

## Advanced Chemical Oxidants For Remediation Of Ground Water Contaminated With Petroleum Hydrocarbon Products: A Review

Ekwuluo, Maurice<sup>1</sup>, Udom G. J.<sup>2</sup> And Osu Charles I.<sup>3</sup>

<sup>1</sup>Rivers State Ministry of Environment, Port Harcourt, Nigeria, Ekwuluomaurice04@gmail.com

<sup>2</sup>Department of Geology, University of Port Harcourt, Nigeria

<sup>3</sup>Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt. P.M.B. 5323, Port Harcourt, Nigeria. [charsike@yahoo.com](mailto:charsike@yahoo.com)

**Abstract:** This review highlights the various chemical oxidants used for chemical oxidation remediation of ground water contaminated with all manner of petroleum hydrocarbon products. The oxidants include: hydrogen peroxide/Fenton's reagent, sodium per sulphate, permanganates, potassium ferrioxalate, Regeno<sub>x</sub><sup>TM</sup> and Zero valent iron. Application of this oxidants as well as their advantages and disadvantages were discussed.

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### 1. Introduction

Contaminations from oil components can occur during the extraction process in sedimentary basins and as a result of storage tank leaks, including gasoline stations and during marine transport (oil tankers) (Watts *et al.*, 2000). Moreover, during its processing a large volume of hydrocarbon-rich wastewater is generated, which, if left untreated, causes serious environmental impacts (Durell *et al.*, 2006; Mota *et al.*, 2008).

According to Valentinetti, (1989), hydrocarbon contamination from petroleum products leaks and spills is the most common ground water pollution problems. It is estimated that there are over two million fuel storage tanks in the United States and any tank can potentially be a pollutant source. Surveys of existing tank facilities show approximately 30 % are leaking (Taylor, 1989). Leaks in underground storage tanks and underground fuel transfer lines are not easy to detect and locate as they are often so small that inventory studies are ineffective in locating the source of pollutant. The rate of dissipation or natural degradation of fuel contamination is extremely slow in many cases and even a small fuel leak can produce serious contamination that is extremely costly to remediate.

Spilled petroleum products often form non-aqueous phase liquid (NAPL) which constitutes environmental contaminant sources having high concentrations of benzene, toluene, ethylbenzene, and xylene (BTEX) isomers and these are the major petroleum hydrocarbon contaminants (Jochen *et al.*, (2002) and Julien *et al.*, (2011). BTEX constituents are volatile and easily dissolve in water; they make up half of the total number of water soluble fractions of gasoline, (Pawlowski *et al.*, 1998). Benzene's low

water solubility of 1.8 g/l at 25 °C, low Henry's constant of 0.23 mg/l at 25 °C, mobility in soil octanol-water partition coefficient of 0.24 and volatility make the creation of ground water treatment scheme quite challenging (ITRC, 2005). It is worthy to note that benzene is also stubborn under anoxic conditions and potentially carcinogenic (USEPA, 1993). The tendency for contaminated soil water to leach into the ground water is largely controlled by forces operating from either the ground surface (infiltration, evaporation) or from the bottom layers of the zone of generation which eventually leads to the development of soil water potential gradient, first in the vertical direction (NRC, 1993). Groundwater contamination from petroleum hydrocarbon has indeed become a major environmental concern because of its wide usage and many contamination incidences. In the United States of America alone, it is reported that there are up to 400,000 contaminated groundwater sites. (Thiruvengkatachari *et al.*, 2008). Currently, both ex-situ and insitu remediation technologies are being improved to solve this environmental problem, (Gavrilescu, 2005). Reports also have it that in recent times, chemical oxidation technologies are becoming more popular, (Hoekstra *et al.*, 2011)); however, it is difficult to select an optimal method and processes at low overall costs (Liquang *et al.*, 2001). Though many techniques have been used to develop support tools for site remediation decision-making, it should be known that carrying out more studies on this subject will help to create management systems for petroleum contaminated sites in which desired remediation methods will be the lowest cost and time efficient as well as guarantee safety of the environment and public health. Many remedial methods are available but chemical oxidation has been

rated high and proven for the remediation of groundwater contaminated with petroleum products (Julien *et al.*, 2011; Thompson *et al.*, 2008). The Greater number of scientific researchers are currently shifting attention to chemical oxidation because it is a preferred remedial alternative to other remediation techniques for hydrocarbon contaminated ground water due to observed limitations of conventional ground water clean-up technologies (Liang *et al.*, 2011).

According to Mulligan *et al.*, (2000), this kind of information is indispensable for decision makers and all stakeholders in the selection of appropriate technology for the treatment of hydrocarbon contaminated groundwater resources. It will also provide among other things, a general overview of chemical oxidation technology by examining various oxidants and their reaction chemistry.

### **Chemical Oxidants**

#### **Hydrogen peroxide and Fenton's reagent**

Hydrogen peroxide, when used alone in the oxidation of organic compounds has an oxidizing power relative to chlorine of 1.31 (Lowe, 2001). When combined with iron (II) salts, Fenton-like reactions occur yielding hydroxyl radicals (OH) with a relative oxidation power of 2.06 in the soil, Iron (II) occurs naturally in the form of iron oxides or can be added to the hydrogen peroxide as iron sulfate. The reaction is as follows:  $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}$  (Lowe, 2001; ITRC, 2001). There also occurs a number of subsequent reactions that can lead to the production of perhydroxyl radical ( $\text{HO}_2$ ) as well as the scavenging of OH. Both hydrogen peroxide and the free radicals will oxidize contaminants of concern, however, their reaction rates vary. Hydrogen peroxide alone and Fenton's reagent react with the longer chain carbon sources before oxidizing the lighter hydrocarbons while Fenton's reagent reacts faster and is much more efficient due to the genesis of free hydroxyl radicals (Cheryl and Gopal, 2015). The hydroxyl radical rapidly reacts non-selectively by attacking and attaching the carbon-hydrogen bonds of contaminant organic compounds. This method has been used to treat many organics such as chlorinated and non-chlorinated solvents, PAHs, esters, pesticides, VOCs, SVOCs, BTEXs, phenols and others (ITRC, 2001; Herbert, *et al.*, 1999). Intermediate compounds formed as a result of the reaction with the hydroxyl radical can then be subsequently oxidized to carbon dioxide and water in the presence of excess oxidant (Herbert *et al.*, 1999). Oxidation reactions with hydrogen peroxide/Fenton's reagent are affected amongst others by  $\text{p}^{\text{H}}$ , reaction time, temperature, catalysts and concentration (Fibresima, 2012). Efficacy of reaction is greatest in conditions of low  $\text{p}^{\text{H}}$  and is minimized in moderate to

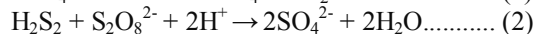
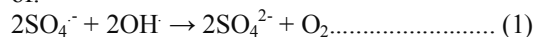
high alkaline environments where the ferrous ion ( $\text{Fe}^{2+}$ ) occurs as a colloidal solid that can reduce the permeability of sub-surface media and thereby lower the reaction efficiency (Yin, and Herbert, 1999).

In an attempt to obtain the optimal  $\text{p}^{\text{H}}$  range required, an acidic solution might be required, which could have a potentially detrimental effect on the surrounding ecosystem. However, it is not always feasible to decrease the  $\text{p}^{\text{H}}$  without excess acid addition due to buffering action of the soil (Xu, 2003). The impact of hydrogen peroxide application on biological activity can go either way. It is possible that Fenton's reagent can adversely affect the microbial populations, eliminating the feasibility of using bioremediation as a companion remediation technique or breakdown of hydrogen peroxide to oxygen and can stimulate the aerobic biological activity (Amarante and David, 2002). Another factor in the use of this technology is the exothermicity of the Fenton's reaction which results in the evolution of substantial quantity of heat and gas. As hydrogen peroxide readily decomposes to water vapor and oxygen, special care is required during the delivery process. The success of treatment is further affected by the presence of competing reactions by free radical (hydroxyl) scavengers such as carbonates, bicarbonates and organic matter commonly present in the subsurface (Cheryl and Gopal, 2015). Advantages of employing this form of oxidant in the treatment of contaminated soil and/or groundwater include: low chemical cost, relatively rapid reaction process and application over a wide range of volatile and semi-volatile organics. Since hydrogen peroxide has been variously applied in the field, there is a range of reliable information available that can be utilized in designing the appropriate remediation plan (Amarante and David, 2002).

#### **Sodium persulfate**

The potential liberation of ammonia gas during injection of ammonia persulfate and potassium persulfate low solubility in water is the main reason for the use of sodium persulfate. The chemical oxidation process consists of the dissociation of persulfate salts to persulfate anions ( $\text{S}_2\text{O}_8^{2-}$ ) which are strong oxidants. As oxidants, persulfate ion is more powerful than hydrogen peroxide, although the hydroxyl radicals generated during hydrogen peroxide are kinetically faster in destroying contaminants. The persulfate anion reaction with natural organic matter is much lower and kinetically slower in the oxidation than the hydroxyl radical. The oxidative strength free radicals ( $\text{SO}_4^{\cdot-}$ ) is increased by the addition of heat or, as in Fenton's system, a ferrous salt or chelated ferric iron. From this medication, the resulting solution is called activated sodium persulfate. E.g. decomposition

of hydrogen peroxide can provide heat for activation of:



The sulphate radical is kinetically faster than the persulfate anion. The use of sodium persulfate has some design considerations which include (Hoeskra, et al., 2011):

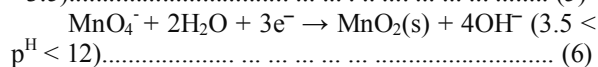
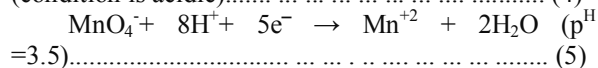
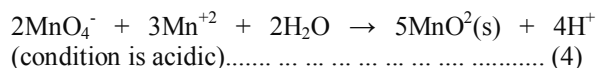
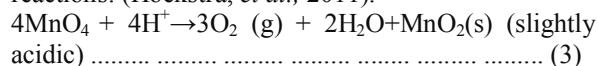
- Persulfate reaction with contaminant of concern is kinetically slower than with hydroxyl radical which results into the possible further distribution of the oxidant before degradation.
- Soft metals (e.g. copper or brass) can be degraded by persulfate.
- Chelated iron when used may increase the longevity of iron in groundwater.
- Within the treatment zone, low  $p^H$  can cause metals to be mobilized.
- The increase of natural organic matter reduces the ratio of the volume of contaminants of concern oxidized per volume of oxidant as this is common with all chemical oxidation applications.

Sodium per sulphate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is the most common persulfate salt used in chemical oxidation applications (Hoekstra, et al., 2011).

#### Permanganates

Permanganates are oxidants that have over the years been used for the treatment of drinking water and wastewater. Permanganate ion has a relative oxidizing power of 1.24 (Manzardo, et al. 2014) it comes either as  $\text{NaMnO}_4$  or  $\text{KMnO}_4$ . Permanganates in reaction with organic compounds produce manganese dioxide ( $\text{MnO}_2$ ) as well as  $\text{CO}_2$  and intermediate organic compounds (Yin and Allen et al., 1999).  $\text{R}^+ \text{MnO}_4^-$ ,  $\text{MnO}_2 + \text{CO}_2$  or  $\text{R}_{\text{ox}} + \text{others}$  where, R = organic contaminant of concern  $\text{R}_{\text{ox}}$  = oxidized intermediate compound.

Organics which have carbon-carbon double bonds; aldehyde groups or hydroxyl groups find permanganate ion, especially useful oxidant. Many processes such as cleaving, hydroxylation hydrolysis, and others lead to the production of intermediates and eventually to carbon dioxide and water (Chapagain, et al., 2006). Manganese dioxide ( $\text{MnO}_2$ ) occurs naturally in soil and so, that produced during the reaction does not pose environmental concerns, though there is some concern about the precipitation of  $\text{MnO}_2$  leading to a decrease in permeability. Manganese is known to exist in multiple valences, occur simultaneously and hence its reactions tend to be effective over a wide  $p^H$  range. Reaction with contaminants of concern can occur either by direct electron exchange or free radical advanced oxidation reactions: (Hoekstra, et al., 2011).



Contaminants that have been oxidized via the use of permanganate include: alkanes, aromatics, phenols, PAHs, pesticides, some organic acids, aldehydes, amines, alcohols, ketones, chlorinated solvents (PCE, TCE), sulphides, MTBE and others (Damm, et al., 2002, Schroth, et al., 2001). Oxidation rate as a result of permanganate is often influenced by  $p^H$ , temperature, the solubility of the target contaminant and the concentration of each contaminant species (Siegrist, et al., 2000).

Advantages of utilizing permanganate for oxidation of contaminants include the following (Cheryl and Gopal, 2015):

1. The oxidation reactions are not exothermic
2. They are readily soluble and has a higher efficiency in water and soil treatment
3. Relatively safe to handle
4. Catalysts are not needed
5. No pH control is required
6. The presence of free radical scavengers in the soil (e.g. carbonate, bicarbonate) has no adverse impact on performance
7. Neither the oxidants nor their by-products are toxic to the local microbial population allowing the use of bioremediation as a companion remediation technology
8. They are more persistent in the subsurface and therefore can migrate by diffusive processes to further regions within the contamination zone.

However, two main difficulties are associated with the use of permanganates: Regulatory concerns regarding the amount of dissolved manganese in an area and the remaining purple colours of unreacted permanganate in groundwater,  $\text{MnO}_2(\text{s})$  precipitate occupies pore space thereby reducing soil permeability and limiting further injections of aqueous oxidants into the contaminated zone (ESTCP, 1999). Permanganates are more expensive than hydrogen peroxide/Fenton's reagent, however, its ease of delivery to the contaminated sites, applicability over a wider  $p^H$  range, higher level of treatability, reliability and high solubility makes remediation of contaminated soil and/or groundwater by permanganate cost effective (Seol et al., 2003).

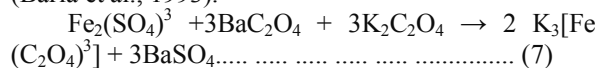
#### Potassium Ferrioxalate

Potassium ferrioxalate (potassium trisoxalatoferate (III), is a chemical compound with formula

$\text{K}_3 [\text{Fe} (\text{C}_2\text{O}_4)_3]$ , which its iron is in the +3-oxidation state. It has a metal complex of an

octahedral transition in which three bidentate oxalate ions are bound to an iron centre. Potassium acts as a counter ion, balancing the  $-3$  charge of the complex. All crystals of the trihydrated form of the complex,  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  are emerald green in colour. When in solution, the salt dissociates to give ferrioxalate anion,  $[Fe(C_2O_4)_3]^{3-}$  which displays fluorescent green colour. Potassium ferrioxalate is at times sometimes used in the measure of light flux (actinometry).

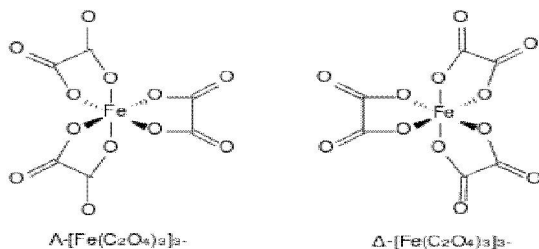
**Preparation:** Potassium ferrioxalate trihydrate crystals are often synthesized by reacting iron (III) sulphate, barium oxalate and potassium oxalate: (Barla et al., 1993).



When the reactants are mixed in water, it precipitates solid  $BaSO_4$  which is removed and the green trihydrate crystallizes from cooled solution. Potassium ferrioxalate could also be synthesised by reacting aqueous iron (III) chloride hexahydrate and potassium oxalate monohydrate.  $FeCl_3 \cdot 6H_2O + 3K_2C_2O_4 \cdot H_2O \rightarrow K_3[Fe(C_2O_4)_3] \cdot 3H_2O + 3KCl + 6H_2O \dots \dots \dots (8)$

In structure, Ferrioxalate complex has  $D_3$  molecular symmetry, in which the iron centre is octahedral. The six Fe–O bond distances are sometimes close to  $2.0 \text{ \AA}$  which indicates that Fe (III) is high spin; as low spin complex displays Jahn–Teller distortions. Ammonium and mixed sodium-potassium salts are isomorphous, similar to complexes  $V^{3+}$ ,  $Al^{3+}$  and  $Cr^{3+}$ .

The ferrioxalate complex shows helical chirality since it could form two non-superimposable geometries. Referencing IUPAC convention, the isomer with the left-handed screw axis is assigned the Greek symbol  $\Lambda$  (lambda) while mirror image with the right-handed screw axis is normally given the Greek symbol  $\Delta$  (delta). (Greenwood *et al.*, 1995).

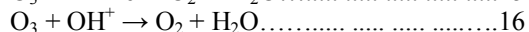


### Ozone:

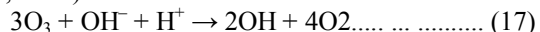
Ozone is a gas that can be emplaced by injection into the vadose zone, by sparging, or by injection of ozonated water. It is highly reactive with a short half-life of about 20 minutes and should be generated close to the treatment area. Unlike other chemical oxidation methods, injection of ozone requires a semi-

permanent remediation system. Also, corrosion resistant piping and injection points are required. The sparge points or injection wells need to be placed closely together and fugitive ozone emissions during production or injection often represent unacceptable risks. A vapor collection system may be necessary according to (Huling and Pivetz 2006). Ozone has the potential to degrade PCE, TCE, DCE, VC, BTEX, phenols, MTBE, TBA, and explosives. But reacts poorly with DCA, PAHs, TCA, PCBs, and pesticides. Ozone reactions with contaminants of concern could come as direct or indirect oxidation with the production of hydroxyl radicals. Direct oxidation involves the direct insertion of ozone molecules into unsaturated carbon-carbon bonds forming an ozonide. Indirect oxidation reaction is faster than direct oxidation and it is caused by its reaction with the hydroxide ion at neutral to basic pH which forms hydroxyl radicals. A chain reaction is usually initiated bringing about the formation of new radicals. Hydroxyl radical formation is enhanced in the presence of ultraviolet light especially in ex-situ application and by reacting with certain cations.

### Equation:

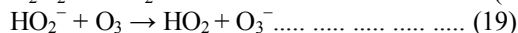
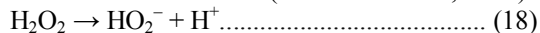


When ozone is applied in combination with hydrogen peroxide it results in increased generation of hydroxyl radicals by reacting peroxide and ozone independently and with intermediate products. The reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical  $O_2^-$  and hydroperoxyl radical  $HO_2$ . By the reaction between ozone and the super-oxide anion radical the ozonide anion radical  $O_3^-$  is Formed, which decomposes immediately giving OH radical. Summarizing, three ozone molecules produce two OH radicals (Gottschalk et al., 2000):



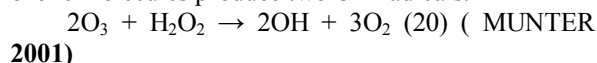
### Ozone + hydrogen peroxide ( $O_3/H_2O_2$ ) – (peroxone)

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of OH radicals (Gottschalk et al., 2000):



The reaction continues along the indirect pathway described above and OH

radicals are produced (Hoigne 1982). The combination of different reaction steps shows that two ozone molecules produce two OH radicals:



Paillard et al., (1988) studied the elimination of atrazine in filtered Seine River water. Results showed better degradation of the pesticide in water treated

with ozone–hydrogen peroxide combination as compared to ozone alone. The optimum H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> mass ratio was from 0.35 to 0.45. The performance of the process depends on the ozone dose, contact time, and alkalinity of water (Duguet et al., 1985), when treating Lake Cholet water, established the importance of H<sub>2</sub>O<sub>2</sub> introduction point: the best performance was achieved when H<sub>2</sub>O<sub>2</sub> was added after the oxidation of highly reactive substances with ozone alone. The implementation of a radical system makes oxidation of refractory molecules possible: it allows getting full advantage of selective molecular ozone reactions before converting the process to non-selective free radical attack. Hydrogen peroxide is a relatively inexpensive, readily available chemical oxidant. It is produced by electrolysis of ammonium bisulphate or by oxidation of alkyl hydroanthraquinones. The electrolytic process consumes approximately 7.7 kWh per 1 kg of H<sub>2</sub>O<sub>2</sub> produced (TECHCOMMENTARY, 1996; MUNTER, 2001).

#### Regeno<sub>x</sub><sup>TM</sup>

Regeno<sub>x</sub><sup>TM</sup> is a proprietary sodium percarbonate blend produced by regeneration which is catalysed to slowly release oxidant over about 30 days. This oxidant operates under alkaline conditions unlike hydrogen peroxide and per sulphates, it does not require the manipulation of subsurface geochemistry. This technology was put in place by regeneration as a prelude to, or concurrent with, enhanced bioremediation. From literature, Regeno<sub>x</sub><sup>TM</sup> is a very effective oxidizer of nearly all common contaminants but must be verified further.

#### Conclusion

Chemical oxidation is a form of oxidation technique known to be the most rapid, cost saving and innovative treatment method for the remediation of soil or ground water contaminated by targeted environmental contaminants of concern. Oxidizing agents commonly used include: hydrogen peroxide catalysed with ferrous in Fenton's reagent (Claudia et al., 2006; John et al., 1993), potassium permanganate (David et al., 2004) and sodium per sulphate (Julien et al., 2011). For proper application of different oxidants, laboratory studies must be carried out to choose the most suitable one and concentration, because each oxidant has its specific advantages and disadvantages.

An increase of dissolved contaminant concentrations in contaminated groundwater most times occurs after treatments as a rebound effect, this has therefore become a vital factor in evaluating effectiveness of source depletion technologies. Most of the previous studies reviewed do not consider the possible effect of these site-specific scenarios on the outcome of the results obtained. Sodium persulfate

application as a preferred oxidative alternative to the widely used oxidants in treating organic compounds in groundwater has been studied and more research on its optimal applicability should be carried out because of their emerging potential for better performance comparative to other oxidants.

#### Corresponding Author:

Osu Charles I  
Department of Pure and Industrial Chemistry,  
University of Port Harcourt, P.M.B 5323 Choba, Port  
Harcourt, Rivers State, Nigeria.  
Telephone: +234 803 7783246  
E-mail: [charsike@yahoo.com](mailto:charsike@yahoo.com)

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