diamine (C$_2$H$_8$N$_2$) was placed in the electrochemical cell. Acetonitrile (CHN) was used as a solvent. About 1 g of SAI carbon was put into the stainless steel basket. The carbon was soaked in reactant solution for half an hour prior to the start of the experiment. During this period of time and throughout the experiment, nitrogen gas was bubbled to stir the solution and also to remove as much oxygen as possible. A current density of 2-4 mA was applied to the electrochemical cell for 5 minutes, and the operation was carried out in room temperature. After the experimental process, the modified activated carbon was rinsed with deionized-distilled water and dried for 24 hours at 105 $^\circ$C and stored.

3.2.4 Activated Carbon Characterization

3.2.4.1 Pore Volume Distribution and Specific Surface Area Determination

The pore volume distribution and specific surface area of GACs were determined by adsorption of argon vapor onto GAC samples by means of isotherms with progressively increasing relative pressures from $10^{-6}$ to 0.993 atm/atm by ASAP 2010 units (Micromeritics Instrument Corporation, Norcross, GA). The sample glass tube that contained the GAC was immersed in a liquid argon bath (99.9% purity) that held at
temperature of 87.3 K. Molecular area of argon was taken to be 0.142 nm². Before obtaining adsorption or desorption isotherms, the carbon sample was degassed for 24 h at 378 K to remove any moisture or adsorbed contaminants that may have been present on the GAC surface. Values of specific surface areas were obtained by the BET (Brunauer-Emmett-Teller) method; and argon adsorption isotherms were interpreted with the Density Functional Theory model provided by Micromeritics. Each sample was analyzed in duplicate.

3.2.4.2 Characterization of Surface Charge Distribution and pHpzc

A Mettler Toledo DL53 titrator (Mettler Toledo, Inc., Columbus, OH) was used to measure the total net surface charge distribution and pH of Point of Zero Charge (pHpzc) of activated carbon. Two NaCl solutions (0.01 and 0.1 N) were used as electrolytes in the titration. Approximately 0.15 g of sample each was added to 200 mL of electrolytes, which were adjusted to pH 10.5 by 0.1 N NaOH. During the titration process, 0.2 mL of 0.04 N HCl was added to the mixture every ten minutes. At the end of the 10 min, the pH was recorded. The end point of titration was set to be 10 mL of HCl addition. The same procedure was carried out for blank samples (only without the addition of carbon) for both electrolyte concentrations. The difference in pH (ΔpH) between blank solution and carbon mixture, when the same amount of titrant was added, is attributed to the ion exchange capacity of carbon. ΔpH is interpreted as directly related to the surface charge of the carbon sample at a certain pH. When the relative surface charge is plotted against pH, the point at which the curves from two electrolytes crosses was taken as the pH at which the absolute charge on the surface is zero (pHpzc). This is the only point where the surface charge is independent of the electrolyte concentration (Newcombe et al. 1993). At the same time, results from titration with 0.01N NaCl were presented as a surface charge distribution after being normalized according to the pHpzc value. Duplicate analyses at both 0.01N and 0.1 N NaCl were conducted, and the standard deviations of the pHpzc and surface charge at pH 7.5 were calculated.

Another method was used to determine the pHpzc in order to corroborate the results obtained by automatic titration. One gram of sample was added to 10 mL of
deionized water and the pH of the mixture (after 24 hour equilibration) was taken as the slurry pH. According to the mass titration method recommended by Noh and Schwarz (1989), the equilibrium pH should be equivalent to the pHpzc. The standard error in the test is proven to be 0.02-0.04 pH units.

3.2.4.3 Elemental Analysis

Elemental analysis was performed by a carbon-hydrogen-nitrogen determinator CHN600 (LECO Corporation, St Joseph, MI). The carbon sample contained in a tin capsule was completely burned out at 900°C. The combustion products determined in this process were CO₂, NOₓ, H₂O and N₂. Any amount of SOₓ formed was removed from the combustion products by CaO before the measurement of C, H, and N. The contents of C and H were measured in an infrared cell, whereas N content was measured by a conductivity cell. Thus the results obtained by this technique only report the nitrogen, carbon and hydrogen content. The oxygen content was calculated by difference assuming that only four elements, C, H, N and O, were present in the carbon samples. Samples were analyzed in triplicate; and the standard deviations for these analyses were calculated.

3.2.4.4 Zeta-potential and pH_{IEP}

A Laer Zee Meter (Model 501- Pen-Kem, Inc., Bedford Hills, NY) was used to measure the zeta-potential (ZP) of carbon samples. 50 mL of 0.01 N NaCl solution was adjusted with 0.1 N HCl or NaOH to different pH values, between 2 and 11. 0.1 g of carbon, ground to less than 45 µm, was added to each of the solutions and stirred for 24 hours. After that, approximately 25 mL of sorbent suspension was injected directly into the electrophoretic cell, and it was placed under microscope where it was automatically illuminated by a laser beam. This was followed by applying an electric field to the cell; the voltage was adjusted manually until the carbon particles inside the cell, as observed by the microscope, were stationary (a minimum of three readings, ZP, were taken within one minute). The average ZP, at each pH value, was plotted against pH at equilibrium.
The isoelectric point (IEP) was taken as the point where the electrophoretic mobility was zero (Julien et al. 1998). Standard deviations of duplicate analysis were calculated.

3.2.4.5 Surface Functional Groups Determination

The determination of acidic surface functional group content was performed using the methods proposed by Boehm (1964). Solutions of NaHCO$_3$, Na$_2$CO$_3$, NaOH and HCl were prepared using deionized-distilled water. Fifty mL of base solution was added to 2-g carbon in a glass bottle. The bottle was sealed and allowed to equilibrate for 24 hours in a rotary shaker. At the end of the equilibration period, the supernatant was titrated using standardized HCl solution. The amount of base consumed by the functional groups on the carbon surface was calculated as the difference in the amount of acid required to titrate the blank to pH 4.5, and the amount of acid required to titrate the supernatant to the same end point. The free “carboxyl” group concentration on the surface was empirically determined as the amount of sodium bicarbonate consumed by the carbon sample (rigorously, this represents functional groups that have pKa’s that are similar to those for carboxyls). “Lactone” content was calculated as the difference between the amounts of sodium carbonate and sodium bicarbonate consumed (and this rigorously represents functional groups that have a pKa similar to those for lactone groups). “Phenolic” group content was determined as the difference between the amounts of sodium hydroxide and sodium carbonate consumed (and this rigorously represents functional groups that have pKa’s that are similar to phenolics, i.e. at high pH). Total acidic group represented the summation of “phenolic”, “lactone” and “carboxyl” group contents.

Basic group content was evaluated by allowing 2 g of GAC to equilibrate with 50 mL of HCl for 24 hours. The basic group content was empirically calculated as the difference between the amounts of NaOH required to reach the end point for the HCl blank and for the supernatant. Samples were analyzed in triplicate.
3.2.4.6 Adsorption Isotherm Experiments

Adsorption isotherm tests were conducted using the bottle-point method. A hundred mL of deionized-distilled water that had been spiked with 2000 ppb of perchlorate was added to glass bottles containing 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 or 1 g of carbon. The bottles were sealed and put on a shaker for 24 h at 20°C. After that, the mixture was filtered through 0.45 µm glass fiber filters to separate the carbon particles, and the aqueous-phase perchlorate concentration was monitored. The test was repeated at each carbon dose. The average equilibrium perchlorate values ($C_e$) from each carbon dose were used to fit the isotherm equations.

3.2.4.7 Kinetic Experiments

Carbon samples ground down to US mesh 325×400 (45-38 µm) were added to 50 mL deionized-distilled water to make a mixture with 1500 mg carbon/L. Fifty mL Redlands water was added to an array of reactor syringes that have been previously cleaned by deionized-distilled water and dried. 0.667 mL of activated carbon mixture was then added to each syringe to make a total of 50 mL mixture that contained 20 mg carbon/L. The syringes were put onto an end-to-end rotary shaker for a predetermined amount of time. After this time, aqueous samples were filtered and analyzed for perchlorate and TOC. The adsorbed perchlorate and TOC were calculated by difference between the initial and subsequent concentrations. The test was repeated for its reproducibility. The average value from the duplicate was taken and shown in the figures. Duplicates for both perchlorate and TOC varied by less than 3-5% from one another.

3.2.4.8 Oxygen Re-adsorption

To appraise the relative extent to which oxygen could readsorb to the ammonia-tailored carbons, the ammonia-tailored carbons were prepared at 500, 600, 700, or 800°C for 60 minutes in a thermogravimetric analyzer (TGA). Then, without opening the TGA to air, the TGA and its contents was cooled to ambient temperature in N$_2$ atmosphere.
Next, the temperature was raised to 105°C under nitrogen, and kept there for 3 hours. Then, with temperature maintained at 105°C, oxygen gas flowed through the TGA chamber at 160 mL/min for 240 minutes; while the TGA monitored mass change. Each sample was duplicated for its oxygen readsorption capacity and the difference between duplicate is less than 4%.

3.2.5 Activated Carbon Regeneration

3.2.5.1 Perchlorate Preloading for Carbon Regeneration

Before regeneration, carbons were first exhausted with perchlorate in RSSCT column or batch loading. In column loading, the perchlorate-containing water (Redlands groundwater) was pumped through the column at predetermined empty bed contact time (EBCT). The carbon in column was deemed exhausted (breakthrough) once the perchlorate concentration in effluent was close to that of the influent. The amount of perchlorate loaded was calculated from integration of the perchlorate breakthrough curve.

In batch loading, 1 g of carbon was mixed with 200 mL of perchlorate-containing solution. The glass bottle contained the mixture was put on a rotary shaker for 24 h. Redlands groundwater spiked to perchlorate concentration 5 mg/L was used as perchlorate-containing solution. The goal of batch loading is to shorten the time of perchlorate exhaustion. After 24 hours, the carbon was separated from the aqueous solution and the amount of perchlorate loaded was calculated from difference in perchlorate concentration of the aqueous solution before and after it was mixed with carbon.

3.2.5.2 Chemical Regeneration

Carbon particle size in chemical regeneration was US mesh 60×80. Before regeneration, carbon was loaded with perchlorate in small columns. Chemical regeneration was conducted by pumping regenerant through the perchlorate-loaded carbon column at the selected EBCTs. Change of EBCT was achieved by changing the
water flow rate. Two methods were tested in chemical regeneration. One was regeneration with calcium thiosulfate. Calcium thiosulfate concentrations of 75, 150, 210, 300 and 350 mg/L as thiosulfate were used to regenerate perchlorate-laden carbon. The other was regeneration by base/acid method. There were two steps in the base/acid regeneration method. First, perchlorate-free water adjusted to pH 12 by NaOH was applied to the GAC beds to desorb the perchlorate from the carbon. Then the beds were washed by water adjusted to pH 2 by concentrated HCl. Perchlorate and pH values were monitored during the regeneration process.

The regeneration efficiency was calculated by comparing the perchlorate desorbed during the regeneration with that of loaded to the carbon during column breakthrough.

3.2.5.3 Thermal Regeneration

Carbon particle size for thermal regeneration was US mesh 200×400. Before thermal regeneration, carbon was loaded with perchlorate using the batch loading method. Thermal regeneration was performed also in a TGA with about 1 g of activated carbon. Changes of mass, temperature and operation time were monitored continuously and data recorded automatically. There were two steps in thermal regeneration. The pyrolytic step was carried out under a constant flow (150 mL/min) of nitrogen for 10 min at temperatures between 600-800°C. It was immediately followed by reactivation either with steam, CO₂ or NH₃ at the same temperature. The gas flow rate was controlled so that 1 g reactivating agent/g carbon was applied every 10 min. For reactivation by steam, deionized-distilled water was injected into the furnace from the bottom at 0.674 mL/min (liquid flow rate) for about 0.67 g carbon sample. Steam was created once the water entered the heated part of the TGA furnace. CO₂ or NH₃ were introduced through the furnace gas port into the TGA furnace. Thermally regenerated samples were coded by T, for thermal regeneration, plus regeneration temperature and regeneration reagent, where C stands for regeneration by CO₂, S stands for steam and N stands for NH₃. For example, T600S stands for thermal regeneration at 600°C by steam. Samples labeled with the
suffix 20 indicate those samples were regenerated for 20 min instead of the 10 min that was applied for all the other samples.

3.2.6 Full-Scale Chemical Regeneration in Texas Street Water Treatment Plant

Texas Street water treatment plant in City of Redlands, CA has 24 GAC contactors. They were initially installed to remove trichloroethylene (TCE) and dibromochloropropane (DBCP) from groundwater. Each vessel contains about 20,000 pounds of GAC, and each vessel was designed to provide a 40-min empty bed contact time (EBCT) at 4.3 MGD, or 30 minutes EBCT at 6.5 MGD, or 20 minutes EBCT at 8.6 MGD. At any given time during water treatment, 12 of these GAC vessels have been in the “lead” mode, and 12 have been in “follow” mode. As conventionally operated for TCE and DBCP removal, when the organic contaminants penetrated half way through the “follow” vessel, the “lead” vessel was taken out of service, and it was thermally reactivated. Then, this “follow” vessel became the new “lead” vessel.

The Texas Street plant has been treating water from Well 31-A. This groundwater originates from within the Crafton-Redlands plume area; and in addition to the TCE and DBCP, this groundwater also contains 62-138 ppb perchlorate. Once perchlorate was detected in this well, the Texas Street plant was shut down.

The Penn State-Redlands team embarked on a full-scale testing program during the summer and fall of 2000. These employed both a virgin Westate GAC and an Iron-oxalic acid pre-tailored GAC. These beds treated Texas Street well water that contained 60-80 ppb perchlorate, until the beds were exhausted in their capacity to adsorb perchlorate. Each of the two test beds contained of about 5000 gallons of GAC and they were operated at an empty bed contact time of 20 min. These tests have been called “full-scale” tests even though each test condition employed only one GAC bed, whereas true full-scale operations would employ two GAC beds in series. In iron and oxalic acid pre-tailoring, a mixture of 500 mg/L ferric chloride (as iron) and 580-mg/L oxalic acid was circulated through Westate GAC for several days. The Non-Tailored (virgin) GAC exhibited initial breakthrough of perchlorate at 1000 BV and 80% breakthrough after
2200 BV; while the Iron-OA pre-tailored GAC exhibited initial breakthrough of perchlorate at 1200 BV and 80% breakthrough after 2500 BV.

In the summer of 2001, full-scale chemical regeneration tests were conducted using the base/acid method for two perchlorate-exhausted carbon beds. Base solution here was perchlorate-free Redlands utility water adjusted to pH around 11-12 by NaOH (50% by weight) solution. Acid solution was the same water adjusted to pH around 2 by hydrochloric acid (36.5~38% by weight). The flow rate was set at 150 gpm. Samples were taken from 4 sampling ports located at 25%, 50%, 75% and 100% of the depth of the carbon bed. Those samples were monitored for perchlorate and pH. Following the chemical regeneration, the carbon bed was tested for its perchlorate removal capacity.
CHAPTER 4
ACTIVATED CARBON TAILORING

4.1 SMALL AND FULL-SCALE COLUMN TEST OF NON-TAILORED
ACTIVATED CARBON FOR PERCHLORATE REMOVAL

The RSSCT perchlorate breakthrough behavior for virgin SAI and Westates GAC has been compared to full-scale response in Figure 4.1. The full-scale trials were conducted in Texas Street Water Treatment Plant, City of Redlands, CA, and employed a US mesh 12×40 (1700-360 µm) bituminous GAC (Westates) (Na et al. 2002). As observed from Figure 4.1, virgin SAI and Westates carbon (both bituminous carbon) showed very similar perchlorate breakthrough profile in RSSCT. When compared with full-scale operation, the perchlorate breakthrough occurred at about 1,100 bed volumes for both the RSSCTs and full-scale conditions.

The 1,100 BV that virgin GAC could remove perchlorate translated to a 6-week operation during the summer of 2001 when Redlands treated their perchlorate-impacted groundwater and purveyed this water to their customers as an interim solution to a summer water shortage. This operation time was too short for economical routine practice. Thus, the research team has sought means of tailoring the GAC so as to increase its adsorption capacity for perchlorate.

The water temperatures in the RSSCT at Penn State were 20-25°C, and the water temperature in full-scale tests at Redlands were 22-28°C. Thus, the temperatures were consistent with one another. The slope of the RSSCT breakthrough curves were steeper than for the full-scale bed, and this occurred here and in other RSSCTs because of the inherent limitations that go into the similitude equation as pertains to the Reynold’s number for the small-scale columns. Specifically, the Reynolds number for the RSSCT was taken to be 0.13 so as to render the similitude equations to be mathematically solvable (as is the standard routine), whereas actual Reynolds number in the RSSCT columns was lower than this.
4.2 OXIDATION BY NITRIC ACID AND PYROLYSIS BY N₂

As shown by both small and full-scale tests, conventional activated carbon had very limited adsorption capacity for perchlorate. One way to enhance carbon’s adsorption capacity for perchlorate is to modify the physical and/or chemical specifics of carbon surface and make it more effective for perchlorate removal. A crucial first step in developing a process in carbon tailoring is to identify the properties that most strongly influence perchlorate uptake. Therefore, the first objective in our research was to clarify which physical and chemical properties are most desirable for improving perchlorate adsorption capacity. A series of commercially available GACs made from a variety of raw materials were investigated for their perchlorate adsorption capabilities.

It was well established that oxidation and pyrolysis in inert atmosphere are effective ways to change chemical characteristics (Considine et al. 2001; Haghseresht et al. 2003; Pereira et al. 2003). One of the commercially available carbons, SAI Carbon, was treated with nitric acid or pyrolyzed in N₂ to temperature as high as 1000°C. It was expected that carbon would obtain different surface chemistry after those treatments. Our goal was to interpret and understand the interactions between perchlorate and the activated carbon surfaces.

Table 4.1 is the physical properties (surface area, pore volume) of those carbons while table 4.2 lists some of their chemical properties (acidity, basicity, oxygen content, pHpzc, surface charge) and perchlorate adsorption capacities represented by bed volume to 4 ppb perchlorate breakthrough in small column tests.
### Table 4.1
Physical properties of the activated carbon samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Micropore (&lt;20 Å) volume (mL/g)</th>
<th>Mesopore (20-500 Å) volume (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAI</td>
<td>874</td>
<td>0.252</td>
<td>0.055</td>
</tr>
<tr>
<td>SOX0.01</td>
<td>880</td>
<td>0.254</td>
<td>0.057</td>
</tr>
<tr>
<td>SOX0.1</td>
<td>868</td>
<td>0.249</td>
<td>0.064</td>
</tr>
<tr>
<td>SOX1</td>
<td>829</td>
<td>0.248</td>
<td>0.068</td>
</tr>
<tr>
<td>SOX6</td>
<td>768</td>
<td>0.231</td>
<td>0.061</td>
</tr>
<tr>
<td>N700</td>
<td>870</td>
<td>0.331</td>
<td>0.075</td>
</tr>
<tr>
<td>N1000</td>
<td>841</td>
<td>0.321</td>
<td>0.084</td>
</tr>
<tr>
<td>Filtrasorb 400</td>
<td>969</td>
<td>0.307</td>
<td>0.108</td>
</tr>
<tr>
<td>Filtrasorb 600</td>
<td>718</td>
<td>0.287</td>
<td>0.035</td>
</tr>
<tr>
<td>Centaur</td>
<td>805</td>
<td>0.306</td>
<td>0.032</td>
</tr>
</tbody>
</table>

### Table 4.2
Chemical properties of the activated carbon samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acidity (mmol/g)</th>
<th>Basicity (mmol/g)</th>
<th>O (%)</th>
<th>pHpzc</th>
<th>Surface charge at pH 7.5 (meq/g)</th>
<th>Bed volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAI</td>
<td>0.34</td>
<td>0.24</td>
<td>8.82</td>
<td>8.35</td>
<td>0.045</td>
<td>1100</td>
</tr>
<tr>
<td>SOX0.01</td>
<td>0.43</td>
<td>0.18</td>
<td>12.2</td>
<td>6.21</td>
<td>-0.003</td>
<td>1020</td>
</tr>
<tr>
<td>SOX0.1</td>
<td>0.62</td>
<td>0.12</td>
<td>13.17</td>
<td>5.62</td>
<td>-0.018</td>
<td>900</td>
</tr>
<tr>
<td>SOX1</td>
<td>0.83</td>
<td>0.10</td>
<td>14.43</td>
<td>3.30</td>
<td>-0.023</td>
<td>560</td>
</tr>
<tr>
<td>SOX6</td>
<td>1.16</td>
<td>0.05</td>
<td>17.77</td>
<td>2.52</td>
<td>-0.028</td>
<td>60</td>
</tr>
<tr>
<td>N700</td>
<td>0.15</td>
<td>0.28</td>
<td>5.04</td>
<td>9.50</td>
<td>0.056</td>
<td>1600</td>
</tr>
<tr>
<td>N1000</td>
<td>0.08</td>
<td>0.35</td>
<td>5.14</td>
<td>9.50</td>
<td>0.067</td>
<td>2460</td>
</tr>
<tr>
<td>Filtrasorb 400</td>
<td>0.37</td>
<td>0.28</td>
<td>6.84</td>
<td>9.48</td>
<td>0.067</td>
<td>1300</td>
</tr>
<tr>
<td>Filtrasorb 600</td>
<td>0.30</td>
<td>0.32</td>
<td>3.25</td>
<td>10.27</td>
<td>0.087</td>
<td>2300</td>
</tr>
<tr>
<td>Centaur</td>
<td>0.27</td>
<td>0.28</td>
<td>4.74</td>
<td>10.01</td>
<td>0.085</td>
<td>1500</td>
</tr>
</tbody>
</table>
It was observed that oxidation by nitric acid (samples marked by SOX plus the nitric acid concentration) at concentration between 0.01 and 0.1 N altered the surface chemistry of the carbon without any significant effect on pore structure and surface area. Both the surface area, micro- and meso-pore volumes of SOX0.01 and SOX0.1 were similar to those of SAI carbon. For carbons treated at nitric acid concentration of 1 and 6 N, there were small decreases in surface area and micropore volume while the mesopore volume increased. It was believed that nitric acid at those concentrations (1 and 6 N) led to the collapse of some micropore walls, which resulted in micropores converted into mesopores thus decrease in micropore volume and increase in mesopores volume (Pereira et al. 2003). As far as chemical properties were concerned (Table 4.2), all nitric acid treated samples had apparent increases in acidity, oxygen content and decrease in basicity. Changes in surface chemistry resulted in decrease in pHpzc and positive surface charge. pHpzc for SAI carbon was 8.35 while it dropped to 5.62 for SOX0.1 and further to 2.52 for SOX6. Carbon surface was positively charged at pH 7.5 for SAI carbon with a positive charge 0.045 meq/g while all oxidized carbons presented negative surface charge at pH 7.5. pH 7.5 was the average pH value of target water (Redlands groundwater) in this research. When nitric acid oxidized samples were tested for perchlorate removal in RSSCT, they showed sharp decrease in bed volume to breakthrough as shown in Table 4.2. SAI carbon could operate 1100 bed volume without detectable perchlorate in effluent. The number dropped to 900 for SOX1. For SOX6, only 60 bed volumes of water were passed through before perchlorate breakthrough. Taking SAI, SOX0.01 and SOX0.1 as an example, as mentioned earlier, no significant changes took place in surface area and pore volumes after the nitric acid oxidation, and the only obvious change is in surface chemistry. Carbon SOX0.01 and SOX0.1 had higher acidity, oxygen content and lower basicity. They also had much lower adsorption capacity for perchlorate based on the bed volume that could operate before perchlorate breakthrough. It appears that physical properties (surface area, pore volume) were similar, perchlorate adsorption decreased with increase in acidity and oxygen content.

Contrary to nitric acid oxidation, pyrolysis in nitrogen atmosphere produced material with the highest basic character. As shown in Table 4.2, pyrolysis increased carbon’s basicity from 0.24 mmol/g for SAI sample to 0.35 mmol/g for N1000. Oxygen
content decreased from 8.82% to 5.14% after SAI carbon was treated in nitrogen for 1 h at 1000°C. In addition, there was decrease in acidity after the pyrolysis process. The carbons obtained more positive surface charge at pH 7.5. pHpzc also increased after the pyrolysis. Condine et al. (2001) revealed that most of the acidic oxygen surface groups should have been removed at temperature higher than 700°C. It was not surprising to find that N1000 had much less acidity and oxygen content than N700. Carbon sample after heat treatment showed decrease in surface area and micropore volume. It was possible that pyrolysis in N₂ caused some micropores to break down and those pores changed into bigger ones as occurred in nitric acid oxidation. The pyrolyzed carbons showed improvement in perchlorate removal. Since there were actually decreases in surface area and micropores after this treatment, the enhancement in perchlorate adsorption capacity was apparently caused by change in surface chemistry.

Besides SAI carbon, several other commercial available carbons with an array of raw materials (section 3.1.1) were also investigated. When three Calgon carbons were compared with SAI carbon, sample Filtrasorb 600 had the best perchlorate adsorption capacity as represented by the bed volume to breakthrough listed in Table 4.2. It achieved a bed volume to perchlorate breakthrough about 2300 as compared with that of 1100 for SAI carbon. However, this carbon had much less surface area and micropore volume than SAI or Filtrasorb 400 and Centaur carbon. It further proved that perchlorate adsorption capacity was not directly linked with physical properties of the carbon surface. It tends to be more related to surface chemistry. Although Filtrasorb 600 had less surface area and micropore volume, it hosted higher basicity and obtained higher positive surface charge at the pH studied.

Overall, it is safe to draw the conclusion that increase in positive surface charge, or carbon basicity may help improve the perchlorate adsorption capacity. Therefore, carbon modification that could increase surface basicity was surely an option to enhance the adsorption capacity for perchlorate. Pyrolysis in nitrogen has shown to be capable of produce basic carbon. But as indicated in Table 4.2, pyrolysis in N₂ for 1 h at 1000°C under nitrogen was only able to double the bed volume performed till breakthrough. Another tailoring method, NH₃ tailoring was investigated next.
4.3 THERMOCHEMICAL TAILORING BY NH₃

4.3.1 Carbon Mass Change during NH₃ Treatment

During NH₃ treatment, a carbon sample was placed in a TGA and kept in a N₂ atmosphere when the furnace was heated to reach a desired tailoring temperature. A slight decrease in carbon mass was observed during this stage. In total, 5.5-6.5% of the initial mass was lost via pyrolysis when the furnace was being heated to 500-800°C. The mass changes during N₂ pyrolysis and ammonia thermal treatment have been presented in Figure 4.2. The differences in mass change between duplicates under the same tailoring conditions were within 5% of one another. Thermal treatment in NH₃ caused increase in carbon mass. All carbons had reached a steady state level of mass gain within 60 minutes of ammonia treatment. This is with the exception of carbons that were treated at 800°C; which gradually lost mass at NH₃ treatment time that exceeded 60 minutes. This mass loss is consistent with the mass loss rate that has been observed when hydrogasification causes the release of methane (CH₄). For example, Cannon et al. (1997) observed a 2% mass loss after 60 min of hydrogasification at 850°C.

The TGA data (Figure 4.2) indicates that within 60 minutes of NH₃ treatment, most of the activated carbon’s reactive sites that could react with ammonia’s thermal species had already undergone such a reaction, and no further reaction occurred after 60 minutes that caused a mass gain. For temperatures of 600-700°C, mass gain amounted to 6.5-8.0% during the 60 min of ammonia treatment. In intriguing contrast, the 800°C samples only gained 2.5% mass; while the 500°C samples gained 4.0%.

Overall, at temperatures between 600 and 700°C, mass gains due to reactions with NH₃ were slightly greater than mass loss during pyrolysis, and thus the net mass increased after tailoring. There was a net mass loss at 500 and 800°C.

It has been reported that oxygen-containing surface groups such as carboxyls or lactones are not thermally stable, and they start to decompose at temperatures as low as 300°C. Phenol or quinone-like structures are more stable and evolve as CO at temperature >500°C (Bansal et al. 1988, Otake and Jenkins 1993). These releases
represent an important fraction of the mass loss during the pyrolysis stage in the ammonia tailoring process. That is, in the nitrogen atmosphere, less stable oxygen-containing surface functional groups evolved as CO$_2$ or CO at elevated temperatures. As the results indicate, the higher the target temperature, the higher the mass loss during the heating (pyrolysis) stage. Suarez et al (1999) also reported that an important consequence of CO and CO$_2$ evolution in an inert thermal environment is the creation of highly reactive edge sites that contain unpaired electrons. The observed increase in mass loss during N$_2$ pyrolysis with the increase of temperature is consistent with the literature that indicates that more reactive sites are created as temperatures rise from 500 to 800°C (Abotsi and Osseo-Asare, 1986; Biniak et al. 1997).

For the study herein, N$_2$ was switched to NH$_3$ immediately after the temperature reached a desired value, and the reactive sites thus created were an important fraction of the sites that subsequently reacted with NH$_3$ radicals. This deposition was depicted by increases in mass and in both hydrogen and nitrogen contents after tailoring. As a result, new nitrogen-containing surface functional groups were created on the carbon surface during this stage. Between 500 and 700°C, the net mass gain increased with the increase of temperature during the NH$_3$ tailoring and this indicated that more reactions between radicals from NH$_3$ decomposition and the carbon surface occurred at higher temperature.

The trend reversed at 800°C, where NH$_3$ treatment increased mass by only 2.5%. This was attributed to the higher hydro-gasification of the formerly created activated carbon edge atoms, and this diminished the mass while nitrogen-incorporation increased the mass (Cannon et al. 1997). The two concurrent phenomena incurred only a slight mass gain.

### 4.3.2 Pore Structure and Specific Surface Area

Table 4.3 lists the micropore volume and specific surface area of virgin (non-tailored) and NH$_3$-tailored carbons while Figure 4.3 shows their cumulative pore volume distribution. The differences in cumulative pore volumes for duplicates were within 3-4% of one another as manifested by the duplicate analysis for SAI-500-60 shown in Figure 4.3 as representative. The differences in surface area between duplicates were within 5-
8% of one another. Both surface area and pore volume showed a trend of increase with the increase of treatment temperature up to 700°C. It has been surmised that the radicals (NH₂, NH and atomic hydrogen) generated from NH₃ decomposition at high temperature would cause some gasification of the carbon material, and it also could have caused degradation of non-carbon impurities.

Table 4.3
Surface area and pore volume of virgin and ammonia-tailored samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Micropore (&lt;20 Å) volume (cm³/g)</th>
<th>Mesopore (20-500 Å) volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>874</td>
<td>0.252</td>
<td>0.055</td>
</tr>
<tr>
<td>SAI-500-30</td>
<td>854</td>
<td>0.271</td>
<td>0.064</td>
</tr>
<tr>
<td>SAI-500-60</td>
<td>861</td>
<td>0.273</td>
<td>0.067</td>
</tr>
<tr>
<td>SAI-500-150</td>
<td>864</td>
<td>0.270</td>
<td>0.064</td>
</tr>
<tr>
<td>SAI-600-30</td>
<td>904</td>
<td>0.301</td>
<td>0.068</td>
</tr>
<tr>
<td>SAI-600-60</td>
<td>890</td>
<td>0.321</td>
<td>0.071</td>
</tr>
<tr>
<td>SAI-600-150</td>
<td>919</td>
<td>0.314</td>
<td>0.073</td>
</tr>
<tr>
<td>SAI-650-30</td>
<td>905</td>
<td>0.324</td>
<td>0.071</td>
</tr>
<tr>
<td>SAI-650-60</td>
<td>906</td>
<td>0.332</td>
<td>0.075</td>
</tr>
<tr>
<td>SAI-650-150</td>
<td>945</td>
<td>0.327</td>
<td>0.072</td>
</tr>
<tr>
<td>SAI-700-30</td>
<td>984</td>
<td>0.330</td>
<td>0.078</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>940</td>
<td>0.334</td>
<td>0.078</td>
</tr>
<tr>
<td>SAI-700-150</td>
<td>976</td>
<td>0.332</td>
<td>0.076</td>
</tr>
<tr>
<td>SAI-800-30</td>
<td>926</td>
<td>0.320</td>
<td>0.074</td>
</tr>
<tr>
<td>SAI-800-60</td>
<td>925</td>
<td>0.321</td>
<td>0.075</td>
</tr>
<tr>
<td>SAI-800-150</td>
<td>893</td>
<td>0.317</td>
<td>0.074</td>
</tr>
</tbody>
</table>

In addition, pore volume distribution of both non-tailored and tailored carbons (Figure 4.3) indicated that the NH₃ tailoring created pores mostly between widths 5-30 Å. There was an increase in pore volume in this pore range while only very small changes were observed in pores with width of 30-500 Å. More micropores were created at 600°C
than at 500°C, and the differences were less pronounced at temperatures above 600°C. The SAI-700-60 hosted the highest pore volume, but this was not statistically higher than SAI-650-60 or SAI-800-60. At the same time, treatment time from 30 to 150 min did show difference in mass change as shown in section 4.1.1. However, Statistics analysis of pore volume and surface area indicates that no significant difference was observed for treatment time at confidence level 95%.

4.3.3 Elemental Analysis

Elemental analysis results of virgin NH₃ tailored carbons are shown in Table 4.4. The data revealed that reactions between the carbon surface and the radicals that were created via NH₃ decomposition increased the nitrogen and hydrogen contents. For instance, hydrogen content increased from 0.54% for virgin SAI to 0.79% for SAI-500-60, and nitrogen increased from 0.64% for virgin SAI to 1.62% for SAI-500-60. Overall, nitrogen contents ranged from 1.61-1.69% after ammonia tailoring. Statistical analysis of the nitrogen content indicated that the differences between virgin and all tailored carbons were significant to the 95% confidence interval for all temperatures. However, the differences between one tailored carbon and another were not significant to the 95% confidence interval. This means that NH₃ tailoring increased the nitrogen contents on the carbon surface when compared with virgin carbon while treatment temperature, whether it was 500 or 800°C, did not make a statistically significant difference in nitrogen content.

Oxygen content was around 8.8% for virgin SAI GAC, 7.3-8.7% for the carbons treated at from 500 to 800°C. Because of cumulative errors (when measuring oxygen by difference), the oxygen standard deviations were ±0.35 to 0.65 for these oxygen values. Changes in oxygen content were attributed to two factors: 1) loss of oxygen-containing surface functional groups as CO₂ or CO during elevated temperature treatments, and 2) chemisorption of oxygen back onto the carbon after it cooled down to ambient temperature. Although all tailored samples were kept in a vacuum desiccator between elemental analysis measurements, samples encountered some contact with air during the handling and analyzing process, which typically amounted to hours for any given sample. It has been reported that thermally treated carbon will take up oxygen from air or water,
and oxygen-containing surface functional groups are re-formed (Mendendez et al. 1996; Tessmer et al. 1997; Al-degs et al. 2000). Oxygen content thus obtained reflected what occurred during both thermal treatment and subsequent exposures to air. Oxygen contents thus usefully represent the oxygen contents of tailored carbon products since exposure to air would be unavoidable in practice.

Table 4.4
Elemental analysis of virgin and NH$_3$ tailored carbons
(after several hours exposure to air at ambient temperature)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>90.0±0.5</td>
<td>0.54±0.04</td>
<td>0.64±0.04</td>
<td>8.82±0.58</td>
</tr>
<tr>
<td>SAI-500-30</td>
<td>90.4±0.4</td>
<td>0.64±0.03</td>
<td>1.67±0.01</td>
<td>7.29±0.44</td>
</tr>
<tr>
<td>SAI-500-60</td>
<td>89.0±0.4</td>
<td>0.79±0.02</td>
<td>1.62±0.03</td>
<td>8.59±0.45</td>
</tr>
<tr>
<td>SAI-500-150</td>
<td>89.1±0.5</td>
<td>0.66±0.03</td>
<td>1.63±0.04</td>
<td>8.61±0.57</td>
</tr>
<tr>
<td>SAI-600-30</td>
<td>90.1±0.3</td>
<td>0.61±0.05</td>
<td>1.63±0.06</td>
<td>7.66±0.41</td>
</tr>
<tr>
<td>SAI-600-60</td>
<td>89.6±0.4</td>
<td>0.65±0.02</td>
<td>1.63±0.01</td>
<td>8.12±0.43</td>
</tr>
<tr>
<td>SAI-600-150</td>
<td>90.2±0.3</td>
<td>0.65±0.02</td>
<td>1.64±0.04</td>
<td>7.51±0.36</td>
</tr>
<tr>
<td>SAI-650-30</td>
<td>90.1±0.4</td>
<td>0.69±0.03</td>
<td>1.66±0.03</td>
<td>7.55±0.46</td>
</tr>
<tr>
<td>SAI-650-60</td>
<td>89.7±0.5</td>
<td>0.68±0.03</td>
<td>1.61±0.02</td>
<td>8.01±0.55</td>
</tr>
<tr>
<td>SAI-650-150</td>
<td>89.8±0.6</td>
<td>0.65±0.02</td>
<td>1.69±0.02</td>
<td>7.86±0.64</td>
</tr>
<tr>
<td>SAI-700-30</td>
<td>89.3±0.3</td>
<td>0.71±0.04</td>
<td>1.65±0.03</td>
<td>8.34±0.37</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>89.7±0.3</td>
<td>0.73±0.04</td>
<td>1.61±0.01</td>
<td>7.96±0.35</td>
</tr>
<tr>
<td>SAI-700-150</td>
<td>89.8±0.4</td>
<td>0.75±0.02</td>
<td>1.62±0.04</td>
<td>7.83±0.46</td>
</tr>
<tr>
<td>SAI-800-30</td>
<td>89.2±0.6</td>
<td>0.73±0.02</td>
<td>1.62±0.03</td>
<td>8.45±0.65</td>
</tr>
<tr>
<td>SAI-800-60</td>
<td>89.0±0.3</td>
<td>0.87±0.03</td>
<td>1.61±0.02</td>
<td>8.52±0.35</td>
</tr>
<tr>
<td>SAI-800-150</td>
<td>89.1±0.5</td>
<td>0.81±0.02</td>
<td>1.61±0.05</td>
<td>8.48±0.57</td>
</tr>
</tbody>
</table>
4.3.4 Surface Charge Distribution and pHpzc

Figure 4.4 show the surface charge distribution of carbon samples. Statistics analysis at confidence level 95% showed that treatment time was not a significant factor influencing the surface charge distribution. Therefore, only those treated for 60 min were shown here.

There was an increase in positive surface charge, compared with that of virgin SAI, in all tailored samples at near-neutral pHs encountered in our target water (pH 7.0-8.0, City of Redlands groundwater). At pH 7.5, the surface charge of virgin SAI was only about 0.045 meq/g GAC. Surface charge increased with increasing treatment temperature up to 0.094 meq/g at 700°C, and then back down to 0.072 meq/g at 800°C. With a standard deviation within ±0.008 meq/g GAC (Table 4.5), it is discerned that the surface charge at pH 7.5 for SAI-700-60 was truly higher than for the other thermal conditions.

Table 4.5 compares the slurry pH value to the pHpzc as determined by titration. As indicated in this table, slurry pH values were within experimental error range of the pHpzc values and followed the same trend; thus confirming the titration results. The advantage of using the slurry pH method was that it is much easier to conduct and was less demanding for equipment. However, slurry pH presents only one point as pHpzc; whereas the titration curve offers a range of surface charge data over a span of pH.
Table 4.5
pHpzc by titration, slurry pH and surface charge

<table>
<thead>
<tr>
<th>Sample</th>
<th>pHpzc by titration</th>
<th>Slurry pH</th>
<th>Surface charge at pH 7.5 (meq/g GAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>8.35±0.03</td>
<td>8.55±0.03</td>
<td>0.045±0.005</td>
</tr>
<tr>
<td>SAI-500-30</td>
<td>9.20±0.02</td>
<td>9.20±0.02</td>
<td>0.068±0.004</td>
</tr>
<tr>
<td>SAI-500-60</td>
<td>9.30±0.04</td>
<td>9.26±0.04</td>
<td>0.078±0.005</td>
</tr>
<tr>
<td>SAI-500-150</td>
<td>9.50±0.02</td>
<td>9.23±0.02</td>
<td>0.075±0.004</td>
</tr>
<tr>
<td>SAI-600-30</td>
<td>9.80±0.03</td>
<td>9.72±0.02</td>
<td>0.078±0.005</td>
</tr>
<tr>
<td>SAI-600-60</td>
<td>9.90±0.02</td>
<td>9.78±0.03</td>
<td>0.085±0.005</td>
</tr>
<tr>
<td>SAI-600-150</td>
<td>9.90±0.01</td>
<td>10.23±0.04</td>
<td>0.084±0.006</td>
</tr>
<tr>
<td>SAI-650-30</td>
<td>9.50±0.03</td>
<td>9.77±0.02</td>
<td>0.084±0.008</td>
</tr>
<tr>
<td>SAI-650-60</td>
<td>9.89±0.03</td>
<td>9.86±0.02</td>
<td>0.087±0.005</td>
</tr>
<tr>
<td>SAI-650-150</td>
<td>9.90±0.04</td>
<td>10.00±0.02</td>
<td>0.087±0.007</td>
</tr>
<tr>
<td>SAI-700-30</td>
<td>9.40±0.04</td>
<td>9.42±0.03</td>
<td>0.092±0.006</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>9.95±0.04</td>
<td>9.90±0.04</td>
<td>0.094±0.005</td>
</tr>
<tr>
<td>SAI-700-150</td>
<td>9.90±0.02</td>
<td>9.83±0.04</td>
<td>0.097±0.005</td>
</tr>
<tr>
<td>SAI-800-30</td>
<td>9.84±0.04</td>
<td>9.66±0.04</td>
<td>0.085±0.004</td>
</tr>
<tr>
<td>SAI-800-60</td>
<td>9.90±0.03</td>
<td>9.86±0.04</td>
<td>0.072±0.005</td>
</tr>
<tr>
<td>SAI-800-150</td>
<td>9.85±0.04</td>
<td>9.86±0.03</td>
<td>0.074±0.003</td>
</tr>
</tbody>
</table>

Results reported in Table 4.5 show an increase of pHpzc from 8.35 to 9.95 between virgin SAI and SAI-700-60. The pHpzc stayed at about 9.90 for samples treated at temperatures higher than 600°C. pHpzc and slurry pH had a general trend of increase with the increase of treatment time at temperatures between 500-700°C. For example, at temperature 650°C, SAI-650-30 had a pHpzc 9.50 while pHpzc was 9.89 ad 9.90 for SAI-650-60 and SAI-650-150 respectively. The exception occurred for samples treated at 800°C, SAI-800-30 had pHpzc 9.84 which increased to 9.90 for SAI-800-60 then it dropped to 9.85 for SAI-800-150. The same trend was shown in the mass change results.
800°C treated sample gained mass under NH₃ in the first 60 min, and mass loss was observed after that. The hydrogasification after 60 min by 800°C treatment which caused mass loss must have also changed the surface chemistry which resulted in the decrease in carbon basicity as manifested by decrease in pHpzc.

Although data in Figure 4.4 showed less positive charge density at 500 and 800°C compared to 600 and 700°C, elemental analysis (Table 4.4) shows that all the thermally treated samples contained similar nitrogen contents. Studies have shown that oxygen-containing groups are more likely to contribute negative surface charge at near-neutral pHs, and these functional groups can notably include carboxyls, which have pKa’s in the 2-5 pH range (Zeid et al. 1995; Thrower 1994). The lower surface charge at 500 and 800°C is attributed to either (a) the increased presence of oxygen containing functional groups; or (b) a distinction in the nature of nitrogen-containing speciation; or (c) both.

4.3.5 Zeta-potential/Electrophoretic Mobility

Figure 4.5 presents the zeta-potential distribution of carbon samples over the pH range from 5-11. The zeta potential represents the external surface charge of a particle as a function of pH; i.e. the surface charge that affects external particle mobility. The point where the curves cross the X-axis, at zero voltage, is taken as the isoelectric point (IEP) of the external surface. The external surface of a carbon particle will be positively charged at pH values below the pH_{IEP}. Results in Figure 4.5 also indicate that the thermal treatment in ammonia shifted the pH_{IEP} to basic pH values. This is considered to be a consequence of the change in surface functional groups after tailoring. The basic surface functional groups created by nitrogen-incorporation rendered the carbon more basic, and created a surface that was more positively charged at low pH. The highest increase of pH_{IEP} (see Figure 4.5) is about 1.8 pH units for SAI-700-60.

Table 4.6 also lists the pHpzc and pH_{IEP} and the difference between them. The pHpzc is 1.9 to 2.5 units higher than the pH_{IEP} for both the virgin and tailored GAC’s. This means that the chemisorption of oxygen back onto the carbon was considerably more extensive on the external portion of the GAC grains than on the internal portion.
Thus, the oxygen chemisorption phenomenon was a diffusion-limited process; i.e. it manifested itself as a “shrinking core” phenomenon.

An interesting relationship can be discerned by comparing the trends of the surface charge titration data to the trend of zeta potential data. The zeta potential exhibited net negative values over much of the pH range above 6.3-7.5, and this depicted the external potential of these carbons samples. In contrast, the surface charges exhibited net positive values over the pH range below 9.0-10.5, and this reflected the charge of both the internal and external surfaces. For examples, as shown in Figure 4.4, the surface charge for SAI-700-60 was 0 meq/g at pH 9.95, 0.08 meq/g at pH 7.6 and increased to 0.15 meq/g at pH 5.7. In comparison, Figure 4.5 shows that the external zeta potential of SAI-700-60 was -55 mV at pH around 10, was 0 at pH 7.7, and rose to 10 mV at pH 5.7. The surface area of the internal surfaces was considerably higher than that of the external surfaces. The comparison highlights the extent to which oxygen chemisorption following thermal treatment occurred most extensively on the exterior surface of the carbon grains.

From the results of pHpzc and pHiep, the pHpzc values were 1.8 to 2.5 units higher than the pHiep values. Menendez et al (1995) claimed that the difference (pHpzc-pHiep) reflects surface charge distribution, with values >0 corresponding to more negatively charged external than internal particle surfaces, and values close to zero corresponding to more homogeneous distribution of the surface charge. Similarly, it can be deduced that reactions between ammonia-treated carbons herein exhibited more positive internal charge for various temperatures since pHpzc-pHiep of all tailored samples were in the range of 1.8-2.5. SAI-800-60 showed the highest difference in pHpzc-pHiep compared with virgin SAI, and this was attributed to higher oxygen adsorption on the external particle surface subsequent to thermal treatment. Also, SAI-800-60 exhibited steepest titration slope in the pH 3-5 range indicating that the carbon contained more carboxyl groups.
Table 4.6

pHpzc and pH_{IEP}

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH_{pzc} by titration</th>
<th>pH_{IEP}</th>
<th>pH_{pzc}-pH_{IEP}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>8.35±0.03</td>
<td>6.10±0.02</td>
<td>2.25</td>
</tr>
<tr>
<td>SAI-500-30</td>
<td>9.20±0.02</td>
<td>7.35±0.04</td>
<td>1.85</td>
</tr>
<tr>
<td>SAI-500-60</td>
<td>9.30±0.04</td>
<td>7.44±0.03</td>
<td>1.86</td>
</tr>
<tr>
<td>SAI-500-150</td>
<td>9.50±0.02</td>
<td>7.56±0.02</td>
<td>1.94</td>
</tr>
<tr>
<td>SAI-600-30</td>
<td>9.80±0.03</td>
<td>7.41±0.02</td>
<td>2.39</td>
</tr>
<tr>
<td>SAI-600-60</td>
<td>9.90±0.02</td>
<td>7.45±0.02</td>
<td>2.45</td>
</tr>
<tr>
<td>SAI-600-150</td>
<td>9.90±0.01</td>
<td>7.48±0.03</td>
<td>2.42</td>
</tr>
<tr>
<td>SAI-650-30</td>
<td>9.50±0.03</td>
<td>7.52±0.02</td>
<td>1.98</td>
</tr>
<tr>
<td>SAI-650-60</td>
<td>9.89±0.03</td>
<td>7.56±0.01</td>
<td>2.33</td>
</tr>
<tr>
<td>SAI-650-150</td>
<td>9.90±0.04</td>
<td>7.54±0.04</td>
<td>2.36</td>
</tr>
<tr>
<td>SAI-700-30</td>
<td>9.40±0.04</td>
<td>7.67±0.02</td>
<td>1.73</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>9.95±0.04</td>
<td>7.70±0.02</td>
<td>2.25</td>
</tr>
<tr>
<td>SAI-700-150</td>
<td>9.90±0.02</td>
<td>7.78±0.03</td>
<td>2.12</td>
</tr>
<tr>
<td>SAI-800-30</td>
<td>9.84±0.05</td>
<td>7.38±0.02</td>
<td>2.46</td>
</tr>
<tr>
<td>SAI-800-60</td>
<td>9.90±0.03</td>
<td>7.45±0.02</td>
<td>2.45</td>
</tr>
<tr>
<td>SAI-800-150</td>
<td>9.85±0.04</td>
<td>7.25±0.02</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Overall, NH₃ tailoring at the most favorable elevated temperatures (600-700°C) was able to create nitrogen-containing surface functional groups on the carbon surface as proven by the increase in nitrogen content of the tailored samples while increasing the surface area and micropore volume. The newly created surface functional groups also made the carbon surface more positively charged at the pHs encountered in our target water as shown both by the increase in surface charge density, pH_{pzc} and pH_{IEP} values.

Carbon surface chemistry data garnered by others who treated activated carbon with ammonia provide insight into the structures of surface groups. Jansen and van
Bekkum reported that the surface chemistry of activated carbons following amination (NH\textsubscript{3}) or ammonoxidation (50% NH\textsubscript{3}, 50% air) is dependent on treatment temperature.

Stohr and Boehm (1991) suggested reactions with NH\textsubscript{3} or its radicals at elevated temperatures (600-900°C). Carboxylic, hydroxyl and Ether-like oxygen react with NH\textsubscript{3} leading to amide, nitrile, amine and pyridine- or acridine-like nitrogen created on the carbon surface.

Virgin SAI carbon used in our research contained 8.8% in oxygen-content. Temperatures chosen during NH\textsubscript{3} tailoring were at the same range as those of Stohr and Boehm (1991). Steady decreases in mass were observed during the N\textsubscript{2} pyrolysis, which is in part attributed to gasification of oxygen-containing groups at elevated temperatures. It is, therefore, highly possible that similar conversion of surface groups occurred in the tailored carbons in our research.

Numerous authors have appraised the speciation of nitrogen that appears in coal-based and wood-based materials and several have appraised the nitrogen speciation when activated carbons have been thermally treated with ammonia (Stohr et al. 1991; Pels et al. 1995; Stanczyk et al. 1995; Xie et al. 2000). Studies thus far indicate that nitrogen appears progressively more in ring structures (which have more delocalized charge) as temperatures rise to 800°C or higher and the nitrogen appears more in attached substitute groups (such as amides and amines which have localized charge) as temperatures decline below 700°C. These distinctions may have played a role in the surface charge distribution and pH\textsubscript{pzc} values of ammonia-tailored carbons.

In summary, tailoring temperature plays a significant role in the tailoring process. At low temperature (<500°C), it appears that the carbon’s reaction with NH\textsubscript{3} was very limited as shown by the small increase in carbon mass in NH\textsubscript{3} atmosphere at 500°C. Tailoring at 600-700°C saw significant increases in carbon mass, while 800°C caused the highest mass loss.

Taking into account not only the mass change, but also the results in nitrogen content, specific surface area, pore volume distribution, surface charge distribution, we concluded that the optimum tailoring temperature is between 650 and 700°C. At this temperature range, the tailoring achieved the same or higher surface area, surface charge and pore volume when compared with those from other temperatures. The carbon tailored
at 700°C exhibited the most favorable positively charged surface at near neutral pH and this corresponded to a higher perchlorate adsorption as shown below.

### 4.3.6 RSSCT for Perchlorate Breakthrough

As shown in section 4.1.1, mass change during ammonia thermal treatment reached a plateau level after 60 minutes. As described at length above, mass change during ammonia thermal treatment reached a plateau level after 60 minutes, and nitrogen content ranged from 1.61-1.69% for carbons treated at all temperatures (500-800°C) and durations of time (30-150 min). Inspection of the data for surface area, pore volume, pHpzc and slurry pH reveals that the balance of these four parameters was somewhat more favorable after 60 minutes of ammonia thermal treatment than for other time duration. Thus, for representative comparison, only carbons that were tailored in ammonia for 60 minute were tested for their perchlorate adsorption behavior.

The perchlorate breakthrough profiles in rapid small-scale column tests of five NH₃ tailored and virgin (non-tailored) SAI carbon have been presented in Figure 4.6. As shown in the figure, the bed volumes of water treated till initial 4 ppb perchlorate breakthrough is 3,500 to 4,400 for the tailored carbons, compared to 1,100 for virgin SAI. The bed volumes to initial breakthrough reached 4,400 for SAI-700-60, which performed the best of all the tested carbons. This represented a 4-fold increase over the virgin SAI carbon. Overall, between 500 and 700°C, carbon bed life for perchlorate increased with increasing ammonia-tailoring temperature, and then declined at 800°C. Perchlorate breakthrough test for SAI-700-30 showed a smaller bed volume to breakthrough than SAI-700-60 while SAI-700-60 and SAI-700-150 had the similar adsorption capacity. This indicates that 60 min was enough; further treatment time had little or no effect on perchlorate adsorption capacity. The result was in consistence with the results from pore volume, surface area and surface charge, that is, 60 min treatment had the best combined effect on activated carbon for its perchlorate capability.

Figure 4.7 presents perchlorate breakthrough profiles for two of the tailored carbon samples (SAI-500-60 and SAI-700-60) that were each tested twice by the RSSCT
protocol to show their reproducibility. As indicated by Figure 4.7, the RSSCT results were quite reproducible with deviation between two runs of less than 1%.

Table 4.7 summarizes some of the physical and chemical characteristics for virgin SAI, carbons tailored for 60 min in ammonia and carbons pyrolyzed in N₂.

As a check to discern the significance of ammonia in this tailoring process, ammonia tailored carbon was compared with those pyrolyzed in N₂ for 60 min at temperatures of 700 and 1000°C. As shown in Table 4.7, there were only small differences between ammonia-tailored and nitrogen-pyrolyzed carbons relative to surface area and pore volume. Also, the pHpzc values were only slightly lower for nitrogen-pyrolyzed (pHpzc=9.50) than for ammonia-tailored carbons (pHpzc=9.89-9.95). The main differences between the carbons treated by N₂ pyrolysis and ammonia tailoring were in N-content, surface charge at pH 7.5 and the bed volume till 4 ppb perchlorate breakthrough. The N700 and N1000 carbons had no increase in nitrogen content whereas ammonia-tailoring increased nitrogen content to 1.61-1.63% after 60 min treatment. Also, N₂ exposure incurred only a slight increase in surface charge (to 0.056-0.067 meq/g carbon from 0.045meq/g for the virgin SAI carbon). In comparison, ammonia treatment doubled the positive surface charge (to 0.08-0.094 meq/g carbon). It is noted that a number of papers have shown that N₂ treatment at 700-1000°C will remove oxygenated functionality from a carbon surface. However, the N₂-pyrolyzed surface can become re-oxygenated following ambient exposure to oxygen (Dandekear et al. 1998; Figueiredo et al. 1999; Nowak et al. 2004). The increase in positive surface charge was mainly due to the elimination of acidic oxygen-containing functional groups. It appears that the ammonia tailoring process was able to create carbon with a greater positive surface charge by creating nitrogen-containing surface groups, and this was not the case following mere N₂ pyrolysis.
Table 4.7
Physical and chemical characteristics for virgin SAI, ammonia-tailored carbons and nitrogen-pyrolyzed carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Micropore volume (cm$^3$/g)</th>
<th>Mesopore volume (cm$^3$/g)</th>
<th>N (wt%)</th>
<th>pHpzc</th>
<th>Surface charge at pH 7.5 (meq/g)</th>
<th>Bed volume to 4 ppb perchlorate breakthrough</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>874</td>
<td>0.252</td>
<td>0.055</td>
<td>0.64</td>
<td>8.35</td>
<td>0.045</td>
<td>1100</td>
</tr>
<tr>
<td>SAI-500-60</td>
<td>861</td>
<td>0.273</td>
<td>0.067</td>
<td>1.62</td>
<td>9.30</td>
<td>0.078</td>
<td>3750</td>
</tr>
<tr>
<td>SAI-600-60</td>
<td>890</td>
<td>0.321</td>
<td>0.071</td>
<td>1.63</td>
<td>9.90</td>
<td>0.085</td>
<td>4130</td>
</tr>
<tr>
<td>SAI-650-60</td>
<td>906</td>
<td>0.332</td>
<td>0.075</td>
<td>1.61</td>
<td>9.89</td>
<td>0.087</td>
<td>4380</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>940</td>
<td>0.334</td>
<td>0.078</td>
<td>1.61</td>
<td>9.95</td>
<td>0.094</td>
<td>4390</td>
</tr>
<tr>
<td>SAI-800-60</td>
<td>925</td>
<td>0.321</td>
<td>0.075</td>
<td>1.61</td>
<td>9.90</td>
<td>0.072</td>
<td>3510</td>
</tr>
<tr>
<td>N700</td>
<td>870</td>
<td>0.331</td>
<td>0.075</td>
<td>0.67</td>
<td>9.50</td>
<td>0.056</td>
<td>1600</td>
</tr>
<tr>
<td>N1000</td>
<td>841</td>
<td>0.321</td>
<td>0.084</td>
<td>0.64</td>
<td>9.50</td>
<td>0.067</td>
<td>2460</td>
</tr>
</tbody>
</table>

In addition, statistical analysis indicates that there is significant correlation between bed volume to initial breakthrough versus positive surface charge ($R^2=0.956$) as shown in Figure 4.8. The higher the positive surface charge, the higher the bed volume to perchlorate breakthrough. Surface charge at pH 7.5 was tabulated herein since the perchlorate-containing Redlands water had a pH between 7 and 8.

Table 4.8 lists correlation coefficients for several physical-chemical features of the carbons versus bed volumes to 4 ppb perchlorate breakthrough. These correlations include virgin, nitrogen-pyrolyzed and ammonia-tailored carbons. It shows that correlations between bed volumes versus carbon surface area, micropore volume, mesopore volume of tailored carbons were all below 0.35, indicating negligible correlation.
Table 4.8

Correlation coefficient ($R^2$) between physical-chemical features listed and bed volume till 4 ppb perchlorate breakthrough for virgin SAI, ammonia-tailored and nitrogen pyrolyzed carbons (p-value< 0.05)

<table>
<thead>
<tr>
<th>Feature</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>0.345</td>
</tr>
<tr>
<td>Micropore volume (&lt;20 Å)</td>
<td>0.215</td>
</tr>
<tr>
<td>Mesopore volume (20-500 Å)</td>
<td>0.151</td>
</tr>
<tr>
<td>Surface charge</td>
<td>0.956</td>
</tr>
</tbody>
</table>

Elemental analysis indicates that oxygen content of ammonia-tailored carbons was in 7.3-8.6% range at the time of analysis (section 4.3.3). It was noted that some of the GAC’s oxygen contents did not remain at a stable level, and for the ammonia-tailored carbons, their oxygen content possibly could rise up to 0.5% over time. When adsorbing negatively charged species such as perchlorate, it is important to create an activated carbon that will not chemisorb oxygen, because the oxygenated functional groups (such as carboxyls or lactone) could repel the perchlorate. During bench-scale testing or full-scale operations, oxygen could readсорb either out of the air during GAC storage, or out of the water undergoing treatment that contains dissolved oxygen.

In this light, the authors herein sought to determine whether the nature of ammonia tailoring affected the extent to which oxygen could be adsorbed. Figure 4.9 is the oxygen re-adsorption results for ammonia-tailored carbons. The resultant oxygen adsorption profiles (Figure 4.9) indicate that oxygen adsorption increased with increasing temperature of ammonia tailoring. For duplicate experiments, mass gain (mass of oxygen-readsorption) values were within 1-3% of each other. After 240 minutes, the SAI-500-60 adsorbed 500 µg oxygen/g of GAC, while the SAI-700-60 adsorbed 1,800 µg/g (i.e. 0.18% mass), and the SAI-800-60 adsorbed 2,400 µg/g (i.e. 0.24% mass). On the basis of these results, one discerns that the SAI-700-60 was more stable relative to oxygen readsoption than was SAI-800-60, and the authors propose that this
characteristic contributed to the higher perchlorate removal performance of the SAI-700-60, when compared to the SAI-800-60.

In comparison to these oxygen readorption values, the Penn State team also monitored oxygen readsoption for a lignite based activated carbon that was pyrolyzed in nitrogen at 850°C, and then experienced oxygen adsorption at 105°C, via the same protocol as above (Nowack et al. 2004). In this case, the nitrogen-pyrolyzed carbon adsorbed 5,000 µg /g within 60 minutes and 6,500 µg /g (0.65% mass) within 240 minutes. Thus, ammonia-tailoring created a more stable surface than did nitrogen pyrolysis, relative to readsorbing oxygen.

4.3.7 Aqueous-Phase Nitrate Adsorption

Besides perchlorate, the nitrate concentration in water was also monitored during the RSSCT experiments. The Redlands water contained 7-8 mg/L nitrate as N. For virgin SAI carbon, during the whole small column operation period, effluent nitrate concentration was between 5.5-6.5 mg/L as N while effluent nitrate concentration for tailored carbons ranged from 3.0-5.0 mg/L as N. It appeared that the ammonia tailoring process improved perchlorate adsorption capacity without damaging its capacity for other anions.

4.3.8 Equilibrium Adsorption of perchlorate

Adsorption isotherms of perchlorate onto both ammonia-tailored and non-tailored carbons are displayed in Figure 4.10. These tests employed deionized distilled water which was spiked with 2 mg/L of perchlorate. Each data point represents the average of two experiments, and the C_e values for these were within 4% of each other. It was observed that adsorption capacity reaches an equilibrium value beyond which there was a negligible change in the residue perchlorate concentration (Figure 4.10). The distribution of perchlorate between liquid phase and the solid adsorbent phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the most popular isotherm models. The equilibrium data was fitted to Freundlich in the linear
form. The plot for model fitting is shown in Figure 4.11. The isotherm fitted well with a correlation coefficient ranged from 0.94-0.97.

Table 4.9 lists the Freundlich constant (K) and the exponent (1/n) for these carbons, relative to the expression $q_e = kC_e^{1/n}$. This table also lists the adsorbed perchlorate loading ($q_e$) that corresponded to equilibrium perchlorate concentration ($C_e$) of 4 and 70 ppb. At a $C_e$ of 4 ppb perchlorate, the SAI-700-60 achieved a perchlorate loading ($q_e$) of 2.4 mg/g, whereas the virgin SAI carbon adsorbed 1.5 mg/g. SAI-600-60, SAI-700-60 and SAI-800-60 had $q_e$ values (at $C_e$ 4 and 70 ppb) that are statistically distinct from that of virgin SAI carbon.

The K’s for these perchlorate isotherms ranged from 17 to 28 (mg/g)(L/mg)$^{1/n}$. K for virgin SAI was the lowest and SAI-700-60 had the highest K. The 1/n values ranged from 0.4 to 0.5 for all carbons. These K values reflect a low-to-moderate adsorption when compared to K’s for organic compounds. In comparison, Snoeyink and Summers (1999) lists values of 17-28 (mg/g)(L/mg)$^{1/n}$ for adsorption onto conventional activated carbon of such compounds as methyl ethyl ketone, phenol, bromodichloromethane and 1,3 dichloropropane.
Table 4.9

Freundlich isotherm parameters for perchlorate adsorption

(distilled-deionized water spiked with 2 mg/L of perchlorate)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Virgin SAI</th>
<th>SAI-500-60</th>
<th>SAI-600-60</th>
<th>SAI-700-60</th>
<th>SAI-800-60</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K (mg/g)/(mg/L)^1/n</strong></td>
<td>17.41</td>
<td>20.05</td>
<td>27.20</td>
<td>27.40</td>
<td>24.42</td>
</tr>
<tr>
<td><strong>1/n</strong></td>
<td>0.40</td>
<td>0.43</td>
<td>0.45</td>
<td>0.49</td>
<td>0.42</td>
</tr>
<tr>
<td>q_e (mg/g) at C_e=4 ppb</td>
<td>1.51±0.08</td>
<td>1.50±0.05</td>
<td>1.90±0.05</td>
<td>2.40±0.06</td>
<td>2.42±0.05</td>
</tr>
<tr>
<td>q_e (mg/g) at C_e= 70 ppb</td>
<td>7.25±0.11</td>
<td>7.41±0.12</td>
<td>7.94±0.12</td>
<td>8.94±0.09</td>
<td>8.96±0.16</td>
</tr>
<tr>
<td>Perchlorate adsorption at per mol N at C_e=70 ppb in isotherm test (meq perchlorate/mol N)</td>
<td>278±10</td>
<td>630±9</td>
<td>658±11</td>
<td>776±8</td>
<td>768±9</td>
</tr>
<tr>
<td>Perchlorate adsorption at per mol N at 70 ppb breakthrough in RSSCT (meq perchlorate/mol N)</td>
<td>40.5±1.4</td>
<td>70.4±1.2</td>
<td>99.5±5.4</td>
<td>104.8 ±3.2</td>
<td>67.4±2.3</td>
</tr>
</tbody>
</table>

The isotherm tests employed deionized-distilled water, and it has been recognized that the perchlorate adsorption capacity is lower than this when it competes with NOM or other anions. As a reflection of the relative perchlorate adsorption while using deionized-distilled water, when the C_e was 70 ppb, the ammonia-tailored carbons adsorbed 7.3-9.0 mg ClO_4^-/g carbon, and this amounted to 630-780 meq ClO_4^-/mol N within the GAC (Table 4.9). In contrast, when ammonia-tailored carbons removed perchlorate during RSSCT from Redlands water that contained NOM and competing anions, the carbons at full breakthrough (effluent perchlorate concentration 70 ppb) adsorbed 0.8-1.2 ClO_4^-/mg/g GAC, and this amounted to about 70-105 meq ClO_4^-/mol N (Table 4.9) within the GAC.
These RSSCT values were about an order of magnitude lower than for the isotherm in deionized-distilled water.

The nitrogen that was incorporated into the activated carbon during ammonia-tailoring exhibited a greater propensity to adsorb perchlorate than did the nitrogen that was native within the activated carbon structure. For example, during the RSSCT experiments, the virgin SAI removed 40 meq ClO$_4^-$/mol N, while the SAI-700-60 removed 105 meq ClO$_4^-$/mol N.

The trends regarding perchlorate removal were the same for the RSSCT and isotherm tests. However, the RSSCT results revealed a greater difference among GACs than did the isotherms. The RSSCT results revealed a 4-fold increase in bed volumes; with 4,400 bed volumes to 4 ppb perchlorate breakthrough for the SAI-700-60 versus 1,100 bed volumes for virgin SAI. In contrast, the isotherm tests showed only a 60% improvement in $q_e$ (at $C_e=4$ ppb) for SAI-700-60 as compared to virgin SAI. The difference in the magnitudes of comparison could be in part attributed to the differences in initial concentration and effects of competition.

In the isotherm tests, the initial perchlorate concentration was spiked up to 2000 ppb in deionized-distilled water, whereas the RSSCT employed natural Redlands water that contained 70-78 ppb perchlorate plus other competing anions. The differences in perchlorate performance were greater when natural water was employed in the RSSCTs and these results highlight the finding that the ammonia-tailoring created functional groups that were selective for perchlorate adsorption.

4.3.9 Kinetics of Adsorption

The batch kinetics of perchlorate adsorption by the tailored GACs is presented in Figure 4.12. These experiments were conducted with Redlands water that contained 70-78 ppb perchlorate, 330 µS of conductivity and 2.4-2.6 mg/L TOC.

The tailored GAC’s achieved considerably higher perchlorate removal than did the virgin SAI. For virgin SAI, most perchlorate adsorption occurred during the first 10 minutes, and perchlorate adsorption capacity was very limited. After a contact time of 60 min, only about 13% of perchlorate was adsorbed. The tailored carbons, however,
adsorbed 22-27% of perchlorate after 60 min. Perchlorate adsorption reached pseudo-equilibrium after 60 min, and not much more decline in perchlorate was observed for a contact time >60 min. The highest perchlorate removal occurred with sample SAI-700-60, which removed 27%. Overall, virgin SAI, after 180 min, adsorbed 0.36 mg ClO$_4^-$/g GAC, whereas SAI-700-60 adsorbed more than twice that, 0.75 ClO$_4^-$/g GAC. This value is quite close to the 1.2 mg ClO$_4^-$/g GAC that was computed for RSSCT’s of Redlands water with SAI-700-60. These two values in natural water were an order of magnitude lower than the 7.3-9.0 mg ClO$_4^-$/g GAC adsorption from deionized-distilled water that was shown in Figure 4.10 for C$_e$=70 ppb. The disparity reflects differences occurring when using lower initial perchlorate concentration and the competition caused by other anions and NOM.

The same water samples were also tested during this series of kinetic experiments for their TOC adsorption as shown in Figure 4.13. Whereas virgin SAI removed 47% of the TOC after 60 min; the SAI-700-60 removed 55%, and this represented a slight improvement. Further reduction in TOC was observed after 60 min. It is well recognized that the natural organic matter that comprises TOC includes organic compounds with a wide range of molecular size and composition. Organic compounds with larger molecular size need more time to penetrate into carbon pores, thus resulting in longer time to achieve pseudo-equilibrium. In addition, much of the TOC has a negative charge; thus its adsorption would have a similar phenomenological response as negatively charged perchlorate. Monitoring of TOC during the RSSCT for perchlorate removal of ammonia-tailored carbons indicate that there was a 30-45% removal of TOC by ammonia-tailored carbons while virgin SAI removed only 20% of the TOC during the operation process. Overall, the ammonia-tailoring process was able to improve perchlorate adsorption without causing damage to carbon adsorption for organic compounds or other anions. It’s safe to say that the ammonia-tailoring process enhances perchlorate removal by improving the carbon’s selectivity for perchlorate.

Overall, ammonia tailoring was successful in increasing the basicity of activated carbon as represented in the increase in nitrogen content and pHpzc values for tailored samples. The fact that there is negligible correlation between surface area, pore volume and perchlorate adsorption bed volume is in consistency with the results from the
oxidation and pyrolysis in \( \text{N}_2 \). It is safe to say that perchlorate adsorption is more closely related to the surface chemistry than to the physical characteristics for the carbons in this research. This may be because the perchlorate concentration is very low in the target water. Surface area of activated carbon is not a limiting factor in perchlorate adsorption. At breakthrough point, only a fraction of surface area available was occupied by perchlorate. The results so far shows that instead of looking for a carbon that has larger surface area or more pore volume in the size of perchlorate, modification of surface chemistry appears to be a more realistic option to improve activated carbon’s adsorption capacity.

4.4 ELECTROCHEMICAL TREATMENT

In light of the results from \( \text{NH}_3 \) tailoring, certain improvement in perchlorate adsorption capacity was observed after the treatment. For example, after the carbon was tailored at 700 \( ^\circ \text{C} \) for 60 minutes, the bed volume till breakthrough in small scale column test was 4,400 in contrast with only 1000-1200 bed volume for non-tailored carbon. The results from \( \text{NH}_3 \) tailoring gave us an idea about what we could do to modify carbon so as to make it more perchlorate-orientated. The essence of \( \text{NH}_3 \) tailoring is that the process was able to incorporate nitrogen-containing groups onto carbon surface without damaging, in some cases even increasing the surface area or pore size distribution of the treated carbons. The direct effect of those surface functional groups was to increase the positive surface charge, which helped the ultimate perchlorate adsorption. It is also important that the results from \( \text{NH}_3 \) treated samples strongly indicate that as far as perchlorate is concerned, carbon surface chemistry played a significant role in adsorption.

Therefore, the author tried to explore other ways of nitrogen group incorporation onto carbon surface. Electrochemical chemical tailoring by nitrogen-containing organic compounds deposition appears to be a promising option.

Figure 4.14 shows the surface charge distribution and pHpzc of carbons tailored by electrochemical tailoring using ethylene diamine (\( \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)). The electrical current was set to be between 2-4 mA. The tests employed ethylene diamine concentration of 0.05 and 0.1 M. The reaction time was 5 min.
Electrochemical tailoring using ethylene diamine was able to increase both the net positive surface charge and pHpzc when compared with virgin SAI as shown in Figure 4.14. For instance, carbon tailored with 2 mA current and 0.1 M ethylene diamine had 0.055 meq/g positive surface charge (at pH 7.5) and pHpzc 9.52. As shown previously, the surface charge of virgin SAI is 0.045 meq/g at pH 7.5 and pHpzc 8.35. Overall, there is about 1 pH unit shift to basic in the pHpzc after electrochemical treatment. Little changes were observed both in specific surface area and micropore volume as shown in table 4.10 and in pore volume distribution (Figure 4.15). Since no high temperature or gas was involved in the tailoring, it was expected that the tailoring shouldn’t change much of the carbon pore structure. The surface area and pore volume distribution results also reveal that incorporation of ethylene diamine did not block the pores. Rapid small-scale column test (RSSCT) for perchlorate in Figure 4.16 showed bed volume till perchlorate breakthrough ranged from 1,800 to 2,400.

Table 4.10
Specific surface area and micropore volume (width <20 Å) for electrochemically tailored carbons (5 min exposure to electrolytic current)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Micropore (&lt;20 Å) volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>846</td>
<td>0.312</td>
</tr>
<tr>
<td>I=2mA, 0.05 M C₂H₈N₂</td>
<td>839</td>
<td>0.311</td>
</tr>
<tr>
<td>I=2mA, 0.1 M C₂H₈N₂</td>
<td>851</td>
<td>0.311</td>
</tr>
<tr>
<td>I=4mA, 0.05 M C₂H₈N₂</td>
<td>842</td>
<td>0.312</td>
</tr>
<tr>
<td>I=4mA, 0.1 M C₂H₈N₂</td>
<td>849</td>
<td>0.312</td>
</tr>
</tbody>
</table>

Electrochemically treated carbon was also analyzed for its elemental composition. Table 4.11 is the C, H, O and N contents of tailored carbons. Carbon tailored by this electrochemical method had higher nitrogen content than non-tailored virgin SAI. Nitrogen content after tailoring ranged from 1.74-1.79%. The numbers were even higher than carbon tailored by ammonia (N content 1.61-1.69%) (Chen et al. 2004). The results
indicate the designed electrochemical tailoring was effective in incorporating nitrogen-containing groups onto carbon surface. Electrochemically tailored carbon also had less amount of oxygen (7.17-7.54%) than virgin SAI (8.80%) and carbons tailored by ammonia (8.00-8.28%). Oxygen content on carbon surface was affected not only by oxygen-containing functional group evolution during the tailoring process but also by exposure to air afterwards. Carbon treated at thermal conditions tends to subsequently take up oxygen from air due to the unoccupied reactive sites on carbon surfaces. Those reactive sites were created by the gasification of carbon or other atoms such as oxygen that exists at the edge of the carbon matrix.

No gasification of edge atoms could have occurred during electrochemical treatment. It’s unlikely that there would be much oxygen uptake by exposure. The decrease in oxygen content appears to be due to the replacement by nitrogen-containing groups of the sites that had previously been occupied by oxygen-containing groups during the electrochemical tailoring. It was also possible that oxygen-containing surface functional groups were simply eliminated by reactions that occurred via the electrochemical conditions. For example, the mass compositions presented in Table 4.11 could be explained by a reaction in which a release of carboxyls as CO₂.

Table 4.11
Elemental analysis of electrochemically tailored carbons
(5 min exposure to electrolytic current)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>90.0±0.4</td>
<td>0.54±0.04</td>
<td>0.64±0.02</td>
<td>8.82±0.46</td>
</tr>
<tr>
<td>I=2mA, 0.05 M C₂H₈N₂</td>
<td>90.5±0.5</td>
<td>0.30±0.03</td>
<td>1.74±0.02</td>
<td>7.46±0.55</td>
</tr>
<tr>
<td>I=2mA, 0.1 M C₂H₈N₂</td>
<td>90.7±0.4</td>
<td>0.32±0.04</td>
<td>1.78±0.04</td>
<td>7.20±0.48</td>
</tr>
<tr>
<td>I=4mA, 0.05 M C₂H₈N₂</td>
<td>90.4±0.3</td>
<td>0.31±0.04</td>
<td>1.74±0.04</td>
<td>7.52±0.38</td>
</tr>
<tr>
<td>I=4mA, 0.1 M C₂H₈N₂</td>
<td>90.5±0.3</td>
<td>0.34±0.02</td>
<td>1.79±0.03</td>
<td>7.37±0.35</td>
</tr>
</tbody>
</table>
The carbon tailored by electrochemical method obtained higher nitrogen content (1.74-1.79%) than those tailored by ammonia (1.61-1.69%). However, the ammonia tailored carbon obtained higher pHpzc and positive surface charge. This is because these two tailoring method created nitrogen-containing surface groups with different structures. The groups that were created by ammonia tailoring contained more positive surface charges at the pH studied.

Barbier et al. (1990) tried to bond diamine onto activated carbon fiber in an electrochemical system in order to improve the toughness of the carbon fiber. They suggested two reactions dominate the bonding process as followed:

\[
\begin{align*}
\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{NH}_2^+ + 2\text{H}^+ &\rightarrow \text{C}-\text{NH}_2^+-\text{CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{e} \\
\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{NH}_2^+ + 2\text{H}^+ &\rightarrow \text{C}-\text{NH}_2^+-\text{CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{e} \\
\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{NH}_2^+ + 2\text{H}^+ &\rightarrow \text{C}-\text{NH}_2^+-\text{CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{e} \\
\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{NH}_2^+ + 2\text{H}^+ &\rightarrow \text{C}-\text{NH}_2^+-\text{CH}_2\text{-CH}_2\text{-NH}_2 + 2\text{e} \\
\end{align*}
\]

The authors also pointed out that one quarter of the ethylene diamine bonding was in 4-2 configuration while three fourths are bridged in 4-1 configuration. As obvious
from 4-1 or 4-2 bonding, ethylene diamine was oxidized during the process, thus increased the nitrogen content of the carbon surface.

Ethylene diamine was bonded onto the carbon surface in this research as proven by increase in the nitrogen contents by elemental analysis. Contrary to the expectation, there is little increase in the positive surface charge as shown in Figure 4.15. It is possible that ethylene diamine thus bonded was not protonated at the pH values encountered in the target water of this research (pH around 7-8). Therefore, to achieve the increase the positive surface charge density, nitrogen-containing organic compounds that could be protonated pH 7-8 should be tried in future research.

Results from electrochemical carbon tailoring with ethylene diamine as the reagent showed some encouraging results. The bed lives doubled after the treatment at the best. The major advantage of this method is that it took only around 5 minutes for the treatment to complete. And the test was carried out under room temperature. The whole system was relatively simple and well understood (electrical cell). However, in the preliminary test, acetonitrile (CHN) was used as solvent and LiClO₄ as the supporting electrolyte. Those chemicals are relatively expensive and not very environmentally friendly. Research on alternatives is one of the fields that also need to be further explored in the future.
Figure 4.1: Full and small-scale perchlorate breakthrough profile with Redlands water ($C_0=70-78$ ppb)
Figure 4.2: Mass change during N\textsubscript{2} pyrolysis and NH\textsubscript{3} tailoring
Figure 4.3: Cumulative pore volume distributions of non-tailored (virgin) and NH$_3$-tailored SAI carbons
Figure 4.4: Surface charge distribution of non-tailored (virgin) and NH$_3$-tailored SAI carbons (temperature 500-800°C)
Figure 4.5: Zeta-potential distribution of non-tailored (virgin) and NH$_3$ tailored carbons
Figure 4.6: RSSCT of perchlorate breakthrough with Redlands water by virgin and ammonia tailored SAI carbons ($C_0$=70-78 ppb)
Figure 4.7: RSSCT test reproducibility with Redlands water ($C_0=70-78$ ppb)
Figure 4.8: Correlation between surface charge and bed volume to 4ppb perchlorate breakthrough

R² = 0.956
Figure 4.9: Oxygen-readsorption of ammonia-tailored carbons
Figure 4.10: Perchlorate adsorption isotherm by virgin and tailored SAI carbons with deionized-distilled water that is spiked with 2 mg/L perchlorate ($C_e$ in mg/L, $q_e$ in mg/g)
Figure 4.11: Freundlich plot for adsorption of perchlorate on virgin SAI and ammonia tailored carbons
Figure 4.12: Perchlorate adsorption kinetics study of virgin and tailored SAI carbons ($C_0=70-78$ ppb)
Figure 4.13: TOC adsorption kinetics study of virgin and tailored SAI carbons at pH 7.5 \((C_0=2.4-2.6\text{ mg/L})\)
Figure 4.14: Surface charge distribution of electrochemically tailored carbon.

- Virgin SA1
- I=2 mA, 0.05 M C₂H₈N₂ (pHₚzc=9.15)
- I=2 mA, 0.1 M C₂H₈N₂ (pHₚzc=9.52)
- I=4 mA, 0.05 M C₂H₈N₂ (pHₚzc=9.40)
- I=4 mA, 0.1 M C₂H₈N₂ (pHₚzc=9.50)
Figure 4.15: Pore volume distribution of electrochemically tailored carbons
Figure 4.16: Perchlorate breakthrough profiles of electrochemically tailored carbons ($C_0=70-78$ ppb)
Activated carbon has been widely used to remove both organic and inorganic contaminants in water and wastewater treatment facilities. The most common practice in the application of carbon is regeneration after exhaustion. The status of exhaustion is normally determined by the acceptable level of target contaminant in the effluent. The regenerated material is able to enter another cycle of operation. The cost for regeneration has proved to be much more economical than if the carbon has to be 100% replaced once exhausted (Leng et al. 1996).

Various studies have been conducted on the regeneration since the rapid development in the use of activated carbon in both municipal and industrial sectors. Among all the methods, the most practiced two are thermal and chemical regeneration. Thermal regeneration usually is carried out in a multi-hearth furnace or a rotary kiln at elevated temperature. It’s expected that adsorbed impurities would desorb by volatilization and oxidized at high temperature. The application of thermal regeneration is restricted by several factors. First, it’s not feasible for each facility using carbon to set up thermal regeneration unless necessary. Spent carbon is usually returned to reactivation facilities for regeneration. The cost involved in carbon transportation is an essential part of the overall cost of activated carbon treatment. Secondly, carbon loss due to oxidation and attrition has to be replaced which is another factor affects the cost of the process. Also, adsorbate is usually destroyed in thermal regeneration. Precious resources could be wasted because of this. Finally, air pollution may arise from the regeneration process if the heat treatment can’t completely destroy the adsorbate or harmful by-products may be produced especially in the case the contaminant is organics such as PCB (Liu et al.1985).

As for chemical regeneration, generally, a solvent is introduced to dissolve the adsorbate from the carbon surface. It’s usually carried out on the spot, which means that no transportation is necessary such as in thermal regeneration. This is an important advantage in the situation where frequent regeneration is required. In addition, chemical regeneration is seldom carried out at high temperature; carbon loss due to oxidation is
reduced remarkably. Also, in most cases desorption is carried out by dissolution of adsorbate into the regenerant, therefore, it’s possible to recover the adsorbate. However, reports on chemical regeneration have pointed out that the main disadvantage of chemical regeneration is its inability to completely recover the adsorption capacity of the carbon. Newcombe and Drikes (1991) achieved a regeneration efficiency of 90% in a procedure using a base followed by acid wash to regenerate carbon after adsorption of humic acid. In a research to evaluate the regeneration ability of a wide range of regenerants, both organic and inorganic for mono-substituted benzene compounds exhausted carbons, a wide range of regeneration efficiency was observed (from as low as 14.7% to 99.1%) depending on both the regenerant and adsorbate (Martin and Ng, 1984). In this research, regeneration was aimed at carbon exhausted with perchlorate.

5.1 PERCHLORATE LOADING

Before regeneration, carbon samples were preloaded with perchlorate in small columns or in batch method. Perchlorate loading in chemical regeneration study was loaded in column using Redlands groundwater with perchlorate concentration 50-75 ppb. Figure 5.1 is typical of the loading profile. The amount of perchlorate preloaded is obtained by integration of the breakthrough profile. Based on the figure, the preloaded perchlorate is about 0.16 and 0.54 mg perchlorate/g carbon respectively for virgin SAI and SAI-700-60. In addition, according to the figure, there is perchlorate breakthrough after about 1,100 and 4,500 bed volumes for virgin SAI and SAI-700-60 respectively.

For thermal regeneration, carbon was loaded in batch using Redlands groundwater with perchlorate concentration spiked to 5000 ppb. After 24 h of contact, about 0.41 mg perchlorate/g carbon was loaded onto virgin SAI carbon and the number was 0.80 mg perchlorate/g carbon for ammonia tailored carbon SAI-700-60.
5.2 CHEMICAL REGENERATION

In the former research of chemical regeneration of perchlorate-exhausted carbon in our group, sodium borohydride was used as the regenerant (Na et al. 2000). However, sodium borohydride is somewhat expensive, and its use has raised some issues related to its vigorous reaction rate. During this research, other chemical regenerants were explored.

Two regenerants were tested in chemical regeneration. One was regeneration with calcium thiosulfate. Calcium thiosulfate concentrations of 75, 150, 210, 300 and 350 mg/L as thiosulfate were used to regenerate perchlorate-laden carbon.

The other was base/acid method. Perchlorate-free water adjusted to pH 12 (base cycle) and pH 2 (acid cycle) were used as regenerant. The water used in the test is groundwater from City of Redlands, CA after perchlorate was removed by activated carbon. It’s has been well recognized that the surface chemistry have a great effect on the adsorption. At pH higher than pHpzc (pH of point of zero charge), the net surface charge of carbon is negative while at pH lower than pHpzc, it’s positive. As for perchlorate, it’s negatively charged in water and adsorbed mainly as anion. Therefore, the theory behind this base/acid method is that at high pH, the perchlorate adsorbed is pushed off the carbon surface that is negatively charged because of the electrostatic repulsion between them. The carbon is then washed in the acid (pH 2) so that the surface is more positively charged and ready for the next cycle of perchlorate removal.

5.2.1 Chemical Regeneration with Calcium Thiosulfate

Chemical regeneration was first tested on spent virgin SAI to see which of the two is better before tried on ammonia-tailored carbon.

Calcium thiosulfate concentrations of 75, 150, 210, 300 and 350 mg/L as thiosulfate were used to regenerate perchlorate-laden carbon at empty bed contact time (EBCT) 20 min. Figure 5.2 is the calcium thiosulfate regeneration of perchlorate-exhausted SAI carbon. It reveals that it needs at least a concentration of 210 mg/L as
thiosulfate to regenerate the carbon. At concentration less than 210 mg/L, only a small amount of perchlorate was desorbed. For thiosulfate concentration greater than 210 mg/L, the highest rate of removal appeared to be at about 80-100 bed volumes. Perchlorate concentration in effluent can reach as high as 1800 ppb at 80 bed volumes for regeneration with 350 mg/L of thiosulfate. Overall, for regenerant with 210, 300 and 350 mg/L as thiosulfate, perchlorate desorption was 40, 65 and 63% respectively of the perchlorate preloaded. These values are computed by considering the volumes of effluent multiplied by the concentration of perchlorate. When dividing this value by the mass of perchlorate that was preloaded, the result represents the percent of perchlorate removed by regeneration. This value can be used as a predictor of the potential carbon performance that can be expected during the next adsorption cycle. The figure also indicates that, for regenerant concentration higher than 210 mg/L, after 150 bed volumes, there was little further perchlorate desorption. Extending the operation time beyond 150 bed volumes would not help much to restore the adsorption capability. In addition, the higher the regenerant concentration, the faster the rate perchlorate is desorbed. For example, at 350 mg/L of thiosulfate, the peak of perchlorate desorption occurs at about 60 bed volumes while at 210 mg/L, it did not happen until 170 bed volumes of regenerant.

Next, the effect of EBCT was investigated during the chemical regeneration by calcium thiosulfate. The EBCT ranged from 3.72 to 20 min. Figure 5.3 shows the results of perchlorate that was desorbed at various EBCTs and at the calcium thiosulfate concentration of 300 and 350mg/L as thiosulfate. When the EBCT was relatively low, the concentration of calcium thiosulfate made a difference, for example, at EBCT equaled to 3.72 min, perchlorate removal by calcium thiosulfate of 350mg/L is much greater than that at 300mg/L. With the increase of EBCT, this difference narrowed. When the EBCT reached up to 16 min, perchlorate removed by these two solutions was almost the same. From these figures, we can also see that perchlorate removed during the regeneration of carbon increased with the increase of EBCT. The highest effluent concentration of perchlorate can be up to 2000 ppb when employing an EBCT of 20 min.

Figure 5.3 also shows the total percentage of perchlorate removed at EBCT values of 3.72, 8, 12, 16 and 20min. At lower EBCT, the percentage was relatively small, with
only about 22% and 34% removed at 300 and 350mg/L respectively at EBCT 3.72 min while it reached 65% and 63% at EBCT 20 min.

Overall, to have at least 60% perchlorate desorption, about 150 bed volumes of regenerant containing no less than 300 mg/L as thiosulfate is necessary.

5.2.2 Base/Acid Regeneration

Figure 5.4 is regeneration of virgin SAI by the base/acid method at EBCT 20 min. As shown in the figure, perchlorate concentration in regenerant fluid peaked soon after the start of the regeneration. The highest perchlorate concentration (4,500 ppb) in effluent occurred at around 20 bed volumes. There was little further desorption after 60 bed volumes. Compared with the results of regeneration by calcium thiosulfate at 350 mg/L, the rate of desorption for perchlorate by base/acid method is higher than that by thiosulfate regeneration. The percent of perchlorate desorbed by base/acid method is about 92.5% after 100 bed volumes compared with that of 66.5% for thiosulfate regeneration. Little or no perchlorate was detected during the acid wash process.

By comparing both the regeneration efficiency and the bed volume of regenerant needed, base/acid method appears to be more promising as a candidate.

Regeneration of SAI-700-60 by base/acid method was conducted as of virgin SAI. Figure 5.3 also includes perchlorate concentration in effluent vs. bed volume of regenerant for SAI-700-60. It takes about 80 bed volumes of regenerant to complete the regeneration. After that, only a very small amount of perchlorate was desorbed. Most of the perchlorate desorption occurred between 10-40 bed volumes with the highest perchlorate concentration about 7000 ppb at 15 bed volumes. Overall, about 94.2% of preloaded perchlorate was successfully desorbed by regeneration after 100 bed volumes. Like virgin SAI regeneration, no detectable perchlorate was found in the effluent during the acid cycle.

Figure 5.5 is the effluent pH changes in base and acid cycle for virgin SAI and SAI-700-60. For both samples, during the base cycle, the pH increased to around 11.5 after about 20 and 15 bed volumes respectively, which also corresponds to the period when the perchlorate concentration peaked in the effluent. And pH values kept at 11.2-
11.7 for the rest of the regeneration. During the acid cycle, effluent pH dropped from 11.5 to 4.5 after about 20 and 30 bed volumes respectively for virgin SAI and SAI-700-60. Previous research has shown that NH$_3$ tailored carbon has more basic surface functional groups than virgin SAI. Differences in surface chemistry may be the main reason for the rate in pH increase and decrease for these two carbons. Overall, after 40 bed volumes, the pH values of effluent stayed at around 3.7 and 4.0 for virgin SAI and SAI-700-60 respectively. Therefore, for regeneration hereafter, 100 bed volumes of base (pH 12) and 50 bed volumes of acid (pH 2) were recommended.

### 5.2.3 Small-Scale Perchlorate Reloading after Repeated Base/Acid Regeneration

Both regenerated virgin SAI and SAI-700-60 were tested for perchlorate reloading in RSSCT. The influent is groundwater from City of Redlands, CA with perchlorate 50-75 ppb during the test period. Figure 5.6 and 5.7 show the perchlorate breakthrough curves for repeatedly regenerated virgin SAI and SAI-700-60. Results indicate that less than 10% reduction in carbon bed life was observed after the first regeneration for both samples while repeated exhaustion and regeneration thereafter had no obvious effect on the adsorption capacity. The bed lives kept at around 1,150 and 4,250 after the second and third regeneration for virgin and SAI-700-60 respectively.

There were about 100 bed volumes of effluent from the base cycle with perchlorate 690 and 4500 ppb respectively for virgin SAI and SAI-700-60. The pH is about 11.5. 50 bed volumes of waste were produced in the acid cycle with no detectable perchlorate and pH around 2.5. The wastes were mixed in the disposal process with a final pH around 9.5 and perchlorate concentration about 450 and 3000 ppb for virgin SAI and SAI-700-60 regeneration respectively. Thus produced wastewater can either be combined into sewage system or would be much easier to remove by a biological process since its high perchlorate concentration.
5.3 FULL-SCALE CHEMICAL REGENERATION

Two carbon beds were exhausted with in Texas Street Water Treatment plant during a testing program conducted during the summer and fall of 2000. The one bed contained a virgin Westates bituminous GAC, and the other was with Iron-oxalic acid tailored GAC. The Iron-OA tailoring process included circulating a mixture of 500 mg/L ferric chloride (as iron) and 580 mg/L oxalic acid the Westates GAC for several days. The Non-Tailored (virgin) GAC exhibited initial 4 ppb breakthrough of perchlorate at 1000 BV while the Iron-OA tailored GAC exhibited initial breakthrough of perchlorate at 1200 BV (Figure 5.8).

5.3.1 Regeneration by Base/Acid Method

In RSSCT, base/acid method was found to be capable of removing more than 90% of preloaded perchlorate. Full-scale investigation on base/acid method regeneration was conducted in summer of 2001. The carrier water for these chemical regenerations originated from the City of Redlands water distribution system, and it originated from surface water treatment plants or from other wells that were not contaminated with perchlorate. Herein, the carrier water was identified as City water.

There are 24 GAC beds in the Texas Street Plant that are divided into two rows. The 12 beds on the west side are labeled 1a, 1b to 6a, 6b while that on the east side are 7a, 7b to 12a, 12b. The layout of the plant is shown in Figure 5.9.

Two GAC beds, that is, 1b and 7b were regenerated during the summer 2001. The 7b bed had been filled with virgin Westates bituminous GAC that had been pre-Tailored with iron and oxalic acid during the summer of 2000, and it has been identified as the “Iron-OA Tailored GAC” herein. The 1b bed was filled with virgin Westates bituminous GAC that had not been pre-tailored with iron and oxalic acid and it has been identified as the “Non-Tailored GAC” herein. As have been mentioned, during the summer of 2000, both the “Iron-OA Tailored and Non-Tailored beds were loaded with perchlorate as it treated the Texas Street Plant well water.
5.3.1.1 Perchlorate Released during Chemical Regeneration

Two pumps, one for base (NaOH) and one for acid (HCl) were used during regeneration for pumping concentrated NaOH and HCl out of the storage tank, to adjust the pH of water during both base and acid cycles. According to the base pump capacity, the base and acid flow rates during the regeneration were set to 150 gpm, which corresponded to an empty bed contact time (EBCT) of 33 min. The base and acid flows progressed from the bottom to the top of the GAC beds, which is opposite to the flow direction that had occurred during the previous perchlorate adsorption step.

Perchlorate release during the base step of chemical regeneration is shown in Figure 5.10 and 5.11 for the Non-Tailored (1b) and Iron-OA Tailored (7b) beds respectively. Perchlorate desorbed only during the base cycle, and no detectable concentration of perchlorate desorbed during the acid cycle. The figures show the change of perchlorate concentration versus bed volumes of base processed through the entire bed during the regeneration, as monitored from sampling ports that were nominally located at the 25%, 50%, 75% and effluent levels. It is noticed that in addition to these bed volumes of base, the GAC beds also received considerable City water flow (i.e. without base), which was interspersed with the base flow. These City water flows occurred as the regeneration conditions were started up and as operational difficulties were overcome. Overall, these flows amount to roughly 5-10 BV during startup plus 25-30 BV during operation for the Non-Tailored GAC, and to 15-18 BV during operation for the Iron-OA Tailored GAC. For the Non-Tailored GAC (Figure 5.10), the perchlorate removal was almost complete after about 100 BV along with 25-35 BV of City water that contained no base. For the Iron-OA Tailored (Figure 5.11), the perchlorate removal was effectively complete following 120 BV of base plus roughly 16 BV of City water that contained no base. Overall, for both these two beds, the highest concentration of perchlorate from the effluent could be as high as 8000 ppb. For the Non-Tailored GAC, the perchlorate concentration reached up to 8000 ppb after 30 BV, and it had dropped to 800 ppb after 80 BV. At 115 BV of base treatment, the effluent perchlorate concentration had dropped to
about 30 ppb. For the Iron-OA Tailored GAC, effluent perchlorate concentration reached 6000-7000 ppb at 40-80 BV, and it dropped to 30 ppb after 120 BV.

When compared with the perchlorate that loaded onto the carbon beds during the summer and fall 2000, the Figure 5.10 desorption values represent about 97.9% of the perchlorate that had been initially loaded onto the Non-Tailored bed. Likewise, Figure 5.11 desorption values represent 82.6% of the perchlorate that had been initially loaded onto the Iron-OA Tailored bed. When taking into account the bed volumes of City water that rinsed through these beds during chemical pump breakdown or pipe leakage, the actual percentage of perchlorate desorbed would be about 92-96% for the Non-Tailored bed and 79-81% for the tailored bed. This is comparable to the RSSCT results obtained in the Penn State University lab, which showed about 95% perchlorate desorption from the Non-Tailored carbon and 82% perchlorate desorption Iron-OA Tailored carbon.

For both beds, about 420-450 gallons of concentrated NaOH (50% NaOH) and 450-500 gallons of concentrated HCl (36% HCl) were needed to adjust the pH during the two-step regeneration. In other words, 420-450 gallons NaOH was consumed to increase the pH of City water (at flow 150 gpm) from about 8 to 12 and 450-500 gallons of HCl was consumed to adjust the pH of the City water to about 2 based on the 150 BV regeneration. It was 0.16-0.23 gpm for NaOH and 0.23-0.26 gpm for HCl corresponding to the City water flow rate of 150 gpm for the whole 150 BV regeneration.

5.3.1.2 pH Change of the GAC Beds during the Regeneration

The pH change during regeneration was monitored by taking samples from the 25%, 50%, 75% and 100% (effluent) sample ports. For the Non-Tailored bed, influent pH during the base cycle remained at 12.0-12.3 throughout the regeneration cycle (Table 5.1). Table 5.1 also shows pH change from all four sample ports. pH in effluent generally remained 0.3-1.0 pH units below the influent level, and it dropped to 10.3-10.8 during the 60-80 BV time frame, when the bed had been experiencing considerable rinsing by City water. The pH value of the 25%, 50% and 75% ports generally mimicked the effluent pH levels. For the Iron-OA Tailored GAC bed, influent pH remained at 12.0 throughout the base cycle (Table 5.2). Effluent pH rose from 6.5 initially up to 11.9 after 12 BV, and it
remained there for the rest of the base regeneration cycle. Interestingly, it took longer time (20BV) for the 75% port to reach 11.5-12.0.

Table 5.1

pH change during base cycle of Non-Tailored GAC (1b) bed regeneration

<table>
<thead>
<tr>
<th>Bed volume</th>
<th>Influent</th>
<th>25% port</th>
<th>50% port</th>
<th>75% port</th>
<th>Effluent (100% port)</th>
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Table 5.2

pH change during base cycle of Iron-OA-tailored GAC (7b) bed regeneration

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<th>Bed volume</th>
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<th>50% port</th>
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<th>Effluent (100% port)</th>
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During the acid cycle, for the Non-Tailored carbon bed, influent pH remained at 1.8-2.0 throughout, while effluent pH remained at 2.2-2.4 throughout (Table 5.3). However, the pH values at the intermediate points took a long time to drop. For example, the pH at the 75% port remained above pH 7.5 until 120 BV, and did not drop to the 2.0-2.2 range until 150 BV had been processed. For the Iron-OA-Tailored bed, influent pH remained at 2.0-3.0 throughout, but effluent pH dropped only gradually, taking 20 BV to reach 5.0, and 75 BV to reach 2.0 (Table 5.4). Intermediate pH dropped even more gradually. At the 75% port, the pH remained above 8.8 until 80 BV, and pH had dropped to 2.7 only after 110 BV.
Table 5.3  
*pH change during acid cycle of Non-Tailored GAC (1b) bed regeneration*

<table>
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<tr>
<th>Bed volume</th>
<th>Influent</th>
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<th>75% port</th>
<th>100% port (effluent)</th>
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Table 5.4  
*pH change during acid cycle of Iron-OA-Tailored GAC (7b) bed regeneration*

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<th>Bed volume</th>
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These acid cycle pH trends indicate that short-circuiting occurred during the acid cycle, which may have been caused by calcium carbonate build-up within either of the GAC beds during the pH 12 conditions. It might also have been caused by iron hydroxide precipitation within the Iron-OA Tailored GAC. Indeed, a rust color was observed when collecting samples from the intermediate ports during both the acid regeneration cycle, and the subsequent perchlorate reloading cycle. Moreover, there was also evidence of short-circuiting during the perchlorate reloading cycle, as discussed below.

5.3.2 Operational Hurdles

Several operational hurdles had to be resolved during this demonstration testing. The first of these was that activated carbon could clog the feed pipe that fed chemical regenerant through the bottom of the GAC bed. This is because this 4” stainless steel pipe had been originally designed to feed activated carbon slurry into this vessel, when the vessel was being initially filled with GAC. As such, this pipe hosted no back-flow prevention screen, and this meant that activated carbon could (and sometimes did) back down through this fill pipe. Although other pipes that come up through the bottom of the vessels did have well screens, these pipes were constructed of steel, and they were therefore not suitable for carrying low pH water. To counter this clogging during this demonstration testing, City water was forced back through the stainless steel pipe at roughly 600 gpm (9 gpm/ft²) for several minutes. This inadvertently caused washout of some of the GAC grains.

Ultimately, if full-scale operation of this base-acid chemical regeneration protocol were to be applied, it was recommended that well screens should be installed that are removable in these stainless steel feed lines so that the activated carbon could not clog them.

The second operational hurdle pertained to corrosion. Initially, the concentrated acid was fed directly in the vicinity of weld in stainless steel pipe, and the weld corroded and leaked. The problem was remediated by feeding the HCl into the middle of the 4” PVC pipe cross section; such that the concentrated HCl was instantly diluted by water to pH 2 before it has any opportunity of contact with the stainless steel piping.
5.3.3 Perchlorate Reloading from Well Water after Chemical Regeneration

After the chemical regeneration protocol was completed, the GAC beds were again tested for their capacity to remove perchlorate from well water. Just before embarking on this reloading, (i.e. after GAC washout during chemical regeneration), the depth of carbon in the GAC beds was measured. The carbon surfaces in Non-Tailored carbon bed (1b) and Iron-OA Tailored carbon bed (7b) beds were 0.90 m (2’11”) and 0.83 m (2’9”) respectively below the base of the manway, which was near the top of the carbon reactor. So the volume occupied by carbon is 5400 gallon in Non-Tailored carbon bed and 5540 gallon in the Iron-OA Tailored one.

The second cycles of reloading perchlorate from well water onto GAC in the two regenerated carbon started after the chemical regeneration was completed and the carbon surface heights were measured. To compare with the full-scale results from summer of 2000, the empty bed contact time was also set at 20 min which corresponding to a water flow of 250 gpm. During this second cycle, the influent perchlorate concentration ranged from 75-100 ppb, and averaged 85 ppb. Figure 5.12 and 5.13 are the breakthrough curves from the Non-Tailored and Iron-OA Tailored carbon beds from all four sampling ports. These figures indicate that for Non-Tailored carbon, there was detectable effluent perchlorate following 220 BV of operation, and this gradually rose to 80% breakthrough after 1350 BV of water treatment service. In comparison, the Iron-OA Tailored carbon beds yielded detectable effluent perchlorate after about 150 BV and this gradually rose to 80% breakthrough after 1350 BV.

This breakthrough occurred far more rapidly than what had been observed during second-cycle RSSCT experiments that was previously conducted in Penn State Univ. lab and a number of follow up experiments were conducted to discern the cause for this paradox, as discussed below.
5.3.4 Scavenger Bed

The 1a bed at Texas Street Plant, which had virgin carbon, was used as a scavenger bed to adsorb the perchlorate that had been removed from the Non-Tailored carbon (1b) and Iron-OA Tailored (7b) beds during the regeneration. The effluent pH from the base cycle stayed at about 12 during the whole regeneration process for both the Non-Tailored GAC bed and the Iron-OA Tailored GAC bed as can be seen from Table 5.1 and 5.2. To make sure the perchlorate would be successfully readsorbed in the scavenger bed, the pH of effluent from the base cycle of regenerant solution (pH about 12) was adjusted to a lower pH. This pH dropped to about 8-9 by HCl during the first about 120 BV of processing the Non-Tailored GAC. Due to a capacity restriction of the acid pump the pH could not be adjusted to lower values. After 120 BV the pH was adjusted to 6.5-7.5 for all subsequent conditions when a new higher-capacity acid pump was installed. Figure 5.14 and 5.15 identify the aqueous-phase perchlorate concentration of various ports of the scavenger bed during the regeneration cycles of the Non-Tailored carbon bed and the Iron-OA Tailored carbon bed. Figure 5.14 data shows that there was a clear wave front of perchlorate being chromatographically pushed through the scavenger bed by the base. The highest concentration experienced from each sampling port occurred gradually. When the pH was too high due to insufficient capacity from the initial acid pump, there is a clear jump of perchlorate concentration that indicates that a pH 8-9 was insufficient for the re-adsorbing perchlorate onto this scavenger bed. After 120 BV had been processed, a new acid pump with high capacity was installed; the influent pH was able to stay at about 6.5-7.5. As can be seen from the Figure 5.15, the whole bed regained some adsorption capacity, and the water-phase perchlorate concentration dropped dramatically. This adsorption capacity continued well into the adsorption of perchlorate from the following regeneration for Iron-OA Tailored carbon bed, as shown in Figure 5.15. Results from perchlorate adsorption in scavenger bed indicate that solution pH is an important factor in perchlorate adsorption. Carbon was able to adsorb more perchlorate at lower pH.
About 450-500 gal of concentrated HCl (36% by weight) was used to drop the pH of the base regenerant to pH 6-9 for these 150 BV of water, and this amounted to 5-6 gallons of concentrated acid per 10,000 gallows of pH 12 regenerant.

5.3.5 Follow-up RSSCT Base/Acid Regeneration Tests at Penn State Lab

In light of the above full-scale tests, it can be said that although base/acid regeneration was successful in RSSCT at Penn State, the protocol exhibited confounding complications that appeared to compromise performance during the full-scale testing at Redlands during the summer of 2001. Several hypotheses were explored for why these large discrepancies in performance could have occurred. These hypotheses include:

(1) There were true difference between the simulated RSSCT scaling computations and full-scale performance that were manifest for the second cycle of reloading that had not appeared during the first cycle.

(2) The RSSCT experiments that were conducted before the summer of 2001 employed deionized distilled water as the carrier for the base and acid. In contrast, the full-scale chemical regeneration testing employed City water from Redlands. Perhaps the additional ions in the City water caused less efficient chemical regeneration than in deionized water.

(3) During RSSCT experiments that were conducted before the summer of 2001, we first loaded perchlorate onto GAC grain by means of a batch protocol that aimed to mimic flow-through perchlorate loading. The batch loading used Redlands water that was spiked with a higher level of perchlorate. Perhaps this batch cycle loading did not appropriately depict the adsorption balance between perchlorate and other competing anions that would occur during flow-through conditions that employed the native (70-100 ppb) levels of perchlorate.

(4) The longer duration of pH 12 base exposure damaged the activated carbon during full-scale tests, whereas it had not caused such damage with shorter exposure time during the earlier RSSCT tests.

(5) A precipitation of calcium carbonate, iron hydroxide, or some other species caused the activated carbon beds to be short-circuiting during the base regeneration, acid regeneration, and perchlorate reloading cycles. This deleteriously diminished the
chemical regeneration efficiency, and therefore also diminished subsequent perchlorate removal performance.

(6) Perhaps there were true differences between the SAI and Westates bituminous activated carbons. Perhaps the SAI carbon, which had been used in our Penn State RSSCT tests, contained weak-base type surface functional groups, whereas the Westates carbons, which had been used at full-scale, contained strong-base type surface functional groups.

(7) Perhaps the long standby duration between fall 2000 and summer 2001 had allowed perchlorate to wedge its way into GAC pores in such a way as to render them less accessible to chemical regeneration.

(8) Perhaps there were performance-related differences between Redlands Texas Street well water and Redlands’ other sources of potable water that originates from surface water treatment plants and other wells.

To test these hypotheses, we embarked on a series of RSSCT tests as follows:

RSSCT operations were set up to test hypothesis 1 (scaling simulation), 2 (perchlorate loading using DI water in RSSCT), 3 (batch loading) and 4 (long exposure to base solution), which was carried out by Penn State research team.

In order to test the first hypothesis (scaling simulation) for why the regenerated carbon experienced the earlier than expected breakthrough, RSSCT experiments was repeated to simulate these full-scale tests. The tests employed regenerated Westates carbon that was taken from the top of the regenerated Non-Tailored and Iron-OA Tailored GAC beds. RSSCT tests employed the same Redlands groundwater and empty bed contact time as in full-scale reloading after regeneration.

As far as second hypothesis is concerned, Redlands water instead of DI water was used in batch loading. The carbon exhausted with perchlorate by batch loading was then regenerated by base/acid method and afterwards tested for perchlorate reloading in small-scale column.

And column loading instead of batch loading was investigated for chemical regeneration to test hypothesis 3. The fourth hypothesis was that the length of exposure to the base at full scale caused the GAC to be damaged. To test this base degradation hypothesis, 50 BV of GAC-treated Redlands water at pH 12 was recirculated through a
column of virgin GAC for one week. The goal was to create an environment in which the pH within the column would remain at pH 12. This was to simulate what could have happened at full scale where the pH should be relatively constant due to the constant input of fresh feed. Raw Texas Street water (i.e. that contained perchlorate) was then passed through the column to test the ability of the GAC to adsorb perchlorate following these treatments.

Results from these tests indicate that only hypothesis 4 (long exposure to base solution) was a possible reason for the shorter-than-expected bed life of chemically regenerated carbon in full scale.

The fifth hypothesis was that precipitation caused excessive short-circuiting in the vessels at Redlands following chemical regeneration. Based on the pH monitoring during the acid cycle of regeneration (Table 5.5 and 5.6), the pH of effluent reached that of the influent almost immediately once the operation started, whereas the pH from sampling port of 25%, 50% and 75% changed only gradually. This can be well explained by the short-circuiting in the bed. One of the potential causes of the short-circuiting is the formation of calcium carbonate precipitation during the base cycle, which could block the pores between carbons so that the water could not be evenly distributed.

The sixth hypothesis developed was that although the SAI GAC used in the lab and the Westates GAC used in Redlands are both bituminous carbons, there are some significant differences between them, particularly in the surface chemistry. A virgin Westates GAC was tested for base/acid regeneration in RSSCT using the same protocol as SAI GAC. The GAC was loaded with perchlorate from Redlands water using a flow-through process. It was next regenerated using the base/acid method, and then evaluated for its ability to adsorb perchlorate following regeneration. Figure 5.16 is the perchlorate breakthrough profile of Westates GAC using Redlands groundwater before and after chemical regeneration. It indicates that virgin Westates GAC operated about 1150 bed volume before perchlorate breakthrough, which is essentially the same as that of SAI GAC (1100 bed volume). After chemical regeneration, there was perchlorate breakthrough after only 240 bed volumes. Therefore, the SAI and Westates GAC had similar performance as far as perchlorate removal was concerned. The hypothesis that SAI and Westates GAC are essentially different could be dismissed.
With regard to hypothesis 7 (prolonged holding of perchlorate), we noted that during full-scale tests, we desorbed 79-96% of the perchlorate; whereas in RSSCT experiments, we desorbed 82-95% of the perchlorate as discussed above. Since these numbers are essentially the same, we can discount this hypothesis.

On the basis of the above follow-up RSSCT testing, it appears that pH 12 base degradation of the carbon and precipitation-induced short-circuiting were the major causes for the diminished full-scale performance.

5.4 THERMAL REGENERATION

Thermal regeneration is aimed at regenerating perchlorate-exhausted carbon at the same time destroying the adsorbed perchlorate so as to restore its capacity for next cycle of application. It’s reported that perchlorate starts to decompose at temperature 400-500°C (Long et al. 2000). Therefore, it’s expected that adsorbed perchlorate would decompose at thermal regeneration temperatures (usually higher than 600°C). Thermal reactivation is the most commonly used regeneration method especially where the carbon usage is huge. Water treatment facilities usually do not install in-situ thermal regeneration system but simply used that was provided by carbon industry.

As shown in chapter 4, ammonia tailoring at 600-700°C was able to improve GAC’s adsorption capacity to four-fold of its non-tailored counterpart. Virgin SAI carbon could operate 1100 bed volume without perchlorate breakthrough while that of SAI-700-60 (carbon tailored at 700°C for 60 min) had a bed volume to breakthrough 4400-4500. NH₃ tailoring caused change in surface chemistry of activated carbon, which is directly reflected in the increase of positive surface charge density.

The objectives of this study on thermal reactivation of ammonia-tailored GAC therefore have been: (1) to discern the impact of the thermal regeneration process on the surface chemistry of ammonia-tailored carbons; (2) to determine the effect of regeneration on the perchlorate adsorption capacity of tailored carbons; (3) to test whether perchlorate could be removed through multiple cycles of water treatment service and thermal reactivation.
Three thermal regeneration gases were tested: steam, carbon dioxide and NH₃. The first two of these gases or their mixture have been widely employed in thermal regeneration of GAC. NH₃ was chosen because it was also the chemical that was used in carbon tailoring.

5.4.1 Mass Loss

During regeneration, mass loss occurs because of both adsorbate gasification and GAC oxidation (Sebastiani et al. 1994). Control of mass loss is important because it determines how much makeup carbon would be needed when the regenerated carbon returns to operation in the water treatment facility. Mass loss is directly linked to regeneration time, temperature and the regeneration agent. Table 5.5 shows the mass loss during regeneration by steam, CO₂ and NH₃ at a variety of temperatures. Duplicate analyses showed that variation between two samples regenerated under the same conditions was about 0.3%. As shown in Table 5.5, regeneration by steam caused the most mass loss after 10 min of regeneration or 1 g steam/g carbon. At 700-800°C, 10-12% of mass was lost for steam regeneration. Mass loss for regeneration by NH₃ and CO₂ stayed at about 5-8% after 10 min. In general, the mass loss increased with the increase of regeneration temperature by the same regeneration agent. Mass loss also increased with the increase of regeneration time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loss (%)</th>
<th>Sample</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAI70060</td>
<td>--</td>
<td>T800N</td>
<td>7.95</td>
</tr>
<tr>
<td>T600S</td>
<td>7.31</td>
<td>T600C</td>
<td>3.58</td>
</tr>
<tr>
<td>T700S</td>
<td>10.12</td>
<td>T700C</td>
<td>4.12</td>
</tr>
<tr>
<td>T800S</td>
<td>12.24</td>
<td>T700C20</td>
<td>6.35</td>
</tr>
<tr>
<td>T600N</td>
<td>4.88</td>
<td>T800C</td>
<td>6.54</td>
</tr>
<tr>
<td>T700N</td>
<td>5.23</td>
<td>T800C20</td>
<td>7.23</td>
</tr>
</tbody>
</table>
5.4.2 Apparent Density

The measurements and calculations of apparent density (AD) were conducted in accordance with ASTM procedure (ASTM 1983). Conventionally, apparent density is the value most often used to determine whether a GAC has been properly regenerated, and it has proven to be a useful parameter for monitoring the effectiveness of the regeneration process when activated carbons have been loaded with natural organic matter. In such case, most favorable regeneration corresponds to restoring AD to the virgin AD or slightly higher. When the GAC was regenerated to an AD higher than the virgin AD, chars formed during pyrolytic stage of thermal regeneration was not completely removed and porosity may be lost. But when AD was a lot lower than that of the virgin GAC, it may mean that the GAC was over-regenerated. Micropores were lost by gasification and the friability of GAC may be increased (de Vooys, 1983). AD is much easier to monitor than pore volume distribution or adsorption capacity. It does not need costly equipments to measure, and therefore, was often used as an indicator to control the regeneration process.

AD was determined for each GAC before and after regeneration. Duplicate analysis showed the variation between two samples regenerated under the same condition to be about 0.005 g/cm³. Apparent densities of regenerated carbons are presented in Table 5.6. The original SAI-700-60 had an AD of 0.450 g/cm³ and the regenerated carbons had AD’s of 0.440-0.452 g/cm³.

Ten minute regeneration by steam or NH₃ at 600 or 700°C achieved AD very close to that of SAI-700-60, while AD for T800S or T800N was relatively lower. The low ADs for T800S and T800N indicated that regeneration at 800°C by steam or NH₃ was possibly too harsh, and the carbon was slightly over-regenerated. Generally, carbons regenerated by CO₂ showed decrease in AD with increase in time and temperature at 600 and 700°C. There was a greater decrease in AD values when regeneration time was extended to 20 min (2 g CO₂/g GAC) at temperatures of 700 and 800°C. Overall, if judged only by AD values, regeneration by 600 and 700°C by steam or NH₃ appeared to be able to restore the capacity of the carbon. In the case of CO₂ regeneration, no
significant difference was observed for all regenerated carbons in AD values when compared with original SAI-700-60.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Apparent density (g/cm³)</th>
<th>Sample</th>
<th>Apparent density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAI</td>
<td>0.440</td>
<td>SAI-700-60</td>
<td>0.450</td>
</tr>
<tr>
<td>T600S</td>
<td>0.449</td>
<td>T600C</td>
<td>0.452</td>
</tr>
<tr>
<td>T700S</td>
<td>0.449</td>
<td>T700C</td>
<td>0.452</td>
</tr>
<tr>
<td>T800S</td>
<td>0.440</td>
<td>T700C20</td>
<td>0.444</td>
</tr>
<tr>
<td>T600N</td>
<td>0.446</td>
<td>T800C</td>
<td>0.445</td>
</tr>
<tr>
<td>T700N</td>
<td>0.450</td>
<td>T800C20</td>
<td>0.445</td>
</tr>
<tr>
<td>T800N</td>
<td>0.442</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.4.3 Surface Area and Pore Volume Distribution

Table 5.7 lists the specific surface area, micropore volumes and mesopore volumes of SAI-700-60 and its regenerated variants. Also, as a representative, Figure 5.17 shows the cumulative pore volume distribution of carbon regenerated by CO₂. The differences in cumulative pore volumes for duplicates were within 5% of one another. The differences in surface area between duplicates were within 10% of one another. There was significant difference between pore volumes, but there was no significant different in surface areas between SAI-700-60 and its regenerated variants. In general, micropore volume decreased after regeneration when compared with original SAI-700-60. The loss of micropore volume showed a tendency to be more pronounced with the increase of regeneration temperature and time. For instance, micropore volume of T600C was 0.325 mL/g, and it dropped to 0.315 mL/g for T800C and 0.312 mL/g for T800C20. On the contrary, mesopore volume increased with increasing temperature and time (Table 5.7).
Thus, gasification of the carbon structure during the regeneration process converted micropores into mesopores.

For regeneration by steam and NH₃, a considerable percent (about 7.5%) of the micropore volume was lost by regeneration at 800°C for 10 min.

Table 5.7
Surface area and pore volume of regenerated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Micropore (&lt;20 Å) volume (mL/g)</th>
<th>Mesopore (20-500 Å) volume (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAI</td>
<td>874</td>
<td>0.252</td>
<td>0.055</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>984</td>
<td>0.330</td>
<td>0.078</td>
</tr>
<tr>
<td>T600S</td>
<td>955</td>
<td>0.324</td>
<td>0.078</td>
</tr>
<tr>
<td>T700S</td>
<td>969</td>
<td>0.308</td>
<td>0.082</td>
</tr>
<tr>
<td>T800S</td>
<td>1028</td>
<td>0.310</td>
<td>0.084</td>
</tr>
<tr>
<td>T600N</td>
<td>932</td>
<td>0.320</td>
<td>0.084</td>
</tr>
<tr>
<td>T700N</td>
<td>935</td>
<td>0.318</td>
<td>0.082</td>
</tr>
<tr>
<td>T800N</td>
<td>920</td>
<td>0.305</td>
<td>0.096</td>
</tr>
<tr>
<td>T600C</td>
<td>906</td>
<td>0.325</td>
<td>0.075</td>
</tr>
<tr>
<td>T700C</td>
<td>912</td>
<td>0.320</td>
<td>0.076</td>
</tr>
<tr>
<td>T700C20</td>
<td>925</td>
<td>0.319</td>
<td>0.086</td>
</tr>
<tr>
<td>T800C</td>
<td>921</td>
<td>0.315</td>
<td>0.084</td>
</tr>
<tr>
<td>T800C20</td>
<td>936</td>
<td>0.312</td>
<td>0.086</td>
</tr>
</tbody>
</table>
5.4.4 Elemental Analysis

Elemental analysis results of virgin SAI, NH₃ tailored SAI-700-60 and regenerated carbons are shown in Table 5.8 together with standard deviations.

The data revealed that ammonia tailoring increased the nitrogen and hydrogen contents. Hydrogen content increased from 0.54% for virgin SAI to 0.73% for SAI-700-60, and nitrogen increased from 0.64% for virgin SAI to 1.61% for SAI-700-60. However, regeneration in steam or CO₂ caused decreases in both hydrogen and nitrogen contents. As shown in Table 5.8, the hydrogen contents dropped to 0.3-0.5% for carbons regenerated by steam or CO₂, compared to 0.74% for SAI-700-60. Changes in nitrogen contents were even more highly dependent on the individual regeneration agent employed. Samples regenerated by steam exhibited the highest decrease in nitrogen contents (to 0.6-0.8%) followed by CO₂ regenerations (0.92-0.99%) then NH₃ regeneration (0.94-1.04%).

Overall, there was less H and N for steam regenerated carbon than for SAI-700-60. So the steam removed H and N heteroatoms during the regeneration process. Following steam regeneration, the N content returned to the level that it had been before the carbon was tailored by ammonia. Carbon regenerated by ammonia had as much H as for SAI-700-60 and 2/3 as much N while carbons regenerated by CO₂ had H close to virgin SAI but 2/3 as much N as SAI-700-60. Thus, the steam stripped off more N heteroatoms that had been chemisorbed during ammonia-tailoring than did the ammonia regeneration or CO₂ regeneration.
Table 5.8
Elemental composition of regenerated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAI</td>
<td>90.0±0.5</td>
<td>0.54±0.04</td>
<td>0.64±0.04</td>
</tr>
<tr>
<td>SAI-700-60</td>
<td>89.7±0.3</td>
<td>0.73±0.04</td>
<td>1.61±0.01</td>
</tr>
<tr>
<td>T600S</td>
<td>90.8±0.3</td>
<td>0.47±0.04</td>
<td>0.79±0.05</td>
</tr>
<tr>
<td>T700S</td>
<td>90.7±0.4</td>
<td>0.36±0.03</td>
<td>0.62±0.04</td>
</tr>
<tr>
<td>T800S</td>
<td>89.8±0.4</td>
<td>0.32±0.02</td>
<td>0.60±0.02</td>
</tr>
<tr>
<td>T600N</td>
<td>91.4±0.2</td>
<td>0.67±0.03</td>
<td>1.04±0.02</td>
</tr>
<tr>
<td>T700N</td>
<td>91.2±0.1</td>
<td>0.69±0.04</td>
<td>1.01±0.03</td>
</tr>
<tr>
<td>T800N</td>
<td>90.5±0.1</td>
<td>0.67±0.03</td>
<td>0.94±0.04</td>
</tr>
<tr>
<td>T600C</td>
<td>91.1±0.3</td>
<td>0.51±0.03</td>
<td>0.98±0.04</td>
</tr>
<tr>
<td>T700C</td>
<td>91.0±0.1</td>
<td>0.44±0.04</td>
<td>0.96±0.04</td>
</tr>
<tr>
<td>T700C20</td>
<td>91.3±0.3</td>
<td>0.38±0.02</td>
<td>0.99±0.03</td>
</tr>
<tr>
<td>T800C</td>
<td>91.1±0.1</td>
<td>0.37±0.02</td>
<td>0.96±0.03</td>
</tr>
<tr>
<td>T800C20</td>
<td>91.1±0.2</td>
<td>0.30±0.03</td>
<td>0.92±0.02</td>
</tr>
</tbody>
</table>

Waer et al. (1992) suggested the following reactions during regeneration by steam and CO₂:

\[
\begin{align*}
H_2O + C(s) & \rightarrow CO(g) + H_2(g) \quad (5-1) \\
CO_2 + C(s) & \rightarrow 2CO(g) \quad (5-2) \\
CO + H_2O(g) & \rightarrow CO_2 + H_2 \quad (5-3)
\end{align*}
\]

Where C(s) is the carbonaceous char produced during pyrolysis.

For sites on carbon surface that had heteroatoms, such as hydrogen or oxygen, bonded to form functional groups, it is possible that gasification would occur during the regeneration process and thus initiated loss of heteroatoms as shown in the following reactions:

\[
C\cdot(H) \rightarrow C(s) + CH_4 \quad (5-4)
\]
\[
C'(O) \rightarrow C(s) + CO
\]  
(5-5)

For ammonia tailored carbons, the loss of hydrogen or nitrogen during regeneration can therefore be explained by the gasification that would occur under the regeneration conditions. Although, there is currently very little research about how nitrogen-containing functional groups react during the regeneration, it is possible that the same kind of gasification also occurred to those groups. In addition, functional groups reacted in different ways to various regeneration gases proven by the difference in elemental composition of the regenerated products from same temperature and time but different gases.

One thing interesting about regeneration by NH\textsubscript{3} was that instead of gaining nitrogen as observed during NH\textsubscript{3} tailoring, carbon lost some of the nitrogen during regeneration. NH\textsubscript{3} tailoring and NH\textsubscript{3} regeneration employed the similar temperatures. Longer times were used in tailoring than in regeneration. But according to the mass change during ammonia tailoring, the gain of mass during ammonia tailoring started right away. So it was expected that carbon may react the same way as in tailoring. The difference is that during regeneration, the carbon surface was saturated with inorganic or organic compound from water. It was assumed, therefore, that those adsorbates not only prevented nitrogen to be incorporated onto carbon surface, they may even react with existing nitrogen groups and resulted in the elimination of some of them. This is proven by the fact that the nitrogen content dropped about 0.6\% after the regeneration in ammonia.

In addition, the gasification of surface heteroatoms generally increases with the increase of temperature and treatment time when the same agent was used. For example, the hydrogen of T600S was 0.47\% and it was 0.36\% and 0.32\% for T700S and T800S respectively.

### 5.4.5 Surface Charge Distribution and pH\textsubscript{pzc}

Table 5.9 is the surface charge at pH 7.5 and pH\textsubscript{pzc} (pH of point of zero charge) for the SAI-700-60 and regenerated carbons.
The SAI-700-60 exhibited a surface charge of 0.094 meq/g carbon at pH 7.5 and a pHpzc of 9.90. When CO₂ regeneration was employed, the carbons exhibited surface charge at pH 7.5 of 0.081-0.085 meq/g, and pHpzc of 9.21-9.31, and these were only slightly lower than that of SAI-700-60. In contrast, carbons regenerated by steam had less than half of the positive surface charge of that for SAI-700-60, and their pHpzc values were also more than 1 unit lower than SAI-700-60. In comparison, the carbon regenerated by NH₃ obtained surface charge at pH 7.5 (up to 0.091 meq/g) and pHpzc values (up to 9.45) that were closest to SAI-700-60.

Table 5.9
Surface charge and pHpzc of regenerated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface charge at pH 7.5 (meq/g)</th>
<th>pHpzc</th>
<th>Sample</th>
<th>Surface charge at pH 7.5 (meq/g)</th>
<th>pHpzc</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAI-700-60</td>
<td>0.094</td>
<td>9.90</td>
<td>T800N</td>
<td>0.084</td>
<td>9.04</td>
</tr>
<tr>
<td>T600S</td>
<td>0.048</td>
<td>8.98</td>
<td>T600C</td>
<td>0.082</td>
<td>9.31</td>
</tr>
<tr>
<td>T700S</td>
<td>0.045</td>
<td>8.45</td>
<td>T700C</td>
<td>0.085</td>
<td>9.21</td>
</tr>
<tr>
<td>T800S</td>
<td>0.045</td>
<td>8.31</td>
<td>T700C20</td>
<td>0.084</td>
<td>9.24</td>
</tr>
<tr>
<td>T600N</td>
<td>0.089</td>
<td>8.57</td>
<td>T800C</td>
<td>0.081</td>
<td>9.24</td>
</tr>
<tr>
<td>T700N</td>
<td>0.091</td>
<td>9.45</td>
<td>T800C20</td>
<td>0.084</td>
<td>9.21</td>
</tr>
</tbody>
</table>

5.4.6 Rapid Small-Scale Column Test (RSSCT) for Perchlorate Removal

Before column test for perchlorate removal, part of the regenerated carbon was separated and undergone a chemical regeneration process (base/acid) method developed previously in our group in Penn State University. It has proven that during the base cycle of the regeneration, perchlorate desorbed when perchlorate-free water adjusted to high pH (around 12) passed through carbon. After 100 bed volumes of pH 12 water, more than 95% of the loaded perchlorate could desorb. Part of the each regenerated carbon was washed with about 200 bed volumes of deionized-distilled water adjusted to pH 12. No
perchlorate was detectable in the collected effluent. This indicates that perchlorate was destroyed during the thermal regeneration process.

Perchlorate breakthrough profiles by RSSCT of regenerated carbons were shown in Figure 5.18, 5.19 and 5.20. These profiles are compared to SAI-700-60 (shown in dashed line) for which initial 4 ppb perchlorate breakthrough occurred at 4400.

Carbons regenerated by NH₃ (Figure 5.20) achieved bed volumes to initial breakthrough of 4000-5000, which were similar to that of SAI-700-60. Regeneration by CO₂ at 600 and 700 °C for 10 min only restored part of the perchlorate adsorption capacity (i.e. 3000-3600 BV to initial breakthrough). However, extending the CO₂ regeneration time to 20 min or raising the temperature to 800 °C was fully effective in regenerating the carbon (4000 to 4400 BV to initial breakthrough). T700C20, T800C and T800C20 all had significantly higher bed volume than T600C and T700C. In addition, T700C20 had a higher bed volume than T800C suggesting that changing regeneration time was more effective than changing the temperature.

Patrick (1995) pointed out that CO₂ had a lower diffusion into carbon’s porous network and lower reaction rate than steam due to its larger molecular dimension and higher activation energy barrier than H₂O. Extending regeneration time means that more CO₂ could reach deeper into pores of the activated carbon, thus greater regeneration efficiency.

5.4.7 Perchlorate Adsorption vs. Surface Charge

In earlier research, the authors observed that perchlorate adsorption was closely related to surface chemistry (chapter 4). As shown in chapter 4, carbons were either tailored by ammonia at temperatures 500, 600, 700 and 800 °C or pyrolyzed in N₂ at 700 and 1000 °C for 60 min. In general, the higher the positive surface charge and pHpzc, the higher the adsorption capacity for perchlorate (R²=0.956).

Figure 5.21 is the correlation between surface charge and bed volume to initial 4 ppb perchlorate breakthrough of carbons tailored by ammonia and carbons regenerated by steam, carbon dioxide and ammonia. There was good correlation between surface charge and bed volume to initial perchlorate breakthrough with R²=0.946. The strong
correlation further confirmed that perchlorate adsorption is a charge related process. Carbon’s surface chemistry played an important role.

5.4.8 Repeated Thermal Regeneration

Two SAI-700-60 samples were loaded with perchlorate in RSSCT and regenerated by CO₂ and NH₃ respectively. The RSSCT perchlorate loading and regeneration were repeated for three times to see the effect of repeated regeneration as would occur in practice.

Figure 5.22 depicts the perchlorate breakthrough profiles of carbon regenerated by CO₂ at 800°C for 20 min (T800C20) and Figure 5.23 depicts performance when regenerated by NH₃ at 700°C for 10 min (T700N). Table 5.10 is the elemental analysis of those regenerated samples.

As shown in Figure 5.22, CO₂ regeneration achieved only slight decrease in carbon bed life after up to three cycles whereas NH₃ regeneration (Figure 5.23) achieved even a small increase. And nitrogen content (Table 5.10) did not change with the successive regenerations. Indeed, the nitrogen-containing functional groups left over after the first cycle of regeneration appeared quite stable in subsequent cycles. This may also explain the reason why there is no further drop of bed volume for perchlorate. The stabilized carbon surface chemistry guaranteed a certain amount of perchlorate capacity.

Mass loss during repeated regeneration was also less than that during the first cycle. Mass loss ranged from 3-4.5% during subsequent regenerations via either CO₂ or NH₃ thermal treatment.

These data indicate that the NH₃ and CO₂ regeneration not only restored the perchlorate capacity but also disengaged other anions that competed with the perchlorate for adsorption.
Table 5.10
Elemental analysis of repeatedly regenerated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T800C20-1st cycle</td>
<td>91.1±0.2</td>
<td>0.30±0.03</td>
<td>0.92±0.02</td>
</tr>
<tr>
<td>T800C20-2nd cycle</td>
<td>90.8±0.2</td>
<td>0.34±0.02</td>
<td>0.90±0.04</td>
</tr>
<tr>
<td>T800C20-3rd cycle</td>
<td>90.5±0.4</td>
<td>0.32±0.03</td>
<td>0.87±0.03</td>
</tr>
<tr>
<td>T700N-1st cycle</td>
<td>91.2±0.1</td>
<td>0.69±0.04</td>
<td>1.01±0.03</td>
</tr>
<tr>
<td>T700N-2nd cycle</td>
<td>91.0±0.1</td>
<td>0.74±0.04</td>
<td>0.98±0.03</td>
</tr>
<tr>
<td>T700N-3rd cycle</td>
<td>91.1±0.1</td>
<td>0.74±0.05</td>
<td>1.04±0.03</td>
</tr>
</tbody>
</table>
Figure 5.1: Perchlorate breakthrough profile in small-column tests for virgin SAI and SAI-700-60 ($C_0=70-78$ ppb)
Figure 5.2: Regeneration of perchlorate-exhausted virgin SAI by calcium thiosulfate (concentration by thiosulfate)
Figure 5.3: Effect of EBCT on chemical regeneration by calcium thiosulfate (concentration by thiosulfate)
Figure 5.4: Base/acid regeneration of perchlorate-exhausted virgin SAI and SAI-700-60
Figure 5.5: pH change in effluent during base and acid cycles of regeneration
Figure 5.6: Perchlorate breakthrough profile for repeatedly regenerated (base/acid method) virgin SAI ($C_0=75-80$ ppb)
Figure 5.7: Perchlorate breakthrough profile for repeatedly regenerated (base/acid method) SAI-700-60
Figure 5.8: Perchlorate loading onto Non-Tailored and Iron-OA Tailored GAC during Summer 2000 (Courtesy of Bob Parette).
Figure 5.9: Layout of Texas St. Water Treatment Plant, City of Redlands, CA
Figure 5.10: Regeneration of Non-Tailored carbon bed by base/acid
Figure 5.11: Regeneration of Iron-OA Tailored carbon bed by base/acid
Figure 5.12: Perchlorate reloading from well water onto Non-Tailored carbon bed
(influent perchlorate concentration $C_0=75-100$ ppb)
Figure 5.13: Perchlorate reloading from well water onto Iron-OA Tailored carbon bed (influent perchlorate concentration $C_0=75-100$ ppb)
Figure 5.14: Scavenger bed perchlorate levels during Non-Tailored carbon bed regeneration
Figure 5.15: Scavenger bed perchlorate levels during Iron-Tailored carbon bed regeneration (BV represents the beds of water that passed through the Iron-OA Tailored GAC bed)
Figure 5.16: Perchlorate breakthrough profile of virgin Westates GAC by RSSCT
Figure 5.17: Cumulative pore volume distribution of carbon regenerated by CO₂
Figure 5.18: RSSCT for perchlorate breakthrough of carbons regenerated by steam
Figure 5.19: RSSCT for perchlorate breakthrough of carbons regenerated by CO₂
Figure 5.20: RSSCT for perchlorate breakthrough of carbons regenerated by NH$_3$
Figure 5.21: Correlation between bed volume and surface charge for ammonia-tailored carbons and these regenerated with steam, CO₂ and NH₃.
Figure 5.22: Perchlorate breakthrough by carbons repeatedly regenerated by CO₂
Figure 5.23: Perchlorate breakthrough by carbons repeatedly regenerated by NH$_3$
CHAPTER 6
CONCLUSIONS

- Small-scale column tests (RSSCT) were effective in predicting full-scale carbon bed operation.
- For Redlands water (~75 ppb ClO₄⁻), virgin bituminous GAC was able to treat 1100 BV before perchlorate was detected in the effluent. This would correspond to 1 month of removal at the Texas Street plant if a 20 minute EBCT was used. For Redlands water, virgin GAC is not an economically attractive approach for perchlorate removal.
- Carbon tailoring by ammonia at temperature between 500 and 800°C was employed to improve carbon’s adsorption capacity. Ammonia thermal tailoring acted as activating agent at temperatures higher than 500°C, and it caused both physical and chemical changes to the carbons. Micropores were created in the process, which were reflected in the increase of surface area and micropore volume. Results from elemental analysis showed that nitrogen was incorporated in the tailoring process, and this increased the number of basic groups. The net effect of the tailoring is shown in an increase of about 1 to 2 units on the pHpzc and pHIEP of carbon samples.
- Rapid small-scale column tests revealed remarkable improvement in perchlorate adsorption when conventional bituminous GAC was thermally tailored in ammonia at 500-800°C. The most favorable improvement occurred between temperatures of 650-700°C. After the tailoring procedure, a 4-fold increase in bed volume to initial perchlorate breakthrough was observed in the case of sample SAI-700-60. Characterization of both tailored and virgin SAI carbon revealed strong correlation between carbon surface chemistry and perchlorate adsorption. Bed volume to initial perchlorate breakthrough increased with the increase of positive surface charge density.
- Ammonia tailoring was also able to enhance the carbon’s adsorption for TOC, although it showed a smaller improvement for TOC adsorption than for
perchlorate adsorption. This is important because perchlorate contamination is often entangled with organic contamination such as in the case of Redlands water in this research. Overall, NH$_3$ tailoring appears to be an effective way to enhance the adsorption of perchlorate from aqueous solution.

- Ammonia tailored carbon was thermally regenerated by CO$_2$, NH$_3$ and steam at temperatures between 600-800°C. Regenerating gas played an important role in the final products. Overall, CO$_2$ and NH$_3$ regeneration were able to restore most of the perchlorate adsorption capacity of modified carbons. Regeneration process removed some of the nitrogen-containing surface functional groups. Repeated thermal regeneration indicates that there was no further decrease in bed life for perchlorate adsorption up to three cycles.

- Carbon tailoring by electrochemical method using ethylene diamine was effective in incorporating nitrogen-containing groups onto carbon surface in only 5 min of reaction time and at ambient temperature. The resulted carbon was less effective than ammonia-tailored carbons though it offered higher nitrogen content. The difference was attributed to the difference in the structures of nitrogen-containing groups created by the two tailoring process. The nitrogen groups created by ammonia-tailoring process were more positively charged at the pH of the target water.

- Nitric acid oxidation and pyrolysis in nitrogen were also widely used to change the surface chemistry of carbon. Nitric acid oxidation was able to greatly increase the surface acidity and oxygen content. Carbons thus obtained were more negatively charged as reflected in surface charge and pH$_{pzc}$ values. It was also possible that carbon physical properties could be kept intact if the right conditions were chosen in the oxidation process. But extreme oxidation condition would cause the collapse of pore walls and resulted in decrease in surface area or pore volume. On the other hand, pyrolysis under inert gas atmosphere effectively removed acidic oxygen-containing surface groups and increased basicity at high temperatures. There was also change in physical properties after heat treatment.

- Perchlorate adsorption tests showed that carbon with perchlorate removal was highly related to surface chemistry. Carbon oxidation by nitric acid was
detrimental to perchlorate adsorption even in the cases there was little change in surface area and pore volume distribution. In general, carbon surface that was less acidic and presents more positive charges would have a greater perchlorate adsorption capacity.

- Between two of the most commonly applied regeneration method, chemical regeneration was more suitable for situations where frequent regeneration is necessary or in places where there is long transportation between the water treatment and regeneration facilities.

- Chemical regeneration of carbons bed exhausted with perchlorate was tested both in small column tests and in full-scale. In small scale column tests, Two regenerants were tested. For regeneration by calcium thiosulfate, it needs about 150 bed volumes of regenerant (300mg/L as thiosulfate or higher) to achieve perchlorate desorption greater than 60%. Compared with regeneration by calcium thiosulfate, the base/acid method needs less regenerant (100 bed volumes) to complete the regeneration. The perchlorate desorbed (92.5%) is also higher than by calcium thiosulfate. Therefore, base/acid method was recommended for perchlorate-exhausted carbon regeneration.

- Base/acid method was also quite effective in regenerating spent NH₃ tailored carbon. As much as 94% of the perchlorate was desorbed after 100 bed volumes. Column tests revealed that repeated regeneration saw a less than 10% reduction in bed life after first cycle of loading and regeneration which may be due to the incompleteness of chemical regeneration. No further decline in bed life was observed for the second and third cycles of perchlorate loading and regeneration.

- Base/acid method in full-scale regeneration at Texas Street Water Treatment was carried out in the summer of 2001 on two carbon beds. Both were exhausted with perchlorate in the previous year. Results from regeneration stage were in consistence with the small-scale column test in Penn State University lab. More than 95% of the previously loaded perchlorate was removed during the base cycle after 100 bed volume.

- The discrepancy between small and full scale operation of base/acid regeneration occurred in perchlorate reloading stage. Instead of restoring the perchlorate
adsorption capacity, regenerated carbon bed had a bed life about 20% of the original. Follow-up tests revealed that long immersion of carbon in base solution (due to mechanical problem) was detrimental to carbon surface. Short-circuiting occurred during the reloading process was proven to be another factor that caused the poor performance of base/acid regeneration.

- Overall, carbon tailoring combined with effective regeneration is sure to give granular activated carbon a competitive edge in its application on perchlorate removal.
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