

# Mineral matter removal from anthracite by high-temperature chlorination

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Mineral matter was removed from anthracite by heating in 0.1 MPa  $\text{Cl}_2$  at 600–1400°C. The mineral matter undergoes carbothermic reduction, followed by chlorination of metals to volatile chlorides. Removal of mineral matter increases the porosity of the coal and enhances the accessibility of additional mineral matter to  $\text{Cl}_2$ . Exposure to  $\text{Cl}_2$  results in the fixation of chlorine on the anthracite, thereby affecting the electrical resistivity of the resulting carbon.

(Keywords: anthracite; demineralization; chlorination)

Anthracites are a valuable resource. They are high in carbon content, and low in volatile matter and sulfur content. In addition to their use as a fuel, they have many other uses, including reduction of metal oxides, production of metal carbides, electrodes, and activated carbon, and fillers for plastics. Their performance and value in their non-fuel uses are affected by the amount and nature of the mineral matter which they contain. A low mineral matter content is desirable.

This study explored the use of chlorination at elevated temperatures to reduce the mineral matter content of a Pennsylvania anthracite high in kaolinite and quartz. Chlorination of ores and minerals is commonly used commercially to convert oxides to metal chlorides. Carbon is used as the reductant, converting the oxide to a metal before reaction with  $\text{Cl}_2$  to produce a volatile chloride. In addition to upgrading of the quality of the anthracite by chlorination, the main metal chlorides produced (Si, Al, Fe and Ti) have commercial value.

## EXPERIMENTAL

### Anthracite

Anthracite from the St Nicholas breaker of the Western Middle field of Pennsylvania was chosen for the chlorination study. The sample, originally egg coal (~7.5 cm in size), was reduced in size using a jaw crusher and disc mill, yielding size fractions 991–833, 589–417, 351–208, 147–104, 74–43 and <43  $\mu\text{m}$ . The average size of the <43  $\mu\text{m}$  fraction was ~15  $\mu\text{m}$ . Chemical analysis of a typical 351–208  $\mu\text{m}$  fraction, used in most of this study, is given in Table 1. A spectrochemical analysis of the ash is given in Table 2 for the major elements present in the anthracite. Trace elements and their amounts found in Pennsylvania anthracites are listed elsewhere<sup>1</sup>.

### Reactor system

A flow diagram of the reactor system is shown in Figure 1 and described in complete detail elsewhere<sup>2</sup>. The reactor consisted of two concentric tubes: an inner tube of impermeable graphite and an outer tube of porcelain. The space between the tubes was filled with fine alumina powder. Threaded metal sleeves, machined from Hastelloy C, were cemented on the outer ends of the reactor tube. This permitted the use of water-cooled end caps which, together with Teflon gaskets, provided an airtight seal on the reactor tube assembly.

The temperature inside the reactor tube was determined indirectly, by comparison of millivolt readings of two similar thermocouples, one inside the reactor tube and the other outside. This calibration was performed in the presence of flowing  $\text{N}_2$ , since the thermocouple inside the reactor could not be used in the presence of flowing  $\text{Cl}_2$ . During actual runs, reaction temperatures were determined from readings on the thermocouple outside the reactor.

### Chlorination

The reactor was first brought to the required operating temperature (600–1400°C) in  $\text{N}_2$  flowing at 150  $\text{cm}^3 \text{min}^{-1}$ . To commence a run, the water connections to the outlet cap were removed and the outlet cap was unscrewed from the reactor. A boat of spectroscopic graphite containing a known weight of anthracite (~20 g) was then slowly inserted into the reactor. The time required to insert the boat into the reactor, screw the outlet cap in place, and reattach the water connections was ~4 min. Immediately after this, the  $\text{N}_2$  flow was shut off and  $\text{Cl}_2$  was admitted to the reactor tube at the desired flow rate. After the specified chlorination time, the  $\text{Cl}_2$  flow was discontinued and the system was flushed with  $\text{N}_2$  at a flow rate of 500  $\text{cm}^3 \text{min}^{-1}$  for 30 min. The sample in the boat was then removed from the reactor and separated into three portions: 4–5 g for chemical analysis, 2 g for

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electrical resistivity measurements, and the remainder for determination of surface area. Blank runs were also conducted, in which the samples were subjected to the same temperature and time conditions but with Cl<sub>2</sub> replaced by N<sub>2</sub>.

*Analysis and testing*

*Chemical analyses.* Moisture, ash, sulfur, carbon, hydrogen, and volatile matter were determined according to ASTM methods. The limit of duplicability for the carbon and hydrogen determinations was 0.07 and 0.3 wt% respectively, and that for the ash was 0.3 wt%.

**Table 1** Chemical analysis of anthracite (wt% as-received)

Carbon	88.3
Hydrogen	2.0
Ash	7.6
Moisture	1.3
Sulfur	0.6
Chlorine	nil
Volatile matter	3.2

**Table 2** Spectrochemical analysis of anthracite ash (wt%)\*

SiO <sub>2</sub>	54
Al <sub>2</sub> O <sub>3</sub>	30
Fe <sub>2</sub> O <sub>3</sub>	5.7
TiO <sub>2</sub>	2.0
V <sub>2</sub> O <sub>5</sub>	0.05
MgO	0.67
MnO	0.07
CaO	1.6

\*Cu, Ni, Na and Cr were also detected but not measured

*Spectrochemical analyses of ash.* The ash from the chemical analyses was kept for analysis of its constituents by the procedure described by Joensuu and Suhr<sup>3</sup>.

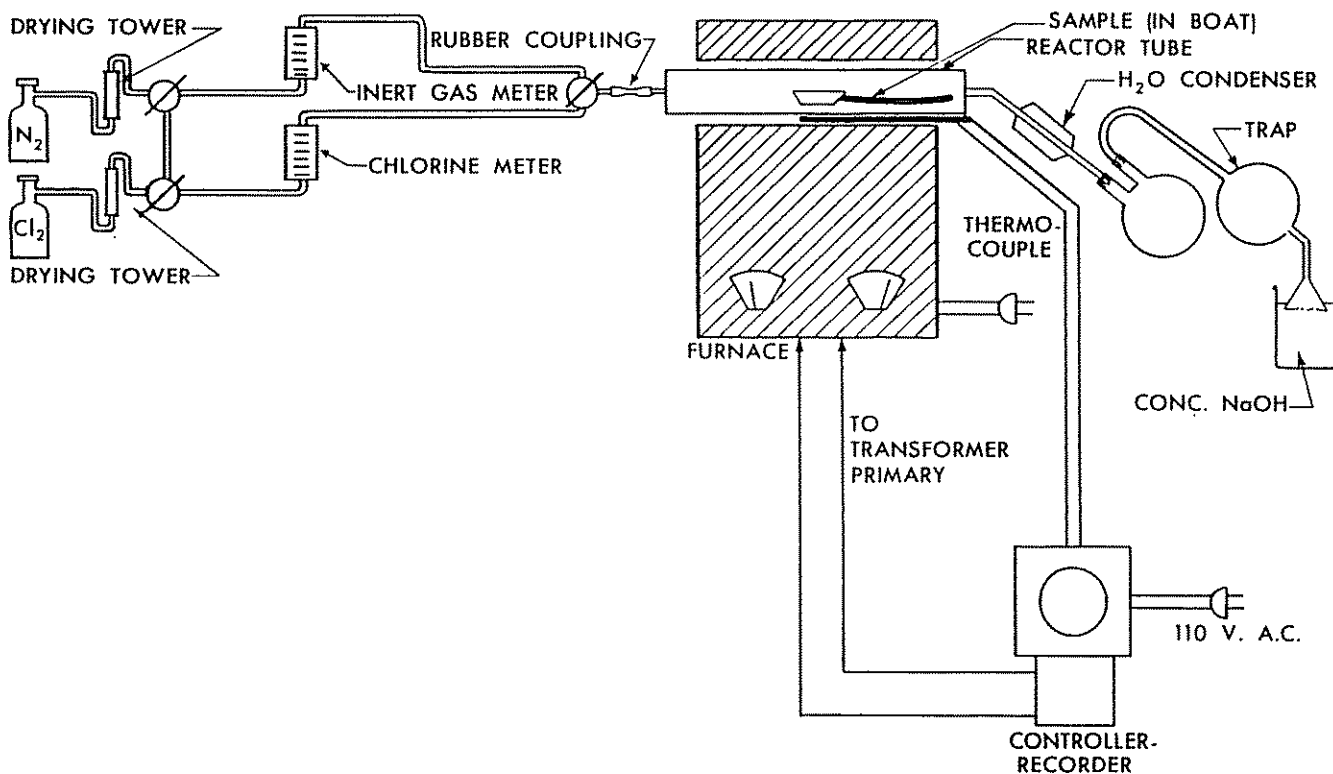
*Electrical resistivity measurements.* These were made at room temperature by confining 2 g of sample between two brass-tipped steel pistons (one of which was graduated) in a glazed steatite holder (38 mm o.d., 13 mm i.d., 51 mm long). The holder, constituting one arm of a Kelvin bridge, was mounted in a hydraulic press. Before the anthracite sample was placed in the steatite holder, it was outgassed overnight in a vacuum oven at 105°C. The samples were then placed in a desiccator and allowed to cool.

*Surface area measurements.* Surface areas were determined from adsorption isotherms of N<sub>2</sub> (-196°C) using the BET equation<sup>4</sup>. An equilibration time of 30 min was allowed at each adsorption point. Using ~4 g of sample, surface areas could be duplicated to ±2%.

**RESULTS**

*Effect of operating variables on ash removal*

Chlorination runs were initially made at temperatures of 800, 1000, 1200 and 1400°C. Samples of 351–208 μm anthracite were held in the reactor for 1 h at temperature under Cl<sub>2</sub> flow, followed by 0.5 h under N<sub>2</sub> flow. For comparison, blank runs were made in which anthracite samples were held for 1.5 h in N<sub>2</sub>. Results are summarized in Table 3. For runs under N<sub>2</sub>, there is little decrease in ash content on thermal treatment up to 1200°C, but some ash reduction is achieved at 1400°C. For runs under Cl<sub>2</sub>, significant reduction in ash is achieved by



**Figure 1** Flow diagram of reactor system

thermal treatment at 800–1000°C. Further increases in temperature to 1400°C result in little additional reduction in ash content. Thermal treatment in both N<sub>2</sub> and Cl<sub>2</sub> results in a monotonic decrease in hydrogen content of the anthracite with increasing temperature. The hydrogen content is reduced more sharply by heat treatment under Cl<sub>2</sub> than under N<sub>2</sub>.

Spectrochemical analyses<sup>2</sup> of the ash remaining in the samples after heat treatment showed that in N<sub>2</sub>, the percentages of eight major elements in the ash changed little up to 1400°C. In contrast, in runs under Cl<sub>2</sub>, iron was preferentially removed; titanium and calcium were more difficult to remove. For example, at 1400°C the following amounts were removed: ~83% of Si and Al; ~93% of Fe; ~60% of Ti; and ~75% of Ca. At 1000°C, the following amounts were removed: ~80% of Si and Al; ~84% of Fe; ~47% of Ti; and ~33% of Ca.

The runs so far discussed were conducted at a gas flow rate of 65 cm<sup>3</sup> min<sup>-1</sup>. To check for possible effects of Cl<sub>2</sub> mass transport rate in the main gas stream on rate of ash removal, additional runs were made at Cl<sub>2</sub> flow rates of 194 and 387 cm<sup>3</sup> min<sup>-1</sup>. Up to 1200°C, no effect of flow rate on ash removal was observed in 1 h runs. In another run the possibility that anthracite bed height affected ash removal was examined: after 1 h at 1200°C, the upper and lower layers of anthracite were separated. Within experimental error, both layers had the same ash content, showing that there was a negligible concentration gradient of Cl<sub>2</sub> through the bed. Hence mass transport of Cl<sub>2</sub> through the bed had a negligible effect on reaction rate<sup>5</sup>.

The effect of anthracite particle size on ash removal rate was studied using six different size ranges, each treated for 1 h at temperatures of 1000, 1200 and 1400°C. Chemical analyses of these size fractions in the original are given in Table 4. Note that the <43 μm fraction had a particularly high ash content. Figure 2 summarizes the ash removal results. At each reaction temperature, the percentage of original ash remaining decreases with decreasing particle size of anthracite chlorinated.

Table 3 Chemical analyses (wt%) of chlorinated anthracites and blank samples

Temperature (°C)	Blank			Chlorinated		
	Ash	C	H	Ash	C	H
Original	7.6	88.3	2.0	—	—	—
800	7.7	86.7	1.2	6.3	84.3	0.6
1000	7.8	90.1	0.6	1.8	91.5	0.2
1200	7.5	91.9	0.4	1.4	95.7	0.2
1400	6.8	91.4	0.2	1.2	96.9	0.1

Table 4 Chemical analyses of different size fractions of anthracite (wt% as-received)

Size (μm)	Ash	VM	H	C
991–883	7.9	3.4	2.5	87.2
589–417	7.9	3.6	2.2	86.8
351–208	7.8	3.7	2.0	87.4
147–104	6.8	4.2	2.4	87.5
1–43	7.7	4.4	2.4	86.1
<43	10.3	5.1	2.4	83.8

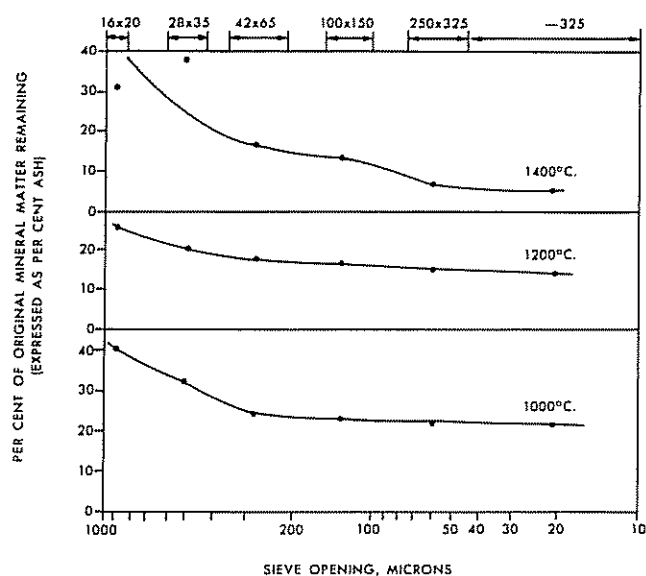


Figure 2 Effect of particle size on mineral matter removal for 1 h chlorination at different temperatures

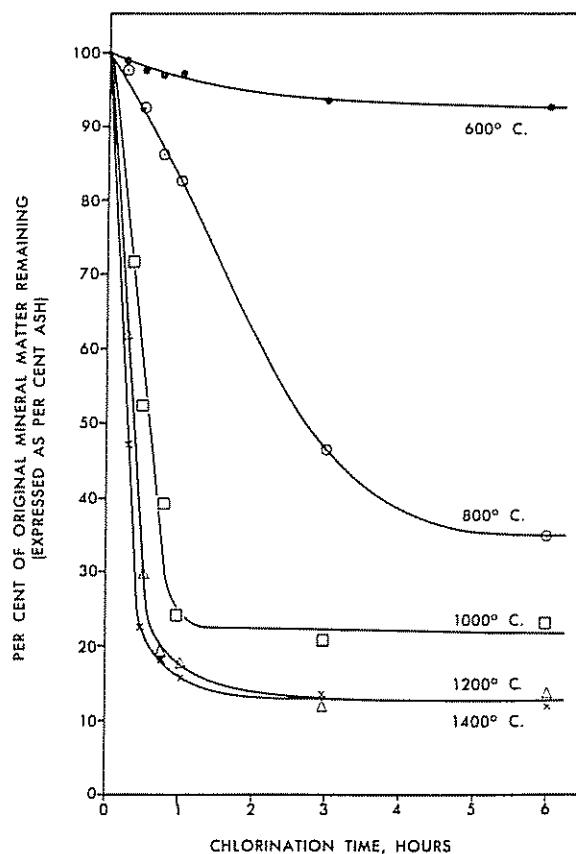


Figure 3 Effect of time and temperature on mineral matter removal from 351–208 μm anthracite by chlorination

Chlorination of the <43 μm fraction at 1400°C for 1 h is particularly effective in removing ash, reducing it from 10.3 wt% in the original anthracite to 0.56 wt% in the chlorinated sample.

Chlorinated runs were conducted on the 351–208 μm fraction to obtain rate curves at 600, 800, 1000, 1200 and 1400°C, with chlorination times of 15, 30, 45, 60, 180 and 360 min. The results are summarized in Figure 3. Each

data point on this graph represents a separate run. Marked differences in removal rates are seen. At the extremes, only ~8% of the ash is removed at 600°C in 6 h, but as much as ~85% at 1400°C. However, little additional ash is removed as the chlorination time is extended beyond 1 h at 1400°C. The results of additional runs at 1200°C for chlorination times of 4–12 min, presented in Figure 4, show that in fact most of the ash removal is accomplished within 12 min.

As discussed later, heat treatment of anthracite at elevated temperatures in an inert gas produces changes in it. For example, at 1200°C it lowers the surface area measured by gas adsorption, and it effects significant changes in the mineral matter. It was therefore of interest to determine the effect of such heat treatment on the subsequent ease of ash removal by chlorination. Anthracite was heated in He slowly to 850°C, held for 30 min, then heated to 1480°C and held for 3 h. Figure 5 summarizes the results of subsequent chlorination runs at 1200°C and different times. As expected, pretreatment significantly reduced the ease of mineral matter removal.

The effect of Cl<sub>2</sub> partial pressure on the rate of ash removal was studied at 1200°C. Figure 6 summarizes the results for atmospheres varying from pure Cl<sub>2</sub> to a 25:75 v/v mixture of Cl<sub>2</sub> and N<sub>2</sub>. At short reaction times the partial pressure of Cl<sub>2</sub> has a particularly marked effect

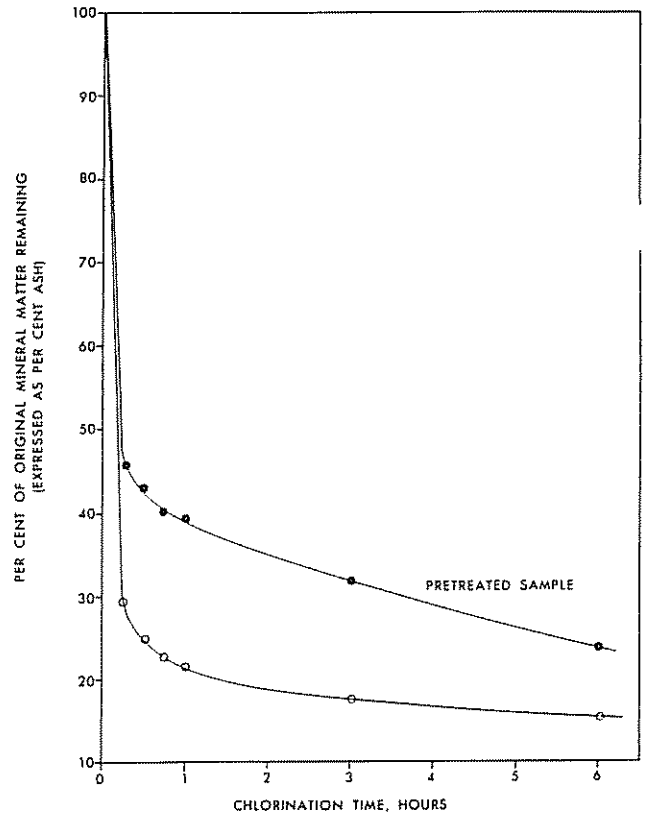


Figure 5 Effect of thermal pretreatment of anthracite on subsequent mineral matter removal by chlorination at 1200°C

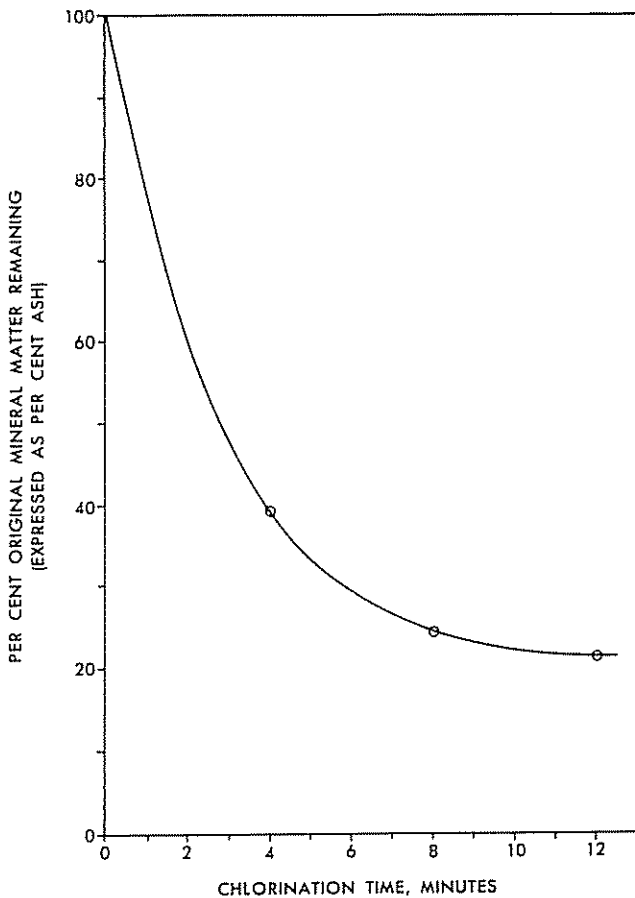


Figure 4 Mineral matter removal from 351–208 μm anthracite for short chlorination times at 1200°C

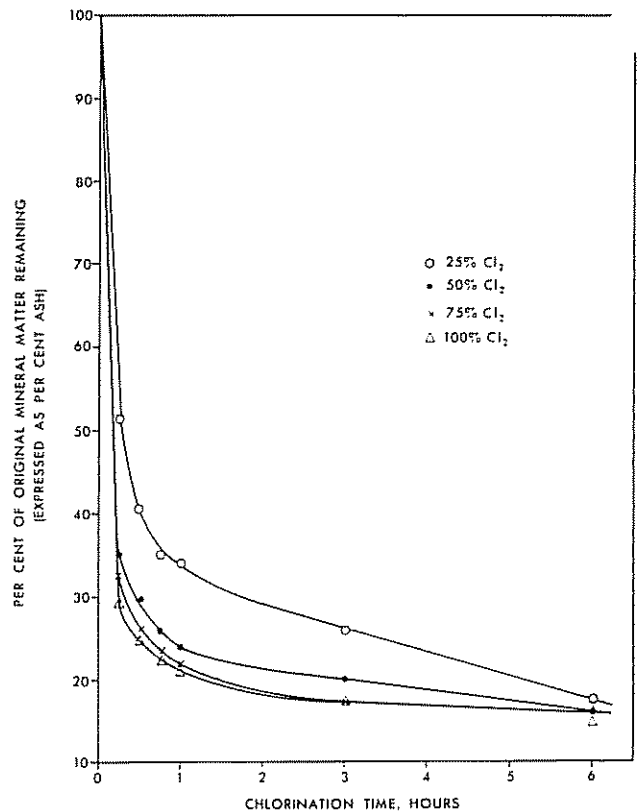


Figure 6 Effect of Cl<sub>2</sub> partial pressure on mineral matter removal from 351–208 μm anthracite at 1200°C

on the amount of ash removed. For example, at 15 min, ~71% of the ash is removed using 100% Cl<sub>2</sub> but only 52% using 25 vol.% Cl<sub>2</sub> in the gas stream. As the chlorination time increases, the effect of Cl<sub>2</sub> pressure on ash removal decreases, until at 6 h essentially the same amount of ash is removed at all Cl<sub>2</sub> pressures.

#### Effect of chlorination on surface area

Anthracite samples (351–208 μm) were heated at various temperatures for 1 h in either inert gas or Cl<sub>2</sub>, followed by measurement of surface area by N<sub>2</sub> adsorption at –196°C. The results are summarized in Table 5. Chlorinated samples have higher specific surface areas than the original anthracite and samples heated in inert gas under all conditions studied. The specific surface area passes through a maximum with increasing chlorination temperature.

#### Effect of chlorination on electrical resistivity

Electrical resistivities of samples heat-treated in N<sub>2</sub> and Cl<sub>2</sub> for 1 h at a series of temperatures are summarized in Figure 7. For both gases, they decrease with increasing heat-treatment temperature, the decrease being particularly marked between 725 and 1000°C. At each temperature, the resistivity of the chlorinated samples is lower.

## DISCUSSION

#### Removal of mineral matter from anthracite by chlorination

As mentioned previously, the major minerals in Pennsylvania anthracites are clays (primarily kaolinite) and quartz, which constitute upwards of 90 wt% of the total mineral matter in some cases<sup>1</sup>. Upon heating, kaolinite loses some water of hydration and adsorbed water at ~105°C<sup>6,7</sup>. This is followed by the loss of combined water between 550 and 600°C from hydroxyl groups surrounding the aluminium atoms, resulting in the formation of an amorphous phase of intimately mixed

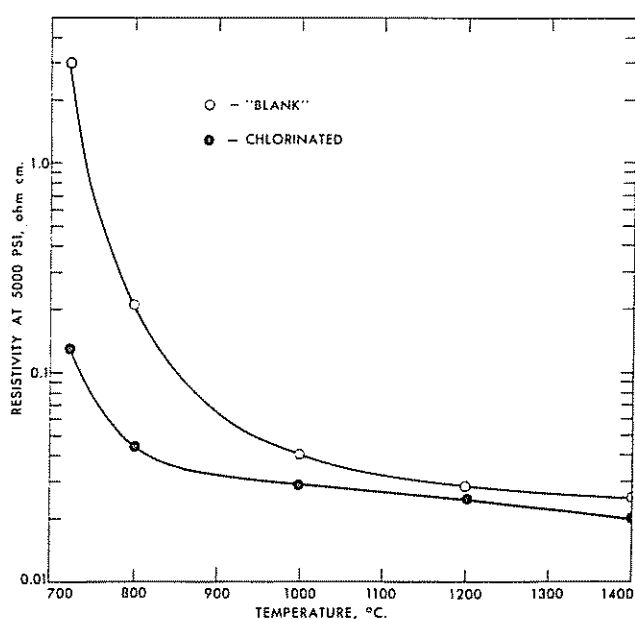


Figure 7 Change in electrical resistivity with heat treatment temperature for anthracite heated in N<sub>2</sub> and Cl<sub>2</sub>

Table 5 Surface areas (m<sup>2</sup> g<sup>-1</sup>) of chlorinated anthracites and blank samples

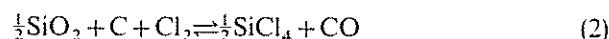
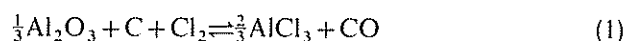
Temperature (°C)	Blank	Chlorinated
Original	1.8	–
800	<1	5.4
1000	<1	24
1200	<1	8.4
1400	<1	2.3

Table 6 Chlorine fixation on anthracite and carbon blacks (from ref. 19)

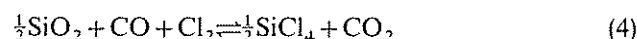
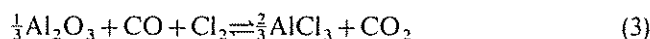
HTT (°C)	Time at HTT (h)	VM loss in N <sub>2</sub> (wt%)	Chlorine fixed (wt%)
St Nicholas anthracite			
600	4.5	1.9	13.3
700	4.5	2.4	17.5
800	2.8	3.3	14.7
900	2.0	4.4	10.7
Excelsior black			
600	1.8	2.9	12.7
700	1.0	–	10.4
900	1.0	8.5	6.0
1200	1.0	–	1.9
Acetylene black			
800	1.0	nil	1.1
1000	1.0	nil	0.9
1200	1.0	nil	0.9

SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (metakaolin). Metakaolin remains unaltered up to ~950–1000°C, at which stage it becomes converted either to a spinel-like form of γ-alumina or to mullite (2SiO<sub>2</sub>·3Al<sub>2</sub>O<sub>3</sub>). With further increase in temperature, the γ-alumina is replaced by increasing amounts of mullite<sup>6</sup>. Quartz, which is the stable phase of SiO<sub>2</sub> up to ~870°C, undergoes a crystallographic phase transition above this temperature to tridymite, which is the stable phase up to ~1470°C.

Oxides of Si and Al are called refractory oxides because of the strong affinity of these elements for oxygen<sup>8</sup>. Thus in the presence of Cl<sub>2</sub> but in the absence of carbon, it is thermodynamically unfavourable to convert these metal oxides to metal chlorides in the temperature range used in this study. In contrast, in the presence of the reducing agent carbon, the conversion of the metal oxides to metal chlorides by the following reactions is thermodynamically favourable in that temperature range:



The use of CO as a reducing agent by the reactions



is also thermodynamically possible. However, Almagro<sup>9</sup> has shown that the reduction of mineral matter in refuse from high-ash anthracite is retarded when 20 or 50% CO is introduced into the Cl<sub>2</sub> stream at 1000 or 1200°C. As shown below, see shortly, there are only small amounts of CO in the volatile matter released from anthracite upon heating.

The rate of mineral matter removal from anthracite

can depend on a number of resistances and their combination: the inherent chemical rate of reduction of metal oxides (or metal sulfides in the case of pyrite) by carbon, the inherent chemical rate of chlorination of metals by  $\text{Cl}_2$ , and the rates of diffusion of reactants into and products out of the porous anthracite char. At a given temperature, the inherent rate of reduction of metal oxides by carbon (a topochemical type of reaction) is proportional to the interfacial contact area between the two solid phases. The inherent rate of metal chlorination in turn depends on the surface area of the metal and the pressure of  $\text{Cl}_2$  at the metal surface. However, the inherent rate of the latter reaction will be reduced if diffusion limitations lead to a diminution of  $\text{Cl}_2$  pressure and/or a build-up of metal chloride pressure at the metal surface.

Consider the different steps (resistances) involved in reducing the mineral matter (ash) content of coal. For the carbothermic reduction of metal oxides, an attempt can be made to estimate the interfacial contact area between oxide and char surface. O'Gorman<sup>10</sup> subjected Pennsylvania anthracite to low-temperature ashing (LTA) to recover its mineral matter. Its surface area, as measured by  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$ , was  $7.7\text{ m}^2\text{ g}^{-1}$ . He also found<sup>1</sup> that the ratio (by weight) of LTA mineral matter to ash was 1.18. Therefore, the mineral matter surface area per unit mass of coal is  $0.69\text{ m}^2\text{ g}^{-1}$  taking an ash content of 7.6 wt.%. Now if it is assumed that the mineral matter is cubic in shape and that the interfacial area between mineral matter and coal consists of only one face of the cube, this interfacial area per unit mass of coal is  $\sim 0.12\text{ m}^2\text{ g}^{-1}$ . Since most of the mineral matter in the anthracite in fact consists of the clay-like mineral kaolinite, which is flaky, the interfacial area will be somewhat greater than that calculated assuming a cubic shape. No data exist, to the authors' knowledge, which allow the calculation of a specific rate constant for the reduction of the oxides of silicon or aluminium by carbon. Khalafalla and Haas<sup>11</sup> studied the carbothermic reduction of 210–149  $\mu\text{m}$  particles of quartz. They concluded that reduction primarily occurs in a highly reactive transitional phase as quartz is being transformed to cristobalite at  $\sim 1470^\circ\text{C}$ . A transitional phase may also be the active phase when quartz is transformed to tridymite at lower temperatures.

The fact that the rate of ash removal increased with decreasing particle size of the anthracite means that mass transport of  $\text{Cl}_2$  into the particle and/or metal chlorides out of the particle partly controlled the reaction rate. It is concluded that reaction proceeded as described by zone-II kinetics<sup>5</sup>. It did not occur in zone I, where the rate is independent of particle size of reactant, or in zone III, where the reaction rate would increase with increasing  $\text{Cl}_2$  flow rate.

Consider the question of mass transport resistance to reaction. Anthracite is a molecular sieve material<sup>12–15</sup>. That is, most of its surface area is located in small micropores. The microporosity has been characterized in particular by measuring rates of uptake of  $\text{CO}_2$  at  $25^\circ\text{C}$  and  $\text{N}_2$  at  $-196^\circ\text{C}$ . Carbon dioxide has a kinetic diameter ( $\sigma$ ), as calculated from its minimum equilibrium cross-sectional diameter, of 0.33 nm;  $\text{N}_2$  has  $\sigma = 0.36\text{ nm}$ . Despite this small difference in diameter,  $\text{CO}_2$  has much greater access to the micropores in anthracite than does  $\text{N}_2$ . Whereas the  $\text{N}_2$  area of the 351–208  $\mu\text{m}$  fraction is only  $1.8\text{ m}^2\text{ g}^{-1}$ , the  $\text{CO}_2$  area of the same fraction is

$\sim 230\text{ m}^2\text{ g}^{-1}$ <sup>14</sup>. As the anthracite is heated to elevated temperatures in an inert gas, the particles shrink (densify), resulting in a monotonic decrease in both the  $\text{N}_2$  and  $\text{CO}_2$  surface areas with increasing heat treatment temperature<sup>16</sup>. This increases the resistance to mass transport and can result in the increased closure of pore apertures to the reacting gas,  $\text{Cl}_2$ . This results in a balance between pore closure as a result of particle shrinkage and pore opening because of mineral matter removal. Ultimately, pore closure predominates as the chlorination temperature is increased, with the result that the specific surface area of chlorinated anthracite passes through a maximum, as seen in Table 5. The fact that ash removal is incomplete at each temperature is thought to be due primarily to the inaccessibility of the ash behind closed pores. Ultimately, mineral matter can be essentially completely removed from anthracite if chlorination is conducted at sufficiently high temperatures ( $2250^\circ\text{C}$ )<sup>17</sup>. However, it is thought that in this case the elements residing in closed pores diffuse along crystallite boundaries in the anthracite and thus gain access to chlorine. This diffusion is a process of high activation energy which can occur only at elevated temperatures.

#### Take-up of chlorine by anthracite during chlorination

It has been known for some time that if coals containing hydrogen and oxygen complexes associated with aromatic groups are heated in a  $\text{Cl}_2$  atmosphere, chlorine can be added to the coal<sup>18</sup>. The chlorine is tightly bound to the coal and can be removed only by heating to higher temperatures. The chlorine is added by two pathways. In one, it interacts with hydrogen, displacing it to produce  $\text{HCl}$  and chemisorbed chlorine:



In the other, hydrogen and oxygen complexes thermally removed from aromatic groups and the periphery of small trigonally bonded carbon crystallites, producing highly reactive nascent carbon sites on which chlorine is dissociatively chemisorbed. Whether chlorine is in fact added to the carbon, as in the two pathways just discussed, depends on whether a chlorine atom collides with a nascent carbon site before the site undergoes rehybridization to a less active form. This rehybridization will be considered shortly. If all the hydrogen in the St Nicholas anthracite were replaced by chlorine, the anthracite would contain  $\sim 42\text{ wt}\%$  chlorine.

Stacy *et al.*<sup>19</sup> studied the fixation of chlorine on St Nicholas anthracite and carbon blacks. Chlorination at heat treatment temperature was discontinued when the weight increase was  $< 2\%$   $\text{h}^{-1}$ . The results are summarized in Table 6. Excelsior black and acetylene black have surface areas ( $\text{N}_2$ ,  $-196^\circ\text{C}$ ) of 207 and  $64\text{ m}^2\text{ g}^{-1}$  respectively. These results reveal certain important facts. The amount of chlorine fixed depends on two factors: the amount and nature of the functional groups in the precursor, and the temperature at which the chlorine is fixed. As seen for acetylene black, which has negligible functional groups (or volatile matter), chlorine fixation is very small. Comparison of the amount of chlorine fixed on St Nicholas anthracite and Excelsior black demonstrates that the chemical nature of the volatiles is also important. At  $900^\circ\text{C}$  say, 8.5 wt% volatiles are released from the Excelsior black, compared with

4.4 wt% from the anthracite, but Excelsior black has fixed considerably less chlorine. This is because most of the volatile matter released from the anthracite is hydrogen<sup>20</sup>, whereas most of that released from Excelsior black consists of the oxides of carbon. Hydrogen is more efficient, per unit mass, at fixing chlorine. The effect of temperature on chlorine fixation is a balance between two factors. Increasing temperature results in the release of more volatiles and hence potentially the fixation of more chlorine. However, as the temperature rises, the tendency of chlorine to desorb from sites at which it is chemically bonded increases. It is seen that at higher temperatures the stability of chemisorbed chlorine is the dominant factor.

#### *Effect of chlorination on electrical resistivity*

The electrical resistivity results appear to be consistent with Pinnick's studies<sup>21</sup> on low-temperature carbonaceous materials. From electrical resistivity and infrared absorption measurements, Pinnick showed that the energy gap between the upper valence and conduction bands for these materials is substantial and that consequently their intrinsic electrical conductivity should be low. He concluded that conduction in these materials can be attributed chiefly to positive charge carriers. These positive carriers are produced as a result of the removal of hydrogen and oxides of carbon from the periphery of aromatic platelets during heat treatment. That is, some of the  $\sigma$  electrons from peripheral carbon atoms, which formed valence bonds with hydrogen etc., are left unpaired; a  $\pi$  electron can now jump from the  $\pi$  band into the  $\sigma$  state, forming a spin pair. The effect of this is to remove an electron from the  $\pi$  band and to create a hole or positive charge carrier.

The electrical resistivity data for St Nicholas anthracite treated in  $N_2$  are as expected. With increasing heat treatment temperature the fraction of peripheral aromatic carbon atoms covered by functional groups decreases. This decreased coverage results in an increase in the number of positive charge carriers and hence a decrease in electrical resistivity.

The effect of chlorination on the electrical resistivity of the anthracite also appears reasonable. At each heat treatment temperature, the presence of  $Cl_2$  results in a lower resistivity than in  $N_2$ . As discussed by Puri<sup>18</sup>, only a fraction of the hydrogen removed from carbon by chlorination is substituted by chlorine. Therefore, even though some chlorine is also chemisorbed on new peripheral carbon sites after removal of the oxides of carbon from anthracite, the fraction of the surface covered by hydrogen plus oxygen is greater after heat treatment in  $N_2$  than that covered by hydrogen plus oxygen plus chlorine after heat treatment in  $Cl_2$ . Differences in resistivity were particularly marked at a heat treatment temperature of 725°C. At this temperature, marked thermal removal of hydrogen from peripheral aromatic

platelets has just commenced. However, when the anthracite is heated in  $Cl_2$  instead of  $N_2$ , much additional hydrogen is removed, as is seen in *Table 3*.

## CONCLUSIONS

Mineral matter in anthracite can be removed to a considerable extent by heating in  $Cl_2$  at temperatures up to 1400°C. The mineral matter first undergoes a carbothermic reduction reaction, followed by chlorination. The rate of mineral matter removal is a function of anthracite particle size and  $Cl_2$  partial pressure. As a result of chlorination, the carbonaceous solid fixes considerable chlorine, primarily by interaction with hydrogen to produce HCl and a Cl atom which is chemisorbed. Such interaction reduces the electrical resistivity of the resulting carbon.

## ACKNOWLEDGEMENT

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