



(86) Date de dépôt PCT/PCT Filing Date: 2006/12/08
(87) Date publication PCT/PCT Publication Date: 2007/06/14
(45) Date de délivrance/Issue Date: 2013/09/24
(85) Entrée phase nationale/National Entry: 2008/06/09
(86) N° demande PCT/PCT Application No.: GB 2006/004591
(87) N° publication PCT/PCT Publication No.: 2007/066125
(30) Priorité/Priority: 2005/12/10 (GB0525193.9)

(51) Cl.Int./Int.Cl. *B09C 1/06* (2006.01),
F23G 7/14 (2006.01)

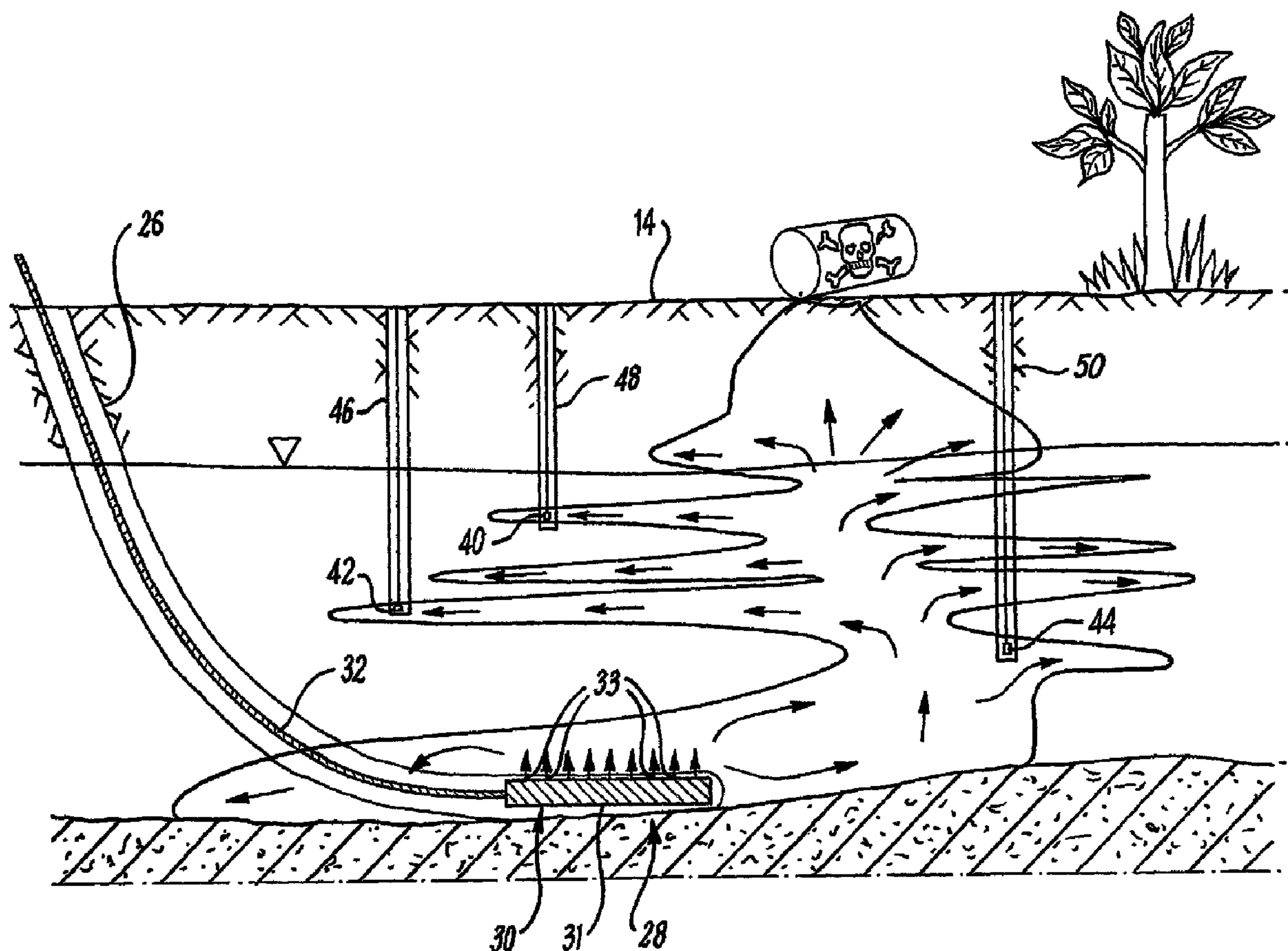
(72) Inventeurs/Inventors:
GERHARD, JASON, GB;
TORERO, JOSE, GB;
PIRONI, PAOLO, GB;
SWIZTER, CHRISTINE, GB;
REIN, GUILLERMO, GB

(73) Propriétaire/Owner:
THE UNIVERSITY COURT OF THE UNIVERSITY OF
EDINBURGH, GB

(74) Agent: EMERY JAMIESON LLP

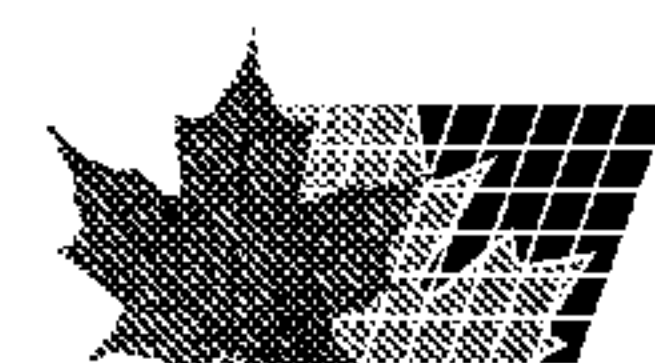
(54) Titre : PROCEDE ET APPAREIL POUR DECONTAMINER LE SOL

(54) Title: METHOD AND APPARATUS FOR REMEDIATING CONTAMINATED LAND



(57) Abrégé/Abstract:

The invention relates to a method and apparatus for remediating land (10) that is contaminated by a combustible material (12), in particular, land contaminated with non- aqueous phase liquids (NAPLs). In an embodiment of the invention, a method for



(57) **Abrégé(suite)/Abstract(continued):**

remediating land that is contaminated by a combustible material is disclosed which includes the steps of locating a subterranean volume (16) of combustible material such as a DNAPL (12) in land (10) to be remediated, and igniting the combustible material (12) to combust the material and thereby remediate the land (10). By monitoring combustion of the material, combustion may be optimised by, for example, supplying an oxidant or a combustion suppressant.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 June 2007 (14.06.2007)

PCT

(10) International Publication Number
WO 2007/066125 A3

(51) International Patent Classification:
B09C 1/06 (2006.01) **F23G 7/14** (2006.01)

(21) International Application Number:
PCT/GB2006/004591

(22) International Filing Date:
8 December 2006 (08.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0525193.9 10 December 2005 (10.12.2005) GB

(71) Applicant (for all designated States except US): **THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURGH** [GB/GB]; 1-7 Roxburgh Street, Edinburgh EH8 9TA (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **GERHARD, Jason** [CA/GB]; 45 Merchiston Crescent, Edinburgh EH10 5AH (GB). **TORERO, Jose** [PE/GB]; 71 South Clerk Street (2F2), Edinburgh EH8 9PP (GB). **PIRONI, Paolo** [IT/GB]; 1/6 East Parkside, Edinburgh EH16 5XJ (GB). **SWIZTER, Christine** [US/GB]; 35 (3F3) Mentone Terrace, Edinburgh EH9 2DF (GB). **REIN, Guillermo** [ES/GB]; 27/2 Oxford Street, Edinburgh EH8 9PQ (GB).

(74) Agent: **KENNEDYS PATENT AGENCY LIMITED**; 185 St Vincent Street, Glasgow G2 5QD (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

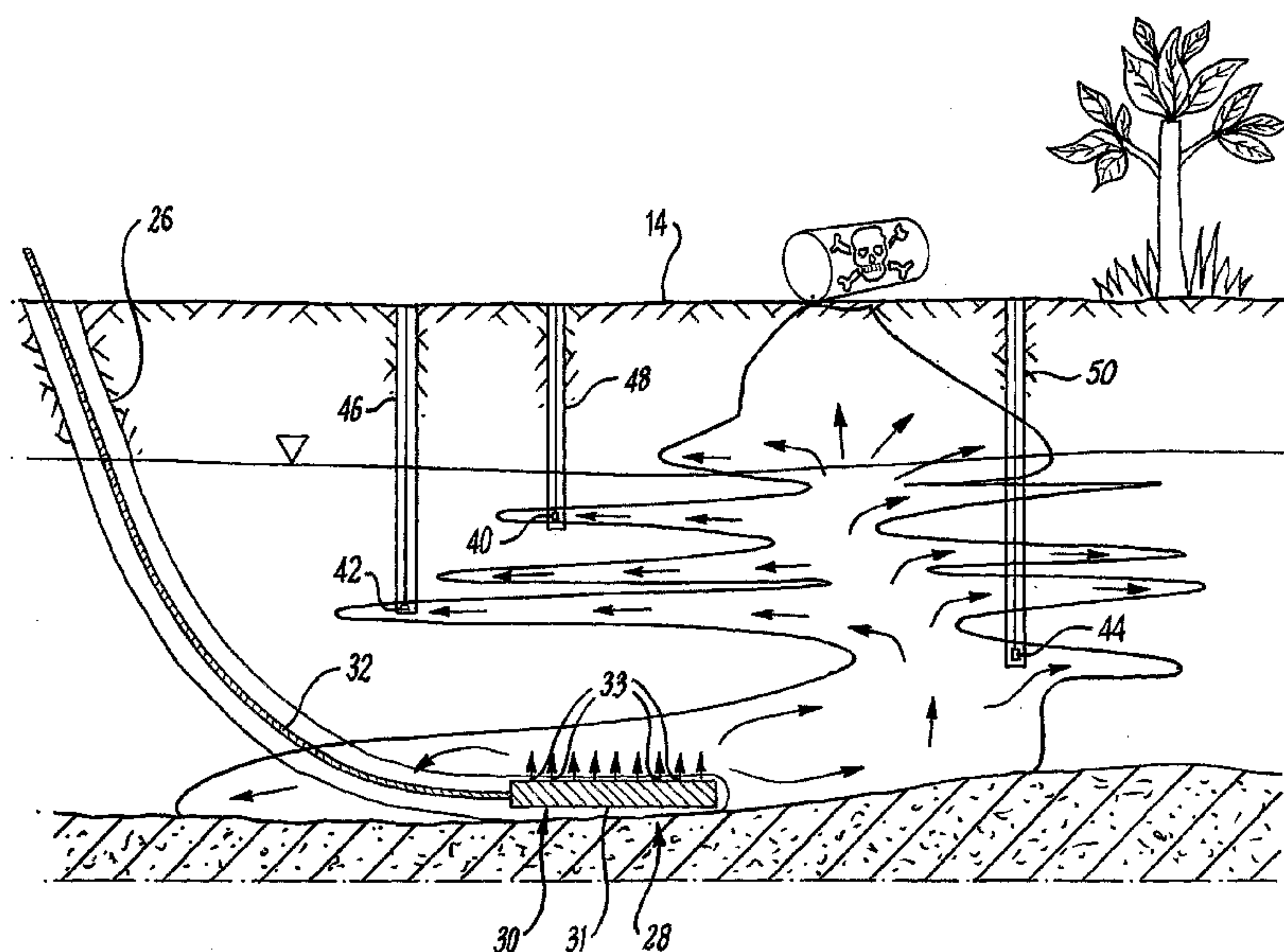
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR REMEDIATING CONTAMINATED LAND



(57) Abstract: The invention relates to a method and apparatus for remediating land (10) that is contaminated by a combustible material (12), in particular, land contaminated with non- aqueous phase liquids (NAPLs). In an embodiment of the invention, a method for remediating land that is contaminated by a combustible material is disclosed which includes the steps of locating a subterranean volume (16) of combustible material such as a DNAPL (12) in land (10) to be remediated, and igniting the combustible material (12) to combust the material and thereby remediate the land (10). By monitoring combustion of the material, combustion may be optimised by, for example, supplying an oxidant or a combustion suppressant.

WO 2007/066125 A3

WO 2007/066125 A3



(88) Date of publication of the international search report:

15 November 2007

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

1 **Method and apparatus for remediating contaminated land**

2

3 The present invention relates to a method and apparatus
4 for remediating or cleaning land that is contaminated by
5 a combustible material. In particular, but not
6 exclusively, the present invention relates to an improved
7 method and apparatus for the remediation of areas of land
8 contaminated with non-aqueous phase liquids (NAPLs).

9

10 The contamination of ground water and surface water by
11 historical unsound disposal practices and continuing
12 accidental releases of hazardous industrial chemicals
13 affects thousands of sites worldwide. Among the most
14 common and problematic of these chemicals are immiscible
15 organic liquids, particularly non-aqueous phase liquids
16 (NAPLs). NAPLs that are lighter than water are known as
17 LNAPLs; these include petrol (gasoline) and diesel.
18 NAPLs that are denser than water are known as DNAPLs;
19 these include chlorinated solvents such as
20 trichloroethylene (TCE) and tetrachloroethylene (PCE),
21 polychlorinated biphenyls (PCBs) and complex hydrocarbon
22 mixtures (such as coal tar and creosotes). NAPLs pose a
23 serious and long term threat to water quality, due to
24 their prevalence, toxicity, persistence, and resistance
25 to standard remediation efforts.

26

1 The United Kingdom Environment Agency has indicated that
2 there are up to 20,000 sites in England and Wales
3 affected by NAPL contamination, and which require
4 treatment under the United Kingdom Environmental
5 Protection Laws. Indeed, it is estimated that
6 chlorinated solvents alone account for approximately 30%
7 of ground water pollution instances in England and Wales.
8 In the United States, the US Department of Defence
9 estimates that approximately 11% of its 3,000 plus
10 solvent impacted sites have DNAPL source zones remaining
11 in the subsurface. Source zones are sub-surface regions
12 containing immiscible liquid (NAPL), which can persist
13 for decades or even centuries, and which continue to
14 release dissolved phase contamination at concentrations
15 in ground water which are usually well above those
16 considered to present a risk to human health. In
17 addition, these compounds are typically volatile and
18 therefore also partition into the air phase present in
19 the soil above the water table, from where these vapours
20 can migrate above ground and into buildings. As such,
21 NAPL source zones are responsible for persistent
22 contamination of land, water and air.

23
24 A wide range of industries have produced NAPLs over the
25 past century, including by-products and waste derived
26 from: coal tar derived from gas manufacture (from coal),
27 creosotes from wood preserving operations, and solvents
28 used in the degreasing of electrical components and for
29 dry cleaning. Contamination of the subsurface occurred
30 by these immiscible organic liquids occurred at locations
31 of manufacture, transport, storage, use, and disposal.
32 In particular, in the past, it was common and permitted
33 practice to dispose of these materials by pouring them
34 into the ground after use. Only in the past 20 years
35 has the risk from NAPLs been recognized, their handling
36 been regulated, and approaches to the remediation of NAPL

1 contaminated sites been sought. However, NAPLs are
2 highly persistent in the subsurface and difficult to
3 address satisfactorily with current remedial techniques.
4 When recovered to the surface, they are hazardous to
5 handle and costly to treat or dispose of safely.

6
7 Industrial by-product/waste materials typically form
8 liquid or liquid/gas deposits, although in the case of
9 certain materials, solid deposits may also be present.
10 One typical situation where solid contaminants may be
11 present is on sites where organic chemical explosives
12 have been manufactured, and where production process
13 and/or manufacturing process discharges have occurred.
14 The discharges involved in the manufacture of the organic
15 explosives 2,4,6-trinitrotoluene (TNT), 2,4-
16 dinitrotoluene (DNT), hexahydro-1,3,5-trinitro-1,3,5-
17 triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-
18 tetrazocine (HMX) are particularly problematic. This is
19 because, under circumstances where the environmental
20 temperatures are significantly lower than the discharge
21 water temperatures (not uncommon - groundwater is
22 typically at 10°C), explosives may precipitate out of
23 solution and create a separate solid phase material in
24 the soil.

25
26 Another organic contaminant found as a solid phase in the
27 subsurface is purifier waste, resulting from the cooling
28 and purification of gas freshly manufactured from coal (a
29 common practice in the early to mid 1900's). During the
30 process, impurities were removed by passing the gas
31 through "purifier beds" made up of either lime or wood
32 chips impregnated with iron filings. The beds of purifier
33 would eventually load up with tar and other materials and
34 become unusable. This purifier waste (also referred to
35 as "box waste") had a tendency to spontaneously ignite if
36 left uncovered and was either shipped off site to

1 landfills or used to fill low-lying areas on site.
2 Purifier Waste is typically found as a dark mixture of
3 wood chips with pieces of solid (typically tar) mixed in.

4
5 Several methods for dealing with NAPLs have been put
6 forward, with varying success. For example, the standard
7 way of dealing with areas of land contaminated with NAPLs
8 is excavation and disposal, otherwise known as "dig and
9 dump". This consists of identifying and exhuming the
10 contaminated soil and transporting it to a landfill site,
11 where it is deposited. However, this practice simply
12 moves the contamination problem from one area to another
13 while often increasing the risk of exposure by bringing
14 the NAPLs above ground. This practice is now frowned
15 upon as unsustainable, and has recently become much more
16 expensive in the UK due to new legislation and landfill
17 tax.

18
19 The first in-situ (i.e., within the ground) method that
20 has been used in an effort to deal with NAPLs is the
21 "pump and treat" technique. This involves installing a
22 ground water recovery well downgradient of the NAPL
23 source zone. Continuous pumping of the recovery well
24 captures the dissolved phase compounds emanating from the
25 source zone. The recovered contaminated water must be
26 treated at surface. However, this technique is
27 essentially a containment strategy for the dissolved
28 phase plume created by the NAPL, and has been shown to be
29 ineffective at remediating the source zone. As such,
30 they often must be operated indefinitely simply to limit
31 the spread of contaminated ground water.

32
33 Many treatment technologies exist for addressing
34 dissolved phase compounds in groundwater. However, like
35 "pump and treat", these do not address the source zone
36 that continually "feeds" compounds to these groundwater

1 plumes. There exist far fewer technologies for
2 addressing NAPLs themselves in the source zone.

3
4 Various in-situ chemical treatments have been used in an
5 attempt to remove NAPLs from contaminated sites. For
6 example, in one technique, surfactants or alcohols are
7 pumped into the ground through an injection well, and aid
8 the dissolution and mobilisation of NAPL which can then
9 be pumped out of a second, downgradient well. The
10 resulting mixture of NAPL and contaminated water may then
11 be separated at surface into aqueous and non-aqueous
12 phases for treatment and/or incineration. However, this
13 technique suffers from a number of disadvantages. In
14 particular, it involves the continuous addition of
15 expensive and sometimes hazardous chemical additives; may
16 not be particularly effective in some subsurface
17 settings; may lead to remobilization of DNAPLs downwards
18 which worsens the situation; involves fluids that are
19 difficult to separate from NAPLs or recycle; and recovers
20 large volumes of fluids that require treatment.

21
22 A further chemical treatment for the in-situ removal of
23 NAPLs from contaminated sites involves their oxidation.
24 For example, potassium permanganate can be pumped into a
25 contaminated site, which then reacts with the NAPLs by
26 means of an oxidation reaction, to transform the NAPL
27 into nonhazardous compounds. However, the success of
28 this technique can be limited due to the reaction
29 simultaneously forming mineral solids that block the pore
30 space surrounding the NAPL, thereby preventing further
31 contact between the reactants. In addition, the
32 naturally occurring organic material in the soil often
33 exerts a large oxidant demand, requiring additional
34 oxidant to be injected. The use of large volumes of
35 oxidant is typically expensive.

36

1 Biological techniques have also been used in an effort to
2 remediate sites contaminated by NAPLs. Such
3 bioremediation techniques typically involve adding
4 nutrients and an organic food source to contaminated soil
5 such that groups of bacteria in the soil multiply and
6 interact to degrade hazardous compounds. Ex-situ
7 bioremediation involves exhuming the contaminated soil
8 and treating in a reactor or in mounds at ground surface.
9 In-situ bioremediation has been implemented for treating
10 dissolved phase compounds downgradient of the source
11 zone, acting as a plume containment strategy but not
12 reducing NAPL volume. There have been recent efforts to
13 make bioremediation possible within the source zone
14 itself; while some success been shown in some laboratory
15 experiments, this has yet to be demonstrated in the
16 field.

17
18 Several problems exist with bioremediation of NAPL source
19 zones. The continuous input of additives (organic
20 substrates and nutrients) can make the treatment costly.
21 In addition, it is necessary to obtain a site specific
22 balance of bacteria, food and nutrients for every
23 contaminated site. The bioremediation technique is
24 therefore site specific. Another problem associated with
25 bioremediation techniques is that of 'biofouling', in
26 which the pore space near the NAPLs and the pumping wells
27 become blocked by excessive microbial growth.
28 Furthermore, not all contaminated sites have the
29 requisite bacteria naturally present at the site. In
30 these situations, known biological degraders would need
31 to be injected as well, in a process known as 'bio-
32 augmentation'. However, in certain jurisdictions this
33 practice is actively discouraged, and in many cases is
34 not allowed, due to restrictions on the implantation of
35 non-native organisms.

36

1 The in situ (i.e., in the subsurface) chemical and
2 biological treatment techniques described above all
3 involve injecting fluids into the subsurface upgradient
4 of the source zone and rely on subsequent contact between
5 the chemicals and the NAPL. However, a significant
6 problem with all such fluid injection techniques is that
7 achieving the desired flush of the source can be
8 problematic. Fluid bypassing often occurs where the
9 injected fluid tends to flow around the NAPL thereby
10 limiting its exposure to and thus contact with a portion
11 of the injected chemical. This occurs for primarily two
12 reasons: NAPLs tend to rest upon low permeability lenses
13 of subsurface material (e.g., silts or clays) which
14 naturally divert flow away from them; and the NAPL itself
15 blocks the pore spaces causing water or an injected fluid
16 to flow more easily and quickly around the source zone.
17 In addition, dilution of the injected fluids may cause
18 their concentrations to decrease such that their
19 effectiveness is diminished.

20

21 Another approach which has been employed in an effort to
22 rid contaminated sites of NAPLs involves thermal
23 remediation techniques, including steam flushing,
24 electrical resistance heating (ERH), and electrical
25 conductive heating (ECH). The benefits of thermal
26 remediation technologies are that they may reduce the
27 NAPL mass in a matter of months to years (in comparison
28 to years to decades for the more passive technologies
29 discussed above), and that they can be effective in low
30 permeability media, since heat conduction is generally
31 less affected than the flow of fluids by hydraulic
32 properties.

33

34 Steam flushing involves the injection of steam to the
35 sub-surface to volatilize and decrease the viscosity of
36 the NAPLs, thus assisting their mobilization towards a

1 withdrawal well. ERH and ECH involve the implantation of
2 large electrodes into the ground (at the source zone),
3 and sustained heating of the water and/or soil itself.
4 Thermal methods typically heat the subsurface to a
5 temperature of approximately 100°C. In so doing, they
6 aim not to destroy the contaminants in situ but rather to
7 change their phase and/or properties so that they can be
8 mobilized and recovered. A primary remediation mechanism
9 is to volatilise NAPL compounds such that they may be
10 collected from the air phase in the subsurface or at
11 ground surface. Also common is recovery of liquid that
12 is mobilized due to its reduced viscosity. In some
13 cases, some NAPL compounds may be thermally degraded as
14 absorbed heat causes endothermic degradation (pyrolysis)
15 or reaction with water (hydrolysis). However, these
16 techniques exhibit varied success and have a significant
17 drawback. Specifically, the techniques require a large
18 and continuous input of energy in order to achieve and
19 maintain a given temperature. Thus, these techniques
20 often prove to be prohibitively expensive.

21

22 In summary therefore, the prior art methods of
23 remediating (or cleaning) sites contaminated with NAPLs
24 generally have significant limitations in terms of the
25 timescales over which they are operated, the
26 effectiveness of the techniques used, and the costs
27 incurred.

28

29 It is amongst the objects of embodiments of the invention
30 to obviate or mitigate at least one of the drawbacks
31 associated with the prior art.

32

33 Further aims and objects of the invention will become
34 apparent from a reading of following description.

35

1 According to a first aspect of the present invention,
2 there is provided a method of remediating land
3 contaminated with a combustible material, the method
4 comprising the steps of:

5 locating a subterranean volume of combustible
6 material in land to be remediated; and
7 igniting the combustible material to combust the
8 material and thereby remediate the land.

9
10 The invention thereby provides a method by which land
11 contaminated with combustible materials may be cleaned or
12 remediated by combusting the materials *in situ*. This
13 overcomes problems associated with prior cleaning
14 techniques such as "dig and dump". Combustion of the
15 material may be self-sustaining in that it may only be
16 necessary to supply sufficient energy to ignite the
17 material; once ignited, combustion of the material may
18 proceed as long as there is sufficient fuel (the
19 combustible material) and oxygen for combustion to take
20 place. This is in contrast with, for example, known
21 thermal remediation processes, which require continuous
22 energy input.

23
24 Materials including many common NAPLs as well as some
25 solid organic contaminants are flammable and contain
26 substantial energy. When burned, they release significant
27 amounts of heat. For example, the heat of combustion
28 (HOC) of TCE and chlordane relative to that of wood are
29 90% and 300%, respectively; shredded tires, with a HOC of
30 only 5% of wood, have been successfully combusted in
31 waste recovery schemes. Combustion involves a self-
32 sustained exothermic reaction of a combustible material
33 in the presence of an oxidant, oxidizing (and thereby
34 destroying) the combustible material in the process.
35 When the combustible material is embedded within a porous
36 media, the porous media has a highly beneficial impact on

1 combustion: the solid acts as energy store and then feeds
2 that energy back into the reaction. This energy feedback
3 mechanism means that an efficient, self-propagating
4 combustion process is possible for conditions that
5 otherwise lead to extinction. Applications in ex-situ
6 incineration, porous burners and enhanced oil recovery
7 indicate significant potential, but the concept of in
8 situ combustion for subsurface remediation is novel.

9

10 It will be understood that the combustible material is
11 subterranean in that it is below ground level or within
12 the subsurface, and may comprise a fluid and/or a solid,
13 or any combination thereof. However, most materials are
14 anticipated as being predominantly in a fluid phase. It
15 will also be understood that the subsurface is typically
16 porous and may comprise soil or the like, with
17 combustible liquids typically residing in pores defined
18 between solid particles of the soil (or in the case of
19 fractured rock environments, residing in the network of
20 fractures between blocks of rock/clay and/or in the pore
21 spaces of the rock/clay matrix itself).

22

23 A combustion front may be generated following ignition of
24 the combustible material and may travel outwardly, away
25 from a point of ignition and through the volume of
26 combustible material. The combustion front may follow a
27 path defined by factors including the shape of a fluid
28 volume and a pathway defined along the interconnected
29 pores in the soil. The combustion front should follow the
30 distribution (i.e., path) of the combustible material away
31 from the ignition point without the (above ground)
32 operator knowing in advance the specific distribution
33 (pathways). Thus, the process will also be self-guiding.

34

35 Preferably, the method comprises monitoring combustion of
36 the material. Monitoring combustion of the material may

1 comprise the steps of monitoring one or more parameters,
2 including temperature in the land contaminated with the
3 combustible material, at a plurality of locations.
4 Monitoring combustion may also comprise monitoring by-
5 products of the combustion process such as the
6 constituents and/or volumes of gaseous by-products
7 resulting from combustion of the material. The method
8 may comprise monitoring combustion of the material in
9 real-time, and thus during the combustion process. In
10 many circumstances, existing NAPL remediation techniques
11 are only evaluated in the field by mapping the
12 distribution of NAPL and the downgradient gas/water
13 concentrations before and then after treatment, and
14 looking at the difference to determine the
15 "effectiveness" of the technology. Real-time monitoring
16 provides significant advantages over prior methods.
17 Alternatively, or additionally, the method may comprise
18 monitoring the extent of combustion of the material
19 subsequent to combustion, that is, after combustion has
20 ceased.
21
22 Monitoring combustion of the material, either in real-
23 time or by monitoring the extent of combustion after
24 combustion has ceased, may facilitate determination of
25 the extent to which the material has been combusted and
26 factors including the type of combustion that the
27 material is or has undergone and a rate of progression of
28 a combustion front through the material. For example, if
29 a combustion front is progressing more slowly than
30 anticipated, there may be a relative lack of oxygen
31 present. Alternatively, if the combustion front is
32 progressing faster than anticipated, there may be an
33 excess of oxygen relative to the volume of material.
34
35 Accordingly, by monitoring combustion of the material,
36 action may be taken in order to achieve an optimal or

1 desired form and rate of combustion. For example, the
2 method may comprise monitoring combustion of the material
3 and supplying (or modifying the amount or ratio of the
4 supply of) air/oxygen in one or more locations.
5 Alternatively, the method may comprise supplying
6 additional fuel, such as further combustible material,
7 for example, to assist ignition of the volume of
8 material. Alternatively, the method may comprise
9 supplying a combustion suppressant such as nitrogen or
10 water in order to suppress and thereby control
11 combustion. In a further alternative, the method may
12 comprise deactivating an ignition device (used to ignite
13 the material) and/or reducing or terminating the addition
14 of oxidant, to control (or suppress) combustion. As will
15 be described below, this may control combustion depending
16 upon the type of combustion occurring.

17

18 Flaming combustion refers to combustion that occurs in
19 the gas phase. For example, when an accumulation of NAPL
20 (e.g., kerosene) rests in an open container and is
21 ignited, the heat will continuously volatilise the fuel,
22 and the gaseous fuel combusts producing a flame. Flame
23 combustion is also referred to as homogeneous combustion
24 because at the location where combustion occurs both the
25 oxidant (oxygen in the air) and the fuel are in the same
26 (gas) phase, where they readily mix. Flame combustion
27 consumes the fuel relatively quickly and generates
28 relatively high temperatures (e.g., typically greater
29 than 900 °C).

30

31 Smouldering combustion refers to combustion of a material
32 on the surface of the solid/liquid material itself. For
33 example, when a combustible material (e.g., tobacco) is
34 compacted to form a porous solid (e.g., a cigarette) and
35 is ignited, the oxidant (oxygen) diffuses into the
36 surface of the material and the combustion proceeds on

1 the tobacco surface. Smouldering is referred to as
2 heterogeneous combustion because the oxidant (gas) and
3 the fuel (liquid or solid) are not in the same phase.
4 Smouldering typically proceeds slowly relative to flaming
5 and generates lower temperatures (e.g., typically between
6 400°C and 600°C) but under specific conditions can achieve
7 temperatures above 1000°C. By monitoring and controlling
8 combustion, smouldering combustion can be promoted.

9
10 In particular embodiments, the method may comprise
11 monitoring combustion in order to promote or maintain
12 smouldering of the material. Alternatively, the method
13 may comprise monitoring combustion in order to promote
14 flame combustion. These different combustion regimes may
15 be achieved by monitoring/controlling the supply/ratio of
16 oxidant (air/oxygen/ozone). For example, smouldering, is
17 oxygen deficient so that it can be controlled by managing
18 the oxygen supply; can propagate at lower temperatures;
19 and requires less oxidant. Accordingly, by monitoring
20 combustion and controlling the supply of oxidant,
21 smouldering combustion can be promoted. If required, a
22 combustion suppressant such as nitrogen may be supplied
23 to maintain combustion in a smouldering state. The
24 method may comprise super-adiabatically combusting the
25 material, such that the material undergoes super-
26 adiabatic combustion. In super-adiabatic combustion, the
27 combustion front experiences minimal movement with
28 migration of fuel and oxidizer towards the reaction zone
29 dominating the combustion process.

30

31 The method may comprise controlling the extent of
32 combustion of the material, and may comprise
33 extinguishing combustion after a desired or determined
34 time period; and/or following travel of a combustion
35 front a desired or determined distance through the
36 material and thus at a desired location.

1
2 Extinguishing combustion at a desired time may be
3 achieved as follows. If combustion is not yet thermally
4 sufficient so as to be thermally self-sustaining, and
5 thus an ignition element used to ignite the material is
6 still activated, the ignition device may be deactivated
7 to thereby extinguish combustion. If combustion is
8 progressing in a thermally sufficient, thermally self-
9 sustaining mode, and thus the ignition element is off,
10 but combustion is oxygen deficient/starved so that
11 progression relies on the continued addition of an
12 oxidant (e.g., air/oxygen/ozone), then the flow of
13 oxidant may be reduced or discontinued to thereby
14 extinguish combustion. An alternative way of achieving
15 this will be by diluting the oxidizer flow with a
16 suppressant such as nitrogen or water. If combustion is
17 progressing in the absence of oxidant supply and without
18 a requirement for an ignition device to remain activated,
19 then a combustion suppressant such as nitrogen or water
20 may be injected; this may be of a particular utility for
21 the remediation of land contaminated with chemical
22 explosives which generally have embedded oxidants.
23
24 Extinguishing combustion at a desired location may be
25 achieved by creating one or more combustion barriers. In
26 embodiments of the invention, a site boundary or
27 perimeter may be formed by setting up one or more
28 combustion barriers. The step of forming the one or more
29 barriers may comprise constructing a physical barrier.
30 For example, a rigid sheet-pile wall (e.g., made of
31 steel) may be driven into the subsurface to form a cut-
32 off wall. Or, for example, a time-setting material, such
33 as cementitious material containing bentonite, may be
34 injected into the ground, typically into an excavated
35 trench or borehole, to form a cut-off wall.
36 Alternatively, or in addition, the step of forming the

1 barrier may comprise forming a fluid suppression wall,
2 such as a gas wall, by injecting fluid into the ground in
3 a plurality of locations. For example, a plurality of
4 boreholes/wellbores may be drilled, and/or trenches may
5 be formed (filled with gravel or the like) and a fluid
6 suppressant injected through the boreholes and/or into
7 the trench. These techniques may provide a barrier which
8 extinguishes the combustion process at the boundary
9 thereby defined.

10

11 Preferably the material is a fluid which is non-aqueous
12 and therefore relatively immiscible in water, but may
13 also or alternatively be a solid. The combustible
14 material may be a NAPL, and may in particular be a DNAPL
15 or LNAPL.

16

17 The method may comprise accessing the volume of
18 combustible material from surface. Accessing the volume
19 of material may comprise drilling an access borehole,
20 passage or the like from surface to a location
21 intersecting the volume of material or to a location
22 adjacent the volume of material. This may facilitate
23 subsequent ignition of the combustible material. The
24 borehole or the like may be substantially vertical, or
25 may be a horizontal borehole. It will be understood that
26 a horizontal borehole is one which includes at least a
27 portion which is deviated from the vertical; such
28 boreholes are known in the oil and gas exploration and
29 production industry, and facilitate access to the
30 material volume from a laterally spaced location.
31 Drilling a horizontal borehole may also facilitate
32 subsequent ignition of the material and propagation of a
33 combustion front through the material. This is because
34 the borehole may be directed to intersect the volume at
35 or adjacent a lower boundary or perimeter of the volume.
36 The combustion front may therefore be initiated at the

1 bottom of the contaminated region and propagate upwards.
2 In this fashion, buoyant or forced air flows may be
3 generated, assisting the combustion process. This may
4 promote conservation of energy (heat), improving
5 efficiency of the method, as heat generated during
6 combustion rises or is pushed by a forced air flow
7 upwardly through the land, assisting in self-sustainment
8 of the combustion process. This may make it possible to
9 burn very low concentrations of fuels in the presence of
10 heat sinks (such as areas of or containing relatively
11 large volumes of water). In addition, ignition from
12 below may permit material (NAPLs) that are mobilized by
13 their reduced viscosity (due to increased temperature) to
14 trickle downwards and remain within the combustion zone,
15 thereby still being combusted or alternatively being
16 recovered in the ignition borehole or another borehole
17 dedicated to that purpose.

18

19 In an alternative, the borehole may be directed to
20 intersect the volume of material at or adjacent to an
21 upper boundary and the combustion front propagated
22 downwardly through the material volume. Alternatively,
23 the borehole may be directed to intersect the volume of
24 material at a lateral boundary and the combustion front
25 propagated horizontally across the material volume, or
26 located centrally and combustion propagated outwardly
27 from the centre of the material volume towards its
28 extremities.

29

30 The step of igniting the combustible material may
31 comprise locating an ignition device within or adjacent
32 to the volume of material and may in particular comprise
33 locating the ignition device extending along the borehole
34 or the like from the surface to the location intersecting
35 with or adjacent to the volume of material. Where a
36 combustion regulating fluid (e.g., oxidant or

1 suppressant) is to be injected into the ground, an
2 injection device may be provided with the ignition device
3 and thus co-located in the borehole.

4
5 Preferably, combustion by-products comprising gases and
6 the like are collected for analysis and/or disposal. The
7 combustion by-products may be collected at surface and
8 contained in a suitable storage chamber. Additionally or
9 alternatively, where access to the material volume is
10 achieved through a borehole or the like, the by-products
11 may be returned to surface along the same borehole or
12 other boreholes provided expressly for this purpose.
13 Accessing the combustible fluid volume through a
14 borehole(s) or the like may therefore additionally
15 facilitate capture of gaseous by-products from the
16 combustion process. In the presence of significant
17 amounts of water in the subsurface, a fraction of gaseous
18 products (e.g., carbon dioxide, which is highly soluble)
19 may dissolve into the water and thus not be collected.

20
21 The method may comprise monitoring combustion byproducts
22 in the land following combustion and/or during
23 combustion. This may be achieved by taking and analysing
24 samples of the soil/groundwater.

25
26 According to a second aspect of the present invention,
27 there is provided apparatus for remediating land
28 contaminated with a combustible material, the apparatus
29 comprising an ignition device, the ignition device
30 adapted to be located below ground level for igniting a
31 subterranean volume of combustible material in land to be
32 remediated, to combust the material and thereby remediate
33 the land.

34
35 The ignition device may be adapted to heat the
36 combustible material in order to ignite the material, and

1 may comprise an electric resistance heater. The electric
2 resistance heater may comprise an electric element or
3 wire which heats up when an electric current is passed
4 through the element, and the element may have a corrosion
5 resistant coating or cover adapted to shield the element
6 from corrosive materials.

7
8 Alternatively, the ignition device may be adapted to
9 generate an electrical discharge or spark or other source
10 of heat to thereby ignite the material. If required, the
11 ignition device may comprise a burner or the like,
12 coupled to a fuel supply, for generating a flame or other
13 source of heat to ignite the material. It will be
14 understood that, with certain materials, the flame or
15 other source of heat may only require to be maintained
16 for as long as it takes for the combustible material to
17 ignite.

18
19 The apparatus may comprise at least one fluid injection
20 device for injecting a fluid (particularly a gas) adapted
21 to promote combustion into the material volume, such as
22 an oxidant comprising or containing air/oxygen/ozone.
23 This may facilitate control of combustion of the material
24 by enabling injection of oxidant. The fluid injection
25 device may comprise at least one flow line extending from
26 surface into the volume. Optionally, the fluid injection
27 device may comprise a manifold having a plurality of
28 outlets, the manifold connected to a main fluid supply
29 line, for supply of fluid through a single supply line to
30 a plurality of locations within the volume. The supply
31 line may be contained within the ignition borehole either
32 alongside the ignition device or may be adapted to be
33 inserted subsequent to removal of the ignition device.

34
35 The fluid injection device may also be for supplying a
36 combustion suppressant such as water or nitrogen, into

1 the material volume, for selectively extinguishing
2 combustion, or restricting combustion of uncombusted
3 material. The fluid injection device may comprise
4 separate flow lines for the flow of oxidant/combustion
5 suppressant or may be adapted for selective supply of
6 either.

7
8 The apparatus may comprise at least one sensor for
9 monitoring combustion of the material. Preferably, the
10 apparatus comprises a plurality of sensors spaced
11 throughout the volume. The apparatus may comprise a
12 temperature sensor and/or a gas sensor for determining
13 the volume and/or constituent of gaseous by-products
14 resulting from combustion of the fluid.

15
16 An embodiment of the present invention will now be
17 described, by way of example only, with reference to the
18 accompanying drawings, in which:

19
20 Figure 1 is a schematic, cross-sectional view of an area
21 of land contaminated with a combustible material;

22
23 Figure 2 is a view of the area of land shown in Figure 1
24 during remediation utilising a method according to an
25 embodiment of the present invention;

26
27 Figure 3 is a schematic view illustrating progression of
28 a combustion front through a volume of the combustible
29 material shown in Figure 1;

30
31 Figure 4 is an enlarged schematic view of soil in the
32 contaminated land shown in Figure 1;

33
34 Figure 5 is a view similar to Figure 2 of an area of land
35 contaminated with a combustible material, shown during

1 remediation utilising a method according to an
2 alternative embodiment of the present invention;

3

4 Figure 6 is a view of the area of land contaminated with
5 a combustible fluid shown in Figure 5, shown in a
6 variation on the method of Figure 5;

7

8 Figure 7 is a view of the area of land contaminated with
9 a combustible fluid shown in Figure 5, shown in a further
10 variation on the method of Figure 5;

11

12 Figure 8 is a view of the area of land contaminated with
13 a combustible fluid shown in Figure 5, shown in a still
14 further variation on the method of Figure 5;

15

16 Figure 9 presents a schematic illustration of a equipment
17 utilised in an experiment conducted to prove viability of
18 the method and apparatus of the present invention;

19

20 Figure 10 is a table detailing the results of further
21 experiments conducted to prove viability of the method
22 and apparatus of the present invention; and

23

24 Figure 11 is a graph showing the measured temperature vs.
25 time, as well as the percentage (by volume) of CO and CO₂
26 in the combustion products, measured during a coal
27 tar/sand experiment carried out utilising the equipment
28 of Figure 9.

29

30 Turning firstly to Figure 1, there is shown an area of
31 land 10 which has been contaminated with a combustible
32 material, in particular, a combustible fluid 12. The
33 combustible fluid typically comprises a NAPL and may in
34 particular comprise a DNAPL which may be a chlorinated
35 solvent such as trichloroethylene, tetrachloroethylene,
36 or a complex hydrocarbon mixture such as coal tar or

1 creosote. The DNAPL 12 may have been previously disposed
2 of by pouring onto a surface 14 of the land 10, or may be
3 the result of an accidental spillage. As shown in the
4 Figure, the DNAPL has permeated down through soil 11 in
5 the area 10, and has formed a non-uniform volume or
6 source zone 16 of contamination. It will be understood
7 that the shape of the volume 16 is dependent upon a
8 number of factors including the volume of NAPL released,
9 the physical fluid properties of the NAPL, and the
10 spatial distribution of soil or rock permeability in the
11 region of the land 10. The DNAPL 12 has formed a number
12 of NAPL 'pools' (i.e., areas of stable NAPL that is
13 connected through a large number of pores in the
14 soil/rock) including a lower pool 18, which has
15 accumulated on an impermeable rock layer 20. The DNAPL
16 12 may also include areas of 'residual' NAPL in which
17 disconnected NAPL blobs (single pore) and ganglia
18 (spanning several pores) are trapped in the pore space,
19 typically in a pathway through which NAPL passed but did
20 not accumulate in a pool.

21

22 The DNAPL 12 shown in Figure 1 has permeated down through
23 the soil 11 in the area of land 10 to a level below the
24 current water table 22. Accordingly, over a period of
25 time, compounds within the DNAPL 12 become dissolved out
26 of the volume 16, mixed in with the groundwater, and flow
27 into a watercourse such as a stream, river or the like,
28 creating a pollution problem. The present invention is
29 directed to a method of remediating or cleaning the
30 contaminated area of land 10 (i.e., the source zone), as
31 will now be described with reference also to Figure 2.
32 It will be noted that the method also applies to LNAPL
33 scenarios, except that the LNAPL does not substantially
34 penetrate the water table; rather it forms a lens that
35 sits atop it (and often depresses it locally around the
36 LNAPL pool), as will be described in more detail below.

1
2 It will also be understood that the likely phase or
3 phases of the material present in the volume 16 (liquid,
4 gas/vapour and solid) is dependant upon the contaminant
5 material and environmental conditions such as ambient
6 temperature and pressure, and the presence of
7 groundwater. Thus under other circumstances, gas/vapour
8 and/or solids may also or alternatively be present in the
9 volume 16.

10
11 In general terms, the method comprises remediating the
12 contaminated area of land 10 by firstly locating the
13 subterranean volume of DNAPL 12. This may be achieved by
14 utilising one or a combination of a number of techniques;
15 for example, using remote detection geophysical equipment
16 (not shown), or by drilling and sampling (for soil, gas,
17 or water) a number of test wells or boreholes (not shown)
18 at a number of locations and depths spaced around the
19 surface 14 in a suspected contaminated area of land.
20 This facilitates determination of the general shape and
21 volume 16 of the area of land 10 contaminated with the
22 DNAPL 12. In the illustrated example, and as discussed
23 above, the volume 12 includes a lower pool 18 which rests
24 upon the impermeable rock layer 20; however, such a lower
25 bounding pool is not a prerequisite for the method.

26
27 Once the volume 16 has been located using such
28 techniques, the area of contaminated land 10 is
29 remediated by igniting the DNAPL 12, to thereby combust
30 the DNAPL. This is achieved by drilling a borehole 26
31 from the surface 14, extending through the soil 11 to a
32 location 28 adjacent the lower boundary 24 of the fluid
33 volume 16. Such drilling techniques are known in, for
34 example, the oil and gas exploration and production
35 industry. The borehole 26 is deviated, to facilitate
36 access to the lower boundary 24, although a vertical

1 borehole may be drilled through the volume 16 to the
2 location 28.

3

4 Following drilling of the borehole 26 and, if required,
5 lining with suitable tubing (such as lengths of
6 interconnected casing or liner), a gas injection manifold
7 and a material ignition device 30 is run into the
8 borehole 26 from surface 14 and down to the location 28.

9 The device 30 is connected to control equipment and to a
10 source of compressed air/oxygen/ozone (not shown) at
11 surface 14 via an umbilical 32. The device 30 also
12 comprises a manifold 31 having a plurality of gas outlets
13 33.

14

15 The ignition device 30 includes a sheathed cable heater
16 or wire (not shown) which, when activated, rapidly heats
17 up to in-turn heat the DNAPL 12 that has entered within
18 the screen of the borehole 26 and in the area surrounding
19 the device 30. A suitable material for the cable heater
20 sheath is INCONEL®, although other materials may be
21 utilised. This causes the DNAPL 12 to ignite, thereby
22 commencing combustion of the DNAPL. The sheath protects
23 the heater from exposure to corrosive compounds present
24 in the ground, particularly the DNAPL 12 itself. In an
25 alternative arrangement, when it is desired to combust
26 the DNAPL 12 in the volume 16, an electrical discharge or
27 spark (or indeed any other means of producing heat) is
28 generated by the device 30, by providing a suitable
29 control signal from surface, thereby igniting the DNAPL
30 12. Once the DNAPL 12 has been ignited, a combustion
31 front 34 is generated, as shown in the schematic view of
32 Figure 3, which travels through the volume 16 from the
33 location 28, the combustion front spreading outwardly
34 from the device 30.

35

1 Oxidant may be injected into the subsurface through the
2 ignition borehole manifold 31. The porous nature of the
3 soil 11 in the area of land 10 and the injection of
4 oxidant at the same location as the ignition ensures
5 forward (in the direction of the flow) propagation of the
6 combustion front, whereby energy is recovered from a hot,
7 burnt region 16a of the DNAPL volume and is transferred
8 to an un-burnt region 16b. It is likely that combustion
9 will proceed in smouldering mode, with combustion
10 occurring on the material surface and oxidant diffusing
11 into that surface. Following ignition, the combustion
12 front 34 travels through the volume 16 to combust the
13 remaining pools of DNAPL 12 which are in fluid
14 communication with the pool 18, as indicated by the
15 arrows in Figure 2. Areas of residual DNAPL are
16 combusted as well due to the ability of the porous media
17 to retain and transmit temperatures that support
18 combustion, even when the NAPL is not in continuous fluid
19 connection throughout the pore space. Gaseous by-
20 products of the combustion process pass upwardly through
21 the soil to the surface 14 and may be allowed to pass
22 into the atmosphere, or may be collected for further
23 treatment and/or storage using appropriate collection and
24 storage equipment (not shown). The gaseous by-products
25 may also be drawn off through the borehole 26 (or other
26 installed boreholes for that purpose) and collected in a
27 similar fashion. It is possible that a fraction of the
28 combustion products will condense back to the liquid
29 phase when in contact with cold soil or water above the
30 combustion front. Generally, the combustion products will
31 be expected to be mostly water, CO, and CO₂.
32
33 The method therefore facilitates remediation of the
34 contaminated area of land 10 by combustion of the DNAPLs
35 12 in the volume 16.
36

1 The method and apparatus of the invention will now be
2 described in more detail, with reference also to Figure
3 4, which is an enlarged, schematic illustration of the
4 soil 11 in the contaminated volume 16.

5
6 The DNAPL 12 permeates the soil 11 in the land 10 from
7 the surface 14, and resides within the interconnected
8 pore spaces 36 between soil particles 38, as shown in
9 Figure 4. However, it will be understood that the NAPL
10 can also be contained within open fractures or fissures
11 in a fractured rock/clay environment and/or in the
12 consolidated porous matrix within which the fractures are
13 embedded. Combustion of hydrocarbon fuels such as the
14 DNAPL 12 within a porous matrix like the soil 11
15 generates a self-sustaining exothermic reaction within
16 the pore spaces 36, during which heat is transmitted from
17 the burning DNAPL 12a (Figure 3) to both the pore spaces
18 36 and to the solid matrix (the soil particles 38). The
19 presence of the porous media has a significant,
20 beneficial impact on the combustion process in that the
21 solid particles 38 have a high thermal inertia, thereby
22 heating up and storing energy from the combustion
23 reaction. Transmission of this heat through the porous
24 media and via the heated oxidant (gas) travelling in the
25 same direction as the combustion front can create a pre-
26 heated region ahead of the front. In this way, much of
27 the released energy can be delivered back to the reaction
28 when it reaches the preheated location. Heat losses are
29 therefore small allowing propagation of a combustion
30 front even for very low concentrations of fuel and/or
31 oxidant.

32
33 This energy feedback mechanism thus could result in
34 temperatures in the reaction zone 34 significantly
35 exceeding those typically possible for a given DNAPL 12.
36 The combustion products will release most of their energy

1 to the uncombusted DNAPLs 12b near the combustion (i.e.,
2 reaction) front 34, consequently leaving the immediacy of
3 the combustion front region cold. In this way, an
4 efficient self-propagating combustion process is possible
5 in conditions that would otherwise lead to extinction of
6 the combustion process.

7
8 The propagation rate of the exothermic reaction through
9 the soil may also be significantly influenced by the
10 direction of oxidiser flow, that is the direction of flow
11 of oxygen carrying air. Accordingly, the method may
12 involve the supply of air (or alternative mixtures of
13 oxygen, nitrogen and other gases, e.g., ozone) to the
14 soil in the area 10 during the combustion process.
15 Indeed, the propagation rate of an exothermic reaction
16 through the porous matrix of the soil 11 is significantly
17 influenced by the direction of air (oxidizer) flow.
18 Figure 3 demonstrates how forward propagation uses
19 injected oxidizer (air/oxygen) to recover energy and
20 thereby assists propagation of the reaction. When
21 addressing fuels (NAPLs) of low calorific output, very
22 low fuel concentration, or in the presence of thermal
23 sinks such as water, it is necessary to ensure that most
24 of the energy generated by the exothermic reaction is
25 recovered by the un-burnt fuel and oxidizer. Thus,
26 propagation will generally be in a forward mode, as
27 illustrated in Figure 3. Within forward mode, three
28 regimes can be identified based upon oxidizer flow rate:
29 excess heat causing reaction front acceleration; shortage
30 of heat causing deceleration; and heat accumulation
31 exactly at the reaction front 34. This ideal third
32 condition is known as super-adiabatic combustion. The
33 specific regime achieved in any application can therefore
34 be manipulated depending on the desired outcome, by
35 controlling injection of air/oxygen through the injection
36 device 30, and/or supply of a suppressant such as

1 nitrogen or water, as will be described below. The
2 propagation rate is also affected by pore diameter of
3 the soil and the fraction of porosity occupied by
4 fuel, air and other, non-reacting materials.

5
6 Propagation of a forward reaction front within a porous
7 matrix such as the soil can subsist within a wide
8 range of conditions. The most important variables are
9 the nature of the porous medium, the thermal properties
10 of the combustible material, and the supply of oxygen.
11 For large airflow rates (large oxygen supply), there is a
12 large release of energy and propagation of the reaction
13 front will accelerate. If the oxygen supply is reduced,
14 the energy produced decreases and the reaction front will
15 decelerate, further reduction of the oxygen supply can
16 lead to extinction. Under these conditions, exothermic
17 reactions result mostly from oxidation on the liquid
18 fuels' surface; this mode of combustion is termed
19 smouldering (e.g., a cigarette). Smouldering typically
20 proceeds slowly relative to flaming and generates lower
21 temperatures (e.g., typically between 400°C and 600°C) but
22 under specific conditions can achieve temperatures above
23 1000°C. In addition, smouldering is possible at
24 extremely low air-to-fuel ratios, and even in the absence
25 of any external oxygen supply. Thus a range of operating
26 regimes is possible: slow NAPL smouldering is likely in
27 the absence of air-filled porosity, while periodic or
28 continuous air (oxygen) injection (through the device 30)
29 will increase temperatures and accelerated propagation
30 of the burning front (i.e., remediation) through the
31 source zone.

32
33 Thus to achieve optimum combustion and thereby progress
34 of the combustion front through the volume of DNAPL
35 12, combustion of the DNAPLs may be monitored. This may
36 be achieved by monitoring the temperature of the soil in

1 and around the volume 16 at a number of locations spaced
2 throughout the volume and surrounding soil, using
3 suitable temperature sensors (e.g., thermocouples; three
4 shown in Figure 2 and given the reference numerals 40, 42
5 and 44). These sensors 40, 42 and 44 are located in
6 small boreholes or passages 46, 48 and 50 drilled from
7 the surface 14 into the soil in the volume 16 and
8 surrounding area. Equally, the constituents and/or
9 volume of the gaseous by-products resulting from the
10 combustion process may be monitored either at surface 14
11 or by sampling at various locations throughout the volume
12 16, in a similar fashion as for obtaining temperature
13 data. These gaseous by-products may also or
14 alternatively be extracted through the borehole 26. By
15 monitoring the temperature and constituents/volume of the
16 gaseous by-products, the nature of the combustion
17 occurring can be determined in real-time, enabling
18 modifying action to be taken, if required. For example,
19 by varying oxygen supply with consequential effect upon
20 propagation of the combustion front 34. In the
21 circumstances where air or oxygen is supplied during the
22 combustion process, this may be either on a continuous
23 basis or at periodic intervals, as required. Also,
24 oxidant may be supplied at a single location or at
25 multiple locations to facilitate progress of the
26 combustion front throughout the source zone, as will be
27 described below.

28

29 Turning now to Figure 5, there is shown a view similar to
30 Figure 2 of an area of land contaminated with an LNAPL
31 such as petrol (gasoline), jet fuel, heating oil, or
32 diesel. In the Figure, the area of land is designated
33 100 and the LNAPL is given the reference numeral 112.
34 The LNAPL differs from the DNAPL 12 illustrated in Figure
35 1 in that it is lighter than water and thus tends to
36 collect in pore spaces or cracks in rock/clay formations

1 on or above the existing groundwater table (the
2 groundwater table is essentially the upper surface of the
3 water-saturated zone, above which air partially fills the
4 pore space).

5

6 The method employed in remediating the area of land 100
7 to remove the LNAPL 112 is essentially similar to that
8 described above in relation to Figures 1 to 4, and only
9 the substantial differences will be described herein.
10 Like components of the apparatus utilised to clean the
11 land 100 with the apparatus used to clean the land 10
12 shown in Figures 1 to 4 are given the same reference
13 numerals, incremented by 100.

14

15 In the illustrated embodiment, a vertical borehole 126
16 has been drilled from surface 114 to a location 128
17 adjacent a lower boundary or perimeter of a fluid volume
18 116 of LNAPL 112. An ignition device 130 is inserted and
19 then activated to combust the LNAPL 112 in the fluid
20 volume 116. Combustion of the LNAPL 112 is monitored and
21 by-products optionally collected in the same fashion as
22 that described above.

23

24 Turning now to Figure 6, there is shown a view of the
25 area of land 100 contaminated with LNAPL 112 shown in
26 Figure 5. In Figure 6, however, it is desired to limit
27 travel of the combustion front through the volume 116 of
28 LNAPL from the ignition point, so that the combustion
29 front does not pass into soil present in an area 52.
30 This is achieved by drilling a borehole 54 from surface,
31 running-in a combustion suppressing device 56, and
32 injecting a combustion suppressing fluid 58 (such as
33 water or nitrogen) into the contaminated soil, as
34 indicated by the arrows in the Figure. The injected
35 fluid forms a barrier 60 which restricts passage of the

1 combustion front into uncombusted LNAPL 112 in the area
2 52.

3

4 Turning now to Figure 7, there is again shown a view of
5 the area of land 100 contaminated with LNAPL 112 shown in
6 Figure 5. Once again, it is desired to limit travel of
7 the combustion front through the volume 116 of LNAPL from
8 the ignition point, so that the combustion front does not
9 pass into soil present in an area 52. In the illustrated
10 embodiment, this is achieved by constructing a physical
11 combustion suppressing barrier 62. The barrier 62 is
12 typically formed by excavating a trench 63 and pouring a
13 time-setting bentonite based cementitious material 64 into
14 the trench. Once the material 64 has set, a solid
15 barrier 62 is created preventing travel of the combustion
16 front into the area 52. Alternative methods may be
17 employed for forming the barrier 62. For example, metal
18 sheets (not shown) may be pile-driven into the ground.

19

20 Figure 8 illustrates in schematic plan view the area of
21 land 100 shown in Figure 5. In this case, it is desired
22 to restrict passage of the combustion front into the area
23 52 and also into an area 66 of the ground. The methods
24 illustrated and described in relation to Figures 6 and 7
25 are employed in combination in the method of Figure 8,
26 with the most appropriate technique selected based upon
27 factors including the particular properties of the soil
28 in the contaminated area 100.

29

30 For example, the land in the area 52 may consist largely
31 of rock formations unsuited to the excavating/piling
32 method described in relation to Figure 7. Accordingly,
33 the method of Figure 6 may be followed, with a number of
34 boreholes 54a, 54b and 54c drilled using a drill bit.
35 Combustion suppressing devices in the form of gas supply
36 lines 56a, 56b and 56c (respectively) is installed in

1 each borehole 54 and the suppressant fluid injected
2 through each borehole 54 to form the barrier 60. In
3 contrast, the land in the area 66 may consist largely of
4 soft soil or clay-based formations, and the
5 excavating/piling method of Figure 7 may then be followed
6 to form the barrier 62.

7
8 It will be understood that a number of boreholes 54 may
9 be drilled, spaced around the volume 116, to allow for
10 injection of combustion suppressing fluid during the
11 combustion process, if required. For example, water or
12 nitrogen may be injected during the combustion process in
13 order to maintain smouldering combustion or to suppress
14 the reaction in the event that combustion is being found
15 to speed beyond the desired propagation rates. This may
16 occur when the reaction front approaches the surface. A
17 requirement to inject a combustion suppressant in this
18 fashion may be determined through monitoring of the
19 combustion temperature and the temperature, pressure
20 and/or content of the combustion by-products, as
21 described above.

22
23 Also illustrated in Figure 8 are multiple ignition
24 devices 30a, 30b which are spaced across a width of the
25 volume 116. The devices 30a, 30b are typically activated
26 simultaneously to commence combustion of the LNAPL 112 in
27 the volume 116. Furthermore, a number of oxidant supply
28 boreholes 68a to d are shown, through which an oxidant
29 such as air or oxygen may be injected (as indicated by
30 the arrows 70 a to d). It will be understood that
31 oxidant may be injected during the combustion process in
32 order to promote, sustain, and/or accelerate combustion.
33 For example, in the event that there is insufficient
34 oxygen present even for smouldering combustion to occur,
35 and the combustion is in danger of extinguishing, it may
36 be necessary to inject an oxidant. A requirement to

1 inject oxidant in this fashion may, again, be determined
2 through monitoring of the combustion temperature and the
3 temperature, pressure and/or content of the combustion
4 by-products, as described above.

5
6 It will be understood that combustion of the LNAPL 112
7 may progress from a single ignition point within the
8 volume 116, using one of the devices 30a,b. However, if
9 during progression of the combustion front through the
10 volume 116, monitoring of the combustion process
11 indicates a requirement to ignite the LNAPL 112 at a
12 further location, the other one of the devices 30a,b or
13 even a further device (not shown) may be activated.

14
15 It will be understood that combustion of the LNAPL 112
16 may be thermally self-sufficient in that the or each
17 ignition device 30a,b may be turned off; and may be
18 oxygen sufficient such that no oxidant is required to be
19 supplied through the suppression devices 56. Thus
20 combustion may be self-sustained in that it may be
21 thermally self-sufficient, and/or self-sustained in that
22 it may have sufficient oxygen and thus is not oxygen
23 deficient. Monitoring combustion as described above
24 permits appropriate action to be taken (such as shutting
25 off ignition devices or flow of oxidant) once combustion
26 is self-sufficient. In the event that it is determined
27 that combustion is not thermally sufficient, one or more
28 of the ignition device 30a,b may be maintained in an
29 activated state.

30
31 In general terms, in each of the above described
32 embodiments, it is desired to promote/maintain
33 smouldering combustion, and appropriate remedial action
34 may be taken to promote or maintain such combustion.

35

1 There follows a description of preliminary experiments
2 carried out to verify the validity of the methods and
3 apparatus of the invention described above.

4

5 Equipment and Methods for Preliminary Experiments:

6

7 Equipment:

8

9 Experimental cell: Quartz glass beaker (2 sizes, H.
10 Baumbach & Co., Ltd., Ipswich, UK)

11 1) OD = 103mm, H= 175mm (opaque)

12 2) OD = 106mm, H= 195mm (clear)

13

14 Air diffuser: 8mm coiled copper tube perforated with 2mm
15 holes

16

17 Igniter: 240V, 450W Inconel®-coated cable heater, 3.25mm
18 square cross section x 762mm length (0.128" square cross
19 section x 30" long) (Watlow Ltd, Linby, UK, part
20 #125PS30A48A)

21

22 Gas analysis: CO and CO₂ analyser units (ADC Gas Analysis
23 Ltd, Hoddesdon, UK)

24

25 Thermocouples: 1.5mm and 3mm x 0.5m Inconel® sheath type
26 K thermocouples (RS Components Ltd., Corby, UK, #219-4488
27 (3mm) and #159-095 (1.5mm))

28

29 Data acquisition and recording: Multifunction
30 Switch/Measure Unit (Agilent Technologies, Santa Clara,
31 CA, USA, #34980A)

32

33 Insulation blanket: 240V, 1045W heating tape 2.54cm x 254
34 cm, 1.33W/cm² (Omega Engineering Ltd., Manchester, UK)

35

36 Porous Media (Soil) types:

1

2 a) Coarse quartz sand (Leighton Buzzard 8/16 sand, WBB
3 Minerals, Sandbach, UK)

4 b) Fine quartz sand (Lochaline L60A silica sand, Tarmac
5 Central Ltd., Buxton, UK)

6 c) Peat (field sample)

7 d) Oil sands (field sample; fine sand naturally coated
8 with solidified petroleum)

9

10 Injected oxidant:

11

12 Ambient air, flow rate from zero L/min to approximately
13 20 L/min

14

15 Contaminants:

16

17 a) Freshly manufactured coal tar (Alfa Aesar, Heysham,
18 UK, item #42488; a viscous, multi-component DNAPL)

19 b) Vegetable oil (Sainsbury's Supermarkets Ltd, London,
20 UK; a representative, non-toxic representative viscous
21 LNAPL)

22 c) Dodecane (Fisher Scientific UK Ltd, Loughborough, UK,
23 item #36577-0010; a low viscosity LNAPL)

24 d) Trichloroethylene (TCE) (Fisher Scientific UK Ltd,
25 Loughborough, UK, item #15831-0010; a chlorinated solvent
26 DNAPL)

27 e) 1,2-dichloroethane (DCA) (Fisher Scientific UK Ltd,
28 Loughborough, UK, item #D/1756/15; a chlorinated ethane
29 DNAPL)

30 f) Grease (Electrolube multipurpose MPG50T grease; a
31 viscous, multi-component LNAPL)

32 g) Field sample of coal tar (recently recovered from a UK
33 site upon which a manufactured gas plant operated in the
34 early 1900s; DNAPL)

- 1 h) Solid explosive compound (particulate ammonium nitrate
2 - the primary component of TNT or DNT - mixed with inert
3 components; solid compound that incorporates oxidant)
4 i) Petroleum (naturally occurring solidified coating on
5 oil sands, obtained as part of field sample core).

6
7 Note: In the field, chlorinated solvents are typically
8 not found as pure (i.e., lab grade) chemicals but mixed
9 with up to 30% oil and grease (Dwarakanath, V., R. E.
10 Jackson, and G.A. Pope, 2002. Influence of Wettability
11 on the Recovery of NAPLs from Alluvium. Environmental
12 Science and Technology, 36 (2), 227 -231). Thus, the
13 experiments with solvents employed multi-component
14 mixtures (see Results): 75% TCE + 25% Oil (by weight),
15 75% Dodecane + 25% Oil (by weight), 75% DCA + 25% Grease
16 (by weight).

17
18 Experimental Procedure:

19
20 Figure 9 presents a schematic illustration of the
21 experiment. Preliminary experiments to examine the basic
22 concepts of in situ combustion for remediation of
23 contaminated porous media was carried out in an
24 approximately 1L quartz glass beaker 72 (103mm OD x 175mm
25 H or 106mm OD x 195mm H, *H. Baumbach & Co., Ltd.*). The
26 beaker was filled with a small amount of coarse sand
27 (Leighton Buzzard 8/16 sand, *WBB Minerals*) sufficient to
28 place the air diffuser 74 above the bottom of the beaker
29 by several millimetres. The air diffuser 74 consisted of
30 a length of 8mm copper tubing, bent into a coil and
31 perforated with 1.5-2mm holes along the bottom portion of
32 the tube so that air flow would be directed upward. The
33 chosen porous media was used to bury the air diffuser by
34 several millimetres. The ignition element 76, a coiled
35 3.25mm square cross section x 762mm length Inconel®-
36 coated cable heater (240V, 450W, part #125PS30A48A,

1 *Watlow Ltd*), was placed above the air diffuser 74. The
2 chosen porous media 75 was then added to the beaker to
3 bury the ignition element by 5 centimetres. If the
4 contaminant was a solid, it was mixed with the sand that
5 was emplaced in this step. If the contaminant was a
6 liquid, then it was added subsequently and allowed to
7 percolate downward through the media, typically immersing
8 the cable heater 76. Thus, the emplaced contaminant zone
9 was typically 5 cm height above the ignition element 76.
10 The chosen porous media was then filled to within 5 cm of
11 the top of the apparatus. Three centimetres of fine sand
12 (*Lochaline L60A silica sand, Tarmac Central Ltd.*) were
13 placed at the top of the emplaced porous media to serve
14 as a cap. Up to five 1.5mm or 3mm x 0.5m *Inconel®* sheath
15 Type K thermocouples 78 a to e (parts #219-4488 (3mm) and
16 #159-095 (1.5mm), *RS Components Ltd.*) were inserted into
17 the porous media with their measuring tips exposed at
18 locations of 1 cm intervals above the cable heater 76,
19 with the last thermocouple 78e typically placed outside
20 of the contaminated zone. The thermocouples 78 a to e
21 were connected to a Multifunction Switch/Measure Unit
22 (34980A, *Agilent Technologies*), which logged the data,
23 converted the voltage output to temperature, and passed
24 the results onto a computer.

25
26 The small diameter of the apparatus used in these
27 preliminary experiments means that the system is prone to
28 excessive heat loss (which are not expected in larger
29 experiments or *in situ* applications). To reduce heat
30 losses, the glass beaker 72 was wrapped in heating tape
31 (240V, 1045W, 1.33W/cm², *Omega Engineering, Ltd.*). The
32 heating tape was used turned on first, bringing the
33 system to an elevated (but insufficient for combustion,
34 i.e. approximately 200°C) starting temperature in order to
35 counter heat loss to the surrounding air. Once that
36 temperature was achieved, the cable heater ignition

1 element 76 was turned activated with a current of 1.7
2 Amperes. Shortly afterwards, air flow was initiated,
3 supplied at a flow rate of 20 L/min. Once airflow began,
4 the igniter 76 was allowed to remain on until after the
5 temperature reading from the thermocouple 78a closest to
6 the igniter 76 peaked and began to decrease. CO and CO₂
7 gas measurements (*ADC Gas Analysis Ltd.*) were made of the
8 gas stream exiting the top of the porous media 75, as
9 these are byproducts of combustion. After the ignition
10 element was turned off, air injection was continued, as
11 was temperature, CO and CO₂ recording continued until
12 insignificant CO or CO₂ was present in the offgases and
13 the reaction temperature dropped to levels not likely to
14 support a combustion reaction. After the system had
15 cooled, the porous media 75 was carefully excavated.
16 Photographs were taken to demark the extent of
17 remediation and the degree of remaining contamination was
18 visually evaluated. In some cases, samples were analysed
19 for residual contaminants by gas chromatography; the
20 method follows.

21
22 Gas Chromatography-Mass Spectrometer (GC/MS) was used for
23 the trichloroethylene (TCE) and 1,2-dichlorethane (DCA)
24 experiments. Approximately 10 grams of each soil was
25 placed in a 20mL headspace vial and crimp sealed with a
26 PTFE/silicon septum. The GC/MS method was optimised to
27 identify low levels of DCA and trichloroethylene TCE.
28 Detection limit for TCE and DCA is approximately 0.5 ppm.

29
30 Gas Chromatography-Flame Ionization Detector (GC/FID) was
31 employed for the experiments involving dodecane,
32 vegetable oil and coal tar. Approximately 10g of each
33 sand were placed in a 20mL glass vial. Dichloromethane
34 was added to a level approximately 1cm above the sand.
35 The vials were crimp sealed with PTFE/silicon septa,
36 shaken and placed in a 50oC incubator for 12 hours. The

1 vials were then shaken, sand allowed to settle, and
2 extract removed and transferred to 2mL autosampler vials
3 for analysis. Masses were recorded before and after
4 incubation to ensure limited losses during heating.
5 Detection limit for compounds by this method is
6 approximately 0.5 ppm.

7

8 Results:

9

10 Over 30 experiments have been conducted, examining
11 different ignition sources, experimental setups,
12 equipment devices, fuel types, sand types, etc. A number
13 of those are not presented as they helped to refine the
14 final ignition and experimental processes (outlined in
15 experimental procedure above). This section describes in
16 detail one experiment, that of coal tar combustion in
17 coarse quartz sand, as a representative set of
18 experimental results that followed the described
19 experimental procedure. The results of other experiments
20 using the described procedure are summarised in tabular
21 form in Figure 10.

22

23 Coal Tar Within Coarse Sand Experiment:

24

25 Figure 11 presents the results for the liquid contaminant
26 coal tar within coarse quartz sand, with the graph lines
27 80a to e representative of the measured temperature vs.
28 time at the corresponding thermocouples 78a to e. Figure
29 11 also illustrates the percentage (by volume) of CO and
30 CO₂ in the combustion products.

31

32 The initial temperature rise is associated with the
33 heating tape. In experiments conducted without the tape,
34 a similar temperature rise is observed as a result of the
35 ignition element but the heat is less equally
36 distributed, dominated instead at the lowest thermocouple

1 78a, which is next to the igniter. The scale of the test
2 apparatus results in increased heat losses, which need to
3 be compensated by a low temperature heating tape (i.e.
4 approximately 200°C). It is noted that the heating tape is
5 required only due to the small size of this 'proof of
6 concept' experimental apparatus; in a full scale
7 experimental apparatus, as in the field, the porous media
8 volume is large enough to act as the insulator and
9 therefore heat losses of this type will not occur and
10 such additional heat application will not be required.
11 This is consistent with a theoretical analysis that
12 scales the results to larger systems and with extensive
13 experimental experience in the smouldering combustion of
14 solid porous foam (e.g., cushions) at a variety of
15 scales.

16
17 Figure 11 demonstrates that when the ignition element 76
18 is turned on, the temperature increases rapidly in its
19 immediate vicinity. The temperature increase again
20 accelerates when the air (oxidant) flow is begun. Figure
21 11 demonstrates that *in situ* combustion initiates
22 relatively quickly after this time, as evidenced by the
23 appearance of CO and CO₂, which are gaseous combustion
24 products. Their appearance is taken to coincide with the
25 ignition temperature and ignition time, observed to be
26 400 °C and 57 min in this experiment, respectively. *In*
27 *situ* temperatures typically rise quickly following the
28 onset of combustion, with the maximum temperature taken
29 as the maximum peak achieved in any thermocouple 78 (in
30 this case, the second thermocouple 78b from the ignition
31 element 76).

32
33 In this experiment, the ignition element was turned off
34 10 minutes after combustion began while the oxidant
35 delivery is maintained. After this time, Figure 11
36 illustrates that self-sustaining combustion is observed

1 in this experiment, meaning that the combustion front is
2 propagating through the contaminated zone without the
3 addition of external energy. Evidence for this includes
4 the succession of temperature peaks at successive
5 locations further from the ignition point (e.g., the --
6 sustained maximum temperature between thermocouples 78a
7 and 78b (TC1 and TC2) and the sustained maximum
8 temperature between thermocouples 78c and 78d (TC3 and
9 TC4), as indicated by the graph lines 80a to d. Further
10 evidence is the successive 'cross-over of temperature
11 profile plots (e.g., the temperature at TC4 is still
12 increasing while that at TC3 is decreasing; note that TC5
13 is not within the contaminant zone). Heat is transferred
14 from high temperature to low temperature, thus a cross
15 over indicates that heat is being transferred from
16 Thermocouple 78d (TC4) to Thermocouple 78c (TC3)
17 evidencing that significant heat generation is occurring
18 at the location of Thermocouple 78d (TC4). The continued
19 production of combustion gasses (CO and CO₂) provide
20 further evidence that combustion continued after the
21 ignition element 76 was turned off. The velocity of the
22 propagating combustion front is measured by dividing the
23 spatial distance between thermocouples 78 by the time
24 between maximum temperature peaks; in this case the
25 velocity is estimated at 4.1×10^{-5} m/s. Literature values
26 with different fuels indicate that these are typical
27 smouldering combustion propagation velocities. The
28 final decrease in temperature at each location follows a
29 similar profile, representative of energy dissipation
30 after all of the contaminant has been destroyed and the
31 reaction has locally self-extinguished.

32
33 By way of comparison, the base case experiment was
34 repeated exactly but with no fuel/contaminant in the
35 porous media. The thermocouple 78d (TC 4 - sand only)
36 temperature profile 80f is directly comparable with TC 4

1 from the coal tar experiment. The area under a
2 temperature history is proportional to the energy
3 released during the process, therefore the difference
4 between the two represents the energy produced by the
5 combustion of the contaminant. Estimation of the areas
6 under each curve demonstrates that the energy produced by
7 the combustion process in the immediacy of Thermocouple 4
8 is more than four times greater than the energy delivered
9 by the ignition system at this location. This provides
10 clear evidence that once ignition has been achieved, the
11 energy required for self-sustained propagation can be
12 delivered by the combustion of the contaminant with no
13 further need for subsequent ignition devices. All excess
14 energy will be delivered forwards and thus used to
15 accelerate the reaction front.

16
17 Photographs of the contaminant and porous material were
18 taken both before and after the experiment, which
19 revealed the thoroughness of remediation in the
20 combustion zone: no observable contaminant remained.
21 Physical handling of the remediated soil and comparing
22 bulk density measurements before and afterwards also
23 confirmed no contamination remaining. The photos also
24 showed that the coal tar located beneath the igniter 76
25 (and thus out of the combustion zone) does not get
26 remediated despite being substantially heated; instead
27 the coal tar and sand become partially solidified upon
28 cooling. It was also observed that remediation by *in*
29 *situ* combustion changes the soil colour to red, which is
30 the result of high temperature iron oxidation and is
31 typically observed in soil affected by forest fires where
32 the temperature exceeded 600 °C.

33
34 Gas Chromatography (GC) analysis was utilised to assess
35 the extent to which compounds remained in the soil
36 excavated from the combustion zone. As denoted in the

1 final column of Figure 10, only a trace level of residual
2 compounds were detected, with a signal close to the
3 detection limit of the method and insufficient for
4 quantification.

5

6 Figure 10 presents summary results from 13 other
7 experiments conducted with the same method as described
8 for the coal tar/coarse sand experiment presented.
9 Figure 10 illustrates that in situ combustion was
10 successfully achieved in all of the experiments. This
11 includes 3 additional common NAPLs and two solid
12 materials. The Figure also indicates successful in situ
13 smouldering combustion for a variety of porous media
14 types, for a variety of fluid saturations (both water and
15 NAPL), for field-derived samples as well as laboratory
16 samples, and heterogeneous conditions in the source zone
17 (i.e., combustion zone). In only two experiments was
18 there any contaminant observed to remain in the
19 combustion zone; in these cases channelling of the
20 oxidant clearly caused the oxidant to bypass one location
21 which did not achieve combustion. GC analysis confirmed
22 the virtual elimination of all organic compounds from the
23 combustion zone in the 8 experiments subjected to
24 analysis. The combustion propagation velocities in Figure
25 10 are typical of smouldering combustion being the
26 dominant combustion regime in these experiments.

27

28 Two repeat base case (i.e., coal tar in coarse sand)
29 experiments were conducted and very similar results to
30 those described in Figure 10 were obtained, indicating
31 the reproducibility of the method. A third repeat was
32 conducted but in this case the air flow was terminated at
33 approximately 5 minutes after the ignition element was
34 turned off; in other words, after self-sustaining
35 combustion had been established but before all of the
36 contaminant had been combusted. This experiment

1 demonstrated that combustion ceased in this case very
2 soon after the oxidant input was terminated. This
3 demonstrates that the reaction can be extinguished in by
4 removing the oxidant injection stream. Moreover, upon
5 cooling, the resulting sandpack was found to not be
6 completely remediated, instead containing a substantial
7 solidified mass of heated coal tar and sand. This mass
8 could not be removed from the experimental apparatus;
9 therefore, at this time, the ignition process was applied
10 to the cooled mass and in situ combustion was
11 successfully restarted. At the end of this second
12 combustion phase for this experiment, the sand was easily
13 excavated and no observable coal tar remained in the
14 combustion zone. This indicates that the process can be
15 stopped and successfully restarted and underscores that
16 heating without combustion does not achieve remediation,
17 at least for the case tested.

18
19 The above experimental data clearly demonstrates that the
20 method and apparatus of the present invention is viable
21 for remediating land contaminated with combustible
22 materials such as DNAPLS and LNAPLS *in situ*.

23
24 Existing thermal methods are promising for in-situ NAPL
25 remediation but are prohibitively costly. In the present
26 invention, propagation of a combustion front through a
27 porous medium can be achieved for very low fuel content
28 if the reaction propagates in the forward mode (Figure
29 3). Research has shown that this can be applied to
30 hydrocarbon liquids embedded in the subsurface and that
31 the process can be modulated to propagate in an optimal
32 manner. Energy input may be limited to initial ignition
33 of the NAPL 12 near the base of the source zone 16, after
34 which a self-sustaining reaction may proceed. The
35 technique exhibits the advantages of existing thermal
36 technologies (including effective mass reduction and

1 indifference to permeability contrasts), and will be much
2 more cost-effective since continuous energy input is not
3 typically required (i.e., self-sustaining). Moreover,
4 the combustion front will naturally follow the connected-
5 phase NAPL 12 (i.e., fuel) pathway through the pore
6 spaces 36, even if those are not known/determined in
7 advance. The method and thus the combustion process may
8 therefore be effectively self-guiding. Thus, significant
9 advantages over existing chemical, physical and
10 biological technologies are provided, which often:
11 inefficiently target a much greater subsurface volume
12 than the NAPL 12 itself; rely on expensive chemical
13 additions that tend to bypass contaminant zones and
14 become diluted below effective levels; and are
15 ineffective around low permeability regions upon which
16 the NAPLs 12 tend to accumulate.
17
18 Various modifications may be made to the foregoing
19 without departing from the scope of the present
20 invention.

Claims:

1. A method of remediating land contaminated with a combustible material, the method comprising the steps of:
 - 5 locating a subterranean volume of combustible material in land to be remediated, wherein the land defines a porous matrix and the combustible material is present in the porous matrix;
 - igniting the combustible material to combust the combustible material in a smouldering combustion process by applying heat to the combustible material with
10 an ignition device followed by supplying an oxidant to the combustible material; and
 - when the smouldering combustion process is established, deactivating the ignition device and thereby remediating the land.
2. A method according to claim 1, in which the method comprises controlling
15 at least one of: an extent of heating of the combustible material; a rate of supplying an oxidant to the combustible material; and a rate of supplying a combustion suppressant to the combustible material, to provide the smouldering combustion process.
- 20 3. A method according to claim 2, in which the method further comprises monitoring combustion of the combustible material and performing the controlling step in dependence on the monitoring of the combustion.
4. A method according to claim 3, in which the controlling step is performed
25 to at least one of: establish smouldering combustion; and maintain smouldering combustion.
5. A method according to any one of claims 1 to 4, in which smouldering combustion of the combustible material is maintained in the presence of either of:
30 -a combustible material and an oxidant supplied to the combustible material; or
-a combustion suppressant supplied to the combustible material.

6. A method according to claim 1, in which the land defining the porous matrix consists of at least one of: particulate matter; and a fractured rock environment.
- 5 7. A method according to claim 1, in which the method further comprises monitoring the combustible material for smouldering combustion and deactivating the ignition device when smouldering combustion is present.
- 10 8. A method according to any one of claims 1 to 7 comprising combusting the material in situ.
- 15 9. A method according to any one of claims 1 to 8, in which following ignition of the combustible material a combustion front is generated which progresses away from at least one point of ignition and through the combustible material.
10. A method according to any one of claims 1 to 9 comprising igniting the combustion material at a plurality of locations within the material volume.
- 20 11. A method according to any one of claims 1 to 10, comprising extinguishing combustion after a desired time period.
- 25 12. A method according to claim 11, comprising extinguishing combustion at a desired location by creating one or more combustion barriers.
- 30 13. A method according to any one of claims 1 to 12, comprising combusting the combustible material in a self-sustaining smouldering combustion process.
14. A method according to any one of claims 1 to 13, comprising igniting the material using an ignition device; monitoring combustion and, where the combustion is oxygen starved, supplying an oxidant to maintain combustion; and selectively changing the supply of oxidant to control a propagation rate of combustion.

15. A method to any one of claims 1 to 13, comprising igniting the material using an ignition device; monitoring combustion and, where the combustion is oxygen starved, supplying an oxidant to maintain combustion; and selectively changing the supply of oxidant to extinguish combustion.
16. A method according to any one of claims 1 to 13, comprising igniting the material using an ignition device; monitoring combustion and, where the combustion is not oxygen starved, selectively injecting a combustion suppressant to control a propagation rate of combustion.
17. A method according to any one of claims 1 to 13, comprising igniting the material using an ignition device; monitoring combustion and, where the combustion is not oxygen starved, selectively injecting a combustion suppressant to extinguish combustion.
18. A method according to any one of claims 1 to 17, further comprising injecting, using at least one fluid injection device, an oxidant into the combustible material to modify the rate, degree or extent of the smouldering combustion process.
19. A method as claimed in claim 13, comprising combusting the material in a thermally self-sufficient combustion process.
20. A method as claimed in claim 13, comprising combusting the material in an oxygen sufficient combustion process.
21. A method as claimed in claim 19, comprising igniting the material using an ignition device and, once the combustion process is thermally self-sufficient, deactivating the ignition device.
22. A method as claimed in claim 1, wherein the combustible material is a fluid.

23. A method as claimed in claim 9 or 10, comprising controlling combustion such that the combustion front follows a distribution of the combustible material away from the ignition point.
- 5
24. A method as claimed in claim 1, comprising monitoring temperature in the land contaminated with the combustible material at a plurality of locations.
25. A method as claimed in claim 11, comprising monitoring by-products of the combustion process.
- 10
26. A method as claimed in claim 25, comprising monitoring the constituents and volumes of gaseous by-products resulting from combustion of the material.
27. A method as claimed in claim 1, comprising monitoring combustion of the material in real-time during the combustion process.
- 15
28. A method as claimed in claim 1, comprising monitoring the extent of combustion of the material after combustion has ceased.
- 20
29. A method as claimed in any one of the claims 24 to 28, comprising modifying the combustion of the material by modifying an amount or ratio of a supply of air or oxygen, or by supplying an additional fuel, or by supplying a combustion suppressant, or by deactivating the ignition device, or by reducing or terminating the addition of oxidant.
- 25
30. A method as claimed in claim 29, comprising when an oxidant is supplied, following monitoring of combustion, modifying the flow rate of oxidant supplied.
31. A method as claimed in claim 29 or 30, comprising igniting the material in at least one further location.
- 30

32. A method as claimed in any one of claims 24 to 28, comprising supplying a combustion suppressant in order to suppress and thereby control combustion.

5 33. A method as claimed in claim 1, comprising super-adiabatically combusting the material.

34. A method as claimed in claim 1, comprising monitoring combustion in order to promote smouldering of the material.

10 35. A method as claimed in claim 1, comprising extinguishing combustion following travel of a combustion front a desired distance through the material.

36. A method as claimed in claim 12, comprising forming a combustion boundary by setting up one or more combustion barriers.

15 37. A method as claimed in claim 36, comprising constructing a physical barrier.

38. A method as claimed in claim 37, comprising excavating a trench and supplying a material into the trench to form a cut-off wall.

20 39. A method as claimed in claim 37, comprising pile-driving one or more sheets into the ground to form a cut-off wall.

25 40. A method as claimed in claim 36, comprising forming a fluid suppression wall by injecting a suppressant fluid into the ground in a plurality of locations.

41. A method as claimed in claim 1, comprising accessing the volume of combustible material from surface by drilling an access borehole from surface to a location intersecting the volume of material.

30 42. A method as claimed in claim 41, comprising directing the borehole to intersect the volume at a lower boundary of the volume, and igniting the material to

cause the combustion front to be initiated at the bottom of the volume and to propagate upwards.

43. A method as claimed in claim 41 or 42, comprising locating an igniting device
5 within the borehole and activating the device.

44. A method as claimed in claim 43, comprising collecting combustion by-products for analysis and disposal.

10 45. A method as claimed in claim 1, comprising monitoring combustion by-products in the land following combustion.

46. A method as claimed in claim 1, comprising monitoring combustion by-products in the land during combustion.

15

47. Apparatus for remediating land contaminated with a combustible material, the apparatus comprising an ignition device, the ignition device adapted to be located below ground level for igniting a subterranean volume of combustible material in land to be remediated, to combust the material in a smouldering
20 combustion process and thereby remediate the land.

48. Apparatus as claimed in claim 47, wherein the ignition device is adapted to heat the combustible material in order to ignite the material.

25 49. Apparatus as claimed in claim 47, wherein the ignition device is an electric resistance heater.

50. Apparatus as claimed in claim 49, wherein the heater comprises an electric element having a corrosion resistant coating adapted to shield the element from
30 corrosive materials.

51. Apparatus as claimed in claim 47, wherein the ignition device is adapted to generate an electrical discharge to ignite the material.

52. Apparatus as claimed in any one of claims 47 to 51, comprising at least one fluid injection device for injecting an oxidant into the material volume, to promote and/or modify the rate, degree, or extent of combustion.

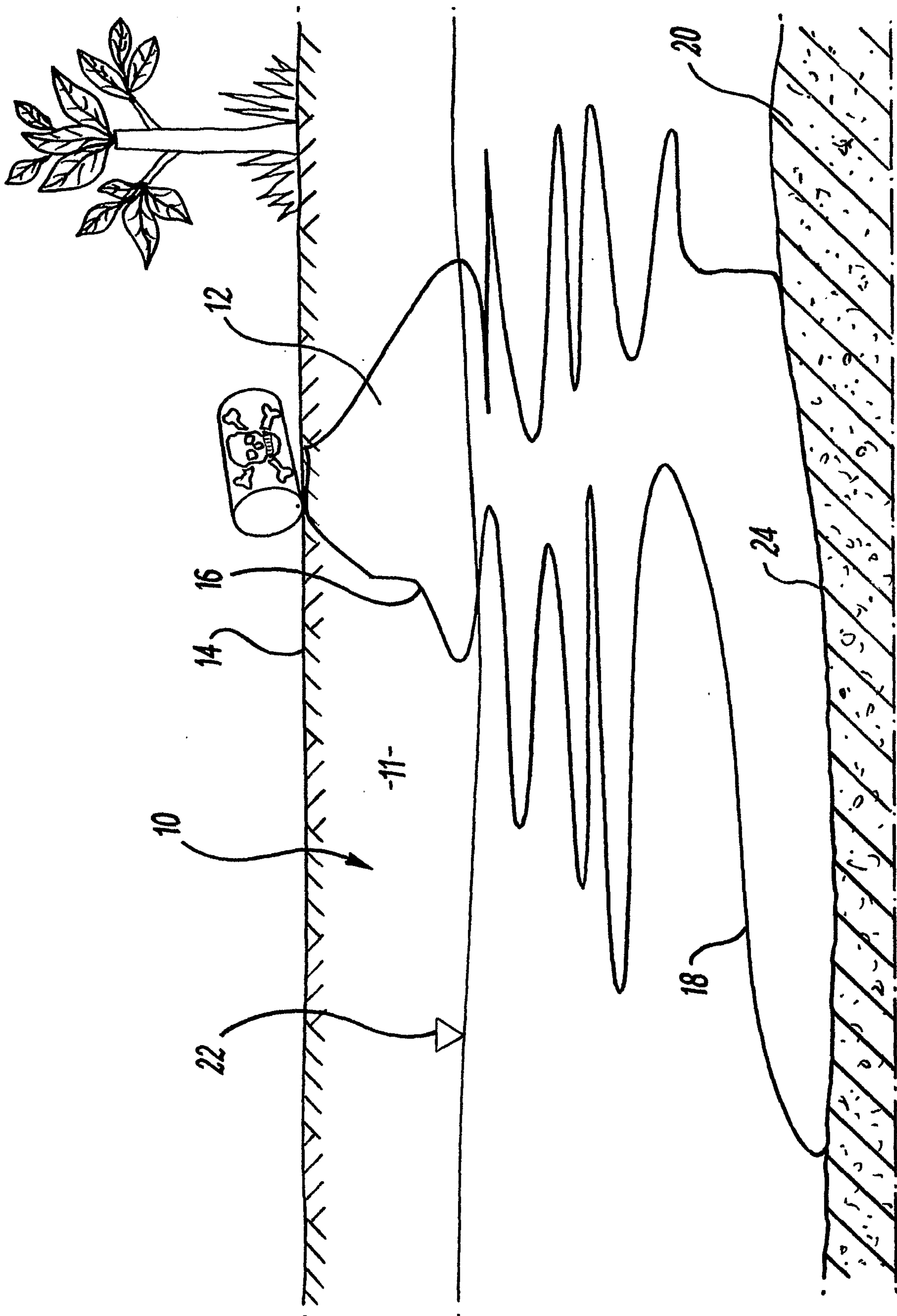
53. Apparatus as claimed in claim 52, wherein the fluid injection device comprises at least one flow line extending from surface into the volume.

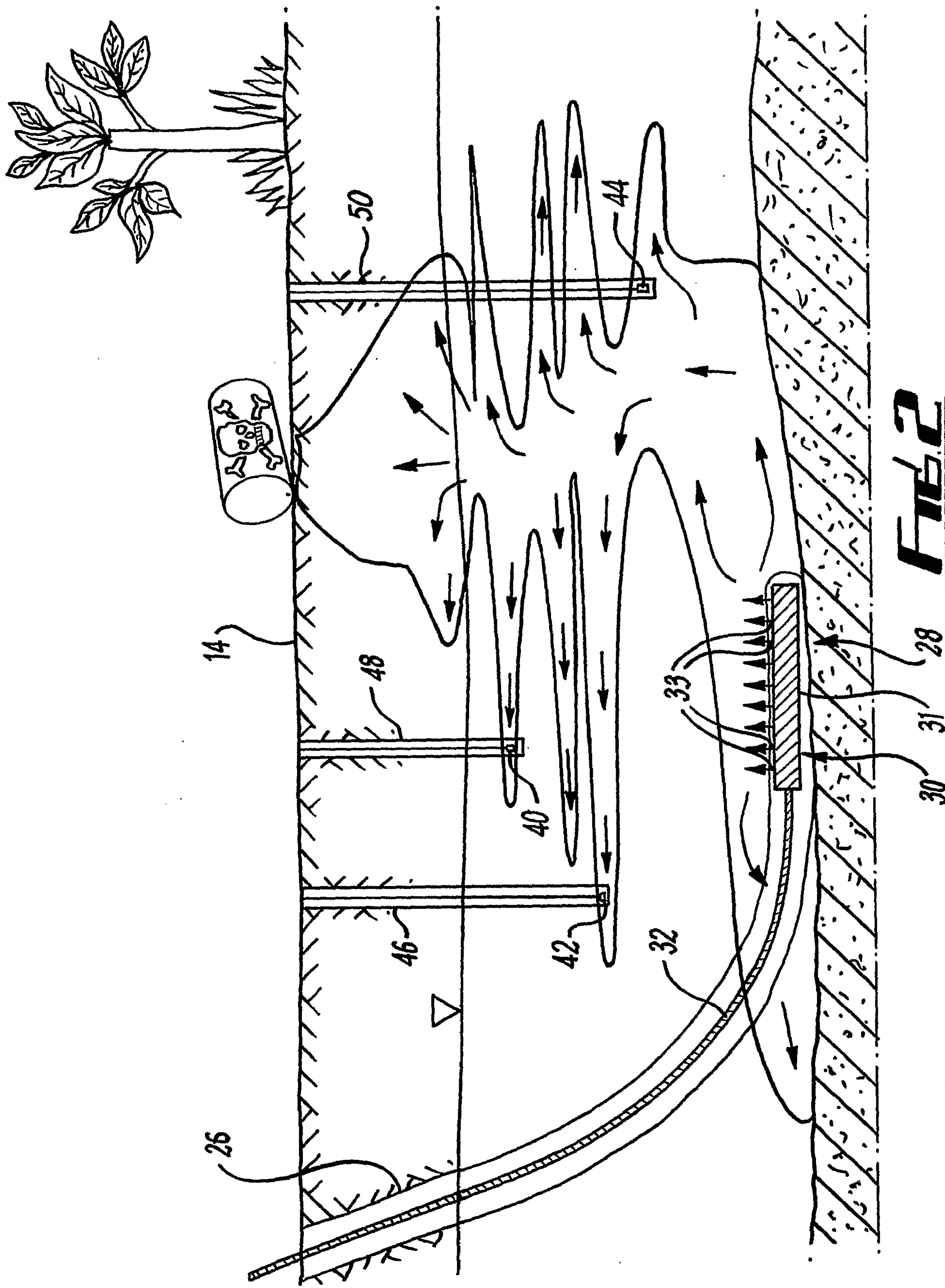
54. Apparatus as claimed in claim 53, wherein the fluid injection device comprises a manifold having a plurality of outlets, the manifold connected to a main fluid flow line, for supply of fluid through a single flow line to a plurality of locations within the volume.

55. Apparatus as claimed in any one of claims 47 to 54, comprising at least one fluid injection device for injecting a combustion suppressant into the material volume, to suppress combustion.

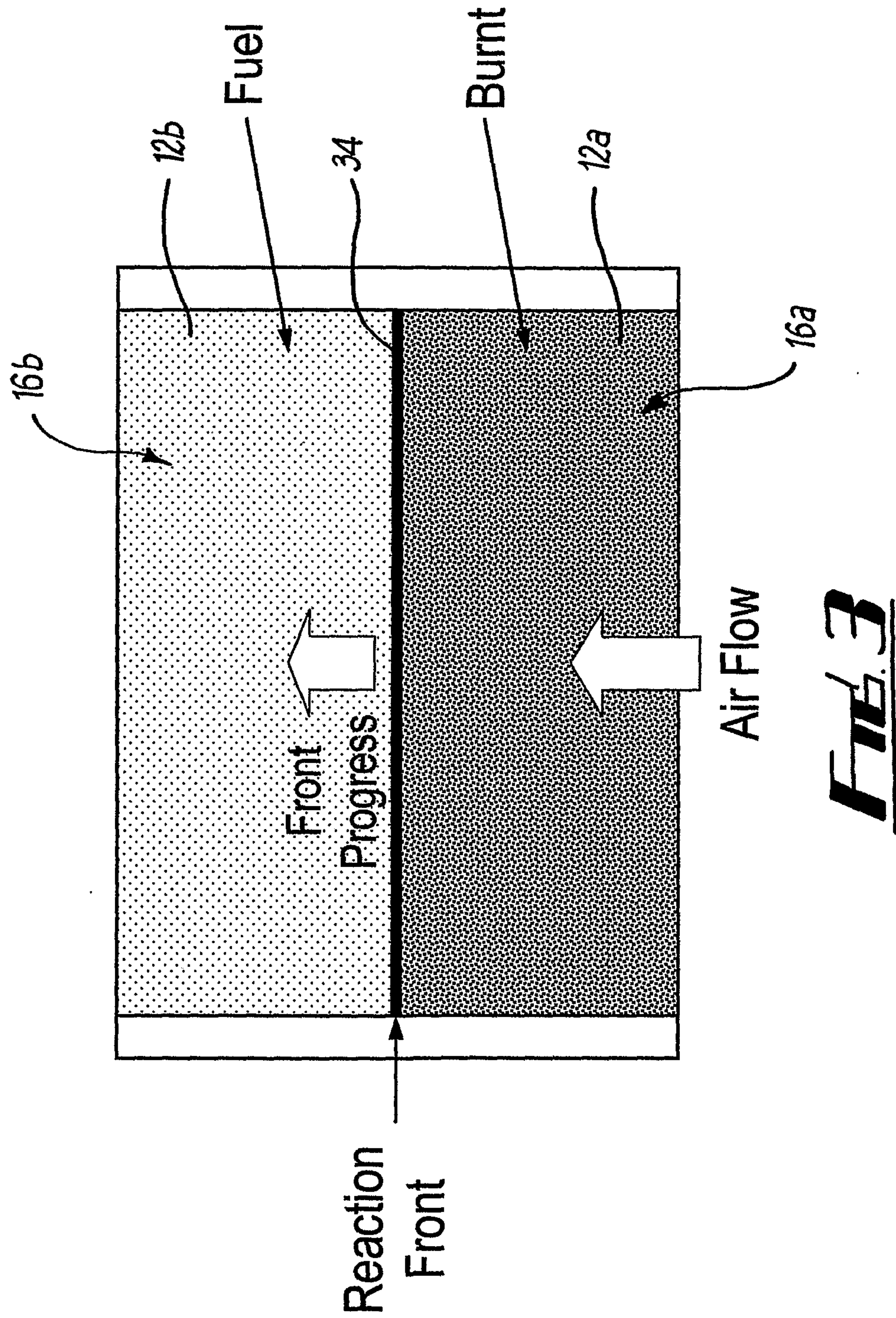
56. Apparatus as claimed in any one of claims 47 to 55, comprising at least one sensor for monitoring combustion of the material.

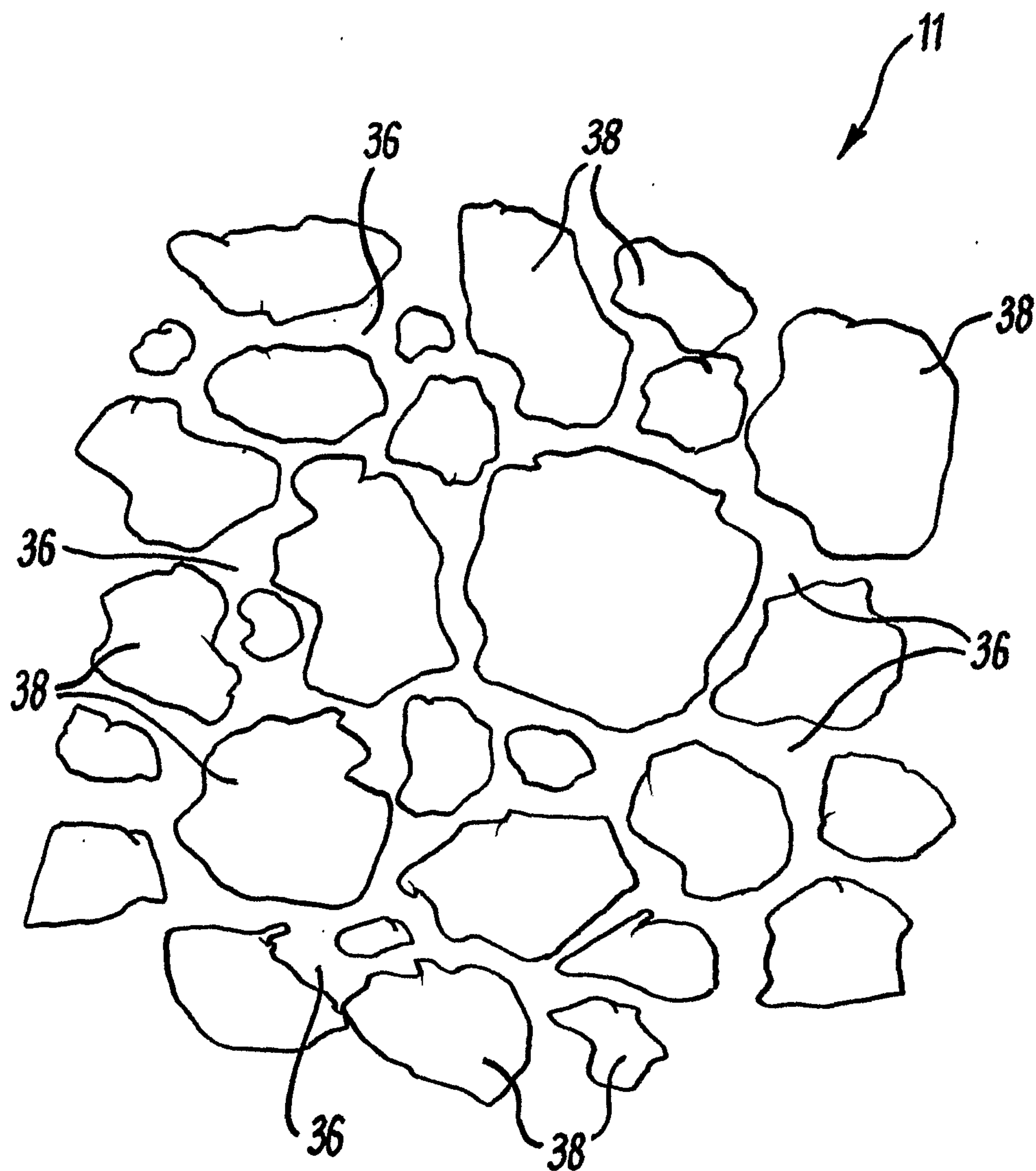
57. Apparatus as claimed in claim 56, comprising at least one sensor selected from the group comprising: a temperature sensor; a pressure sensor; and a gas sensor for determining the volume and constituent of gaseous by-products resulting from combustion of the material.

**Fig. 1**



SUBSTITUTE SHEET (RULE 26)



**FIG. 4**

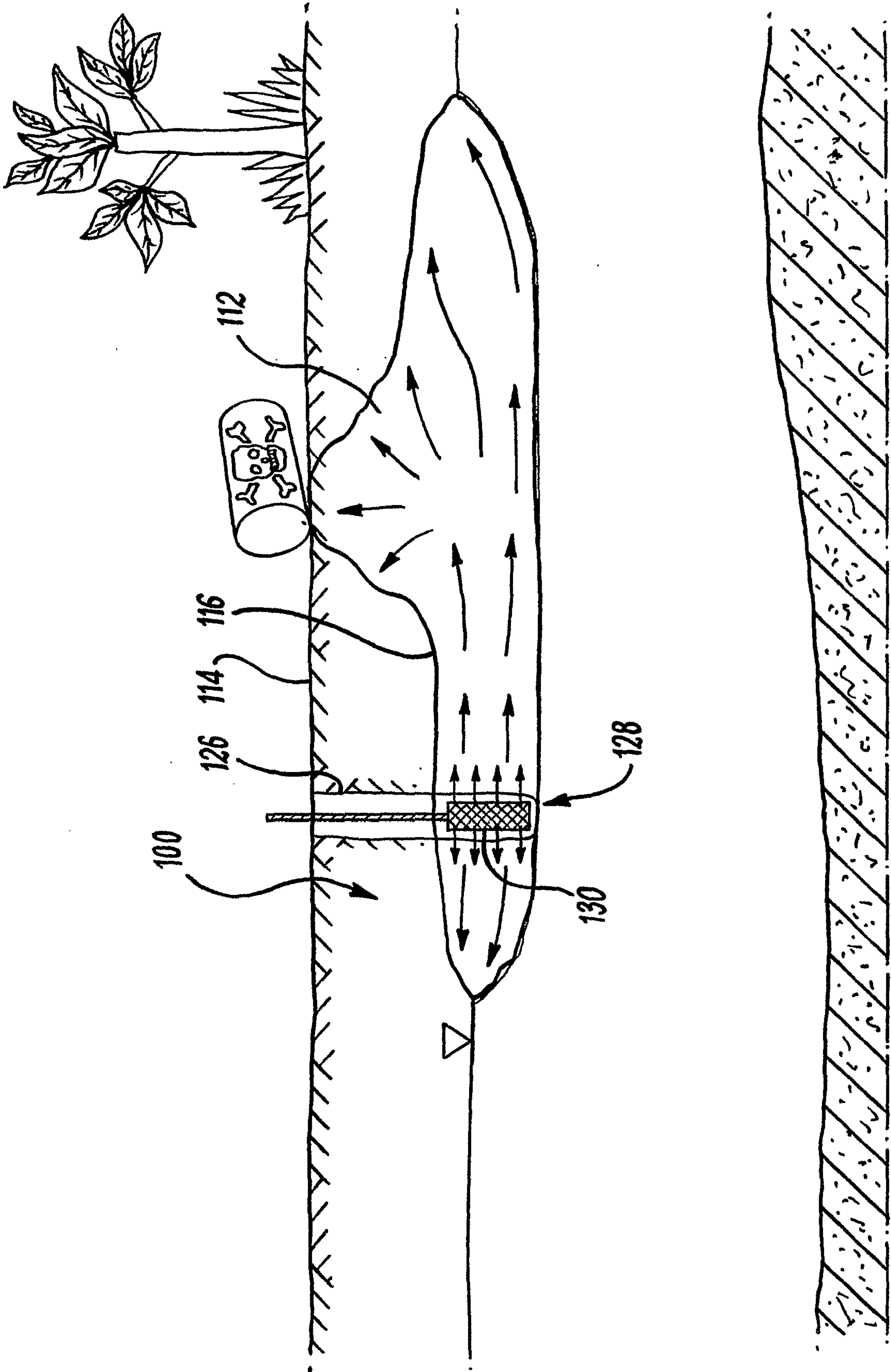


FIG. 5

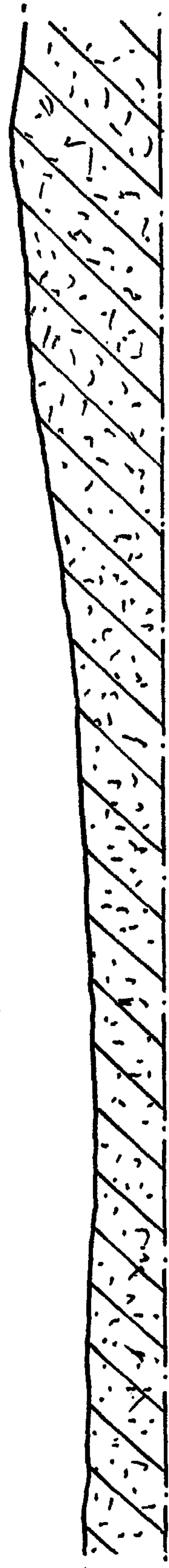
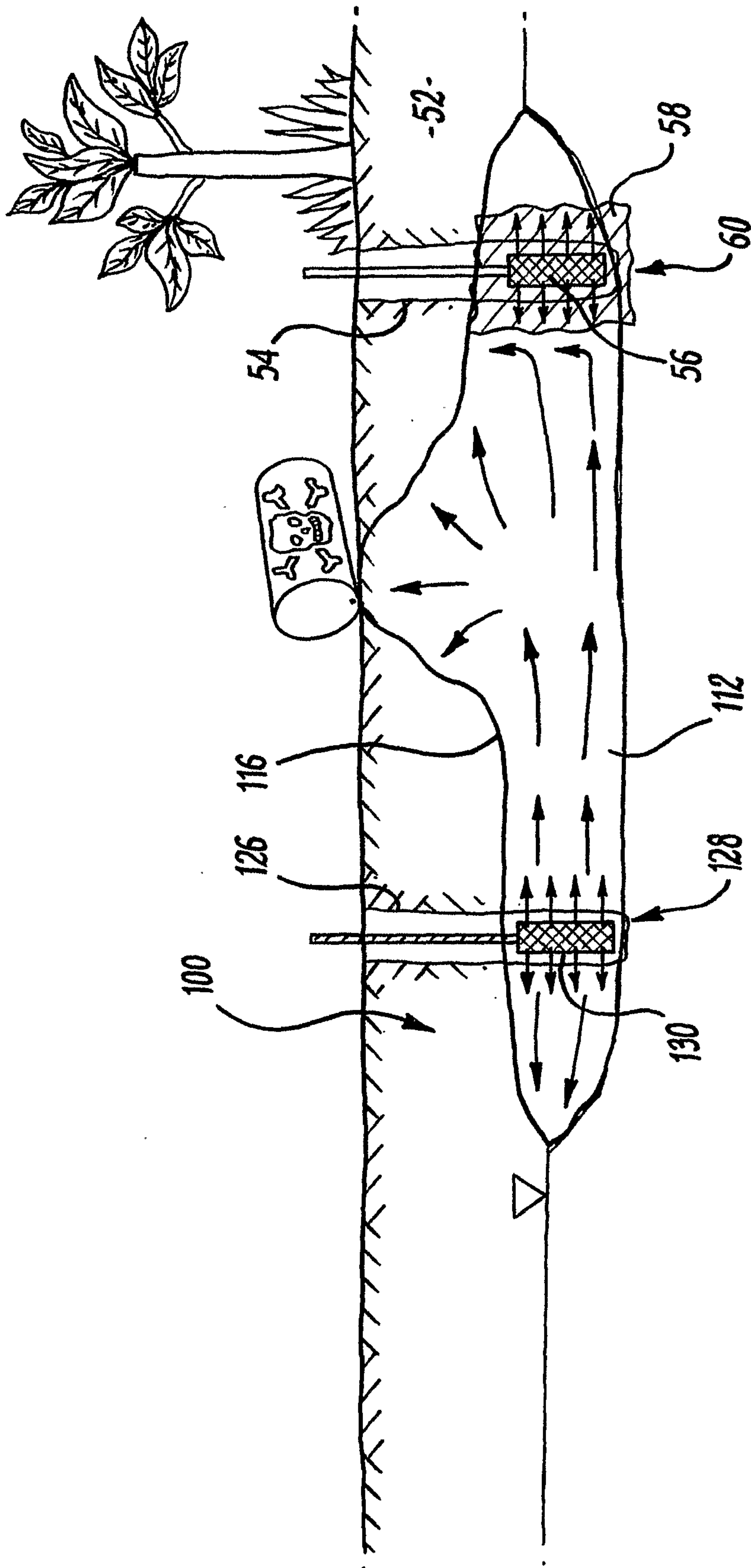
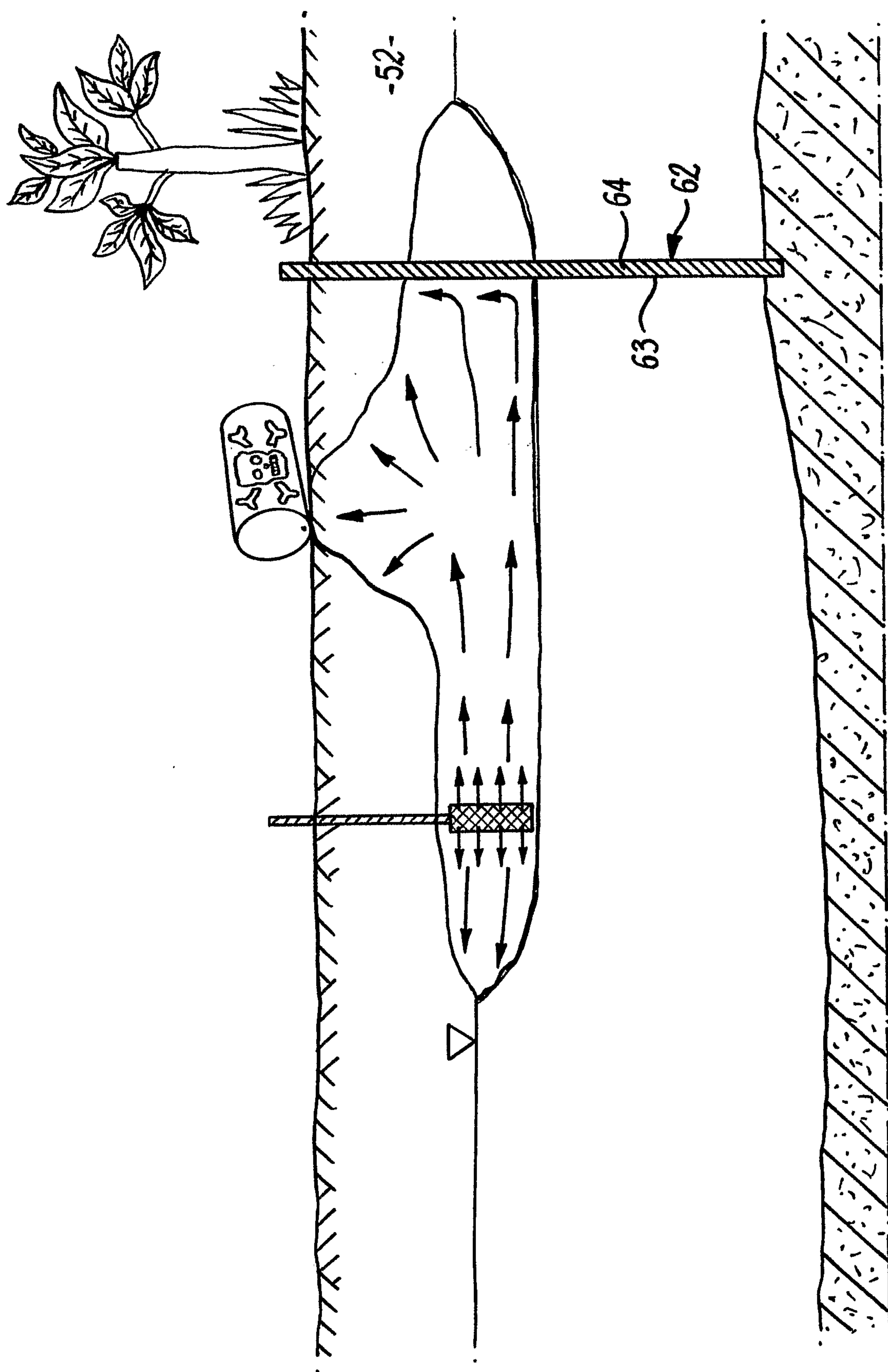
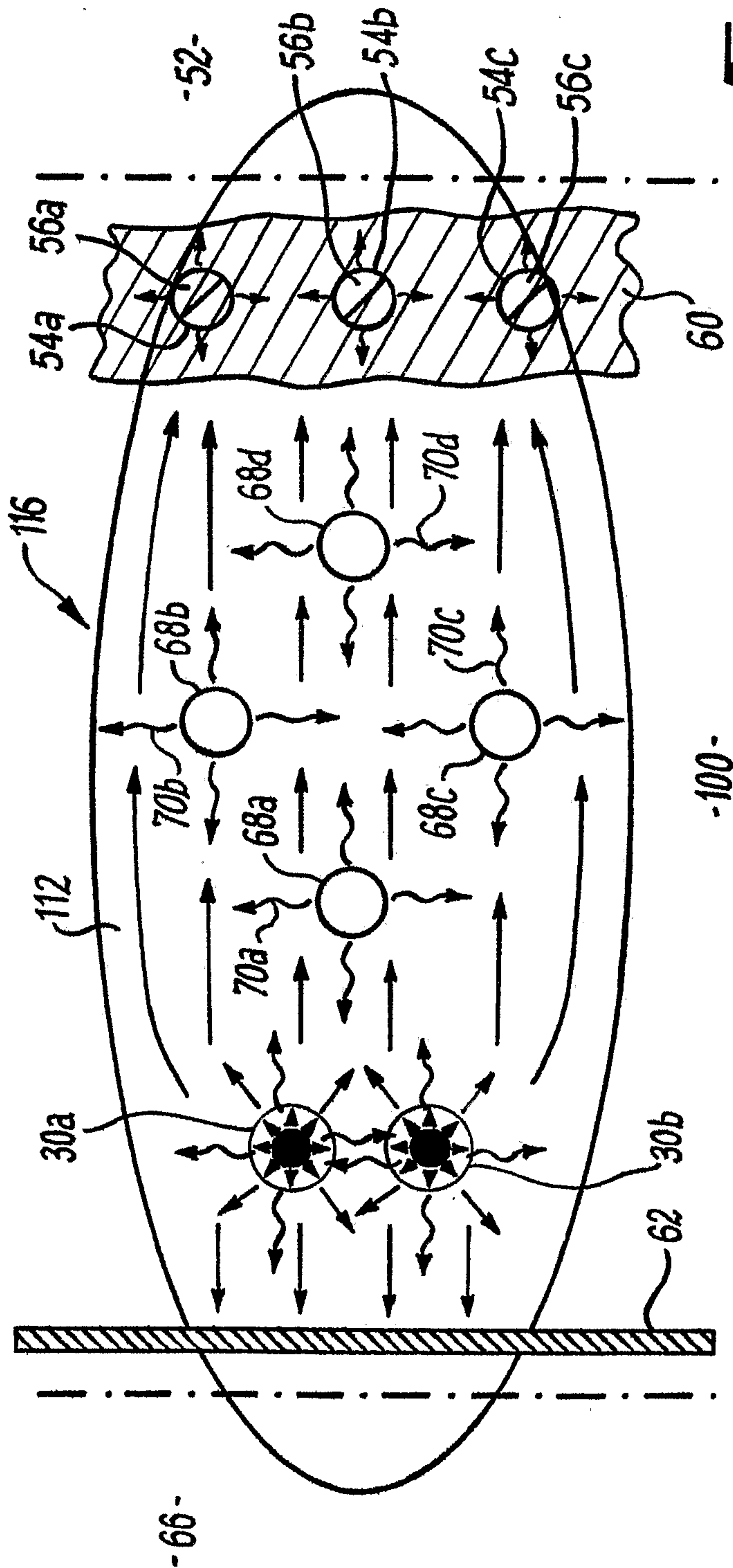


Fig. 6



**Fig. 8**

Limit of NAPL source zone

Ignition and oxidant addition wells

Oxidant addition (and subsurface monitoring and near-surface gas extraction) wells

Oxidant flow (e.g., air)

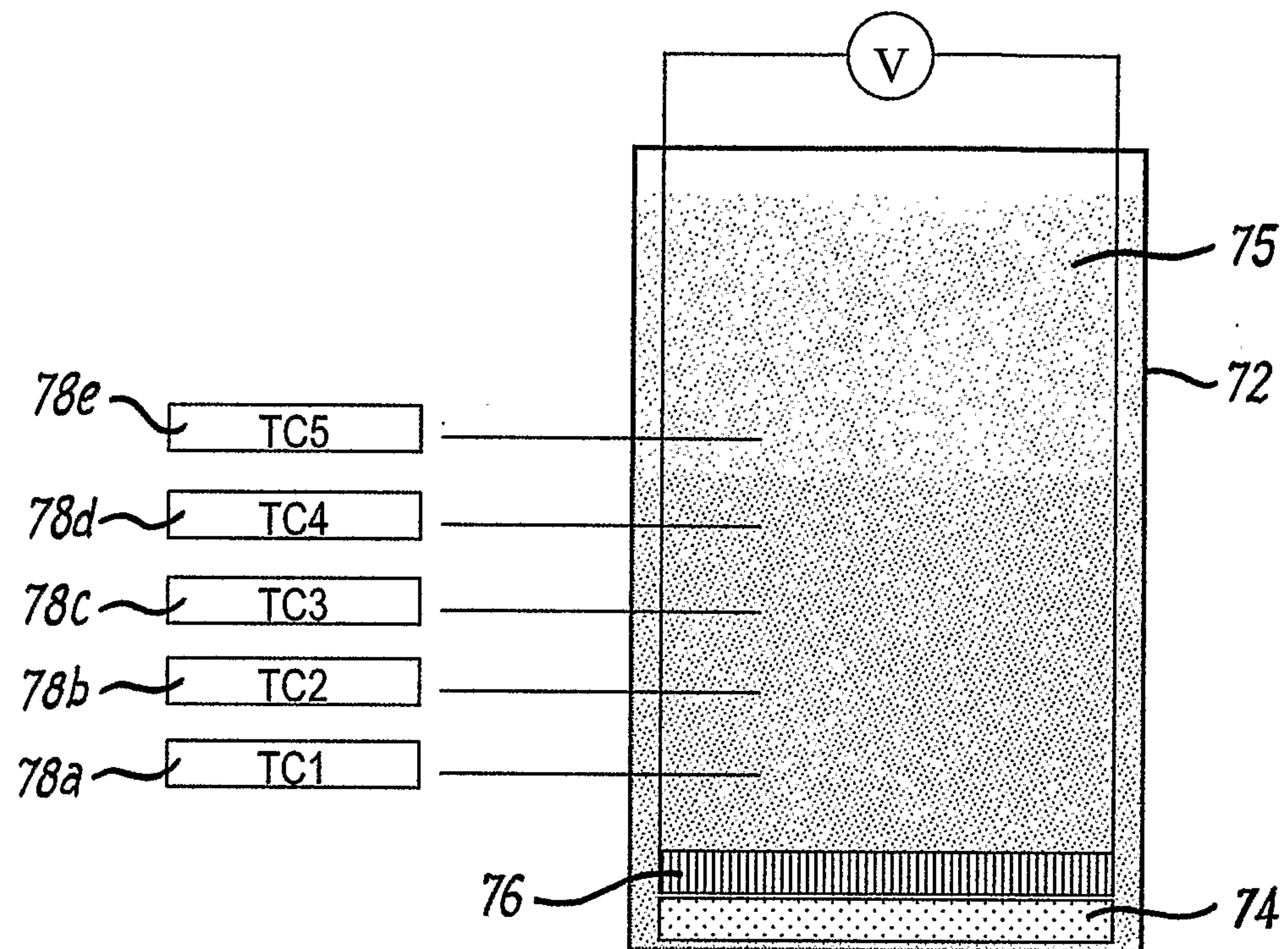
Progress of combustion front (i.e., NAPL destruction)

Boundary for desired treatment

Physical combustion barrier (e.g., bentonite wall or sheet piling)

Gaseous combustion barrier (e.g., nitrogen-sparged reaction-suppression zone)

Gas suppressant injection well

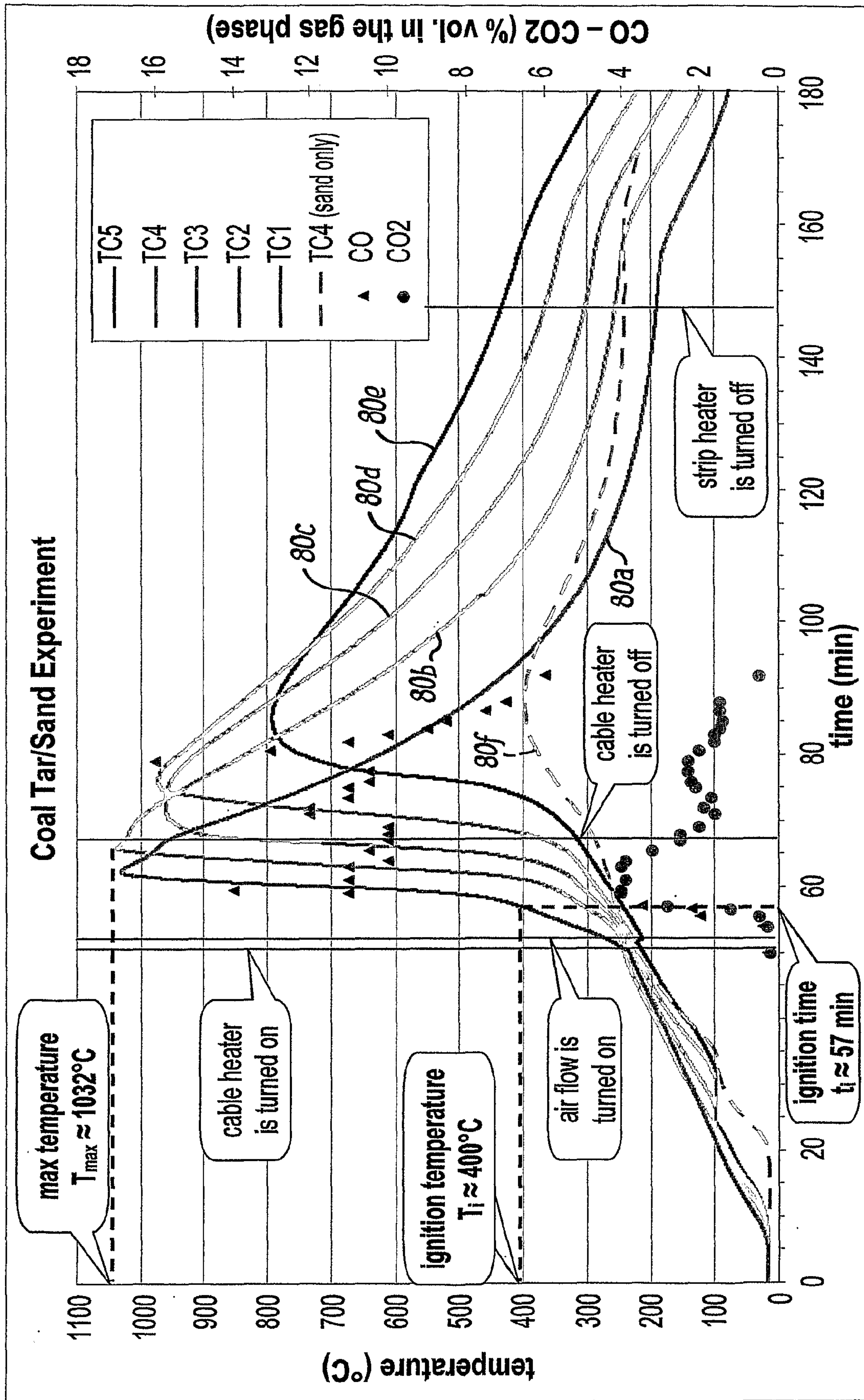
**FIG. 9**

Category	Soil type	Contaminant	Successful In Situ Combustion? (yes/no)	Ignition Temp (°C)	Maximum Temp (°C)	Time to Ignition (including preheating) (min)	Combustion Propagation Velocity (m/s)	Completely Remediated (Visual Inspection)? (yes/no) ¹	Completely Remediated (GC Analysis)? (yes/trace/NA) ²
Base Case	Coarse sand	Coal tar	Yes	400	1032	57	4.1x10 ⁻⁵	Yes	Trace
Vary Contaminant	Coarse sand	Vegetable oil	Yes	203	786	44	-	Yes	Yes
	Coarse sand	Solid Explosive	Yes	192	370	58	-	Yes	NA
	Coarse sand	DCA/grease	Yes	200	688	22	-	Yes	Trace
	Coarse sand	TCE/oil	Yes	350	689	24	-	Yes	Trace
	Coarse sand	Dodecane/oil	Yes	240	660	32	-	Yes	Trace
	Fine sand	Coal tar	Yes	400	822	23	1.4x10 ⁻⁵	No	Trace
Vary Porous Media	2 layers: coarse over fine sand	Coal tar	Yes	425	1139	43	8.3x10 ⁻⁵	Yes	Yes
Heterogeneity	2 contaminated coarse sand layers separated by a clean fine sand layer	Coal tar	yes	400	1139	47	8.3x10 ⁻⁵	Yes	NA
Vary Fluid Saturations	40% water -saturated coarse sand	Coal tar	Yes	470	1040	47	7.4x10 ⁻⁵	Yes	Trace
	Coarse sand	30% Coal tar saturation	Yes	400	715	48	4.4x10 ⁻⁵	No	Yes
Field Samples	Peat	Field coal tar	Yes	300	1010	47	3.5x10 ⁻⁵	Yes	NA
	Fine sand	Field coal tar	Yes	250	1053	52	9.8x10 ⁻⁵	Yes	Trace
	Oil sands (fine sand grain size)	solidified petroleum coating	Yes	300	1066	35	1.7x10 ⁻⁴	Yes	NA

¹ 'Yes' = no observable contaminant remaining in the targeted combustion zone (via feel, smell, eyesight, or bulk density), 'No' = a portion of the combustion zone remained partially contaminated due to channelling of the oxidant around this area; the portion of the combustion zone contacted by oxidant has no observable contaminant remaining.

² 'Yes' = no compounds detected, 'Trace' = compounds detected near detection limit of instrument, amount too small to quantify, 'NA' = not analysed

Fig. 10

**Fig. 11**

