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CA 2830528 A1 2012/09/27

(21) 2 830 528

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2012/03/22
(87) Date publication PCT/PCT Publication Date: 2012/09/27
(85) Entrée phase nationale/National Entry: 2013/09/17
(86) N° demande PCT/PCT Application No.: US 2012/030149
(87) N° publication PCT/PCT Publication No.: 2012/129420
(30) Priorité/Priority: 2011/03/22 (US61/466,258)

(51) Cl.Int./Int.Cl. *C01B 11/02* (2006.01), *C01B 31/24* (2006.01), *C07B 41/00* (2006.01), *C07B 61/00* (2006.01)

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(54) Titre : PRECURSEUR DE DIOXYDE DE CHLORE ET PROCEDES D'UTILISATION
(54) Title: CHLORINE DIOXIDE PRECURSOR AND METHODS OF USING SAME

(57) **Abrégé/Abstract:**

According to one aspect of the invention, a method of converting an oxy halide salt into a halide dioxide in a reaction zone under certain conditions is provided. More specifically, the method includes generating chlorine dioxide from a stable composition comprising an oxy halide salt by introducing said composition to a reducing agent and minimum temperature within the reaction zone. According to another aspect of the invention, a composition for a stable chlorine dioxide precursor comprising an oxy halide salt is provided.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 September 2012 (27.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/129420 A3

(51) International Patent Classification:
C01B 11/02 (2006.01) ***C07B 41/00*** (2006.01)
C01B 31/24 (2006.01) ***C07B 61/00*** (2006.01)

(21) International Application Number:
PCT/US2012/030149

(22) International Filing Date:
22 March 2012 (22.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/466,258 22 March 2011 (22.03.2011) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(88) Date of publication of the international search report:
28 February 2013

WO 2012/129420 A3

(54) Title: CHLORINE DIOXIDE PRECURSOR AND METHODS OF USING SAME

(57) Abstract: According to one aspect of the invention, a method of converting an oxy halide salt into a halide dioxide in a reaction zone under certain conditions is provided. More specifically, the method includes generating chlorine dioxide from a stable composition comprising an oxy halide salt by introducing said composition to a reducing agent and minimum temperature within the reaction zone. According to another aspect of the invention, a composition for a stable chlorine dioxide precursor comprising an oxy halide salt is provided.

CHLORINE DIOXIDE PRECURSOR AND METHODS OF USING SAME

TECHNICAL FIELD

[0001] This invention relates to a composition for a stable, chlorine dioxide precursor and method for using the same to generate chlorine dioxide for petroleum applications, such as, but not limited to, the use of chlorine dioxide in petroleum formations and high temperature gas or liquid streams. More particularly, this invention relates to a composition comprising an oxy halide salt, (e.g., sodium chlorate) as a stable chlorine dioxide precursor for use in petroleum applications.

BACKGROUND

[0002] In the petroleum industry, numerous agents or contaminants can cause damage to or restriction of the production process. Examples of such contaminates can be high-molecular weight polymers (e.g. polyacrylamides, carboxymethylcellulose, hydroxyethylcellulose, CMC, HPG, and Zanthan), bacteria, sulfur, iron sulfide, hydrogen sulfide and similar compounds.

[0003] These contaminants can, in some cases, occur naturally in the formation or be present from prior human interactions. For example, bacteria are commonly introduced to the formation during drilling and workover (e.g. the repair or stimulation of an existing production well) operations. Similarly, during the fracturing process, bacteria are often introduced into the wellbore and forced deep into the formation. More specifically, polymers such as CMC, HPG, Zanthan, and polyacrilomides are added to the fracturing fluid to maintain the proppant in suspension and to reduce the friction of the fluid. Bacteria entrained within this fluid penetrate deep into the formation, and once frac pressure is released, become embedded within the strata in the same manner as the proppant deployed. Additionally, the polymer can also be deposited within the formation, causing damage in its own right.

Typically, conventional "breakers" are added to the fracturing fluid along with the polymer to prevent this problem, but damage to producing wells due to the incomplete destruction of the polymer remains a common occurrence.

[0004] Many bacteria are facultative, that is they can exist in both aerobic or anaerobic conditions using either molecular oxygen or other oxygen sources to support their metabolic processes. For example, under the right conditions, facultative bacteria can use sulfate as an oxygen source and respire hydrogen sulfide, which is highly toxic to humans in addition to being corrosive to steel. Additionally, in a process known in the art as Microbiologically Induced Corrosion (MIC), bacteria will attach to a substrate, such as the wall of a pipe in the wellbore, and form a "biomass" shield around them. Underneath, the bacteria metabolize the substrate (e.g. a mixture of hydrocarbon and metallic iron) and respire hydrogen sulfide, resulting in the metal becoming severely corroded in the wellbore and, eventually, pipe failure and damage to downhole equipment. The respiration and presence of hydrogen sulfide also complicates the refining and transportation process, and attenuates the economic value of the produced hydrocarbon.

[0005] The traditional methods used to address these problems has one or more drawbacks. For example, the present industry practice is to add conventional organic and inorganic biocides, such as quaternary ammonium compounds, chloramines, aldehydes, such as Gluteraldehyde, THPS and sodium hypochlorite, to fracturing fluids with other additives to control bacteria. The efficacy of these conventional biocides, however, is minimal due to the type of bacteria that typically are found in hydrocarbon-bearing formations and petroleum production environments. More particularly, only a small percentage of these bacteria, which are often found in volcanic vents, geysers, and ancient tombs, are active at any one time; the remainder of the population is present in dormant and spore states. The aforementioned conventional biocides have no, or limited, effect on dormant and spore forming bacteria.

Thus, while the active bacteria are killed to some extent, the inactive bacteria survive and thrive once they reach the environmental conditions found within the formation. Additionally, these biocides become inactivated when exposed to many of the components found in petroleum production formations. And, furthermore, microorganisms build resistance to these biocides, thus limiting their utility over time.

[0006] Chlorine dioxide, on the other hand, can inactivate or kill active, dormant and spore forming microorganisms. Unlike conventional biocides, microorganisms do not build a resistance to chlorine dioxide, and it has a low residual toxicity and produces benign end products. Chlorine dioxide is therefore an efficacious biocide, however certain applications have not been possible prior to the invention. For example, although chlorine dioxide can be applied directly to well fluids (for example, fracturing water) for disinfection, it can only be applied at a low dosage to prevent degradation of polymer(s) or other drag reduction additives.

[0007] Embodiments of this invention provide for a stable chlorine dioxide precursor additive. The inventor has found that this chlorine dioxide precursor will remain stable within, for example, well fluids (e.g. a fracturing fluid) or other fluid streams or systems until it enters a zone (e.g. within a subterranean formation) that satisfies certain conditions and reaches a minimum temperature of about 100°F - 110°F. One or more embodiments of the invention, which incorporate this chlorine dioxide precursor into a fracturing fluid, thus provide an *in situ* method for generating and using chlorine dioxide as a polymer oxidant and downhole biocide that does not deplete or attenuate the friction-reducing components of the fracturing fluid until the chlorine dioxide precursor is dispersed into the target zone of the subterranean, hydrocarbon-bearing formation. In these embodiments, the chlorine dioxide precursor reacts with components in the subterranean formation at a certain temperature to form chlorine dioxide therein, which then acts as a polymer oxidant and downhole biocide.

[0008] The inventor has found that the embodiments of the invention provide for results that cannot be accomplished with *ex situ* generated halogen dioxides, such as chlorine dioxide, or other halogen dioxide precursors, such as sodium chlorite. For example, chlorine dioxide cannot be added to well fluids (e.g. fracturing fluid) at high concentrations prior to injection into the wellbore because the chlorine dioxide will prematurely oxidize the polymers and friction-control additives within the fracturing fluid. Similarly, sodium chlorite, sometimes referred to as "stabilized chlorine dioxide," is limited in that it immediately begins to react with weak acids and other components of the fracturing fluids at ambient temperatures, thereby generating chlorine dioxide too soon, which in turn will prematurely oxidize the polymers and friction- control additives within the fracturing fluid. By contrast, embodiments of the present invention remain generally stable until exposed to a minimum temperature and reducing agents (e.g., contaminants) located within a subterranean formation or otherwise provided in a target reaction zone.

[0009] Thus, embodiments of the invention provide for, *inter alia*, a composition that is stable under ambient conditions within a fluid stream or system (for example, the well fluids applied during drilling, completion, workover and fracturing operations), but subsequently reacts within a target reaction zone under specified conditions to produce a halide oxide that is capable of 1) degrading polymers within the target zone (i.e. the subterranean formation); 2) reducing toxic and unwanted sulfur compounds within the target zone (i.e. the subterranean formation and hydrocarbon deposits), and 3) functioning as a biocide that kills or destroys bacteria in active, dormant and spore forms.

BRIEF DESCRIPTION OF THE INVENTION

[0010] One aspect of the invention includes a method for introducing an oxy halide salt into a zone wherein the oxy halide salt comes into contact with a reducing agent resulting in conversion of the oxy halide salt into a halide dioxide, comprising applying or injecting an oxy halide salt into a zone with a reducing agent under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide.

[0011] Another aspect of the invention includes a method of reducing, inactivating, destroying, or eliminating one or more reduced sulfur compounds, comprising the steps of contacting the reduced sulfur compound with an oxy halide salt under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide, thereby reducing, inactivating, destroying, or eliminating one or more reduced sulfur compounds.

[0012] In another aspect of the invention, a method for oxidizing one or more polymers, one or more reduced sulfur compounds or one or more reduced metals, comprises the steps of contacting the polymer, reduced sulfur compound or reduced metal with an oxy halide salt in a reaction zone under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide, thereby oxidizing one or more polymers, one or more reduced sulfur compounds or one or more reduced metals.

[0013] Another aspect of the invention includes a method for inactivating, destroying or killing one or more microbes, comprising contacting the microbe with an oxy halide salt under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide, thereby inactivating, destroying or killing one or more microbes.

DETAILED DESCRIPTION

[0014] The following terms as used herein have the following meanings:

[0015] As used herein, the words "comprise," "has," and "include," and all grammatical variations thereof are each intended to have an open, non-limiting meaning that does not exclude additional elements or parts.

[0016] As used herein, a biocide, or bactericide, is a substance that inhibits, destroys or kills bacteria.

[0017] As used herein, free residual level or residual is the amount of oxidant in a fluid present and available for microbiological control at a given time after the oxidant has reacted with background impurities and contaminants in the fluid. Generally described in units of percentage or ppm.

[0018] As used herein, well fluid is any fluid used in any of the drilling, completion, work over, fracturing and production of subterranean oil and gas wells.

[0019] For the purposes of promoting an understanding of the principles of the invention, reference will now be made to embodiments of the invention and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, and any alterations and further modifications in the described embodiments, and any further applications of the principles of the invention as illustrated therein as would normally occur to one skilled in the art to which the invention relates are contemplated an protected.

[0020] According to one or more embodiments of the invention, a halide dioxide, preferably chlorine dioxide, is generated *in situ* in a target reaction zone. According to one aspect of the invention, the target reaction zone is found within a hydrocarbon-bearing subterranean formation and is the zone within the formation where the target compounds, or contaminants, are located. Furthermore, the target zone may comprise a hydrocarbon deposit, a petroleum deposit, a hydrocarbon or petroleum product formation, or a hydrocarbon or petroleum processing product or equipment. As used herein, the target compounds, or contaminants, are agents located within the subterranean formation that have the potential or propensity to cause damage to or restriction of the petroleum production process, and include high-molecular weight polymers (e.g. polyacrylamides, carboxy-methylcellulose, hydroxyethylcellulose, CMC, HPG, and Zanthan), microbes (e.g. anaerobic and aerobic bacteria), sulfur, iron sulfide, hydrogen sulfide and similar compounds.

[0021] In one or more embodiments, a composition comprises a stable, halogen dioxide precursor concentrate that does not react with the target compounds prior to entering the target reaction zone within the subterranean formation. The halogen dioxide precursor comprises an oxy halide salt, such as sodium chlorate, in solution at a concentration up to about 50% by weight, preferably about 5% to 40% by weight. Although the embodiments and examples disclosed herein refer to sodium chlorate as the oxy halide salt, one of ordinary skill in the art would recognize that other oxy halide salts containing a chlorine in the plus five valence or oxidation state, such as potassium chlorate, calcium chlorate or magnesium chlorate, would fall within the embodiments of this invention. The stable precursor concentrate will typically be added to a fluid stream (e.g. well fluid) at concentrations ranging from about 100 to 10,000 mg/l.

[0022] Although not required, in one or more embodiments, the composition or concentrate comprising the stable chlorine dioxide precursor further comprises additives selected to benefit the type of treatment that is targeted. For example, in certain embodiments, the halogen dioxide precursor further comprises and is premixed with additives, preferably chelants or weak acids, such as citric acid, or wetting agents such as ethylene glycol monobutyl ether. More specifically, in one embodiment, the composition comprises up to about 40% by weight sodium chlorate, up to 20% by weight of a chelating agent, and up to about 10% by weight of a surface active agent. In other embodiments, the composition comprises an aqueous solution of an oxy halide salt and a weak acid, wherein the concentration of the oxy halide salt is between about 5% and 40% and the concentration of the weak acid is between about 5% and 20%. In still other embodiments, more specifically in embodiments wherein the target reaction zone alone supplies a sufficient amount hydrogen ions to allow for the generation of chlorine dioxide, the stable precursor composition does not include any chelating agent.

[0023] Because the target compounds within the target zone react with the stable precursor to form a halogen dioxide, preferably chlorine dioxide, as an end-product of the reaction, a free residual of said halide oxide is generated *in situ* and is available to oxidize other compounds, function as a biocide and control or inactivate microbes located either within or around the target zone. Therefore, in one or more embodiments of this invention, no *ex situ* generator or process is required to generate chlorine dioxide for injection into the subterranean formation and/or gas or liquid streams in order to destroy or reduce polymers, sulfur, reduced sulfur compounds, phenols and other compounds.

[0024] More specifically, in one or more embodiments of the present invention, the premixed composition, or concentrate, comprising said halogen dioxide precursor is stable and not reactive in solutions of polymer, sulfides, and/or weak acids at ambient conditions and temperatures, and more specifically is stable in solutions of polymer, sulfides, and/or weak acids at temperatures in the range of less than about 90°F to 110°F, and more preferably does not react to form chlorine dioxide until the temperature reaches or exceeds about 110°F to 115°F. More specifically, and in the embodiments disclosed herein, the composition is stable at ambient temperatures in, for example, drilling, fracturing, completion, and operational well fluids, including but not limited to drilling muds, fracturing fluids, produced or fresh water, or blends thereof. In still other embodiments of the invention, the composition or concentrate also remains stable at temperatures in the range of less than about 90°F to 110°F when premixed with a low concentration of a strong acid, such as hydrochloric or hydrofluoric acid, wherein the concentration of the strong acid can be in the range of about 0.1 % to 2 %, more preferably 0.2% to 0.5 %. In accordance with the invention, both the selection and concentration of a weak or strong acid is determined by the concentration at which said acid will not react to form chlorine dioxide when it is mixed directly with the oxy halide salt at temperatures in the range of less than about 90°F to 110°F.

[0025] According to the invention, the composition comprising the stable halogen dioxide precursor therefore remains stable until it reaches a target reaction zone, wherein the composition is then exposed to temperatures of at least about 90°F to 110°F, and preferably reaches or exceeds about 110°F to 115°F, and wherein the composition is further exposed or introduced to at least one of or a combination of one or more of the following: a hydrocarbon containing formation, reduced sulfur compounds, elemental sulfur, sulfite, polymer, biomass (i.e. microbes or bacteria), reduced metal ions, and other easily oxidized organic and inorganic compounds. For example, in one or more embodiments, the reduced sulfur compounds are present in a target reaction zone within a subterranean geological formation or material that contains one or more solid, liquid, or gaseous hydrocarbons, or a hydrocarbon deposit, a petroleum deposit, a hydrocarbon or petroleum product formation, or a hydrocarbon or petroleum processing product or equipment. In another embodiment, microbes and reduced sulfur compounds are present in a target reaction zone within a petroleum processing piece of equipment. In still another embodiment, polymers and reduced sulfur compounds are present in a target reaction zone within the fractures of hydrocarbon-bearing subterranean formation.

[0026] Embodiments of the present invention also provide that the concentrate or composition comprising said halogen dioxide precursor is either added to or premixed with a fluid stream, for example a fluid stream being injected into a subterranean wellbore, wherein said fluid stream may include other additives, such as friction reducers, wetting agents, polymers, corrosion inhibitors, sand, proppants, biocides, breakers and other chemicals and wherein the chlorine dioxide precursor is and remains stable in the presence of these additives until it reaches the target reaction zone. Once it reaches the target reaction zone, the halogen dioxide precursor is introduced to a high temperature liquid or gas stream that contains one or more of sulfides, reduced sulfur compounds, polymers, microbial matter or other target compounds. In accordance with the invention, the high temperature fluid or gas stream is at or brought up to temperatures above about 90°F to 115°F, and preferably above about 110°F to 115°F. According to embodiments of this invention, when the halogen dioxide precursor solution reaches the target reaction zone within the formation that contains the conditions set forth above, said precursor composition will react spontaneously to form halogen dioxide (e.g., chlorine dioxide) in said zone. The *in situ* generated halogen dioxide will then destroy polymers and other target compounds, such as reduced sulfur compounds, biomass (e.g. microbes, bacteria), sulfur, phenols, either within, around or after said zone, such that the halogen dioxide formation reaction that initiates in said zone will consume the contaminants.

[0027] In one embodiment, said stable composition or concentrate is premixed offsite and is then transported to the work site. In other embodiments, for example during a hydraulic fracturing operation, said composition can be premixed at the work site in one of the frac tanks or in the blender. The premixed concentrate comprising the stable chlorine dioxide precursor and other additives is then injected into the process stream via a chemical injector system and/or other method that is known to those skilled in the art.

[0028] The dosage rate and concentration of the composition comprising the stable precursor is calculated based on the quantity of chlorine dioxide, or other halogen oxide, that needs to be generated and/or the amount of contaminants that need to be consumed. More specifically, the dosage rate and concentration can be determined based on the nature of the treatment, the characteristics of the fluid or gas stream, the characteristics of the subterranean formation (if applicable), and the contaminants contained therein, as would be determined by those skilled in the art. For example, and in one embodiment, the application ratio to eliminate reduced sulfur compounds and oxidate reduced metal ions is approximately 2.5 to 5:1 chlorine dioxide precursor to target compound by weight.

[0029] When chlorine dioxide or other halogen dioxides are added directly to well fluids (i.e. fracturing fluids) or other fluid streams, they can initially react with dissolved organic and inorganic compounds in the water, thus depleting the amount of free residual available as a biocide and for other intended treatment purposes. Therefore, in one or more embodiments of the present invention, it will be necessary to add an excess of the stable precursor in order to produce a free residual of the halogen dioxide sufficient to achieve the desired bacterial control and/or oxidation of complex organics. In yet another embodiment, if instant biocidal control is desired or required, the stable precursor of the present invention may be incorporated into a water or fluid stream that has already has been dosed with a generated solution of chlorine dioxide or other biocidal agent. More specifically, and by way of example only, chlorine dioxide concentrations of 10 to 20 mg/l or less do not impact the performance of the additives, such polymer(s) or other drag reduction additives, in fracturing fluids. Therefore, in certain embodiments, the composition comprising the stable precursor can be added to raw fracturing water that contains a sufficient residual of chlorine dioxide, for example from about 0.02 to5 mg/l, and preferably from about 1-2 mg/l, to provide primary disinfection of the raw water without prematurely depleting or effecting the performance of the other additives. The addition of this low-residual, generated chlorine dioxide provides primary disinfection and inhibits or prevents biofouling of the mixing and pumping equipment. As described herein, and in accordance with the invention, the composition comprising the stable precursor will not provide appreciable biocidal control until activation it is introduced to the appropriate conditions within the reaction zone, including one or more reducing agents and fluid temperatures at a minimum of about 90°F to 110°F, and preferably at or above about 110°F to 115°F.

[0030] Although the embodiments disclosed hereinabove often refer to the target reaction zone as located within a subterranean formation, in accordance with alternate embodiments that are within the scope of the invention, the reaction zone can also equipment, a pipeline or vessel for extracting, processing, refining, transporting or storage of hydrocarbons. In order to oxidize contaminants in a fluid or gas stream in accordance with the invention in these embodiments, a stable precursor composition or concentrate will comprise up to about 40% of a oxy halide salt, preferably sodium chlorate and may also comprise up to about 20% by weight of a chelating agent. The composition is then introduced via the fluid or gas stream to an environment with a minimum temperature of about 90°F to 100°F, ideally over about 100°F, and more preferably over about 110°F to 115°F, wherein said fluid or gas stream further comprises contaminants such as reduced metal ions, biomass, reduced sulfur compounds, or other reduced organics such as phenols or tertiary alcohols or amines.

[0031] The inventor has also found that, due to the oxidation of sulfides and other contaminants, the generation of chlorine dioxide within a formation in accordance with this invention will affect the affinity of hydrocarbons to non-hydrocarbons, such that the embodiments disclosed herein result in hydrocarbons being released from the subterranean formation in amounts greater than would have occurred without the generation of chlorine dioxide within the formation. More specifically, *in situ* generated chlorine dioxide *via* the stable precursor composition disclosed herein effectuates the removal of hydrocarbons from subterranean formation material, while other oxidants such as hydrogen peroxide, sodium persulfate, sodium peroxide, sodium chlorite, and sodium hypochlorite do not.

Examples

Example 1

[0032] This example illustrates a representative reaction in which chlorine dioxide is formed from a precursor. A chlorine dioxide precursor reacts with reduced contaminant to form chlorine dioxide by gaining an electron from the contaminant.

$$ClO_3^- + Rx \rightarrow ClO_2 + RxO^-;$$

where Rx is the reducing agent providing an electron in the reduction of chlorate to chlorine dioxide.

[0033] The formed chlorine dioxide competes with the stable precursor in the oxidation of the contaminants, and as a reactive free radical oxidizes additional compounds that are non reactive with the precursor. Neither chlorine dioxide nor chlorate react via electrophilic substitution and do not thus form chlorinated organic compounds. One known pathway for chlorate to form chlorine is in the absence of a reducing agent under strong acid conditions, as represented by the following reaction:

$$ClO_3^- + 2HCl \rightarrow ClO_2 + \frac{1}{2} Cl_2 + H_2O$$

[0034] No strong acids are present in the media during the application of the present invention and reducing agents are always present during the chlorine dioxide formation. Mixture of the chlorine dioxide precursor with a strong acid is generally avoided to prevent chlorination and corrosive effects from the resultant chlorine.

Example 2

[0035] A solution was made up of 10% by weight of sodium chlorate, 10% citric acid, and 0.15% hydrochloric acid. Samples of the solution were stored at 80°F, 90°F, 100°F, 110°F, 120°F and 150°F and monitored for sixty days using spectrophotometric analysis for the presence of chlorine dioxide. At no time during the test period was there a physical change in the solution, evidence of off-gassing or evidence of chlorine dioxide production. At the end of the observation period the samples were analyzed for sodium chlorate. No significant change in the concentration was observed. The foregoing study demonstrates that solutions of an oxy halide salt can be formulated with weak acids or low concentrations of strong acids (e.g., hydrochloric acid) without the resultant formation of chlorine dioxide that would prevent their transportation under DOT regulations, or degradation of the product within a normal shelf life period.

Example 3

[0036] Identical examples of the solution used in Example 2 were mixed with the addition of 0.5% Iron Sulfide. Samples of the final solution were stored at 80°F, 90°F, 100°F, 110°F, 120°F and 150°F and monitored for sixty days using spectrophotometric analysis for the presence of chlorine dioxide. At temperatures of up to 110°F, no evidence of reaction or chlorine dioxide formation was observed and hydrogen sulfide gas was evolved into the head space of the samples. At the end of the sixty day cycle chlorate analysis indicated no significant change. The 120°F samples showed a slow degradation of the hydrogen sulfide and yellowing of the solution over a 48 hour period. After 48 hours there was no remaining sulfide within the sample and there was a slight residual of 8-10 ppm chlorine dioxide. The 150°F sample immediately yellowed and consumed the iron sulfide without a release of hydrogen sulfide upon addition and formed a slight 10 to 15 ppm residual of chlorine dioxide. Once iron sulfide was consumed formation of chlorine dioxide ceased. Additional aliquots of iron sulfide resulted in complete destruction of the sulfide and oxidation of the iron to the ferric state. Subsequent analysis of the residual chlorate revealed that chlorate was consumed by approximately a 2.7 chlorate to sulfide weight ratio. The foregoing study demonstrates that the stable chlorine precursor will react at typical production formation conditions to form chlorine dioxide and consume the target contaminants and form sufficient residual chlorine dioxide to kill, inactivate or destroy more stable or resilient contaminants such as bacteria and polymers.

Example 4

[0037] Identical examples of the solution used in Example 2 were mixed with the addition of 5% by weight ground up core material. The materials were sandstone and dolomite in nature, and contained approximately 10 mg/kg of iron sulfide. Samples of the final solution were stored at 80°F, 90°F, 100°F, 110°F, 120°F and 150°F and monitored for sixty days using spectrophotometric analysis for the presence of chlorine dioxide. At temperatures of up to

100°F, there was no evidence of reaction or chlorine dioxide formation, and hydrogen sulfide gas was evolved into the head space of the samples. At the end of the sixty day cycle, chlorate analysis indicated no significant change in chlorate concentration. The 110°F, 120°F and 150°F samples showed a slow degradation of the hydrogen sulfide and yellowing of the solution over a 48 hour period. After 48 hours, there was no remaining sulfide within the sample and there was a slight residual of 8-10 ppm chlorine dioxide. The 150°F sample immediately yellowed and consumed the iron sulfide without a release of hydrogen sulfide upon addition, and formed a slight 10 to 15 ppm residual of chlorine dioxide. Subsequent analysis of the residual chlorate revealed that chlorate was consumed by approximately a 3.2 chlorate to sulfide weight ratio. The foregoing study demonstrates that production zone material can provide sufficient reducing materials for the conversion of a precursor to chlorine dioxide to occur.

Example 5

[0038] In this example, a first flask contained a 0.5 percent solution of sodium sulfide. A second flask contained a solution of 10% sodium chlorate and 10% citric acid. A third flask contained a 5% solution of ferric (iron) sulfate. An inert gas stream purged gases from flask to flask through a gas train. Hydrochloric acid was added to the first flask to evolve hydrogen sulfide gas. The study was conducted at 100°F, 150°F, 175°F and 200°F. At 100°F and 150°F, no reaction was observed within the second flask and hydrogen sulfide reacted with the iron sulfate solution to form iron sulfide in the third flask. Some hydrogen sulfide vented from the third flask. At 175°F, iron sulfide was still formed in the third flask and some hydrogen sulfide vented, but to a much lesser extent. Flask 2 remained clear at the end of the study, but evolved some chlorine dioxide. At 200°F, no iron sulfide formed within the third flask or was vented from the gas train. The solution in flask 2 displayed evidence of chlorine dioxide formation and had a slight residual of chlorine dioxide of approximately 5 mg/l at the conclusion of the study the foregoing study demonstrates that an elevated temperature gas stream has sufficient reducing properties to trigger the conversion of precursor to chlorine dioxide, and that reducing agents within the contaminants can be used as the reductant (hydrogen sulfide) to trigger the conversion with sufficient halo dioxide to result in the elimination of the reductant.

[0039] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

What I claim is:

CLAIMS

1. A method for introducing an oxy halide salt into a zone wherein the oxy halide salt comes into contact with a reducing agent resulting in conversion of the oxy halide salt into a halide dioxide, said method comprising the steps of introducing an oxy halide salt into a reaction zone under conditions in which all or a part of the oxy halide salt is converted into a halide dioxide, wherein said reaction zone comprises a reducing agent.
2. A method for reducing, inactivating, destroying, or eliminating one or more reduced sulfur compounds, said method comprising the steps of contacting the reduced sulfur compound with an oxy halide salt under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide, thereby reducing, inactivating, destroying, or eliminating one or more reduced sulfur compounds.
3. A method for oxidizing one or more polymers, one or more reduced sulfur compounds or one or more reduced metals, said method comprising the steps of contacting the polymer, reduced sulfur compound or reduced metal with an oxy halide salt in a reaction zone under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide, thereby oxidizing one or more polymers, one or more reduced sulfur compounds or one or more reduced metals.
4. A method for inactivating, destroying or killing one or more microbes, said method comprising the steps of contacting the microbe with an oxy halide salt under conditions in which all or a part of the oxy halide salt is converted into the halide dioxide, thereby inactivating, destroying or killing one or more microbes.
5. The method of any of claims 1 to 4, wherein the conditions comprise a temperature greater than about 110°F and, more preferably, greater than about 115°F.

6. The method of claims 1 or 3, wherein the zone comprises geological material that contains one or more solid, liquid, or gaseous hydrocarbons.

7. The method of claims 1 or 3, wherein the zone comprises a hydrocarbon deposit, a petroleum deposit, a hydrocarbon or petroleum product formation, or a hydrocarbon or petroleum processing product or equipment.

8. The method of claims 2 or 4, wherein the reduced sulfur compounds or microbes are present in a geological material that contains one or more solid, liquid, or gaseous hydrocarbons, or a hydrocarbon deposit, a petroleum deposit, a hydrocarbon or petroleum product formation, or a hydrocarbon or petroleum processing product or equipment.

9. The method of any of claims 1 to 4, wherein the oxy halide salt comprises a chlorine in the plus five valence state.

10. The method of claims 1 or 3, wherein the halide dioxide reduces, inactivates, destroys, or eliminates one or more reducing compounds in the zone.

11. The method of any of claims 1 to 4, wherein the oxi halide salt comprises chlorate.

12. The method of any of claims 1 to 4, wherein the conditions comprise a reducing compound, an acid, or a mixture of one or more of said reducing compound and acid.

13. The method of any of claims 1 to 4, further comprising heating the oxy halide salt to a temperature greater than about 110°F, and more preferably greater than about 115°F, prior to or upon entering the reaction zone, or prior to or upon contact with one or more reduced sulfur compounds or one or more microbes.

14. The method of claim 1, wherein the reducing agent comprises elemental sulfur, a reduced sulfur compound, a reduced organic compound or a reduced metal ion, or a mixture thereof.

15. The method of any of claims 1 to 4, wherein the halide dioxide comprises chlorine dioxide.

16. The method of any of claims 1 to 4, wherein the oxy halide salt is blended or mixed with a free residual of chlorine dioxide in the range of about 0.02 to5 mg/l, and preferably in the range of about 1-2 mg/l, prior to introduction into the reaction zone, or prior to contact with the reduced sulfur compound or microbe.

17. The method of any of claims 1 to 4, wherein the oxy halide salt is blended or mixed with an acid prior to introduction into the reaction zone, or prior to contact with the reduced sulfur compound or microbe, and wherein said oxy halide salt and acid do not react to form a halide dioxide prior to being introduced into the reaction zone, or prior to contact with the reduced sulfur compound or microbe.

18. The method of claims 11 or 17, wherein the acid comprises citric, lactic, formic, oxalic, ethanoic, acetic, or propanoic acid, or a mixture of one or more of said weak acids.

19. The method of any of claims 1 to 4, wherein the oxy halide salt is in an aqueous medium.

20. The method of claim 19, wherein the aqueous medium comprises water.

21. A composition comprising an oxy halide salt and an acid that is stable and does not convert to a halide oxide provided an absence of a reducing agent in the composition and a temperature below about 90°F, and more preferably below about 100°F.

22. The composition of claim 21, wherein the oxy halide salt contains chlorine in the plus five valence state.

23. The composition of claim 21, wherein the anion component of the oxy halide salt is chlorate.

24. The composition of claim 21, wherein the acid comprises a weak acid.

25. The composition of claim 24, wherein the weak acid comprises citric, lactic, formic, oxalic, ethanoic, acetic, or propanoic acid, or a mixture of one or more of said weak acids.

26. The composition of claim 21, wherein the acid comprises a strong acid in the range of about 0.1 % to 2 %, more preferably 0.2% to 0.5 %.

27. The composition of claim 26, wherein the strong acid comprises hydrochloric or hydrofluoric acid.

28. The composition of claim 21, wherein the composition further comprises a chelating, a wetting agent or a mixture thereof.

29. The composition of claim 21, wherein the compound can be converted into chlorine dioxide in the presence of a reducing agent when heated to a temperature greater than about 110°F.

30. A stable solution, comprising an aqueous solution of an alkaline metal oxy halide salt and a weak acid, wherein the concentration of the alkaline metal oxy halide salt is between about 5% and 40% and the concentration of the weak acid is between about 5% and 20%, and wherein the stable solution does not react to form a halide dioxide until said solution reaches a minimum temperature of about 110°F, and is exposed to one or more reduced compounds.

31. The stable solution of claim 30, wherein the halide dioxide comprises chlorine dioxide.

32. The stable solution of claim 30, wherein the alkaline metal oxy halide salt comprises sodium chlorate.

33. The stable solution of claim 30, wherein the reduced compound comprises a sulfide, a reduced sulfur compound, a reduced metal, or a mixture of one or more of said compounds.

34. The stable solution of claim 33, wherein the reduced metal comprises Fe(II).

35. The stable solution of claim 30, wherein the minimum temperature and reduced compounds are introduced when the stable solution enters or becomes in contact with a geological material comprising one or solid, liquid, or gaseous hydrocarbons, a hydrocarbon deposit, a petroleum deposit, a hydrocarbon or petroleum product formation, or a hydrocarbon or petroleum processing product or equipment.

36. A method of generating chlorine dioxide, comprising introducing a stable composition comprising sodium chlorate into a reaction zone comprising one or more reduced compounds under conditions in which all or a part of the sodium chlorate is converted into chlorine dioxide, thereby generating chlorine dioxide.

37. The method of claim 36, wherein the stable solution further comprises an acid.

38. The method of claim 36, further comprising heating the solution to a minimum temperature of about 110°F to 115°F, or wherein the reaction zone has a minimum temperature of about 110°F to 115°F.

39. The method of claim 36, wherein the reaction zone comprises geological material that contains one or solid, liquid, or gaseous hydrocarbons.

40. The method of claim 36, wherein the reaction zone comprises a hydrocarbon deposit, a petroleum deposit, a hydrocarbon or petroleum product formation, or a hydrocarbon or petroleum processing product or equipment.

41. The method of claim 36, wherein the chlorine dioxide is sufficient to reduce, inactivate, destroy, or eliminate one or more reducing compounds in the zone.

42. The method of claim 36, wherein the reaction zone comprises one or more sulfur compounds or one or more microbes.

43. The method of claim 36, wherein the reduced compound comprises elemental sulfur, a reduced sulfur compound, a reduced organic compound or a reduced metal ion.

44. The method of claim 36, wherein the reduced compound is selected from a sulfide, a reduced sulfur compound, or a reduced metal.

45. The method of claim 44, wherein the reduced metal comprises Fe(II).

46. The method of claim 37, wherein the acid comprises citric, lactic, formic, oxalic, ethanoic, acetic, or propanoic acid, or a mixture of one or more of said weak acids.

47. The method of claim 36, wherein the solution comprises an aqueous medium.

48. The method of claim 47, wherein the aqueous medium comprises water.

49. The method of claim 36, wherein the minimum temperature and/or the reduced compounds are introduced when the stable solution enters a hydrocarbon producing formation.

50. The method of claim 36, wherein the reaction zone provides hydrogen ions sufficient to generate chlorine dioxide when the stable solution enters said reaction zone.

51. The method of any of claims 1 to 4 or 36, wherein the reaction zone is equipment, a pipeline or vessel for extracting, processing, refining, transporting or storage of hydrocarbons.