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Modified Activated Carbon Perchlorate Sorbents

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A new method for improving the selectivity of activated carbons for adsorbing perchlorate has been developed. The technique involves alkylation of functional groups present on the activated carbon surface. The modified activated carbons typically have adsorption capacities 5-10 times that of the parent activated carbon. The technique is believed to mainly alkylate the oxygen surface groups rather than the nitrogen surface groups.
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Executive Summary

Background
Perchlorate contamination of ground and surface water is an ongoing problem at a number of sites, principally in the Western United States. The contamination is a result of historical activities such as previously acceptable disposal procedures and testing of solid rocket motors[1]. Perchlorate is highly soluble and environmentally mobile; one result of this behavior is the presence of up to 8 ppb of perchlorate in Lake Mead at the inlet to Las Vegas’ municipal water system due to migration of perchlorate from the Kerr-McGee site near Henderson, NV[1]. The health effects of exposure to low levels of perchlorate are not well known, but state action levels for perchlorate in drinking water are as low as 1 ppb[2]. The Department of Defense (DoD) is responsible for perchlorate remediation in many of these sites, and development of innovative approaches to remediate this problem has been an active area of research sponsored by SERDP.

A number of technologies are used for perchlorate remediation[1, 3-5]. The most widely used approach is ion exchange using strong-base anion exchange resins and traditional pump and treat technology. One drawback of this approach has been the relatively low selectivity of commercial resins for perchlorate, which renders a large fraction of their anion exchange capacity unusable[6]. More recently, highly selective anion exchange resins have been prepared, but are much more expensive[5-7]. The most promising technology for perchlorate remediation is bioremediation by perchlorate reducing bacteria to destroy perchlorate under anaerobic conditions[2, 8]. This is a particularly attractive approach for the in situ degradation of perchlorate in groundwater. However, bioremediation of perchlorate is ineffective if other electron acceptors, especially oxygen and nitrate, are present. Therefore, bioremediation of perchlorate contaminated surface water is generally ineffective. In addition, bioremediation is not acceptable for treating drinking water in the United States.

Objective
The goal of this research is to develop inexpensive granular modified activated carbon anion exchange materials (GMACs), derived from granular activated carbon (GAC), that have a high selectivity for perchlorate and can be produced in a manner analogous to the production of gas-activated carbon. The aim is to develop inexpensive materials for use in treating drinking water. Ideally, these materials would be inexpensive enough for use in a single-use system without regeneration. These materials could also be used in conjunction with bioremediation as an attachment surface for perchlorate reducing bacteria. This is a “SEED-like” proposal aimed specifically at synthesizing GMACs and determining their suitability as perchlorate adsorbents.

Results
The main hypothesis/assumption inherent in this work is that the pyridinic nitrogen sites in activated carbon can by alkylated to produce cationic sites that are similar to those found in certain strong base anion exchange resins. A number of approaches were used to increase the nitrogen content in activated carbons and techniques for alkylating these carbon materials were developed. The most effective alkylated carbon materials had ~15 times the perchlorate adsorption capacity of the parent activated carbon. However, increasing the nitrogen content had little or no effect on the perchlorate adsorption capacity of the activated carbons. Consequently, the main hypothesis that the nitrogenous sites in activated carbon can be alkylated appears to be false. Instead, alkylation appears to increase the net positive charge of the activated carbons by
alkylating the anionic oxygen surface sites and converting them to neutral species as well as converting some neutral oxygen sites into cationic sites. While alkylation greatly increases the selectivity of the cationic sites for perchlorate, the fact that this approach does not seem capable of increasing the number of cationic surface sites strongly suggests that modified activated carbons are not promising materials for perchlorate remediation since perchlorate selective ion exchange resins can perform the same task more economically.
Technical Objective.
The primary research objective is to modify activated carbon by creating additional quaternary ammonium sites and measure the capacity and selectivity of these activated carbons for perchlorate adsorption. The secondary research objective is to determine whether GMACs can be prepared using only gaseous reagents under conditions similar to those used to prepare conventional gas-activated carbon. The primary hypothesis is that the nitrogenous sites in activated carbon can be alkylated and the resulting quaternary ammonium sites will behave similarly to those present in strong base anion exchange resins.

Background.

Perchlorate Contamination and Remediation Techniques
Perchlorate contamination of ground and surface water is an ongoing problem at a number of sites, principally in the Western U.S. The contamination is a result of previously acceptable disposal practices and testing of solid rocket motors[1, 3]. Perchlorate is highly soluble and environmentally mobile; one result of this behavior is the presence of 8 ppb of perchlorate in Lake Mead due to migration of perchlorate from the Kerr-McGee site near Henderson, NV. The health effects of exposure to low levels of perchlorate are not well understood, and there is no current federal guideline for perchlorate contamination for groundwater. However, the perchlorate guidelines for a number of states vary from 1 ppb to 18 ppb, and the EPA draft assessment suggested a drinking water standard of 1 ppb perchlorate[2]. The responsibility for perchlorate remediation at many of these sites falls to DoD.

Although alternative technologies for perchlorate remediation include membrane filtration (reverse osmosis) and phytoremediation, they are either energy or water inefficient or are at a very early stage of development. For this reason, the background discussion here will be limited to bioremediation and ion exchange, which are currently used for perchlorate remediation[1, 3-5].

The most attractive approach to perchlorate remediation is bioremediation by perchlorate reducing bacteria[2, 8]. These organisms utilize perchlorate as an electron acceptor in respiration and reduce it to chloride. This remediation technology is applied in a number of different ways (including bacteria attached to solid media such as activated carbon, or batch reduction in stirred tank), but the general advantages and disadvantages are the same. The major advantages of bioremediation are low cost, especially for in situ bioremediation, and the fact that perchlorate is destroyed rather than simply removed. Bioremediation has been employed in ex situ, pump and treat facilities and in permeable barriers for shallow groundwater where anaerobic conditions are created using mushroom compost[2]. The latter example is especially interesting since conventional permeable reactive barriers containing zero valent iron are ineffective for treating perchlorate due to the slow kinetics of the reaction of perchlorate with iron metal[9].

While bioremediation is a very attractive technology, it is not applicable to all situations. When other electron acceptors, especially nitrate or oxygen, are present, reduction of perchlorate is suppressed because other electron acceptors are used preferentially to perchlorate[2, 8]. Therefore, bioremediation of perchlorate in this manner is not effective for treating surface water in situ. Bioreduction of perchlorate is also suppressed in systems with high total dissolved solids,
such as the brine generated by regeneration of anion exchange resin[10]. In addition, bioremediation is a not currently accepted treatment for drinking water in the U.S. although drinking water is currently treated using biological activated carbon (BAC).

The most mature technology for perchlorate remediation is ion exchange[1, 3-5]. The major advantages gained by using anion exchange to remove perchlorate are that the process is well understood and that ion exchange is an accepted method for treating drinking water. Ion exchange has a number of drawbacks such as the generation of perchlorate containing waste brine. A number of technologies have been developed to address this particular problem, including electrochemical destruction of perchlorate and destruction of perchlorate by acidic ferrous chloride[11]. Another drawback is the less than ideal perchlorate selectivity of conventional anion exchange resins (shown in Fig. 1A&B)[7]. As a result, only part of the exchange capacity of these resins can be utilized for perchlorate sorption[6]. This problem has been addressed by creating bifunctional resins (shown in Fig. 1C) that have a much higher affinity for perchlorate and can utilize more of their exchange capacity. However, these resins are much more expensive than conventional resins[5]. More recently, the production of N-nitrosamines from tertiary amines leached from these quaternary ammonium resins has emerged as a problem when using these resins to treat drinking water [12-14].

The affinity of ion exchange materials is generally expressed by the distribution coefficient, $K_d$, which is the equilibrium concentration of an ion on the resin (in mol kg$^{-1}$) divided by its concentration in solution (in mol L$^{-1}$). For the bifunctional resins, $K_d$($\text{ClO}_4^-$) > $3 \times 10^6$ mL g$^{-1}$ have been reported, which is approximately 5 times better than the best monofunctional, commercial resin (shown in Fig 1B) [6]. The distribution coefficient is also an indication of the selectivity of the ion exchange materials; materials with large distribution coefficients for perchlorate are highly selective for perchlorate and have a high capacity for perchlorate adsorption (mmol g$^{-1}$). Materials with smaller distribution coefficients have either low perchlorate selectivity or low perchlorate adsorption capacity or both.
Perchlorate selectivity in anion exchange resins is largely governed by the low energy of hydration of perchlorate, which is considerably smaller than those of the anions commonly found in groundwater (listed in Table 1) [15, 16]. The energy, $\Delta G_{\text{exch}}$, of exchanging a given anion, $A^-$, for perchlorate is the difference in their hydration energies, $G_{\text{hyd}}$, minus the difference in energies of their interactions with the ion exchange resin, $G_{\text{res}}$, as shown in equation 1.

$$
\Delta G_{\text{exch}} = (\Delta G_{\text{hyd},A^-} - \Delta G_{\text{hyd},\text{ClO}_4^-}) - (\Delta G_{\text{res},A^-} - \Delta G_{\text{res},\text{ClO}_4^-})
$$

(1)

Anions that are more strongly hydrated than perchlorate also interact more strongly with the ion exchange resin, so both terms in parentheses in Eq. 1 are negative. Therefore, one way to increase the perchlorate selectivity of the resin is to make the magnitude of the term $(\Delta G_{\text{res},A^-} - \Delta G_{\text{res},\text{ClO}_4^-})$ as small as possible by decreasing the strength of the interaction of anions with the resin. This is the strategy used in designing the perchlorate selective, bifunctional resins shown in Fig. 1C[7]. The interaction of the anions with the benzyltrimethylammonium group is much weaker than that of the benzyltrimethylammonium or benzyltripropylammonium group of the strong base type I and nitrate-selective resins, respectively, due to the decreased coulombic interaction created by the bulky alkyl group. The magnitude of the term $(\Delta G_{\text{res},A^-} - \Delta G_{\text{res},\text{ClO}_4^-})$ is also the reason that weak base anion exchange resins generally have poor perchlorate selectivity. The protonated ammonium group of weak base resins can interact strongly with the anion through hydrogen bonding, which results in poor perchlorate selectivity.
Table 1. Energies of Hydration, $\Delta G_{\text{hyd}}$, of Singly-Charged Anions\[15\].

<table>
<thead>
<tr>
<th>Anion</th>
<th>$\Delta G_{\text{hyd}}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO$^-$</td>
<td>-90</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>-88</td>
</tr>
<tr>
<td>F$^-$</td>
<td>-87</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>-80</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-79</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>-72</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-69</td>
</tr>
<tr>
<td>ClO$_3^-$</td>
<td>-67</td>
</tr>
<tr>
<td>I$^-$</td>
<td>-64</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>-56.6$^a$</td>
</tr>
<tr>
<td>ReO$_4^-$</td>
<td>-56.2$^a$</td>
</tr>
<tr>
<td>TcO$_4^-$</td>
<td>-54.0$^a$</td>
</tr>
</tbody>
</table>

a) Data from reference \[16\].

Anion Exchange by Activated Carbon

Unmodified activated carbon adsorbs perchlorate by anion exchange[17, 18]. Ordinary GAC has a moderate distribution coefficient, $\sim 2 \times 10^4$ mL g$^{-1}$, but GAC has a very low number of exchange sites, $2 \times 10^3$ meq g$^{-1}$[17]. Because of the low number of sites, it is more informative to compare the distribution coefficients per meq, $K_{\text{dm}}$, which is $K_d$ divided by the ion exchange capacity of the material in meq g$^{-1}$. The distribution coefficient of GAC, $K_{\text{dm}}$(ClO$_4^-$), is approximately $10^7$ mL meq$^{-1}$, which is comparable to that of the perchlorate selective bifunctional resin, $K_{\text{dm}}$(ClO$_4^-$) $> 10^6$ mL meq$^{-1}$[6]. So, GAC possesses few anion exchange sites that are highly selective for perchlorate. Unfortunately, this represents the only detailed study of the ion exchange of perchlorate by activated carbon.

Recent work by Cannon and coworkers has shown that the perchlorate adsorption capacity of GAC may be increased by treatment with ammonia at high temperatures [18, 19]. These ammonia treated carbons have three to four times the capacity of the precursor carbon material. Their work clearly demonstrates that the ammonia treatment increases the nitrogen content of the activated carbon as well as the net positive charge of the activated carbon. While the nature of the cationic site responsible for the ion exchange is not addressed directly, it is assumed to be a protonated pyridinic site (weak base ion exchange).

Although adsorption of perchlorate by activated carbon has not been extensively studied, adsorption of pertechnetate, TcO$_4^-$, has received a greater amount of attention. Since $\Delta G_{\text{hyd}}$ is very similar for both anions (see Table 1), their ion exchange behavior is similar. Distribution coefficients for perchlorate should be $\sim 20\%$ smaller than those of pertechnetate since perchlorate is more strongly hydrated [16]. A study of the pH dependence of pertechnetate adsorption showed that GAC possess two distinct sets of weak-base anion exchange sites[20]. The more abundant have a $pK_a$ $\sim 4$ and have a concentration of $\sim 0.5$ meq g$^{-1}$. The less numerous sites have a $pK_a$ $\sim 9$, but their concentration was not quantified. In other studies of adsorption of pertechnetate on activated carbon, the distribution coefficient varies from $10^3$ mL g$^{-1}$ to $10^6$ mL g$^{-1}$[21-23]. Overall, these studies show that activated carbon has a good selectivity for
pertechnetate, but few cationic exchange sites and pertechnetate adsorption is pH dependent with diminished capacity at higher pH.

The weak-base anion exchange behavior of activated carbon can be understood by examining the identities of its functional groups. Figure 2 shows an idealized graphene plane of activated carbon and the functional groups applicable to anion exchange[24, 25]. The functional group that is calculated to be the strongest base is actually the oxygen-based pyronic group (Fig. 2C), which is calculated to have a pKₐ between 7.5 to 12[25]. This is the functional group that is most likely responsible for anion exchange by activated carbon at neutral pH. The high selectivity of this site for perchlorate is due to the weakness of its interaction with anions, resulting from delocalization of the charge of the cationic site.

![Figure 2. Sites on Active Carbon Related to Anion Exchange. A) Pyridinic, B) Quaternary Nitrogen, C) Pyridonic, D) Protonated Pyridinic (pKa ~ 4), E) Stable Pyrylium Cation.](image)

The functional group responsible for anion exchange at lower pH is most likely the protonated pyridinic sites (Fig. 2D), which should have a pKa ~5[25]. The distribution coefficient for pertechnetate adsorption by this site is somewhat smaller than that of the pyrone as expected for a weak-base ion exchange site[20, 22]. Studies of the nitrogen containing functional groups present in activated carbon show that pyridinic groups can be prepared by treating activated carbon with a variety of different nitrogen containing molecules including ammonia, pyridine, or urea, at elevated temperatures[24, 26-29]. Heating to 800°C produces activated carbon containing 2 to 7 wt. % nitrogen mainly present as pyridinic sites (Fig. 2A)[24, 27]. Heating to higher temperatures transforms the pyridinic groups into quaternary nitrogen sites (Fig. 2B)[24, 27].

Both the quaternary sites and pyridinic sites are interesting from the standpoint of anion exchange. The quaternary site should have a very high affinity for perchlorate depending upon how its positive charge is compensated within the graphene sheet. The charge of the quaternary sites is somewhat delocalized, and activated carbon that contains a large number of these sites should be very effective at removing perchlorate by ion exchange.
The ability to produce a large number of pyridinic sites in activated carbon is particularly interesting due to the similarity of these sites to the weak-base ion exchange sites in the poly-(4-vinylpyridine) ion exchange resin, Reillex™-HP (Fig. 3B). Although Reillex™-HP is not particularly selective for pertechnetate, its methylated derivative, Reillex™-HPQ (Fig. 3D) is very selective for pertechnetate with $K_d > 10^4 \text{mL g}^{-1}$[30]. In comparison, the bifunctional, perchlorate-selective resins have very similar distribution coefficients for pertechnetate adsorption, $K_d = 5 \times 10^4 \text{mL g}^{-1}$[7]. Reillex™-HPQ is a relatively expensive anion exchange resin used in highly oxidizing environments, such as nitric acid, because the methylpyridinium group is resistant to electrophilic attack that degrades ordinary, polystyrene based anion exchange resins.

Figure 3. Comparison Between Pyridinic Sites in Activated Carbon and poly(4-vinylpyridine). A) Pyridinic Site, B) Reillex-HP™ [poly(4-vinylpyridine)], C) Methylated Pyridinic Site, D) Reillex-HPQ™ [methylated poly(4-vinylpyridine)]

The similarity between the pyridinic sites in activated carbon and the pyridine group of Reillex™-HP suggests that the pyridinic sites can be alkylated to give a strong base anion exchange material (GMAC) with high selectivity for perchlorate analogous to Reillex™-HPQ. The main advantage of activated carbon is its low cost ($0.80 \text{lb}^{-1}$ or $24 \text{ft}^{-3}$)[31] compared with conventional ion-exchange resin (Fig. 1B, ~$200 \text{ft}^{-3}$)[5]; the bifunctional, perchlorate selective resin is more expensive. Although GMAC would be more expensive than activated carbon, it could still be considerably less expensive than ion-exchange resin. Estimating the selectivity of GMAC is difficult, but based on the analogy of the structures of the methylated pyridinic group and the methylated pyridinium group of Reillex™-HPQ and the selectivity of activated carbon for pertechnetate, the perchlorate selectivity of GMAC should be very high. Although the perchlorate adsorption capacity of GMAC can be estimated from the wt. % N (1 wt. % N is equivalent to 0.83 meq g$^{-1}$), the proton adsorption capacity of activated carbon containing largely pyridinic sites is ~0.8 meq g$^{-1}$ regardless of the wt. % N. Consequently, the anticipated perchlorate adsorption capacity of GMAC is ~1 meq g$^{-1}$, which is less than commercial ion exchange resins (2-3 meq g$^{-1}$), but the distribution coefficients of GMAC and commercial resins should be similar since GMAC should have greater perchlorate selectivity.

**Perchlorate Remediation by GMAC**

The main application addressed by this proposal is removal of perchlorate from drinking water. The proposed technology is to use GMAC in place of ordinary GAC or ion exchange resin to adsorb perchlorate. Although this could be accomplished using conventional ion-exchange resin, the use of a less expensive material (GMAC) would be more economical if the material has
sufficient perchlorate selectivity and adsorption capacity. Ideally, GMAC would be used as a single use adsorbent rather than being regenerated. Whether this is economically feasible depends upon the actual cost of producing GMAC versus the cost of ion-exchange resin and the added capital costs of the regeneration equipment.

GMAC could also be used as an anion exchange material in conventional pump and treat remediation systems. Whether this would be economical depends upon the perchlorate concentration in the influent and how well GMAC withstands regeneration. More interesting is the potential for using GMAC in conjunction with bioremediation, especially in BAC treatment. Ordinary GAC is an excellent support material for bacteria used in a BAC filter for water treatment[32, 33]. BAC treatment is highly effective for removing dissolved organic compounds (DOC) from water because of the synergy between adsorption of these compounds on GAC and development of the bacterial community. During the initially phase of operation, DOC is largely adsorbed by GAC; however, once the bacterial community has been established, DOC is largely destroyed by the bacteria and the sorption capacity of GAC regenerated[32]. Since BAC filters require periodic backwashing to prevent clogging by biofilm, the contaminant must remain strongly adsorbed to the GAC, which is the case for DOC. Unfortunately, although BAC filters initially work well for perchlorate reduction, they fail following backwashing due to desorption of perchlorate from GAC[17, 34]. This situation could be remedied by the use of GMAC in place of GAC. Since GMAC would strongly adsorb perchlorate, the problem of perchlorate desorption following backwashing would be minimized, and BAC treatment could potentially be used for perchlorate remediation.

An additional advantage presented by GMAC is that regulatory approval should be relatively simple since GMAC is a form of activated carbon, which is already approved for use in a wide variety of applications.

Materials and Methods.

General
Deionized (DI) water was purified using a Milli-Q system. All chemicals were reagent grade and used as received. pH was measured using a VWR Symphony pH meter, which was calibrated either at pH 4 and 7 or pH 4 and 10 immediately prior to use. The activated carbon (AC) used was GC12x40 provided by General Carbon, and is derived from bituminous coal. Prior to use, CG12x40 (100 g) was washed with 6M HCl (250 mL) for 12 hours followed by rinsing with DI water until the rinse water had the same pH as the DI water. Pyromex® oxygen stabilized polyacrylonitrile (PAN) was provided by Toho Tenax America. Elemental analysis were determined by the University of California - Berkeley microanalytical laboratory. BET surface areas were determined by Materials Synergy, Oxnard, California.

Activated Carbon Treated with Ammonia (NAC)
Activated carbon (10 g) was weighed into a horizontal tube furnace and held in place with quartz wool. The furnace was purged with air and heated to 400°C for 4 hours. At this point, the furnace was purged with nitrogen for 5 minutes and then purged with mixture of ammonia and nitrogen (~9:1) and heated to 700°C for 4 hours. The AC was allowed to cool under the flowing NH₃/N₂. The resulting carbon had a strong ammonia odor and was treated under vacuum until the pressure was less than 30 mTorr. Yield: 8.95 g.
Activated Carbon Treated with Urea-formaldehyde Resin (UAC)[35]
To 35 mL of formaldehyde solution (37% in water) was added 2 drops of 12 M HCl, and the solution was heated to 90°C. Urea (6.07 g, 101 mmol) was added resulting in a vigorous exothermic reaction. The reaction mixture was cooled to 60°C and stirred for 30 min. Activated carbon (48.62 g) was added until incipient wetness. The mixture was dried at 140°C overnight. Dried mixture (10 g) was placed in a tube furnace, purged with nitrogen, and heated to 800°C under nitrogen purge. The carbon material was washed with DI water until the pH was neutral and dried at room temperature on a glass filter. Yield 7.11 g.

Ammonia Treated UAC (NUAC)
UAC (10 g) was placed in a tube furnace and purged with nitrogen for 10 minutes. The gas was changed to a ~9:1 mixture of ammonia and nitrogen and the furnace was heated to 800°C for 4 hours. The carbon was then purged with nitrogen and the furnace was allowed to cool under a nitrogen purge. The carbon was treated under vacuum until the pressure was less than 30 mTorr at 100°C. Yield: 8.44 g.

Activated Carbon Treated with Hydrogen (HAC)
AC (4.8 g) was placed in a tube furnace and purged with 10% hydrogen in argon. The furnace was heated to 800°C for 1 hour and allowed to cool to room temperature under the same gas. The carbon was washed with DI water until the pH was neutral and dried on the glass filter. Yield 4.64 g.

Methyl Chloride Alkylated Activated Carbon
Methyl chloride (MeCl) treatment was carried out in a tube furnace generally in conjunction with some other technique. The example here is for HAC. Activated carbon (HAC, 5.0 g) was loaded into a tube furnace and purged with 10% hydrogen in argon. The furnace was heated to 800°C for 1 hour. The furnace was cooled to 500°C and purged with methyl chloride. The furnace was maintained at 500°C for 30 minutes under a slow purge of methyl chloride and cooled to room temperature. The resulting material was washed with water (extremely acidic) then stirred with 2 g of ammonium acetate in 50 mL of water for 30 minutes. The material filtered and washed on the filter with 1 L of DI water then dried at 100°C under vacuum. Yield 5.16 g. The MeCl treated carbons have the prefix “A,” for alkylated and suffix “MeCl”: the MeCl alkylated, hydrogen treated carbon is AHAC-MeCl.

Note: During the synthesis of sample ANUAC-MeCl, the methyl chloride cylinder became empty, and it is likely that air leaked into the furnace as it cooled.

Dimethyl Sulfate Alkylated Activated Carbon
Dimethyl sulfate (Me₂SO₄) treatment was carried out on activated carbon already treated to increase it nitrogen content. The example here is for NUAC. Activated carbon (NUAC, 3.0 g) was weighed into a Teflon lined stainless steel autoclave. Dimethyl sulfate (4.5 mL) was added and the autoclave was sealed and heated to 107°C for 16 hrs. The material was removed from the autoclave and washed with acetone (3 x 25 mL). The carbon was suspended in HCl (1 M, 120 mL) and heated to reflux for 16 hr to destroy residual Me₂SO₄. The material was filtered, washed with NaHCO₃ (5%, 100 mL) then with 1 L DI water and dried on the glass filter. Yield 3.03 g.
The Me$_2$SO$_4$ treated carbons have the prefix “A,” for alkylated and suffix “Me$_2$SO$_4$”: the Me$_2$SO$_4$ alkylated, NUAC carbon is ANUAC-Me$_2$SO$_4$.

**Methyl Iodide Alkylated Activated Carbon** [36]
Activated carbon (10.0 g) was suspended in 100 mL tetrahydrofuran and tetra-n-butylammonium hydroxide (5 mL) was added. The mixture was stirred for 2 hr, and methyl iodide (MeI, 1 mL) was added. The mixture was stirred overnight. The activated carbon was removed by filtration and dried under vacuum. The carbon was washed with 1 L water and allowed to dry on the filter. Yield (9.40 g). The MeI treated carbons have the prefix “A,” for alkylated and suffix “MeI”: the MeI alkylated, AC carbon is AAC-MeI.

**Polyacrylonitrile Activated Carbon (PANC)**
Pyromex® fibers were washed with acetone (3x20 mL) then placed in a tube furnace and purged with nitrogen. The furnace was heated to 1000°C then furnace was purged with carbon dioxide for one hour at 1000°C. The furnace was purged with nitrogen and allowed to cool to 380°C. The furnace was purged with MeCl and allowed to cool under a slow MeCl purge. The carbon was washed with 1 L water and dried under vacuum. Yield 0.95 g.

**Activated Carbon Treated with Other Chemical Elements**
Activated carbon was treated at incipient wetness with the desired chemical element dissolved in water. The carbon was dried on a glass filter the heated in a tube furnace under 10% hydrogen in argon and treated with MeCl at 300 to 500°C. The following is the example for iron.

Ferrous chloride tetrahydrate (1.99g) was dissolved in HCl (0.1M, 7 mL) and added to 10.0 g of AC in a plastic centrifuge tube. The tube was shaken vigorously to distribute the solution on the activated carbon. The carbon was dried on a fritted glass filter overnight. The carbon was placed in a tube furnace and purged with 10 % hydrogen in argon then heated to 800°C for 1 hour. The furnace was cooled to 500°C and purged with MeCl, the furnace was held at 500°C for 30 min then allowed to cool to RT. The carbon was washed with 200 mL water then stirred in 50 mL water containing 1 g ammonium acetate for one hour. The material was washed with 2 L water and dried on a fritted glass filter. Yield 11.92 g.

**Absorption Isotherm Experiments**
Activated carbon was weighed into a set of eight 50 mL polypropylene centrifuge cones. The mass of the activated carbon in the tubes was nominally 80 mg, 60 mg, 40 mg, 30 mg, 20 mg, 10 mg, 5 mg, and 0 mg although the exact value varied somewhat. To each of the tubes was added 25 mL of either 200 μM NH$_4$ReO$_4$ in DI water or 10.0 μM NaClO$_4$ in a synthetic groundwater (0.21 mM NaCl, 0.35 mM Na$_2$SO$_4$, 0.11 mM NaNO$_3$, and 1.5 mM NaHCO$_3$). The tubes were placed on a sample rocker and rocked for 20 hours. The ReO$_4^-$ or ClO$_4^-$ concentrations and the pH were then determined for each tube.

**Perchlorate Analysis**
Perchlorate concentrations were determined using a Dionex DX150 Ion Chromatograph with a 4 mm AS16 column a 4 mm AG16 guard column. The samples were first filtered through a 0.22 μM filter, and the samples with high concentrations of perchlorate (samples containing <30 mg of activated carbon) were diluted by 10 x prior to analysis.
**Perrhenate Analysis**

Perrhenate concentrations were determined spectrophotometrically. Either 1.00 or 2.00 mL of solution was added to a 5 mL volumetric flask followed by 1.30 mL of α-furildioxime (16 mM in acetone) and 1.0 mL Sn²⁺ (0.3 M in 3 M HCl) and water to make 5.00 mL. The solutions were allowed to stand for 1 hour and the absorption at 532 nM was measured using an Ocean Optics spectrometer. Absorption was corrected for a blank containing the reagents without perrhenate, and the extinction coefficient was determined from the absorbance of the sample that did not contain activated carbon (ε~7400 cm⁻¹ M⁻¹).

**X-ray Photoelectron Spectroscopy (XPS)**

Samples were powdered with a small ball mill (Wig-L-Bug) and placed on small (1 mm square) pieces of conductive carbon tape on a stainless steel sample stage. The samples were evacuated to <10⁻⁸ mTorr. Spectra were recorded using the High-pressure photoemission spectroscopy endstation of beamline 11.0.2 of the Advanced Light Source. Photon binding energy was referenced to the carbon peak at 284.5 eV. Spectra were analyzed using the program Fitt. A Tougaard background was used for all spectra. For the graphitic carbon peak an asymmetric Doniach-Sunjic lineshape with α (asymmetry parameter) fixed at 0.19 [37]. All other peaks were fit using a pseudoVoigt lineshape. For all peaks, the Lorenzian linewidth was fixed a value determined by the core-hole lifetime. The peak energies and intensities were allowed to vary and a single Gaussian linewidth was used for all peaks except the carbon carboxylate/π−π∗ shake up peak, for which the linewidth was allowed to vary independently.

**Slurry pH Measurements**

1.0 g of powdered activated carbon was suspended in 10.0 mL of DI water and placed on a sample rocker. Samples were rocked for 20 hours, and the pH was determined.

**Results and Accomplishments.**

As stated in the introduction, the goal of this project was to increase the perchlorate absorption capacity of activated carbon. This goal was to be accomplished in two ways. First, the number of potential cationic ion exchange sites in activated carbon was to be increased by increasing the nitrogen content of activated carbon. Second, the perchlorate selectivity of activated carbon was to be increased by alkylation of the weak base ion exchange sites to convert them into strong base sites. Inherent in this approach are hypotheses that the nitrogen groups are the weak base ion exchange sites and that the pyridinic nitrogen groups can be alkylated in the same way as their molecular analogs. The first of these hypotheses is somewhat speculative, but the second hypothesis did not seem speculative at the outset of this project. Ultimately, both of these hypotheses proved to be inconsistent with the results of this project. The results are separated into synthetic studies, absorption studies, and x-ray photoelectron spectroscopy (XPS) studies of the modified activated carbon materials. The conclusion section includes a discussion of the effect of these chemical treatments on the functional groups on the activated carbon surface and absorption of perchlorate.

**Synthesis of Modified Activated Carbon**

The synthetic studies largely fall into two categories: alkylation of activated carbon and enhancement of nitrogen content. The goal of this project was to increase the nitrogen content in pyridinic sites and then to alkylate these sites. Three different approaches were used to increase
the nitrogen content of the activated carbons: ammonia treatment, urea-formaldehyde resin treatment, and using polyacrylonitrile (PAN) as a precursor. These carbons were subjected to different techniques to alkylate the functional groups present on the activated carbon surface.

The goal of alkylation of activated carbon is to convert the weak-base ion exchange sites into strong-base sites. Successfully converting the sites should increase the selectivity of activated carbon for poorly solvated anions, such as perchlorate, perrhenate (ReO₄⁻) or pertechnetate (TcO₄⁻) as described in the introduction. In comparison to unmodified carbon, alkylated carbon should behave at neutral pH like unmodified carbon behaves at low pH. In the case of pertechnetate, the absorption capacity of unmodified carbon at pH=1 is ~3 times that at neutral pH [20]. Properties of the modified activated carbons are listed in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>pH (slurry)</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>BET surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent activated carbon</td>
<td>AC</td>
<td>8.82</td>
<td>85.2</td>
<td>0</td>
<td>0.33</td>
<td>1107</td>
</tr>
<tr>
<td>AC alkylated with methyl chloride</td>
<td>AAC-MeCl</td>
<td>8.73</td>
<td>89.76</td>
<td>0.38</td>
<td>0.35</td>
<td>788</td>
</tr>
<tr>
<td>AC alkylated with methyl iodide</td>
<td>AAC-MeI</td>
<td>9.19</td>
<td>89.19</td>
<td>1.25</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Ammonia treated AC</td>
<td>NAC</td>
<td>9.14</td>
<td>88.16</td>
<td>0.38</td>
<td>1.48</td>
<td>1070</td>
</tr>
<tr>
<td>NAC alkylated with Me₂SO₄</td>
<td>ANAC-Me₂SO₄</td>
<td>5.23</td>
<td>79.36</td>
<td>0.71</td>
<td>1.19</td>
<td>1075</td>
</tr>
<tr>
<td>AC treated with urea-formaldehyde resin</td>
<td>UAC</td>
<td>10.21</td>
<td>79.94</td>
<td>0.13</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>Ammonia treated UAC</td>
<td>NUAC</td>
<td>10.23</td>
<td>73.12</td>
<td>0.19</td>
<td>1.28</td>
<td>1035</td>
</tr>
<tr>
<td>NUAC alkylated with Me₂SO₄</td>
<td>ANUAC-Me₂SO₄</td>
<td>3.63</td>
<td>81.8</td>
<td>0.96</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>NUAC alkylated with MeCl</td>
<td>ANUAC-MeCl</td>
<td>6.62</td>
<td>86.13</td>
<td>0.55</td>
<td>2.29</td>
<td>802</td>
</tr>
<tr>
<td>Hydrogen treated AC</td>
<td>HAC</td>
<td>9.02</td>
<td>86.32</td>
<td>0.16</td>
<td>0.36</td>
<td>1072</td>
</tr>
<tr>
<td>HAC alkylated with MeCl</td>
<td>AHAC-MeCl</td>
<td>3.90</td>
<td>87.4</td>
<td>0.2</td>
<td>0.26</td>
<td>880</td>
</tr>
<tr>
<td>Polyacrylonitrile activated with CO₂, treated with H₂, and alkylated with MeCl</td>
<td>PANC</td>
<td>82.48</td>
<td>0.88</td>
<td>6.82</td>
<td></td>
<td>305</td>
</tr>
</tbody>
</table>
As shown in Table 2, treatments to increase nitrogen content functioned as anticipated in that both urea treatment and ammonia treatment increased the nitrogen content of the activated carbon. In addition, the slurry pH, which loosely follows the point of zero charge of the carbon surface, varies as expected. Treatment with either nitrogen or urea produces a more basic functional groups (or decrease the number of acidic functional groups) present on the carbon surface as anticipated. Subsequent treatment with alkylation agents lowers the solution pH as the basic sites are alkylated. In the case of Me$_2$SO$_4$ treatment, the low slurry pH is believed to be due to slow hydrolysis of MeSO$_4^-$ adsorbed on the activated carbon. The origin of the low pH in the HAC-MeCl sample is unknown.

**Perrhenate Absorption by Modified Activated Carbons**

Due to several problems with perchlorate analysis by ion chromatography, initial characterization of the absorption properties of activated carbons was performed using perrhenate (ReO$_4^-$) rather than perchlorate. Colorimetric analysis of perrhenate concentrations were much more reliable; however, low concentrations (1-10 ppb) of perrhenate could be measured by this technique. The hydration energy of perrhenate is almost identical to that of perchlorate (see Table 1) and the difference in partitioning of the two ions in solvent extraction studies is ~4% [16]. Consequently, perrhenate is an excellent surrogate for perchlorate, and the perrhenate absorption by activated carbon is directly comparable to perchlorate absorption.

The absorption isotherms were modeled using the Langmuir isotherm, where $C_{\text{sol}}$ is the concentration in solution (in mol L$^{-1}$), $C_{\text{ads}}$ is the amount adsorbed on carbon (in mol kg$^{-1}$), $N_L$ is the number of sites and $K$ is the equilibrium coefficient [38]. For a few samples, a significantly better fit was produced using the Toth isotherm, shown in Eq 3, where $t$ is the heterogeneity parameter [39, 40]. In particular, adsorption of perrhenate by HAC and ANAC-Me$_2$SO$_4$, was not particularly well modeled by the Langmuir isotherm, which indicates that the cationic sites in these samples possess a greater degree of heterogeneity than other samples. Although the Toth isotherm produces a better fit to the data and consequently a more accurate determination of the absorption capacity of the activated carbon, using the Toth isotherm model leads to a loss of physical insight provided by $K$ and $N_L$. Consequently, the Langmuir isotherm model parameters are also included in Table 3 for materials in which the Toth isotherm better describes the adsorption of perrhenate. An additional figure of merit $K_d$ at $C_{\text{sol}} = 10^{-6}$ M (100 ppb), where $K_d = C_{\text{ads}}/C_{\text{sol}}$, is an indication of how well the material would work at concentrations more similar to those found in affected environments. Moreover, $K_d$ at $10^{-6}$ M provides a useful means for comparison the of the absorption capacity of the different materials regardless of the model used to describe the adsorption isotherm.

\[
C_{\text{ads}} = N_L \frac{K C_{\text{sol}}}{1 + K C_{\text{sol}}} \tag{2}
\]

\[
C_{\text{ads}} = N_L \frac{K C_{\text{sol}}}{1 + (K C_{\text{sol}})^t} \tag{3}
\]

The effects of ammonia treatment and alkylation on the absorption properties of activated carbon are quantified in Table 3 along with results from Chen, et al. on perchlorate absorption by
activated carbon and ammonia treated activated carbon [18]. The most striking result obtained from the analysis of the perrhenate absorption isotherms is that the number of exchange sites, $N_L$, seems to vary only very slightly during chemical modification. This is in marked contrast to the amount of nitrogen in the activated carbons: both ammonia treated carbons, NAC and NUAC, contain five times as much nitrogen as does AC, and PANC contains at least 10 times as much nitrogen as AC. Moreover, in NAC and NUAC the added nitrogen should be present at the pore walls since it was added after activation of the carbon. However, NAC and NUAC have only approximately twice as many cationic sites as AC, and PANC, with ten times the amount of nitrogen, has approximately the number of cationic sites as AC. On the other hand, the selectivity, $K$, of the cationic sites for poorly solvated anions varies widely. Ammonia treatment has little effect on the selectivity. Hydrogen treatment increases $K$ as well as $N_L$. Finally alkylation increases $K$ by approximately a factor of 5 although this varies somewhat.

### Table 3. Perrhenate Absorption Data by Modified Activated Carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH$^a$</th>
<th>$K$</th>
<th>$N_L$</th>
<th>$K_d$ (10$^6$M)</th>
<th>$10^3 K_d$ /BET</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>NA</td>
<td>6.5E+04</td>
<td>0.143</td>
<td>8.8E+03</td>
<td>7.9E+03</td>
</tr>
<tr>
<td>AAC-MeCl</td>
<td>8.67</td>
<td>4.2E+05</td>
<td>0.143</td>
<td>4.3E+04</td>
<td>5.4E+04</td>
</tr>
<tr>
<td>AAC-MeI</td>
<td>8.64</td>
<td>2.8E+05</td>
<td>0.256</td>
<td>5.7E+04</td>
<td></td>
</tr>
<tr>
<td>NAC</td>
<td>9.04</td>
<td>9.3E+04</td>
<td>0.152</td>
<td>1.3E+04</td>
<td>1.2E+04</td>
</tr>
<tr>
<td>ANAC-Me$_2$SO$_4$</td>
<td>7.29</td>
<td>6.9E+05</td>
<td>0.273</td>
<td>1.1E+05</td>
<td>1.0E+05</td>
</tr>
<tr>
<td>UAC</td>
<td>8.77</td>
<td>4.2E+04</td>
<td>0.309</td>
<td>1.3E+04</td>
<td></td>
</tr>
<tr>
<td>NUAC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANUAC-Me$_2$SO$_4$</td>
<td>7.72</td>
<td>2.8E+05</td>
<td>0.236</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANUAC-Me$_2$SO$_4$ (t=0.175)$^b$</td>
<td>7.72</td>
<td>5.2E+07</td>
<td>0.753</td>
<td>7.5E+04</td>
<td></td>
</tr>
<tr>
<td>ANUAC-MeCl</td>
<td>7.69</td>
<td>5.8E+05</td>
<td>0.223</td>
<td>8.1E+04</td>
<td>1.5E+05</td>
</tr>
<tr>
<td>HAC</td>
<td>9.04</td>
<td>2.2E+05</td>
<td>0.210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAC (t=0.054)$^b$</td>
<td>9.04</td>
<td>5.3E+13</td>
<td>27.3</td>
<td>6.5E+04</td>
<td>3.5E+04</td>
</tr>
<tr>
<td>HAC-MeCl</td>
<td>5.12</td>
<td>1.2E+06</td>
<td>0.263</td>
<td>1.4E+05</td>
<td>1.6E+05</td>
</tr>
<tr>
<td>PANC, H$_2$/MeCl</td>
<td>8.12</td>
<td>4.7E+05</td>
<td>0.145</td>
<td>4.6E+04</td>
<td>1.5E+05</td>
</tr>
<tr>
<td>SAI $^c$</td>
<td></td>
<td>6.9E+04</td>
<td></td>
<td>7.9E+04</td>
<td></td>
</tr>
<tr>
<td>SAI-500-60 $^c$</td>
<td></td>
<td>7.4E+04</td>
<td></td>
<td>8.6E+04</td>
<td></td>
</tr>
<tr>
<td>SAI-600-60 $^c$</td>
<td></td>
<td>9.7E+04</td>
<td></td>
<td>1.1E+05</td>
<td></td>
</tr>
<tr>
<td>SAI-700-60 $^c$</td>
<td></td>
<td>8.9E+04</td>
<td></td>
<td>9.5E+04</td>
<td></td>
</tr>
<tr>
<td>SAI-800-60 $^c$</td>
<td></td>
<td>9.3E+04</td>
<td></td>
<td>1.0E+05</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $K_d$ for ClO$_4^-$ rather than for ReO$_4^-$

$^b$ pH of sample with 100 mg carbon in 25 mL 0.200 mM ReO$_4^-$.  

$^c$ Data for Toth isotherm

$^d$ Data from reference[18]. SAI is unmodified activated carbon, SAI-xxx-60 are activated carbons tailored with ammonia at xxx °C.
The result of the changes in $K$ and $N_1$ are corresponding changes in the absorption capacity at $10^{-6}$ M. Simply alkylating the activated carbon increases its capacity by a factor of 5. Treatment of the activated carbon with either ammonia or nitrogen, followed by alkylation increases its absorption capacity by approximately an order of magnitude. In comparison to the ammonia tailored carbon reported by Cannon and coworkers, the alkylated carbons are not significantly better. In the case of the SAI carbons, ammonia treatment does not result in a large increase in capacity for absorption of perchlorate from deionized water. However, the parent SAI carbon has very good absorption properties to begin with.

The effects of different chemical modifications of the activated carbon surfaces are more clearly illustrated by directly comparing the absorption isotherms. Figure 4 shows the $\text{ReO}_4^-$ absorption isotherm of the parent AC along with the isotherms of the chemically reduced carbons: NAC, UAC, and HAC. In comparison to the parent, AC, ammonia treatment slightly increases the number of absorption sites as well as the selectivity, which is in good agreement with the results of Chen, et al. Treatment with urea-formaldehyde resin greatly increases the number of sites, but the sights have approximately the same selectivity as those in the parent activated carbon. Finally, hydrogen treatment somewhat increases the number of sites, but greatly increases the selectivity of the sites.

![Figure 4. Isotherms for Absorption of Perrhenate on Activated Carbons (AC) Modified by Treatment with Ammonia (NAC), Urea-formaldehyde Resin (UAC), and Hydrogen (HAC). Data are Indicated by the Symbol and Least Squares Fit of the Langmuir Isotherm to the Data is Indicated by the Solid Lines. For HAC, the Toth Isotherm was used.](image)

The effect of ammonia treatment (or urea treatment) followed by alkylation is illustrated in Figure 5. On first inspection, these results seem very promising. Alkylation of carbon can be accomplished using a very strong alkylating agent, dimethyl sulfate, at elevated temperature. Use of this reagent requires an additional step to destroy the residual dimethyl sulfate, which is highly toxic, and to destroy the remaining methyl sulfate, $\text{CH}_3\text{OSO}_3^-$, which is not particularly
hazardous but has a low solvation energy. Any remaining methyl sulfate will compete with perchlorate (or perrhenate) for adsorption sites on the activated carbon. Destruction of the methyl sulfate and dimethyl sulfate was accomplished by treating the activated carbon in 0.6 M NaHCO₃ or 1 M HCl at reflux for 12 hours followed by neutralization. The more aggressive HCl reflux, used in the synthesis of ANUAC-Me₂SO₄, appears to result in the hydrolysis of some of the alkylated functional groups on the carbon surface as indicated by the much greater heterogeneity of the interactions of the cationic sites with the perrhenate. For comparison, ANAC-Me₂SO₄ was treated with 5% NaHCO₃, and its isotherm is in good agreement with the Langmuir model, which indicates much less heterogeneity in the interaction of the cationic sites with the perrhenate. Of greater utility is the alkylation of the activated carbon using methyl chloride (MeCl), which can be performed by treating the activated carbon directly with gaseous MeCl. Furthermore, MeCl is far less toxic than dimethyl sulfate and the methyl chloride treatment does not require solvent. Regardless of the alkylation methodology, the cationic sites have a much greater selectivity for perrhenate. However, the number of cationic sites (~ 0.2 meq g⁻¹) is disappointingly low; much lower than the amount of nitrogen, 1 wt. % or 0.8 meq g⁻¹, added by ammonia or urea-formaldehyde/ammonia treatment.

Figure 5. Isotherms for Absorption of Perrhenate on Activated Carbons (AC) Modified by Treatment with Ammonia (NAC), Ammonia Treated Carbon Alkylated with Dimethylsulfate (ANAC-Me₂SO₄), Carbon Treated Urea-formaldehyde Resin and Ammonia Then Alkylated Using Methyl Chloride (ANUAC-MeCl) or Dimethyl Sulfate (ANUAC-Me₂SO₄). Data are Indicated by the Symbol and Least Squares Fit of the Langmuir Isotherm to the Data is Indicated by the Solid Lines. For ANUAC-Me₂SO₄, the Toth Isotherm was used.

The uncertainty caused by the low number of cationic sites in comparison to the number of nitrogen sites is underscored by the effect of alkylation alone on the absorption of ReO₄⁻ by activated carbon as illustrated in Figure 6. Treatment with methyl chloride clearly increases the selectivity for ReO₄⁻, but does not greatly affect the number of cationic sites. On the other hand,
treatment with methyl iodide (MeI) increases both the selectivity and the number of sites. Interestingly, the methyl iodide treatment described here has been widely used in treating coal to increase its solubility in organic solvents. Based on work by Liotta and others, the methyl iodide treatment is known to mainly alkylate oxygen-based functional groups, especially carboxylates and phenolates [36, 41]. It can also alkylate the carbon sites, and can be reasonably expect to alkylate pyridinic sites if they are present at the pore surface [41].

Based on the initial assumptions that alkylation of activated carbon would convert the neutral pyridinic sites into cationic alkyl pyridinium sites, MeCl alkylation of the parent activated carbon, AC, was carried out as a control experiment to demonstrate that this treatment had little effect without first increasing the nitrogen content of the carbon. However, the results indicated that other reactivity was occurring. Therefore, the methyl iodide alkylation was performed. The greatly increased number of cationic sites strongly implies that the important functional groups in determining the absorption behavior are oxygen-based (pyronic, phenolic, and carboxylic sites) rather than nitrogen sites as initially hypothesized.

![Graph showing isotherms for absorption of perrhenate on activated carbons modified by treatment with methyl chloride gas at 500°C (AAC-MeCl), and activated carbon suspended in tetrahydrofuran treated with tetra-n-butylammonium hydroxide followed by methyl iodide (AAC-MeI). Data are indicated by the symbol and least squares fit of the Langmuir isotherm to the data is indicated by the solid lines.]

**Figure 6. Isotherms for Absorption of Perrhenate on Activated Carbons (AC) Modified by Treatment with Methyl Chloride Gas at 500°C (AAC-MeCl), and Activated Carbon Suspended in Tetrahydrofuran Treated with Tetra-n-butylammonium Hydroxide Followed by Methyl Iodide (AAC-MeI). Data are Indicated by the symbol and least squares fit of the Langmuir isotherm to the data is indicated by the solid lines.**

The hypothesis that the oxygenated functional groups control the selectivity of anion absorption by activated carbon is strongly supported by the effect of hydrogen treatment and subsequent alkylation as illustrated in Figure 7. In particular, AHAC-MeCl has both a greater concentration of cationic sites and better perrhenate selectivity than ANUAC-MeCl even though AHAC-MeCl contains very little nitrogen, < 0.3%.

As an additional probe of the role of nitrogen in adsorption of anions, a small number of activated carbons were prepared from polyacrylonitrile (PAN). These activated carbons (PANC)
typically have a high nitrogen content (5-10 wt %, depending on synthesis conditions) and surface areas similar to coal derived activated carbon. None of these carbons were exceptionally effective for adsorbing perrhenate, and most of them had very poor adsorption characteristics. The PANC with the greatest capacity was prepared by from oxidatively stabilized PAN, which was then pyrolyzed, activated with carbon dioxide, then treated with hydrogen followed by methyl chloride. As shown in Table 3, when normalized for surface area, the perrhenate absorption of the PANC is the same as that of the functionalized activated carbon.

![Figure 7. Isotherms for Absorption of Perrhenate on Activated Carbons (AC) Modified by Treatment with Hydrogen (HAC) and by Treatment with Hydrogen Followed by Treatment with Methyl Chloride (AHAC-MeCl). Data are Indicated by the Symbol and Least Squares Fit of the Langmuir Isotherm to the Data is Indicated by the Solid Lines. For HAC, the Toth Isotherm was used.](image)

Perchlorate Absorption from Synthetic Groundwater by Modified Activated Carbons
Perchlorate absorption measurements were limited to measurements of the isotherm for adsorption of perchlorate from simulated groundwater (0.21 mM NaCl, 0.35 mM Na₂SO₄, 0.11 mM NaNO₃, and 1.5 mM NaHCO₃) containing 10.0 µM ClO₄⁻ (0.99 ppm ClO₄⁻). In comparison to the perrhenate absorption isotherms, these isotherms only examine the roughly linear, low-loading (Henry’s Law) region of the isotherm. For this reason, K and N_L are strongly correlated, and K_d at 10⁻⁶ M is the more useful metric. Data for selected materials along with the performance of the ammonia tailored SAI carbons, which were estimated from column breakthrough data are given in Table 4.
As indicated by the data in Table 4, the alkylated activated carbons perform better than their unalkylated precursors; however, the difference in performance is much smaller than for removal of perrhenate from DI water. The alkylated carbons have only 3-4 times the adsorption capacity of the parent material in comparison to the approximately 10 times greater capacity for adsorption of perrhenate from deionized water. The alkylated carbons have smaller capacities than the ammonia tailored carbons. However, this is not a completely valid comparison for two reasons. The SAI carbons were ground to 200x400 mesh whereas the carbons materials used here were all 12x40 mesh. More importantly, ground water contains divalent metal ions, Ca\(^{2+}\) in particular, that can ion-exchange onto the anionic surface sites of activated carbon. While this is also true for Na\(^{+}\), adsorption of Ca\(^{2+}\) onto an anionic surface site will generate an additional cationic surface site. With these factors in mind, the alkylated carbons seem to have similar performance to the ammonia treated carbons.

X-ray Photoelectron Spectroscopy of Modified Carbons
The carbon, nitrogen, and oxygen functional groups were examined by x-ray photoelectron spectroscopy (XPS) with the aim of determining the changes in functional groups caused by the chemical modifications of the activated carbons. Due to the low concentration of anion exchange sites (~0.2 meq g\(^{-1}\), or ~0.4 wt. %) makes this effort particularly challenging if the changes are largely due to carbon speciation since carbon comprises ~80% of these samples. However, if the changes are to the nitrogen or oxygen functional groups, then XPS has a reasonably good chance of detecting the changes to these functional groups.

In addition to providing information about speciation of the different elements, XPS provides elemental composition of the surfaces examined. This information is given in Table 5 along with the results from combustion analysis. Note that the samples examined by combustion analysis were in equilibrium with water vapor and part of their mass is adsorbed water, which is presumably the major source for the difference in %C between the two analytical techniques.
The most obvious difference between the two types of analysis is the large difference in % N. There is no obvious reason for the difference. The most obvious correlation between the composition of the materials and the perchlorate absorption capacity is the inverse correlation between % O and the perchlorate absorption capacity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C (EA)</th>
<th>%H (EA)</th>
<th>%N (EA)</th>
<th>%C (XPS)</th>
<th>%O (XPS)</th>
<th>%N (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0.33</td>
<td>93.2</td>
<td>6.8</td>
<td>0.0</td>
</tr>
<tr>
<td>AAC-MeCl</td>
<td>94.1</td>
<td>5.9</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AAC-MeI</td>
<td>95.9</td>
<td>4.1</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>88.16</td>
<td>0.38</td>
<td>1.48</td>
<td>94.4</td>
<td>5.6</td>
<td>0.6</td>
</tr>
<tr>
<td>ANAC-Me₂SO₄</td>
<td>79.36</td>
<td>0.71</td>
<td>1.19</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MAC</td>
<td>79.94</td>
<td>0.13</td>
<td>1.14</td>
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<td></td>
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<tr>
<td>NMAC</td>
<td>73.12</td>
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</tr>
<tr>
<td>ANMAC-Me₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td>95.6</td>
<td>4.4</td>
<td>0.6</td>
</tr>
<tr>
<td>ANMAC-MeCl</td>
<td></td>
<td></td>
<td></td>
<td>94.4</td>
<td>5.6</td>
<td>0.8</td>
</tr>
<tr>
<td>HAC</td>
<td>94.0</td>
<td>6.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAC-MeCl</td>
<td>94.0</td>
<td>6.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN, CO₂, N₂</td>
<td>94.2</td>
<td>5.8</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN, CO₂, H₂, MeCl</td>
<td>94.5</td>
<td>5.5</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The C 1s XPS spectra of the carbon materials were deconvoluted as shown in Figure 8. The spectrum is dominated by a large, asymmetric peak at 285.5 eV due to the graphitic carbons. The asymmetry of the peak is due to the conductivity of the sample and not to the distribution of carbon atoms associated with ether, carbonyl, or carboxylate functional groups commonly used to fit this peak [26, 37, 42]. The spectra of all conductive carbon materials (graphite, glassy carbon, and activated carbon) have the same large, asymmetric peak due to conductive carbon. Consequently, the C 1s XPS spectra of these samples actually contain little information. In addition to the graphitic carbon peak, a peak at 291 eV is prominent and is assigned to a combination of carboxylic carbon and the π to π* shake-up peak [26]. A small peak at 286 eV is also present and is assigned to carbon singly bonded to either oxygen (phenolic) or nitrogen (pyridinic or quaternary nitrogen) as well as sp³ carbon [26].
Figure 8. C 1s XPS Spectrum of AC. Data are Indicated by Small Dots, the Fit is Indicated by the Red Line Obscured by the Dots the Green Line Corresponds to Graphitic Carbon, Background is the Blue Line, and Peaks at ~ 286 and 291 eV are Orange and Black, Respectively.

The results from fitting the C 1s spectra of a variety of samples are shown in Figure 9. As noted above, there is little useful information present in these spectra. The spectra of the PANC carbons are quite different from those derived from AC as suspected. The main differences are that the PANC carbons contain a large amount of nitrogen, and consequently, the peak at 286 eV is much larger and the PANC carbons seem much less graphitic than the carbons derived from AC. The only other difference is in sample ANUAC-MeCl, which contains a higher than expected amount of carbon bonded to oxygen (or nitrogen or chlorine). This is not unexpected for this sample as it was suspected that the furnace leaked during its preparation. As noted above, there is little to indicate the effect of chemical modification in these spectra. The other observation worth noting is that the parent AC is quite graphitic and does not contain many functional groups.
The O 1s XPS spectra were fit using pseudoVoigt peaks and the model described by Pamula, et al. using four peaks at specific binding energy as follows: ~531 eV (C=O groups in carboxylate), ~532.5 eV (C=O groups in ketone, and C-OH in phenolic groups), ~533.5 eV (C-OH groups in carboxylic acids, C-O-C groups in esters and aryl ethers) [43]. The deconvolution of the O 1s XPS spectrum is shown in Figure 10, and the spectra and fits for all of the samples are shown in Figure 11.
Figure 10. Deconvolution of O 1s XPS Spectrum of AC. Assignment of Peaks is as given in Text.
Figure 11. O 1s XPS Spectra of Modified Activated Carbons. Data are Indicated by Dots, and Fits are Indicated by Red Lines.
The N 1s XPS spectra were fit using pseudoVoigt peaks and the model described by Biniak, et al. using two peaks at specific binding energy as follows: 398.5 eV (pyridinic groups) and 401 eV (quaternary nitrogen and pyridone groups) while contributions from other nitrogen functional groups are possible, only these two peaks were observed in these samples [26]. N 1s XPS spectra were only observable for the activated carbons treated with ammonia or urea/ammonia or for the PAN derived carbons. The spectra and fits are shown in Figure 12.

Figure 12. N 1s XPS Spectra of Modified Activated Carbons. Data are Indicated by Dots, and Fits are Indicated by Red Lines.
The fitting results are given in Table 6 along with the capacity of the samples for ReO$_4^-$ adsorption at $10^{-6}$ M. As suggested by the effect of chemical modification on the affinity of these materials for ReO$_4^-$ or ClO$_4^-$, the presence or absence of nitrogen groups is not correlated with absorption capacity. In addition, although the different oxygen peaks are slightly correlated with absorption capacity, none of the correlations are significant at the 95% confidence level.

Table 6. Combined Results from XPS Analysis of Modified Carbon Samples.

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>284.4</th>
<th>286.0</th>
<th>290.5</th>
<th>531.2</th>
<th>532.8</th>
<th>533.8</th>
<th>536.9</th>
<th>401.0</th>
<th>398.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assignment</td>
<td>a</td>
<td>b</td>
<td>C</td>
<td>d</td>
<td>e</td>
<td>f</td>
<td>g</td>
<td>h</td>
<td>i</td>
</tr>
<tr>
<td>Sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>8.8E+03</td>
<td>87.1</td>
<td>3.2</td>
<td>3.0</td>
<td>1.8</td>
<td>1.8</td>
<td>1.9</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>AAC-MeCl</td>
<td>4.2E+04</td>
<td>87.6</td>
<td>3.8</td>
<td>2.7</td>
<td>1.2</td>
<td>1.8</td>
<td>1.8</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>AAC-MeI</td>
<td>5.7E+04</td>
<td>91.9</td>
<td>0.9</td>
<td>3.1</td>
<td>1.1</td>
<td>1.4</td>
<td>1.5</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>NAC</td>
<td>1.3E+04</td>
<td>88.7</td>
<td>2.9</td>
<td>2.9</td>
<td>1.2</td>
<td>1.7</td>
<td>1.7</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>ANMAC-Me$_2$SO$_4$</td>
<td>5.1E+04</td>
<td>89.2</td>
<td>3.0</td>
<td>3.4</td>
<td>0.7</td>
<td>1.0</td>
<td>1.6</td>
<td>1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>ANMAC-MeCl</td>
<td>8.1E+04</td>
<td>77.1</td>
<td>15.0</td>
<td>2.3</td>
<td>0.8</td>
<td>2.0</td>
<td>1.8</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>HAC</td>
<td>3.8E+04</td>
<td>89.0</td>
<td>2.0</td>
<td>3.0</td>
<td>1.1</td>
<td>1.7</td>
<td>1.8</td>
<td>1.4</td>
<td>0.0</td>
</tr>
<tr>
<td>HAC-MeCl</td>
<td>1.4E+05</td>
<td>87.5</td>
<td>3.4</td>
<td>3.1</td>
<td>1.3</td>
<td>1.3</td>
<td>1.9</td>
<td>1.6</td>
<td>0.0</td>
</tr>
<tr>
<td>PAN, N$_2$ low</td>
<td></td>
<td>74.4</td>
<td>16.7</td>
<td>3.1</td>
<td>0.7</td>
<td>2.9</td>
<td>2.2</td>
<td>0.1</td>
<td>1.4</td>
</tr>
<tr>
<td>PAN, CO$_2$, MeCl</td>
<td>4.6E+04</td>
<td>77.2</td>
<td>17.2</td>
<td>0.0</td>
<td>1.0</td>
<td>2.2</td>
<td>1.8</td>
<td>0.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Correlation w/ $K_d$</td>
<td>1.00</td>
<td>-0.16</td>
<td>0.14</td>
<td>0.06</td>
<td>-0.24</td>
<td>-0.32</td>
<td>0.21</td>
<td>0.24</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

a) Graphitic carbon  
b) Carbon singly or doubly bonded to a heteroatom and sp$^3$ carbon  
c) Carbon in carboxylates plus $\pi$ to $\pi^*$ shake-up peak  
d) Carbonyl oxygen of carboxylates  
e) Carbonyl oxygen of ketones, oxygen in phenolic groups  
f) Hydroxyl oxygen in carboxylates, ether oxygen in esters and phenyl ethers  
g) Adsorbed water and/or oxygen  
h) Quaternary nitrogen  
i) Pyridinic nitrogen  
j) $K_d$ for ReO$_4^-$ adsorption with $C_{sol} = 10^{-6}$ M
The O 1s data in Table 6 can be rearranged as follows to yield more specific information about the functional groups present on the activated carbon surface. The number of carboxylate groups is determined from the peak at 531.2 eV, and the number of ketone and phenolic groups is determined from the peak at 532.8 eV. The number of ether groups is determined by subtracting the area of the peak at 531.2 eV from the area of the peak at 533.8 eV. The N 1s data already corresponds to specific functional groups. When the O 1s and N 1s data is interpreted in this manner, it is possible to compare the number of functional groups determined from the O 1s and N 1s spectra with the number of functional groups suggested by the C 1s spectra. Each carboxylate functional group will contribute to the peak at 290.5 eV in the C 1s spectra. The other functional groups contribute to the area of the peak at 286 eV in the C 1s spectra in proportion to the number of carbon atoms to which they are bonded (ketones and phenolic groups contain one carbon, ethers and pyridinic groups contain 2 carbons, and quaternary sites contain 3 carbons). These results are combined in Table 7.

Table 7. Functional Group Composition (in mol. %) Determined from the XPS Spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kd</th>
<th>C⁷</th>
<th>C⁺</th>
<th>C⁻</th>
<th>CO₂R</th>
<th>C=O</th>
<th>C-O-C</th>
<th>O₂H₂O</th>
<th>N-Q</th>
<th>N-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>8.8E+03</td>
<td>87.1</td>
<td>3.2 (1.9)</td>
<td>3.0 (1.8)</td>
<td>1.8</td>
<td>1.8</td>
<td>0.0</td>
<td>1.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>AAC-MeCl</td>
<td>4.2E+04</td>
<td>87.6</td>
<td>3.8 (3.1)</td>
<td>2.7 (1.2)</td>
<td>1.2</td>
<td>1.8</td>
<td>0.6</td>
<td>1.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>AAC-MeI</td>
<td>5.7E+04</td>
<td>91.9</td>
<td>0.9 (2.2)</td>
<td>3.1 (1.1)</td>
<td>1.1</td>
<td>1.4</td>
<td>0.4</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NAC</td>
<td>1.3E+04</td>
<td>88.7</td>
<td>2.9 (4.2)</td>
<td>2.9 (1.2)</td>
<td>1.2</td>
<td>1.7</td>
<td>0.6</td>
<td>1.0</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>ANMAC-Me₂SO₄</td>
<td>5.1E+04</td>
<td>89.2</td>
<td>3.0 (4.3)</td>
<td>3.4 (0.7)</td>
<td>0.7</td>
<td>1.0</td>
<td>0.9</td>
<td>1.1</td>
<td>0.3</td>
<td>0.3</td>
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<tr>
<td>ANMAC-MeCl</td>
<td>8.1E+04</td>
<td>77.1</td>
<td>15.0 (6.1)</td>
<td>2.3 (0.8)</td>
<td>0.8</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>HAC</td>
<td>3.8E+04</td>
<td>89.0</td>
<td>2.0 (3.0)</td>
<td>3.0 (1.1)</td>
<td>1.1</td>
<td>1.7</td>
<td>0.7</td>
<td>1.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>HAC-MeCl</td>
<td>1.4E+05</td>
<td>87.5</td>
<td>3.4 (2.4)</td>
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<td>1.6</td>
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</tr>
<tr>
<td>PAN, N2</td>
<td>74.4</td>
<td>16.7 (12.8)</td>
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<td>0.7</td>
<td>2.9</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN, CO₂, MeCl</td>
<td>4.6E+04</td>
<td>77.2</td>
<td>17.2 (9.1)</td>
<td>0.0 (1.0)</td>
<td>1.0</td>
<td>2.2</td>
<td>0.8</td>
<td>0.4</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Correlation with Kd</td>
<td>1.00</td>
<td>-0.16</td>
<td>0.14</td>
<td>0.06</td>
<td>-0.24</td>
<td>-0.32</td>
<td>0.35</td>
<td>0.24</td>
<td>-0.05</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

a) Graphitic carbon
b) Carbon singly or doubly bonded to a heteroatom and sp³ carbon. Number in parenthesis is the amount of these kinds of carbons predicted from the functional group distribution.
c) Carbon in carboxylates plus π to π* shake-up peak. Number in parenthesis is the amount carbon in carboxylate groups predicted from the functional group distribution.
As with the raw XPS data, the correlations between $K_d$ and the concentrations of functional groups are weak: the confidence limits for correlations of 0.24 and 0.35 are 63% and 81%, respectively. However, the strongest of these correlations is for oxygen containing functional groups rather than nitrogen groups, and the correlations can be interpreted in a straightforward manner. The groups that are anionic (carboxylate and possibly some phenols) at pH $\sim$ 8 decrease the net positive charge on the carbon surface, and therefore decrease the affinity of the carbon surface for ReO$_4^-$ and ClO$_4^-$. On the other hand, ethers are produced when the phenolic sites are alkylated, so an increase in the number of ether sites decreases the number of anionic phenolic sites and increases net positive charge of the carbon surface. It is also possible that neutral pyrone (C=O) sites may be alkylated to produce cationic pyrylium sites (C-O-C) on the carbon surface and to increase the net positive charge of the carbon surface. Unfortunately, alkylation does not appear to produce the desired quaternary ammonium sites as evidenced by the fact that all of the ammonia treated carbon samples have approximately the same ratio of quaternary nitrogen to pyridinic nitrogen despite the fact that two of these samples have been treated with alkylating agents. If the pyridinic nitrogen sites were being alkylated, one would expect that the ratio of quaternary nitrogen to pyridinic nitrogen would increase. In the case of PANC treated with MeCl, alkylation of the pyridinic sites may have occurred, but this in the only sample in which this may have happened.

### Activated Carbon Treated with Other Elements

From the preceding results, the nature of the cationic sites on the activated carbon surface has not been clearly established. Although the cationic sites are likely functional groups that contain oxygen and carbon, the parent activated carbon contains a number of other chemical elements in significant concentration. For this reason, it seemed worthwhile to determine the effect on ReO$_4^-$ adsorption capacity of increasing the amount of these elements in activated carbon; results of these experiments are reported in Table 8. In all of these cases, the carbons were treated with aqueous solutions by the incipient wetness method and dried under air. The impregnated carbons were then treated at high temperature using 10% H$_2$ in Ar followed by MeCl at 500°C. As shown in Table 8, none of these treatments improved the sorption capacity of the activated carbon.

#### Table 8. Adsorption Properties of Carbon Treated with Other Elements.

<table>
<thead>
<tr>
<th>Sample$^a$</th>
<th>K</th>
<th>$N_L$</th>
<th>$K_d (10^{-8}M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAC-MeCl</td>
<td>1.2E+06</td>
<td>0.26</td>
<td>1.4E+05</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>1.5E+06</td>
<td>0.13</td>
<td>8.1E+04</td>
</tr>
<tr>
<td>CoCl$_2$</td>
<td>7.7E+04</td>
<td>0.14</td>
<td>9.7E+03</td>
</tr>
<tr>
<td>Na$_3$BO$_3$</td>
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<td>0.13</td>
<td>5.2E+04</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>7.8E+05</td>
<td>0.13</td>
<td>5.6E+04</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.11</td>
<td>3.4E+04</td>
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<tr>
<td>H$_3$PO$_4$</td>
<td>no adsorption</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*$^a$* Carbon was treated with these compounds such that the element was present at ~1 meq g$^{-1}$
Conclusions.

The goal of this project was to functionalize activated carbon by increasing the nitrogen content and alkylating the nitrogen sites, so that the resulting material would be similar in capacity and selectivity to perchlorate selective ion-exchange resins. Clearly, the project failed to achieve this goal. The main reason for this failure is that this approach does not increase the number of cationic sites in activated carbon. Although the selectivity of the ion exchange sites for perchlorate or perrhenate is very good ($K \sim 10^5$-$10^6$) and would be sufficient to achieve the goal of this project, the number of sites is far too low ($N_L \sim 0.2$ meq g$^{-1}$) for these materials to be competitive with ion exchange resins even when the much lower cost of activated carbon is taken into account.

Although the project did not achieve its goal, the results of the project are interesting. Previous work by Chen, et al. clearly demonstrates that the perchlorate sorption capacity of activated carbon is strongly correlated with the net positive charge on the carbon surface, which is consistent with the postulated mechanism for perchlorate removal by activated carbon, perchlorate ion exchange onto cationic sites on the carbon surface [18, 19]. Since the treatment that increased the positive surface charge of the activated carbon was tailoring with ammonia, it was reasonably hypothesized that the ammonia treatment was creating additional cationic sites in the form of basic pyridinic groups that would be protonated at pH 7.5. These groups are also important to the main hypothesis involved in this research project: that pyridinic sites can be alkylated to create strong base anion exchange sites in activated carbon. This hypothesis is particularly attractive since it is in good agreement with molecular chemistry and provides a straightforward mechanism for increasing the number of ion exchange sites on the activated carbon surface. Unfortunately, both hypotheses appear to be incorrect.

While alkylation, or at least treatment of activated carbon with alkylating agents, does strongly increase the overall sorption capacity of activated carbon for perchlorate or perrhenate, it does this by increasing the selectivity than by increasing the number of ion exchange sites as clearly shown by the absorption isotherm experiments. Regardless of which model is used to describe the isotherm, the number of exchange sites is only $\sim 0.2$ meq g$^{-1}$ as indicated by the “plateau” in the absorption capacity of these materials at high $C_{sol}$.

Explanation of the Effect of Alkylation on Perchlorate Selectivity of AC

Although the goal of this project was to alkylate nitrogenous groups on the activated carbon surface, the effects of alkylation and treatment with the reducing gases ammonia and hydrogen as well as the results of the XPS studies strongly suggest that these chemical modification mainly change the nature of the oxygen containing functional groups rather than the nitrogenous groups. First, pyridinic groups are very unlikely to be protonated at pH 7.5 since the $pK_a$s of protonated pyridine, quinoline, and acridine are 5.15, 4.85, and 5.60, respectively. The protonated primary amines (anilines) have similarly low $pK_a$s. Consequently, the effect of ammonia treatment on perchlorate absorption is not likely to be due directly to the presence of protonated nitrogenous functional groups. Second, results from direct alkylation of the activated carbon (AAC-MeCl and AAC-MeI) as well results from hydrogen treated activated carbon (HAC and HAC-MeCl) suggest that the other basic sites are already be present on the activated carbon surface.
Chen, et al., clearly show that the ClO$_4^-$ sorption capacity of activated carbon is strongly correlated with the net positive charge on the carbon surface [18, 19]. Although the authors attribute this to an increase in the number of cationic sites, this is not the only explanation. Activated carbon contains both cationic, basic groups, most likely pyrone groups, and anionic, acidic groups, mainly carboxylic groups, and the effect of ammonia treatment on the net positive charge of the carbon surface can also be explained by a decrease in the number of anionic groups on the activated carbon surface. This is also consistent with the effect of hydrogen treatment on the activated carbon surface since it is known that thermal treatment of AC under reducing atmospheres enhances the decomposition of carboxylic groups relative to treatment under inert atmosphere [44]. Furthermore, this explanation is strongly consistent with the effects of alkylation on absorption of perrhenate and perchlorate. The effect of alkylation by methyl iodide by the Liotta method is especially consistent with this postulate since this procedure is known to largely alkylate oxygenated groups (although in coals rather than in activated carbons) [36]. All of these effects are summarized cartoon form in Figure 13. Interestingly, alkylation does not appear to convert the pyridinic sites into cationic alkylpyridinium sites as hypothesized.

In addition to removing anionic groups from the carbon surface, the chemical modifications may alter the cationic groups on the carbon surface. Ammonia tailoring introduces quaternary nitrogen sites into the interior of the graphene sheets. The presence of these sites should make the pyrone groups more basic in analogy to the effect of ether groups described by Suarez, et al.; consequently, more pyrone groups should protonated at pH 7.5 [25]. Alkylation should increase the number of cationic sites by alkylating the neutral pyrone groups producing stable pyrylium groups at neighboring ether sites in analogy to protonation of pyrone groups. This result is consistent with the XPS data reported here. The pyrylium sites are expected to have high selectivity for poorly solvated anions since the positive charge is delocalized and the interaction of the pyrylium site with an associated anion will be weak.

Outlook for Perchlorate Removal by Activated Carbon
A new technique, alkylation, for increasing the selectivity of activated carbons for perchlorate or other poorly solvated anions has been developed. This chemical modification can be performed in solution (treatment with MeI, treatment with Me$_2$SO$_4$) or in the gas phase (treatment with MeCl, treatment with H$_2$ or NH$_3$ followed by MeCl). The gas phase treatments could be implemented in conjunction with the usual synthesis of activated carbon, and the resulting materials should be relatively inexpensive. Nevertheless, it is doubtful that these materials can compete with perchlorate ion exchange resins for use in treating drinking water. The capacity of the ammonia tailored activated carbons is $\sim$10$^4$ bed volumes (BV)[18] and may increase that capacity, but only by a factor of 4 or 5 at best, and might not increase it at all. On the other hand, perchlorate selective ion exchange resins have capacities ranging from 10$^5$ to 10$^6$ BV [6].

Although the ion exchange resins are expensive (up to 10 times as expensive as activated carbon) and the cost of activated carbon and ion exchange resin per BV of water treated may be similar, the use of activated carbon is still more expensive due to the addition costs required to either install larger sorbent beds or replace the sorbent beds more frequently. The only advantage that the modified activated carbons may have over ion exchange resins is that the activated carbons will not shed amines that can form N-nitrosamines upon contact with chloramines [13]. However, the latter issue can be addressed by UV treatment of the effluent to destroy the N-nitrosamines.
Figure 13. Changes in the Activated Carbon Surface Caused by Chemical Modification.
References
5. Perchlorate Contamination Treatment Alternatives. 2003, California Environmental Protection Agency, Department of Toxic Substances Control, Office of Pollution Prevention and Technology Department.


