

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
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☐ Additional inventors are being named on the _____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

METHOD FOR ACCELERATED DECHLORINATION OF MATTER

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ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification Number of Pages

9

☐ CD(s), Number

☒ Drawing(s) Number of Sheets

1

☐ Other (specify)

☐ Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☒ Applicant claims small entity status. See 37 CFR 1.27.

☒ A check or money order is enclosed to cover the filing fees

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☐ Payment by credit card. Form PTO-2038 is attached.

FILING FEE
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\$80.00

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☒ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE

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Date

1/3/03

REGISTRATION NO.
(if appropriate)

30,057

Docket Number:

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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Date: 1.3.03

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS: Michael Scalzi
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FILED: Herewith

FOR: METHOD FOR ACCELERATED DECHLORINATION OF MATTER

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TRANSMITTAL LETTER

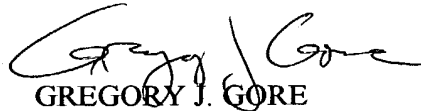
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Dear Sir:

Enclosed herewith for filing in the above-captioned provisional patent application is a specification including labeled drawings, a Provisional Application For Patent Cover Sheet, a Certificate of Mailing, a check in the amount of \$80.00, and a return receipt postcard.

Commissioner is hereby authorized to charge Deposit Account 071733 for any deficiencies or credits in payment fees.

Respectfully submitted,



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To the Assistant Commissioner for Patents:

This is a **PROVISIONAL** patent application for an invention entitled

METHOD FOR ACCELERATED DECHLORINATION OF MATTER

by Michael Scalzi of Doylestown, Pennsylvania, and Wade Meese of Worthington, Ohio, both
citizens of the United States of America.

BACKGROUND OF THE INVENTION

Through the years, chlorinated solvents have had a large impact on several industries, including pharmaceuticals, chemical processing, food extraction, dry cleaning and metal cleaning. With wide spread use and improper handling and storage, extensive soil and water damaged has occurred. Due to their toxicity, carcinogenicity and persistence in the environment, Chlorinated solvents are listed by the United States Environmental Agency as high priority pollutants. If left untreated, chlorinated solvents could remain unchanged for period of fifty years or more. The most common chlorinated solvents used are Methylene Chloride, tetrachloroethene, trichloroethene, carbon tetrachloride, chloroform, tetrachloroethane, dichloroethene and vinyl chloride. Carbon tetrachloride is s

systematic poison of the nervous system, the intestinal tract, the liver, and the kidneys. Vinyl chloride and Methylene chloride are known carcinogens, and could also effect the nervous system, the respiratory system, the liver, the blood, and the lymph system.

Chlorinated solvents are often found in separate phase mixtures commonly referred to as dense nonaqueous-phase liquids ("DNAPLs"). DNAPLs are visible, denser-than-water, separate oily phase materials in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces. Chlorinated solvents partition into the water phase to create a dissolved contaminant plume when in contact with water. Thus, creating a long-term, continuing source of contamination as the soluble constituents slowly dissolve into moving groundwater.

One common technique for treating contaminated matter is the "pump-and-treat" methods in which contaminated groundwater is pumped to the surface, cleaned chemically or by passing the groundwater through a bioreactor, and is reinjected into the groundwater. This process is carried out over a long period of time. Various factors complicate the removal of these contaminants from the environment. They are very volatile, highly mobile, denser than water, and generally found in the environment as mixtures of products with different degrees of chlorination.

SUMMARY OF THE INVENTION

Anaerobic microorganisms have the capability to decompose a wide range of highly chlorinated compounds. However, anaerobic microorganisms are at a disadvantage in that their growth is slow when compared to that of aerobic organisms. In-situ they are at an even greater disadvantage due to the partitioning of the targeted substrates into the soil matrix. In the accelerated dechlorination of soil and water contaminated with chlorinated solvents, anaerobic microorganisms are stimulated, increasing the rate of biological mineralization of the solvents.

The method provided utilizes a treatment process consisting of a colloidal suspension of iron powder, polylactate ester (electron donor), such as glycerol tripolylactate, xylitol pentapolylactate, and sorbitol hexapolylactate (slow release hydrogen donors), chemical oxygen scavengers (reducing agents) in solution with essential nutrients (ortho-phosphate and nitrogen compounds), vitamin stimulants such as B2 and B12 delivered via compressed gases: N or CO2 so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products. The incorporation of the B12 acts as both a enzymatic stimulus for the anaerobic

action and a surface catalyst of the iron particle. The core element of the B12, cobalt, enhances the surface oxidation action of the iron further

A closed delivery system is used to deliver the process utilizing a combination of gas and liquid delivery systems. All of the vessels are interconnected and valved, allowing for mixings, washings, filling, and discharge of materials via pressure vessels or mechanical pumping systems. The system utilized allows for a variety of dissimilar compounds to be delivered via a single injection line. Further, the switching between feed systems is accomplished without any loss of pressure to the delivery line eliminating the common problems experienced from the vacuum developed down-hole as pressure is released and reapplied. Lastly, the current system is fully self-contained requiring no electrical supply. The only site utility requirement is an available water source for slurry preparation.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an In-Situ Delivery System – Flow Diagram

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides the method for accelerated dechlorination of matter contaminated with chlorinated solvents utilizing mechanisms associated with zero valent iron oxidation. With the combination of lactic acid, oxygen scavengers, nutrients and zero valent iron, when added to matter contaminated with chlorinated solvents, can provide a reducing environment. The compounds have utility in aiding the destruction or inactivation of chlorinated solvents.

Iron powder, when added with other compounds to provide a source of electron donors, nutrients, and reducing agents, will stimulate naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents. In order to keep an anaerobic environment, nitrogen or carbon dioxide gas are used to propel all injections into the subsurface. The gas are first injected into the subsurface at approximately 175 pounds per square inch until a significant pressure drop is observed at the injection pressure vessel. This process is referred to as pre-injection fracturing with the intent of opening pathways into the subsurface for the injections. These pathways are believed to be those more permeable pathways along which chlorinated solvents are more likely to have migrated, both in the vadose and saturated zones. Liquid and liquid-entrained injectants are then delivered with pressurized gas to the pathways that are produced during the fracturization step. Based on the change in pressure observed at the compressed nitrogen supply, approximately 4 million cubic feet of gas (70°F and one atmosphere pressure) are injected into the subsurface of the site.

Chemical oxygen scavengers (reducing agents) are then injected to remove oxygen from groundwater and soil moisture immediately after fracturization of the subsurface, facilitating the anaerobic conditions that are preferred for the reductive dehalogenation of chlorinated solvents by indigenous bacteria. The resulting environment contains a wide spectrum of inorganic, biochemical, and enzymatic redox systems. Along with the reducing agents, nutrients are added to the injection in order to support microbial activity.

In an anaerobic environment, zero valent iron is then injected. Zero valent iron has a moderately low toxicity and a good reducing power so that it can rapidly reduce higher concentrations of dissolved phase chlorinated solvents when injected via direct chemical reactions. Zero valent iron will continue to react with dissolved chlorinated solvents in groundwater until it is completely oxidized by chlorinated solvents, oxygen, or other oxidants that contact residual concentrations of zero valent iron. Under normal environmental conditions, zero valent iron is capable of being oxidized and reduced back and forth.

With the addition of an electron donor source to provide hydrogen, the biodegradation process is initiated. A polylactate ester, such as glycerol tripolylactate, xylitol pentapolyolactate, or sorbitol hexapolyolactate, is now injected

with the intent of being cometabolized by indigenous anaerobic bacteria to produce dechlorinating conditions necessary for indigenous anaerobic bacteria to biodegrade residual concentrations of chlorinated solvents. This slow release process is controlled over time, maintaining a slow delivery of hydrogen at low concentrations which drives the anaerobic reductions. The lactic acid is then metabolized by indigenous bacteria to produce hydrogen, which can then be metabolized by chlorinated solvent degrading bacteria. Lactic acid, hydrogen, nutrients, and bacteria then move with groundwater, enhancing the attenuation of chlorinated solvents as they move through the aquifer over a period of months.

In order to cleanse the injection line of the viscous polylactate ester, a reducing agent is once again injected. The oxygen scavenger also promotes an anaerobic environment, stimulating the microorganisms. With the injections complete, a post injection line purge is performed. The gas is injected to clear the lines of any remaining reducing agents. With the clean line, the next injection location is prepared.

EXAMPLE 1

A site known to be contaminated with chlorinated solvents was geologically mapped. After determination of the subsurface contaminate concentrations, characteristics and the direction of flow of ground water, a series of injection points were drilled. Contaminate concentrations of cis-1,2-DCE prior to the biodegradation process ranged from 6.6 ppb to 69 ppb. The initial concentration of VC ranged from 0.97 to 2 ppb. The initial concentration of TCE ranged from 0.23 to 12.0 ppb.

After determining the levels of the contaminants, biodegradation was initiated and maintained by the addition of iron powder, lactate, reducing agents, vitamin stimulants, and delivered by compressed gases. The process was repeated once every 60 days for 4 months. Iron powder was chosen for two primary reactions with chlorinated solvents. The first being, the anaerobic iron corrosion reaction in which water is dissociated to form hydrogen gas, and the direct absorption of a chlorinated hydrocarbon onto the surface of the iron, followed by reductive dehalogenation. Four mechanisms are at work during the reductive process. First, the ZVI acts as a reductant by supplying electrons directly from the metal surface to an absorbed halogenated compound. Next, hydrogen gas is generated by the anaerobic corrosion of the metallic iron by water. Third, metallic iron may act as a catalyst for the reaction of hydrogen with the halogenated hydrocarbon using the hydrogen produced on the surface of the iron metal as the result of anaerobic corrosion with water. Fourth, solubilized ferrous iron can also act as a reductant, albeit at a rate at least an order of magnitude slower.

At the end of the 4 month process, microbial process are strongly active as demonstrated by the disappearance of Tetrachloroethane, 1,1-TCA, and dichloromethane. The alkaline conditions over the four months would suggest that the chloride production observed is primarily due to the microbial dechlorination process. The 4,600 ppb increase in chlorides observed over the period suggest significant microbial activity. There appears to be no toxicity issues in any of the areas on site and there has not been any microbial accumulation of intermediates of the degradation pathways. As a by-product of the program, benzene has also been addressed in those areas where it has been found in the groundwater samples.

What is claimed is:

1. A coordinated and synergistic process for stimulating the biodegradation of chlorinated solvents in an aqueous subsurface and saturated soil environment through growth and stimulation of bacteria and oxidation of dissolved phase compounds via the action of iron particles including in an anoxic environment:

- (a) the addition of iron powder as a colloidal suspension such that a layer of dispersed iron particles is formed within the soil; and
- (b) providing electron donors, one that is an inorganic compound capable of supplying an electron wet in an aqueous environment, another which is an organic compound which releases electrons over time through its decomposition to dehalogenating bacteria as a stimulus for anaerobic biodegradation of chlorinated solvents; and
- (c) providing a reducing agent to remove oxygen from groundwater and soil moisture immediately prior to the introduction of stimulation agents, facilitating the anaerobic conditions that are preferred for the reductive dehalogenation of chlorinated solvents by bacteria; and
- (d) providing nutrients comprising of phosphorus- and nitrogen-containing compounds such that biological growth is not inhibited by these limiting factors,
- (e) providing essential enzymes, such as vitamin B2 and B12, to support and stimulate anaerobic microbial activity,
- (f) a delivery process via compressed gases such as N or CO2 as not to oxygenate an anaerobic process wherein a liquid solution is injected into the contaminated matter and
- (g) a sequence of delivery such that
 - 1. a pressurized gas is introduced so as to establish horizontal delivery pathways subsurface,
 - 2. a slurry containing nutrients and oxygen scavenger (reducing agent) is introduced subsurface into the saturated and vadoze zone in such quantity as to influence both zones driving these area anoxic,
 - 3. a colloidal suspension of iron particles within the nutrient/reducing agent slurry is introduced immediately following the environmental preparation achieved in the prior step,
 - 4. a heated organic compound capable of releasing electrons at low concentrations over time which drives the anaerobic reductions, containing 1 to 100 micromolar concentrations of vitamin B12, cyanocobalamin, and 10 to 1000 micromolar concentrations of riboflavin, 7,8-dimethyl-10'-(1'-d-ribyl) isoalloxazine, is introduced immediately following the iron suspension introduction,

5. a slurry containing nutrients and oxygen scavenger (reducing agent) is introduced subsurface into the saturated and vadoze zone in such quantity as to further influence both zones while driving the injectants further into the formation and
 6. a pressurized gas is injected so as to drive all materials into the formation and clean all delivery lines within the system.
2. A process according to claim 1, wherein the chlorinated solvent is at least one member selected from the group consisting of trichloroethene, tetrachloroethene, dichloroethene isomers consisting of cis-1,2-dichloroethene, trans-1,2-dichloroethene and 1,1-dichloroethene, carbon tetrachloride, dichloromethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane.
 3. The process according to claim 2, wherein the pH for the reaction is between 3.5 and 8.5.
 4. The bioremediation process of claim 1 wherein the microorganisms comprise anaerobic microorganisms.
 5. The bioremediation process of claim 1 which is carried out in situ.
 6. The bioremediation method of claim 4 wherein the anaerobic microorganisms comprise bacteria from the group of methanogens, acetogens, ethanogens, dehalogenators, denitrifiers, and mixture thereof.

METHOD FOR ACCELERATED DECHLORINATION OF MATTER_{av}**Abstract**

Anaerobic microorganisms have the capability to decompose a wide range of highly chlorinated compounds. However, anaerobic microorganisms are at a disadvantage in that their growth is slow when compared to that of aerobic organisms. In the accelerated dechlorination of matter contaminated with chlorinated solvent, anaerobic microorganisms are stimulated causing a faster breakdown.

The method provided utilizes a treatment process consisting of zero valent iron, lactate, nutrients, chemical oxygen scavengers (reducing agents), vitamin stimulants such as B2 and B12 all delivered via compressed gases: N or CO₂ so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products.

FIG. 1

