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(54) Title: DESTRUCTION OF PCBS ON CONCRETE AND BRICK MATERIALS

(57) Abstract: Methods for remediating contaminants on porous materials using surfactant-enhanced in situ chemical oxidation (S-ISCO) are presented.

DESTRUCTION OF PCBS ON CONCRETE AND BRICK MATERIALS

[0001] The present invention relates to methods for remediating contaminants on porous materials using surfactant-enhanced in situ chemical oxidation (S-ISCO).

[0002] This application claims the benefit of U.S. Provisional Application Number 61/251,704, filed October 14, 2009, which is hereby incorporated by reference in its entirety.

BACKGROUND

[0003] There are a large number of sites contaminated with chemicals that can have detrimental effects on public health and the environment. For example, soils, aquifers, landfills, buildings, and building materials have been identified as containing such contaminants. In addition to the potential or actual detrimental effects on public health and the environment, the contaminated sites can represent an economic loss in that the sites often cannot be put to productive use until they are remediated. Various methods for remediating contaminated soils and aquifers have been proposed and/or implemented. For example, such remediation methods are described in the following: international application number PCT/US2007/007517, filed March 27, 2007, published as PCT Publication WO2007/126779; U.S. provisional application number 60/785,972, filed March 27, 2006; U.S. Patent Application No. 12/068,653, filed February 8, 2008, published as US2008/0207981; U.S. Patent Application No. 12/771,210, filed April 30, 2010; international application PCT/US2008/008905, filed July 23, 2008, published as WO2009/014697; U.S. provisional application number 60/935,033, filed July 23, 2007; U.S. Patent Application No. 12/670,373, filed January 22, 2010; international application PCT/US2008/011228, filed September 26, 2008 published as WO2009/042223; U.S. provisional application number 60/960,341, filed September 26, 2007; U.S. Patent Application No. 12/680,170, filed March 25, 2010; international application PCT/US2008/011235, filed September 26, 2008, published as WO2009/042228; U.S. provisional application number 60/960,340, filed September 26, 2007; U.S. Patent Application No. 12/680,103, filed March 25, 2010; international application PCT/US2008/011229, filed September 26, 2008, published as WO2009/042224; U.S. provisional application number 60/960,347, filed September 26, 2007; U.S. Patent Application No. 12/667,478, filed March 18, 2010; international application PCT/US2009/001549, filed March 11, 2009, published as WO2009/114145; U.S. provisional application number 61/064,553, filed March 11, 2008; international application

PCT/US2009/001550, filed March 11, 2009, now published as WO2009/114146; U.S. provisional application number 61/064,554, filed March 11, 2008; U.S. provisional application number 61/071,526, filed May 5, 2008; international application PCT/US2009/044402, filed May 18, 2009, published as WO2009/140694; U.S. provisional application number 61/071,785, filed May 16, 2008; U.S. Patent Application No. 12/667,384, filed April 13, 2010; international application PCT/US2010/050781, filed September 29, 2010; U.S. provisional application number 61/246,953, filed September 29, 2009; U.S. Patent Application No. 12/893,826, filed September 29, 2010; international application PCT/US2010/052546, filed October 13, 2010; U.S. provisional application number 61/251,458, filed October 14, 2009; U.S. Patent Application No. 12/903,866, filed October 13, 2010; international application PCT/US2010/052520, filed October 13, 2010; U.S. provisional application number 61/251,291, filed October 13, 2009; international application PCT/US2010/052337; U.S. provisional application number 61/251,452, filed October 14, 2009; U.S. provisional application number 61/251704, filed October 14, 2009; U.S. provisional application number 61/251,710, filed October 14, 2009; and U.S. provisional application number 61/251,693, filed October 14, 2009; all of which are hereby incorporated by reference in their entirety.

[0004] Widespread environmental contaminants that have proven difficult to remediate are the polychlorinated biphenyls (PCBs). Prior to a federal ban in 1979, polychlorinated biphenyls (PCBs) were used widely, for example, in transformers and as plasticizers and dyes. 1.4 billion pounds of PCBs were manufactured in the U.S. prior to 1977. PCBs are now recognized as toxic, carcinogenic, and environmentally persistent, that is, stable and resistant to degradation. The term PCB encompasses 209 individual compounds (congeners) having varying toxicity. PCBs were released to the environment as components of, for example, transformer, compressor, hydraulic, and heat transfer oils, and contaminated soils and sediments as well as construction materials and features such as concrete, bricks, and pipes. 150,000 tons of PCBs reside in landfills.

SUMMARY

[0005] In a method according to the present invention, a plant-derived surfactant is applied to the surface of a material that includes a contaminant, so that the plant-derived surfactant solubilizes the contaminant. An oxidant can also be applied to the surface, so that the oxidant degrades the contaminant. For example, the oxidant can be applied to the surface simultaneously with, after, or before applying the plant-derived surfactant. The contaminant and the plant-derived surfactant can form an emulsion. The plant-derived surfactant can penetrate into the material and/or extract the contaminant from the material. For example, the plant-derived surfactant can include an extract, pressing, juice, or portion of a plant, such as the pulp, seed, or rind, or a chemically modified extract, pressing, juice, or portion of a plant, such as the pulp, seed, or rind, or a combination. For example, the plant-derived surfactant can include a non-ionic surfactant derived from castor oil, a non-ionic surfactant derived from coconut oil, and combinations. For example, the oxidant can include a persulfate, sodium persulfate, a peroxide, hydrogen peroxide, calcium peroxide, or a combination. Ultraviolet light or visible light can be used to irradiate the surface, alone or in conjunction with an oxidant, for example, for photolytic degradation. An activator can be applied to the surface along with irradiation of the surface with visible or ultraviolet light. For example, an octahedral molecular sieve, titanium dioxide, and/or doped titanium dioxide can be applied to the surface and the surface can be irradiated with ultraviolet light and/or visible light. For example, the contaminant can include a hydrocarbon, an aromatic hydrocarbon, a halogenated hydrocarbon, a halogenated aromatic hydrocarbon, a chlorinated hydrocarbon, a chlorinated aromatic hydrocarbon, a polychlorinated biphenyl (PCB), a non-aqueous phase liquid (NAPL), a light NAPL, a dense NAPL, an oil, a transformer oil, a hydraulic oil, a compressor oil, a metal machining lubricant fluid, or a combination of these. For example, the contaminated material treated can include a manmade material, a natural material, a porous material, a material porous to water, a material porous to oil, a material having an open cell foam structure, a closed cell foam structure, and/or a cellular structure, concrete, brick, clay, a clay material, a fired clay material, adobe, terra cotta, earth, packed earth, sand, stone aggregate, wood, drywall, gypsum, pressboard, plywood, linoleum, ceramic or marble tile, a material used in the building or construction industry, paper, a pipe material, lumber, a processed wood material, polyvinyl chloride, or a combination.

[0006] After application of the surfactant, for example, after a predetermined period following application of the surfactant, for example, 1, 2, 3, 6, or 12 hours, 1, 2, 3, 7, 10, 11, 14, or 21 days, or 1, 2, 3, 6, or 12 months after application, the concentration of the contaminant in the material within an 0.5 inch depth of the surface can be reduced to less than about 20000, 10000, 5000, 2000, 1000, 500, 200, 100, 50, 25, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, or 0.001 ppm. After application of the surfactant, for example, after a predetermined period following application of the surfactant, for example, 1, 2, 3, 6, or 12 hours, 1, 2, 3, 7, 10, 11, 14, or 21 days, or 1, 2, 3, 6, or 12 months after application, the concentration of the contaminant in the material within an 0.5 inch depth of the surface can be reduced to less than about 90%, 80%, 67%, 50%, 20%, 10%, 5%, 2%, 1%, 0.5%, 0.2%, or 0.1% of the initial concentration of the contaminant.

[0007] In a method according to the present invention, an activator is applied to the surface, as well as the plant-derived surfactant and the oxidant. For example, the activator can include a metal, iron, a zero valent metal, zero valent iron, a metal chelate, an iron chelate, Fe-TAML (iron tetra-amido macrocyclic ligand), an octahedral molecular sieve, titanium dioxide, doped titanium dioxide (for example, metal-doped titanium oxide), or a combination of these.

[0008] In a method according to the present invention, the oxidant is applied to the surface simultaneously with the plant-derived surfactant. Alternatively, the oxidant can be applied to the surface after applying the plant-derived surfactant or before applying the plant-derived surfactant. A first quantity of oxidant can be applied to the surface before applying the plant-derived surfactant, a second quantity of oxidant can be applied to the surface with the plant-derived surfactant, and/or a third quantity of oxidant can be applied to the surface after the plant-derived surfactant has been applied. Ultraviolet light or visible light can be applied, in addition to or instead of an oxidant.

[0009] In a method according to the present invention, in addition to applying a plant-derived surfactant and/or an oxidant to the surface, mechanical vibration, sound waves, ultrasound waves, heat, and/or infrared radiation is applied to the surface of the material.

[0010] In a method according to the present invention, in addition to applying a plant-derived surfactant and/or an oxidant to the surface, a base and/or an acid is applied to the surface of the material. For example, the base can include a mineral base, an organic base, a strong base, a weak base, an alkaline earth metal hydroxide, an alkali metal hydroxide, sodium hydroxide, potassium hydroxide, or a combination. For example, the acid can include a mineral acid, an organic acid, a strong acid, a weak acid, sulfuric acid, a hydrohalogen acid, hydrochloric acid, nitric acid, citric acid, peracetic acid, or a combination.

[0011] In an embodiment according to the present invention, a composition includes a manmade porous material, a contaminant within the pores of the manmade porous material, a plant-derived surfactant in an amount effective to solubilize the contaminant, and an oxidant in an amount effective to oxidize the contaminant.

BRIEF DESCRIPTION OF THE FIGURES

[0012] Figure 1 presents a photograph of vials containing the PCB Aroclor 1254, water, and VeruSOL-3 surfactant at various concentrations. A vial serving as a first control contained water with no Aroclor or VeruSOL-3, and a vial serving as a second control contained 50 mg of Aroclor and water, but no VeruSOL-3.

[0013] Figure 2 presents a graph showing concentration of Aroclor 1254 as a function of the concentration of VeruSOL-3, with solubility enhancement factors β indicated.

[0014] Figure 3A presents photographs of a vial containing PCB solubilized with VeruSOL-3 and a control vial containing PCB in water. Figure 3B presents photographs of a vial containing PCBs solubilized with VeruSOL and vials containing the solubilized VeruSOL and alkaline persulfate or green nano iron activated persulfate.

[0015] Figure 4 presents a bar graph showing the concentration of Aroclor 1254 in the vials shown in Figs. 3A and 3B.

[0016] Figure 5 presents a bar graph showing the concentration of Aroclor 1254 in a sample of solubilized Aroclor 1254 and in samples subsequently treated with Fe-TAML catalyzed hydrogen peroxide and green nano zero valent iron catalyzed hydrogen peroxide, respectively.

[0017] Figure 6 presents a bar graph showing the concentration of Aroclor 1254 in the liquid phase of PCB contaminated concrete blocks treated with VeruSOL-3 alone, treated with VeruSOL-3 and sodium persulfate, treated with VeruSOL-3 and hydrogen peroxide, and treated with VeruSOL-3, hydrogen peroxide, and sodium persulfate.

[0018] Figure 7 presents a bar graph showing the concentration of Aroclor 1254 within solid concrete blocks that were contaminated with PCB. Concentrations are shown for a control sample of a PCB contaminated concrete block that was not subsequently treated, as well as for PCB contaminated concrete blocks that were treated with VeruSOL-3 alone, treated with VeruSOL-3 and sodium persulfate, treated with VeruSOL-3 and hydrogen peroxide, and treated with VeruSOL-3, hydrogen peroxide, and sodium persulfate.

DETAILED DESCRIPTION

[0019] Embodiments of the invention are discussed in detail below and in the attached figures. In describing embodiments, specific terminology is employed for the sake of clarity. However, the invention is not intended to be limited to the specific terminology so selected. A person skilled in the relevant art will recognize that other equivalent parts can be employed and other methods developed without parting from the spirit and scope of the invention. All references cited herein are incorporated by reference as if each had been individually incorporated.

[0020] Remediation of polychlorinated biphenyls (PCBs) in the environment has been challenging as the result of many factors. One such factor is the highly hydrophobic nature of PCBs, making them unavailable for aqueous phase destruction reactions. Because of their extremely low aqueous solubilities, phase PCBs or PCBs present in various organic matrices, such as transformer oils, hydraulic oils, compressor oils, and waste oils can be difficult to remediate through chemical oxidation. Because of the recalcitrance in the environment, PCBs historically used in hydraulic, compressor, and transformer oils, and grouting materials, when accidently released to contact construction materials present a challenging matrix for remediation. As a result, in traditional remediation approaches PCB contaminated concrete and bricks generally require grinding removal of the surface of the concrete or brick, or complete demolition followed by disposal in a TSCA regulated landfill meeting the requirements of 40 CFR § 761.75 if concentrations exceed 50 ppm (parts per million).

[0021] Plant-oil based surfactants effectively emulsify pure PCB oil and PCB oils in transformer and compressor oils. Solubility enhancement factors in the solubilized phase, beyond that in water alone, approach 2000. Destruction of PCBs with homolog specific analysis of the surfactant emulsified solution is effective using either peroxide- or persulfate-based advanced oxidation processes. Advanced oxidation reactions, such as photooxidation, catalyzed hydrogen peroxide, activated persulfate, and some combinations of these can degrade PCB congeners. For example, treatment of a PCB in an aqueous medium with persulfate can reduce the PCB concentration to less than one-half of the initial value within 2 hours.

[0022] The plant-oil based surfactants can act to micellularize organic liquid contaminants in water. As such, the plant-oil based surfactants act to enhance the apparent solubility of the organic liquid contaminants in water. The contaminant can reside on the surface of or within the structure of the micelle. The process of micellularization is also referred to as emulsification or solubilization in the present text.

[0023] In an embodiment according to the present invention, a plant-derived surfactant is applied to the surface of a material that includes a contaminant, so that the plant-derived surfactant solubilizes the contaminant. The contaminant and the plant-derived surfactant can form an emulsion. An oxidant can be applied to the surface, so that the oxidant degrades the contaminant.

[0024] A simultaneous or sequential application of surfactants and oxidants, such as free radical oxidants, can be effective at desorption and destruction of PCBs in a contaminated manmade material, concrete, bricks, and/or a material porous to water. For example, the VeruSOL surfactant, derived from extracts of plants, can be applied to the contaminated surface, and can be sequentially followed by treatment with an oxidant to cause free radical oxidation of the contaminant. Alternatively, the VeruSOL surfactant can be applied simultaneously with oxidant to the contaminated surface to cause free radical oxidation of the contaminant.

[0025] For example, the contaminated material to treat can be clay, a clay material, a fired clay material, adobe, terra cotta, earth, packed earth, sand, stone aggregate, wood, drywall, gypsum, pressboard, plywood, linoleum, ceramic or marble tile, a material used in the building or construction industry, paper, and/or a pipe material.

[0026] Porous to water can mean that water can penetrate the material, for example, by flowing through channels in the material or by diffusing through the material. The material can have an open cell foam structure, a closed cell foam structure, and/or a cellular structure. For example, the plant-derived surfactant can penetrate into and/or extract contaminant from the material.

[0027] For example, the oxidant can be applied to the surface of a material simultaneously with, before, and/or after applying the plant-derived surfactant.

[0028] In an embodiment according to the invention, an activator is applied to the surface of a material. For example, the activator can be a metal, iron, a zero valent metal, zero valent iron, a metal chelate, an iron chelate, Fe-TAML (iron tetra-amido macrocyclic ligand), an octahedral molecular sieve, titanium dioxide, doped titanium dioxide (for example, metal-doped titanium dioxide), or a combination. For example, a titanium dioxide and/or doped titanium dioxide activator can be applied to the surface of the material, and the surface of the material can be irradiated with visible and/or ultraviolet light. The light can stimulate photocatalytic activity of the titanium dioxide, for example, in the production of hydroxyl radicals from water, and can promote the degradation of contaminants such as PCBs.

[0029] In an embodiment according to the invention, mechanical vibration, sound waves, ultrasound waves, heat, infrared radiation, visible light radiation, and/or ultraviolet radiation can be applied to the surface of the material. The infrared, visible light, and/or ultraviolet radiation can itself promote the degradation of a contaminant, such as a PCB, or can work in conjunction with a photocatalyst, such as titanium dioxide, or another photoactive substance applied to the surface of the material to promote degradation of a contaminant, such as a PCB. In an embodiment according to the invention, a base can be applied to the surface of the material. For example, the base can be alkali metal hydroxide, sodium hydroxide, and/or potassium hydroxide. In an embodiment according to the invention, an acid can be applied to the surface of the material.

[0030] In an embodiment, after a predetermined period following application of the surfactant, for example, 1, 2, 3, 6, or 12 hours, 1, 2, 3, 7, 10, 11, 14, or 21 days, or 1, 2, 3, 6, or 12 months after application, the concentration of contaminant in the material within an 0.5 inch depth of the surface is reduced to less than about 20000, 10000, 5000, 2000, 1000, 500, 200, 100, 50, 25, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, or 0.001 ppm (parts per million). In an embodiment, after a predetermined period following application of the surfactant, for example, 1, 2, 3, 6, or 12 hours, 1, 2, 3, 7, 10, 11, 14, or 21 days, or 1, 2, 3, 6, or 12 months after application, the concentration of contaminant in the material within an 0.5 inch depth of the surface is reduced to less than about 90%, 80%, 67%, 50%, 20%, 10%, 5%, 2%, 1%, 0.5%, 0.2%, or 0.1% of the concentration of contaminant prior to application of the surfactant.

[0031] As used herein, the term "surfactant" includes surfactant compounds, cosolvent compounds, and mixtures. The term "plant oil based surfactants" are surfactants having at least one plant oil. As used herein, the term "plant-derived surfactant" means a surfactant having at least one plant-derived material.

[0032] “Contaminant” encompasses any organic compound present in a location that, by its presence, diminishes the usefulness of the location for productive activity or natural resources, or would diminish such usefulness if present in greater amounts or if left in the location for a length of time. The location may be subsurface, on land, in or under the sea or in the air. “Contaminant” thus can encompass trace amounts or quantities of such a substance. Examples of productive activities include, without limitation, the following: recreation; residential use; industrial use; habitation by animal, plant, or other life forms, including humans; and similar such activities. Examples of natural resources are aquifers, wetlands, sediments, soils, plant life, animal life, and ambient air quality. As used herein "contaminated" means containing one or more contaminant. Contaminated soil, contaminated groundwater, or contaminated wastewater may each include one or more contaminants.

[0033] According to an exemplary embodiment of the invention, the plant-derived surfactant and/or plant-oil based surfactant can include a substance made from a naturally occurring biodegradable plant oil. A surfactant and/or cosolvent can be or can be derived from a plant extract or a biodegradable plant extract, that is, it can be plant derived. For example, the plant-derived surfactant can include an extract, pressing, juice, and/or portion of a plant or a chemically modified extract, pressing, juice, and/or portion of a plant.

[0034] Additionally or alternatively, the surfactant can comprise a substance made from castor oil, coca oil, coconut oil, soy oil, tallow oil, cotton seed oil, or a naturally occurring plant oil. Additionally or alternatively, the surfactant can comprise VeruSOL-1, VeruSOL-2, VeruSOL-3, VeruSOL-4, VeruSOL-5, VeruSOL-6, Citrus Burst 1, Citrus Burst 2, Citrus Burst 3, or E-Z Mulse. Additionally or alternatively, the surfactant can comprise ALFOTERRA 53, ALFOTERRA 123-8S, ALFOTERRA 145-S, ALFOTERRA L167-7S, ETHOX HCO-5, ETHOX HCO-25, ETHOX CO-5, ETHOX CO-40, ETHOX ML-5, ETHAL LA-4, AG-6202, AG-6206, ETHOX CO-36, ETHOX CO-81, ETHOX CO-25, ETHOX TO-16, ETHSORBOX L-20, ETHOX MO-14, S-MAZ 80K, T-MAZ 60 K 60, TERGITOL L-64, DOWFAX 8390, ALFOTERRA L167-4S, ALFOTERRA L123-4S, or ALFOTERRA L145-4S. As mentioned previously, the surfactant can include a surfactant/co-solvent mixture, in which case, the co-solvent can include, for example, dilimnone, terpinoids, alcohols, and/or plant-based solvents. Further examples of surfactants and surfactant/co-solvent mixtures include terpenes, citrus-derived terpenes, limonene, d-limonene, castor oil, coca oil, coconut oil, soy oil, tallow oil, cotton seed oil, and a naturally occurring plant oil. The surfactant and/or cosolvent can be a nonionic surfactant, such as ethoxylated soybean oil, ethoxylated castor oil, ethoxylated coconut fatty acid, and amidified, ethoxylated coconut fatty acid. For example, a composition of surfactant and cosolvent can include at least one citrus terpene and at least one surfactant. A citrus terpene may be, for example, CAS No. 94266-47-4, citrus peels extract (citrus spp.), citrus extract, Curacao peel extract (Citrus aurantium L.), EINECS No. 304-454-3, FEMA No. 2318, or FEMA No. 2344. A surfactant may be a nonionic surfactant. For example, a surfactant may be an ethoxylated castor oil, an ethoxylated coconut fatty acid, or an amidified, ethoxylated coconut fatty acid. An ethoxylated castor oil can include, for example, a polyoxyethylene (20) castor oil, CAS No. 61791-12-6, PEG (polyethylene glycol)-10 castor oil, PEG-20 castor oil, PEG-3 castor oil, PEG-40 castor oil, PEG-50 castor oil, PEG-60 castor oil, POE (polyoxyethylene) (10) castor oil, POE(20) castor oil, POE(20) castor oil (ether, ester), POE(3) castor oil, POE(40) castor oil, POE(50) castor oil, POE(60) castor oil, or polyoxyethylene (20) castor oil (ether, ester). An ethoxylated coconut fatty acid can include, for example, CAS No. 39287-84-8, CAS No. 61791-29-5, CAS No. 68921-12-0, CAS No. 8051-46-5, CAS No. 8051-92-1, ethoxylated coconut fatty acid, polyethylene glycol ester of coconut fatty acid, ethoxylated coconut oil acid, polyethylene glycol monoester of coconut oil fatty acid, ethoxylated coco fatty acid, PEG-15 cocoate, PEG-5 cocoate, PEG-8 cocoate, polyethylene glycol (15) monococoate, polyethylene glycol (5) monococoate, polyethylene glycol 400 monococoate, polyethylene glycol monococonut ester, monococonate polyethylene glycol, monococonut oil fatty acid ester of polyethylene glycol, polyoxyethylene (15) monococoate, polyoxyethylene (5) monococoate, or polyoxyethylene (8) monococoate. An amidified, ethoxylated coconut fatty acid can include, for example, CAS No. 61791-08-0, ethoxylated reaction products of coco fatty acids with ethanolamine, PEG-11 cocamide, PEG-20 cocamide, PEG-3 cocamide, PEG-5 cocamide, PEG-6 cocamide, PEG-7 cocamide, polyethylene glycol (11) coconut amide, polyethylene glycol (3) coconut amide, polyethylene glycol (5) coconut amide, polyethylene glycol (7) coconut amide, polyethylene glycol 1000 coconut amide, polyethylene glycol 300 coconut amide, polyoxyethylene (11) coconut amide, polyoxyethylene (20) coconut amide, polyoxyethylene (3) coconut amide, polyoxyethylene (5) coconut amide, polyoxyethylene (6) coconut amide, polyoxyethylene (7) coconut amide, an alkyl polyglucoside, an alkyl polyglucoside-based surfactant, a decyl polyglucoside, or an alkyl decylpolyglucoside-based surfactant. Examples of surfactants derived from natural plant oils are ethoxylated coca oils, coconut oils, soybean oils, castor oils, corn oils, and palm oils. Many of these natural plant oils are U.S. FDA GRAS. VeruSOL-3, other VeruSOL surfactants, and S-ISCO technology, products, and services are available from VeruTEK Technologies, Inc. ALFOTERRA surfactants are available from Sasol North America. Citrus Burst surfactants are available from Florida Chemical. Ethox, Ethal, and Ethsorbox surfactants are available from Ethox Chemicals. S-Maz and T-Maz surfactants are available from BASF. Tergitol and DOWFAX are available from Dow Chemical.

[0035] Additional surfactants and surfactant/co-solvent mixtures, and details regarding the same, are described in the aforementioned U.S. Published Patent Application No. 2008/0207981.

[0036] According to an exemplary embodiment of the invention, the activator may include a metal, a transition metal, a chelated metal, a complexed metal, a metallorganic complex, and hydrogen peroxide. Examples of activators which are other external agents or conditions include heat, temperature, and high pH. Examples of activators include a metal, iron, Fe(II), Fe(III), a metal chelate, an iron chelate, iron-EDTA, Fe(II)-EDTA, Fe(III)-EDTA, iron-citric acid, Fe(II)-citric acid, Fe(III)-citric acid, a zero valent metal, such as a nanoscale zero valent metal, zero valent iron, such as nanoscale zero valent iron (e.g., zero valent iron particles having a diameter in the range of from about 1, 2, 5, 10, 20, 50, 100, 200, or 500 nm to about 2, 5, 10, 20, 50, 100, 200, 500, or 1000 nm), hydrogen peroxide, high pH, and heat. In some cases an alkali metal EDTA compound, such as sodium EDTA, may serve as an activator. Additional activators and details regarding the same are described in the aforementioned U.S. Published Patent Application No. 2008/0207981. In other embodiments, the activator may be an Fe-TAML compound. Fe-TAML compounds are described, for example, in U.S. Patents 5,847,120, 5,876,625, 6,011,152, 6,051,704, 6,054580, 6,099,586, 6,100,394, 6,136,223, 6,241,779, and 7,060,818, which are hereby incorporated by reference in their entirety.

[0037] According to an exemplary embodiment of the invention, the oxidant can be a chemical oxidant such as a permanganate, an alkali metal permanganate, potassium permanganate, molecular oxygen, ozone, a persulfate, an alkali metal persulfate, sodium persulfate, an activated persulfate, a percarbonate, an activated percarbonate, a peroxide, an alkali earth peroxide, calcium peroxide, or hydrogen peroxide, or ultraviolet (uV) light or any combination of these oxidants with or without uV light. Additional oxidants and details regarding the same are described in the aforementioned U.S. Published Patent Application No. 2008/0207981.

[0038] According to embodiments of the invention, contaminants include dense nonaqueous phase liquids (DNAPLs), light nonaqueous phase liquids (LNAPLs), polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, pesticides, polychlorinated biphenyls and various organic chemicals, such as petroleum products. Examples of contaminants include volatile organic compounds, semi-volatile organic compounds, non-aqueous phase liquids (NAPLs), chlorinated solvents, dense nonaqueous phase liquids (DNAPLs), light nonaqueous phase liquids (LNAPLs), aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), pesticides, halogenated hydrocarbons, halogenated aromatic hydrocarbons, chlorinated hydrocarbons, chlorinated aromatic hydrocarbons, polychlorinated biphenyls (PCBs), benzene, toluene, ethyl benzene, xylene, hydrocarbons, halogenated hydrocarbons, petroleum range hydrocarbons and combinations thereof. A contaminant can include an oil, a transformer oil, a hydraulic oil, a compressor oil, a metal machining lubricant fluid, and combinations.

[0039] Contaminants can be associated with, for example, manufactured gas plant residuals, creosote wood treating liquids, petroleum residuals, pesticide, or polychlorinated biphenyl (PCB) compounds and other waste products or byproducts of industrial processes and commercial activities.

[0040] In an embodiment according to the present invention, a plant-derived surfactant, such as a castor oil derivative, a coconut oil derivative, or VeruSOL-3, is applied to the surface of a manmade porous material that includes a contaminant, such as a PCB, within its pores. The plant-derived surfactant can penetrate into the material and solubilize, emulsify, or suspend the contaminant. The contaminant can thereby be extracted from the pores of the material to the surface of the material. The liquid including the contaminant dissolved, emulsified, or suspended in the plant-derived surfactant can then be gathered from the surface of the material, for example, by using an absorbent substance (such as a sponge), using a vacuum cleaner, wiping the fluid into a container, or rinsing the fluid into a container. The gathered liquid can then be disposed of in a regulatory-compliant manner. Additionally or alternatively, an oxidant can be applied to the surface of the manmade porous material. The oxidant can be dissolved, emulsified, or suspended in the plant-derived surfactant applied to the surface of the material. Alternatively, the oxidant can be applied to the surface of the material in a step separate from the application of the plant-derived surfactant. For example, the oxidant can be applied to the surface of the material before or after the application of the plant-derived surfactant. The oxidant, for example, sodium persulfate and/or hydrogen peroxide, can act to oxidize and destroy the contaminant within the pores of the manmade porous material, and/or can act to oxidize and destroy the contaminant at the surface of the manmade porous material. For example, the oxidant can oxidize and decompose contaminant that is extracted by the plant-derived surfactant from the pores to the surface of the manmade porous material. The oxidant may be included with the plant-derived surfactant in a treatment liquid, so as to facilitate one-step treatment of a manmade porous material. For example, the mixture of plant-derived surfactant and oxidant can be applied to contaminated concrete blocks and allowed to remediate the blocks by oxidizing the contaminant within the pores of the blocks and/or on the surface of the blocks. Alternatively, the plant-derived surfactant alone can be applied to the surface of a contaminated material to extract the contaminant from pores to the surface of the material, and the oxidant can be then applied in a second step to the surface to oxidize and destroy the contaminant on the surface of the material. Such a two-step approach can be useful, for example, to minimize undesired degradation of the interior of the manmade porous material by the oxidant.

EXAMPLE 1: Solubilization of PCB with VeruSOL

[0041] In an experiment, Aroclor 1254, a PCB, was used. 50 mg of Aroclor was placed into each of several 4 mL vials with Sudan IV red hydrophobic dye (to facilitate identification of the non-aqueous phase) and water. In the several vials, the VeruSOL-3 surfactant was added to achieve concentrations of VeruSOL-3 of 1 g/L, 2.5 g/L, 5.0 g/L, and 10 g/L. A first control contained water with no Aroclor or VeruSOL-3, and a second control contained 50 mg of Aroclor and water, but no VeruSOL-3. The concentration of the PCBs was determined with three types of PCB analysis: Aroclor specific analysis, homolog specific analysis, and congener specific analysis. A photograph of the vials is shown in Fig. 1. Aroclor 1254 has a solubility in water of $C_{aq} = 0.869$ mg/L. Figure 2 presents a graph showing the concentration of Aroclor 1254 in the emulsion formed with the VeruSOL-3 along the vertical axis as a function of concentration of VeruSOL-3 along the horizontal axis. The solubility enhancement factor, that is, the ratio of the concentration of Aroclor 1254 in the emulsion with VeruSOL (C_{VS}) over the solubility of Aroclor 1254 in water with no VeruSOL (C_{aq}) is shown as beta (β) = C_{VS}/C_{aq} values. For example, with 2.5 g/L of VeruSOL, the Aroclor 1254 has a concentration in the VeruSOL-3-water emulsion of about 1700 mg/L, a solubility enhancement of about 1946 times over that of Aroclor 1254 in water without VeruSOL-3. Thus, VeruSOL-3 as a surfactant effectively promotes the emulsification of PCBs. The concentrations of PCBs (for example, Aroclor 1254) in a sample, in the experiments of this Example 1, as well as in the experiments of Examples 2-4, discussed below, were determined with a technique based on EPA Method 8082 using a gas chromatograph/electron capture detector. PCB congeners (SW846 8082) from Mitkem Laboratories were used as the PCBs in this Example 1. These PCB congeners were also used as analytical standards.

EXAMPLE 2: Oxidation of Emulsified PCB

[0042] In an experiment, the PCB Aroclor 1254 was emulsified in water with VeruSOL-3 (at a concentration of 2 g/L) as the surfactant. The left-hand photograph in Fig. 3 shows the Aroclor-VeruSOL-3-water emulsion in the vial at left. The vial at right served as a control and contained Aroclor and water, but no VeruSOL. The vials were shaken for 72 hours and then allowed to settle for 24 hours. The Aroclor-VeruSOL-3-water emulsion was then used in tests of the ability of various compositions to oxidize the Aroclor PCB. The right-hand photograph in Fig. 3 shows results after 5 days of treatment with an oxidant composition. The first vial, at left, represents a control, in which no oxidant composition was added to the Aroclor-VeruSOL-3-water emulsion. In the second vial from the left, an alkaline-activated persulfate (sodium persulfate activated with the base sodium hydroxide) had been added to the emulsion. The clarity of the fluid after 5 days indicated that the persulfate had oxidized and degraded the Aroclor PCB. In the third vial, at right, a mixture of persulfate and zero valent iron nanoparticles had been added to the emulsion. The zero valent iron nanoparticles were formed by a green process using plant extracts as set forth in international application PCT/US2009/044402, filed May 18, 2009 (published as WO2009/140694 A2 on June 3, 2010); the description in this international application is hereby incorporated by reference. The clarity of the fluid after 5 days indicated that the persulfate had oxidized and degraded the Aroclor PCB. The graph presented in Fig. 4 shows that the Aroclor emulsion treated with persulfate for five days and the Aroclor emulsion treated with the iron nanoparticles for five days have a concentration of Aroclor 1254 that is only one-fifth of the concentration in the control vial which sat for five days without the addition of persulfate.

[0043] In another set of tests, the Aroclor-VeruSOL-3-water emulsion was treated in one case with hydrogen peroxide and iron tetra-amido macrocyclic ligand (Fe-TAML) as a catalyst, and in a second case with hydrogen peroxide and the iron nanoparticles produced by the green method. Figure 5 presents a graph comparing the concentration of Aroclor in the treated emulsions with an untreated control emulsion. In the case of treatment of the emulsion with the combination of hydrogen peroxide and Fe-TAML, 73.1% of the Aroclor 1254 was destroyed. In the case of treatment of the emulsion with the combination of hydrogen peroxide and the iron nanoparticles, 84.6% of the Aroclor 1254 was destroyed.

EXAMPLE 3: Destruction of PCBs in Contaminated Concrete

[0044] In a set of experiments, concrete from a former manufacturing facility that was contaminated with PCBs was treated with a mixture of VeruSOL-3 and activated persulfate (also referred to herein as S-ISCO treatment). That is, the concrete cores taken from a warehouse floor of the manufacturing facility were treated by statically applying to the surface of the concrete a S-ISCO aqueous-based treatment liquid including 100 g/L of the oxidant sodium persulfate and 10 g/L of VeruSOL-3 (which included plant-derived surfactant), with the S-ISCO liquid adjusted with sodium hydroxide to a pH of about 12 to activate the persulfate (a pH above about 10.5 can activate persulfate). The treatment liquid was statically applied to the surface of the concrete in that it was passively applied, with no externally-induced mixing of the treatment liquid with the concrete (for example, no pulverizing of the concrete surface to homogenize the concrete with the liquid). To assess the distribution and concentration of PCBs in the concrete, samples were chipped from the upper 0.5 inch depth of the concrete (0 to 0.5 inch depth) and from the 0.5 to 1 inch depth of the concrete before treatment and after an 11-day treatment with the surface-applied S-ISCO liquid. Samples were also were taken of the treatment liquid remaining on the surface of the concrete after the 11-day treatment; this residual liquid was termed the SPLP (synthetic precipitation leaching procedure) extract.

[0045] The concentrations of various Aroclor PCBs in four concrete samples before treatment, as well as in a grease material obtained from concrete, all obtained from the manufacturing facility, are presented in Table 1.

Concrete: Initial (Pre-Treatment) Baseline PCB Aroclor Concentrations					
PCBs [μg/kg]	Sample A (0 – 0.5 in.)	Sample B (0.5 - 1 in.)	Sample C (0 – 0.5 in.)	Sample D (0.5 - 1 in.)	Sample E Grease
PCB-1016	ND	ND	ND	ND	ND
PCB-1221	ND	ND	ND	ND	ND
PCB-1232	ND	ND	ND	ND	ND
PCB-1242	ND	ND	ND	ND	ND
PCB-1248	*	*	ND	ND	*
PCB-1254	*	*	ND	ND	*
PCB-1260	*	*	10,000	*	*
PCB-1262	ND	ND	ND	ND	ND
PCB-1268	ND	ND	ND	*	ND
Total PCBs	26,000	7,900	10,000	4,300	120,000
Reporting Limit	3,600	3,400	3,400	360	19,000

ND = None Detected

* = The analysis indicated that the Aroclor species designated may have been present; however, the concentration of the species could not be identified. Therefore, the total PCB concentration is shown in the penultimate row of the table.

Table 1

[0046] The concentration of the PCB congeners in the four concrete samples after 11 days of treatment with the treatment solution is presented in Table 2, along with a comparison with the initial (pre-treatment) concentration of total PCBs and the percent reduction in PCB concentration achieved by the treatment. There were no PCBs detected in the SPLP extract (the residual treatment liquid) from the concrete following treatment. The limit of detection was 1.0 µg/L; that is, the concentration of PCBs in the SPLP extract was less than this value.

Concrete: Final (Post-Treatment) PCB Congener Concentrations					
PCBs [µg/kg]	Sample A (0 – 0.5 in.)	Sample B (0.5 - 1 in.)	Sample C (0 – 0.5 in.)	Sample D (0.5 - 1 in.)	
PCB-1016	ND	ND	ND	ND	
PCB-1221	ND	ND	ND	ND	
PCB-1232	ND	ND	ND	ND	
PCB-1242	ND	ND	ND	ND	
PCB-1248	ND	ND	ND	ND	
PCB-1254	ND	ND	*	*	
PCB-1260	*	*	*	*	
PCB-1262	ND	ND	ND	ND	
PCB-1268	*	*	ND	ND	
Final (Post-Treat) PCBs	5,100	2,000	5,300	2,500	
Initial (Pre-Treat) PCBs	26,000	7,900	10,000	4,300	
Percent Reduction	80.5%	74.7%	47.0%	46.5%	
Reporting Limit [µg/kg]	3,300	330	970	330	

ND = None Detected

* = The analysis indicated that the Aroclor species designated may have been present; however, the concentration of the species could not be identified. Therefore, the total PCB concentration is shown in the penultimate row of the table.

Table 2

EXAMPLE 4: Destruction of PCBs in Porous Concrete

[0047] In a set of experiments, a solution of 500 ppm (parts per million on a weight basis) Aroclor 1254 PCB in transformer oil (from Supelco Analytical Standards) was applied to very porous concrete blocks for a duration of 7 days, designated CB-2 through CB-6. No PCB was applied to the concrete block CB-1, which served as a blank control. The PCB contaminated blocks were then treated with solutions of VeruSOL-3 alone, VeruSOL-3 and activated sodium persulfate, VeruSOL-3 and catalyzed hydrogen peroxide, and VeruSOL-3 and a mixture of activated sodium persulfate and catalyzed hydrogen peroxide for a duration of 11 days. 1 mL of 10 N sodium hydroxide was used as the activator of the sodium persulfate; thus, the activated sodium persulfate is also referred to as "alkaline persulfate". 1 mL of 5 μM Fe-TAML was used as the catalyst for the hydrogen peroxide. Tables 3A and 3B present a summary of the test conditions for six samples, CB-1 through CB-6.

Protocol: Oxidation Tests on Porous Concrete Blocks Contaminated with PCBs		
Sample	**Test Condition**	**Test Summary**
CB-1	Blank Control	Uncontaminated Concrete Block
CB-2	PCB Control	Concrete Block Contaminated with 500 ppm Aroclor 1254 in Transformer Oil (500 ppm A 1254): Untreated
CB-3	VeruSOL-3 alone	Concrete Block Contaminated with 500 ppm A 1254: VeruSOL-3 Treated (VeruSOL-3 desorbed PCBs)
CB-4	S-ISCO Alkaline Persulfate	Concrete Block Contaminated with 500 ppm A 1254: S-ISCO Treated
CB-5	S-ISCO Catalyzed Hydrogen Peroxide	Concrete Block Contaminated with 500 ppm A 1254: S-ISCO Treated
CB-6	S-ISCO Catalyzed Hydrogen Peroxide and Alkaline Persulfate	Concrete Block Contaminated with 500 ppm A 1254: S-ISCO Treated

Table 3A

[0048] Table 3B shows how the reagents were applied to the PCB contaminated samples CB-3 through CB-6. In a first treatment step, Phase I, only the surfactant VeruSOL-3 (VS-3) at a concentration of 300 g/L in water was applied to the contaminated sample. In a subsequent, second treatment step, Phase IIA, the oxidant sodium persulfate at a concentration of 500 g/L in water was applied to the sample CB-4; the oxidant hydrogen peroxide at a concentration of 30% in water (on a volumetric basis) was applied to the samples CB-5 and CB-6. In a subsequent, third treatment step, Phase IIB, the catalyst sodium hydroxide at a concentration of 10 N in water was applied to the sample CB-4; the catalyst Fe-TAML at a concentration of 5 μM in water was applied to the samples CB-5 and CB-6. Subsequent, fourth and fifth treatment steps, were applied to the sample CB-6 only: sodium persulfate at a concentration of 500 g/L in water was applied as Phase IIIA, and this was followed by the application of sodium hydroxide at a concentration of 10 N in water as Phase IIIB.

Sample	**Solubilization Phase**	**Oxidation Phase**			
	Phase I	**Phase IIA**	**Phase IIB**	**Phase IIIA**	**Phase IIIB**
	Surfactant	**Oxidant**	**Catalyst**	**Volume Oxidant Solution**	**Catalyst**
CB-1	None	0	0	0	0
CB-2	None	0	0	0	0
CB-3	300 g/L VeruSOL-3 (VS-3)	0	0	0	0
CB-4	300 g/L VS-3	500 g/L Sodium Persulfate	1 mL 10 N NaOH	0	0
CB-5	300 g/L VS-3	30% H_2O_2	1 mL 5 µM Fe-TAML	0	0
CB-6	300 g/L VS-3	30% H_2O_2	1 mL 5 µM Fe-TAML	50 mL of 500 g/L Sodium Persulfate	1 mL 10 N NaOH

Table 3B

[0049] Figure 6 presents the concentration in the liquid phase (that is, in the treatment solution) following the 11-day treatment of the concrete blocks (also termed the concrete bricks) designated CB-3 through CB-6 with solutions of VeruSOL-3 alone, VeruSOL-3 with sodium persulfate and sodium hydroxide (collectively termed alkaline persulfate), VeruSOL-3 with hydrogen peroxide and catalyst (Fe-TAML), and VeruSOL-3 with hydrogen peroxide, catalyst, sodium persulfate, and sodium hydroxide, respectively. The left-most bar of Fig. 6 shows the concentration of the Aroclor 1254 PCB in the liquid phase for concrete block CB-3 treated with only VeruSOL-3 (no oxidant) as 28,000 µg/L. That is, the VeruSOL-3 extracted the PCB from the concrete block, solubilizing or emulsifying the PCB into an oil in water emulsion. Figure 6 also shows that the oxidant compound(s) in the solutions used to treat concrete blocks CB-4 through CB-6 destroyed more than 99% of the Aroclor 1254 PCB extracted into the liquid phase present at the surface of the concrete blocks.

[0050] To assess the distribution and concentration of PCBs within the concrete, samples were chipped from the upper 0.5 inch depth of the concrete (0 to 0.5 inch depth) and from the 0.5 to 1 inch depth of the concrete before treatment and after the 11-day treatment with the treatment solutions. Figure 7 presents the final concentration within the concrete blocks CB-2 through CB-6. The solution of Aroclor 1254 PCB in transformer oil was initially applied to concrete block CB-2 as well as to blocks CB-3 through CB-6. However, block CB-2 was not subsequently treated with VeruSOL-3 or oxidant, and, therefore, served as a control. The Aroclor 1254 PCB was at a concentration of about 5700 µg/kg in the control block CB-2. The concentration of Aroclor 1254 PCB within the concrete blocks subsequently treated with VeruSOL-3 or oxidant was lower, indicating the extraction and/or destruction of PCB by the oxidant. In concrete block CB-3, treated only with VeruSOL-3, 28% of the PCB within the block was extracted into the liquid phase (also see Fig. 6). In concrete block CB-4, treated with VeruSOL-3 and activated sodium persulfate, the concentration of PCB decreased by 33%, indicating that the PCB was destroyed by the oxidant within the pores of the concrete block and/or extracted by the VeruSOL-3 and destroyed in the liquid phase at the surface of the concrete block (also see Fig. 6). In concrete block CB-5, treated with VeruSOL-3 and catalyzed hydrogen peroxide, 39% of the PCB was destroyed. And in concrete block CB-6, treated with VeruSOL-3, catalyzed hydrogen peroxide, and activated sodium persulfate, 40% of the PCB was destroyed.

[0051] Thus, the experiments for which results are shown in Figs. 6 and 7 showed that VeruSOL-3 extracted PCB from porous concrete blocks and that activated sodium persulfate, catalyzed hydrogen peroxide, and a combination of catalyzed hydrogen peroxide and activated sodium persulfate each destroyed through oxidation a large fraction of the PCB present in the blocks. The oxidants acted effectively in the liquid phase, so that greater than 99% of PCB present in the liquid phase was destroyed.

[0052] The embodiments illustrated and discussed in this specification are intended only to teach those skilled in the art the best way known to the inventors to make and use the invention. Nothing in this specification should be considered as limiting the scope of the present invention. All examples presented are representative and non-limiting. The above-described embodiments of the invention may be modified or varied, without departing from the invention, as appreciated by those skilled in the art in light of the above teachings. It is therefore to be understood that, within the scope of the claims and their equivalents, the invention may be practiced otherwise than as specifically described.

WE CLAIM:

1. A method comprising applying a plant-derived surfactant to the surface of a manmade porous material that includes a contaminant, the plant-derived surfactant being in an amount effective to solubilize the contaminant within the material.

2. The method of claim 1, wherein the plant-derived surfactant is selected from the group consisting of a non-ionic surfactant derived from castor oil, a non-ionic surfactant derived from coconut oil, and combinations.

3. The method of claim 1, further comprising applying an octahedral molecular sieve, titanium dioxide, and/or doped titanium dioxide to the surface and irradiating the surface with ultraviolet light and/or visible light.

4. The method of any one of claims 1-2, further comprising applying an oxidant to the surface, so that the oxidant degrades the contaminant.

5. The method of claim 4, wherein the contaminant and the plant-derived surfactant form an emulsion.

6. The method of any one of claims 4-5, wherein the plant-derived surfactant extracts the contaminant from the material.

7. The method of any one of claims 4-6, wherein the plant-derived surfactant penetrates into the material.

8. The method of any one of claims 4-7, wherein the oxidant is selected from the group consisting of a persulfate, sodium persulfate, a peroxide, hydrogen peroxide, calcium peroxide, and combinations.

9. The method of any one of claims 4-7, wherein the oxidant is selected from the group consisting of a persulfate and sodium persulfate.

10. The method of any one of claims 4-9, wherein the oxidant is applied to the surface simultaneously with the plant-derived surfactant.

11. The method of any one of claims 4-9, wherein the oxidant is applied to the surface after applying the plant-derived surfactant.

12. The method of any one of claims 4-9, wherein the oxidant is applied to the surface before applying the plant-derived surfactant.

13. The method of any one of claims 4-12, further comprising applying an activator to the surface.

14. The method of claim 13, wherein the activator is selected from the group consisting of a metal, iron, a zero valent metal, zero valent iron, a metal chelate, an iron chelate, Fe-TAML, an octahedral molecular sieve, titanium dioxide, doped titanium dioxide, and combinations.

15. The method of any one of claims 4-14, wherein the plant-derived surfactant comprises an extract, pressing, juice, or portion of a plant or a chemically modified extract, pressing, juice, or portion of a plant.

16. The method of any one of claims 4-15, wherein the contaminant is selected from the group consisting of a hydrocarbon, an aromatic hydrocarbon, a halogenated hydrocarbon, a halogenated aromatic hydrocarbon, a chlorinated hydrocarbon, a chlorinated aromatic hydrocarbon, a polychlorinated biphenyl (PCB), a non-aqueous phase liquid (NAPL), a light NAPL, and a dense NAPL.

17. The method of any one of claims 4-15, wherein the contaminant is selected from the group consisting of an oil, a transformer oil, a hydraulic oil, a compressor oil, and a metal machining lubricant fluid.

18. The method of any one of claims 4-17, wherein the material is selected from the group consisting of concrete, brick, a fired clay material, adobe, terra cotta, drywall, pressboard, plywood, linoleum, ceramic tile, and marble tile.

19. The method of any one of claims 4-17, wherein the material is selected from the group

consisting of lumber, a processed wood material, paper, and polyvinyl chloride.

20. The method of any one of claims 4-19, further comprising applying a base to the surface of the material.

21. The method of claim 20, wherein the base is selected from the group consisting of an alkali metal hydroxide, sodium hydroxide, potassium hydroxide, and combinations.

22. The method of any one of claims 4-19, further comprising applying an acid to the surface of the material.

23. The method of claim 22, wherein the acid is selected from the group consisting of sulfuric acid, hydrochloric acid, nitric acid, citric acid, peracetic acid, and combinations.

24. The method of any one of claims 4-23, further comprising applying mechanical vibration, sound waves, ultrasound waves, heat, and/or infrared radiation to the surface of the material.

25. The method of any one of claims 4-24, further comprising irradiating the surface with ultraviolet light.

26. The method of claim 25, further comprising applying an activator to the surface.

27. The method of claim 25, further comprising applying an octahedral molecular sieve, titanium dioxide, and/or doped titanium dioxide to the surface.

28. The method of any one of claims 4-27, wherein following application of the surfactant, the concentration of the contaminant in the material within an 0.5 inch depth of the surface is reduced to less than about 20000 ppm.

29. The method of any one of claims 4-27, wherein following application of the surfactant, the concentration of the contaminant in the material within an 0.5 inch depth of the surface is

reduced to less than about 10000 ppm.

30. The method of any one of claims 4-27, wherein following initial application of the surfactant, the concentration of the contaminant in the material within an 0.5 inch depth of the surface is reduced to less than about 5000, 2000, 1000, 500, 200, 100, 50, 25, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, or 0.001 ppm.

31. The method of any one of claims 4-27, wherein following initial application of the surfactant, the concentration of the contaminant in the material within an 0.5 inch depth of the surface is reduced to less than about 90%, 80%, 67%, 50%, 20%, 10%, 5%, 2%, 1%, 0.5%, 0.2%, or 0.1% of the initial concentration.

32. A composition comprising a manmade porous material, a contaminant within the pores of the manmade porous material, a plant-derived surfactant in an amount effective to solubilize the contaminant, and an oxidant in an amount effective to oxidize the contaminant.

33. The composition of claim 32, wherein the manmade porous material is selected from the group consisting of concrete, brick, a fired clay material, adobe, terra cotta, drywall, pressboard, plywood, linoleum, ceramic tile, and marble tile.

34. The composition of claim 32, wherein the manmade porous material is selected from the group consisting of lumber, a processed wood material, paper, and polyvinyl chloride.

AROCLOR 1254 - PCBs WITH THE S-ISCO PROCESS

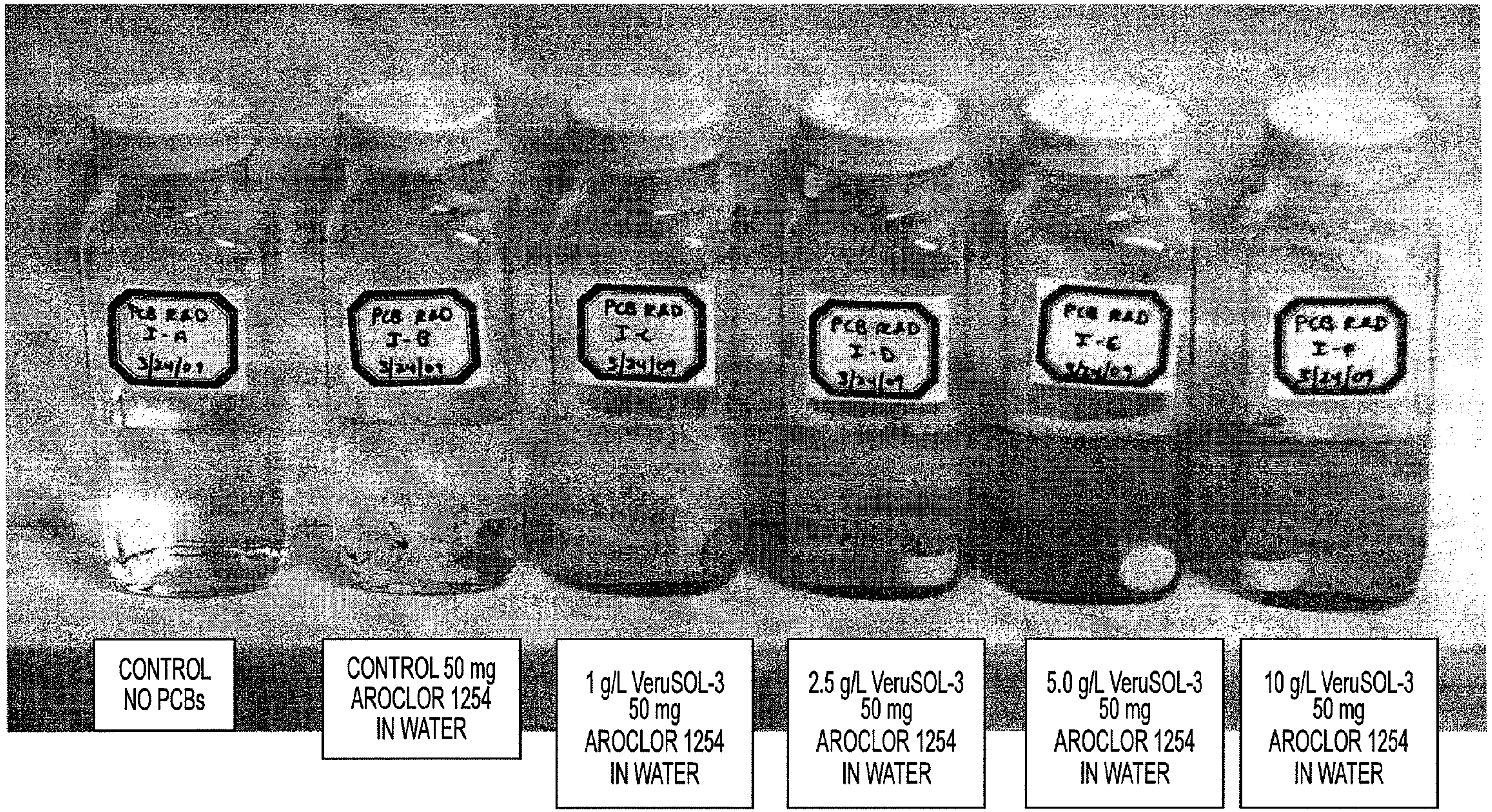
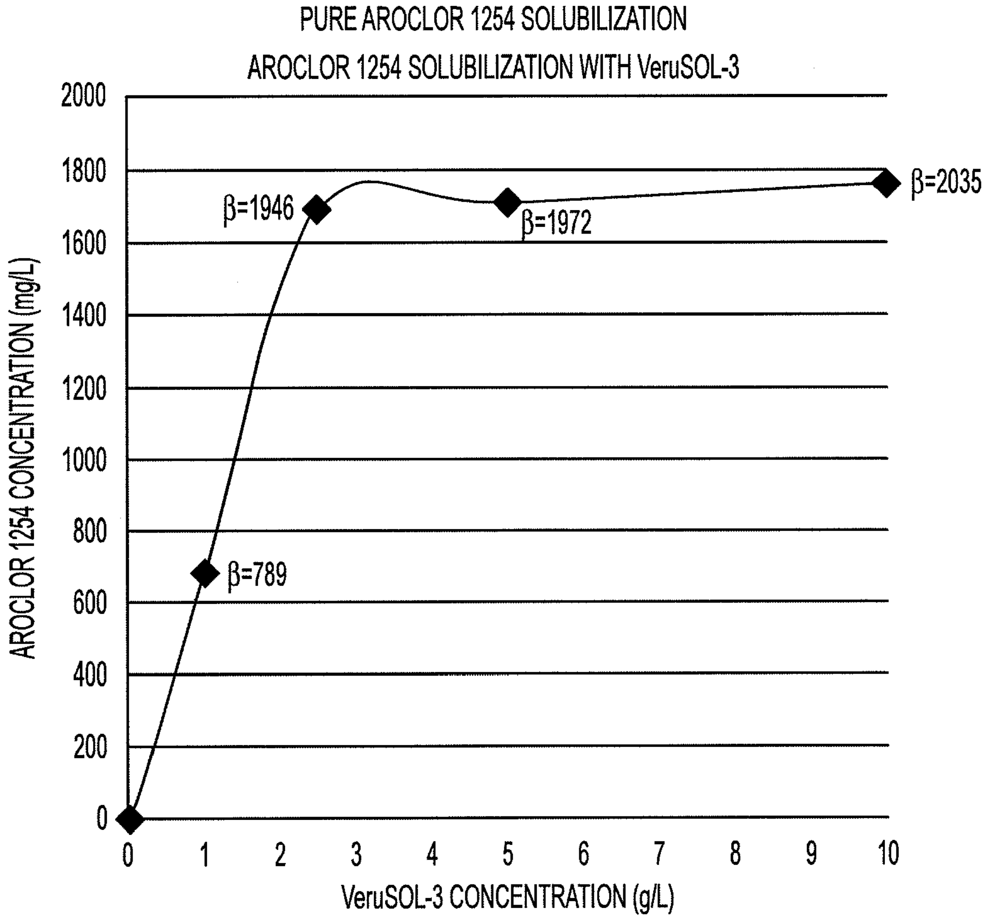


FIG. 1



NOTE: β=SOLUBILITY ENHANCEMENT FACTOR (C_{VS}/C_{aq}); C_{aq} = 0.869 mg/L
HOMOLOG SPECIFIC ANALYSIS

FIG. 2

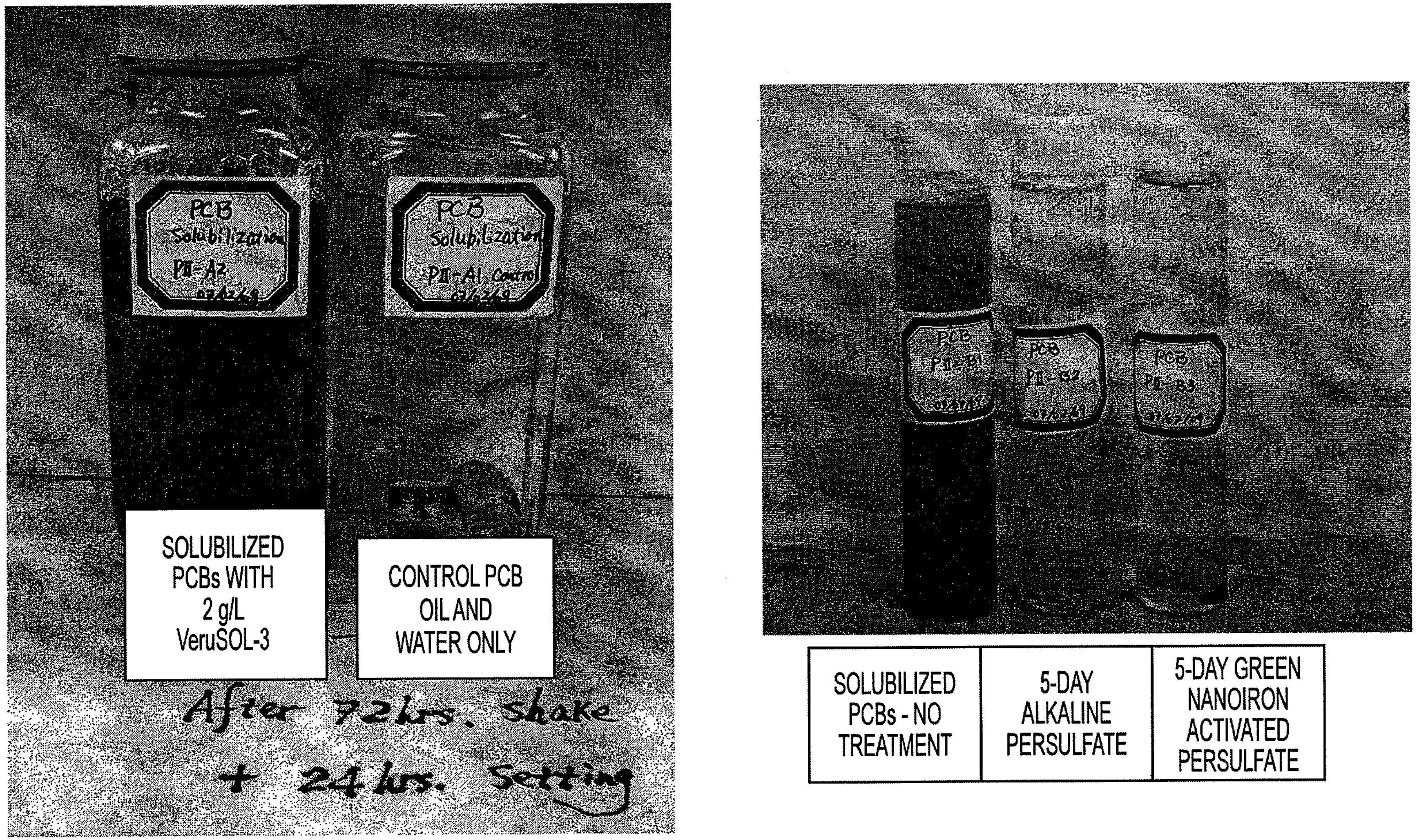

PCB
Solubilization
PII-A2
PCB
Solubilization
PII-A1 Control
SOLUBILIZED PCBs WITH 2 g/L VeruSOL-3
CONTROL PCB OIL AND WATER ONLY
After 72hrs. shake
+ 24hrs. Setting
PCB
PII-B1
PCB
PII-B2
PCB
PII-B3
SOLUBILIZED PCBs - NO TREATMENT
5-DAY ALKALINE PERSULFATE
5-DAY GREEN NANOIRON ACTIVATED PERSULFATE

FIG. 3

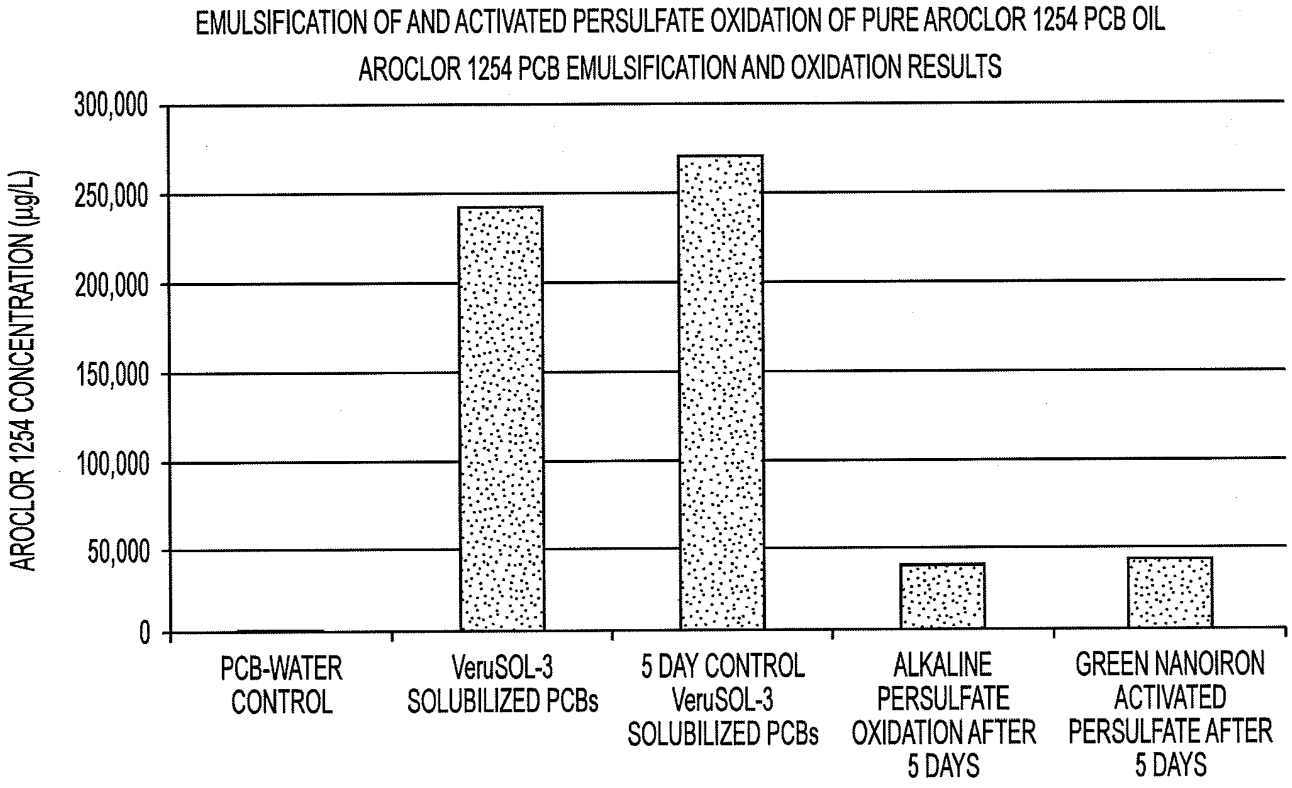

EMULSIFICATION OF AND ACTIVATED PERSULFATE OXIDATION OF PURE AROCLOR 1254 PCB OIL
AROCLOR 1254 PCB EMULSIFICATION AND OXIDATION RESULTS
AROCLOR 1254 CONCENTRATION (µg/L)
300,000
250,000
200,000
150,000
100,000
50,000
0
PCB-WATER CONTROL
VeruSOL-3 SOLUBILIZED PCBs
5 DAY CONTROL VeruSOL-3 SOLUBILIZED PCBs
ALKALINE PERSULFATE OXIDATION AFTER 5 DAYS
GREEN NANOIRON ACTIVATED PERSULFATE AFTER 5 DAYS

FIG. 4

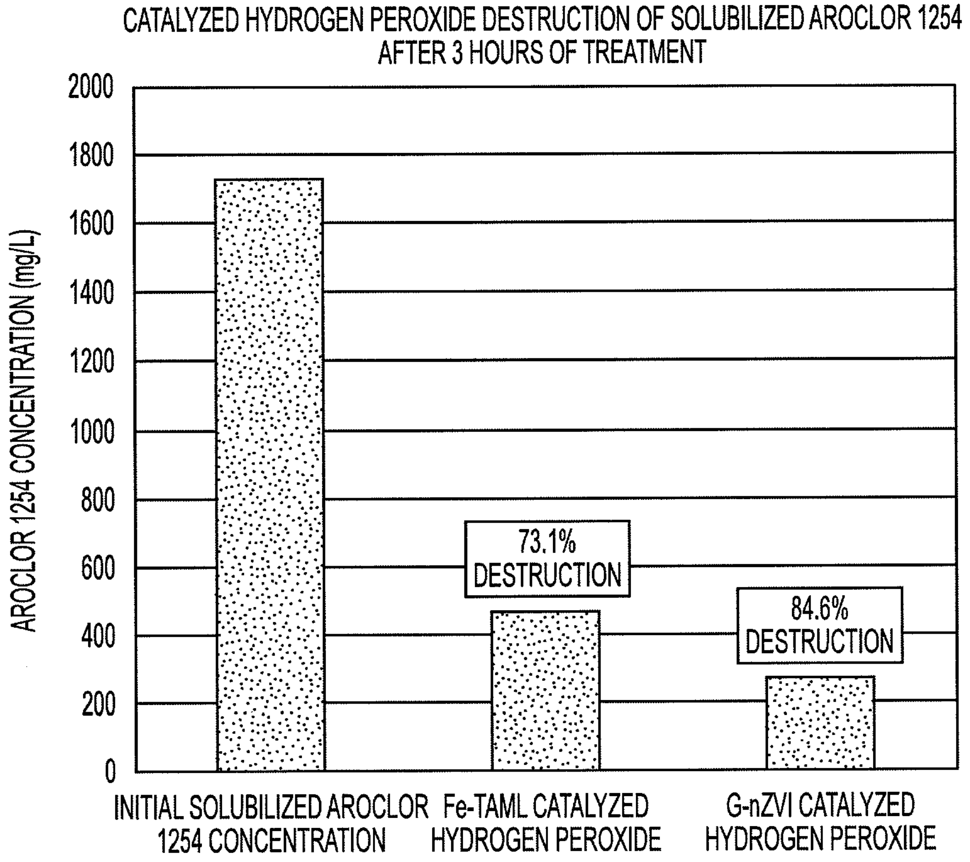

CATALYZED HYDROGEN PEROXIDE DESTRUCTION OF SOLUBILIZED AROCLOR 1254
AFTER 3 HOURS OF TREATMENT
AROCLOR 1254 CONCENTRATION (mg/L)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
73.1% DESTRUCTION
84.6% DESTRUCTION
INITIAL SOLUBILIZED AROCLOR 1254 CONCENTRATION
Fe-TAML CATALYZED HYDROGEN PEROXIDE
G-nZVI CATALYZED HYDROGEN PEROXIDE

FIG. 5

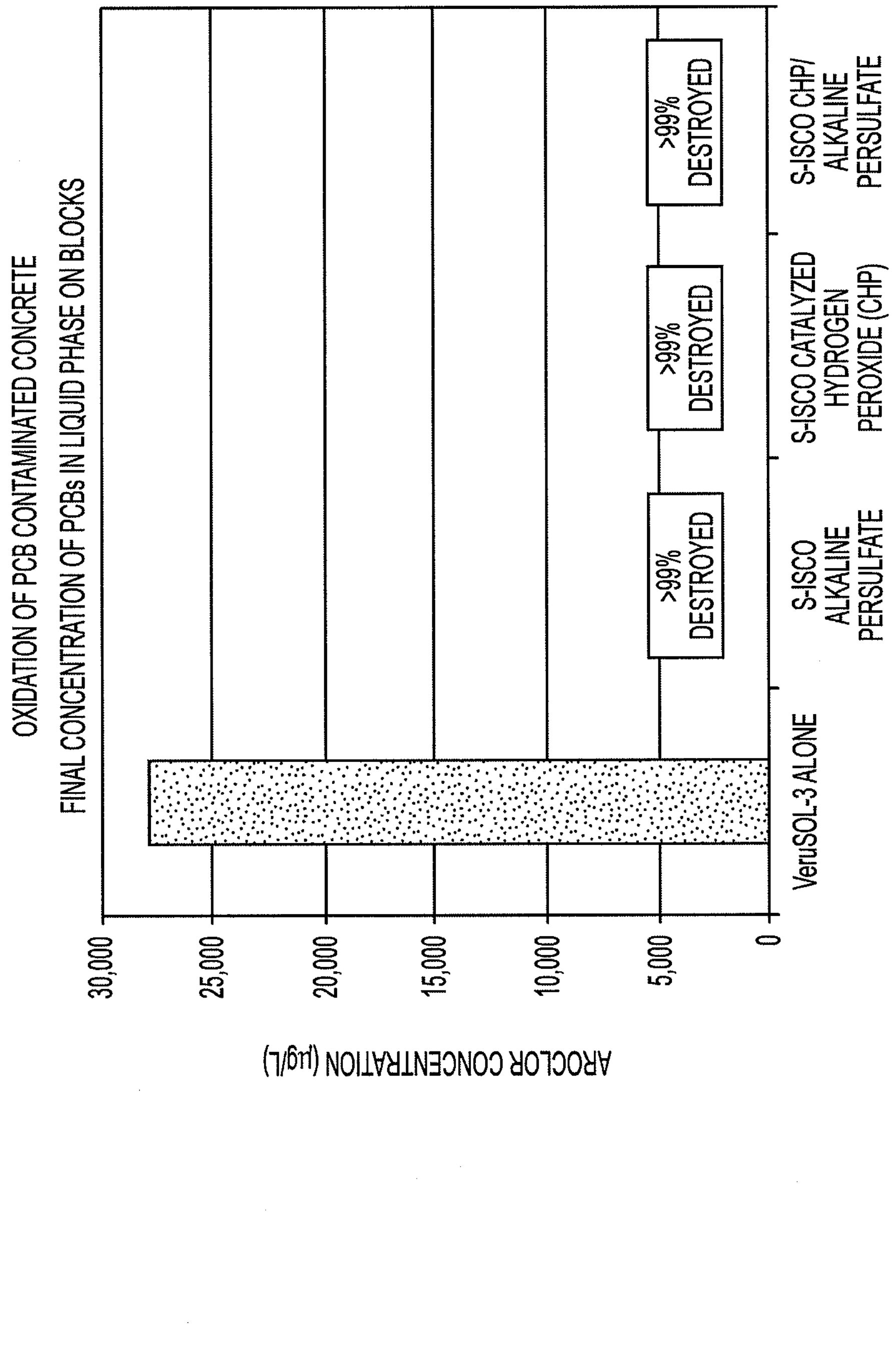

OXIDATION OF PCB CONTAMINATED CONCRETE
FINAL CONCENTRATION OF PCBs IN LIQUID PHASE ON BLOCKS
AROCLOR CONCENTRATION (µg/L)
30,000
25,000
20,000
15,000
10,000
5,000
0
VeruSOL-3 ALONE
>99% DESTROYED
S-ISCO ALKALINE PERSULFATE
>99% DESTROYED
S-ISCO CATALYZED HYDROGEN PEROXIDE (CHP)
>99% DESTROYED
S-ISCO CHP/ ALKALINE PERSULFATE

FIG. 6

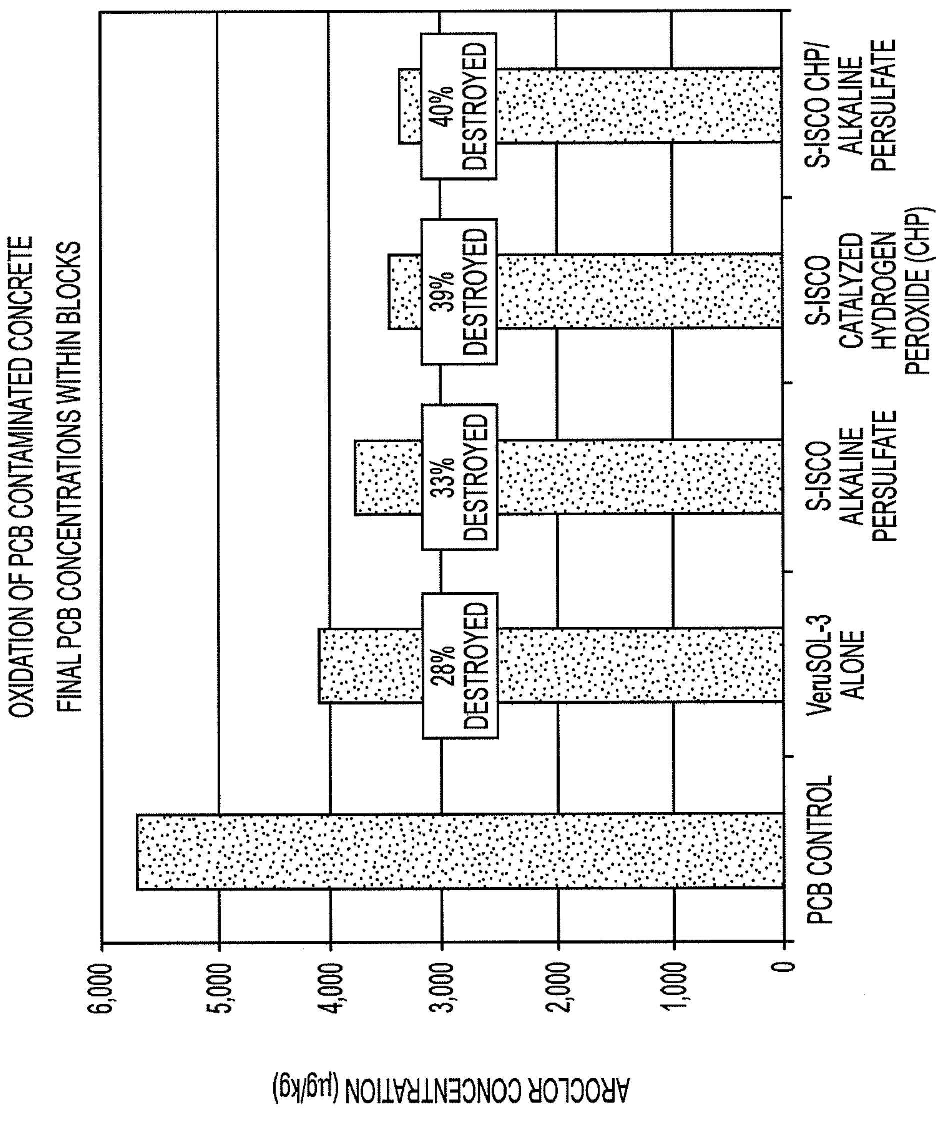

OXIDATION OF PCB CONTAMINATED CONCRETE
FINAL PCB CONCENTRATIONS WITHIN BLOCKS
AROCLOR CONCENTRATION (µg/kg)
6,000
5,000
4,000
3,000
2,000
1,000
0
PCB CONTROL
VeruSOL-3 ALONE
28% DESTROYED
S-ISCO ALKALINE PERSULFATE
33% DESTROYED
S-ISCO CATALYZED HYDROGEN PEROXIDE (CHP)
39% DESTROYED
S-ISCO CHP/ ALKALINE PERSULFATE
40% DESTROYED

FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/52657

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A62D 3/00; C11D 1/00 (2010.01)
USPC - 510/108
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)
IPC(8)L: A62D 3/00; C11D 1/00 (2010.01)
USPC: 510/108

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 510/110, 364, 365

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (PGPB,USPT,USOC,EPAB,JPAB); Google Scholar. Search terms used: castor, coconut; adobe, brick, clay, concrete, drywall, octahedral molecular sieve, pressboard, terra cotta; plywood, linoleum, ceramic tile, lumber, paper; polyvinyl chloride; surfactant; titanium dioxide; ultra-violet, ultraviolet, UV

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2008/0207981 A1 (HOAG et al.) 28 August 2008 (28.08.2008), entire document, especially: para [0001], [0011]-[0014], [0023], [0048], [0053], [0060], [0071]-[0077], [0096]	1, 2, 4, 5, 32 3, 33, 34
Y	US 2008/0255498 A1 (HOULE et al.) 16 October 2008 (16.10.2008), para [0175], [0230], [0514], [0515]	3, 33, 34
A	US 2004/0134857 A1 (HULING et al.) 15 July 2004 (15.07.2004), para [0006], [0052], [0064]-[0065], [0077], [0149]	1-5, 32-34
A	US 6,517,802 B1 (XIAO et al.) 11 February 2003 (11.02.2003), col. 12, ln 12-20; col. 15, ln 25-28	1-5, 32-34
A	US 2003/0166466 A1 (HOKE et al.) 4 September 2003 (04.09.2003), para [0018], [0030], [0118], [0120]	1-5, 32-34

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"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)
"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
"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
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 26 November 2010 (26.11.2010)	Date of mailing of the international search report 09 DEC 2010
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/52657

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-31
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.