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Gilmore et al.

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(54) **METHODS AND APPARATUSES FOR REAGENT DELIVERY, REACTIVE BARRIER FORMATION, AND PEST CONTROL**

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(63) Continuation-in-part of application No. 09/429,235, filed on Oct. 28, 1999, now abandoned.

(51) **Int. Cl.**[7] **B09C 1/08**

(52) **U.S. Cl.** **405/128.5**; 405/128.15; 405/128.75

(58) **Field of Search** 405/128, 129, 405/50, 258, 263, 264, 269, 128.1, 128.15, 128.25, 128.3, 128.45, 128.5, 128.7, 128.75

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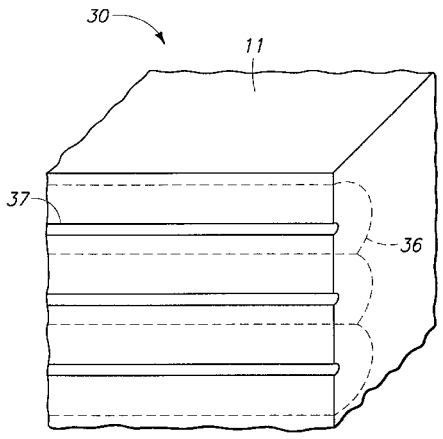
(57) **ABSTRACT**

A reagent delivery method includes positioning reagent delivery tubes in contact with soil. The tubes can include a wall that is permeable to a soil-modifying reagent. The method further includes supplying the reagent in the tubes, diffusing the reagent through the permeable wall and into the soil, and chemically modifying a selected component of the soil using the reagent. The tubes can be in subsurface contact with soil, including groundwater, and can be placed with directional drilling equipment independent of groundwater well casings. The soil-modifying reagent includes a variety of gases, liquids, colloids, and adsorbents that may be reactive or non-reactive with soil components. The method may be used inter alia to form reactive barriers, control pests, and enhance soil nutrients for microbes and plants.

139 Claims, 5 Drawing Sheets



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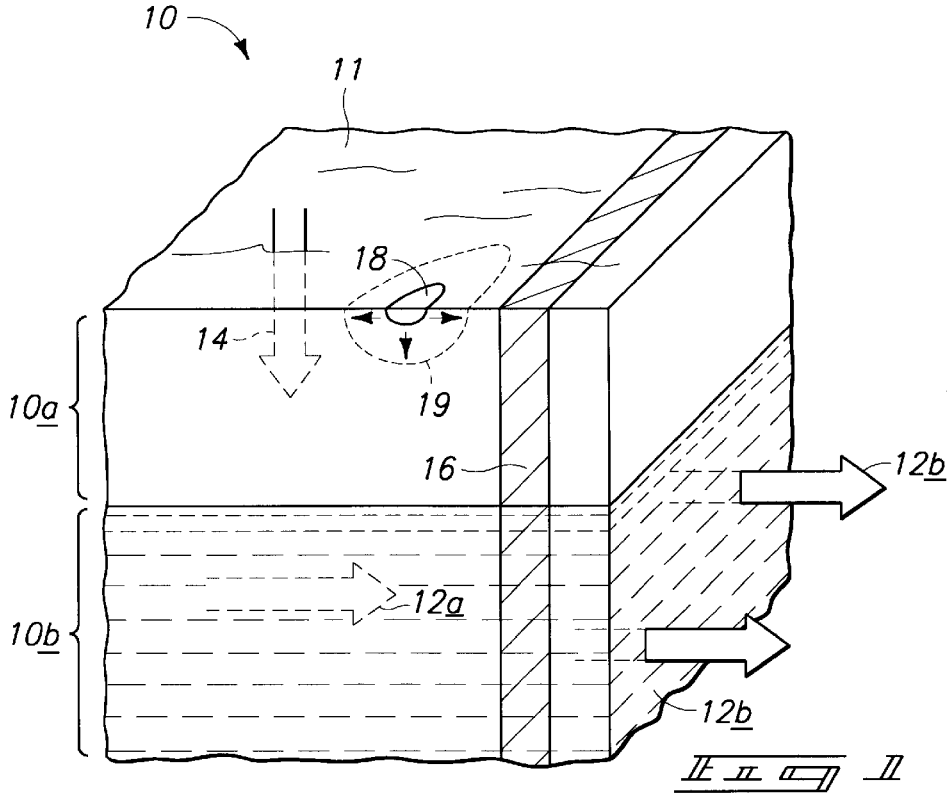
10
11
18
14
19
10a
16
12b
12a
10b
12b

Fig. 1

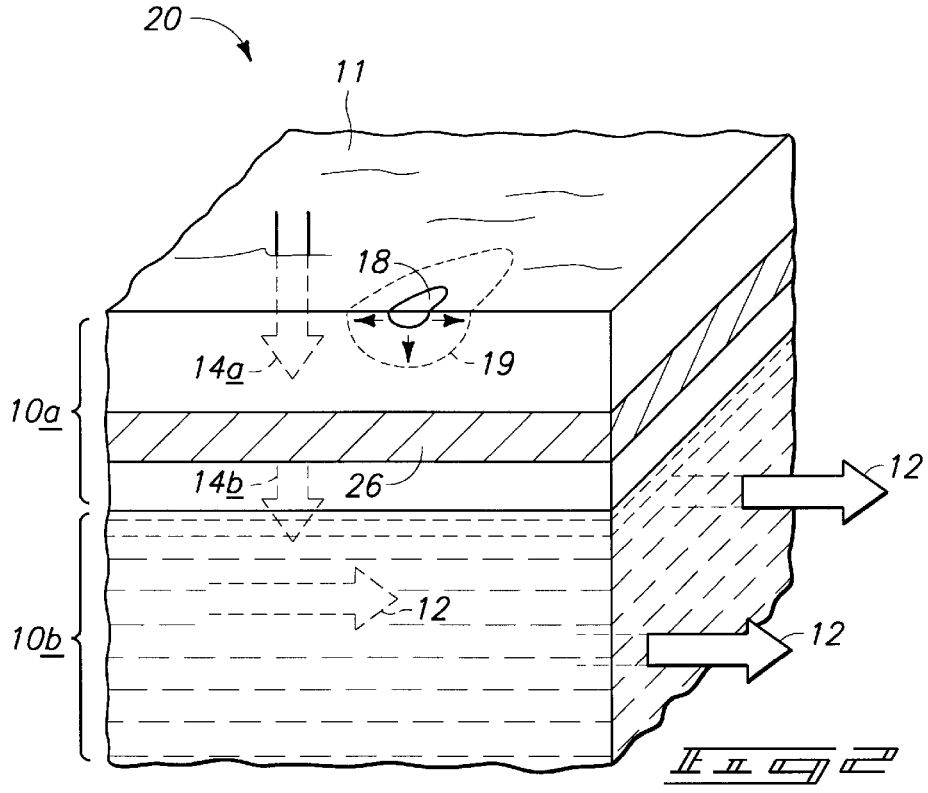
20
11
18
14a
19
10a
14b
26
12
10b
12
12

Fig. 2

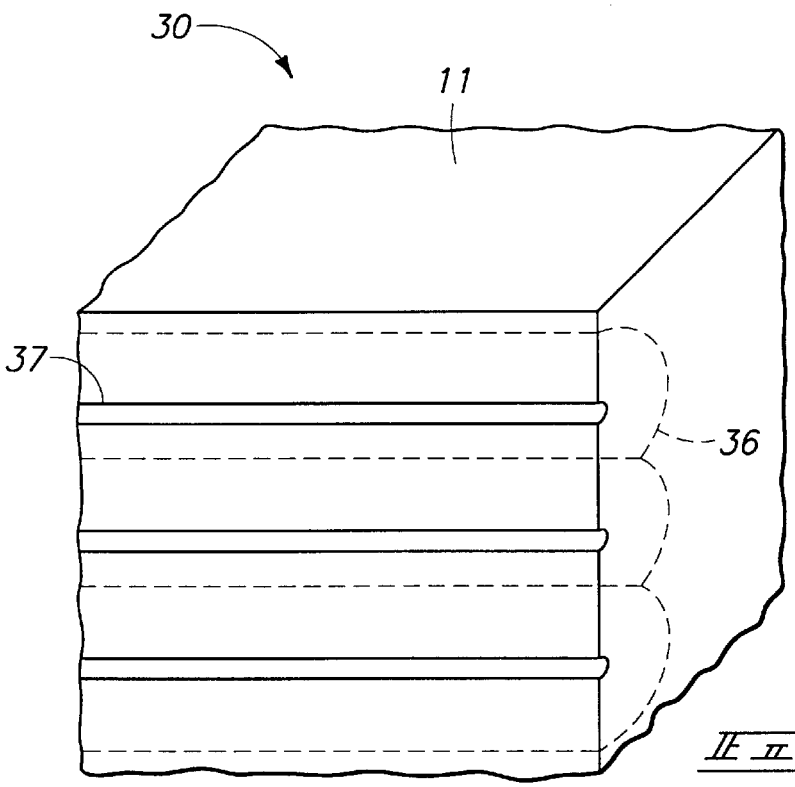

Fig 3

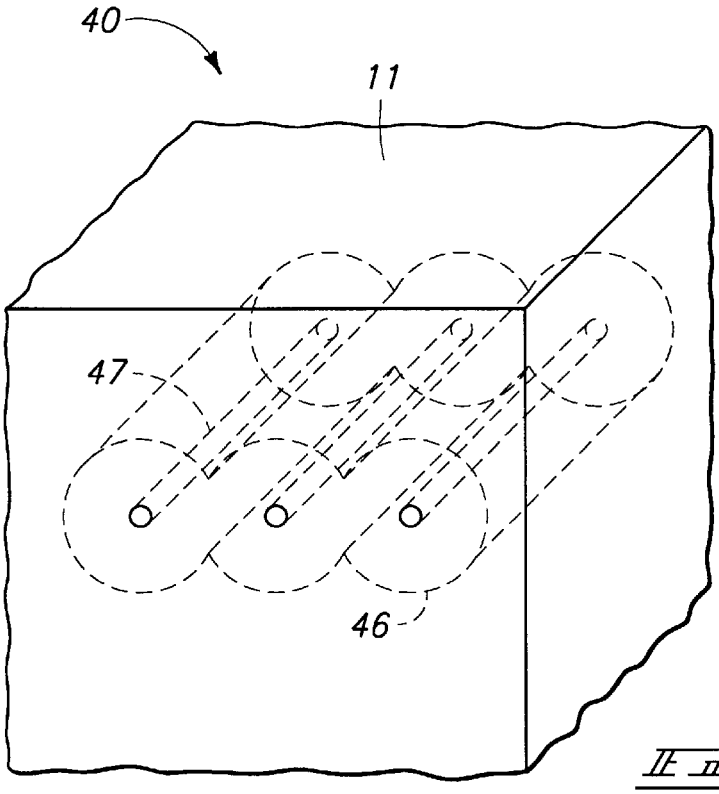

Fig 4

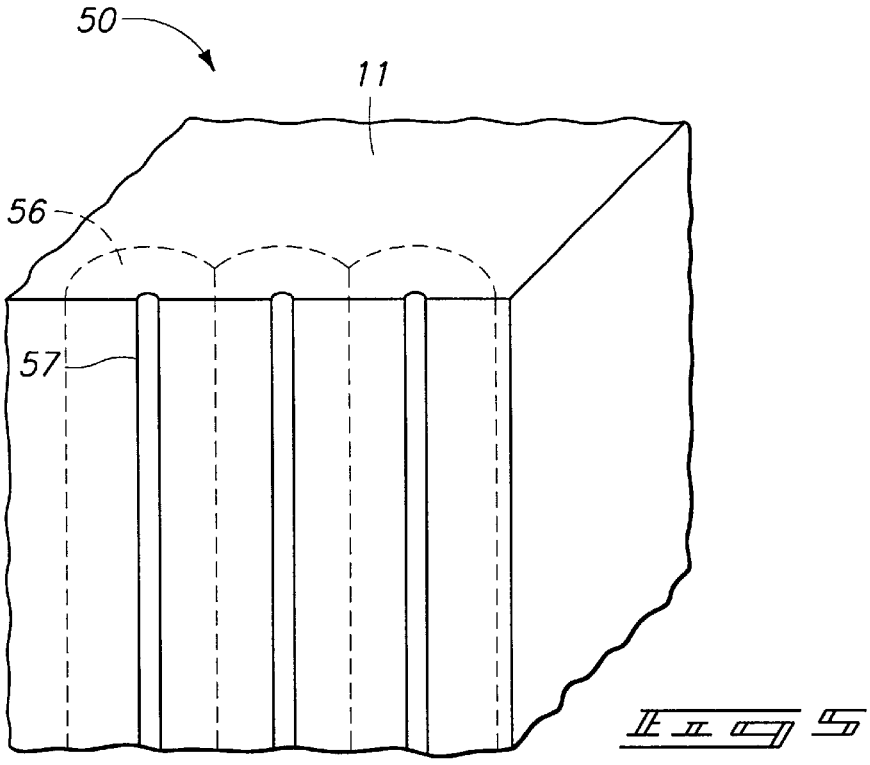

Fig 5

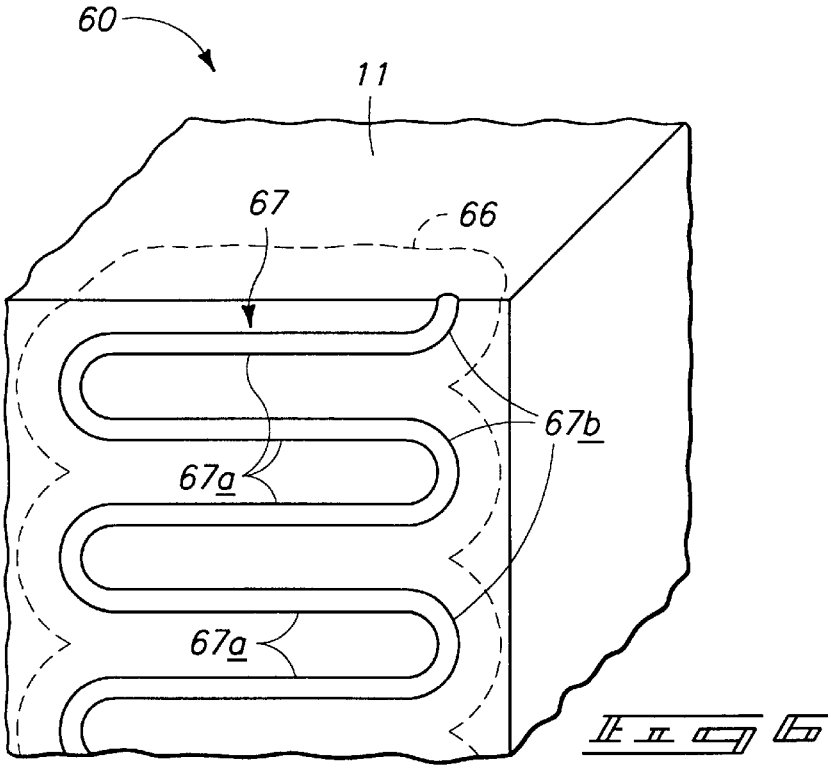

Fig 6

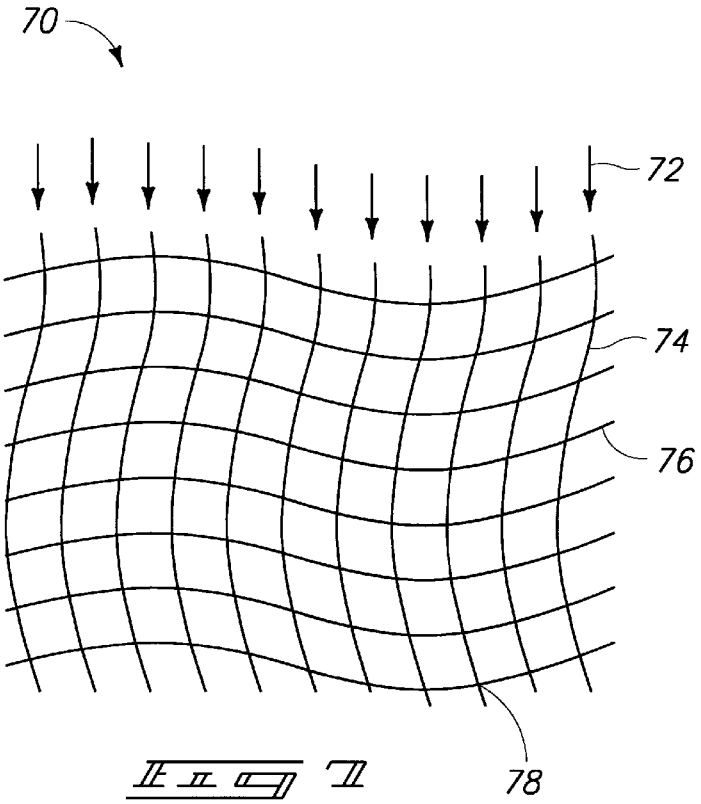

Fig 7

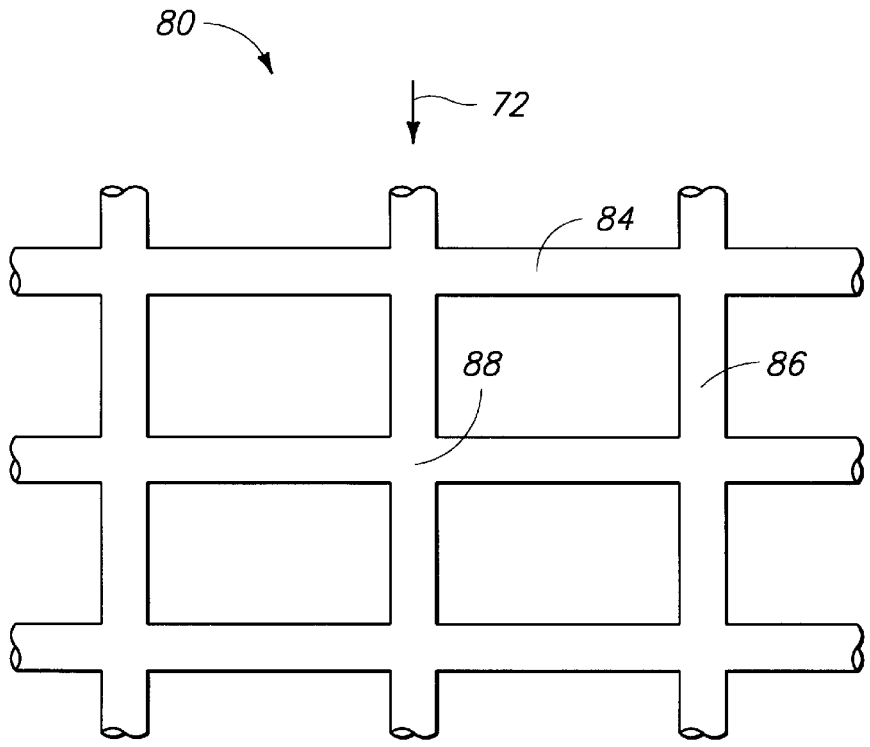

Fig 8

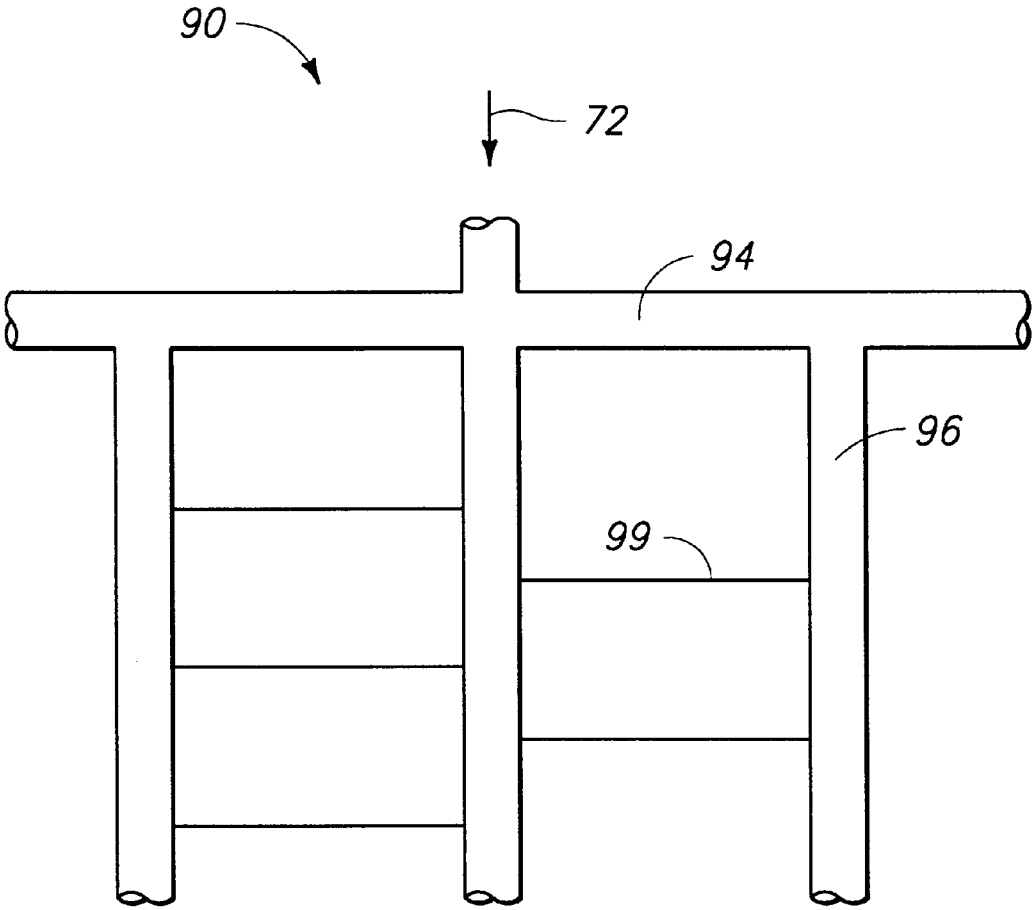

Fig 9

METHODS AND APPARATUSES FOR REAGENT DELIVERY, REACTIVE BARRIER FORMATION, AND PEST CONTROL

This patent is a Continuation-In-Part Application of U.S. patent application Ser. No. 09/429,235 filed on Oct. 28, 1999 now abandoned.

This invention was made with Government support under Contract Number DE-AC0676RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

TECHNICAL FIELD

The invention relates to methods and apparatuses for delivering reagents, forming reactive barriers, and controlling pests.

BACKGROUND OF THE INVENTION

One persistent global challenge is the management and remediation of pollution. Pollution can take several forms, one of which includes land or soil pollution. Soil at a variety of depths beneath the ground surface can become contaminated with pollutants from a wide variety of sources. Soil pollution includes contamination of soil in the Vadose zone, meaning soil that is not saturated with water between the ground surface and a point below the ground surface where the soil becomes saturated with water. Soil pollution can also occur in groundwater, meaning any regions of the soil below the Vadose zone that are saturated with water.

Contamination from a point source in the Vadose zone can disburse outward from the source. Contaminants can also disburse from the Vadose zone into underlying groundwater. Groundwater typically has a gradient or flow pattern, wherein groundwater flows through the saturated soil matrix while solid soil particles remain in place. Accordingly, when contaminants reach groundwater, the contaminants can potentially spread with the groundwater more rapidly than they would otherwise from dispersion in the Vadose zone.

The problem of contaminants spreading by dispersion in the Vadose zone, groundwater flow, or other mechanisms is widely recognized. Accordingly, a wide variety of methods and apparatuses have been developed to counteract contamination of increasingly large areas of soil caused by contaminants spreading.

One such technology provides the creation of reactive barriers in soil that can be contacted with contaminated groundwater or dispersion from contaminated Vadose zone soil. A reactive barrier can be established by digging a trench into which a reactive substance can be placed and then backfilling the trench. One such reactive substance includes zero-valent iron in the form of iron filings that acts as a reducing agent on a variety of contaminants. Groundwater containing targeted contaminants can flow through the iron filings deposited in a trench and flow out of such iron filings as treated groundwater.

While some success has been achieved in establishing reactive barriers in trenches, the life of such a barrier is finite. Depending on a variety of conditions, including the level of contamination, the reagents in the barrier will ultimately be consumed. Once the reaction with contaminants ceases, additional reactive materials must again be placed in a trench and backfilled to continue the treatment of groundwater in situ.

It would be very unusual for a reactive barrier, as described above, to maintain its reactivity long enough to effectuate complete treatment of groundwater contaminants. Rather, the most common circumstance is that protection against spreading of contamination will endure for a time and then cease. Thus, a need exists for reactive barriers that will persist long enough to prevent contaminant spreading as long as the contamination exists. Such reactive barriers are needed to alleviate the spreading of groundwater contamination as well as Vadose zone contamination. Without such advances, the current challenges of isolating and remediating soil contamination will continue to exist.

SUMMARY OF THE INVENTION

In accordance with one aspect of the invention, a reagent delivery method includes positioning reagent delivery tubes in contact with soil. The tubes can include a wall that is permeable to a soil-modifying reagent. The method further includes supplying the reagent in the tubes, diffusing the reagent through the permeable wall and into the soil, and chemically modifying a selected component of the soil using the reagent. The tubes can be in subsurface contact with soil, including groundwater, and can be placed with directional drilling equipment independent of groundwater well casings. The soil-modifying reagent includes a variety of gases, liquids, colloids, and adsorbents that may be reactive or non-reactive with soil components. In accordance with various aspects of the invention, the method may be used to form reactive barriers, control pests, enhance soil nutrients for microbes and plants, and serve other functions.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

FIGS. **1–6** are perspective views of various isometric soil portions.

FIGS. **7–9** are side views of exemplary reagent distribution matrices.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

FIG. **1** illustrates a soil portion **10** including a Vadose zone **10***a* and an area of water-saturated soil (i.e., groundwater) **10***b*. In the context of this document, the terms "soil" or "soil portion" comprise all matter at and below the ground surface, regardless of its location or composition. For example, matter at and below the floor of a body of water is within the meaning of "soil." Accordingly, marine sediment is considered soil. Also accordingly, "soil" and "soil portion" include all of the solid, liquid, and/or gaseous components of such soil.

Vadose zone **10***a* extends from a ground surface **11** downward to the point where soil becomes saturated with water and groundwater **10***b* begins. Multiple regions of water-saturated soil can exist below Vadose zone **10***a* forming a variety of groundwater regions or aquifers. Regions of unsaturated soil may also exist below groundwater regions or aquifers. FIGS. **1** and **2** have been drawn in simplified form for the sake of explanation but do not limit the present invention to application in only one groundwater region, aquifer, or other soil portion saturated with water. FIG. **1** also illustrates a direction of flow for a contaminated

groundwater flow **12***a* in groundwater **10***b*. The infiltration of a surface water flow **14** is indicated downwardly from ground surface **11** into Vadose zone **10***a* and toward groundwater **10***b*. Sources of surface water flow **14** include, for example, rainfall and above-ground bodies of water. An area of a modified soil **16** is formed in soil portion **10**. A contaminant source **18** is also illustrated along with a boundary line for a disbursed contaminant **19**. FIG. **2**, illustrating soil portion **20**, includes all the elements of soil portion **10** illustrated in FIG. **1**, except that an area of a modified soil **26** is provided in the alternative to modified soil **16**.

One difference between modified soil **16** and modified soil **26** is their respective orientation. Modified soil **16** is shown oriented approximately vertically and extending from ground surface **11** through Vadose zone **10***a* and into groundwater **10***b*. Depending on the intended function for modified soil **16**, such modified soil may or may not extend fully through soil portion **10** as shown in FIG. **1**. Rather, it is conceivable that modified soil **16** can only exist within Vadose zone **10***a*, within groundwater **10***b*, or in some other configuration. Similarly, modified soil **26** can exist at any depth below ground surface **11**, including zero depth, or at ground surface **11**. It is further conceivable that modified soil **16** can be oriented in some fashion other than indicated in FIG. **1**, approximately vertically, or in FIG. **2**, approximately horizontally. For selected purposes, some of which are described herein, certain advantages may exist to orienting modified soil **16** approximately vertically and modified soil **26** approximately horizontally.

One aspect of the present invention provides a method for reagent delivery that includes positioning one or more reagent delivery tubes in contact with the soil. If desired, the reagent delivery tubes can be in subsurface contact with the soil. At least a portion of at least one of the tubes can comprise a wall that is permeable to a soil-modifying reagent. The reagent can be supplied into the tube, diffusing the reagent through the permeable wall and into the soil. Once in the soil, the reagent can be used to chemically modify a selected component of the soil. Soil components can include any solid, liquid, and/or gas, in particular, groundwater and components within its liquid phase. Notably, the reagent delivery tubes can be positioned in a variety of configurations to accomplish the above-described aspect of the present invention, as well as other aspects. Accordingly, the above-described reagent delivery method can be used to establish an area of modified soil, such as modified soil **16** or modified soil **26**. The approximately vertical orientation of modified soil **16**, the approximately horizontal orientation of modified soil **26**, or some other orientation can be established by the positioning of the reagent delivery tubes.

There exists at least three mechanisms envisioned by the present invention in which soil or its properties can be modified. First, a reagent can react directly with a contaminant or other soil component. Second, a secondary reaction of a reagent with a contaminant can occur, such as when oxygen enhances already existing microbial reactions. Third, modification of soil components or soil properties can cause existing soil components to react with contaminants. Such is the case when hydrogen sulfide reduces existing iron oxide in soil, thus allowing reduced iron to react with contaminants or other components. Sodium dithionite can also be used to reduce naturally occurring iron in soil. Iron can also be introduced into soil as a colloid. Other reducing agents include ammonium oxalate. Examples of adsorbents include quaternary ammonium amine compounds and surface-modified clay colloids.

FIG. **3** illustrates a soil portion **30** including reagent delivery tubes **37** in subsurface contact with a soil as indicated by their position below ground surface **11**. A reagent is supplied in tubes **37** and diffused through the permeable walls and into soil portion **30** as indicated by a boundary surrounding each tube **37** indicating the extent of a modified soil **36**. In FIG. **3**, the areas of modified soil **36** surrounding tubes **37** are shown to overlap. Tubes **37** are positioned substantially parallel to one another and a majority of tubes **37** are approximately coplanar. More specifically, each of tubes **37** lie in the same approximately vertical plane and, thus, all of tubes **37** are coplanar. Accordingly, the overlapping areas of modified soil **36** form a substantially vertical overall area of modified soil analogous to modified soil **16** shown in FIG. **1**. It is conceivable that tubes **37** could also be positioned substantially parallel to one another, but with less than a majority of tubes **37** being substantially coplanar. Depending on the particular arrangement, an overall area of modified soil analogous to modified soil **16** shown in FIG. **1** could nevertheless be formed.

It should be noted that soil portion **30** of FIG. **3** is presented in a more simplified form compared to soil portions **10** and **20** in FIGS. **1** and **2**. Even though no distinction is made in soil portion **30** as to a Vadose zone or groundwater, modified soil **36** can exist in any Vadose zone, groundwater, and/or other region of a soil portion presented herein or otherwise in existence.

Further note should be made that each of tubes **37** possesses a longitudinal axis that is oriented within about 45° of horizontal. More specifically, assuming ground surface **11** is approximately horizontal, each of tubes **37** is also approximately horizontal. The advantages to be obtained by orienting reagent delivery tubes within about 45° of horizontal are surprising. Once such advantage is that such positioning allows the use of directional drilling equipment to emplace tubes **37**. Directional drilling equipment is currently being used in the placement of electrical and other underground transmission cables. The technology allows placement of such cables at varying depths and horizontal runs of varying lengths. If a horizontal run is not desired, then the technology will allow an angled run, for example within about 45° of horizontal.

Placing tubes **37** approximately horizontal can provide several advantages. One advantage is that delivery of reagent to a large region in the path of moving groundwater can be accomplished with minimal disturbance of the ground surface. From a starting location, a tube **37** can be extended to a distance as great as the directional drilling equipment will reach. Subsequent tubes **37** may be placed at other depths, perhaps from the same starting location, to establish a desired arrangement of tubes **37**. If conventional vertical well casings were instead used for reagent delivery, then conventional drilling equipment would set up and drill every several feet for each well casing. Thus, tubes **37** can be placed to intercept groundwater with a minimum of access holes relative to convention techniques. Further, tubes **37** could be placed to maximize contact with a selected geologic strata that may preferentially contain contaminants.

Tubes **37** may also be placed substantially parallel and substantially coplanar with directional drilling equipment. Given potential variations in precise placement of tubes **37**, some misalignment from exactly parallel or an exact plane may occur, but can be acceptable in many cases. Areas of modified soil **36** can be designed to overlap such that substantially parallel and substantially coplanar tubes **37** nevertheless provide a desired effect.

Another advantage of the various aspects of the present invention is that minimal energy is required to operate the technology. A reagent flow can be provided to the apparatus using a gravity-fed tank or container. Alternatively, a pump can be utilized to supply the apparatus. Gaseous reagents can similarly be provided from a pressure-regulated vessel. As a result of such features, the present invention can be considered to provide a semi-passive reactive barrier. Such is opposed to a passive reactive barrier, one example of which is solid iron filings placed in a trench and backfilled.

Still another advantage of the various aspects of the invention is that enhanced delivery of reagents to surrounding soil can be achieved. Reagents may be supplied to modify soil in bulk form, that is, for gases, as gas bubbles, and for liquids, as droplets or stream flow. Particularly in the case of gases, bubbles do not diffuse reagents into soil in an efficient manner. By comparison, molecular diffusion of reagents through a permeable wall and into surrounding soil provides the reagents in a form that will readily modify selected soil properties or components. If bubbles are instead provided, then the reagents in the gas bubbles can diffuse from bubbles into the same molecular form provided from a reagent delivery tube with a permeable wall. Accordingly, improved modification and dispersion of reagents delivered through a tube can be provided in the various aspects of the present invention.

A variety of materials may be used to enable molecular diffusion through a permeable wall of a reagent delivery tube. Generally, such materials are preferably substantially amorphous. A highly cross-linked polymer material may hinder diffusion, but a less cross-linked material can allow more diffusion. A material that is completely amorphous, with no particular ordered arrangement of molecules and/or atoms, will often allow the most diffusion. The desired degree to which the material comprising a permeable wall is amorphous may depend on the particular reagents to be diffused and the desired diffusion rate. A few examples of suitable materials include silicone tubing, neoprene tubing (synthetic rubber available from Norton Performance Plastics in Wayne, N.J.), and TYGON (TM) tubing (silicone tubing also available from Norton Performance Plastics). Natural rubber, gum rubber, substantially amorphous polyurethane, and substantially amorphous polyethylene may also be suitable.

Conventionally, subsurface reagent delivery equipment has utilized installation of a perforated or otherwise porous well casing. Once installed, reagents can be directly injected into the conventional well casing and thereafter diffuse into surrounding soil. By comparison to the various aspects of the present invention, subsurface reagent delivery through a perforated well casing is rather limited and ineffective. Placing perforated well casings in the positions shown for tubes **37** in FIG. **3** would require excavation and backfilling. Yet, directional drilling equipment can quite easily place tubes **37** parallel to one another in a vertical plane, wherein tubes **37** are placed at varying depths below ground surface **11**. Further, placing reagent delivery tubes in contact with soil provides release of reagent directly to an affected area.

Other methods for placing tubes **37** in the described positions are also available. For example, one tube **37** can be placed in the bottom of a trench which is then backfilled to the point where a second tube **37** is to be placed. Successive backfilling and placement of additional tubes **37** will result in the orientation illustrated in FIG. **3**. In more detail, such a method includes exposing subsurface soil, placing one or more of tubes **37** in contact with the subsurface soil, and backfilling the exposed subsurface soil.

FIG. **4** illustrates soil portion **40** wherein reagent delivery tubes **47** are positioned in subsurface contact with soil portion **40** below ground surface **11**. By supplying a reagent in tubes **47**, an area of modified soil **46** can be established surrounding each tube **47**. In FIG. **4**, the longitudinal axis of each tube is oriented approximately horizontally, tubes **47** are approximately parallel, and each tube **47** is approximately coplanar. However, in contrast to tubes **37** in FIG. **3**, tubes **47** in FIG. **4** are positioned in an approximately horizontal plane. Accordingly, the overlapping areas of modified soil **46** form an overall area of modified soil similar to modified soil **26** illustrated in FIG. **2**. The positions shown in FIG. **4** are also conducive to placement either by directional drilling equipment or by exposing subsurface soil and backfilling after placing tubes in contact with the subsurface soil. As an alternative to FIG. **4**, tubes **47** could be arranged radially, extending outward from a common area of origin. Tubes **47** could still be positioned in an approximately horizontal plane, but they would not be parallel.

FIG. **5** illustrates soil portion **50** with tubes **57** positioned with their longitudinal axes approximately vertical. Even though tubes **57** are not within about 45° of horizontal, tubes **57** are approximately parallel and approximately coplanar. Thus, the overlapping areas of modified soil **56** form an overall area of modified soil similar to modified soil **16** illustrated in FIG. **1**. Tubes **57** can be placed using directional drilling equipment or by exposing subsurface soil and backfilling after placing tubes **57** in contact with the subsurface soil. As an alternative to FIG. **5**, tubes **57** could be arranged radially, extending downward from a common area of origin. Tubes **57** could still be positioned in an approximately vertical plane, but they would not be parallel.

In FIG. **6**, soil portion **60** includes ground surface **11** below which tube **67** is placed in subsurface contact with soil. Tube **67** includes a plurality of parallel tubular sections that are approximately linear. Linear sections **67***a* are shown with their longitudinal axis oriented approximately horizontally. Alternatively, although not shown, the longitudinal axes of linear sections **67***a* could be oriented approximately vertically or at some other position. Tube **67** further includes one or more curved sections **67***b* joined to linear sections **67***a* to form a serpentine pattern.

Although linear sections **67***a* of tube **67** are approximately parallel and approximately coplanar in the shown configuration, other configurations are, of course, possible. A plane defining the relative position of linear sections **67***a* is approximately vertical in the shown configuration. Tube **67** thus produces an area of modified soil **66** that is approximately vertical, resembling modified soil **16** of FIG. **1**. Alternatively, tube **67** can be oriented as shown but with the plane defining the position of linear sections **67***a* oriented approximately horizontally. In such a configuration, an area of modified soil would be produced resembling modified soil **26** of FIG. **2**.

The various tubes of FIGS. **3**, **4**, and **6** individually comprise a major portion sized and oriented to provide an individual vertical distance of reagent distribution in the soil and an individual horizontal distance of reagent distribution in the soil greater than the vertical distance. In FIG. **5**, unless the length of tubes **57** is unusually shallow, the horizontal distance of reagent distribution is less than the vertical distance. If the length of tubes **57** is less than the horizontal distance of reagent distribution indicated by the area of modified soil **56**, then the horizontal distance of reagent distribution could be greater than the vertical distance for tubes **57**.

FIG. **6** further illustrates tube **67** including one or more curved sections and a plurality of approximately linear

sections, wherein the major portion of each tube comprises one of the linear sections. Also in FIGS. **3**, **4**, and **6**, a longitudinal axis of the major portion of one or more individual tubes is oriented within about 45° of horizontal. As described, individual tubes are more specifically oriented approximately horizontally.

The various tubes of FIGS. **3–6** can be in subsurface contact with both soil and groundwater. Further, selected portions of the tubes may be permeable to a soil-modifying reagent while other portions are not permeable. Thus, selected portions of soil can receive the reagent diffusing through the permeable wall while other portions do not. Such a configuration would allow a tube to extend from ground surface **11** through Vadose zone **10***a* and into groundwater **10***b* without releasing any reagent into Vadose zone **10***a*, but instead affecting groundwater **10***b* or a portion thereof.

The materials and constructions of the tubes can vary depending on the reagent to be dispersed with the tubes. In one aspect of the invention, the permeable wall of a reagent delivery tube can comprise a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell. By this means, a thin permeable liner can be provided with structural integrity sufficient so that it can be placed in subsurface contact with soil. It may further be desirable that the opening in the shell forming the permeable wall comprise pores that are intrinsic to a material comprising the shell. Pores intrinsic to a material can be distinguished from orifices mechanically formed in a shell. Of course, tubes can be used having a permeability intrinsic to the material comprising a shell such that no permeable liner is required.

The permeability of the permeable wall of a tube depends upon the particular reagent to be delivered. The particular reagent depends upon the objective of modifying the soil. One advantage of the present invention is that it chemically modifies a selected component of the soil using the reagent. The soil modifying reagent can comprise a gas, a liquid, a colloid, or yet other materials, but preferably a gas. Any of such reagents may further be described as a reducing agent, an oxidizing agent, a microbe, an enzyme, or an adsorbent. Each of such reagents may chemically modify a selected component in the soil. The soil may be chemically modified by treating a contaminant found therein. Alternatively, a reagent may produce a chemically modified component of the soil that in turn reacts with a soil contaminant, even though the reagent does not directly react with a soil contaminant. Examples of a few soil contaminants include a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

Another advantage of the present invention is that it can modify a selected property or component of at least one of the soil and groundwater using a gaseous reagent. In such case, a gas permeable tube wall is preferred. Possible soil modifying reagents to accomplish such an advantage include a reducing agent, an oxidizing agent, an oxygen source, an oxygen displacer or scavenger, a microbial nutrient, a co-metabolite, a pesticide, a fertilizer, or a herbicide, each of which may be provided in a gaseous form.

Some of such reagents are not reactive with soil components, while others can be selected to react with a soil contaminant. Gaseous reducing agents and oxidizing agents may chemically modify components of the soil, including contaminants. An oxygen source can be used to enhance a microbial reaction occurring in the soil, wherein the microbial reaction chemically modifies a selected component of the soil. Thus, supplying an oxygen source modifies the property of oxygen content in soil, rather than modifying a particular component of soil. Providing an oxygen displacer or scavenger is analogous except that an anoxic condition can be created. Generally, an anoxic condition might be desired for other microbial reactions. A microbial nutrient can provide a similar enhancement. A pesticide may also be supplied to provide the advantage of pest control in a selected soil portion. Fertilizer may be provided to enhance plant growth in a selected soil portion. A herbicide may be provided to suppress plant growth in a selected soil portion.

Another aspect of the invention comprises a reactive reagent reacting with a selected component of the soil. Accordingly, creating an area of modified soil as depicted in FIGS. **1–6** can create a rechargeable reactive barrier. That is, a reactive reagent may be supplied from reagent delivery tubes to a selected soil portion where the reagent will react with existing selected components in such soil portion. As illustrated in FIG. **1**, contaminated groundwater **12***a* flows through modified soil **16**. Assuming modified soil **16** is a rechargeable reactive barrier, contaminants or other soil components moving with contaminated groundwater flow **12***a* will pass through the rechargeable reactive barrier for treatment. Treated groundwater flow **12***b* then flows out from the rechargeable reactive barrier. A continuous supply of reactive reagent into modified soil **16** will match the continuous supply of soil contaminants or other components flowing with groundwater **10***b*.

Referring to FIG. **2**, assuming modified soil **26** is a rechargeable reactive barrier, any contaminant or other soil component infiltrating with contaminated surface water flow **14***a* will pass through the rechargeable reactive barrier. Treated surface water flow **14***b* then enters groundwater **10***b*. One potential use for such a method is in preventing contamination of groundwater with organic and inorganic byproducts of a cattle feed lot, including viruses. Other analogous uses are also conceivable. Examples of reactive reagents, which happen to be gaseous reactive reagents, include chlorine, sulphur dioxide, bromine, acetylene, ozone, hydrogen sulfide, or combinations thereof. Some of such reagents can provide reaction with a selected component in the soil and subsequent reaction of the selected component with a soil contaminant. Of course, a gaseous, reactive reagent can also react directly with a contaminant.

A rechargeable, reactive barrier may similarly be established through a microbial reaction. Such microbial reactions can be enhanced by providing an oxygen source or an oxygen displacer or scavenger as required by the particular type of reaction. A microbial nutrient or a co-metabolite are other reagents that may be supplied according to the present invention to enhance the microbial reaction.

In another aspect of the invention, pest control can be provided by positioning one or more reagent delivery tubes in contact with a soil. At least a portion of at least one of the tubes can comprise a wall that is permeable to a pest control reagent. The pest control reagent can be supplied in the tube and diffused in an effective amount through the permeable wall and into the soil. If desired, the reagent delivery tubes can be in subsurface contact with the soil. One potential agricultural aspect includes placing reagent delivery tubes in furrows of an agricultural field and supplying pesticide. An example of a pest is a root nematode. Such a method can enhance the safety of using some pesticides, such as methyl bromide, and also reduce the amount required by localizing application in the area most needed.

Another use of pesticide reagent delivery tubes involves protecting subsurface structures from pest damage or infes-

tation. Examples of pests include termites and ants. Tubes may be positioned an effective distance from a subsurface structure to effectuate a pest control in soil juxtaposed with the structure. Such may be accomplished with directional drilling equipment, the trench and backfill method described above, or perhaps other methods. In a similar manner, plant control can be provided by positioning one or more herbicide reagent delivery tubes in contact with a soil. Such may be useful in suppressing plant growth in designated areas and suppressing root damage of subsurface structures.

FIGS. **7–9** illustrate further aspects of the present invention with their depiction of a few examples of alternative embodiments to the reagent delivery tubes illustrated in FIGS. **3–6**. One difference between the tubing of FIGS. **3–6** and the tubing of FIGS. **7–9**, is that the latter are linked together such that a preselected spacing between tubing sections is provided and maintained when the apparatuses are positioned in or on soil. Because of the linked feature, the apparatuses of FIGS. **7–9** will generally be installed in trenches or other excavations that are then backfilled. Notably, such trenches or other excavations exposing the subsurface soil may be constructed in a manner that allows the apparatuses of FIGS. **7–9** to be positioned in an approximately vertical plane, an approximately horizontal plane, or even some other plane. Further, assuming that the apparatuses of FIGS. **7–9** are at least somewhat flexible, the apparatuses could be oriented such that tube sections are not necessarily coplanar. For example, such apparatuses could be placed in a curved trench or some other nonplanar trench or excavation.

Nevertheless, because the apparatuses of FIGS. **7–9** include reagent delivery tube sections, they may be used in the methods described above to form modified soil portions, such as modified soil **16**, modified soil **26**, or yet other areas of modified soil. It is not presently anticipated that the apparatuses of FIGS. **7–9** can be installed using directional drilling equipment. Nevertheless, it is conceivable that currently existing or later developed equipment could potentially be used to position the apparatuses of FIGS. **7–9**. A method may be used other than one requiring exposure of subsurface soil, placement of the apparatuses, and backfilling the exposed subsurface soil.

In FIG. **7**, a magnified view of a geotextile fabric forming a matrix **70** is illustrated. A reagent flow **72** can be introduced into hollow tubular sections **74**, hollow tubular sections **76**, or both. Matrix **70** of FIG. **7** can be a woven fabric, wherein tubular sections **74** and tubular sections **76** intersect at cross-overs **78**. Since tubular sections **74** and tubular sections **76** intersect at cross-overs **78**, they can additionally be linked in some fashion at cross-overs **78**. If matrix **70** is woven then tubular sections **74** and **76** will likely remain in their respective positions without some sort of link at cross-overs **78**. However, if matrix **70** is not woven or if the gaps between approximately parallel tubular sections s are large enough to allow shifting, then such linking may be desired.

It is further noted that only a portion of tubular sections **74** or **76** may comprise reagent delivery tubes and yet matrix **70** may still accomplish soil modification as described above. A variety of configurations are conceivable. For example, only tubular sections **74**, as shown in FIG. **7**, may be used to deliver reagent, while tubular sections **76** simply provide a woven, fabric-like feature or some other spacer-type of feature. Accordingly, tubular sections **76** may be substituted for other structures that are not tubular and might not function as reagent delivery tubes. Further, for example, only a selected portion of tubular sections **74** might be used for reagent delivery. Because the boundary of modified soil can extend beyond the diameter of an individual tubular section **74**, the reagent delivery tubes in matrix **70** need not be directly adjacent to one another. Some number of tubular sections **74** or other non-tubular structures can exist between the tubular sections **74** used for reagent delivery. Even so, the overlapping boundaries of modified soil around individual reagent delivery tubes can still provide an area of modified soil such as modified soil **16**, modified soil **26**, or some alternative.

In FIG. **8**, a matrix **80** is illustrated wherein reagent flow **72** is supplied through tubular sections **84** and tubular sections **86**. Tubular sections **84** and **86** intersect to form reagent distribution junctions **88**. Because tubular sections **84** and **86** are linked by distribution junctions **88**, reagent flow **72** supplied at a single tubular section, or a few tubular sections, will quickly spread throughout matrix **80**. The spacing between parallel tubular sections **84** and parallel tubular sections **86** may be greater than the distance between parallel tubular sections **74** and **76** illustrated in FIG. **7**. A greater distance may be warranted given the potentially increased cost of fabricating matrix **80** with distribution junctions **88**, as compared to a woven fabric of matrix **70** with cross-overs **78**. FIG. **8** illustrates matrix **80** as having distribution junctions **88** at each intersection of tubular sections **84** and **86**. Nevertheless, it is conceivable that distribution junctions **88** may only be provided at a portion of the intersections.

In FIG. **9**, a matrix **90** is illustrated wherein reagent flow **72** is supplied into a tubular section **94** which distributes reagent flow **72** to multiple tubular sections **96**. Tubular sections **96** are further provided with one or more spacers **99** to maintain tubular sections **96** in an approximately parallel configuration. Thus, FIG. **9** represents simply one additional variation on the reagent delivery apparatuses described in FIGS. **7** and **8**. Other variations are, of course, encompassed by the present invention.

Depending on the placement and configuration of the apparatuses of FIGS. **7–9**, such apparatuses can accomplish reagent delivery wherein one or more reagent delivery tubes are in contact with a soil. At least a portion of at least one of the tubes can include a wall that is permeable to a reagent. If desired, the reagent delivery tubes can be in subsurface contact with the soil. Preferably, the tubes can individually comprise a major portion sized and oriented to provide an individual vertical distance of reagent distribution in the soil and an individual horizontal distance of reagent distribution in the soil greater than the vertical distance. As illustrated in FIGS. **7–9**, a reagent delivery apparatus may also be provided comprising a reagent distribution matrix. At least a portion of the matrix can include a plurality of parallel tubular sections and a wall permeable to the reagent, the wall being in contact with a soil, perhaps in subsurface contact.

Each of FIGS. **7–9** further illustrates how such an apparatus can comprise one or more spacers extending between adjacent tubular sections. Such structures can comprise a dual function of both a spacer and a tubular section. The longitudinal axis of at least a portion of the tubular sections in the apparatuses in FIGS. **7–9** can be oriented within about 45° of horizontal. Thus, the unique tubing orientation of FIGS. **3** and **4** can be provided by the apparatuses of FIGS. **7–9**.

In yet another aspect of the present invention, a reagent delivery apparatus can comprise a reagent distribution matrix, wherein at least a portion of the matrix comprises a wall permeable to reagent, a first plurality of parallel tubular

sections, and a second plurality of parallel tubular sections. If desired, the reagent delivery tubes can be in subsurface contact with the soil. The longitudinal axis of at least a s portion of the first tubular sections can be substantially perpendicular to a longitudinal axis of at least a portion of the second tubular sections. FIGS. **7** and **8** each illustrate such an apparatus.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

What is claimed is:

1. A reagent delivery method, comprising:

positioning one or more reagent delivery tubes in contact with a soil, at least a portion of at least one of the tubes comprising a wall that is permeable to a soil-modifying reagent;

supplying the reagent in the tube;

diffusing the reagent through the permeable wall and into the soil; and

chemically modifying a selected component of the soil using the reagent;

wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

2. The method of claim **1**, wherein the one or more reagent delivery tubes are positioned in subsurface contact with the soil.

3. The method of claim **1**, wherein the soil comprises marine sediment.

4. The method of claim **1**, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

5. The method of claim **4**, wherein the openings comprise pores intrinsic to a material comprising the shell.

6. The method of claim **1**, wherein the positioning the tubes further comprises orienting a longitudinal axis of one or more of the tubes within about 45° of horizontal.

7. The method of claim **1**, wherein the positioning the tubes further comprises placement with directional drilling equipment.

8. The method of claim **1**, wherein the positioning the tubes further comprises:

exposing a subsurface soil;

placing one or more of the tubes in contact with the subsurface soil; and

backfilling the exposed subsurface soil.

9. The method of claim **1**, wherein the soil-modifying reagent comprises a gas.

10. The method of claim **1**, wherein the soil-modifying reagent comprises at least one of a reducing agent, an oxidizing agent, a microbe, an enzyme, or an adsorbent.

11. The method of claim **1**, wherein the tubes contact a groundwater within the soil and the reagent diffuses into the groundwater.

12. The method of claim **1**, wherein the chemically modified component of the soil reacts with a soil contaminant.

13. The method of claim **12**, wherein the soil contaminant comprises at least one of a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

14. A reagent delivery method, comprising:

positioning one or more reagent delivery tubes in subsurface contact with a soil and a groundwater, at least a portion of at least one of the tubes comprising a gas permeable wall;

supplying a gaseous, soil-modifying reagent in the tube; diffusing the gaseous reagent through the permeable tube wall and into at least one of the soil and the groundwater; and

modifying a selected property or component of the at least one of the soil and groundwater using the gaseous reagent;

wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

15. The method of claim **14**, wherein the soil comprises marine sediment.

16. The method of claim **14**, wherein the wall comprises a shell having openings therein and a permeable liner in contact with an inner surface of the shell.

17. The method of claim **16**, wherein the openings comprise pores intrinsic to a material comprising the shell.

18. The method of claim **14**, wherein the positioning the tubes further comprises orienting a longitudinal axis of one or more of the tubes within about 45° of horizontal.

19. The method of claim **14**, wherein the positioning the tubes further comprises placement with directional drilling equipment.

20. The method of claim **14**, wherein the positioning the tubes further comprises:

exposing the subsurface soil;

placing one or more of the tubes in contact with the subsurface soil; and

backfilling the exposed subsurface soil.

21. The method of claim **14**, wherein the soil-modifying reagent comprises at least one of a reducing agent, an oxidizing agent, an oxygen source, an oxygen displacer or scavenger, a microbial nutrient, a pesticide, or a fertilizer.

22. The method of claim **14**, wherein the soil-modifying reagent is not reactive with soil components.

23. The method of claim **14**, wherein a chemically modified component of the soil reacts with a soil contaminant.

24. The method of claim **23**, wherein the soil contaminant comprises at least one of a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

25. A reactive barrier formation method, comprising:

positioning one or more reagent delivery tubes in contact with a soil, at least a portion of at least one of the tubes comprising a wall that is permeable to a reactive, soil-modifying reagent;

supplying the reactive reagent in the tube;

diffusing the reactive reagent through the permeable wall and into the soil; and

reacting the reactive reagent with a selected component of the soil;

wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

26. The method of claim **25**, wherein the one or more reagent delivery tubes are positioned in subsurface contact with the soil.

27. The method of claim **25**, wherein the soil-modifying reagent is in a gaseous form.

28. The method of claim 25, wherein the soil-modifying reagent comprises at least one of chlorine, sulphur dioxide, bromine, acetylene, ozone, hydrogen sulfide, or combinations thereof.

29. The method of claim 25, wherein the tubes contact a groundwater within the soil and the reagent diffuses into the groundwater.

30. The method of claim 25, wherein the selected component comprises a soil contaminant.

31. The method of claim 30, wherein the soil contaminant comprises at least one of a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

32. The method of claim 25, further comprising additionally reacting the reacted selected component with a soil contaminant.

33. A reactive barrier formation method, comprising:

positioning one or more reagent delivery tubes in subsurface contact with a soil and a groundwater, at least a portion of at least one of the tubes comprising a gas permeable wall;

supplying a gaseous, reactive, soil-modifying reagent in the tube;

diffusing the gaseous, reactive reagent through the permeable wall and dissolving the gaseous, reactive reagent into the groundwater; and

reacting the gaseous, reactive reagent with a groundwater contaminant;

wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

34. The method of claim 33, wherein the soil-modifying reagent comprises at least one of chlorine, sulphur dioxide, bromine, acetylene, ozone, hydrogen sulfide, or combinations thereof.

35. The method of claim 33, wherein the groundwater contaminant comprises at least one of a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

36. A reactive barrier formation method, comprising:

positioning one or more reagent delivery tubes in contact with a soil, at least a portion of at least one of the tubes comprising a wall that is permeable to a soil-modifying reagent;

supplying the reagent in the tube;

diffusing the reagent through the permeable wall and into the soil; and

enhancing a microbial reaction occurring in the soil using the reagent, the microbial reaction chemically modifying a selected component of the soil;

wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

37. The method of claim 36, wherein the one or more reagent delivery tubes are positioned in subsurface contact with the soil.

38. The method of claim 36, wherein the soil-modifying reagent is in a gaseous form.

39. The method of claim 36, wherein the soil-modifying reagent comprises at least one of an oxygen source, an oxygen displacer or scavenger, a microbial nutrient, or a co-metabolite.

40. A pest control method, comprising:

positioning one or more reagent delivery tubes in contact with a soil, at least a portion of at least one of the tubes comprising a wall that is permeable to a pest control reagent;

supplying the pest control reagent in the tube; and

diffusing an effective amount of the pest control reagent through the permeable wall and into the soil;

wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

41. The method of claim 40, wherein the one or more reagent delivery tubes are positioned in subsurface contact with the soil.

42. The method of claim 40, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

43. The method of claim 42, wherein the openings comprise pores intrinsic to a material comprising the shell.

44. The method of claim 40, wherein the positioning the tubes further comprises orienting a longitudinal axis of one or more of the tubes within about 45° of horizontal.

45. The method of claim 40, wherein the positioning the tubes further comprises placement with directional drilling equipment.

46. The method of claim 40, wherein the positioning the tubes further comprises:

exposing a subsurface soil;

placing one or more of the tubes in contact with the subsurface soil; and

backfilling the exposed subsurface soil.

47. The method of claim 40, wherein the positioning the tubes further comprises placing tubes an effective distance from a subsurface structure to effectuate pest control in soil juxtaposed with the structure.

48. The method of claim 40, wherein the pest control reagent comprises a gas.

49. A subsurface reagent delivery apparatus, comprising:

one or more reagent delivery tubes in subsurface contact with a soil, at least a portion of the tubes comprising a wall that is permeable to the reagent, wherein the tubes individually comprise a major portion sized and oriented to provide an individual vertical distance of reagent distribution in the soil and an individual horizontal distance of reagent distribution in the soil greater that the vertical distance, and wherein at least a portion of the permeable wall is substantially amorphous, the substantially amorphous portion of the wall permitting molecular diffusion of the reagent into the soil.

50. The apparatus of claim 49, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

51. The apparatus of claim 50, wherein the openings comprise pores intrinsic to a material comprising the shell.

52. The apparatus of claim 49, wherein a longitudinal axis of the major portion of one or more individual tubes is oriented within about 45° of horizontal.

53. The apparatus of claim 49, wherein one or more of the tubes contact a groundwater within the soil.

54. The apparatus of claim 49, wherein the tubes form a subsurface serpentine pattern comprising one or more curved sections and a plurality of approximately linear sections, wherein the major portion comprises one of the linear sections.

55. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix, wherein at least a portion of the matrix comprises a plurality of parallel tubular sections and a wall permeable to a reagent, the wall being in subsurface contact with a soil, wherein at least a portion of the permeable wall is substantially

amorphous, the substantially amorphous portion of the wall permitting molecular diffusion of the reagent into the soil.

56. The apparatus of claim **55**, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

57. The apparatus of claim **56**, wherein the openings comprise pores intrinsic to a material comprising the shell.

58. The apparatus of claim **55**, wherein one or more of the tubular sections contact a groundwater within the soil.

59. The apparatus of claim **55**, further comprising one or more curved sections joined to the tubular sections, forming a subsurface serpentine pattern.

60. The apparatus of claim **55**, wherein a majority of the tubular sections are approximately coplanar in an approximately horizontal plane.

61. The apparatus of claim **55**, wherein a majority of the tubular sections are approximately coplanar in an approximately vertical plane.

62. The apparatus of claim **55**, further comprising one or more spacers extending between adjacent tubular sections.

63. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix in subsurface contact with a soil, wherein at least a portion of the matrix comprises a wall permeable to a reagent and a plurality of parallel tubular sections and wherein the longitudinal axis of at least a portion of the tubular sections is oriented within about 45° of horizontal and wherein at least a portion of the permeable wall is substantially amorphous, the substantially amorphous portion of the wall permitting molecular diffusion of the reagent into the soil.

64. The apparatus of claim **63**, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

65. The apparatus of claim **64**, wherein the openings comprise pores intrinsic to a material comprising the shell.

66. The apparatus of claim **63**, wherein one or more of the tubular sections contact a groundwater within the soil.

67. The apparatus of claim **63**, further comprising one or more curved sections joined to the tubular sections, forming a subsurface serpentine pattern.

68. The apparatus of claim **63**, wherein a majority of the tubular sections are approximately coplanar.

69. The apparatus of claim **68**, wherein the approximately coplanar tubular sections are in an approximately vertical plane.

70. The apparatus of claim **68**, wherein the approximately coplanar tubular sections are in an approximately horizontal plane.

71. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix, wherein at least a portion of the matrix comprises a wall permeable to a reagent, a first plurality of parallel tubular sections, and a second plurality of parallel tubular sections and wherein a longitudinal axis of at least a portion of the first tubular sections is substantially perpendicular to a longitudinal axis of at least a portion of the second tubular sections, and wherein at least a portion of the permeable wall is substantially amorphous, the substantially amorphous portion of the wall permitting molecular diffusion of the reagent into the soil.

72. The apparatus of claim **71**, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

73. The apparatus of claim **72**, wherein the openings comprise pores intrinsic to a material comprising the shell.

74. The apparatus of claim **71**, wherein at least a portion of the first and second tubular sections intersect to form one or more reagent distribution junctions.

75. The apparatus of claim **71**, wherein a majority of the tubular sections are approximately coplanar.

76. The apparatus of claim **75**, wherein the approximately coplanar tubular sections are in an approximately vertical plane.

77. The apparatus of claim **75**, wherein the approximately coplanar tubular sections are in an approximately horizontal plane.

78. A reagent delivery method, comprising:

positioning one or more reagent delivery tubes in contact with a soil, at least a portion of at least one of the tubes comprising a wall that is permeable to a soil-modifying reagent;

supplying the reagent in the tube;

delivering the reagent through the permeable wall and into the soil; and

chemically modifying a selected component of the soil using the reagent;

wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

79. The method of claim **78**, wherein the one or more reagent delivery tubes are positioned in subsurface contact with the soil.

80. The method of claim **78**, wherein the soil comprises marine sediment.

81. The method of claim **78**, wherein the openings comprise pores intrinsic to a material comprising the shell.

82. The method of claim **78**, wherein the positioning the tubes further comprises orienting a longitudinal axis of one or more of the tubes within about 45° of horizontal.

83. The method of claim **78**, wherein the positioning the tubes further comprises placement with directional drilling equipment.

84. The method of claim **78**, wherein the positioning the tubes further comprises:

exposing a subsurface soil;

placing one or more of the tubes in contact with the subsurface soil; and

backfilling the exposed subsurface soil.

85. The method of claim **78**, wherein the soil-modifying reagent comprises a gas.

86. The method of claim **78**, wherein the soil-modifying reagent comprises at least one of a reducing agent, an oxidizing agent, a microbe, an enzyme, or an adsorbent.

87. The method of claim **78**, wherein the tubes contact a groundwater within the soil and the reagent diffuses into the groundwater.

88. The method of claim **78**, wherein the chemically modified component of the soil reacts with a soil contaminant.

89. The method of claim **88**, wherein the soil contaminant comprises at least one of a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

90. A reagent delivery method, comprising:

positioning one or more reagent delivery tubes in subsurface contact with a soil and a groundwater, at least a portion of at least one of the tubes comprising a gas permeable wall;

supplying a gaseous, soil-modifying reagent in the tube;

delivering the gaseous reagent through the permeable tube wall and into at least one of the soil and the groundwater; and

modifying a selected property or component of the at least one of the soil and groundwater using the gaseous reagent;

wherein the wall comprises a shell having openings therein and a permeable liner in contact with an inner surface of the shell.

91. The method of claim **90**, wherein the soil comprises marine sediment.

92. The method of claim **90**, wherein the openings comprise pores intrinsic to a material comprising the shell.

93. The method of claim **90**, wherein the positioning the tubes further comprises orienting a longitudinal axis of one or more of the tubes within about 45° of horizontal.

94. The method of claim **90**, wherein the positioning the tubes further comprises placement with directional drilling equipment.

95. The method of claim **90**, wherein the positioning the tubes further comprises:

exposing the subsurface soil;

placing one or more of the tubes in contact with the subsurface soil; and

backfilling the exposed subsurface soil.

96. The method of claim **90**, wherein the soil-modifying reagent comprises at least one of a reducing agent, an oxidizing agent, an oxygen source, an oxygen displacer or scavenger, a microbial nutrient, a pesticide, or a fertilizer.

97. The method of claim **90**, wherein the soil-modifying reagent is not reactive with soil components.

98. The method of claim **90**, wherein a chemically modified component of the soil reacts with a soil contaminant.

99. The method of claim **98**, wherein the soil contaminant comprises at least one of a metallic ion, a hydrocarbon, or a halogenated hydrocarbon.

100. A pest control method, comprising:

positioning one or more reagent delivery tubes in contact with a soil, at least a portion of at least one of the tubes comprising a wall that is permeable to a pest control reagent;

supplying the pest control reagent in the tube; and

delivering an effective amount of the pest control reagent through the permeable wall and into the soil;

wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

101. The method of claim **100**, wherein the one or more reagent delivery tubes are positioned in subsurface contact with the soil.

102. The method of claim **100**, wherein the openings comprise pores intrinsic to a material comprising the shell.

103. The method of claim **100**, wherein the positioning the tubes further comprises orienting a longitudinal axis of one or more of the tubes within about 45° of horizontal.

104. The method of claim **100**, wherein the positioning the tubes further comprises placement with directional drilling equipment.

105. The method of claim **100**, wherein the positioning the tubes further comprises:

exposing a subsurface soil;

placing one or more of the tubes in contact with the subsurface soil; and

backfilling the exposed subsurface soil.

106. The method of claim **100**, wherein the positioning the tubes further comprises placing tubes an effective distance from a subsurface structure to effectuate pest control in soil juxtaposed with the structure.

107. The method of claim **100**, whereon the pest control reagent comprises a gas.

108. A subsurface reagent delivery apparatus, comprising: one or more reagent delivery tubes in subsurface contact with a soil, at least a portion of the tubes comprising a wall that is permeable to the reagent, wherein the tubes individually comprise a major portion sized and oriented to provide an individual vertical distance of reagent distribution in the soil and an individual horizontal distance of reagent distribution in the soil greater that the vertical distance, and wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

109. The apparatus of claim **108**, wherein the openings comprise pores intrinsic to a material comprising the shell.

110. The apparatus of claim **108**, wherein a longitudinal axis of the major portion of one or more individual tubes is oriented within about 45° of horizontal.

111. The apparatus of claim **108**, wherein one or more of the tubes contact a groundwater within the soil.

112. The apparatus of claim **108**, wherein the tubes form a subsurface serpentine pattern comprising one or more curved sections and a plurality of approximately linear sections, wherein the major portion comprises one of the linear sections.

113. A subsurface reagent delivery apparatus, comprising: one or more reagent delivery tubes in subsurface contact with a soil, at least a portion of the tubes comprising a wall that is permeable to the reagent, wherein the tubes individually comprise a major portion sized and oriented to provide an individual vertical distance of reagent distribution in the soil and an individual horizontal distance of reagent distribution in the soil greater that the vertical distance, wherein the tubes form a subsurface serpentine pattern comprising one or more curved sections and a plurality of approximately linear sections, wherein the major portion comprises one of the linear sections.

114. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix, wherein at least a portion of the matrix comprises a plurality of parallel tubular sections and a wall permeable to a reagent, the wall being in subsurface contact with a soil, wherein the wall comprises a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

115. The apparatus of claim **114**, wherein the openings comprise pores intrinsic to a material comprising the shell.

116. The apparatus of claim **114**, wherein one or more of the tubular sections contact a groundwater within the soil.

117. The apparatus of claim **114**, further comprising one or more curved sections joined to the tubular sections, forming a subsurface serpentine pattern.

118. The apparatus of claim **114**, wherein a majority of the tubular sections are approximately coplanar in an approximately horizontal plane.

119. The apparatus of claim **114**, wherein a majority of the tubular sections are approximately coplanar in an approximately vertical plane.

120. The apparatus of claim **114**, further comprising one or more spacers extending between adjacent tubular sections.

121. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix, wherein at least a portion of the matrix comprises a plurality of parallel tubular sections and a wall permeable to a reagent, the wall being in subsurface contact with a soil, the matrix further comprising one or more curved sections joined to the tubular sections, forming a subsurface serpentine pattern.

122. A subsurface reagent delivery apparatus, comprising: a reagent distribution matrix in subsurface contact with a

soil and a plurality of parallel tubular sections, wherein the longitudinal axis of at least a portion of the tubular sections is oriented within about 45° of horizontal and wherein at least a portion of the matrix comprises a wall including a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

123. The apparatus of claim **122**, wherein the openings comprise pores intrinsic to a material comprising the shell.

124. The apparatus of claim **122**, wherein one or more of the tubular sections contact a groundwater within the soil.

125. The apparatus of clime **122**, further comprising one or more curved sections joined to the tubular sections, forming a subsurface serpentine pattern.

126. The apparatus of claim **122**, wherein a majority of the tubular sections are approximately coplanar.

127. The apparatus of claim **122**, wherein the approximately coplanar tubular sections are in an approximately vertical plane.

128. The apparatus of claim **122**, wherein the approximately coplanar tubular sections are in an approximately horizontal plane.

129. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix, a first plurality of parallel tubular sections, and a second plurality of parallel tubular sections and wherein a longitudinal axis of at least a portion of the first tubular sections is substantially perpendicular to a longitudinal axis of at least a portion of the second tubular sections and wherein at least a portion of the matrix comprises a wall including a shell having openings therein and a reagent permeable liner in contact with an inner surface of the shell.

130. The apparatus of claim **129**, wherein the openings comprise pores intrinsic to a material comprising the shell.

131. The apparatus of claim **129**, wherein at least a portion of the first and second tubular sections intersect to form one or more reagent distribution junctions.

132. The apparatus of claim **129**, wherein a majority of the tubular sections are approximately coplanar.

133. The apparatus of claim **132**, wherein the approximately coplanar tubular sections are in an approximately vertical plane.

134. The apparatus of claim **132**, wherein the approximately coplanar tubular sections are in an approximately horizontal plane.

135. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix, wherein at least a portion of the matrix comprises a wall permeable to a reagent, a first plurality of parallel tubular sections, and a second plurality of parallel tubular sections and wherein a longitudinal axis of at least a portion of the first tubular sections is substantially perpendicular to a longitudinal axis of at least a portion of the second tubular sections and wherein a majority of the tubular sections are approximately coplanar.

136. The apparatus of claim **135**, wherein the approximately coplanar tubular sections are in an approximately vertical plane.

137. The apparatus of claim **135**, wherein the approximately coplanar tubular sections are in an approximately horizontal plane.

138. The method of claim **78**, wherein a portion of the permeable wall is substantially amorphous and molecular diffusion of the reagent occurs through the substantially amorphous portion of the permeable wall.

139. A subsurface reagent delivery apparatus, comprising:

a reagent distribution matrix in subsurface contact with the soil, wherein at least a portion of the matrix comprises a wall permeable to a reagent and a plurality of parallel tubular sections and wherein the longitudinal axis of at least a portion of the tubular sections is oriented within about 45 degrees of horizontal, the matrix including one or more curved sections joined to the tubular sections, forming a subsurface serpentine pattern.

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