



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : E02D 3/00, B09B 3/00, C02F 1/72	A1	(11) International Publication Number: WO 94/18396 (43) International Publication Date: 18 August 1994 (18.08.94)
(21) International Application Number: PCT/US94/01533 (22) International Filing Date: 10 February 1994 (10.02.94) (30) Priority Data: 08/017,478 12 February 1993 (12.02.93) US (60) Parent Application or Grant (63) Related by Continuation US 08/017,478 (CIP) Filed on 12 February 1993 (12.02.93) (71)(72) Applicant and Inventor: VIGNERI, Ronald, J. [US/US]; 1723 Verrazanno Drive, P.O. Box 517, Wilmington, NC 28405-0517 (US). (74) Agents: KLAUBER, Stefan, J. et al.; Klauber & Jackson, Continental Plaza, 4th floor, 411 Hackensack Avenue, Hackensack, NJ 07601 (US).		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD AND SYSTEM FOR REMEDIATION OF GROUNDWATER CONTAMINATION 		
(57) Abstract A method for remediating a hydrocarbon-contaminated region of a subterranean body of groundwater (10) to destroy or reduce the initial concentration levels of hydrocarbon contaminants. A plurality of mutually spaced wells (12, 14, 16, 18) are provided which intersect the groundwater (10) region. A treating flow of acetic acid is provided from one or more of the wells into the groundwater region, to establish acidic conditions. A turbulent flow of an aqueous solution of ferrous ion into the groundwater (10) region is generated for mixing with the acidified groundwater (10), thereby providing a catalyst for disassociation of hydrogen peroxide. A treating flow of hydrogen peroxide solution from one or more of the wells (12, 14, 16, 18) into the groundwater region is then provided, so that the hydrogen peroxide may undergo a Fenton-like reaction in the presence of the acidic conditions and ferrous ion to generate hydroxyl free radicals for oxidizing the contaminants. An apparatus system for practising the method is also disclosed.		

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**METHOD AND SYSTEM FOR REMEDIATION
OF GROUNDWATER CONTAMINATION**

BACKGROUND OF INVENTION

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This invention relates generally to the beneficial treatment of organics-contaminated water, and more specifically relates to method and apparatus for remediating groundwater which has become contaminated with hydrocarbons, PCB's, aromatic solvents, chlorinated solvents, pesticides and the like.

Groundwater contamination, typically arising from petroleum storage tank spills or from intentional or accidental discharge of liquid hydrocarbons or compositions containing same, has become a problem of increasing concern in virtually all areas of the world where human activities occur. Aside from contamination of this type which results from industrial complexes, it has unfortunately been found that even suburban neighborhoods which would appear to be havens from such phenomena, have increasingly been found to the consternation of the residents to harbor pools of hydrocarbon pollutants, the source of which is very commonly automobile service station sites at which antiquated or abandoned storage tanks have released gasoline, fuel oils, lubricants and the like into the local groundwater. Other common sources of such noxious material can include dry cleaning establishments and/or manufacturers or distributors of the tetrachloroethane which is used in dry cleaning. Other well-known hazardous hydrocarbon materials include polychlorinated phenols (e.g. PCB's), pentachlorophenols (PCP's), and various aliphatic and aromatic hydrocarbons, as for example gasoline, benzene, naphthalene and various petroleum and petroleum derivative products. Certain particularly pernicious compounds of this type are often considered under the grouping "BTEX", which is understood

by those familiar with the art to refer to benzene, toluene, ethyl benzene and the xylenes (m-, p-, and o-). The BTEX content of groundwater or other contaminated sites is frequently regarded as a principle measure of the acceptability of the water in question for human consumption and use and other purposes.

Various remediation techniques have been utilized in the past for treatment of groundwater which has been thus contaminated. Among the most predominate type of systems in present use are those based on so-called "pump and treat" technology. In this method the contaminated groundwater and possibly a phase-separated product is withdrawn from a recovery well sunk into the groundwater and pumped to an above ground treatment facility. Various treatment techniques are thereupon used, such as diffused air treatment and air stripping. Inline filters can also be used; and similarly carbon adsorption can serve to remove contaminants from the displaced groundwater. Systems of the pump and treat type are considered expensive to install and operate. In many instances they basically result in separation or adsorption of the contaminants, and while purified water may result from the treatment, the problem often remains of disposing of the contaminants which have thus been separated.

In recent years increasing interest has also been evidenced in bioremediation technology. The technology has been of great interest, but its effective use in treating groundwater has been limited. The procedures are very complex, involving the use of expensive and complex reactors, and can cause adverse geochemical reactions, and can even introduce new toxic compounds beyond those which are being treated.

Pursuant to the foregoing, techniques have been sought

which would serve to directly treat the contaminated groundwater in both effective and economical fashion.

It has long been recognized that the hydrocarbons
5 representing the source of contamination in the subject
matter of interest, can by ordinary chemical reactions be
oxidized to harmless constituents. In principle, all
such hydrocarbons can under proper conditions be oxidized
to harmless end products, such as water and carbon
10 dioxide. To date, practical methodology to achieve such
results, however, have not been widely adopted. Among
the strong oxidizing agents which in principle could
serve these purposes is hydrogen peroxide, a composition
which is readily available and at reasonable cost. Some
15 efforts have indeed been made to utilize this oxidizing
agent for these purposes. In Brown et al., U.S. Patent
No. 4,591,443, for example, an aqueous solution
containing hydrogen peroxide, together with a compound
for controlling the mobility of the aqueous solution by
20 modifying the viscosity or other flow properties, is
introduced into a permeable subterranean formation. It
is not contemplated that the groundwater can be treated
directly in this disclosure.

25 Forte et al., U.S. Patent No. 4,167,973, discloses the
use of strong oxidizing agents, which can include
hydrogen peroxide, for treating contaminated water and
the like which has been withdrawn from an underground
source and is thereupon treated in a mixing device. The
30 methodology is therefore of the pump and treat system
type, and the treatment of the groundwater is not in
situ.

Other patents of interest include U.S. Nos. 4,927,293 to
35 Campbell, and 4,978,508 to Hansen et al.

Among the other deficiencies of the prior art, is the

failure to define a system wherein a strong oxidizing agent such as hydrogen peroxide may be directly injected into groundwater in a manner such that it can react in situ with the hydrocarbon contaminants present in same, while at the same time providing techniques to assure the efficacy of the said method.

Pursuant to the foregoing it may be regarded as an object of the present invention to provide a method and system which enable economical, effective and rapid treatment of groundwater contaminated with hydrocarbons, so as to destroy the said hydrocarbons or reduce same to a level below that which is considered detrimental to human use.

It is a further object of the present invention to provide a method and apparatus of the foregoing character, which utilizes safe and readily available treatment chemicals, and which moreover results in output products which are harmless and safe.

It is a still further object of the invention to provide a method and apparatus which can be practiced with use of relatively simple equipment, and by relatively unskilled personnel.

25

SUMMARY OF INVENTION

The present invention utilizes the well-known Fenton's reaction in which hydrogen peroxide reacts with Fe^{+2} ion to produce OH. free radical according to the equation $\text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow \text{OH.} + \text{OH}^- + \text{Fe}^{+3}$. The OH. free radical is an extremely powerful oxidizer which effectively reacts with organic contaminants to produce carbon dioxide and water.

Thus in accordance with the present invention, a method is provided for remediating a hydrocarbon-contaminated region of a subterranean body of groundwater to destroy

or reduce the initial concentration levels of hydrocarbon contaminants. Pursuant to the invention a plurality of mutually spaced wells are provided which intersect the groundwater region. A treating flow of acetic acid is provided from one or more of the wells into the groundwater region, to establish acidic conditions therein. A turbulent flow of an aqueous solution of ferrous ion is introduced into the groundwater region, for mixing with the acidified groundwater, thereby providing a catalyst for disassociation of hydrogen peroxide. A treating flow of hydrogen peroxide solution is then provided from one or more of the wells into the groundwater region, the hydrogen peroxide undergoing a Fenton-like reaction in the presence of the acidic conditions and ferrous ion to generate hydroxyl free radicals for oxidizing the contaminants.

During the acidification step the groundwater region is typically brought to a pH of from 3.0 to 4.0. The existence of acceptable continuity and well interflow paths for the region are determined by monitoring pH changes at each other of said wells as a function of time to detect a pH drop of at least 0.2.

Between the acidification step and the introduction of ferrous ion, as well as between the ferrous ion introduction and the addition of hydrogen peroxide, potable water is injected from the same said wells in place of acetic acid and ferrous ion solutions, to provide a transient buffer zone between the compositions introduced during such steps thereby delaying the reaction achieved in the final step until the plume has extended further into the groundwater region.

Where acetic acid is used for the acidification step, it is typically flowed as a solution at a rate of 5 to 10 gallons/min, wherein said solution includes from 10% to

100% by weight of acetic acid. The total amount of acetic acid flowed into the region is typically from 1 to 3% by volume of the effective volume of contaminated water which is treated, based on a 100% acetic acid solution. The Fe^{2+} ion is provided as an aqueous solution of ferrous sulfate heptahydrate, the total volume of the solution flowed into said region being from 0.5 to 3% of the effective volume of the contaminated water which is treated, based on a 100% by weight solution of said heptahydrate. The treating flow of hydrogen peroxide is at the typical rate of 0.1 to 10 gallons of hydrogen peroxide per minute per well, expressed on the basis of a 35% by weight solution of hydrogen peroxide.

15 The total said treating flow of hydrogen peroxide solution is typically 1 to 5% by weight of the effective volume of contaminated water which is treated, expressed on the basis of a 100% solution of hydrogen peroxide.

20 Pursuant to a further aspect of the invention there is provided a method of remediating a hydrocarbon-contaminated subterranean static plume of groundwater to destroy or reduce the initial concentration levels of hydrocarbon contaminants, comprising the steps of:

25 providing a plurality of mutually spaced wells intersecting said static plume groundwater; measuring the change in water depth at each of said wells following atmospheric precipitation, to determine by common depth changes the likelihood of said plume; confirming the existence of the static plume by generating a test flow of a solution of hydrogen peroxide or acetic acid from one of said wells and monitoring the absence of pH changes at each other of said wells as a function of time; and providing a treating flow of solutions of

35 acetic acid, of ferrous ion, and of hydrogen peroxide from each of said wells to establish a radial sweep about each said well, the total volumes and respective

concentrations of treating solutions being effective to bring about a Fenton-like reaction generating hydroxyl free radicals for oxidizing said contaminants.

5 Thus it will be seen that in the general mode of practicing the invention, a method is provided for remediating a hydrocarbon-contaminated region of a subterranean body of groundwater to destroy or reduce the initial concentration levels of hydrocarbon contaminants,
10 wherein acidic conditions are established at the groundwater region; and flows of aqueous solutions of ferrous ion and of hydrogen peroxide are introduced into the groundwater region, for mixing with the acidified groundwater. The hydrogen peroxide thus undergoes a
15 Fenton-like reaction in the presence of the acidic conditions and ferrous ion to generate hydroxyl free radicals for oxidizing said contaminants.

In a further aspect of the invention, a system is
20 provided for remediating a hydrocarbon-contaminated region of a subterranean body of groundwater to destroy or reduce the initial concentration levels of hydrocarbon contaminants. The system includes a plurality of mutually spaced wells which intersect the groundwater
25 region. Means are provided for pumping a treating flow of acetic acid from one or more of the wells into the groundwater region, to establish acidic conditions. Further means serve to introduce a turbulent flow of an aqueous solution of ferrous ion into the groundwater
30 region, for mixing with the acidified groundwater, thereby providing a catalyst for disassociation of hydrogen peroxide; and means are provided for pumping a treating flow of hydrogen peroxide solution from one or more of the wells into the groundwater region, the
35 hydrogen peroxide undergoing a Fenton-like reaction in the presence of the acidic conditions and ferrous ion to generate hydroxyl free radicals for oxidizing the

contaminants.

In the course of practicing the invention, the treating flow is periodically stopped and a determination made of the hydrocarbon contaminant levels at each said well, the process being continued until the initial contaminant concentration levels drop below predetermined acceptable values. The treating flow may additionally contain reaction surface enhancing reagents, i.e. reagents such as dispersions of lime or the like, which increase or provide surfaces at which the reaction between the near-Fenton solution and the hydrocarbon contaminants may occur. Other additives can also be employed to modify the rheology of the treating flow; and stabilizers and the like may be present in the hydrogen peroxide solution to inhibit premature reaction or decomposition of the oxidizer.

The reaction products of the method constitute innocuous substances, principally water and carbon dioxide predominantly with some associated oxygen and trace element oxidations all of which are lower order of concentrations. Peroxide cleaves aromatic ring structures, and oxidizes the resulting straight-chain or branched-chain alkanes. The oxidation proceeds through progressively shorter hydrocarbon chains, eventually resulting in carbon dioxide and water. The peroxide reduction leaves no hazardous residue itself. The hydrogen peroxide may be used in concentrations of from about 1% to 70% by weight solutions, which are available commercially from many sources.

Typical flow rates used in the foregoing process can be of the order of 0.1 to 36 gallons of hydrogen peroxide solution per minute per well, expressed on the basis of a 35% by weight solution of hydrogen peroxide.

In a preferred mode of practicing the present invention, the existence of acceptable continuity and well interflow paths for the groundwater region to be treated is established by initially generating a test flow of a solution of hydrogen peroxide from one of the wells and monitoring pH changes at each other of the wells as a function of time. A pH drop of at least 0.2 is considered to be indicative of satisfactory conditions. The pH changes are characteristic of the REDOX reactions involved in the invention and are believed to result from the formation of carboxylic acids during the reaction between the hydrogen peroxide and hydrocarbons. Typical such products are acetic acid and certain alkyls. None of these components are hazardous, but if desired, they can be neutralized as part of the overall treatment process. Subsequent to detecting the said pH drop, a treating flow of the hydrogen peroxide solution is then provided from one or more of the wells. The treating flow is again periodically stopped and the hydrocarbon contaminant levels measured at each well until the initial concentration levels drop below predetermined acceptable values. Initial acetic acid injection alone can also be used to induce the above pH drop.

Typical treating flows are at the rate of 0.1 to 36 gallons of the three treatment solutions per minute per well, depending in part upon the concentrations of the solutions used and the contamination levels. The treating flow is provided under a pressure not more than the hydrostatic head relative to ground surface at the point of treating flow discharge from the well. If the pressure exceeds this, it is possible for some of the reactants to pass upwardly through the porous overburden and create undesirable conditions on the ground surface. Very typically in most installations the treating flow is under a pressure of about 6 to 40 psig, subject to the boundary condition indicated in the foregoing.

The total treating flow of the three treatment solutions will generally be in the range of 0.1 to 10% by weight of the effective volume of contaminated water which is to be treated, expressed on the basis of a 35% solution of hydrogen peroxide. The "effective volume" is considered for purposes of this specification includes not only the pooled or possibly slowly flowing groundwater region per se, but as well the overburden which defines the region between the top of the groundwater and the overlying surface accessible to atmosphere. This is considered appropriate in that the communication between overburden and groundwater is such that water can flow with relative ease between the surface overburden and groundwater, and hence in calculating quantities of treating reactants, account should desirably be taken of this factor. "Effective volume" also reflects the apparent interflow from adjacent regions into the region being treated. Boundary interflow can be evaluated by observing how rapidly the pH may change as a function of time at the various wells after a test flow is completed, i.e. a relatively rapid change will indicate that flow from adjacent regions is relatively high, leading to an adjustment in the initially calculated effective volume of the order of 10 to 20%.

The total volume utilized in the test flow is typically .05 to 0.1% by weight of the effective volume of the contaminated water, expressed on the basis of a 35% hydrogen peroxide solution unless free product (e.g. floating oils etc.) is present which requires volume increases of factors which can typically be as high as 10.

In typical treatment arrangements pursuant to the invention at least three injection wells are utilized which are spaced about the periphery of the groundwater

region to be treated. The test flow is injected at one said well and the pH changes are monitored at the other said wells.

5 In a further aspect of the invention, it has been found that in addition to the pH change serving as a sensitive indicator of interflow and continuity, temperature changes also resulting from the aforementioned REDOX reactions may serve as an additional monitoring
10 parameter. Thus in this aspect of the invention the temperature changes are monitored at one or more other of the wells during the test flow process. A temperature rise of at least 2°F at each well spaced from the injection well is considered a confirmatory indicator of
15 the acceptable continuity and well interflow paths.

In the special case in which a static plume is found to exist, same being indicated by observing following moderate atmospheric precipitation that the water levels
20 in the plurality of spaced wells show common changes in height, the treatment regime involves confirming the existence of the static plume by generating a test flow of the three treating solutions from one of the said wells and monitoring the absence of pH changes at each
25 other of the said wells as a function of time. A treating flow of the Fenton-like reactant solutions from each of the wells is then provided at a representative rate of 0.1 to 36 gallons/minute to establish a radial sweep about each said well, the total volume of treating
30 solution being again from 0.1 to 10% by weight of the effective volume of contaminated water expressed on the basis of a 35% hydrogen peroxide solution.

BRIEF DESCRIPTION OF DRAWINGS

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The invention is diagrammatically illustrated, by way of example, in the drawings appended hereto in which:

FIGURE 1 is plan elevational view, diagrammatic in nature of the topography of a site at which groundwater is to be treated;

5 FIGURE 2 is a cross-sectional view taken along the line 2-2' of Figure 1, and illustrating in the subterranean characteristics of the mapped portion of Figure 1; and

10 FIGURE 3 is a schematic cross-sectional view through a representative monitoring and injection well of the type utilized in Figures 1 and 2. The control elements used in connection with the method and system are schematically illustrated in this Figure.

15

DESCRIPTION OF PREFERRED EMBODIMENT

Referring to Figures 1 and 2, plan and cross-sectional views are shown of a typical site in which the method of
20 the invention may be utilized. Contours and topography are indicated by appropriate indicia in feet and inches. The groundwater reservoir to be treated is shown in outline at 10 in Figure 1, at which it is seen that four monitoring and injecting wells 12, 14, 16 and 18 are
25 provided, generally around the periphery of the groundwater reservoir 10 to be treated. As best seen in the cross-sectional view of Figure 2, each of the wells extend to intersect groundwater reservoir 10. Reservoir 10 may be considered to be polluted with various organic
30 contaminants of the type previously discussed. The groundwater reservoir 10 lies atop an impermeable clay layer 20 underneath which bedrock 22 is present. Atop the groundwater reservoir, in order is a silty sand with clay and some gravel layer 24; a silty sand with clay and
35 gravel layer 26; and finally a sand with silt and gravel layer 28. The soil layers atop the reservoir are generally porous and permit with relative ease

communication of atmospheric precipitation with the said reservoir. The present reservoir 10 may be considered as not being a static plume; i.e. flow to and from same is readily possible, although obviously is impeded by the surrounding surfaces and boundaries.

Details of a specific monitoring and injection well 30 are seen in Figure 3. A borehole 32 is provided in which a well casing 34 typically of a PVC material, is inserted as a liner. This liner, as is well known in the art, is provided beneath seal 35 with a slotted well screen 36, i.e. the PVC is provided with multiple fine slots to create the screened effect. A sand/gravel pack 37 surrounds slotted screen 36. An injection string 38 extends to the interior of the well. A valve 40 is provided and a temperature transducer 42 and a pressure transducer 44 are connected to the upper, i.e. above-ground portion of injection string 38 between valve 40 and a valve 46. A quick connect assembly is provided at 48. Schematically shown in Figure 2 are a series of supply tanks 50, 52, 54, 56, 58 and 60, respectively being used for the hydrogen peroxide treating solution, catalyst, stabilizer, enhancer, acids, and alkalies as required. Additional tanks may be provided e.g. when more than one catalyst is used. Pumps 62, 64, 66 and 68 may dispense these components to the quick connect assembly and thereby to the injection and monitoring well 30. Each of the pumps are under control of a control station 70 including a control console 72. Monitoring display 74 provides data and information to the operator, including pressures and temperatures from the transducers at 42 and 44. A chart recorder 76 is similarly provided at the control station 70. A portable test set 78 may be used to establish such parameters as pH, temperature, salinity, conductivity and the like. When needed, deionized water from tank 80 and potable water from tank 82 can also be provided via pumps 84 and 86 to the quick

- connect assembly 48. The entire system is highly portable; an A.C. power generator 88 is provided, and may be driven by a gasoline or other motor. This provides power for all control units including the central control station 70. It will be appreciated that a monitoring flow can be withdrawn from the well, as can a treating or test flow be injected via the well into the groundwater which the well intersects.
- 10 The volume of groundwater reservoir 10 is known in advance from the plurality of wells, which have served to establish the level of the reservoir and depth of the water in same, and the general contours of same. It will be clear that from these considerations the effective volume, i.e. including the reservoir and overburden is calculable -- which effective volume may include a 10 to 20% additive factor for porous flow to adjacent zones which are lateral to the region of interest. In the course of operating the present system, and pursuant to the foregoing discussion, the existence of acceptable continuity and well interflow paths for the region to be treated is established by generating a test flow from one of the wells and monitoring pH changes at the other of the wells as a function of time. A pH drop of at least 0.2 is taken as indication of satisfactory well interflow paths and continuity. Thereafter the treating flow of hydrogen peroxide solution is initiated from the tank 62. As also mentioned, and in advance of this, an initiation catalyst can be injected from tank 52, as can the other additives if desired, such as stabilizers from tank 54, enhancers from tank 56, and acid and alkali adjustments from tanks 58 and 60.

- Among the additives which may be utilized in the present process, are silicate-based inorganic polymers which can serve as finely divided high surface area powders used as adsorbent catalysts. Finely divided iron filings and

potable water can be used as an initiation catalyst by injection in advance of the treating solutions. Other initiation catalyst water solutions include molybdenum, nickel, silver, platinum, and gold, all of which can be added in catalytically effective quantities. Powdered lime can be used as an enhancer with water to encourage saturated alkanes, i.e. unleaded gas and oil, to adsorb onto the lime surface along with hydrogen peroxide. Other additives such as hydralizable polymers can be used to increase viscosity and control diffusion through the groundwater. Various viscosity modifiers in a potable water mix can include ordinary compatible household laundry soaps, mixtures of sodium hydroxide and sodium lauryl sulfate, lime, magnesium oxide, diatomaceous earth anionic, cationic and nonionic polymers. Alkaline agent enhancers may be used to accelerate aromatic ring structures dehalogenation and decomposition. Also, as known in the art of conducting reactions with hydrogen peroxide, stabilizer solutions can be used, including amino trimethylene phosphonic acid; and other organophosphorus compounds. It should be appreciated that the reactions between hydrogen peroxide and hydrocarbons are not per se of the present invention, and the invention encompasses use of various catalysts and other additives which facilitate or accelerate these reactions as are known in the art.

The invention is further illustrated in the following example, which is illustrative of the efficacy of the present invention, without being, however, intended to be delimitative thereof.

Example

In this Example the site remediated pursuant to the invention was an abandoned lamp manufacturing plant at which a subterranean groundwater reservoir similar to

that in Figures 1 and 2 was present, which was heavily contaminated with hydrocarbons and chloroethanes. Four wells were sunk into the reservoir, generally about the periphery of the reservoir. Depth characteristics for the reservoir and initial BTEX and chloroethane contamination was measured, and are shown in Table I.

In order to establish the acceptability of continuity and well interflow paths, an 80% acetic acid solution was injected into Well No. 1 (situated updip in the groundwater reservoir structure) at a rate of 6 gallons per minute for a period appropriate to provide 0.1% by weight of the effective volume of contaminated water in the reservoir. The effective volume included the relatively porous overburden and a 10% additive factor based on groundwater reservoir structure extending beyond the cleanup site boundaries. pH at Wells No. 2, 3 and 4 at the start of the test flow was 6.9 avg. After a period of 1 day, pH was found to have dropped to 5.5 at No. 2, to 6.1 at No. 3, and to 6.7 at No. 4, indicating acceptable continuity and well interflow paths.

In a first cycle of treatment 1.4% by weight of the effective contaminated water volume to be treated, of the 80% acetic acid solution, followed by 20% ferrous sulfate solution, followed by a 35% H_2O_2 solution was injected via each well at a rate of 6.0 gallons per minute with injection quantities of 120, 240, 90, and 120 gallons respectively. After 7 days, measurements of the BTEX and chloroethane levels at the four wells were determined. One month later the same injection procedure was repeated using the same 1.4% of treating solution (by weight of the effective volume of contaminated groundwater). BTEX measurements were repeated 10 days after the second injection. Data for the foregoing are tabulated in Table I below:

Table I

	<u>Well 1</u>	<u>Well 2</u>	<u>Well 3</u>	<u>Well 4</u>
Initial Total BTEX Chloroethane (ppm)	1.8 10.2	1100 1.6	30 1.9	0.7 1.1
First Treatment (%)	1.4	1.4	1.4	1.4
Total BTEX Chloroethane (ppm)	0.01 5.3	0.05 0.40	0.01 0.36	0.01 0.11
Second Treatment (%)	1.4	1.4	1.4	1.4
Total BTEX Chloroethane (ppm)	0.08 0.09	ND* 0.16	0.03 0.006	ND* 0.007

*Non-Detectable

The reduction in BTEX levels is seen to be remarkable.
 The BTEX was partially in a free-product phase on top of
 5 the groundwater, so most of the free cycle chemistry was
 used up in reducing this free-product.

While the present invention has been particularly set
 forth in terms of specific embodiments thereof, it will
 10 be understood in view of the instant disclosure that
 numerous variations on the invention are now enabled to
 those skilled in the art which variations yet reside
 within the present teachings. Accordingly the invention
 is to be broadly construed and limited only by the scope
 15 and spirit of the claims now appended hereto.

WHAT IS CLAIMED IS:

1 1. A method for remediating a hydrocarbon-
2 contaminated region of a subterranean body of groundwater
3 to destroy or reduce the initial concentration levels of
4 hydrocarbon contaminants, comprising the steps of:

5
6 (a) providing a plurality of mutually spaced
7 wells intersecting said groundwater region;

8
9 (b) providing a treating flow of acetic acid
10 from one or more of said wells into said groundwater
11 region, to establish acidic conditions therein;

12
13 (c) introducing a turbulent flow of an aqueous
14 solution of ferrous ion into said groundwater region, for
15 mixing with said acidified groundwater, thereby providing
16 a catalyst for disassociation of hydrogen peroxide; and

17
18 (d) providing a treating flow of hydrogen
19 peroxide solution from one or more of said wells into
20 said groundwater region, said hydrogen peroxide
21 undergoing a Fenton-like reaction in the presence of said
22 acidic conditions and said ferrous ion to generate
23 hydroxyl free radicals for oxidizing said contaminants.

1 2. A method in accordance with claim 1, wherein in
2 step (a) said groundwater region is brought to a pH of
3 from 3.0 to 4.0.

1 3. A method in accordance with claim 1, wherein
2 during step (b) the existence of acceptable continuity
3 and well interflow paths for the said region are
4 determined by monitoring pH changes at each other of said
5 wells as a function of time to detect a pH drop of at
6 least 0.2.

1 4. A method in accordance with claim 1, wherein
2 between steps (b) and (c) and between steps (c) and (d)
3 potable water is injected from the same said wells in
4 place of acetic acid and ferrous ion solutions, to
5 provide a transient buffer zone between the compositions
6 introduced during steps (b), (c) and (d), thereby
7 delaying the reaction of step (d) until the plume of
8 injected miscible reactants has extended further into
9 said groundwater region.

1 5. A method in accordance with claim 1, wherein
2 said acetic acid is flowed as a solution at a rate of 5
3 to 10 gallons/min.

1 6. A method in accordance with claim 5, wherein
2 said solution includes from 10% to 100% by weight of
3 acetic acid.

1 7. A method in accordance with claim 1, wherein the
2 total amount of acetic acid flowed into said region is
3 from 1 to 3% by volume of the effective volume of
4 contaminated water which is treated, based on a 100%
5 acetic acid solution.

1 8. A method in accordance with claim 7, wherein the
2 Fe^{2+} ion is provided as an aqueous solution of ferrous
3 sulfate heptahydrate, the total volume of said solution
4 flowed into said region being from 0.5 to 3% of the
5 effective volume of the contaminated water which is
6 treated, based on a 100% by weight solution of said
7 heptahydrate.

1 9. A method in accordance with claim 8, wherein the
2 treating flow of said hydrogen peroxide is at the rate of
3 0.1 to 10 gallons of hydrogen peroxide per minute per
4 well, expressed on the basis of a 35% by weight solution

5 of hydrogen peroxide.

1 10. A method in accordance with claim 1, wherein
2 the total said treating flow of hydrogen peroxide
3 solution is 1 to 5% by weight of the effective volume of
4 contaminated water which is treated, expressed on the
5 basis of a 100% solution of hydrogen peroxide.

1 11. A method of remediating a hydrocarbon-
2 contaminated subterranean static plume of groundwater to
3 destroy or reduce the initial concentration levels of
4 hydrocarbon contaminants, comprising the steps of:

5
6 (a) providing a plurality of mutually spaced
7 wells intersecting said static plume groundwater;

8
9 (b) measuring the change in water depth at each
10 of said wells following atmospheric precipitation, to
11 determine by common depth changes the likelihood of said
12 plume;

13
14 (c) confirming the existence of the static
15 plume by generating a test flow of a solution of hydrogen
16 peroxide or acetic acid from one of said wells and
17 monitoring the absence of pH changes at each other of
18 said wells as a function of time; and

19
20 (d) providing a treating flow of solutions of
21 acetic acid, of ferrous ion, and of hydrogen peroxide
22 from each of said wells to establish a radial sweep about
23 each said well, the total volumes and respective
24 concentrations of treating solutions being effective to
25 bring about a Fenton-like reaction generating hydroxyl
26 free radicals for oxidizing said contaminants.

1 12. A method for remediating a hydrocarbon-
2 contaminated region of a subterranean body of groundwater

3 to destroy or reduce the initial concentration levels of
4 hydrocarbon contaminants, comprising:

5
6 establishing acidic conditions at said
7 groundwater region; and

8
9 introducing flows of aqueous solutions of
10 ferrous ion and of hydrogen peroxide into said
11 groundwater region, for mixing with said acidified
12 groundwater; said hydrogen peroxide undergoing a Fenton-
13 like reaction in the presence of said acidic conditions
14 and said ferrous ion to generate hydroxyl free radicals
15 for oxidizing said contaminants.

1 13. A method in accordance with claim 12, wherein
2 said groundwater region is acidified to a pH of from 3.0
3 to 4.0.

1 14. A method in accordance with claim 13, wherein
2 said acidic conditions are brought about by introducing a
3 flow of an acetic acid solution; the total amount of
4 acetic acid flowed into said region being from 1 to 3% by
5 volume of the effective volume of contaminated water
6 which is treated, based on a 100% acetic acid solution.

1 15. A method in accordance with claim 14, wherein
2 the Fe^{2+} ion is provided as an aqueous solution of ferrous
3 sulfate heptahydrate, the total volume of said solution
4 flowed into said region being from 0.5 to 3% of the
5 effective volume of the contaminated water which is
6 treated, based on a 100% by weight solution of said
7 heptahydrate.

1 16. A method in accordance with claim 15, wherein
2 the total amount of treating solution of hydrogen
3 peroxide solution is 1 to 5% by weight of the effective
4 volume of contaminated water which is treated, expressed

5 on the basis of a 100% solution of hydrogen peroxide.

1 17. A method in accordance with claim 1, wherein
2 the treating flows of steps (a), (b) and (c) are provided
3 under a pressure not more than the hydrostatic head
4 relative to surface at the point of treating flow
5 discharge from said well.

1 18. A method in accordance with claim 17, wherein
2 the treating flow is provided under a pressure of from 6
3 to 40 psig.

1 19. A method in accordance with claim 17, wherein
2 the total said treating flow of hydrogen peroxide
3 solution is 0.1 to 10% by weight of the effective volume
4 of contaminated water which is treated, expressed on the
5 basis of a 35% solution of hydrogen peroxide.

1 20. A method in accordance with claim 1, further
2 including determining the existence of acceptable
3 continuity and well interflow paths for the said region
4 by generating a test flow of a solution of hydrogen
5 peroxide or acetic acid from one of said wells and
6 monitoring pH changes at each other of said wells as a
7 function of time to detect a pH drop of at least 0.2.

1 21. A method in accordance with claim 20, wherein
2 the total volume in the test flow is 0.05 to 0.1% by
3 weight of the effective volume of contaminated water,
4 expressed on the basis of a 35% solution of hydrogen
5 peroxide, and is injected at the rate of 0.3 to 10
6 gallons/minute and at a pressure which is not more than
7 the hydrostatic head relative to surface at the point of
8 treating flow discharge from said well.

1 22. A method in accordance with claim 1, including
2 at least 3 said wells, which are spaced about the

3 periphery of said groundwater region.

1 23. A method in accordance with claim 20, wherein
2 said test flow is injected at one said well and the said
3 pH change monitored at said other wells.

1 24. A method in accordance with claim 20, further
2 including in step (b), monitoring temperature changes at
3 one or more other of said wells to detect a temperature
4 rise of at least 2°F as a confirmatory indicator of said
5 acceptable continuity and well interflow paths.

1 25. A method in accordance with claim 1, wherein at
2 least one of said treating solutions further includes a
3 reaction surface enhancing reagent.

1 26. A method in accordance with claim 1, wherein
2 the treating flow is periodically stopped and the
3 hydrocarbon contaminant levels measured at each said
4 well, until the said initial contaminant concentration
5 levels drop below predetermined acceptable values.

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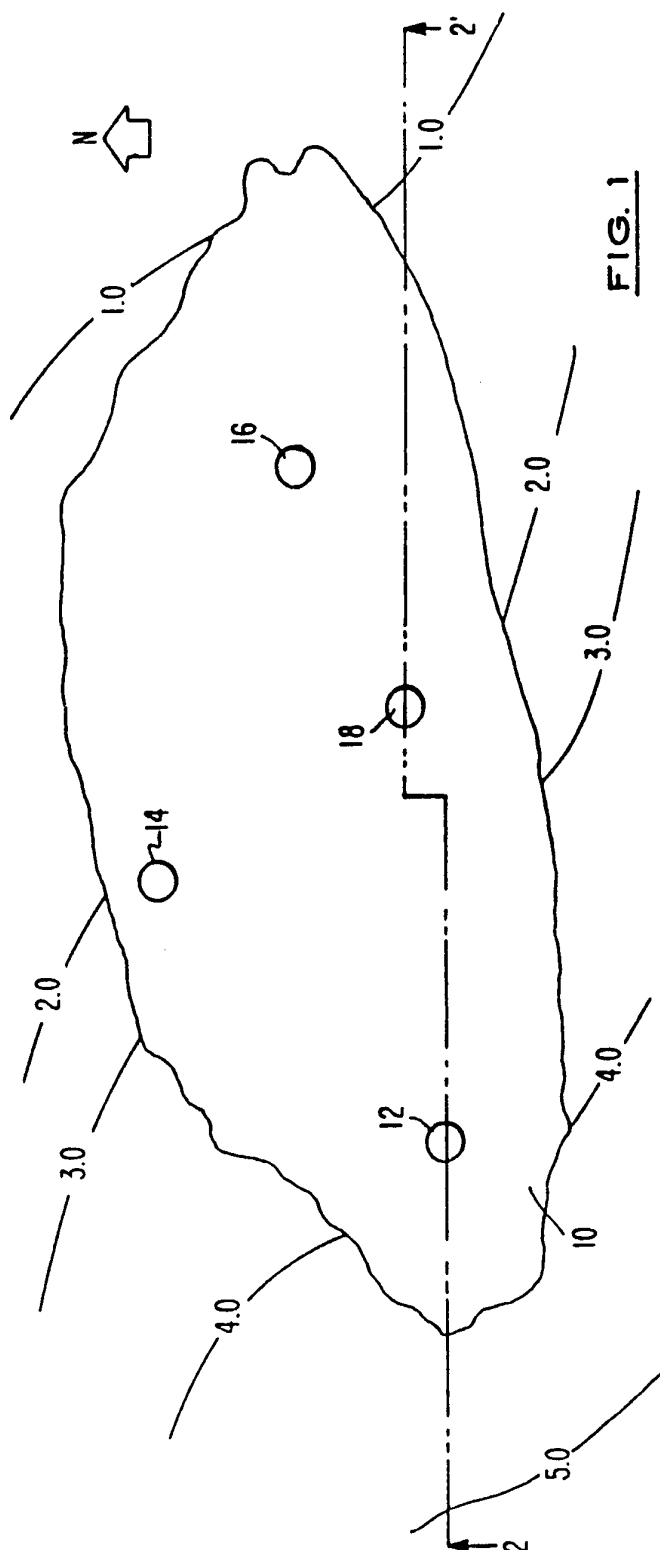


FIG. 1

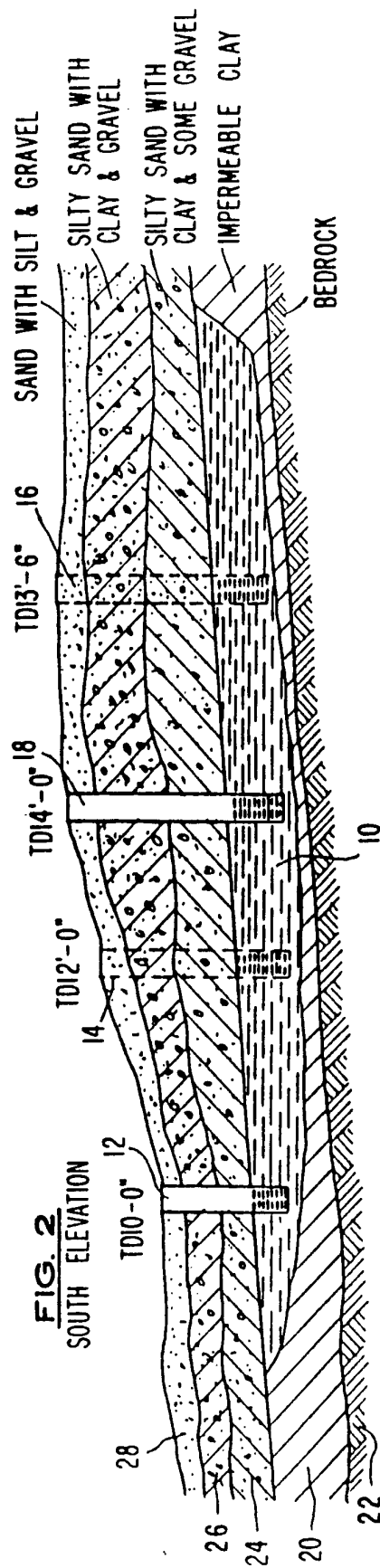


FIG. 2
SOUTH ELEVATION

2 / 2

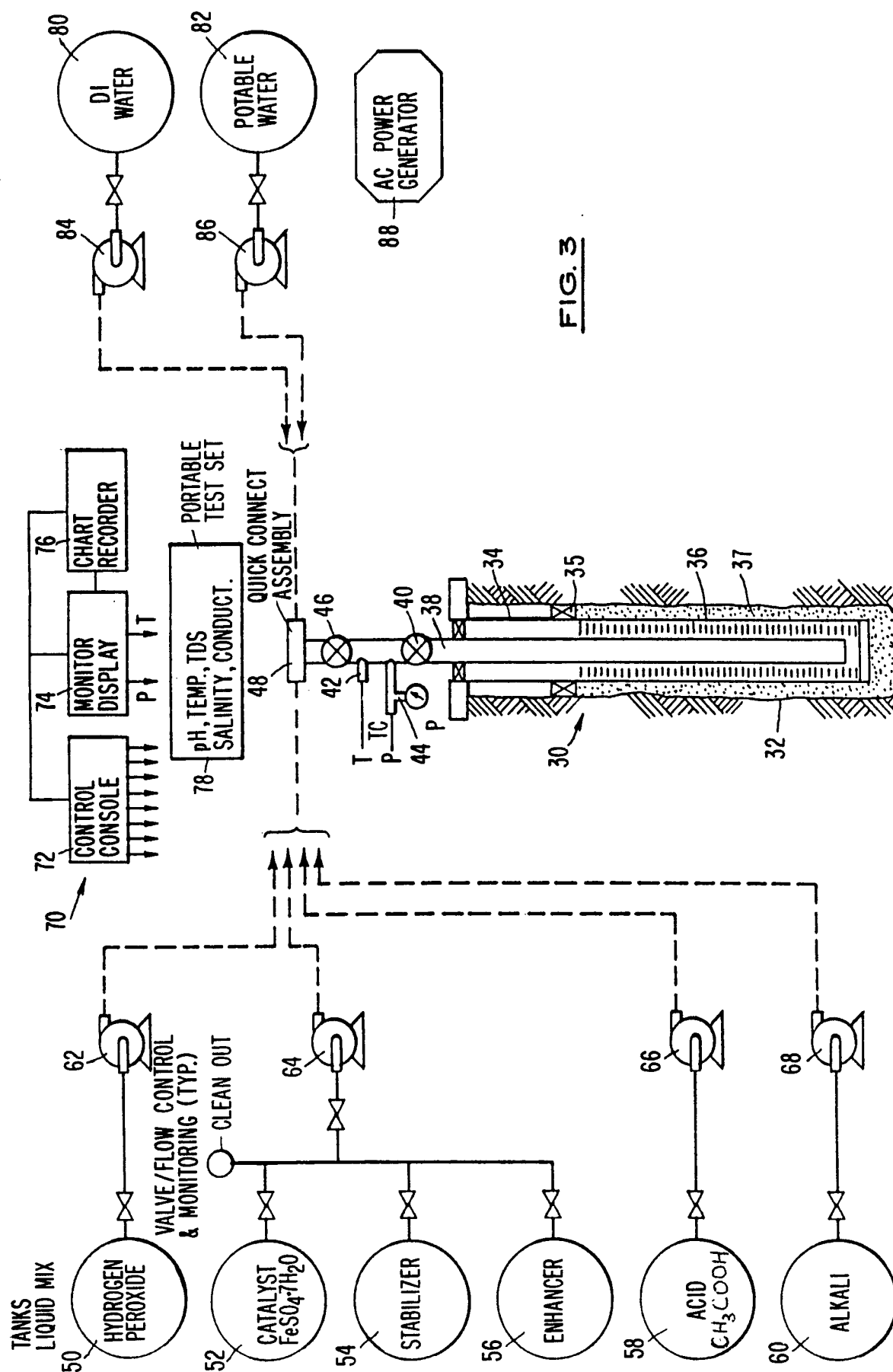


FIG. 3

INTERNATIONAL SEARCH REPORT

ational application No.
PCT/US94/01533

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :E02D 3/00; B09B 3/00; C02F 1/72

US CL :405/128, 52, 263

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 405/128, 52, 263, 129, 258; 166/268, 300, 310; 210/747, 758, 759

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,167,973 (FORTE ET AL) 18 September 1979 see the entire document	1-26
A	US, A, 4,591,443 (BROWN ET AL) 27 May 1986 see the entire document	1-26
A	US, A, 4,978,508 (HANSEN ET AL) 18 December 1990 see the entire document	1-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 13 April 1994	Date of mailing of the international search report APR 25 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer DAVID H. CORBIN Telephone No. (703) 308-2168