Kinetics of Spent Activated Carbon Regeneration

Pyrolysis and regeneration kinetics of 11 spent activated carbons were studied using a thermal balance and a fluidized bed reactor. The adsorbates were aromatic compounds with different types and number of side groups, and most of the side groups were lost on pyrolysis, leaving a residue about equal to the weight of the aromatic portion of the adsorbate. The residues from alkyl phenols reacted with oxygen at 770-920 K at rates up to 12 times the rate for the base carbon. There was a similar increase in oxygen chemisorption indicating increased number of active sites. The adsorption capacity of the carbons was mostly recovered by pyrolysis, even though the surface area and pore volume were reduced by the residue. Some oxidative regeneration is probably necessary to restore adsorption capacity for repeated use.

Peter Harriott
Alan Tat-Yan Cheng
Chemical Engineering Department
Cornell University
Ithaca, NY 14853

Introduction

Activated carbons have been used for many years in the removal of organic pollutants from wastewater, in purification processes, and in chemical separations. Spent carbons are often regenerated and reused, and a variety of chemical, biological, and thermal regeneration processes are available. When the adsorbates include high molecular weight or strongly bound aromatic compounds, as is often the case in wastewater treatment, thermal regeneration at high temperature is generally used.

Thermal regeneration is carried out in a variety of devices including fluidized beds, rotary kilns, multiple-hearth furnaces, and transport-line reactors. Thermal regeneration processes usually involve drying at 105 to 110°C, desorption of volatile organics and pyrolysis of adsorbed organics by heating to 700–800°C, and gasification of the carbonaceous residue. Gasification is generally carried out with water vapor at 800–900°C, and natural gas or other fuel is burned to supply the heat needed for the process, which includes such steps as the endothermic steam-carbon reaction. Carbon dioxide and air are also used as oxidizing agents, but the gasification conditions are very different for each. The carbon-carbon dioxide reaction is slow and endothermic and must be carried out at temperatures over 1000°C. The carbon-oxygen reaction, on the other hand, is exothermic and quite rapid at 600°C, and gasification conditions have to be closely monitored to control the highly exothermic reaction. Some of the base carbon or original adsorbent is lost by gasification reactions, and typical commercial units are said to recover only 75–90% of the base carbon fed. With detailed information about the pyrolysis process and the oxidation characteristics of the residue, it might be possible to control the pyrolysis and gasification steps so that there is little loss of base carbon or adsorptive capacity per cycle.

A number of studies have explored the fundamental aspects of regeneration. The temperature-programmed pyrolysis of several organic adsorbates on three types of carbon was studied by Suzuki et al. (1978). In their classification, Group I compounds vaporized completely on heating. Group II compounds decomposed in approximately first-order fashion and left a small residue. The main problem in regeneration is Group III compounds, which are mostly aromatics, and leave a large residue, up to 60% of the weight of the adsorbed material. Urano et al. (1982) and Tipnis and Harriott (1986) found similar results, but the amount of residue for a typical Group III compound, such as phenol, varies quite a bit with the type of carbon and with pyrolysis conditions.

More complex models for the pyrolysis of adsorbates have been proposed. Chihara et al. (1981a) found that adsorbed sucrose decomposed rapidly at about 200°C, but the residue continued to react slowly as the temperature was increased until only 2% residue remained at 600°C. Two-stage pyrolysis was also observed with an alkylbenzene sulfonate, but the final residue was a greater fraction of the initial deposit. Activation energies for the pyrolysis of adsorbed p-nitrophenol and Emulgen 913 were obtained by Hashimoto et al. (1982). These workers also showed how the thermogravimetric curves for complex mix-

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Correspondence concerning this paper should be addressed to P. Harriott.
The present address of A.T. Cheng is Union Carbide Corp., Tarrytown, NY 10591.

tures of adsorbates could be fitted using a distribution of activation energies and frequency factors. However, it is not certain that such a complex model is needed for the pyrolysis step if the limiting step in regeneration is removal of the residue from pyrolysis. A method of estimating the amount of residue from pyrolysis and its reactivity to oxygen and steam should lead to more efficient regeneration processes.

There is not much information on the kinetics of gasification of the carbonaceous residues left after pyrolysis. When only a small amount of residue is present, it is difficult to distinguish the reaction of the residue from the reaction of the exposed carbon adsorbent. For example, in the studies of Chihara et al. (1981b) pyrolysis of adsorbed sucrose left only 2.7% residue, and the reaction rate with steam was about the same as for the base carbon. Recent work by Krebs and Smith (1985) using similar conditions showed no effect of 10% phenol residue on the reactivity to steam.

Significant differences in reactivity were found by Tipnis and Harriott (1986) for oxidation at 415–500°C of base carbons and carbons with residues from p-nitrophenol. The rate of reaction went through a maximum with residue loading, and based on initial rates, the residue was 10–15 times as reactive (per unit weight) as the base carbon. However, for steam gasification at 900°C, only small differences between spent and fresh carbons were found. The deposits formed by pyrolysis may be very reactive when first formed but loose reactivity on heating to the temperature needed for steam gasification.

In this study, samples of spent carbon were prepared using a purified commercial carbon and 11 adsorbates, including many substituted phenols. The amount of residue left after pyrolysis was measured and shown to correlate with the aromatic content of the adsorbate. For many samples, the reactivity of the residue to oxygen and the amount of oxygen chemisorbed were measured. The results give some insights into the nature of the residue and may lead to improved regeneration procedures.

Experimental

The experimental studies were made with a purified sample of Calgon RC, a coal-derived carbon with a modest surface area of 1,210 m^2/g and a high ash content of 14.6%. To minimize catalytic effects, most of the ash was removed by acid washing, as described in a previous publication (Cheng and Harriott, 1986). The carbon was screened and the 50–100 μm fraction retained for kinetic tests.

Spent carbons were prepared by adsorption from aqueous solutions of phenol or substituted phenols. Samples were allowed to equilibrate for 24 hours at room temperature in a sealed flask placed in a rocker. The carbon was collected by filtration and dried at 100°C. The concentration of phenolic compound in the filtrate was determined by UV spectrometry and used to calculate the loading on the carbon. Tests with different initial concentrations were made to get adsorption isotherms.

The spent carbons were pyrolyzed in N_2 to determine the amount of residue from different adsorbates and to prepare samples for oxidative tests. Pyrolysis was carried out at 700°C in a crucible placed in a horizontal tubular furnace. The sample was kept in the hot zone for about 10 minutes and then moved to the end section and allowed to cool before being removed and weighed.

The kinetics of residue oxidation were studied using a TGA apparatus (Perkin-Elmer TGS-2) with a temperature programmer and recorder. Samples of 2–3 mg were placed on a 5–8 mm platinum pan suspended inside a ceramic furnace, 10 mm diameter × 20 mm long. The furnace is surrounded by a 25-mm Pyrex tube through which inert or reactant gases are passed. Nitrogen or helium were used as carrier gases at flow rate of about 200 cm^3/min, and most runs were made with 5.0 or 7.5% oxygen in the gas. The temperature just below the pan was measured with a thermocouple calibrated using the magnetic transition temperature for different alloys placed in the pan. The TGA was also used for chemisorption measurements at 300 to 400°C. Prior to chemisorption, samples were held for 30 minutes in nitrogen at 700°C to remove absorbed gases.

A small fluidized bed reactor, 3.8 cm × 60 cm, was also used for regeneration studies. The reactor was made of stainless steel with a packed preheater and a sintered metal distribution plate below the bed and a 9 cm × 25 cm disengaging chamber above the reactor. Product gases and gas samples were withdrawn through stainless steel filters at the top of the disengaging chamber. The reactor and preheater were electrically heated, and movable probes were used to measure the temperature and pressure drop in the bed. Another tube was used to collect solid samples from the bed during a run. Gases from the reactor were cooled, dried over silica gel, and sent to a Varian 3700 gas chromatograph. With a 0.6 cm × 180 cm Poropak-Molecular Sieve dual column, concentrations of CO, CO_2, O_2, and N_2 were measured and used to calculate the rate of carbon oxidation.

The gas velocity used for fluidization tests was 1.0 to 1.2 cm/s, which is several times the minimum fluidization velocity of 0.15 cm/s but less than the estimated minimum bubbling velocity of 1.5 cm/s. In this range of velocities, the bed exhibits particulate fluidization with an expansion of 20 to 30%. For kinetic calculations the gas was assumed to be in plug flow through the bed, but the solids were assumed to be mixed. This may seem to be a contradiction, but in the absence of bubbles, there is little backmixing or bypassing of gases, yet the turbulent motion of the solids is enough to eliminate any temperature gradients and make the solid phase nearly uniform.

About 10 g of spent carbon were used for a fluid bed test. After the carbon was charged, it was heated in nitrogen at 700°C at the rate of about 10°C/min. It was then held at 700°C for 10 minutes before lowering the temperature to about 500°C for oxidation tests. Further details are given by Cheng (1985).

Results and Discussion

Adsorption and pyrolysis tests were made using Calgon RC powdered carbon and 11 aromatic compounds. Several of the compounds are phenols found in waste streams from wood processing and coal liquefaction plants. All the materials showed strong adsorption even at low solute concentrations. Isotherms for some alkyl phenols are shown in Figure 1, and Table 1 gives the constants obtained by fitting the data to Langmuir isotherms.

$$q = \frac{bCQ}{1 + bC}$$

Both the adsorption constant b and the capacity Q increase with the number or size of the hydrocarbon side groups on phenol. At low concentration, the solutes are expected to adsorb in a flat configuration on the basal plane of the graphitic crystallites (Mattson et al., 1969). The wide range of b values reflect

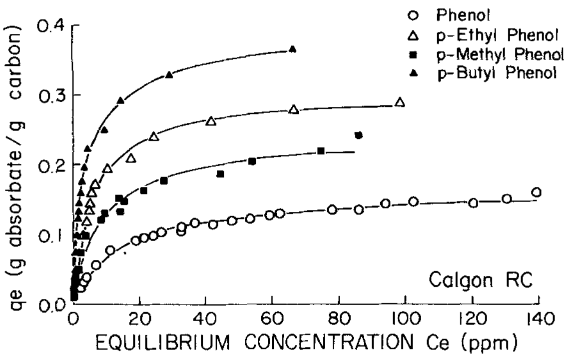

Figure 1. Adsorption isotherms for alkyl phenols.

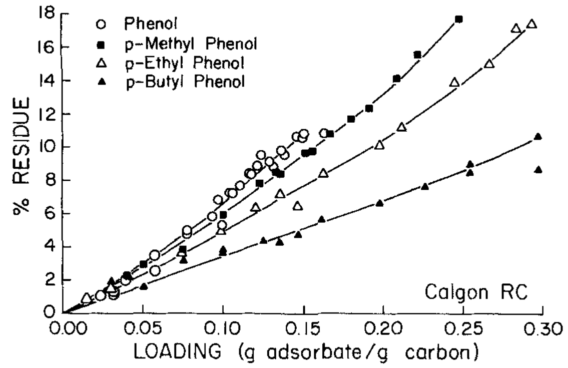

Figure 2. Residue from pyrolysis of alkyl phenols.

changes in strength of adsorption because of differences in polarity. However, the several-fold range of Q values indicates an inconsistency in the use of Langmuir isotherms, since the Q values should correspond to complete surface converge. For the substituted phenols the capacity on a molar basis, Q', actually increases with molecular weight, even though the bigger molecules have a greater specific surface area. Assuming 45 $Å^2$ for the typical specific surface area, a coverage of 3 mmol/g corresponds to 540 m^2/g, only 45% of the total BET surface of 1,210 cm^2/g. About 20% of the total surface is in pores smaller than the phenol molecules, and there is probably also some reduction in available surface area when molecules adsorbed on one side of a slit-shaped pore block access to other sites. However, if these geometric effects were dominant, the values of Q' for substituted phenols would have been less than the value for phenol, which is not the case. The range of values for Q and Q' may be due to heterogeneity of the surface or to interactions between adsorbed molecules.

Pyrolysis Tests

The amount of residue from pyrolysis of the adsorbates was determined by correcting the weight loss for the loss of the base carbon measured in blank runs. The percent residue refers to the weight of residue per unit weight of base carbon.

The amount of residue from pyrolysis of adsorbed phenols increased nearly linearly with adsorbate loading, Figure 2. For a given loading, the amount of residue decreased with increasing molecular weight of the adsorbate, suggesting that the residue comes mainly from the aromatic ring and that the side groups are lost on pyrolysis. Similar results were obtained when comparing methyl phenol with trimethyl phenol or phenol with chlorophenol and bromophenol. The data for several adsorbates are brought together by plotting the amount of residue against adsorbate loading on a molar basis in Figure 3. The straight line shows the residue expected from just the carbon atoms in the aromatic ring, which would be 0.072 g/g base carbon for a loading of 1 mmol/g. Most of the data fall only slightly below this line, which is consistent with loss of all the side groups on pyrolysis but loss of only a small fraction of the ring carbons. The data for sodium benzoate fall above the line, but this might be expected because of sodium salts left on the surface.

The pyrolysis of p-nitrophenol and p-hydroxybenzoic acid, Figure 4, show different trends than for alkylphenols. For low loadings, the residue increases linearly with loading and is about 0.8 the value predicted based on the aromatic carbons. The residue then increases more slowly with loading, and for p-hydroxybenzoic acid, it levels off at about 4% residue. The smaller amounts of residue are probably caused by reaction of oxygen in the side groups with aromatic carbons in adjacent rings, a process which is more likely at high surface concentrations of the adsorbed molecules.

To allow for multiple ring compounds, an aromatic ratio can be defined as the total weight of the aromatic carbon atoms divided by the molecular weight. Based on the data for phenols, the ratio of the weight of residue to the adsorbed weight is expected to be 0.8 to 0.9 times the aromatic ratio. For 2-naphthol, the aromatic ratio is 0.834, and pyrolysis tests showed the residue to be 0.75 times the adsorbate loading, which is 0.90 times the aromatic ratio.

Some of the published studies of adsorbate pyrolysis are com-

Table 1. Langmuir Coefficients for Calgon RC Carbon

Solute	M	b L/mg	Q g/g	Q' mmol/g
phenol	94.1	0.085	0.147	1.56
p-methyl/phenol	108.1	0.169	0.212	1.96
p-ethyl phenol	122.2	0.195	0.293	2.40
2,4,6 trimethyl phenol	136.2	0.319	0.343	2.52
p-t-butyl phenol	150.2	0.448	0.319	2.12
p-bromo phenol	173.0	0.292	0.385	2.23
p-chloro phenol	128.6	0.277	0.258	2.01
p-nitro phenol	139.1	0.899	0.228	1.64
p-hydroxy benzoic acid	138.1	1.133	0.221	1.60
2-naphthol	144.2	0.316	0.50	3.47
sodium benzoate	144.2	0.786	0.105	0.73

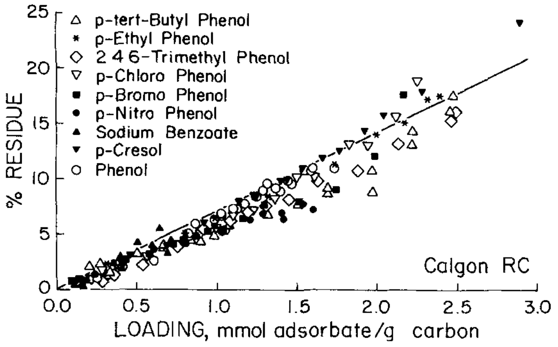

Figure 3. Pyrolysis residue as a function of molar loading.

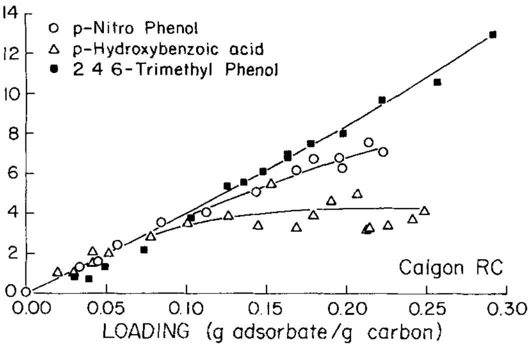

Figure 4. Residue from pyrolysis of oxygenated phenols.

pared with our results in Figure 5. Only the phenol data of Suzuki et al. (1978) were included, since their TGA plot for phenol permitted determination of weight loss at 700°C. For the other compounds, only the residue left at 800°C was reported, and there may have been significant weight loss between 700°C and 800°C. The results of Amicarelli et al. (1979) for phenol and aniline are close to our values, though their pyrolysis temperature was not specified. The pyrolysis studies of Tipnis and Harriott (1986) also show good agreement with the current work. Exact agreement among different experimenters is not expected, because the rate of heating and the type of carbon have some influence on the amount of residue formed during pyrolysis.

Oxidation of Residues

If the residues from pyrolysis of various adsorbates come primarily from the aromatic carbons, the deposits should have similar properties. The reactivity of the deposits can be estimated by comparing the reaction rate for different amounts of residue with that for the base carbon. Typical weight loss curves are shown in Figure 6. In most cases there was a slight increase in weight due to oxygen chemisorption, and then the rate of reaction gradually increased. The rate at 0.5 to 2.5% burnoff was taken as the initial rate. The initial oxidation rates for residues from alkyl phenols, measured at 500°C with 7.5% 0_2, are shown in Figure 7. The reaction rate increases nearly linearly with the amount of residue and then levels off above 10–15% residue. There is little difference in the activity for residues from the four adsorbates. The initial slope of the plot indicates that the deposits are 12–15 times as active as the base carbon on a unit weight basis. This agrees with the 15-fold ratio reported for deposits from p-nitrophenol on a Westvaco carbon (Tipnis and Harriott, 1986).

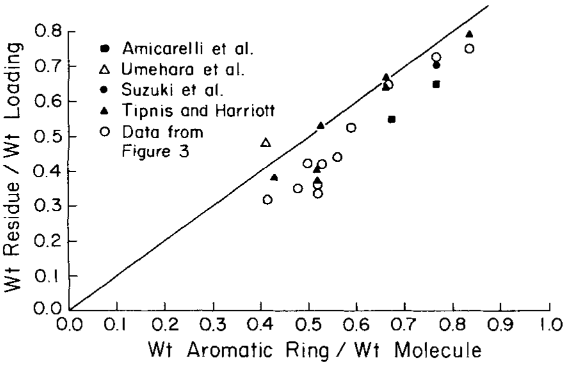

Figure 5. Comparison of pyrolysis ratio and aromatic ratio.

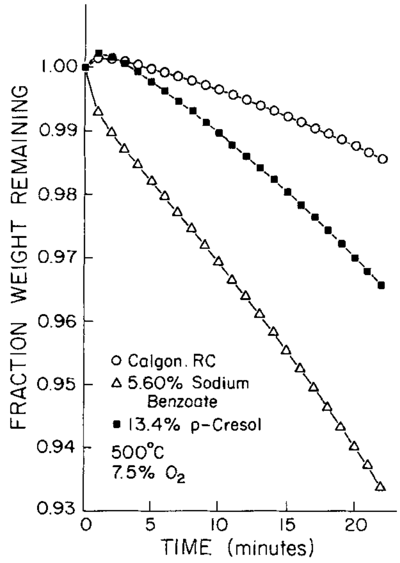

Figure 6. Initial burnoff profiles for fresh and spent carbons.

It is not possible to calculate the reactivities on a unit area basis, since the surface area of the deposits and the base carbon can't be determined separately. However, if the residue has a graphitic structure and forms a layer one atom thick, 0.1 g of residue would have a surface area of 130 m^2, enough to cover only a small fraction of the total surface area. This amount of residue doubles the reactivity of the sample, so the deposit must be at least tenfold more reactive than the base carbon on an area basis. The higher reactivity may be due to a greater fraction of the atoms being at the edge of graphite islands or crystallites. The reaction of graphitic carbons is thought to occur primarily at the crystallite edges and not by direct attack on the basal plane. The residues from chlorophenol or bromophenol were also more reactive than the base carbon, as shown in Figure 8. The increase was somewhat more than for deposits from phenol but less than that found for the alkyl phenols, Figure 7. The absence of a pronounced inhibiting or catalytic effect indicates that most of the halogens are lost on pyrolysis, leaving a carbon deposit much like that from other aromatic compounds.

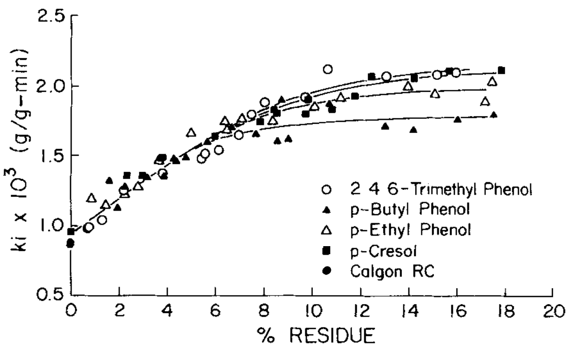

Figure 7. Initial oxidation rates for phenol residues.

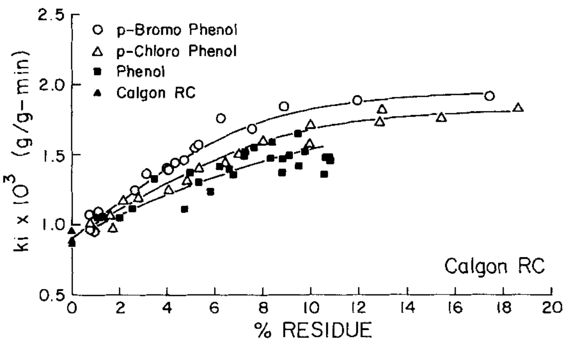

Figure 8. Oxidation rate for residue from halogenated phenols.

The effect of temperature on reactivity to oxygen was studied for carbon containing 4.5% residue from *p*-bromophenol. For temperatures of 500 to 640°C, the activation energy was 32 kcal/mol. At higher temperature, the activation energy was only 13 kcal/mol, in agreement with the data for Calgon RC. The break shown in Figure 9 marks the transition from a surface reaction to the rate of oxygen chemisorption as the controlling step, as was shown by Cheng and Harriott (1986), and is not due to mass transfer effects.

Chemisorption of Oxygen

The higher oxidation rate of pyrolysis residues indicates a greater number of active sites than on an equal area of base carbon. Two methods of measuring the surface oxygen were used to see if there was a correlation between reactivity and the amount of chemisorbed oxygen. In most oxidation tests the sample weight increased to a maximum after oxygen was admitted and then decreased with time, as shown in Figure 6. The maximum weight gain (called equilibrium oxygen) was taken as a measure of the chemisorbed oxygen, though the actual amount of surface oxygen must be greater than this, because some carbon is removed by the time the maximum is reached. The second method was to chemisorb oxygen at 300–400°C, where the rate of oxidation is very low.

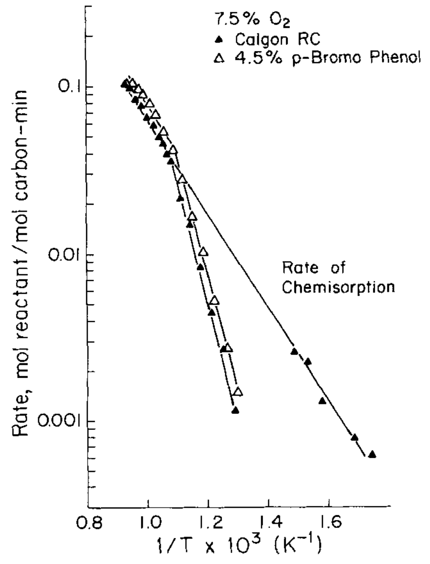

Figure 9. Arrhenius plot for *p*-bromophenol residue.

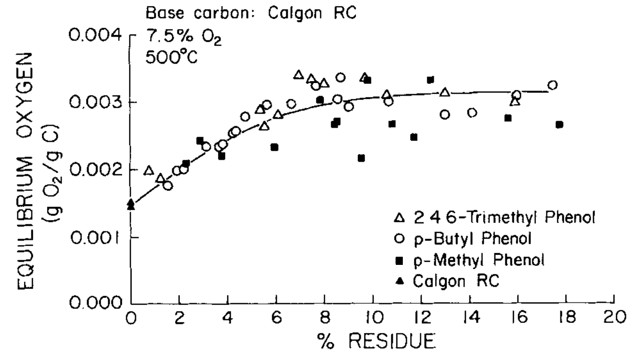

Figure 10. Chemisorption of oxygen by alkylphenol residues.

The amount of oxygen adsorbed under reactive conditions is shown in Figure 10 for carbons with residues from alkyl phenols. The equilibrium oxygen increases with percent residue to values about twice that for the base carbon. The increase is about the same as the increase in reactivity shown in Figure 7. However, the residues from halogenated phenols showed no change or a decrease in equilibrium oxygen, Figure 11, even though the residues were more reactive than the base carbon.

Chemisorption tests at low temperature were made only for carbon with *p*-cresol residues. The rate of chemisorption was higher than for the base carbon, as were the rates of oxidation in the medium and high temperature ranges, Figure 12. However, the total oxygen chemisorbed at 300°C corresponded to an active surface area (ASA) of 25.5 m^2/g, only slightly higher than the ASA of 21.9 m^2/g for Calgon RC. Thus increased chemisorption of oxygen generally means increased reactivity to oxygen, but there are not enough results for a quantitative correlation.

Catalytic Effects

Minerals present in the ash of adsorbent carbons can change the reactivity of the carbons and the pyrolysis residues. The carbons used in this work were purified to minimize such effects, but a few tests were made to explore the effect of residual sodium on reactivity. Spent carbons were prepared by adsorbing sodium benzoate on Calgon RC and pyrolyzing at 700°C. The reactivity to oxygen at 500°C increased with the amount of residue, as shown in Figure 13. With only 5% residue, the rate was 3.5 times that for the base carbon. For the same amount of resi-

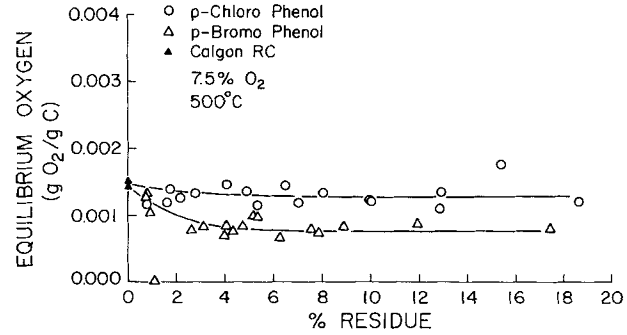

Figure 11. Chemisorption of oxygen by residues from halogenated phenols.

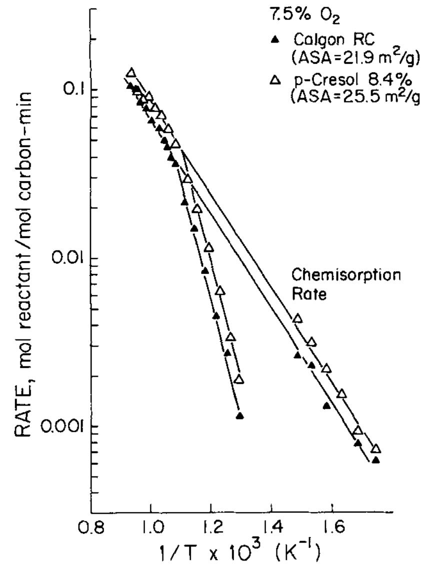

Figure 12. Arrhenius plot for *p*-cresol residue.

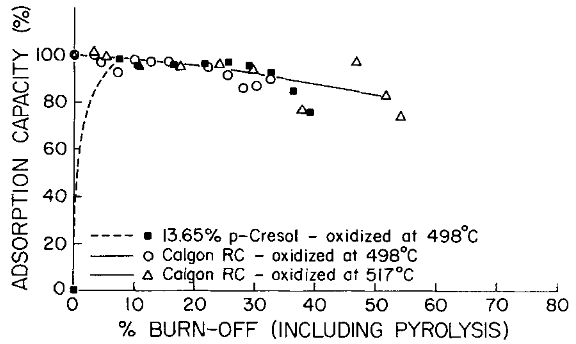

Figure 14. Adsorption capacity after regeneration.

due from other adsorbates, the increase in rate was about 50%. Thus, the sodium salts increased the rate two–three fold, but the separate effects on the residue and on the base carbon were not determined. A similar effect of sodium sulfate on the gasification rate was noted by Umehara et al. (1983b). Chemisorption measurements at 240–300°C for the sodium-containing residue showed a severalfold increase in adsorption rate over the base carbon and a slightly lower activation energy of 10 kcal/mol.

Regeneration Efficiency

The goal of regenerating spent carbon is to recover the adsorptive capacity without much loss of carbon. Calgon RC loaded with 13.7% *p*-cresol residue was pyrolyzed at 700°C in the fluid bed and then oxidized at 498°C. Samples removed from the bed were tested for adsorptive capacity in a standard solution of cresol. The relative adsorption capacity is shown as a function of percent burnoff in Figure 14 along with data for the base carbon. The base carbon lost 3.4 wt. % by pyrolysis before oxygen was admitted, but the adsorptive capacity per gram was about the same. With oxidation there was a slow decline in adsorption capacity to about 80% of the base value at 50% burnoff. The spent carbon showed similar behavior, though the first data point is for 7.6 wt % loss, which includes pyrolysis of the adsorbate and the base carbon. The dashed line suggests the probable recovery of adsorption capacity if pyrolysis is incomplete. The spent carbon after pyrolysis has about 10% residue, which covers more than 10% of the surface, yet the adsorption capacity is the same as for the original carbon. Therefore the residue must have about the same affinity for adsorbate molecules as the base carbon.

Pyrolysis alone is not sufficient for regeneration of carbon that is to be used several times, since the residue partly fills some pores, and further cycles of adsorption and pyrolysis would lead to pore blockage and a large reduction in adsorption capacity. Oxidation can remove most of the residue, but some reaction of the base carbon is inevitable, which leads to a loss in weight and a weakening of the structure. The efficiency of regeneration is defined here as the fraction of original weight remaining times the relative adsorption capacity per unit weight. Since the weight of carbon plus pyrolysis residue is greater than the weight of the starting carbon, the regeneration efficiency is slightly greater than 100% after pyrolysis as shown in Figure 15. However, the efficiency then drops rapidly with burnoff even though the capacity per gram decreases only slightly. At 15% burnoff the regeneration efficiency is about 90%, and most of the residue should be removed, since it is much more reactive than the base carbon. Tests over several cycles of adsorption, pyrolysis, and oxidation are needed to establish the best regeneration conditions for a particular adsorption process, but the controlled oxidation at moderate temperature seems a promising alternative to high temperature regeneration with steam.

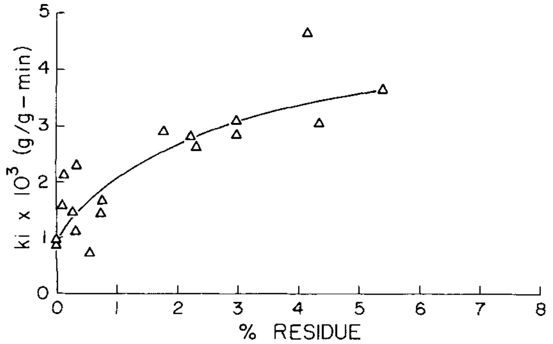

Figure 13. Oxidation rate for residue from sodium benzoate.

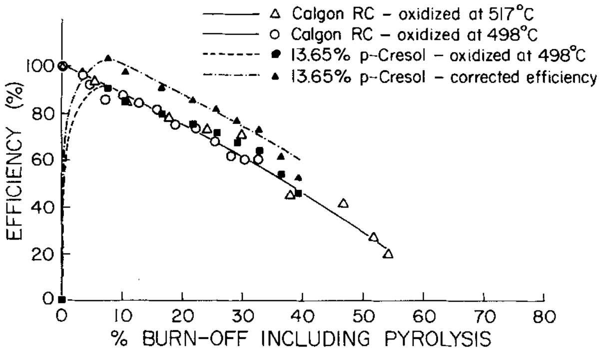

Figure 15. Regeneration efficiency as a function of burnoff.

Notation

b = adsorption constant, Eq. 1, L/mg
c = solute concentration, mg/L
M = molecular weight
Q = adsorption capacity g/g carbon
Q' = adsorption capacity, mmol/g carbon

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