HU000035667T2

(19) **HU** (11) Lajstromszám: **E 035 667** (13) **T2**

MAGYARORSZÁG
Szellemi Tulajdon Nemzeti Hivatala

EURÓPAI SZABADALOM
SZÖVEGÉNEK FORDÍTÁSA

(21) Magyar ügyszám: **E 05 752764**
(22) A bejelentés napja: **2005. 05. 26.**

(96) Az európai bejelentés bejelentési száma:
EP 20050752764
(97) Az európai bejelentés közzétételi adatai:
EP 1755799 A1 **2005. 12. 15.**
(97) Az európai szabadalom megadásának meghirdetési adatai:
EP 1755799 B1 **2017. 09. 27.**

(51) Int. Cl.:

C02F103/06	*(2006.01)*
B09C 1/08	*(2006.01)*
C02F 1/68	*(2006.01)*
C02F 1/72	*(2006.01)*
B09C 1/00	*(2006.01)*
B09C 1/10	*(2006.01)*

(86) A nemzetközi (PCT) bejelentési szám:
PCT/EP 05/052409
(87) A nemzetközi közzétételi szám:
WO 05118170

(30) Elsőbbségi adatok:
574864 P **2004. 05. 27.** **US**

(73) Jogosult(ak):
SOLVAY SA, 1120 Bruxelles (BE)

(72) Feltaláló(k):
BOULOS, Noel, Bellaire, Texas 77401 (US)
MCNEILLIE, Alastair, Humble, Texas 77346 (US)
MUESSIG, Jason, Houston, Texas 77027 (US)

(74) Képviselő:
Danubia Szabadalmi és Jogi Iroda Kft.,
Budapest

(54) **Szennyezőanyagok kombinált kémiai oxidációja/elősegített bioremediációja**

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 755 799 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
27.09.2017 Bulletin 2017/39

(21) Application number: **05752764.0**

(22) Date of filing: **26.05.2005**

(51) Int Cl.:
C02F 103/06 $^{(2006.01)}$
B09C 1/08 $^{(2006.01)}$
B09C 1/10 $^{(2006.01)}$
B09C 1/00 $^{(2006.01)}$
C02F 1/68 $^{(2006.01)}$
C02F 1/72 $^{(2006.01)}$

(86) International application number:
PCT/EP2005/052409

(87) International publication number:
WO 2005/118170 (15.12.2005 Gazette 2005/50)

(54) COMBINED CHEMICAL OXIDATION/ASSISTED BIOREMEDIATION OF CONTAMINANTS

KOMBINIERTE CHEMISCH-OXYDATIV UNTERSTÜTZTE BIOREINIGUNG FÜR VERSCHMUTZTES MATERIAL

COMBINAISON D’OXYDATION CHIMIQUE/BIOREMEDIATION ASSISTEE DE CONTAMINANTS

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR

(30) Priority: **27.05.2004 US 574864 P**

(43) Date of publication of application:
28.02.2007 Bulletin 2007/09

(73) Proprietor: **SOLVAY SA**
1120 Bruxelles (BE)

(72) Inventors:
- **BOULOS, Noel**
  Bellaire, Texas 77401 (US)
- **MCNEILLIE, Alastair**
  Humble, Texas 77346 (US)
- **MUESSIG, Jason**
  Houston, Texas 77027 (US)

(74) Representative: **Vande Gucht, Anne et al**
Solvay S.A.
Département de la Propriété Industrielle
Rue de Ransbeek, 310
1120 Bruxelles (BE)

(56) References cited:
US-A- 5 741 427
US-A- 6 160 194
US-A1- 2002 110 509

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The invention relates to a method for cleaning contaminated materials such as soil and water.

[0002] Additional advantages and other features of the present invention will be set forth in part in the description that follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from the practice of the present invention. The advantages of the present invention may be realized and obtained as particularly pointed out in the appended claims. As will be realized, the present invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the present invention. The description is to be regarded as illustrative in nature, and not as restrictive.

Summary of the Invention

[0003] The invention objectives are accomplished, in general, by the combined use of metal (e.g., Fe) chelates, especially transition metal chelates, and a source of peroxide, especially Mg, Ca, and/or Zn peroxide or sodium percarbonate (PCS) or hydrogen peroxide. An underlying concept is the reaction of hydrogen peroxide which is used as such or which is generated from, e.g., PCS or CaO_2, with a metal chelate. One advantage of a metal chelate is that it is kept in solution under alkaline conditions allowing the H_2O_2 to react with the metal generating a modified Fenton process thereby producing hydroxyl free radicals which are very strong oxidants that degrade contaminants.

Background of the Invention

[0004] The strongest oxidizing agent suitable for soil and groundwater remediation is the hydroxyl free radical. The typical way to generate OH radicals is through the Fenton system using H_2O_2 and ferrous ions at pH 3-4. Hydroxyl free radicals can also be generated by the use of a combination of ozone and H_2O_2 or UV and H_2O_2.

[0005] While these technologies are effective, they suffer from some drawbacks:

- Fenton technology is only suitable at a low pH, hence the need to acidify which requires the use of stainless steel piping and is expensive.
- Ozone/H_2O_2 technology requires on site generation of ozone and can be expensive.
- UV/H_2O_2 technology is not suitable for in-situ remediation.

[0006] Hydrogen peroxide solutions are available in several concentrations. The typical concentration used in soil remediation is the 35% grade. This is further diluted to lower concentrations for example 5-12%, before introduction in the contaminated material to be treated.

[0007] Sodium percarbonate (PCS) is a peroxyhydrate composed of sodium carbonate and H_2O_2. Its solubility in water is ~12%. Upon dissolution in water, it releases its components and the resulting solution contains both soda ash and H_2O_2.

[0008] Calcium and magnesium peroxide are solid peroxygens that are insoluble in water. When they are mixed with water, they slowly release oxygen at their natural pH (> pH 10). They are used in soil and groundwater remediation to provide oxygen to aerobic bacteria thereby enhancing their capability of degrading various contaminants.

[0009] As the pH is lowered, CaO_2 and MgO_2 generate increasingly larger quantities of H_2O_2. For example, at a pH 8, approximately 60% of the active content of CaO_2 can be generated in the form of H_2O_2.

[0010] Whereas OH radicals can be generated at any pH due to H_2O_2 decomposition, the optimal use of this process for chemical oxidation occurs at a pH of 3-4 whereby the Fe ions remain soluble, and cycle between a ferrous and a ferric state.

[0011] US patent 6,268,205 discusses the use of inorganic peroxides in conjunction with buffers and catalyst such as ferrous or ferric sulfate. The pH of such system is adjusted to 7-9. Under these conditions, the metal peroxides will release their activity partially as H_2O_2 and partially as oxygen. This allows for the initial chemical oxidation to take place starting the break up of the contaminants. The oxygen is then released more slowly, which will assist bioremediation over a period of several months. Although OH radicals can be generated from H_2O_2 at this pH, Fe will precipitate as ferric hydroxide. The net result is a reduced generation of OH radicals and clogging of the medium with the precipitated ferric hydroxide.

[0012] US patents 5,741,427 and 6,319,328 are related to the use of Fe salts or chelates that are dissolved in water, the solution is maintained at pH 5-8, and then injected to a soil that has already been injected with an oxidizing agent. This pH is lower than the pH claimed in the above patent and would lead to a very fast release of H_2O_2 from the solid peroxides. The order of addition claimed results in a reduced activation of H_2O_2 as the peroxide would be partially decomposed prior to the injection of the metal chelate.

[0013] US patent 6,843,618 is related to a method of decontaminating soil and ground water containing organic contaminants and divalent metal compounds. It comprises the steps of first treating such soils and ground water with an effective amount of an aqueous solution containing a peroxide and a water soluble chelating agent for a time sufficient to have the water soluble chelating agent chelate at least one of the divalent metals of the divalent metal compounds present in the soil and ground water. Next, the chelated metals are brought into contact with the peroxide to catalytically convert the peroxide to an oxidizing agent. Finally, the last step is contacting the organic contaminants in the soil and ground water with the oxidizing agent to oxidize the organic contaminants to environmentally safe, non-toxic compounds. US 6 160 194 A discloses the step of a method where the contaminated material is contacted with both a metal chelate and a peroxide.

Detailed Description of the Preferred Embodiments of the Invention

[0014] The invention is related to a method for the combined chemical oxidation/assisted bioremediation of contaminated materials, comprising contacting a contaminated material with at least one metal chelate and at least two peroxide compound.

[0015] The contaminated material is in most cases soil or water. The metal chelate and the peroxide compound are as described above.

[0016] According to the method of the present invention, the metal chelate can be added to the contaminant/medium and/or a chelating agent can be added to a medium that already contains a transition metal such as Fe whereby the metal chelate forms in situ. According to the method of the present invention, the metal chelate should be added before or together with the sodium percarbonate or hydrogen peroxide, preferably before. In other cases, the metal chelate is first added to the contaminated material in a first stage, then in a second stage the first peroxide compound is added, preferably sodium percarbonate or H_2O_2, and then the second peroxide compound is added preferably one of Ca, Mg, and Zn peroxides.

[0017] A preferred embodiment of the invention includes the use of at least one metal chelate, especially transition metal chelate, such as a Fe chelate, either as such, or in the form of the metal salt (e.g., ferrous or ferric salt) and a separate ligand (all of which are hereinafter referred to as "metal chelate"). The metal chelate can either be added together with all other components of a peroxide solution or slurry, or separate injections or additions to the material being treated may be made whereby the peroxide solution or slurry is added either before, during or after the metal chelate. Alternatively, the chelating agent may be added to the material being treated (e.g., soil) in order to chelate with metals such as Fe in the ground. A buffer can be also added either in the peroxide solution or slurry, or with the metal chelate to adjust the pH, preferably to 7-9. Preferred transition metals other than Fe include Mn and Cu, and are in particular those capable of generating OH radicals from H_2O_2. Optionally, products that are considered nutrients to microbes can also be added either separately or in combination with other products in a solution or slurry. As appropriate, some products may be injected or mixed in their dry form. Metal chelates described in US 5,741,427 and US 6,319,328 can be used herein. A preferred metal is Fe. Preferred chelating agents (ligands) include EDTA, citric acid, nitrilotriacetic acid, EDTA acid types, diethylenetriaminepentaacetic acid, hydroxyethylenediaminetriacetic acid, methylglycinediacetic acid, phosphonates, and the TRILON ® chelating agents of BASF, the brochure for which is incorporated herein by reference.

[0018] One objective of the invention is to create a dual acting system for catalytic oxidation of contaminated materials in soil and groundwater using oxidizing products in combination with a chelated metal catalyst (e.g., transition metal) as well as the generation of oxygen for assisted bioremediation. The chelating agent can be mixed in with the metallic catalyst or applied separately if sufficient amounts of the metallic catalyst already exist in the material to be treated. The chelating agent should be added first, to allow for its reaction with the metals of the water, soil, etc. The chelating agent may for example be dosed at a level of 0.01-0.5% of, e.g., sodium percarbonate by moles. One suggested application rate is 0.1%. If a metal chelated complex is used, this can be of any transition metal but in particular of iron, manganese and copper, and is preferably added first.

[0019] The soil contaminants that can be effectively treated include petrochemicals, chlorinated organics, pesticides, energetics, perchlorates, etc.

[0020] Application can be accomplished in any manner, for example by introducing the solid, solution, or suspension in the material to be treated in any manner known in the art. Alternatively the peroxide (e.g., sodium percarbonate (PCS)) can be dissolved and introduced as a solution.

[0021] All components mentioned herein may be used as mixtures of such.

[0022] The relative amounts of invention compounds are not limited. Preferably, the mole ratio of metal chelate to peroxide is 0.01-10 metal chelate / peroxide, more preferably less than 1, for example 0.05, 0.1, 0.2, 0.3, etc. With regard to treatment, the amount of invention components applied to the material being treated is not limited, and can range for example from a ratio of for example 0.0016 to 160,185 (invention components in g/ L of material being treated). A generally useful range is 160 mg/L-24g/L, for example 3.2 g/L - 16 g/L . A preferred range of dosing is up to 2,000 mg/L.

[0023] The source of peroxide may be any known in the art, for example any one or combination of CaO_2, MgO_2, PCS and/or H_2O_2. Preferred are CaO_2 and one of PCS or H_2O_2. While not bound by any theory, it is believed that the addition of H_2O_2 or PCS results in the immediate presence of H_2O_2, which quickly starts the oxidation reaction. The reaction then continues as a result of the slow release of H_2O_2 from the other sources, such as CaO_2 and/or MgO_2. The latter two products also generate oxygen for long term assisted bioremediation.

[0024] The peroxide compound (such as CaO_2) is typically added as a slurry. Two examples of typical concentrations are for instance about 20% by weight and about 35% by weight. The slurry could be more dilute if the material being treated is very porous.

[0025] Alternatively, the peroxide compound can be added as solid particles. They could be used in the soil remediation application as a solid mixed with the soil or as a solid mixed with another invention component. The solid particles can be used in the form of a powder or as granules. Granules of inorganic peroxides are described in the European patent application of SOLVAY filed under the number EP 05104226.5 on 19.05.2005, the content of which is incorporated herein by reference.

[0026] When the peroxide compound is sodium percarbonate, it can be used in the form of a solution or a suspension. Concentrations can be for example 8% by weight in the case of a solution and for example 20% by weight in the case of a suspension. A particularly suitable sodium percarbonate product has particles with a mean particle size in the range of from 100, to 400 μm. A 100 μm product may offer advantages in handling because it is a finer material compared to classical products. It is easier to dissolve and pumping its suspension is also easier. Sodium percarbonate can also be mixed with the soil in a solid form either by simple mixing or by incorporation with the machine that is excavating the soil during excavation.

[0027] The metal chelate is typically added in the form of a solution. The solution concentration can be for example 4% by weight. The metal chelate can be prepared ex situ, for instance in the case of a Fe chelate it can be prepared ex situ by mixing an iron salt such as FeSO4 with the chelating agent solution. One way to do this consists in mixing 0.9kg Fe salt with 7.6L of 40% chelating agent solution (3kg of chelant (100%)), and by diluting this solution four fold

[0028] The combined chemical oxidation / assisted bioremediation treatment according to the invention can further be combined with any other suitable treatment.

[0029] This invention has advantages over US patent 6,268,205 in that the metal chelate has a greater ability to catalyze the chemical oxidation as, e.g., Fe hydroxide would not precipitate. This approach is also better than US patents 5,741,427 and 6,319,328 in that the higher pH will allow for the slow release of oxygen over a greater period of time, thus assisting the naturally occurring microbes in degrading the contaminant.

[0030] The current invention also has advantages over US patent 6,843,618 in that it allows for both chemical oxidation and assisted bioremediation of contaminants. Further, the chemical oxidation can occur in two stages encompassing an immediate oxidation followed by an extended reaction due to the slow release of H_2O_2 and oxygen from the CaO_2 or MgO_2 or ZnO_2. This invention also allows for the addition of the various components in any suitable sequence which improves the effectiveness of treatment.

[0031] The above written description of the invention provides a manner and process of making and using it such that any person skilled in this art is enabled to make and use the same, this enablement being provided in particular for the subject matter of the appended claims, which make up a part of the original description.

Example 1

[0032] Soil and groundwater at a former fuel distribution demonstration site were contaminated with petroleum hydrocarbon from 19 former underground storage tanks (USTs) over the one acre property. Depth to groundwater (DTW) in the primary source treatment area was approximately 4.9 m below ground surface (m bgs) and ranged as deep as 6.7 m bgs over the remainder of the plume. The aquifer primarily consisted of clayey sand with low levels of naturally occurring organic carbon. Soil contamination primarily existed from the base of the UST excavation depth of approximately 4 m bgs and into the groundwater. The excavated UST pits were primarily backfilled with soft sedimentary rock allowing high infiltration rates during precipitation events. The soil has high in iron content.

[0033] Free-phase petroleum 1.2 to 2.1cm thick was consistently detected in the two wells located in the primary source area prior to treatment. However, source area dissolved phase concentrations were low due either to continued influx of uncontaminated groundwater or because the contaminants were highly adsorbed in the soil with very little product extractable from the dissolved phase. Contaminant concentrations downgradient indicate that low concentrations are likely the result of fresh influx of groundwater.

[0034] The existence of free-phase hydrocarbons warranted a dual stage remedial approach including chemical oxidation and bioremediation treatment. Chemical oxidation with sodium percarbonate was initiated to quickly reduce sorbed phase and free phase petroleum constituents, as well as supply an oxygen boost to the aquifer. Calcium peroxide was applied concurrently to provide a slow release source of hydrogen peroxide as well as oxygen for enhancing aerobic microbial growth. In the presence of high concentrations of contaminants, it is difficult to supply enough oxygen to sustain aerobic microbal growth and resultant contaminant degradation. Application of calcium peroxide alone for the purpose of enhancing bioremediation would not be effective on high contaminant or free-phase concentrations. The dual stage approach was initiated only in the primary source area, the majority of the site was treated with calcium peroxide alone.

[0035] The dual stage application is the topic of this example. The source area injection grid was designed on approximately 5 foot centers to promote contact of contaminants with high concentration of the chemicals. Treatment was applied to the superficial ten feet 3 m of groundwater and 30 cm of unsaturated soils immediately above the groundwater table by injecting chemicals in the form of a suspension or solution through the 2.54 cm rods of a Geoprobe Model 6600 geoprobe direct push truck mounted rig.

[0036] The chemicals were applied as follows in each injection:

- First a suspension of calcium peroxide in water was injected at a depth of 5.8-7.9 m bgs. The suspension was ~28% prepared using 34 kg calcium peroxide suspended in 454 L of water.
- The soil contained a high Fe content, therefore a chelating agent was added and allowed to react with Fe in the soil in order to produce the Fe chelate. The chelating agent was immediately injected after the injection of the calcium peroxide slurry and in a similar manner at a depth of 4.6-5.8 m bgs. Approximately 30 L of Trilon M solution (39-41% methylglycinediacetic acid - MGDA-Na_3) were diluted with water in a ratio of 1:10 chelant to water.
- After a period of 2-4 hours, the sodium percarbonate was injected at a depth of 4.6-5.8 m bgs. The aqueous solution/suspension had a concentration of 8-12% and about 34 kg sodium percarbonate were used.

[0037] The hydraulic conductivity of the formation was great enough that significant back pressure did not occur during injection.

[0038] A second injection was made after 23 weeks without adding the chelating agent as it was considered that the Fe chelate formed after the first injection was still present in the soil.
Groundwater samples from site wells located within and outside of the contaminant plume were collected for laboratory analyses 7 weeks prior to the initial treatment and 13,23, and 40 weeks after the initial injection. Field physicochemical measurements have been collected monthly following the initial injection.

Results

[0039] During the initial injection of sodium percarbonate, a brown foam was observed at the surface resulting from the reaction of the oxidant and petroleum contaminated groundwater. This resulted in the elimination of the free-phase contaminants. It is assumed a similar reaction occurred throughout the contaminated zone in the subsurface. The low levels of naturally occurring organic carbon allowed the reaction to occur primarily upon the contaminants.

[0040] The following tables show the effect of treatment. In summary

- Disappearance of the **free product** at the source area where the injection was made, with a drop from ~2.1 cm to no detection after 32 weeks.
- **BTEX (benzene, toluene, ethylbenzene, xylenes) and naphthalene** concentration.
    - In the source area, these contaminants were adsorbed onto the soil and could not be detected in the aqueous phase. Upon treatment, their levels first increased in the aqueous phase through desorption and then dropped in concentration over the period of the treatment.
    - A downgradient well that had a large concentration of these contaminants showed a decrease in contaminants level over the treatment period. After 40 weeks, some rebound was observed likely due to the consumption of the peroxide compounds, requiring a re-injection.
- **Specific conductance** is an indication of dissolved organics. The higher the value, the greater the dissolved organics. Specific conductance dropped after treatment but rebounded later indicating an additional amendment application is needed to continue product degradation.
- **Oxidation Reduction Potential** (ORP) is an indication of the oxidizing potential of the medium. In a completely treated soil, this value should be positive. In this case, due to the very high contamination, the value remained negative throughout the treatment but slowly increased.
    - **Source area:** increased from -162 to -16 mV after 40 weeks.
    - **Immediately downgradient:** increased from -153 to +332 mV but dropped later to -2 mV after 40 weeks.

[0041] Overall, the treatment has been highly successful at eliminating the free-phase hydrocarbons in the primary source area. A third dual stage application is planned to reduce the sorbed phase petroleum hydrocarbons in the unsaturated zone above the treatment area.

Source Area (MW-7)	**7 weeks before treatment**	**Weeks since Treatment**						
		4	**9**	**13**	**17**	**23**	**32**	**40**
Benzene - µg/L	nd			80		42		16
Toluene - µg/L	nd			35		nd		6.0
Ethylbenzene - µg/L	nd			370		9		67
Xylenes (total) - µg/L	nd			750		19		160
MTBE - µg/L	nd			nd		nd		nd
Isopropylbenzene (cumene) - µg/L	nd			36		nd		nd
Naphthalene - µg/L	11			110		7		19
Free product sheen - ft	0.07	0.04	0.04	0.01	0.02	0.02	0.00	0.00
Specific conductance - ohms	na	2,108	1,620	937	1,117	1,030	1,345	1,525
ORP-mV	na	-162	-180	-163	-138	-136	-108	-16
pH	na	6.3	5.7	6.0	6.2	6.5	6.5	6.5
Immediately downgradient MW-6	**7 weeks before treatment**	**Weeks since Treatment**						
		4	**9**	**13**	**17**	**23**	**32**	**40**
Benzene - µg/L	2,300			49		67		850
Toluene - µg/L	23			nd		nd		8
Ethylbenzene - µg/L	40			nd		nd		26
Xylenes (total) - µg/L	1,000			33		31		250
MTBE - µg/L	25			nd		nd		8
Isopropylbenzene (cumene) - µg/L	45			nd		nd		14
Naphthalene - µg/L	29			nd		nd		nd
Free product sheen - ft	-	-	-	-	-	-	-	-
Specific conductance - ohms	2,050	1,160	824	651	779	608	1,458	2,418
ORP - mV	-153	-24	311	332	3	163	-41	-2
pH	6.5	6.1	6.0	6.0	6.4	6.4	6.1	6.6
nd = non detected na = not available (not measured)								

Example 2

[0042] Another site was contaminated with Diesel Range Organics (DRO) and petroleum hydrocarbons. The water table was high in this site as it is located next to a river. The depth to the groundwater (DTW) was about 4.3 m.

Application

[0043] Due to the low iron at this site a ferrous chelate was formed ex-situ prior to injection.

[0044] The injections were done as follows:

1. 0.9 kg of ferrous sulfate were mixed with 7.6 L of chelant (Trilon M). Several hours later, the solution was diluted with water at a volume ratio of 1:4 chelate:water.
2. The solution was equally applied in 16 wells as the Geoprobe rods were advanced through the water table.
3. As the rods were pulled out of the hole, a sodium percarbonate slurry was pumped at a concentration of 20%. About 21 kg sodium percarbonate were injected in each well (340 kg sodium percarbonate were used for the 16 holes).
4. This was followed by injecting a 20% calcium peroxide slurry. About 7.7 kg of calcium peroxide were injected in each well (125 kg CaO_2 suspended in 606 L of water for the 16 holes). This material was also applied from the bottom up.

[0045] The 16 injection points were installed in a circle around the monitoring well, with 8 located at 1.5 m from the monitoring well, and the other 8 located at a distance of 3 m from the monitoring well.

Results

[0046] A few wells showed a dramatic increase in dissolved oxygen shortly after injection.

Centre Area (MW-23)	**5 days before treatment**	**Days from Treatment**		
		1	**7**	**30**
Specific conductance - ohms	568	533	546	657
ORP - mV	-109.6	247	127	126
Dissolved oxygen conc. - mg/L	1.48	1.17	1.49	2.29
pH	7.13	7.01	7.16	8.29

Claims

1. A method for the combined chemical oxidation/assisted bioremediation of contaminated materials, comprising contacting a contaminated material with at least one metal chelate and at least two peroxide compounds comprising one of H_2O_2 and sodium percarbonate, and one of Ca, Mg and Zn peroxides, the metal chelate comprising a Fe chelate and being added before or together with the sodium percarbonate or hydrogen peroxide.

2. The method according to Claim 1, wherein said material is soil or water.

3. The method of Claim 1 or 2, wherein the metal chelate can be added to the contaminant/medium and/or a chelating agent can be added to a medium that already contains a transition metal such as Fe whereby the metal chelate forms in situ.

4. The method according to any one of claims 1 to 3, wherein a buffer is added to adjust the pH to a value of from 7 to 9.

5. The method according to any one of claims 1 to 4, wherein the one of Ca, Mg and Zn peroxide is added in a first stage, the metal chelate is added in a second stage, and the one of sodium percarbonate and hydrogen peroxide is added in a third stage.

6. The method according to any one of claims 1 to 4, wherein the metal chelate is added in a first stage, the one of hydrogen peroxide and sodium percarbonate is added in a second stage, and the one of Ca, Mg and Zn peroxide is added in a third stage.

7. The method according to any one of claims 1 to 4, wherein the metal chelate is added in a first stage, the one of Ca, Mg and Zn peroxide is added in a second stage and the one of hydrogen peroxide and sodium percarbonate is added in a third stage.

Patentansprüche

1. Verfahren zur kombinierten chemischen Oxidation / unterstützten Biosanierung verunreinigter Materialien, welches das Inkontaktbringen eines verunreinigten Materials mit mindestens einem Metallchelat und mindestens zwei Peroxidverbindungen umfasst, wobei letztere einen der Stoffe H_2O_2 und Natriumpercarbonat und eines der Peroxide von Ca, Mg und Zn umfassen, wobei das Metallchelat ein Fe-Chelat umfasst und vor dem Natriumpercarbonat beziehungsweise Wasserstoffperoxid zugesetzt wird oder gemeinsam mit diesem.

2. Verfahren nach Anspruch 1, wobei ist sich bei dem Material um Erdboden oder Wasser handelt.

3. Verfahren nach Anspruch 1 oder 2, wobei das Metallchelat dem verunreinigenden Stoff / dem Medium zugesetzt werden kann und/oder ein Chelatbildner einem Medium zugesetzt werden kann, das bereits ein Übergangsmetall wie etwa Fe enthält, wobei sich das Metallchelat in situ bildet.

4. Verfahren nach einem beliebigen der Ansprüche 1 bis 3, wobei ein Puffer zugesetzt wird, um den pH auf einen Wert von 7 bis 9 einzustellen.

5. Verfahren nach einem beliebigen der Ansprüche 1 bis 4, wobei das eine der Peroxide von Ca, Mg und Zn in einem ersten Stadium zugesetzt wird, das Metallchelat in einem zweiten Stadium zugesetzt wird und der eine der Stoffe Natriumpercarbonat und Wasserstoffperoxid in einem dritten Stadium zugesetzt wird.

6. Verfahren nach einem beliebigen der Ansprüche 1 bis 4, wobei das Metallchelat in einem ersten Stadium zugesetzt wird, der eine der Stoffe Wasserstoffperoxid und Natriumpercarbonat in einem zweiten Stadium zugesetzt wird und das eine der Peroxide von Ca, Mg und Zn in einem dritten Stadium zugesetzt wird.

7. Verfahren nach einem beliebigen der Ansprüche 1 bis 4, wobei das Metallchelat in einem ersten Stadium zugesetzt wird, das eine der Peroxide von Ca, Mg und Zn in einem zweiten Stadium zugesetzt wird und der eine der Stoffe Wasserstoffperoxid und Natriumpercarbonat in einem dritten Stadium zugesetzt wird.

Revendications

1. Procédé pour l'oxydation chimique/bioremédiation assistée combinées de matières contaminées, comprenant la mise en contact d'une matière contaminée avec au moins un chélate de métal et au moins deux composés peroxydes comprenant l'un du H_2O_2 et du percarbonate de sodium et l'un des peroxydes de Ca, de Mg et de Zn, le chélate de métal comprenant un chélate de Fe et étant ajouté avant ou conjointement avec le percarbonate de sodium ou le peroxyde d'hydrogène.

2. Procédé selon la revendication 1, dans lequel ladite matière est un sol ou de l'eau.

3. Procédé selon la revendication 1 ou 2, dans lequel le chélate de métal peut être ajouté au contaminant/milieu et/ou un agent chélatant peut être ajouté à un milieu qui contient déjà un métal de transition tel que Fe moyennant quoi le chélate de métal se forme *in situ.*

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel un tampon est ajouté pour ajuster le pH à une valeur de 7 à 9.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'un des peroxydes de Ca, de Mg et de Zn est ajouté dans une première étape, le chélate de métal est ajouté dans une deuxième étape et l'un du percarbonate de sodium et du peroxyde d'hydrogène est ajouté dans une troisième étape.

6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le chélate de métal est ajouté dans une première étape, l'un du peroxyde d'hydrogène et du percarbonate de sodium est ajouté dans une deuxième étape et l'un des peroxydes de Ca, de Mg et de Zn est ajouté dans une troisième étape.

7. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le chélate de métal est ajouté dans une première étape, l'un des peroxydes de Ca, de Mg et de Zn est ajouté dans une deuxième étape et l'un du peroxyde d'hydrogène et du percarbonate de sodium est ajouté dans une troisième étape.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 6268205 B **[0011] [0029]**
- US 5741427 A **[0012] [0017] [0029]**
- US 6319328 B **[0012] [0017] [0029]**
- US 6843618 B **[0013] [0030]**
- US 6160194 A **[0013]**
- EP 05104226 A **[0025]**

Szabadalmi igénypontok

1. Eljárás szennyezett anyagok kombinált kémiai oxidációjára/elősegített bioremediációjára, amely tartalmazza a szennyezett anyag érintkeztetését legalább egy fém-keláttal és legalább két peroxid vegyülettel, amely H_2O_2 és nátrium-perkarbonát egyikét és Ca-, Mg- és Zn-peroxidok egyikét tartalmazza, a fém-kelát tartalmaz egy Fe-kelátot, és a nátrium-perkarbonát vagy hidrogén-peroxid előtt, vagy azzal együtt adjuk hozzá.

2. Az 1. igénypont szerinti eljárás, ahol az anyag talaj vagy víz.

3. Az 1. vagy 2. igénypont szerinti eljárás, ahol a fém-kelátot hozzáadhatjuk a szennyezőhöz/közeghez és/vagy egy kelátképző szert hozzáadhatunk egy közeghez, amely már tartalmaz egy átmenetifémet, mint a Fe, így a fém-kelát in situ képződik.

4. Az 1-3. igénypontok bármelyike szerinti eljárás, ahol puffert adunk hozzá, így a pH-t 7-9 értékre állítjuk be.

5. Az 1-4. igénypontok bármelyike szerinti eljárás, ahol a Ca-, Mg- és Zn-peroxidok egyikét egy első szakaszban adjuk hozzá, a fém-kelátot egy második szakaszban adjuk hozzá, és a nátrium-perkarbonát és hidrogén-peroxid egyikét egy harmadik szakaszban adjuk hozzá.

6. Az 1-4. igénypontok bármelyike szerinti eljárás, ahol a fém-kelátot egy első szakaszban adjuk hozzá, a hidrogén-peroxid és nátrium-perkarbonát egyikét egy második szakaszban adjuk hozzá, és a Ca-, Mg- és Zn-peroxidok egyikét egy harmadik szakaszban adjuk hozzá.

7. Az 1-4. igénypontok bármelyike szerinti eljárás, ahol a fém-kelátot egy első szakaszban adjuk hozzá, a Ca-, Mg- és Zn-peroxidok egyikét egy második szakaszban adjuk hozzá, és a hidrogén-peroxid és nátrium-perkarbonát egyikét egy harmadik szakaszban adjuk hozzá.