A method for increasing the effectiveness of a permeable treatment wall is described. The method includes the introduction of ultrasonic radiation in or near the wall. A permeable treatment wall is also described which has an ultrasonic radiation generating transducer in or near the wall. Permeable treatment walls are described as having either a well vertically extending into the wall, or a rod vertically extending into the treatment wall. Additionally, a method for adapting a permeable treatment wall to allow for the introduction of ultrasonic radiation in or near the wall is described.

11 Claims, 4 Drawing Sheets
FIG. 1
FIG. 4

- NO ULTRASOUND
- ULTRASOUND 30 MINUTES

TIME (MIN)

TCE CONC. (ppmv)
FIG. 5

FIG. 6

FIG. 7a FIG. 7b FIG. 7c FIG. 7d
USE OF ULTRASOUND TO IMPROVE THE EFFECTIVENESS OF A PERMEABLE TREATMENT WALL

ORIGIN OF THE INVENTION

The invention described herein was made in performance of work under a NASA contract and is subject to the provisions of Public Law 96-517 (35 U.S.C. §202) in which the contractor has elected not to retain title.

BACKGROUND OF THE INVENTION

Halogenated solvents are used by a wide range of industries including dry cleaners, electronic equipment manufacturers, metal parts fabricators, insecticide and herbicide producers, military equipment manufacturers, etc. These solvents replaced petroleum derived mineral spirits and have distinct advantages because of their nonflammability. The persistence and mobility of these hydrocarbons in the subsurface was largely unanticipated, therefore historical disposal practices have led to widespread groundwater contamination. For example, trichloroethylene (TCE) has been found at more than 79 of 1300 National Priority List sites, primarily as a groundwater contaminant.

Chlorinated solvents fall into the category of dense non-aqueous phase liquids (DNAPLs). DNAPLs are heavier than water and therefore sink below the groundwater table until they encounter a layer through which they cannot pass. As they move downwards, DNAPLs leave behind a smearing trace of their migration pathway before eventually pooling on a confining unit or perhaps within a crevice of a fractured rock. Most DNAPLs can dissolve in aqueous environments, yet they do so in such small quantities that the original contaminant pool functions as a subsurface contamination source. The portion of the contaminant that does dissolve is typically at concentrations which exceed allowable groundwater standards.

Treatment of halogenated hydrocarbon contaminated groundwater is usually accomplished by pumping the groundwater to the surface and removing the contaminant through oxidation or air stripping. Pump-and-treat remediation systems have experienced limited success with respect to DNAPLs. Capillary pressure holds DNAPL at residual saturation which can represent significant contamination. Consequently, removal of the contaminant from the subsurface is extremely time consuming, and therefore cleanup goals are rarely achieved. However, even though the pump-and-treat method is not a particularly successful remediation technology, it has proven to be a highly efficient tool for containment of the contaminant.

Because of the limited degree of success in remediating contaminated sites with technologies which attempt to remove the contaminant from the subsurface and pump it to a treatment system, recent efforts have focused on the physical, biological, or chemical treatment of these contaminants in situ.

A permeable treatment wall (PTW) is an alternative remediation technology which does not require groundwater to be pumped to a treatment facility. Instead contaminated groundwater is passively treated in situ. Permeable treatment walls, as shown in FIG. 1, are vertical cells which are installed subsurface near a contaminant source. PTWs are designed to have a greater permeability than the surrounding soils, and are typically constructed using a high permeability sand mixture comprising a zero-valent metal. PTWs have been successfully demonstrated in several field studies and offer potential economic savings over other halogenated solvent treatment methods.

SUMMARY OF THE INVENTION

The invention provides a method for increasing the effectiveness of a permeable treatment wall, comprising introducing ultrasonic radiation in or near the wall.

The invention also provides a permeable treatment wall comprising an ultrasonic radiation generating transducer in or near the wall. The permeable treatment wall can comprise a well vertically extending into the wall, the well having a lining and an opening such that the ultrasonic radiation generating transducer can be lowered into the opening. Alternately, the ultrasonic radiation generating transducer can comprise a rod vertically extending into the treatment wall and an ultrasonic generator coupled to an upper end of the rod.

Additionally, the invention includes a method for adapting a permeable treatment wall to allow for the introduction of ultrasonic radiation in or near the wall, comprising inserting an ultrasonic radiation generating transducer into the subsurface in or near the wall, or inserting an ultrasonic radiation generating transducer into a well which is in or near the wall, and which is suitable for receiving the transducer. This latter method may further comprise a first step of constructing the permeable treatment wall.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 illustrates a side view of an in situ PTW;
FIG. 2 illustrates the effects of ultrasound on TCE half life in the column studies of Example 2;
Fig. 3 illustrates TCE destruction with iron (100 mesh) as measured in Example 3; Fig. 4 illustrates TCE destruction with magnesium metal as measured in Example 4. Fig. 5 illustrates a PTW where ultrasonic radiation is introduced into the area of a PTW using an in-well technique; Fig. 6 illustrates a PTW where ultrasonic radiation is introduced into the area of a PTW using a rod; and Figs. 7a–d illustrate some embodiments of the rod of FIG. 6.

Detailed Description of the Invention

In the following detailed description of the preferred embodiments of the invention, reference is made to the accompanying figures which form a part hereof, and in which is shown by way of illustration specific embodiments in which the invention may be practiced. It is to be understood that other embodiments may be utilized without departing from the scope of the present invention.

As used herein, the phrase “near said wall” or “near the permeable treatment wall” means a position beyond the outer wall of the PTW but within a distance such that the ultrasonic radiation can produce a beneficial effect on the PTW.

Permeable Treatment Walls

A PTW is conceptually very similar to a concrete slurry wall, except the functions are completely opposite. When used at a remediation site, slurry walls attempt to confine a contaminant plume, thereby preventing its spread to uncontaminated regions. Slurry walls are virtually impermeable by design. PTWs, on the other hand, are permeable and are designed so that larger volumes of water pass through the PTW than through the surrounding soils. As contaminated groundwater flows through a treatment wall, halogenated solvents are chemically altered to give acceptable alternative species. Emerging on the downstream side of the treatment wall is contaminant-free groundwater. No pumps or other aboveground treatment are required, as the natural groundwater gradient carries the contaminant through the treatment wall.

Permeable Treatment Wall Construction

PTWs can be constructed using a mixture of a zero valent metal and a high permeability bulking material. Alternatively, a PTW comprising pure zero valent metal can be used. Four PTW construction techniques have been tried in the field or proposed: 1) traditional excavation and backfilling, 2) slurry trenching, 3) deep-soil mixing, and 4) borehole augering.

Traditional excavation and backfilling can be relatively cheap and expedient if the depth of the excavation is shallow. However, with deeper depths, the shoring of the trench’s side walls becomes a safety issue and can significantly slow down the progress of the excavation. Also, when excavating contaminated wastes, the costs associated with the ultimate disposal of the removed soil may be prohibitive. As a result, the excavation and backfilling method may not be the most economical construction method for large PTWs.

Slurry trenching is most commonly used to construct deep, impervious walls below the subsurface. Typically, the walls are made of concrete and are intended to contain a migrating plume or to divert groundwater away from a contaminant source. During construction of slurry walls, a liquid mixture of water and bentonite (the slurry) is placed in an open trench to support the trench walls. After the excavation, a cement slurry is pumped into the trench to form a permanent wall.

The bentonite performs two functions when constructing a slurry trench. First, it thinly coats the sides of the trench creating what is called a filter cake. The filter cake minimizes slurry seepage outside of the excavation. Additionally, it provides a plane against which the weight of the slurry can push to counteract the lateral hydraulic forces of the surrounding groundwater, thus helping to prevent the trench’s collapse.

The second function of the bentonite is to hold trench soil in solution without settling. The combined densities of the soil and bentonite create a slurry with a density greater than that of groundwater alone. The higher density slurry pushes against the sides of the trench wall helping to prevent its collapse.

When applying traditional slurry trenching construction techniques to permeable treatment walls, bentonite could not be used to perform the two aforementioned functions. The bentonite filter cake permanently creates an impermeable barrier, which defeats the objective of a PTW. However, a natural, biodegradable polymer can be substituted for the bentonite. Typically, the biopolymer maintains an effective filter cake for two weeks before dissolving in water. Once dissolved, the walls of the trench no longer prohibit water from passing through the treatment cell.

This particular method of PTW construction eliminates the time consuming process of installing side braces, which is typically required for the traditional excavation and backfilling method. Unfortunately, the excavated soil disposal cost for this construction method is also high. For civil engineering applications, both trenching techniques usually do not extend to depths beyond 25 m. Deep-soil mixing is a relatively new construction technique to the environmental engineering field. Similar to trenching, deep-soil mixing traditionally increases soil strength and reduces permeability. Where it deviates significantly from trenching is that it does not excavate soils and therefore does not have the associated disposal costs. Deep-soil mixing uses a crane-supported set of leads that guides a series of hollow augers into the subsurface. A cement-based grout is injected through the augers as the mixing shafts penetrate the soil. Once the design depth is reached, the mixing shaft rotation is reversed and the mixing process is repeated as the auger shafts are brought to the surface, leaving behind a soilcrete column.

Deep-soil mixing may be applied to construct permeable treatment walls where sandy soils predominate. Instead of excavating soil down to design depths, only a portion of the excavation occurs; specifically in the upper few feet of the subsurface where there is little chance of finding halogenated contaminants. The mixing augers blend the existing sandy soils with zero valent metal shavings. The upper subsurface is removed to allow volume increases as the mixing action redistributes the soil within the column. Each mixed column of iron and native material then serves as a “pumpless well” drawing water into the column due to its higher hydraulic conductivity relative to the surrounding soil. To date however, deep-soil mixing rigs have not been used to prepare a PTW.

Borehole augering is used throughout the drilling industry for the installation of pumping and monitoring wells. As adapted for PTW construction, this construction method would involve augering to a design depth, filling the borehole through the hollow stem auger with the coarse sand and
null
will be apparent to one skilled in the art that although the pipe has been referred to herein as "slotted," the slots function to facilitate the transfer of ultrasonic radiation from the transducer to the PTW and therefore, any suitable opening is acceptable. Additionally, it may also be possible to use a solid walled pipe in place of the slotted pipe described above.

In Ground technique

As illustrated in FIG. 6, ultrasonic radiation may also be introduced into the area of a PTW 100 using a grooved or turned rod 140, inserted directly into the subsurface, as a transducer. An ultrasound generating device 150 is coupled to an upper, exposed end of the rod for transferring ultrasonic radiation. Commercial ultrasound generating devices are often equipped with a horn made of a specific material. Such a device may be coupled to the rod in any manner suitable for the efficient transfer ultrasonic radiation. The material of a horn will transfer sound at a specific speed. In order to minimize power losses resulting from the transfer of sound from one material to another, the rod should possess a sound transfer velocity which is similar to the sound transfer velocity of the horn material. For example, if the horn is made of Titanium, then a rod material which matches this with respect to sound transfer would be Stainless Steel, 347 ($V_{\text{per}}=5790$ m/sec $V_{\text{stainless}}=6070$ m/sec).

Another significant consideration is the spacing of either the turns or grooves. Preferably, the spacing is in increments of either one-half or equal to the wavelength generated by the ultrasound device. If this spacing is not adhered to, then subsequent sinusoidal waves from the generator will be canceled out by a reflected wave which did not get transferred into the groundwater. For example, if a 20 KHz power source is used, the wavelength of the ultrasonic radiation is approximately 0.285 meters. Therefore, the groove spacing along the rod should preferably be every 0.285 meters or every 0.142 meters.

As illustrated in FIGS. 7a-d, a variety of turn or groove designs are useful for practicing the invention. For example, the turns or grooves may be embodied as a series of horizontal grooves 160, a series of diagonal grooves 170, a series of horizontal raised ridges, or turns, 180, or a series of diagonal raised ridges 190. Ultrasonic radiation is transferred to the groundwater in the space falling between the turns or grooves in the rod. Accordingly, it will be apparent to one skilled in the art that any turn or groove design which allows for the transfer of the ultrasonic radiation is acceptable, and that the designs illustrated in FIGS. 7a-d are not limiting.

The invention will now be illustrated by the following non-limiting Examples.

EXAMPLES

Example 1

Batch Studies

Aqueous samples of trichloroethylene (TCE) were exposed to 20-kHz ultrasound in a 0.5-L Tedlar\textsuperscript{TM} bag. Bag reactors were filled with 0.5 L deionized water and 0 to 2.5 g of iron, and purged with nitrogen. TCE was added in a 5000 ppm methanol solution to achieve final concentrations of 5 to 20 mg/L. Iron was washed with a ten-percent sulfuric acid solution prior to use to remove surface contamination. Bags were placed on a shaker table (160 shakes/min) to maintain well mixed conditions. Samples were removed periodically from the bags and analyzed for TCE. Zero-order batch treatments were conducted for up to 60 days of contact with TCE. Length of sonication varied from 30 minutes to three hours. To minimize temperature impacts during sonication, water was either allowed to flow continuously through the ultrasound bath or the tank was emptied and refilled every 30 minutes. Reagents were obtained from Fisher Scientific, and were used as received. One hundred-mesh iron, obtained from Mallinkrodt Chemicals (Paris, Ky. 40361) was used. Control bags were constructed to evaluate possible sorption and ultrasound effects exclusive of iron treatment.

Results

Batch Studies. A first control, with no iron and no ultrasound exposure, was shaken for two weeks. A second control, contained no iron but was exposed to ultrasound for 30 minutes. TCE data were collected before ultrasound, immediately after exposure and then one hour later. For the control with no ultrasound exposure and no iron, less than two percent of TCE was lost over 14 days. TCE destruction during 30 minutes of sonication alone (no iron) also resulted in less than two percent loss. Fifty-five percent of the experiments were performed in duplicate.

To quantify the results, data were analyzed assuming first-order kinetics. Bags which received ultrasound treatment were monitored, for the purpose of developing rate constants, beginning 24 hours after sonication ended to prevent inclusion of TCE destruction which may have occurred during treatment. Concentrations were transformed to natural logarithms and results of linear regression between transformed concentrations and time were examined. TCE breakdown products, primarily cis-dichloroethene and ethene were found to increase over time, indicating destruction and not simply sorption of TCE onto the iron surface. Iron concentrations, length of sonication, half-lives for TCE disappearance, first order rate constants normalized per m$^2$ iron and length of monitoring period are provided in Table 1.

<table>
<thead>
<tr>
<th>Iron, g/L</th>
<th>US Exposure, hrs</th>
<th>Half-Life, days</th>
<th>1st Order Rate Constant, min$^{-1}$ (&lt;$10^6$)*</th>
<th>Days Monitored Before/After US</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>No Loss\textsuperscript{a}</td>
<td>14/0</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
<td>No Loss\textsuperscript{a}</td>
<td>0/14</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>36.2</td>
<td>7.56</td>
<td>28/0</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>31.2</td>
<td>8.51</td>
<td>Q28</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>24.6</td>
<td>3.71*</td>
<td>28/0</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>21.9</td>
<td>4.17</td>
<td>Q28</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>16.2</td>
<td>3.69*</td>
<td>28/0</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>13.5</td>
<td>3.06*</td>
<td>14/14</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.3</td>
<td>10.3*</td>
<td>Q28</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>5.2</td>
<td>10.5*</td>
<td>14/14</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>5.2</td>
<td>10.6*</td>
<td>14/14</td>
</tr>
</tbody>
</table>

\textsuperscript{a}normalized per m$^2$ iron

Comparison of first order rate constants normalized per m$^2$ of iron suggest that the introduction of ultrasound to reactors containing iron increases reaction rates significantly. Sonication for one-half hour appears to increase reaction rates an average of about 12 percent compared to similar iron concentrations which received no treatment. Regardless of when the ultrasound treatment occurred relative to TCE exposure. However, rate constants nearly tripled (average increase of 184 percent) after a minimum of one
hour of ultrasound treatment. While rate constants continued to increase with increasing length of treatment, the difference in rate increases between one hour and three hours of treatment was less than four percent.

Ultrasonic has been shown to effectively degrade organic compounds, including halocarbons. Much of this work was performed using a horn or probe configuration for the energy delivery system, similar to that used in the current column study, however, some studies used small volumes of samples (25 to 100 mL) and irradiated for periods of up to 3 hours by ultrasonicators operating at a high frequency (such as 530 kHz) or high ultrasonic intensity (approximately 75 W/cm²).

Based on these reports, sonication of a large volume (500 mL) of liquid in an ultrasonic bath operating at 20 kHz with relatively low ultrasonic intensity (0.16 W/cm²) under the conditions described in the Examples herein would not likely provide sufficient energy to degrade significant amounts of TCE. In addition, evaluation of reaction rate constants is delayed sufficiently to exclude these effects. The improvement in TCE destruction is therefore assumed to be due to removal of corrosion products which have accumulated on the iron surface. Scanning electron microscopy (SEM) has also shown that iron “aged” in 200 ppm TCE for 30 days exhibited significant calcification on the surface as compared to “unaged” iron. Following ultrasound application, the SEM showed that the surface was visibly cleaner.

Example 2

Column Studies

Column studies were conducted in an up-flow mode using four different combinations of iron and native aquifer material: 50-mesh iron particles, from Science Kit and Boreal Laboratories, acid-washed heated cast-iron chips from the Peerless Corp., unwashed Peerless iron, and acid-washed heated cast-iron chips from Master Builder’s Supply (Streetsboro, Ohio). The Peerless and Master Builder’s Supply iron chip mesh sizes were distributed as follows: 43 percent of the iron was retained on mesh size 20 and 40 percent on mesh size 40. The remaining fraction of the iron particles included iron dust.

Four Plexiglass columns (10 cm x one-meter) were charged with 20 weight-percent iron and 80 weight-percent construction-grade sand. A fifth control column was charged with only sand. Unbuffered solutions of 15 mg/L TCE in deionized water was allowed to flow through the columns at a rate of 4.7 mL/min. Samples were collected at multiple depths along the columns to monitor TCE destruction. Ultrasound was introduced to the 50-mesh iron column at 50 percent maximum power using a 15.9 mm-diameter stainless-steel long-shaft auger drill bit inserted 15 cm down the bottom of the column and threaded for connection to a Fisher Sonic Dismembrator Model 500 (Watt) ultrasonicator.

Analysis. TCE was analyzed following EPA Method 624. Each sample was injected with 5.0 µL of internal standard, bromochloromethane. A five-ml portion of the sample was transferred to a purge vial. Helium was bubbled through the sample for a period of 15 minutes to transfer the TCE to a Vocabr 3000 trap. The desorption time from the trap was four minutes at 250°C and the trap bake time was seven minutes at 260°C. A Hewlett-Packard gas chromatograph (Model 5890) equipped with a 0.25-mm id, 60-m long Vocel capillary column was programmed for a three-minute hold at 60°C, and a 15°C/min rise to 180°C held for three minutes.

Iron surface area was measured using a Porous Material, Inc. BFET Sorptometer. The 100-mesh iron surface area was found to be 1.76 m²/g.

Results

The results from the column studies are shown in Table 2. The increase in half-lives over time suggests that gradual but significant iron aging has occurred. Comparison of TCE removal by washed and unwashed Peerless iron showed that washed iron is ten times more reactive than unwashed. Surprisingly, little difference was initially observed among the three types of iron used.

### Table 2

<table>
<thead>
<tr>
<th>Column</th>
<th>TCE Half-Life, min</th>
<th>No. of Pore Volumes Passing through Column</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-mesh Iron</td>
<td>240</td>
<td>1-20</td>
</tr>
<tr>
<td>289</td>
<td></td>
<td>200-225</td>
</tr>
<tr>
<td>Peerless Iron</td>
<td>618</td>
<td>300-315</td>
</tr>
<tr>
<td>Master Builder Iron</td>
<td>225</td>
<td>50-60</td>
</tr>
<tr>
<td>Unwashed Peerless</td>
<td>800</td>
<td>80-140</td>
</tr>
<tr>
<td>Peerless Iron</td>
<td>2507</td>
<td>50-60</td>
</tr>
</tbody>
</table>

The effects of ultrasound on the 50-mesh iron column were explored once deterioration in column performance (increased half-life) was observed over an extended period of time (300 plus pore volumes). Ultrasound was introduced at over a one-hour period. An immediate reduction in half-life was observed over the next 30 pore volumes. Unfortunately, air was drawn into the feed bag shortly thereafter, introducing oxygen to the column. The half-life immediately returned to the pre-ultrasound level, presumably due to the build-up of oxidized iron products on the iron surface. Ultrasound was again introduced, and, as can be seen in FIG. 2, half-lives fell dramatically and remained at low levels.

Half-lives calculated for TCE disappearance over the lower section of the column, which contains the probe, and the upper section of the column before and after sonication indicate that impacts of sonication extend beyond the end of the probe. Prior to sonication, the lower half of the column, which receives the highest concentrations of TCE, exhibited a half-life approximately 1.5 times that of the upper section. After sonication, both half-lives dropped significantly. The lower section exhibited a half-life decrease of approximately 70 percent, while the half-life for the upper section of the column dropped 22 percent. Although certainly not to the degree of the lower section, the iron in the upper section of the column appears to have benefitted from sonication.

During the ultrasound application, dispersion of brown colloidal material was observed (iron precipitates). This material tended to be removed further up the column with the advective flow. No increase in pressure drop along the column was experienced after ultrasound treatment which would suggest plugging of the column. Some short-circuiting of TCE down the column was measured during ultrasound introduction. Short-circuiting was not observed for a lithium tracer added to the TCE solution. Therefore, it is assumed that TCE volatilization occurred as a result of local high temperatures induced by ultrasound. Once ultrasound was discontinued, the TCE movement through the column returned to normal.

Example 3

TCE was studied at initial concentrations of up to 20.0 ppmv in batch reactors. The batch reactor consisted of a 3 neck-1 L round bottom flask, kept at constant temperature.
An ultrasound probe was inserted through the center neck and the tip positioned just above the metal (1.0 g iron of various surface areas or magnesium strips). Experiments were conducted with iron metal (various surface areas) or magnesium metal, or a 50-50 mixture of the two, both with and without ultrasound. Also, experiments were done with ultrasound alone (no metal) and a control (no metal or ultrasound). FIG. 3 and FIG. 4 show results for TCE destruction efficiency both with and without ultrasound for iron and magnesium metals, respectively.

All publications, patents, and patent documents are incorporated by reference herein, as though individually incorporated by reference.

What is claimed is:

1. A method for increasing the effectiveness of a permeable treatment wall comprising introducing ultrasonic radiation in or near said permeable treatment wall using an in-well technique.

2. The method of claim 1 wherein the well comprises a slotted pipe or a solid pipe placed into the subsurface in or near the permeable treatment wall.

3. The method of claim 2 wherein the pipe is made of a material with a sound transfer velocity similar to that of groundwater.

4. The method of claim 2 wherein the pipe is made of polyethylene.

5. A method for increasing the effectiveness of a permeable treatment wall comprising introducing ultrasonic radiation in or near said permeable treatment wall using a grooved rod.

6. A method for increasing the effectiveness of a permeable treatment wall comprising introducing ultrasonic radiation in or near said permeable treatment wall using a turned rod.

7. A permeable treatment wall comprising a well vertically extending into the wall, the well having a lining and an opening, and an ultrasonic radiation generating transducer in the well.

8. The permeable treatment wall of claim 7 wherein the lining comprises slots for ultrasonic radiation to pass through.

9. The permeable treatment wall of claim 7 wherein the lining has a sound transfer velocity approximately that of groundwater.

10. A permeable treatment wall comprising a rod vertically extending into the treatment wall, and an ultrasonic generator coupled to an upper end of the rod.

11. The permeable treatment wall of claim 10 wherein the rod includes a grooved or turned exterior surface.