

toluene extraction inefficient, if not impossible. What seems to contradict this explanation somewhat is that fullerenes were also desorbed from such samples upon heating them up to only 350°C and were detected by mass-spectrometry after ionization by low-energy electron capture [6], an analytical technique of lower sensitivity than our HPLC. The only explanation consistent with the apparently discrepant results of Buseck et al. [6] and of this work is that our samples contained very little of the yellowish-brown films, and that other phases of the Shungite are always essentially fullerene free.

We have not examined the Anthraxolite and Thucolite samples for veins of the sort reported to occur in Shungite. These materials, too, might contain efficiently encased fullerenes. Nevertheless, the failure to extract any detectable fullerenes from the six samples of Table 1 does suggest that free fullerene molecules were extremely rare at the surface of the Earth during Precambrian times, and were thus not available for incorporation into parent materials of Anthraxolite, Shungite, and Thucolite. One intriguing, but maybe not very meaningful coincidence is the closeness of the ages of the Sudbury impact of 1850 Myr and the age of the metasediment of Shunga of about 1800 Myr. Were these two sites sufficiently close geographically then for the good fullerene scavengers, which Shunga organics must have been, to have become impregnated with some fullerenes from a Sudbury fallout?

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**Activation of pre-chlorinated anthracite in carbon dioxide and steam**

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Anthracite is a microporous material which can be partially gasified in CO<sub>2</sub> or steam to produce a molecular sieve [1,2] or activated carbon [3,4]. Unfortunately, Pennsylvania anthracites contain a significant concentration of mineral matter which cannot be completely removed by usual preparation techniques. As a result anthracite activation (resulting in removal of

volatile matter and carbon atoms) leads to a final product which in some cases contains an unacceptably high inorganic matter content. Consequently, we have studied the removal of mineral matter from anthracite by heating in 0.1 MPa Cl<sub>2</sub> at temperatures between 600 - 1400°C [5]. Chlorination is quite effective at removing a substantial amount of mineral matter and, as we will see,

yields a material which has desirable properties as a precursor for the production of activated carbon.

Trevorton anthracite, of 42 x 65 Tyler mesh sieve cut, was used in this study. It had the following proximate analysis (fixed carbon, 79.1%; volatile matter, 9.1%; ash, 10.8%; moisture, 1.0%). The sample was devolatilized by holding 3 hr in 0.1 MPa N<sub>2</sub> at 950°C. This was followed by holding 1 hr in 0.1 MPa Cl<sub>2</sub> at 950°C in order to remove most mineral matter as volatile AlCl<sub>3</sub> and SiCl<sub>4</sub> [5]. Samples of devolatilized anthracite and devolatilized/chlorinated anthracite were then activated in either 0.1 MPa CO<sub>2</sub> or 0.1 MPa steam at 950°C. The apparatus used to prepare the samples was described in detail elsewhere [6]. Surface areas, on an ash-containing basis, were calculated from N<sub>2</sub> adsorption isotherms (-196°C) using the BET equation [7]. Samples were analyzed for chlorine according to the method discussed by Eschka [8].

Table 1 summarizes the activation results. Consider activation of the devolatilized anthracite first. The percent weight loss closely equals the percent burn-off on the basis of the starting ash-containing sample. That is, little ash, hydrogen, nitrogen, or sulfur would be lost during activation; and little stable oxygen complex would be formed at 950°C. As discussed previously [3], removal of carbon atoms from a microporous carbon, like anthracite, results first, primarily, in the opening up of closed pores (to N<sub>2</sub>), followed by enlarging of the micropores, and finally the breaking (reacting) through of pore walls, resulting in a decrease in the number of micropores. As a result, the specific surface area of the activated sample first shows a large increase, reaching a maximum value, and then decreasing. The change in surface area with burn-off for anthracite is further affected by the presence of significant ash. That is, the ash has negligible specific

surface area compared to the microporous coaly phase [9]. Its increasing presence with increasing carbon burn-off will make an increasing contribution to lowering the measured surface areas.

Steam is clearly a superior activating agent to CO<sub>2</sub>. Not only is a higher specific surface area developed in steam, but the gasification time required to produce this surface area is much less in steam for the devolatilized anthracite. Clearly the problem is that activation of devolatilized anthracite in either CO<sub>2</sub> or steam yields a product with an unacceptably high ash content.

Now consider results for the activation of the prechlorinated anthracite, as seen in Table 1. In this case, percent weight loss is greater than percent carbon burn-off because of removal of significant chlorine during activation. But this does not affect any of the conclusions now to be drawn. First chlorination of devolatilized anthracite for 1 hr at 950°C has sharply reduced the ash contents of the anthracites. Second, chlorination results in the addition of large amounts of chlorine to the anthracite. As discussed elsewhere [5], it is thought that Cl<sub>2</sub> reacts with hydrogen contained on the anthracite producing HCl and Cl atoms which in turn chemisorb. Third, activation in CO<sub>2</sub> and steam results in a sharp reduction in chlorine content of the anthracite, but steam is much more efficient at chlorine removal than is CO<sub>2</sub>. Fourth, prechlorination of anthracite leads to a superior precursor for the production of a high surface area carbon in either CO<sub>2</sub> or steam. Fifth, prechlorination results in some increase in gasification rate in either CO<sub>2</sub> or steam. This last finding was initially unexpected since it was thought that chemisorbed chlorine would block carbon active sites from attack by CO<sub>2</sub> or steam and result in significant reduction in gasification rates. However, at least two

Table 1  
Activation of Anthracite in Carbon Dioxide and Steam

Activation Time, min	Weight Loss %	Surface Area m <sup>2</sup> /g	Ash %	Chlorine Content %
Devolatilized Anthracite in CO <sub>2</sub>				
0	---	9	9.5	nil
90	50.1	262	17.8	nil
180	62.3	300	23.8	nil
240	74.9	325	33.4	nil
360	78.8	230	37.8	nil
Prechlorinated Anthracite in CO <sub>2</sub>				
0	---	5	2.6	7.7
15	20.2	315	5.1	4.8
30	28.1	500	5.5	4.6
60	42.7	730	6.1	3.9
90	61.2	980	8.5	3.5
120	66.7	1160	9.4	3.0
180	77.7	780	14.2	2.2
Devolatilized Anthracite in Steam				
15	43.2	315	19.9	nil
30	69.9	620	31.9	nil
Prechlorinated Anthracite in Steam				
15	53.0	850	9.3	0.2
30	75.4	760	11.2	0.1

effects of prechlorination appear to counterbalance this effect. First, removal of mineral matter by prechlorination introduced additional transitional and macropores into the anthracite. These pores serve as feeder pores leading to the micropores, resulting in a reduction of diffusional resistance of reacting gas into the particle and, hence, more uniform carbon gasification [10]. Second, as gasification proceeds, chlorine atoms are removed from carbon active sites, producing either  $\text{COCl}_2$  or  $\text{HCl}$ . Left behind are nascent carbon sites of high reactivity [11].

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## CARBON NEWS

### The American Carbon Society: Aims and Scope

The American Carbon Society (ACS), formally the American Carbon Committee, was established in 1957 with the express purpose of organizing US conferences on carbon. Today, the aims and scope of the American Carbon Society are considerably more diverse than those envisioned by its founders. The Society promotes interdisciplinary research and technology in the field of carbon science. Moreover, the Society sponsors a Biennial Conference on Carbon, a major international conference encompassing all areas of carbon science. In the intervening years the Society sponsors the American Carbon Society Workshop, which provides a forum for reporting and discussing single topic carbon research in a more focussed manner than that afforded by the biennial conferences. The ACS promotes carbon science and technology through its Graffin Lecture series, and recognizes excellence in carbon science through the Skakel and Pettinos Awards. Student participation at ACS-sponsored conferences is recognized through the Mrozowski and Walker Awards. *CARBON*, an international journal, is sponsored by the American Carbon Society. *CARBON* is now a monthly publication of approximately 160 pages per issue which publishes papers from numerous foreign countries.

The Society is managed by an elected executive committee and an elected advisory board. Various subcommittees exist, e.g., awards, long-range planning, communications, etc., to further the aims and scope of the Society. Individuals wishing to join the American Carbon Society may obtain further information from the Chair or the Secretary/Treasurer:

Dr. Robert A. Meyer  
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### Announcement

The American Carbon Society is in the initial planning stages for setting up a *moderated usenet group* in order to take advantage of the tremendous resources offered by the INTERNET. The primary objective of this newsgroup on carbon materials would be (1) to bring into **daily contact** people sharing the same interests, and (2) to **exchange information** around the globe in a quick and convenient manner.

As a show of support for this initiative, please send your e-mail address (plus any comments or suggestions) to either Ljubisa Radovic (lrr3@psu.edu) or Julius Jortner (jortnerjul@delphi.com).

### 1996 American Carbon Society Workshop

June 10-  
12, 1996

A workshop on Carbon Materials for the Environment, sponsored by the American Carbon Society, will be held in Charleston, South Carolina, USA. The workshop will highlight the diverse ways carbon materials are used to minimize and remediate environmental pollution. Because of its major role in these respects, it is expected that activated carbon will take center stage. However, papers and discussions on other carbon materials will be strongly encouraged if there is demonstrable association between the material and protection of the environment.

Discussion topics will include:

- removal of gaseous pollutants, including volatile organic compounds (VOCs), direct flue gas injection, and NO<sub>x</sub> and SO<sub>x</sub> reduction;
- adsorption of liquid pollutants, including industrial and municipal waste water treatment and ground water remediation;
- solvent recovery applications;
- catalysts or catalyst supports;
- automotive applications, including evaporative gasoline emission control, on-board refueling, and cabin-air filtration;
- energy storage systems, including alternative automobile fuels such as natural gas, hydrogen and electricity;