

## Thermal conversion of gasworks contaminated soil into carbonaceous adsorbents

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### Abstract

Contaminated soil from a gaswork site has been successfully converted into a carbonaceous adsorbent utilising  $ZnCl_2$  as an activating agent. The organic contamination, consisting of coal tars, phenols and associated compounds, was converted into a carbonaceous material. Extensive reduction (95%) in the cyanide content of the soil after treatment was observed and entrapment of metallic contamination within the carbonaceous matrix has been observed through XRF analysis. Surface area and porosity analysis by gas adsorption indicates surface areas ranging from 110 to 570  $m^2/g$ , and development of microporosity within the carbons. The complex contamination within the soils has influenced the development of adsorption characteristics within the samples, and sulphur, in particular, appears to play a major part in the development of this.

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### 1. Introduction

World demand for adsorbing materials is continually increasing as the developed world expands regulation of industrial and domestic discharges into the environment [1, 2]. The established industrial processes are frequently relying on secondary and tertiary methods to limit their waste discharges, which very often involve active carbon adsorption technology for aqueous and gaseous streams. Traditional sources of feedstock for carbonaceous adsorbent production, which include wood, coal, lignite, coconut shells and peat [3], are finite, and much interest is being expressed in the use of alternative renewable precursors [4].

Previous work by the authors has successfully converted a high volume hazardous waste from the edible oil industry into a carbonaceous adsorbent, with potential for use in batch adsorption applications [5, 6]. The objective of this work was to

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investigate another, more hazardous problematic bulk waste, contaminated soil, by converting it into a reusable, inert carbonaceous product.

### *1.1. Contaminated soil*

The causes of contaminated soil are extremely numerous, and the resulting contamination is often complex and widespread. Some of the industries whose operation has been associated with soil contamination are steel works, petrochemical plants, munitions factories and breakers yards. This current work was concerned with one of the most common type of contaminated site in the UK, abandoned gasworks sites.

The manufacture of town gas was undertaken in the UK for over 150 years. The estimated number of sites which were utilised for this process are approximately 3000 [7]. The sites were originally built on the edges of towns, but with increasing urbanisation of the British population during the 19th and early 20th centuries, and the subsequent expansion of towns, these sites were soon engulfed and became part of the central areas of urban locations. Today, the majority of them are derelict, but because of their prime locations they often have a high development value. Such sites are typically contaminated with a wide range of substances of both an organic and inorganic nature. These include coal tar and its many components [8], ammonia, cyanide (both as complexes and free cyanide), sulphur (all forms) and heavy metals [9]. The contamination is invariably very widespread, and often extensive sub-surface pollution exists due to the practise of re-building on the same site for successive plants, use of process wastes to level ground for site expansion, location of process pipes and process by-product tanks underground (which invariably leaked) and the disposal of process wastes on site.

### *1.2. Site restoration*

Within the United Kingdom, the general approach to contaminated site restoration is to decide on the desired end use for the site and then agree on the remediation required. This usually relies on civil engineering techniques and involves limiting contaminant migration from the site by building underground impermeable layers around, or putting hard cover over, the site [10]. This approach has become increasingly questioned, due to concerns about long-term contamination effects, and numerous cases of severe groundwater contamination. Potential pollution of groundwater supplies is a factor which is frequently being taken into account during the initial stages of development projects, as water supply undertakers in the UK and the National Rivers Authority are increasingly anxious to prevent contamination of existing or potential groundwater resources. Removal of contaminated soil from a site followed by landfill elsewhere is no longer perceived as an adequate response, however, and alternative soil treatments are now being widely researched, especially in the USA and Europe. This work has explored a new approach to contaminated soil treatment by converting it into a reusable carbonaceous adsorbent product, through the utilisation of activated carbon process technology.

### 1.3. Activated carbon

Activated carbon treatment of water to remove pollution has been utilised as a technology for over 60 years [11]. The adsorbent properties of activated carbon were recognised by the Egyptian civilisation who utilised wood char for medicinal purposes. Today, activated carbon is regarded as a commodity material, especially as it often provides the only means of removing certain chemical species, whether harmful or not, from the aquatic or gaseous environment. Its production entails a two stage process, which firstly involves consolidating the carbonaceous portion of the precursor material by controlled heating to minimise carbon volatilisation, whilst forming a char. The second stage is the development of a porous structure within the char which possesses particular adsorption characteristics, this being achieved by selected chemicals or gases. These two steps are termed carbonisation and activation respectively, and this process has been applied to typical samples of contaminated gasworks soil to produce carbonaceous adsorbents whilst rendering the contamination inert, or removing it from the soil system.

## 2. Methodology

Five representative soil samples were collected from a gaswork site undergoing extensive remediation and were a mixture of surface and subsurface samples. The nomenclature in Table 1 was used throughout the work to identify the samples.

### 2.1. Sample pretreatment

All samples were air dried at room temperature to constant weight and large rocks, bricks, etc. were removed before the samples were ground and sieved to less than 2 mm. Representative portions of the samples were removed, and further ground to pass a 150 µm sieve. This fraction was used to perform characterisation of the samples.

Table 1  
Sample nomenclature

Raw (as sampled) soil label	Treated soil label
STA01	STA01C
STA02	STA02C
STA03	STA03C
STA04	STA04C
STA05	STA05C

## 2.2. Soil characterisation

Soil samples were characterised by carbon, metal, cyanide, sulphate and sulphur contents and thermal characteristics.

The carbon analysis was performed using a Perkin Elmer 240 CHN analyser. Metal content was determined by digesting in duplicate the <150 µm portion of the soils (approximately 0.65 g) according to EPA method 3050 [12]. All reagents were Aristar® Grade and distilled water was used throughout the analysis. Spikes of a 100 ppm standard solution containing selected metals, blanks and spiked blanks were run as analytical method controls. All metals were determined using an Applied Research Laboratories 34000 inductively coupled plasma atomic emission spectrophotometer (ICP-AES). Total sulphate [13], total cyanide [14] and free sulphur [15] analysis were performed by Environmental Analysis (St. Leonards, UK).

Portions of the soil samples were analysed for their thermal characteristics using a Stanton Redcroft STA 780 combined thermogravimetric/differential thermal analyser (TG/DTA), using 20 mg portions of soil, with fired alumina as a reference material, heated at 5°C per min in an oxygen-free N<sub>2</sub> atmosphere flowing at 50 ml/min. The data collected by this technique enabled the determination of the optimum temperature conditions for both carbonisation and activation.

## 2.3. Preparation of carbonaceous adsorbents

Previous work within the centre [5, 6, 16] has demonstrated that production of carbonaceous adsorbents from heterogeneous waste materials was successful when using zinc chloride (ZnCl<sub>2</sub>) as an activating agent. The use of ZnCl<sub>2</sub> has been vindicated for other raw materials [17–20] and thus was used throughout this work as the preferred activating agent. The samples were impregnated using a stock solution of a 25% saturated ZnCl<sub>2</sub>, which was added to dry portions of the <2 mm soil fraction, in volumes sufficient to produce soil:ZnCl<sub>2</sub> weight ratios of 1:0.5, 1:1 and 1:2, respectively. As controls, soil samples which were not ZnCl<sub>2</sub> impregnated were also carbonised and activated. Portions of the ZnCl<sub>2</sub> impregnated soil samples were also analysed for their thermal characteristics, in the manner described earlier. From the data collected, the carbonisation and activation temperatures required to produce active carbons were established.

Bulk processing of the samples was performed using a Carbolite HTR 11/150 rotary furnace, using conditions given in Table 2. Post-treatment of the samples involved washing the samples with a 2 M HCl solution at 60°–80°C to remove unreacted ZnCl<sub>2</sub>, acid soluble ash and any traces of sulphur which remained after processing [17–21]. The acid liquors were vacuum filtered off the samples through Whatman® No. 1 filter paper, and the residue rinsed with portions of hot and cold water to remove any remaining acid. All samples were dried overnight at 105°C prior to being ground to pass a 150 µm sieve.

Table 2  
Temperatures chosen for carbonisation and activation

Sample ID	Carbonisation temperature (°C)	Carbonisation time	Activation temperature (°C)	Activation time
STA01	200	120 min for	450	60 min for
STA02	210	all samples	477	all samples
STA03	175		475	
STA04	275		525	
STA05	150		450	

#### 2.4. Product characterisation

Product characterisation consisted of the following parameters: (i) carbon content, (ii) cyanide, sulphate and sulphur analysis, (iii) metal analysis, (iv) aqueous adsorption screening and (v) gas adsorption studies.

These parameters were chosen because the carbon content of the product will influence the adsorbate capacity of the material. If the amount of carbon is low, then detailed examination of the aqueous and gas adsorption parameters is not worthwhile. The carbon analysis for each sample has been converted into a percentage yield. This has been performed using the following formula:

$$\frac{[\text{Weight of product (g)}] \times (\text{measured percentage C in product})}{[\text{Weight of soil used (g)}] \times (\text{measured percentage C in soil})} \times 100$$

= percentage carbon yield.

Aqueous phenol and gaseous nitrogen uptake by carbons are regarded as standard techniques to establish the character of carbonaceous adsorbents. Parameters (ii) and (iii) indicate the effectiveness of the process with regard to the contamination reduction and its inclusion within the carbon lattice.

Carbon content was analysed using a Perkin-Elmer 2400 CHN analyser. Total cyanide, total sulphate and total sulphur content analysis was performed as described earlier. Metal analysis was performed by X-ray fluorescence using a link XR500 instrument, operating at 10 keV with a Cu K $\alpha$  source.

Screening for adsorption capacity was performed in triplicate, using 1 g of sample in 125 ml glass bottles to which 100 ml of aqueous 10 mM phenol (Analar® Grade) or steam distilled and re-crystallised p-nitrophenol (GPR® grade) was added. Adsorbate only samples were also determined to allow for blank corrections. All samples were mixed using a variable speed rotary shaker for 3 h to reach equilibrium at 20 °C + / - 1 °C.

An Omnisorp® 100 automatic gas adsorption analyser operating in continuous mode, using N<sub>2</sub> gas at liquid nitrogen temperatures, was used to measure the surface area of the samples, by application of the BET equation to the data generated. Porosity information was also obtained by this technique.

Table 3  
Carbon analysis results for the untreated soils

Sample ID	Carbon content (%)
STA01	14.57
STA02	49.69
STA03	34.34
STA04	32.93
STA05	18.83

### 3. Results and discussion

#### 3.1. Sample characterisation

##### 3.1.1. Carbon analysis

The carbon value is composed of several components; natural organic material, bacteria, plant material, etc., coal tars and oils, and finally cyanide compounds. The results in Table 3 show how the carbon content of the soil samples vary, with values between 15% and 50%. The samples need to contain as much carbon as possible, as it is this which is being converted into an active char and will increase the potential adsorption capability of the product.

##### 3.1.2. Cyanide, sulphate and sulphur analysis

The values of contamination for these particular species in the raw soil samples are presented in Fig. 1. For comparison the values which were published as guideline

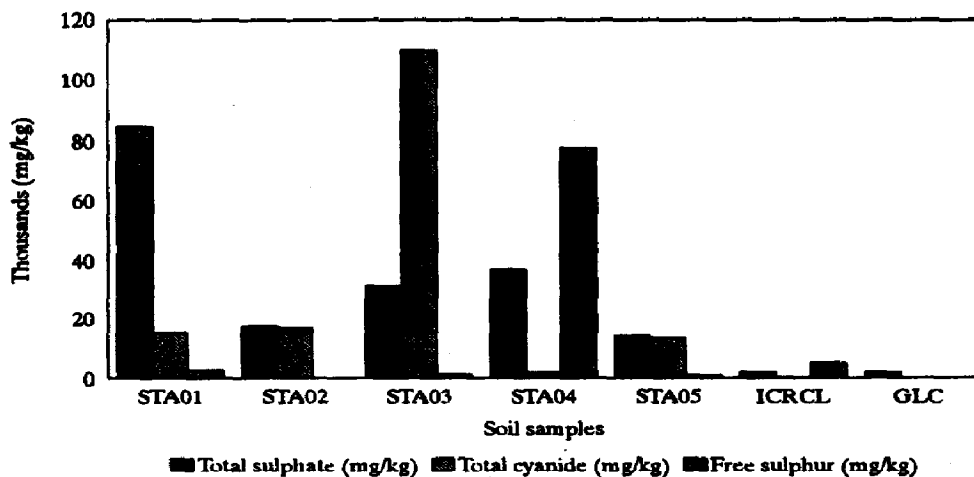


Fig. 1. Contamination levels found in each soil for cyanide, sulphate and sulphur. (ICRCL trigger values and GLC uncontaminated site values shown for reference.)

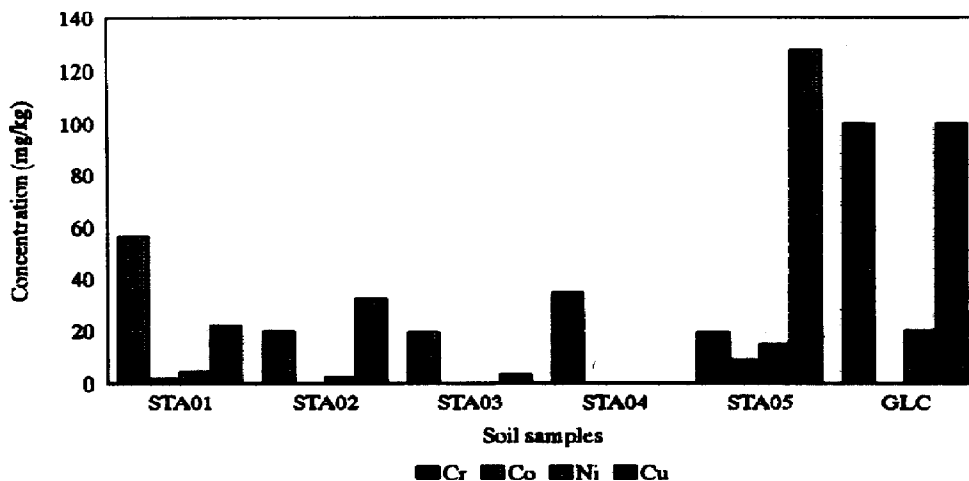


Fig. 2. Concentrations of Cr, Co, Ni and Cu measured in soil samples and together with GLC values for uncontaminated sites.

trigger values for soil contamination by the ICRCCL (Inter-Departmental Committee on the Redevelopment of Contaminated Land) [9] and the GLC (Greater London Council) for uncontaminated sites [22] are also presented. A trigger value is one which indicates that further investigation of the site may be required and subsequently remedial action to correct the contamination levels is needed. It is immediately obvious from comparison with both the GLC and ICRCCL values that all the soil samples used in this study are contaminated and that they exceed the recommended trigger values for at least one of the species determined.

### 3.1.3. Metal analysis

Only Cr, Co, Cu, Ni, Zn, Pb and Mn were examined due to the recognised threat that they pose to the health of plants and animals. Cd has not been discussed because it was only detected in STA05, at a concentration of 5 ppm, and the possible hazard presented by this level of contamination was minor when compared to the levels of Mn, Pb and Zn present in this sample. The data presented in Fig. 2 shows the levels of Cr, Co, Ni and Cu and Fig. 3 the levels of Mn, Zn and Pb contamination which were found in the samples. Typical values for these metals in uncontaminated sites, as reported by Kelly [22], have been shown for comparative purposes.

Consideration of the concentrations of the elements found in samples STA01–STA05 show values which are fairly typical for gaswork sites [7], although STA01 and STA05 are the only samples which exceed the GLC values for uncontaminated sites. STA05 is particularly heavily contaminated, with over 3000 ppm Zn and Mn and 1100 ppm Pb.

STA04 and STA01 exhibited curious behaviour with regard to their Co, Ni and Cu spike recoveries. Both of these samples show that over half of the spikes were not detected. For STA04, the spike is almost completely removed for Co, Ni and Cu. The

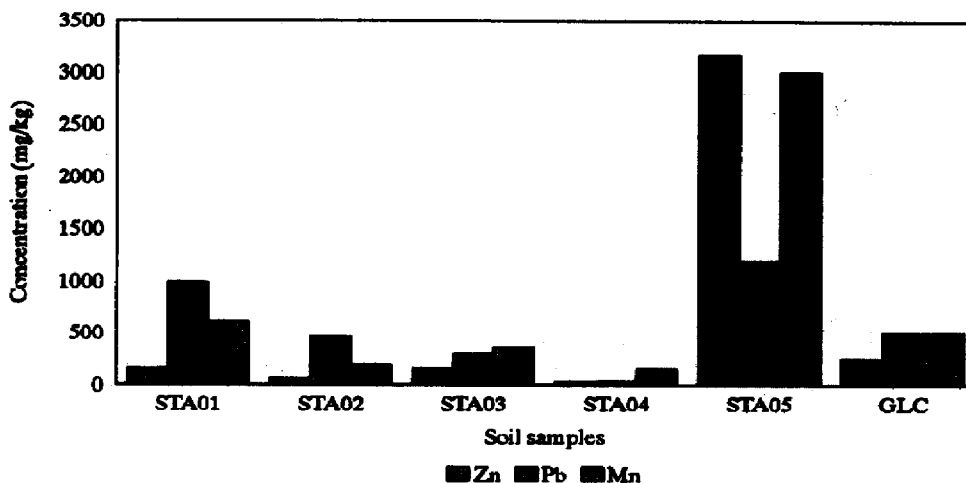


Fig. 3. Concentration of Zn, Pb and Mn found in soil samples together with GLC values for uncontaminated sites.

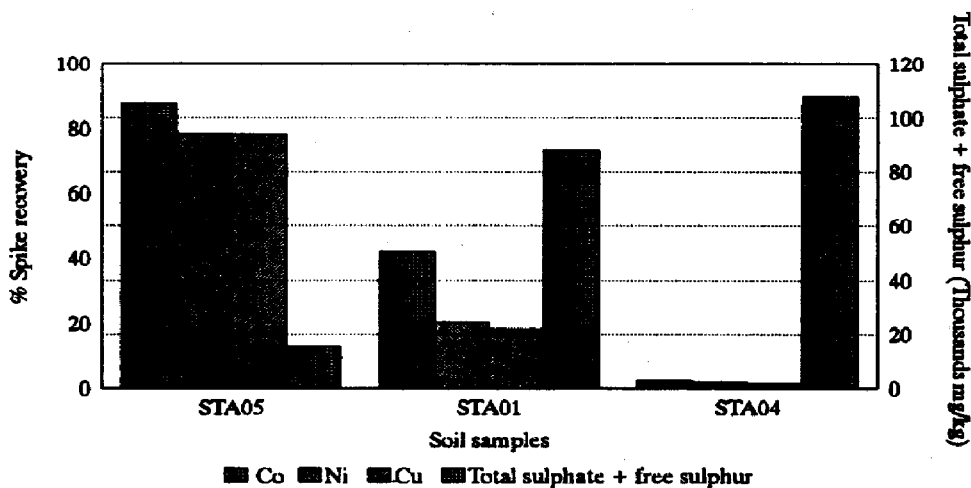


Fig. 4. Effect of increasing amounts of total sulphate and free sulphur species on the recoveries of the elemental spikes for Co, Ni and Cu.

cause of this loss is not clear, but an indication of the possible cause comes from the relative amounts of sulphur species (sulphur and sulphates) in each sample. There is a definite trend in the magnitude of the spike recovery and the amount of sulphur species in each sample, as illustrated in Fig. 4 by the decrease in spike recovery as the sulphur and sulphate content increases. All of the above metals will react with sulphur after gentle heating and the metal sulphide formed is almost insoluble in water, but will dissolve to varying extents under acidic conditions. The sulphate salts of these



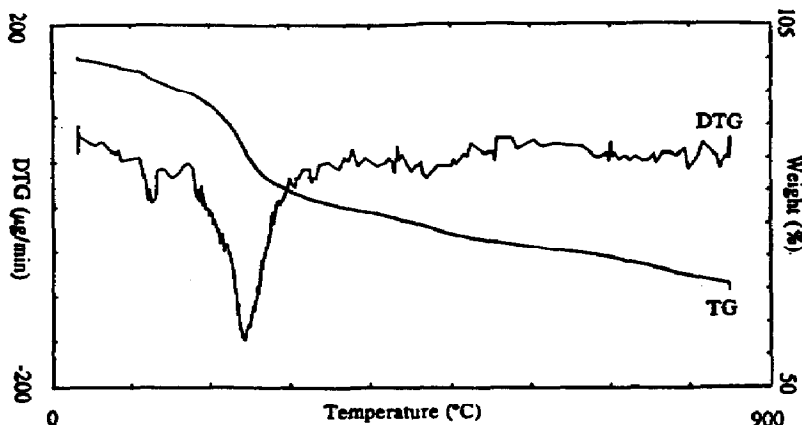


Fig. 5. TG and DTG trace for sample STA01, without the addition of  $\text{ZnCl}_2$ .

metals are also soluble [23]. However, in a review of the properties of metal sulphides by Kolthoff and Moltzau [24], they report several instances of co-precipitation of metal sulphides, particularly in the presence of  $\text{CuS}$  or  $\text{HgS}$ , even under acidic conditions. Hence, it is possible that the elemental spikes were consumed by co-precipitation with sulphides and were not subsequently measured in the digestion method employed. Exact quantification of the fate of these spikes is, however, beyond the scope of this present investigation.

#### 3.1.4. Thermogravimetric analysis

The thermogravimetric analysis of the soil samples indicate at what temperature the reactions involving weight changes are occurring. Each of the five samples show similar characteristics, as described below for STA01.

**3.1.4.1. Soil only samples.** The TG/DTG traces for sample STA01 (soil only) are shown in Fig. 5. The soil exhibits two weight losses which have peaks on the DTG trace at  $120^\circ\text{C}$  and  $243^\circ\text{C}$ , the first peak being loss of residual moisture in the sample and the second carbonisation and breakdown of organic contamination within the sample.

**3.1.4.2.  $\text{ZnCl}_2$  impregnated samples.** The TG/DTG traces for STA01 (with  $\text{ZnCl}_2$ ) are shown in Fig. 6. The effect of the  $\text{ZnCl}_2$  on the thermal characteristics of the soil is readily identified from comparison of Figs. 5 and 6. Addition of  $\text{ZnCl}_2$  to the soil causes the water loss peak to significantly increase, due to the hygroscopic nature of  $\text{ZnCl}_2$ . The organic peak is much reduced in magnitude, indicating that a reduction in volatilisation is occurring and so enhanced carbon retention is resulting. There is also a third peak in the DTG trace at  $510^\circ\text{C}$ , which has been assigned to the presence of  $\text{ZnCl}_2$  on the basis of studies by other workers [25–29].

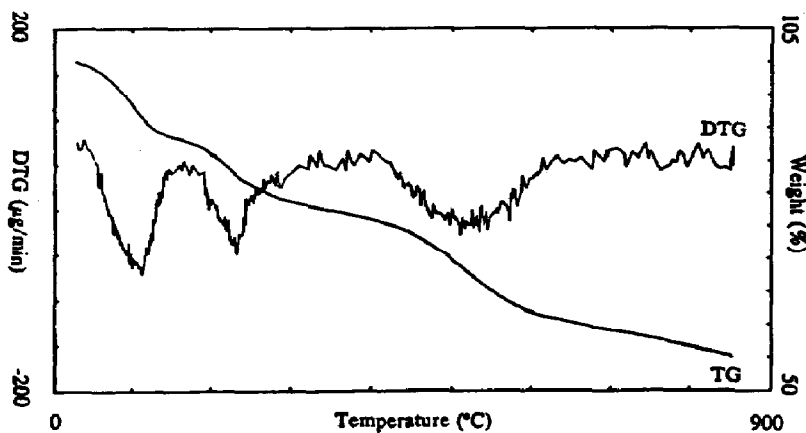


Fig. 6. TG and DTG trace for sample STA01, after the addition of  $\text{ZnCl}_2$ .

The temperatures established from the TG/DTG traces for the preparation of the soil-derived adsorbents are shown in Table 2. The residence time used for the carbonisation and activation was established from the TG trace and previous work [5, 6].

**3.1.4.3. Mechanistic aspects of soil activation and carbonisation.** There is an extensive amount of available literature studying the effect of Lewis acid type compounds (such as  $\text{ZnCl}_2$ ) on the pyrolysis of coals, from which the contamination of these samples is derived from. The proposed mechanism of activation of carbonaceous materials by  $\text{ZnCl}_2$  and by chemical activants in general is by chemical dehydration of the starting material, followed by the attack of the edges of the carbon planes and the removal of tarry material from pores, thus increasing the pore volume of the carbon lattice [3, 4].

However, it has been shown that addition of these compounds to coals increases char formation at the expense of gaseous and tar products under slow heating, whilst the reverse is true for flash pyrolysis. It has also been demonstrated that  $\text{H}_2$  formation readily occurs below  $400^\circ\text{C}$  in the presence of  $\text{ZnCl}_2$  and related compounds, but this is not the case when  $\text{ZnCl}_2$  is absent [25–29]. Work by Jolly et al. [26], using XRD, showed that the  $\text{ZnCl}_2$  added to coal was converted to  $\text{ZnO}$  and then subsequently to  $\text{ZnS}$  after slow heating to  $550^\circ\text{C}$ . They were especially surprised at the detectable presence of  $\text{ZnS}$  because of the low sulphur content of the precursor coal (0.79% w/w). Ibarra et al. [29] have proposed that  $\text{ZnS}$  and  $\text{HCl}$  form when the  $\text{ZnO}$  reacts with  $\text{H}_2\text{S}$  which is one of the pyrolysis products of coals. They also noted that the  $\text{ZnCl}_2$  separates, with the  $\text{Cl}$  finely dispersed in the coal matrix and the  $\text{Zn}$  only being detected where there was an abundance of sulphur. The association of  $\text{Zn}$  with sulphur has also been noted by other workers [25, 27]. Zinc has a high affinity for sulphur, as evidenced by the vigorous manner in which elemental sulphur and zinc powder react when mixed together and warmed [30]. The effect  $\text{ZnCl}_2$  has on coal pyrolysis has thus been suggested to be a form of catalytic cracking, and that this effect

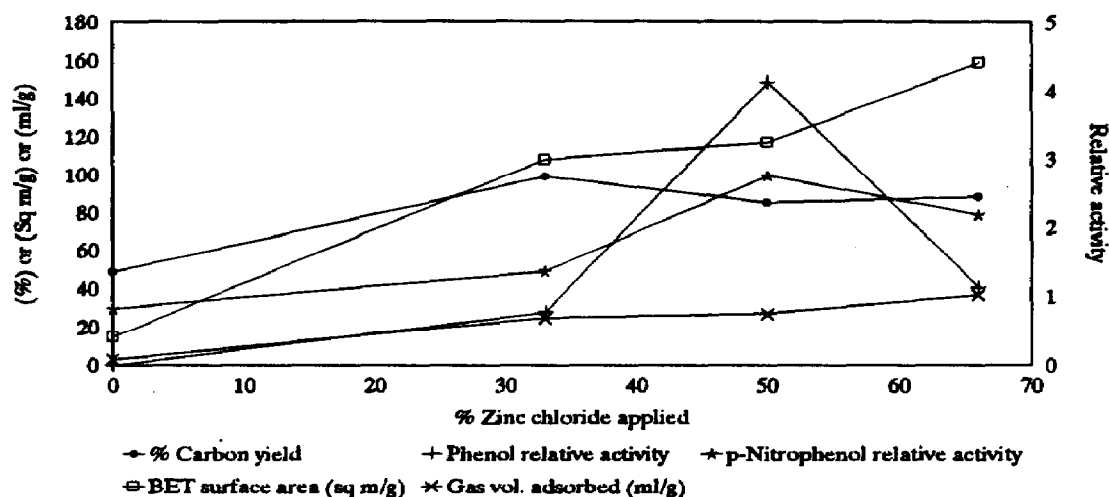


Fig. 7. Comparison of the effect of different ZnCl<sub>2</sub> loadings upon the adsorption related characteristics of soil STA01C.

is influenced by the presence of associated compounds [26, 29]. It is very probable that a similar mechanism is taking place during the carbonisation of these soil samples.

### 3.2. Product characterisation

#### 3.2.1. Carbon analysis

The percentage of carbon yield, calculated in the manner described earlier, illustrates the efficiency of the process in converting the carbonaceous contaminants into a carbon lattice and the effect of different ZnCl<sub>2</sub> loadings. The results in Figs. 7–11 indicate that for the contaminated soil samples, there is no apparent relationship between ZnCl<sub>2</sub> loading and carbon yield. Each sample exhibits a maximum yield at a different ZnCl<sub>2</sub> loading. The maximum carbon yield for samples STA01C and STA02C is at 33% ZnCl<sub>2</sub> loading, samples STA04C and STA05C at 50% ZnCl<sub>2</sub> loading and sample STA03C at 66% ZnCl<sub>2</sub> loading. This is indicative of the complex mixture of the contaminants within the samples which invariably affects the sample behaviour under the carbonisation conditions applied.

#### 3.2.2. Cyanide, sulphate and sulphur analysis

Fig. 12 shows the effect of ZnCl<sub>2</sub> on the presence of cyanide, sulphate and sulphur in the samples. A comparison between samples processed with and without ZnCl<sub>2</sub> indicates that cyanide removal is a purely thermal effect since there are no appreciable differences in cyanide reduction between the two types of samples, which all exhibit at least 95% reduction of their initial cyanide contents.

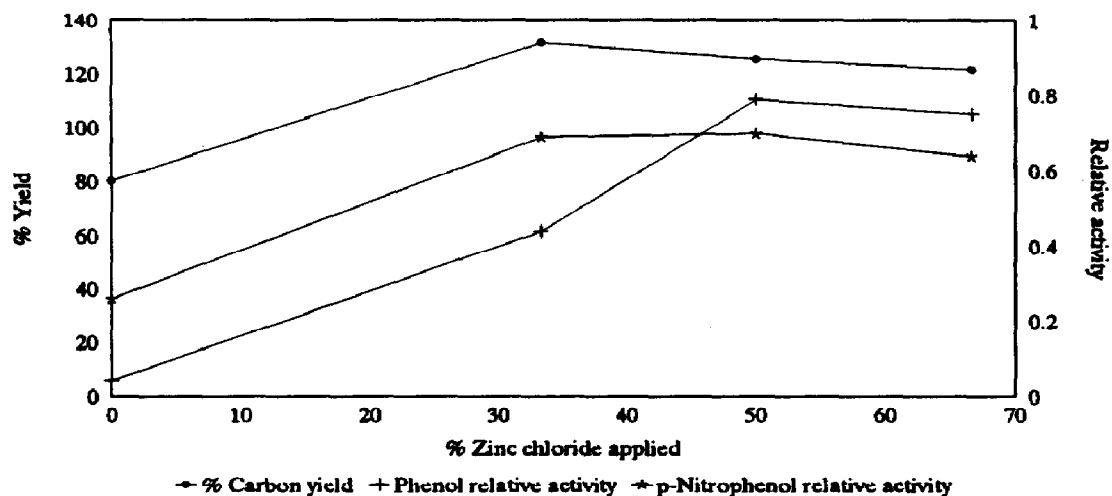


Fig. 8. Comparison of the effect of different  $ZnCl_2$  loadings upon the adsorption related characteristics of soil STA02C.

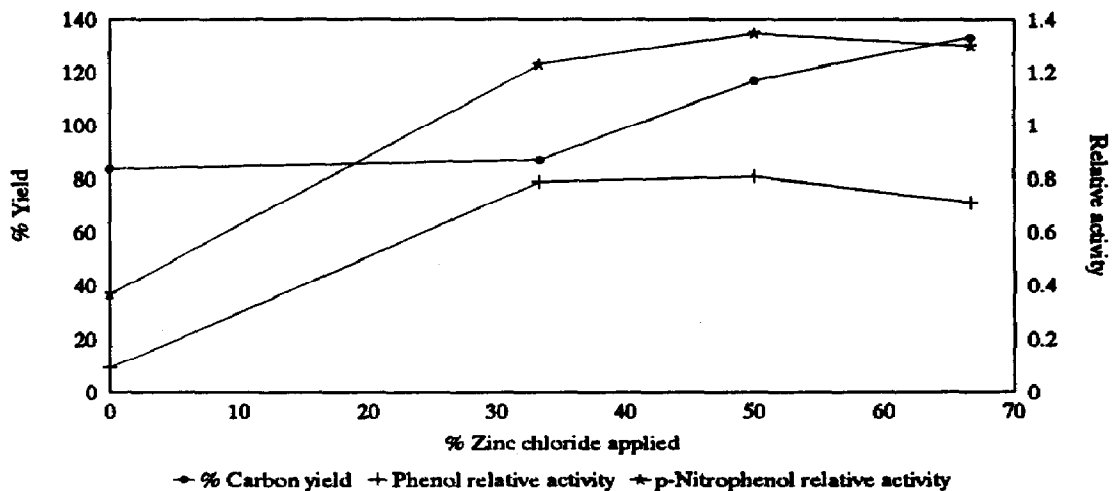


Fig. 9. Comparison of the effect of different  $ZnCl_2$  loadings upon the adsorption related characteristics of soil STA03C.

In contrast, the reduction in the sulphate and sulphur content of the samples fluctuated with all of the samples, and it is considered that there were several factors affecting these parameters, viz.: (1) free sulphur boils at  $444^\circ C$  [23], so during activation sulphur is probably lost by vaporisation; (2) the HCl wash was noted to produce  $H_2S$ ; and (3)  $ZnCl_2$  is considered to react with the sulphur, enhancing its retention within the carbon lattice, as discussed earlier. In addition, conversion of

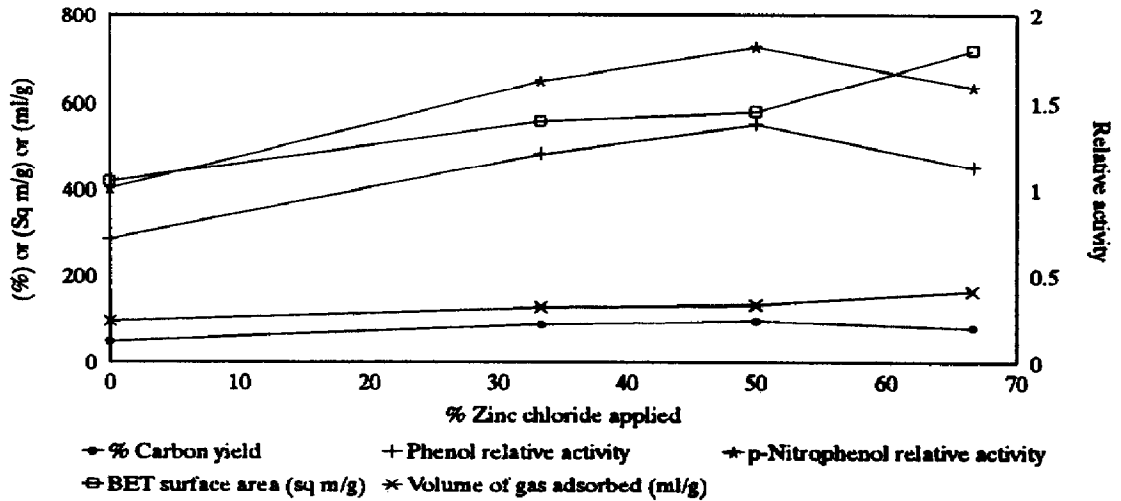


Fig. 10. Comparison of the effect of different  $ZnCl_2$  loadings upon the adsorption related characteristics of soil STA04C.

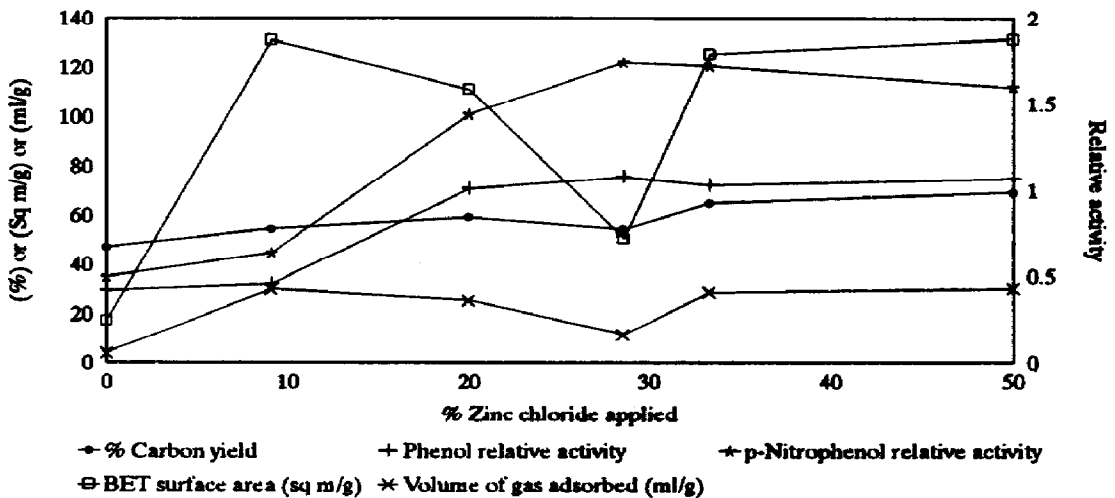


Fig. 11. Comparison of the effect of different  $ZnCl_2$  loadings upon the adsorption related characteristics of soil STA05C.

some of the sulphate to sulphur would be also occurring. This is due to the production of  $H_2$  during carbonisation which will react with any oxygen in the samples. Sulphate is a rich oxygen source, hence reduction will probably occur. Thermal degradation of the sulphate would also be expected [23], but further investigation of the fate of the sulphate species is required before any firm conclusions can be made.

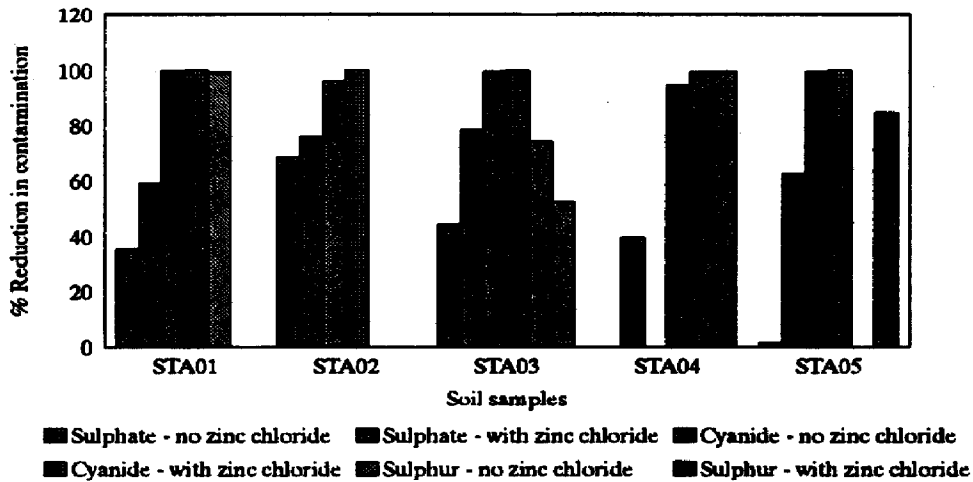


Fig. 12. Effect of addition of  $ZnCl_2$  to the soil samples on concentrations of cyanide, sulphate and sulphur.

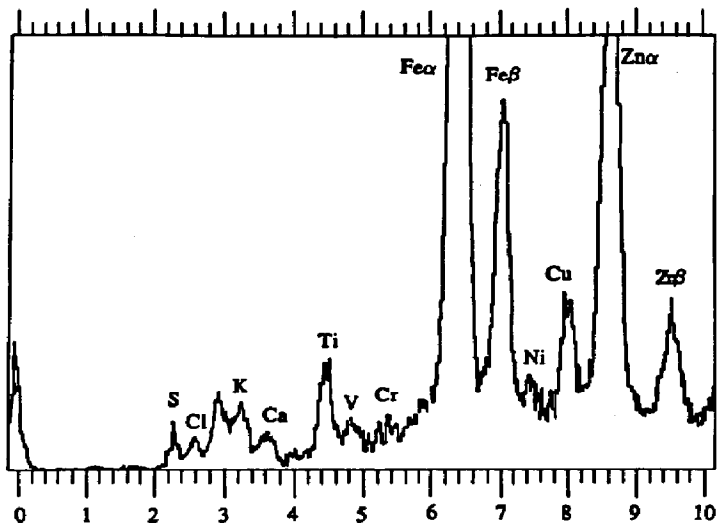


Fig. 13. XRF trace for sample STA02C.

### 3.2.3. Metal analysis

Fig. 13 shows a representative XRF trace which shows that the samples contained large amounts of iron. The zinc content of the  $ZnCl_2$  activated samples is also large, as expected. Traces of sulphur and chlorine can be seen as well as varying amounts of other species such as Ca, V, Ti, Cr, Ni and Cu. The fact that these elements are still present after the HCl wash indicates that they are not readily leached from the samples, and must be strongly retained within the carbon lattice.

Table 4

The percentage of carbon content, phenol and p-nitrophenol percentage adsorption and relative activities for each of the processed soil samples STA01C–STA05C

Soil ID	ZnCl <sub>2</sub> added (w/w) (%)	Carbon (%)	Phenol		p-Nitrophenol	
			Adsorption (%)	Relative activity	Adsorption (%)	Relative activity
STA01C	0.00	15.90	0.00	0.00	13.07	0.82
	33.33	21.71	16.63	0.77	29.42	1.36
	50.00	20.67	44.14	4.13	57.15	4.32
	66.67	21.10	23.56	1.12	46.07	2.18
STA02C	0.00	56.85	2.45	0.04	14.62	0.26
	33.33	57.54	25.05	0.44	39.52	0.68
	50.00	56.18	39.22	0.79	44.26	0.70
	66.67	58.72	21.13	0.75	37.46	0.64
STA03C	0.00	41.84	3.76	0.09	15.37	0.37
	33.33	40.09	31.55	0.79	49.42	0.73
	50.00	37.89	30.63	0.81	51.34	1.51
	66.67	42.42	30.15	0.71	55.14	1.09
STA04C	0.00	63.52	45.70	0.72	63.98	1.01
	33.33	57.13	69.12	1.21	93.22	1.63
	50.00	52.66	72.56	1.38	95.71	1.82
	66.67	59.30	67.05	1.13	94.36	1.59
STA05C	0.00	12.95	5.49	0.42	6.49	0.50
	9.09	14.05	6.46	0.46	9.04	0.64
	20.00	15.22	15.36	1.01	21.99	1.45
	28.57	14.37	15.60	1.08	24.95	1.74
	33.33	17.96	18.49	1.03	30.98	1.73
	50.00	18.17	19.40	1.07	29.16	1.61

### 3.2.4. Aqueous adsorption screening

Table 4 shows the carbon content, phenol and p-nitrophenol adsorption and relative activities, corresponding to each sample. Relative phenol or p-nitrophenol activity has been calculated using the following formula:

$$\frac{[\text{percentage removal of adsorbate by 1 g of product}]}{[\text{percentage carbon in the product}]} = \text{relative activity.}$$

The relative activity reflects the affinity of the carbon in the product for the adsorbates, irrespective of the amount of carbon present. This means that realistic comparisons between the different samples in terms of their adsorption ability can be made, and the success of the process in each case assessed. The results obtained for the processed soil samples are spread over a wide range of values as illustrated by Figs. 7–11.

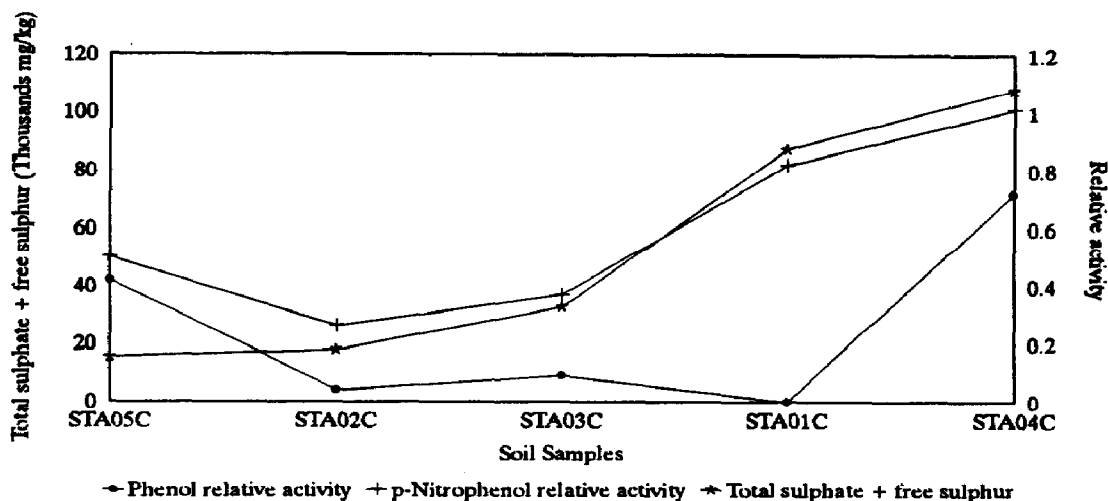


Fig. 14. Effect of the sulphur species in samples STA01C–STA05 on their relative adsorption ability, after preparation without zinc chloride addition.

It is interesting to note that STA01 contained the least carbon of all the soil samples and yet when combined with 50% of its own weight of  $ZnCl_2$  produced the carbon (STA01C) which exhibited the highest relative activity. However, soil STA02, which contained the most carbon (50% w/w), produced activated carbon (STA02C) with the lowest relative activity. This is perhaps indicative of the requirement for further optimisation of the conditions for the carbonisation/activation for the higher organic content samples.

All samples demonstrated that the relative activity increased with the addition of  $ZnCl_2$  up to a maximum of 50% w/w  $ZnCl_2$ , before it started to decline with increasing amounts. The results also indicated that the heterogeneous nature of the samples affected the activation developed by the samples, with their initial composition being a major influence upon the final products' performance as an adsorbent.

The hydrophobicity of p-nitrophenol is the cause of the difference between the percentage adsorption exhibited by the samples for phenol and p-nitrophenol. Sample STA04C exhibits the highest adsorption of all the samples, and the STA04C sample produced without addition of  $ZnCl_2$  has a surprisingly high phenol and p-nitrophenol adsorption (46% and 64%, respectively). Sample STA04C is self-activating and exhibits the second highest relative activities after sample STA01C. The available data for the soil samples treated without  $ZnCl_2$  indicates a relationship between the initial sulphur species content and the relative adsorption activity developed by the products towards phenol and p-nitrophenol. This is clearly shown in Fig. 14, which indicates that the relative activity increases as the sulphur species in each sample increase, except for sample STA05C (for both phenol and p-nitrophenol) and STA01C (for phenol). The lower than expected relative activity of STA01C towards phenol, but not p-nitrophenol, implies that an error may have occurred in the execution of this



Table 5

A comparison of the soil carbons with spent bleaching earth derived carbon and two commercial activated carbons

Sample identity	BET surface area (m <sup>2</sup> /g)	Volume of gas adsorbed (ml/g)	BET <i>c</i> value	Correlation coefficient for BET plot ( <i>r</i> <sup>2</sup> )
STA01C	110	25.31	671	1.0
STA02C	196	45.15	377	1.0
STA03C	219	50.38	630	1.0
STA04C	570	130.94	1775	1.0
STA05C	129	29.74	537	0.9999
SBE	260	59.68	577	1.0
Norit SA4	718	164.98	1646	1.0
BDH charcoal	679	156.05	402	0.9999

experiment. Unfortunately, repetition of this experiment was not possible due to the limited sample quantities which were available.

Carbon STA05C (no ZnCl<sub>2</sub> addition) exhibits a higher relative activity than would be expected if the sulphur species present in that sample were assisting in the development of adsorption activity. The explanation of this result is not obvious with the available data, although the presence of high levels of Zn in this sample (cf. Fig. 3) may indicate that some activation by reaction of the Zn has occurred. The actual process of activation in these samples is extremely complex and appears to involve many variables, whose study is beyond the scope of this work.

### 3.2.5. Gas adsorption studies

BET data for samples STA01C, STA04C and STA05C are presented in Figs. 7, 10 and 11, and support the data for the aqueous adsorption study of the processed soil samples. All the samples exhibit a definite trend with respect to increasing ZnCl<sub>2</sub> application as illustrated by the increased BET surface area and volume of gas adsorbed with ZnCl<sub>2</sub> addition, except, once again, for sample STA05C.

The samples possess microporosity, and as such exhibit a characteristically high BET *c* values [31]. Very large *c* values reveal that the BET equation cannot be applied to gas adsorption information with complete confidence [32], because the values arrived at will be affected by micropore filling effects. Nevertheless, BET data accompanied by a high *c* value does provide an excellent comparative tool for indicating of the relative surface areas of each sample.

Table 5 details the BET data for samples STA01–STA05C activated by 33% ZnCl<sub>2</sub>. For comparison, two commercial carbons and a waste derived adsorbent, spent bleaching earth (SBE), produced by previous work at the centre [5, 6] are also detailed. The most microporous samples, STA04C and Norit SA4, both possess the characteristically high *c* value and possess extensive surface areas. The other soil-derived adsorbents are of a lower surface area than the commercial samples but

compare favourably with the SBE, and the surface areas calculated correlate well with the aqueous adsorption data.

#### 4. Summary and conclusions

This work has demonstrated that it is possible to convert contaminated soil from gaswork sites into a carbonaceous adsorbent using zinc chloride as an activating agent. The samples were highly contaminated with cyanide initially, but after treatment a 95% reduction was achieved. The organic contamination has been converted into a solid carbonaceous lattice, removing the potential hazard which is associated with coal tars, phenols, etc. Initial results have also indicated that the non-volatile metallic contamination is being retained within the carbon lattice formed.

Adsorption capacity within the samples has been developed to varying degrees, with the major controlling factor being the initial carbon content of the soil. The extent of adsorption ability developed has also been shown to be governed by the amount of  $ZnCl_2$  initially added. The optimum amount of  $ZnCl_2$  to be used in the processing of further soil samples, both in terms of product development and economic use, has been established at 33% loading (w/w). Although this does not necessarily represent the amount of  $ZnCl_2$  that produces the highest adsorption activity or surface area in every sample, the results demonstrate that the gain in relative adsorption activity from adding 50% as opposed to 33%  $ZnCl_2$  is negligible.

This work has demonstrated that it is possible to treat contaminated soil and convert it into a material which has potential for reuse as a low grade bulk adsorbent with once-only usage. More work is required to establish the effects of the various components within the soil on the treatment procedure, and ultimately the form of these pollutants during the processing.

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#### References

- [1] N. Haigh, EEC Environmental Policy, 2nd revised addition, Longman, New York, 1990.
- [2] G.B. Davenport, The ChE's Guide to Environmental Law Part 2: The ABC's of Hazardous Waste Legislation, Chemical Engineering Progress, May 1992, pp. 45–50.

- [3] R.P. Bansal, J.-B. Donnet and F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, 1988.
- [4] S.J.T. Pollard, G.D. Fowler, C.J. Sollars and R. Perry, Low-cost adsorbents for waste and wastewater treatment; A review, *Sci. Tot. Environ.*, 116 (1992) 31–52.
- [5] S.J.T. Pollard, C.J. Sollars and R. Perry, A low-cost adsorbent from spent bleaching earth. I: The selection of an activation procedure, *J. Chem. Tech. Biotechnol.*, 50 (1991) 265–275.
- [6] S.J.T. Pollard, C.J. Sollars and R. Perry, A low-cost adsorbent from spent bleaching earth. II: Optimisation of the  $ZnCl_2$  activation procedure, *J. Chem. Tech. Biotechnol.*, 50 (1991) 277–292.
- [7] *Problems Arising From The Redevelopment of Gas Works and Similar Sites*, 2nd edn., ERL/DoE, Nov. 1987. HMSO, London.
- [8] J. Dragun, *The Soil Chemistry Of Hazardous Materials*, Hazardous Materials Control Research Institute, 1988.
- [9] *Guidance on the Assessment and Redevelopment of Gas Works Sites*, ICRCCL Guidance Note 18/79, 5th edn., 1986.
- [10] T. Cairney (Ed.), *Redevelopment of Contaminated Land*, Blackie, 1986.
- [11] M.K.N. Yenkie and G.S. Natarajan, Adsorption equilibrium studies of some aqueous aromatic pollutants on granular activated carbon samples, *Sep. Sci. Technol.*, 26 (1991) 661–674.
- [12] EPA/SW-846, *Test Methods For Evaluating Solid Waste*, Vols. 1a–c and 2, Field Manual, Chemical/Physical Methods, 3rd edn., Environmental Protection Agency, Washington, DC, Office Of Solid Waste And Emergency Response, 1986, PB88-239223.
- [13] Sulphate in Soil, B.S. 1377, 1975, Test 9, B.S. 1377, 1990, Part 3, Method 5.
- [14] *Methods Taken or Adapted from Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, WPCF. Cyanides Methods 4500 A-M, Cyanide and Thiocyanate Methods 4500 A-M.
- [15] P.R. Hesse, Method adapted from Hart, *A textbook of Soil Chemical Analysis*, Murray, London, 1971.
- [16] I. Gee, M.Sc. Thesis, The manufacture of a low-cost adsorbent from a chemical waste, Department of Civil Engineering, Imperial College, London, 1991.
- [17] F. Ruis Beviá, D. Prats Rico and A.F. Marcilla Gomis, Activated carbon from almond shells, chemical activation 1. Activating reagent selection and variables influence, *Ind. Eng. Chem. Prod. Res. Dev.*, 23 (1984) 266–269.
- [18] F. Ruis Beviá, D. Prats Rico and A.F. Marcilla Gomis, Activated carbon from almond shells, chemical activation 2.  $ZnCl_2$  activation temperature influence, *Ind. Eng. Chem. Prod. Res. Dev.*, 23 (1984) 270–271.
- [19] R. Torregrosa and J.M. Martín-Martínez, Activation of lignocellulosic materials: A comparison between chemical, physical and combined activation in terms of porous texture, *Fuel*, 70 (1991) 1173–1180.
- [20] F. Caturla, M. Molina-Sabio and F. Rodríguez-Reinoso, Preparation of activated carbon by chemical activation with  $ZnCl_2$ , *Carbon*, 29 (1991) 999–1007.
- [21] M. Smíšek and S. Černý, Active carbon, manufacture, properties and applications, in: P.L. Robinson (Ed.), *Topics in Inorganic and General Chemistry*, Monograph 12, Elsevier, Amsterdam, 1970.
- [22] R.T. Kelly, *Site Investigation and Materials Problems, Reclamation of Contaminated Land*, Eastbourne 22–25 Oct. 1979, Society of Chemical Industry, paper B2, 1980.
- [23] R.C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 68th edn., CRC Press, 1987–1988.
- [24] I. M. Kolthoff and D.R. Moltzau, Induced precipitations and the properties of metal sulphides, *Chem. Rev.*, 17(3) (1935) 293–325.
- [25] R. Kandiyoti, J.I. Lazaridis, B. Dyrovold and C. Ravindra Weerasinghe, Pyrolysis of a  $ZnCl_2$  impregnated coal in an inert atmosphere, *Fuel*, 63 (1984) 1583–1587.
- [26] R. Jolly, H. Charcosset, J.P. Boudou and J.M. Guet, Catalytic effect of  $ZnCl_2$  during coal pyrolysis, *Fuel Process. Technol.*, 20 (1988) 51–60.
- [27] R.J. O'Brien, G.W. Briers and R. Kandiyoti, Effect of impregnation with  $ZnCl_2$  and other catalysts on coal pyrolysis, *Fuel*, 66 (1987) 711–715.
- [28] H.J. Neuburg, R. Kandiyoti, R.J. O'Brien, T.G. Fowler and K.D. Bartle, Release of chloroform extractable materials from bituminous coals after mild heating, *Fuel*, 66 (1987) 486–492.

- [29] J.V. Ibarra, R. Moliner and J.M. Palacios, Catalytic effects of  $\text{ZnCl}_2$  in the pyrolysis of Spanish high sulphur coals, *Fuel*, 70 (1991) 727–732.
- [30] L. Bretherick (Ed.), *Hazards in the Chemical Laboratory*, 4th edn., Royal Society of Chemistry, 1986, p. 554.
- [31] S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, 2nd edn., Academic Press, New York, 1982.
- [32] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Muscou, R.A. Perotti, J. Rouquérol and T. Siemieniowska, Reporting physisorption data for gas/solid systems, with special reference to the determination of surface area and porosity, *Pure Appl. Chem.*, 57 (1985) 603–619.