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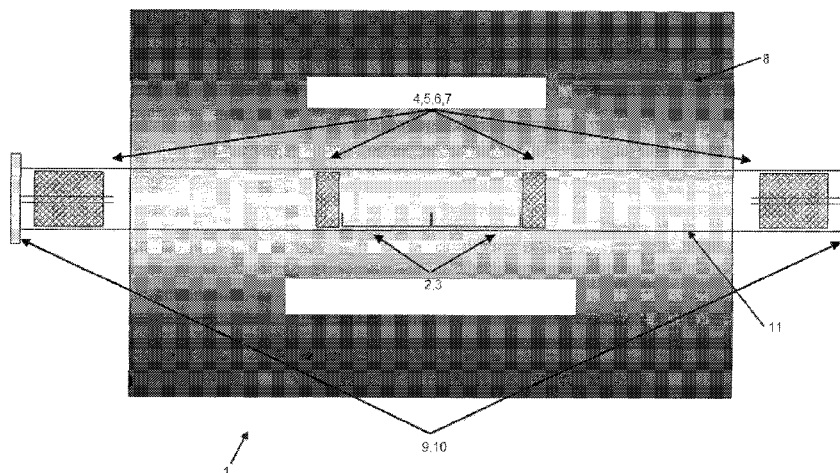


Figure 1

(57) **Abstract:** The present invention relates to activated carbon composites.

Activated Carbon Composites

Description of Invention

5

The present invention relates to activated carbon composites. In particular, the present invention relates to generally dense activated carbon composites. The present invention also relates to a process for the production of such activated
10 carbon composites.

Activated carbon is a form of carbon which has been processed to provide a large surface area, and is therefore extremely porous. 1 gram of a typical activated carbon has a surface area in excess of 500 m². Due to its high
15 surface area, activated carbon is highly porous and provides a large surface area for adsorption and/or chemical reactions.

Activated carbon is often prepared by pyrolysing material with a high carbon content, e.g. charcoal. Pyrolysis usually takes place at around 600-900°C, in
20 an inert atmosphere (e.g. in an argon or nitrogen atmosphere). There are different types of activated carbon, e.g. powdered activated carbon, granular activated carbon, extruded activated carbon, impregnated carbon, polymer coated carbon and other types of activated carbon well known to the skilled person.

25

The adsorption properties of activated carbon have been exploited in the past by the use of activated carbon as a heterogeneous catalyst and in adsorption refrigeration.

30 Activated carbon is often used to trap mercury emissions. When used to trap mercury emissions, activated carbon is often impregnated with iodine or sulphur.

Sigma-Aldrich[®] provides activated carbon in various different forms. One particular form of activated carbon currently sold by Sigma-Aldrich[®] is activated charcoal Norit[®], type Norit CA1 (Sigma-Aldrich[®] product number 97876). This form of activated carbon is said to be applicable to the removal of organic impurities from aqueous solutions in electroplating and in drug research.

All previously known forms of activated carbon are less dense than water, brine and sea water, such that they float on the surface of water or sea water or brine. A typical activated carbon, e.g. forms of activated carbon sold by Sigma-Aldrich[®] as activated charcoal Norit[®], type Norit CA1 (Sigma-Aldrich[®] product number 97876) has an approximate relative density, with respect to water, of 0.250-0.600 (units for this value could be given as g per ml if it was not ratioed to the density of a substance having a known density, i.e. water). In this specification the term relative density is used to mean relative density with respect to water. As such, known forms of activated carbon are less dense than water and float on the surface of water, sea water and brine.

Water pollution is an increasing problem. Environmental agencies are often required to dispose safely of effluent waste, and waste from industrial reaction processes. Furthermore, industrial accidents or the legacy of an industrial heritage can lead to the deposit of toxic and/or harmful wastes in waterways and seas. The sediment may harbour a reservoir of pollutants. Such wastes are harmful to animal and plant life. Previous attempts to "mop-up" water borne hazardous wastes include the introduction of bacteria to "eat-up" harmful waste products, as well as containment methods to skim waste products from the surface of water.

Organic pollutants are one particular form of pollutant which can have toxic effects. For example, polychlorinated biphenyls (PCBs) are a form of organic

pollutants which were, in the past, widely used for many applications. However, PCBs are toxic and persistent organic pollutants.

5 It would, therefore, be preferable to have a substance which can be used to mop-up, i.e. *inter alia* to some extent absorb and immobilise, organic pollutants and other harmful and/or toxic substances from water, for example waterways and seas.

10 The activated carbon composites of the present invention sink in water, sea water and brine. In other words, the activated carbon composites of the present invention are denser than generally pure water (which has a density of 1.0 g per ml at IUPAC's defined standard condition for temperature and pressure), sea water (which has a density of around 1.025 g per ml at IUPAC's defined standard condition for temperature and pressure, but can have
15 different densities which approximate to this value) and brine (brine is water generally saturated with sodium chloride, which has an approximate density of 1.23 g per ml at IUPAC's defined standard condition for temperature and pressure).

20 According to a first aspect of the present invention, there is provided an activated carbon composite comprising activated carbon and at least 53% by weight of inorganic components.

Preferably, wherein the activated carbon composite has from 62% by weight of
25 inorganic components, optionally 70 to 95% by weight of inorganic components.

Advantageously, wherein the activated carbon composite has from any one of 70, 71, 72, 73, 74, 75, 76, 77, 78 or 79 to any one of 80, 81, 82, 83, 84, 85, 86,
30 87, 88, 89, 90, 91, 92, 93, 94 or 95% by weight of inorganic components.

Preferably, wherein the activated carbon composite has 80%, 81%, 82%, 83%, 84%, 85%, preferably 82.43%, by weight of inorganic components.

Advantageously, wherein the activated carbon and the inorganic components
5 are formed in an intimate mixture.

Preferably, wherein the inorganic components comprise, or are, ash components.

10 Advantageously, wherein the ash components comprise calcined clay.

Preferably, wherein the ash components are calcined clay.

Advantageously, wherein the activated carbon composite is denser than water.

15 Preferably, wherein the activated carbon composite is denser than sea water and brine.

Advantageously, wherein the activated carbon composite has a relative
20 density, with respect to water, of at least 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3 or 2.4.

Preferably, wherein the activated carbon composite has a relative density, with
respect to water, of from 1.5 to any one of 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7
25 or 1.6.

Advantageously, wherein the activated carbon composite has a relative
density, with respect to water, of from 1.5 to 2.2.

30 Preferably, wherein the activated carbon composite has a relative density, with
respect to water, of from 1.8 to 2.

Advantageously, wherein the activated carbon composite is in combination with a bulk provider; optionally, wherein the bulk provider is one or more of sand, olivine (the mineral), silica, feldspar, fly ash, clinker, shale, chalk or
5 limestone.

According to a further aspect of the present invention, there is provided a method of preparing an activated carbon composite, wherein the activated carbon composite comprises activated carbon and at least 53% or 62% or
10 70% by weight of inorganic components, and/or has the constituents and/or properties of any one of claims 1 to 14, the method comprising the step of:
heating lignite in a reduced oxygen atmosphere.

Preferably, wherein the reduced oxygen atmosphere is 2% oxygen by mass or
15 less, optionally, 1%, 0.9%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2% or 0.1% or less, or nil% oxygen by mass.

Advantageously, further comprising the step of:
transporting the gases evolved during heating away from the heated
20 lignite, whilst maintaining the reduced oxygen atmosphere.

Preferably, wherein the step of heating lignite in the reduced oxygen atmosphere includes heating the lignite to at least 800°C.

25 Advantageously, wherein the step of heating lignite in a reduced oxygen atmosphere includes heating the lignite to at least 850, 900, 950, 1000, 1050, 1100, 1150 or 1200°C.

Preferably, wherein the reduced oxygen atmosphere comprises nitrogen
30 and/or argon.

Advantageously, wherein the method further comprises the step of, after heating lignite in a reduced oxygen atmosphere, and once much of the organic material has been driven off the lignite in the reduced oxygen atmosphere:

introducing a form of mild oxygenation.

5

Preferably, wherein the form of mild oxygenation is moisture, or an atmosphere containing more oxygen than the reduced oxygen atmosphere or the composition of the gas is the same but the temperature is increased..

10 Advantageously, wherein the method comprises the steps of:

a. introducing lignite into a furnace;
b. purging air from the furnace;
c. increasing the temperature in the furnace to 100°C and holding the temperature for a sufficient time to purge any remaining air from the furnace;
15 d. increasing the temperature in the furnace to 400°C and holding the temperature for a sufficient time to outgas any volatile compounds;

e. increasing the temperature in the furnace to 1000°C and holding the temperature for a sufficient time to provide activated carbon;

20 f. cooling the furnace and the reacted lignite under flowing nitrogen to ambient, or near-ambient, temperature.

In another aspect of the present invention, there is provided activated carbon composite obtainable by the process of any one of the previously mentioned methods.
25

In an additional aspect of the present invention, there is provided the use of activated carbon composite as set out above in the adsorption of pollutants.
30

Preferably, wherein the pollutants are PCBs.

Advantageously, wherein the pollutants are adsorbed from oceans, seas, rivers, lakes, streams, ponds, puddles, filtration beds, and any other natural or man-made body of water.

5

Embodiments of the invention are described below with reference to the accompanying drawings, in which:

Figure 1 is a schematic representation of an apparatus used in a process for preparing activated carbon composites of the present invention.

10

Figure 2 is a picture of the activated carbon composite of the present invention being introduced into synthetic "sea" water containing 3.5% by weight sodium chloride (time since introduction is 0 seconds).

15

Figure 3 is a picture of the activated carbon composite which was introduced into the synthetic "sea" water at a later time than Figure 1, namely, 20 seconds after Figure 1.

Figure 4 is a picture at a still later time than Figure 2, namely, 40 seconds after Figure 2.

20

Figure 5 is a schematic representation of the introduction of the activated carbon composites of the present invention into water.

25

Manufacturing protocol for activated carbon composites

Previous methods of forming activated carbon, as discussed above, have involved the pyrolysis of organic (carbon containing) materials, e.g. wood, coconut husk or polymers. In these earlier methods, it has been a common aim to reduce the amount of inorganic matter in the activated carbon product

30

so as to maximise the surface area of activated carbon for its various uses. In other words, any inorganic material in activated carbon has generally been seen as an impurity.

- 5 The starting material in the production of activated carbon according to the present invention can, in one preferred embodiment, be lignite. The use of lignite as the starting material provides less carbon, more inorganic material, to the ultimately produced activated carbon composites, in comparison to other starting materials commonly used in activated carbon production. Lignite is a
- 10 material which can be obtained from the ground at various sites around the world. Lignite is sometimes referred to as brown coal and is used in power stations for power production, for example in Germany. Compositionally, lignites can vary from location to location. Lignites taken from the ground generally contain from 5-80% by weight organic (carbon based) materials,
- 15 although most common lignites generally contain 25-35% by weight of organic (carbon based) materials, up to around 66% by weight of water and 6 to 19% ash (i.e. inorganic) components. In other words, once the moisture is removed, lignites contain a mixture of inorganic components (e.g. clay like substances) and organic components. Clay is an aluminium silicate which
- 20 contains oxyhydroxide functionality.

The activated carbon of the present invention is formed, in a general sense, by first heating lignite in a reduced oxygen atmosphere. Water (meaning dampness) is removed either before heating (which might have engineering

25 benefits) or during the early part of firing. The reduced oxygen atmosphere is preferably 2% oxygen by mass or less, optionally, 1%, 0.9%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2% or 0.1% or less, or nil% oxygen by mass. The volatile organic compounds are driven from the lignite, e.g. tars, leaving a char (which is similar to charcoal, although it has a higher inorganic component

30 than charcoal). A reduced oxygen atmosphere is used at this stage to prevent complete oxidation of the organic matter in the lignite. The elevated

temperature causes structural transformation and dehydroxylation of the clay component of the lignite, forming calcined clay. In other words, water which had been a structural part of the clay (as hydroxyl groups) is lost during a reaction at this stage. Calcined clay is clay which has been heated and
5 undergone a structural change.

Once much of the organic material has been driven off the lignite in the reduced oxygen atmosphere, moisture is introduced, or some other form of mild oxygenation. This oxygenating atmosphere reacts with the remaining
10 carbonaceous compounds to provide an activated carbon composite which includes activated carbon intimately associated with the inorganic materials, i.e. the calcined clay. The resulting product, the activated carbon composite, is an intimate mixture of ash (i.e. calcined clay and other inorganic components) and activated carbon.

15 A composite is a material which comprises two or more constituent materials with different physical and/or chemical properties. The activated carbon composite of the present invention is termed a composite because it is an intimate mixture of ash (i.e. calcined clay and other inorganic components) and
20 activated carbon. When the activated carbon composite of the present invention is introduced into water, the intimate mixture of activated carbon and ash substantially does not separate, i.e. it remains intimately mixed.

Typical known activated carbons have 5-10% inorganic, i.e. including ash,
25 components, the reminder being activated carbon.

Activated carbon composites of the present invention have from 53%, optionally from 62%, preferably from 70 to 95% by weight ash (i.e. calcined clay and other inorganic) components, the remaining portion being activated
30 carbon. Assuming the density of activated carbon components in the activated carbon composites is approximately $\rho_c = 0.6$ g per ml and assuming the

density of the ash (i.e. calcined clay and other inorganic) is approximately $\rho_{\text{ash}} = 2.4$ per ml, neutral buoyancy is expected at 53% ash (i.e. calcined clay and other inorganic) in water. Assuming the density of activated carbon components in the activated carbon composites is approximately $\rho_c = 0.6$ g per ml and assuming the density of the ash (i.e. calcined clay and other inorganic) is approximately $\rho_{\text{ash}} = 2$ g per ml, neutral buoyancy is expected at 62% ash (i.e. calcined clay and other inorganic) in seawater.

In preferred embodiments, activated carbon composites of the present invention have from any one of 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78 or 79 to any one of 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94 or 95% by weight ash (i.e. calcined clay and other inorganic components), and the remaining portion being activated carbon, and any impurities. In one preferred example, an activated carbon composite of the present invention has 80% by weight ash (i.e. calcined clay and other inorganic components) and 20% activated carbon. In another preferred example, an activated carbon composite of the present invention has 82.43% by weight ash (i.e. calcined clay and other inorganic components) and 17.57% activated carbon.

20

An activated carbon composite according to the present invention can be produced according to the following method, in one non-limiting embodiment.

A system 1 is set up as shown diagrammatically in Figure 1. The system 1 has a tube furnace 11 which is thoroughly purged with nitrogen to remove air before beginning heating. The system also has a heating means 8 which acts to heat the tube furnace 11 to a desired temperature. The heating means 8 can be an oven, a flame, a microwave producing arrangement or any other means which can provide heat to the tube furnace 11 and/or its contents.

30

A thin layer of milled lignite is spread evenly in the bottom of one or both of the 10 cm alumina boats 2,3 (2 grams per boat). It will be appreciated that in other embodiments other numbers of boats may be used, for example, 1, 3, 4, 5 or any other number. It will also be appreciated that the boats 2,3 used may
5 be composed of a different generally inert substance, for example another metal or a ceramic suitable for the temperatures required. In other embodiments, no boats are used, e.g. where heat is applied to the milled lignite in a rotary furnace, a fluid bed arrangement or a moving hearth kiln. Boats are used in this embodiment as containers, to stop the material getting
10 lost.

Baffles 4,5,6,7 are present on either side of the boats 2,3 to encourage transport of volatiles away from the reactant in the boats 2,3. Baffles 4 and 7 (the baffles towards the ends of the tube furnace, adjacent the gas tight seals
15 9, 10) are employed to protect the gas tight seals 9,10 from the high temperature present in the generally central zone of the tube furnace 11. Baffles 5 and 6 (the baffles adjacent to the boats 2,3) are present to regulate gas flow, to encourage transport of volatiles away from the lignite, and to prevent redeposition of organics on the product.

20 Nitrogen is used as a transport gas in one embodiment. In other embodiments, any generally inert gas may be used, for example argon. The nitrogen used as a transport gas is passed through water (not shown) at ambient temperature before entering the tube furnace 11 through an opening
25 in gas tight seal 9, using fibrous filter media (not shown) to ensure sufficient gas-liquid contact. A water trap is used to exclude air on exit from the furnace. A slight positive pressure is maintained at all times during the reaction and the positive pressure forces gaseous products out of the tube furnace 11 through
30 an opening in the gas tight seal 10 at the right hand side of the tube furnace 11 shown in Figure 1. In this embodiment, the damp transport gas acts first to transport away volatile compounds and second as a mild oxidant of the

organic components. In alternative embodiments, other methods of introducing a mild oxidant are employed, including, but not limited to, steam injection or introducing minor amounts of air.

- 5 Gas tight seals 9,10 are provided at the ends of the reaction vessel. In one embodiment input can be regulated by pressure regulators and a needle valve and/or output can be controlled by use of a water trap.

The gas flow used in the non-limiting example was around 500 ml per minute,
10 uninterrupted during the entire reaction cycle and during cooling. Wet transport gas, i.e. gas passed through a water trap, is used throughout in order to avoid the possibility of exposing the materials to oxygen while at high temperature by opening the system.

- 15 The reaction cycle in this non-limiting example was as follows:

1. Introduce lignite into the alumina boats 2,3 and place the lignite containing alumina boats 2,3 into the tube furnace 11.
2. Purge air from the tube furnace 11.
- 20 3. Raise the temperature inside the tube furnace 11 to 100°C at a slow rate (around 2°C per minute). (A relatively slow rate in the raise of temperature was used in this embodiment to permit control of the furnace at low temperatures; a faster increase in temperature could result in overshoot of the desired temperature)
- 25 4. Hold the temperature for 30 minutes to ensure the air is removed from the lignite.
5. Raise the temperature to 400°C at a rate of 10°C per minute.
6. Hold the temperature at 400°C for 60 minutes (outgassing most, if not all, volatile compounds).
- 30 7. Raise the temperature to 1000°C at a rate of 10°C per minute.
8. Hold the temperature for 60 minutes.

9. Cool to ambient, or near-ambient, temperature under flowing nitrogen.
10. Remove the activated carbon composite from the system 1.

Following the above protocol provides activated carbon composites according to the present invention. In one embodiment, the activated carbon composite prepared using the above protocol provided an intimate mixture of 82.43% ash (i.e. calcined clay) and 17.57% activated carbon. The lignite used as the starting material in that particular case was sourced from the Bovey Basin in South Devon.

In other embodiments, different heating rates and gas flow rates are employed.

To provide an activated carbon composite product, which is denser than known activated carbons, according to the present invention, the lignite used as the starting material has a relatively high ash (i.e. inorganic) content, when compared to starting materials used generally to prepare activated carbons. One example of a suitable lignite to be used as the starting material in the method discussed above with respect to Figure 1 is sourced from the Bovey Basin in South Devon, although it will be appreciated that the activated carbon composites of the present invention can be prepared from other lignites or carbonaceous clays, provided the starting material provides a suitable ratio of ash (inorganic components) to organic precursors for formation of activated carbon composites of the present invention.

In the prior art, the preparation of activated carbon concentrated on the solidity or permeability, rather than density relative to water (i.e. the ability to sink) which in this case is imparted by the ash content (inorganic components) of the activated carbon composite.

All previous knowledge in this area focused on purer activated carbon. Following the protocol mentioned above, the activated carbon is a composite because the carbon is intimately associated with calcined clay (from the lignite), which makes the density of the composite of activated carbon and
5 calcined clay higher than water, brine and sea water. As shown in Figures 2-4, the activated carbon composite according to the present invention sinks when added to sea water. Previous activated carbons do not sink (they float) due to their lower density relative to water.

10 Figure 2 shows an activated carbon composite according to the present invention as it is just added to sea water (i.e. at 0 seconds from introduction). Figure 3 shows an activated carbon composite according to the present invention 20 seconds after the introduction shown by Figure 2 (i.e. at 20 seconds from introduction). Figure 4 shows an activated carbon composite
15 according to the present invention 40 seconds after the Figure 3 (i.e. at 60 seconds from introduction).

The activated carbon composite shown to sink in Figures 2-4 was produced according to the method described above (i.e. the activated carbon composite
20 shown to sink in Figures 2-4 is an intimate mixture of 82.43% by weight ash (i.e. calcined clay) and 17.57% activated carbon). In this example, the lignite used as the starting material to prepare the activated carbon composite shown in Figures 2-4 was sourced from Sibelco UK Ltd.'s ballclay deposits in the Bovey Basin. The activated carbon composite shown in Figures 2-4, which is
25 a non-limiting example, has a relative density, with respect to water, of between 1.8 and 2. A range is given for relative density of the activated carbon composite shown in Figures 2-4 to take into account experimental errors. As such, the activated carbon shown in Figures 2-4 sinks in water, sea water and brine.

As is known in the art, dimensions of density are mass / volume. For relative density, one divides one density by another, so the result is a pure number. The word "density" in the present context is often referred to as "specific gravity" in the art. The activated carbons of the present invention are said to
5 have a relative density "with respect to water". A relative density, with respect to water, of between 1.8 and 2 could equally be said to be a density of between 1.8 and 2.0 g per ml.

The density of the activated carbon composites of the present invention was
10 determined using a pycnometer.

The protocol for calculating the relative density of the activated carbon composite shown in Figures 2-4 is as follows (IUPAC's defined standard condition for temperature and pressure are used):

15

Apparatus used:

- Pycnometer
- Balance Sensitive to 0.01 g
- 20 • Portable Vacuum pump(s) capable of maintaining 63.5 cm Hg
- Vacuum desiccator
- Magnetic stirrer and follower
- Stoppered flask with side outlet

25 Preparation of de-aired water:

1. Fill the stoppered flask with the required quantity of distilled water.
2. Place flask on magnetic stirrer to agitate water.
3. Connect to the vacuum pump and switch on.
- 30 4. Disconnect vacuum pump once the bubbling has stopped indicating that there is no more air to be removed.

Procedure (measurement of particle density):

1. Calibrate pycnometer with de-aired distilled water and then dry the
5 pycnometer.
2. Weigh to 2 decimal places 4 g of an oven-dried sample of the activated carbon composite and place in the pycnometer ensuring none of the sample is lost.
3. Fill the pycnometer with distilled water so it is approximately 1/3 to 1/2 full
10 and agitate the mixture to make sure the entire sample is wet. Rinse any portion of the sample adhering to the pycnometer into the slurry.
4. Leave in the dessicator until the bubbling has stopped indicating that there is no more air to be removed.
5. Completely fill the pycnometer with de-aired distilled water ensuring no air is
15 trapped and record the weight.
6. Calculate the particle density (ρ_p) as follows:

$$\rho_p = \frac{W_o}{[W_o + (W_a - W_b)]}$$

- 20 Where: W_o = weight of sample
 W_a = weight of pycnometer filled with water
 W_b = weight of pycnometer filled with sample and water.

The above method of pycnometry exploits the fact that the density of water is
 25 1.0 g per ml at IUPAC's defined standard condition for temperature and pressure. The calculation resolves to a division of the weight of the sample by the weight of water corresponding to the volume of the sample.

Figure 5 shows a schematic representation of the introduction of the activated
 30 carbon composite of the present invention into water, as shown more

specifically in Figures 2-4. In Figure 5, IUPAC's defined standard condition for temperature and pressure are used. The density measurements can be taken at different temperatures and/or pressures.

- 5 In Figure 5, a system 40 for a general test of the density of a sample relative to water, or other liquid, is shown. Water 42 or other liquid, for example sea water or brine, is placed in the liquid receptacle, the water receptacle having a base 44. The water 42 or other liquid in the liquid receptacle forms a surface 43 and a meniscus (not shown) where the surface meets with the edges of the
- 10 water receptacle. Activated carbon composite 41 is introduced onto the surface 43 of the water 42. If the activated carbon composite 41 generally sinks to the base 44, the activated carbon composite 41 is denser than water 42, or other liquid present in the liquid receptacle. If the activated carbon composite 41 generally floats on the surface 43, the activated carbon
- 15 composite 41 is less dense than water 42, or other liquid present in the liquid receptacle.

Activated carbon composites of the present invention typically have a relative density, with respect to water, of from 1.5 to 2.2, i.e. greater than the relative

20 density of brine. Preferably, activated carbon composites of the present invention have a relative density, with respect to water, of from 1.8 to 2.

Activated carbon composites of the present invention have a relative density, with respect to water, of from 1.5 to any one of 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2,

25 2.3 or 2.4. Activated carbon composites of the present invention have a relative density, with respect to water, of from any one of 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3 or 2.4.

In other embodiments, the activated carbon composites of the present

30 invention may be mixed with a bulk provider. Examples of bulk providers include, but are not limited to: sand, olivine (the mineral), silica, feldspar, fly

ash, clinker, shale, chalk, limestone or clay. In these embodiments the activated carbon composites of the present invention may be held together with the bulk provider by a binder. Non-limiting examples of binders include clays, including illites, bentonites and kaolins.

5

The activated carbon composites of the present invention have a higher relative density than known activated carbons. Thus, the present invention provides a material which can be used to mop-up contaminants in polluted water, for example in sea water (at the sea bed, or other levels in the sea, not just the surface). Tests have been conducted which show that the activated carbon composites of the present invention are able to adsorb polychlorinated biphenyl compounds (PCBs).

10

Tables 1 and 2 show partition coefficients calculated for two different samples. The partition coefficients indicate the PCB adsorption potential of each sample.

15

Table 1 shows the partition coefficient calculations for 'Blueguard 3000 C'. 'Blueguard 3000 C' is a combination of olivine (the mineral) with activated carbon prepared from vegetable matter. The activated carbon and olivine in 'Blueguard 3000 C' are not intimately attached because this is a loose mixture. They are held together by a binder. As such, when placed in water, much of the activated carbon floats to the surface of the water and, in the sea for example, can be carried away in a random fashion.

20

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Table 2 shows the partition coefficient calculations for an activated carbon composite according to the present invention, namely, the activated carbon composite described above as formed with reference to the non-limiting exemplary process of manufacture (which is an intimate mixture of 82.43% ash (i.e. mainly calcined clay) and 17.57% activated carbon), and as described

30

with reference to Figures 2-4. The activated carbon composite of Table 2 is denser than water and sinks in water, sea water and brine.

In Tables 1 and 2, the values detailed are as follows:

5

$$K_d = \frac{A_i}{C_i} \text{ (ml/gramme)} = \frac{V_w (C_o - C_i)}{M_{sed} * C_i}$$

$$A_i = \frac{A_i}{C_i} \text{ (gramme/gramme)} = \frac{V_w (C_o - C_i)}{M_{sed}}$$

$K_d =$	Distribution Coefficient or Partition Coefficient (ml/Gramme)
$A_i =$	Concentration of contaminant on the solid at equilibrium (gramme/gramme)
$C_i =$	Total dissolved contaminant concentration remaining in solution at equilibrium (microgramme/ml)
$V_w =$	Volume of Solution (ml)
$C_o =$	Initial concentration of Contaminant (gramme/ml)
$M_{sed} =$	Weight of adsorbant / material (gramme)

The PCBs referred to by number in Tables 1 and 2 are as follows:

- PCB #28 C₁₂H₇Cl₃ 2, 4, 4' – Trichlorobiphenyl
- 10 PCB #52 C₁₂H₆Cl₄ 2,2',5,5' – Tetrachlorobiphenyl
- PCB #101 C₁₂H₅Cl₅ 2,2',4,5,5' – Pentachlorobiphenyl
- PCB #118 C₁₂H₅Cl₅ 2,3',4,4',5 – Pentachlorobiphenyl
- PCB #138 C₁₂H₄Cl₆ 2,2',3,4,4',5' – Hexachlorobiphenyl
- PCB #153 C₁₂H₄Cl₆ 2,2',4,4',5,5' – Hexachlorobiphenyl
- 15 PCB #180 C₁₂H₃Cl₇ 2,2',3,4,4',5,5' - Heptachlorobiphenyl

The adsorption of PCBs for the samples shown in Tables 1 and 2 was found to be above 99.9%.

- 20 As such, the activated carbon composites of the present invention are beneficial.

When used in this specification and claims, the terms "comprises" and "comprising" and variations thereof mean that the specified features, steps or integers are included. The terms are not to be interpreted to exclude the
5 presence of other features, steps or components.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for
10 attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

CLAIMS

1. An activated carbon composite comprising activated carbon and at least
5 53% by weight of inorganic components.
2. An activated carbon composite according to claim 1 wherein the
activated carbon composite has from 62% by weight of inorganic components,
optionally 70 to 95% by weight of inorganic components.
10
3. An activated carbon composite according to any one of claims 1 or 2,
wherein the activated carbon composite has from any one of 70, 71, 72, 73,
74, 75, 76, 77, 78 or 79 to any one of 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90,
91, 92, 93, 94 or 95% by weight of inorganic components.
15
4. An activated carbon composite according to any one of claims 1, 2 or 3,
wherein the activated carbon composite has 80%, 81%, 82%, 83%, 84%, 85%,
preferably 82.43%, by weight of inorganic components.
- 20 5. An activated carbon composite according to any one of claims 1 to 4,
wherein the activated carbon and the inorganic components are formed in an
intimate mixture.
6. An activated carbon composite according to any one of claims 1 to 5,
25 wherein the inorganic components comprise, or are, ash components.
7. An activated carbon composite according to claim 6, wherein the ash
components comprise calcined clay.
- 30 8. An activated carbon composite according to claim 7, wherein the ash
components are calcined clay.

9. An activated carbon composite according to any one of the previous claims, wherein the activated carbon composite is denser than water.
- 5 10. The activated carbon composite of claim 9, wherein the activated carbon composite is denser than sea water and brine.
11. The activated carbon composite of any one of the previous claims wherein the activated carbon composite has a relative density, with respect to
10 water, of at least 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3 or 2.4.
12. The activated carbon composite of any one of the previous claims, wherein the activated carbon composite has a relative density, with respect to water, of from 1.5 to any one of 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7 or 1.6.
- 15 13. The activated carbon composite of any one of the previous claims, wherein the activated carbon composite has a relative density, with respect to water, of from 1.5 to 2.2.
- 20 14. The activated carbon composite of any one of the previous claims, wherein the activated carbon composite has a relative density, with respect to water, of from 1.8 to 2.
- 25 15. The activated carbon composite of any one of the previous claims in combination with a bulk provider; optionally, wherein the bulk provider is one or more of sand, olivine (the mineral), silica, feldspar, fly ash, clinker, shale, chalk or limestone.
- 30 16. A method of preparing an activated carbon composite, wherein the activated carbon composite comprises activated carbon and at least 53% or 62% or 70% by weight of inorganic components, and/or has the constituents

and/or properties of any one of claims 1 to 14, the method comprising the step of:

heating lignite in a reduced oxygen atmosphere.

- 5 17. The method of claim 16, wherein the reduced oxygen atmosphere is 2% oxygen by mass or less, optionally, 1%, 0.9%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2% or 0.1% or less, or nil% oxygen by mass.
- 10 18. The method of claim 16 or claim 17, further comprising the step of:
transporting the gases evolved during heating away from the heated lignite, whilst maintaining the reduced oxygen atmosphere.
- 15 19. The method of any one of claims 16 to 18, wherein the step of heating lignite in the reduced oxygen atmosphere includes heating the lignite to at least 800°C.
- 20 20. The method of claim 19, wherein the step of heating lignite in a reduced oxygen atmosphere includes heating the lignite to at least 850, 900, 950, 1000, 1050, 1100, 1150 or 1200°C.
21. The method of any one of claims 16 or 17, wherein the reduced oxygen atmosphere comprises nitrogen and/or argon.
- 25 22. The method of any one of claims 16 to 21, wherein the method further comprises the step of, after heating lignite in a reduced oxygen atmosphere, and once much of the organic material has been driven off the lignite in the reduced oxygen atmosphere:
introducing a form of mild oxygenation.
- 30 23. The method of claim 22, wherein the form of mild oxygenation is moisture, or an atmosphere containing more oxygen than the reduced oxygen

atmosphere or the composition of the gas is the same but the temperature is increased..

24. The method of any one of claims 16 to 23, wherein the method
5 comprises the steps of:
- a. introducing lignite into a furnace;
 - b. purging air from the furnace;
 - c. increasing the temperature in the furnace to 100°C and holding
10 the temperature for a sufficient time to purge any remaining air from the
furnace;
 - d. increasing the temperature in the furnace to 400°C and holding
the temperature for a sufficient time to outgas any volatile compounds;
 - e. increasing the temperature in the furnace to 1000°C and holding
the temperature for a sufficient time to provide activated carbon;
 - 15 f. cooling the furnace and the reacted lignite under flowing nitrogen
to ambient, or near-ambient, temperature.
25. Activated carbon composite obtainable by the process of any one of
claims 16 to 24.
- 20 26. Use of activated carbon composite according to any one of claims 1 to
15 or 25 in the adsorption of pollutants.
27. The use of claim 26, wherein the pollutants are PCBs.
- 25 28. The use of any one of claims 26 or 27, wherein the pollutants are
adsorbed from oceans, seas, rivers, lakes, streams, ponds, puddles,
filtration beds, and any other natural or man-made body of water.
- 30 29. Activated carbon composite as substantially described herein with
reference to the Figures.

30. Any novel feature or combination of features described herein.

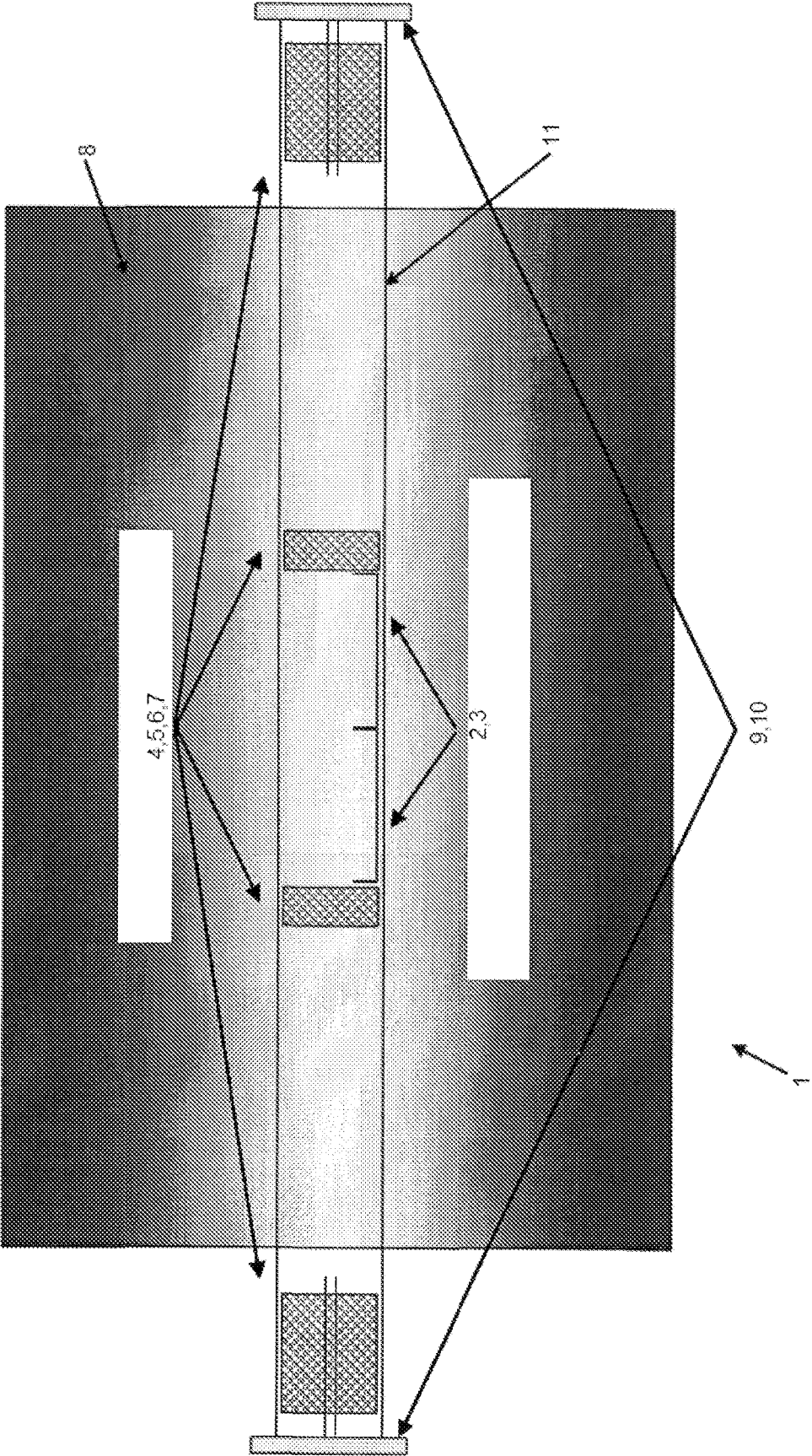


Figure 1

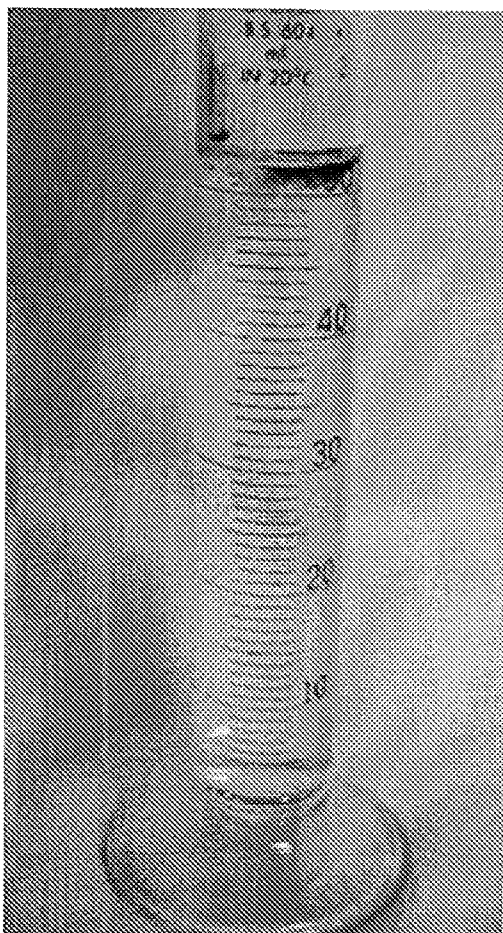


Figure 2

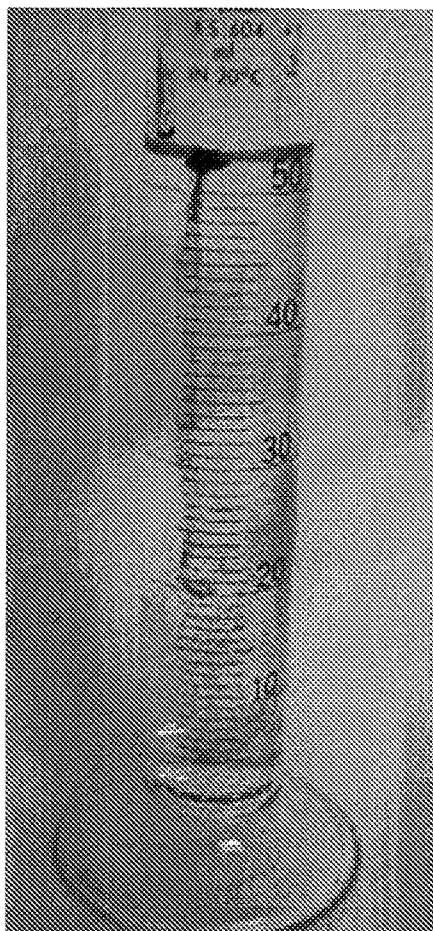


Figure 3

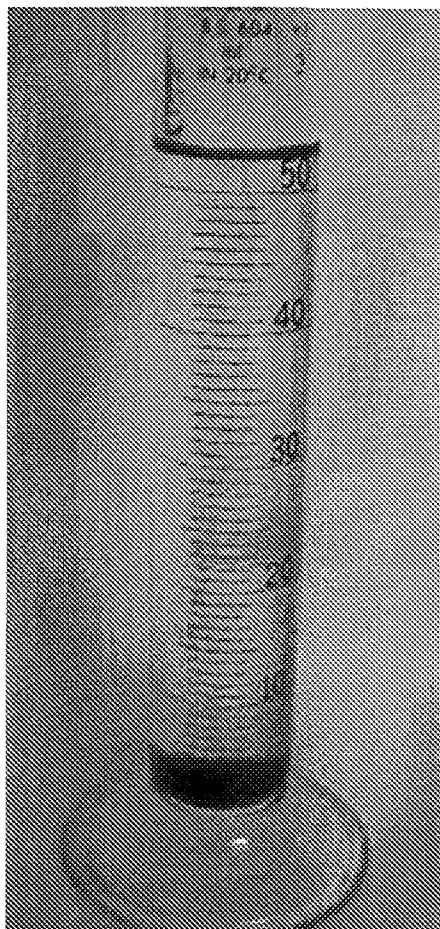


Figure 4

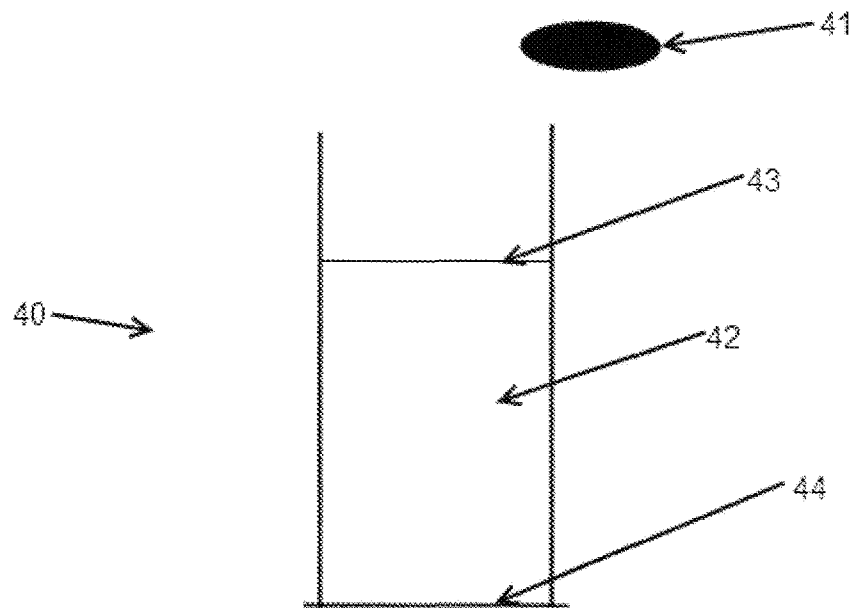


Figure 5

Table 1

	[g/ml] C_o	[μ g/l] C_o	[g] M_{sed}	[ml] V_w	[g/ml] C_i	[μ g/l] C_i	[g/g] A_i	[ml/g] K_d	% Adsorption
BLUEGUARD 3000 C									
PCB # 28	8.50E-05	85.00	100.02	971.63	1.30E-08	0.013	8.26E-04	63,507	99.985
PCB # 52	8.50E-05	85.00	100.02	971.63	2.30E-08	0.023	8.25E-04	35,891	99.973
PCB # 101	8.50E-05	85.00	100.02	971.63	2.20E-08	0.022	8.26E-04	37,523	99.974
PCB # 118	8.50E-05	85.00	100.02	971.63	6.00E-09	0.006	8.26E-04	137,610	99.993
PCB # 138	8.50E-05	85.00	100.02	971.63	1.10E-08	0.011	8.26E-04	75,056	99.987
PCB # 153	8.50E-05	85.00	100.02	971.63	1.00E-08	0.010	8.26E-04	82,562	99.988
PCB # 180	8.50E-05	85.00	100.02	971.63	9.00E-09	0.009	8.26E-04	91,737	99.989
PCB [7]	5.95E-04	595.00	100.02	971.63	9.40E-08	0.094	5.78E-03	61,480	99.984

Table 2

	[g/ml] C_o	[μ g/l] C_o	[g] M_{sed}	[ml] V_w	[g/ml] C_i	[μ g/l] C_i	[g/g] A_i	[ml/g] K_d	% Adsorption
LIGNITE A									
PCB # 28	8.50E-05	85.00	99.03	984.76	3.40E-08	0.034	8.45E-04	24,850	99.960
PCB # 52	8.50E-05	85.00	99.03	984.76	6.30E-08	0.063	8.45E-04	13,407	99.926
PCB # 101	8.50E-05	85.00	99.03	984.76	5.10E-08	0.051	8.45E-04	16,563	99.940
PCB # 118	8.50E-05	85.00	99.03	984.76	1.20E-08	0.012	8.45E-04	70,427	99.986
PCB # 138	8.50E-05	85.00	99.03	984.76	2.10E-08	0.021	8.45E-04	40,240	99.975
PCB # 153	8.50E-05	85.00	99.03	984.76	2.10E-08	0.021	8.45E-04	40,240	99.975
PCB # 180	8.50E-05	85.00	99.03	984.76	1.40E-08	0.014	8.45E-04	60,365	99.984
PCB [7]	5.95E-04	595.00	99.03	984.76	2.16E-07	0.216	5.91E-03	27,382	99.964

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/050959

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 475 461 B1 (OHSAKI TAKUSHI [JP] ET AL) 5 November 2002 (2002-11-05) example 37; table 12	1-15,27, 29,30
X	----- US 4 149 995 A (MURTY HARI N) 17 April 1979 (1979-04-17) example 1 column 1, line 17 - line 25	16-28
X	----- GB 298 546 A (OSKAR SCHOBER) 9 October 1928 (1928-10-09) page 1, left-hand column, line 8 - line 21 page 3, left-hand column, line 3 - right-hand column, line 115 ----- -/-	16,18-24



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

7 September 2012

Date of mailing of the international search report

13/09/2012

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/050959

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MAXIM L. SHCHIPKO ET AL: "Catalytic pyrolysis of Kansk-Achinsk lignite for production of porous carbon materials", FUEL, vol. 74, no. 5, 1 May 1995 (1995-05-01), pages 751-755, XP55033427, ISSN: 0016-2361, DOI: 10.1016/0016-2361(94)00001-8 the whole document -----	16-28
A	SHCHIPKO M L ET AL: "Influence of the origin of chars, produced from lignite by different methods, on features of their activation process", FUEL, IPC SCIENCE AND TECHNOLOGY PRESS, GUILDFORD, GB, vol. 77, no. 6, 1 May 1998 (1998-05-01), pages 527-532, XP004285844, ISSN: 0016-2361, DOI: 10.1016/S0016-2361(97)00251-2 the whole document -----	16-28
A	E. V. VEPRIKOVA ET AL: "Removal of humic substances from water by brown coal sorbents", SOLID FUEL CHEMISTRY, vol. 41, no. 6, 1 December 2007 (2007-12-01), pages 359-363, XP55033499, ISSN: 0361-5219, DOI: 10.3103/S0361521907060079 the whole document -----	16-28
A	US 3 876 505 A (STONEBURNER GEORGE ROBERT) 8 April 1975 (1975-04-08) the whole document -----	16-28
A	US 2005/035062 A1 (HILTZIK LAURENCE H [US] ET AL) 17 February 2005 (2005-02-17) the whole document -----	26-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2012/050959

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6475461	B1	05-11-2002	CA 2191211 A1 03-10-1996
			CN 1154686 A 16-07-1997
			EP 0763509 A1 19-03-1997
			US 6475461 B1 05-11-2002
			WO 9630318 A1 03-10-1996
US 4149995	A	17-04-1979	AU 523490 B2 29-07-1982
			AU 4217078 A 12-06-1980
			BR 7808604 A 28-08-1979
			CA 1116156 A1 12-01-1982
			DD 141154 A5 16-04-1980
			DE 2862253 D1 16-06-1983
			EP 0002674 A1 11-07-1979
			GB 2011359 A 11-07-1979
			IN 150803 A1 18-12-1982
			JP 54094494 A 26-07-1979
			MX 151087 A 28-09-1984
			PH 13744 A 17-09-1980
			PL 212208 A1 05-11-1979
			US 4149995 A 17-04-1979
GB 298546	A	09-10-1928	NONE
US 3876505	A	08-04-1975	AU 475455 B2 26-08-1976
			AU 6314573 A 05-06-1975
			BE 808355 A1 07-06-1974
			CA 1017316 A1 13-09-1977
			DD 108507 A5 20-09-1974
			DE 2361097 A1 12-06-1974
			FR 2209716 A1 05-07-1974
			GB 1415017 A 26-11-1975
			IL 43737 A 31-08-1976
			IT 997921 B 30-12-1975
			JP 49088799 A 24-08-1974
			NL 7316164 A 11-06-1974
			US 3876505 A 08-04-1975
			ZA 7309325 A 30-07-1975
US 2005035062	A1	17-02-2005	NONE