

IN-SITU CHEMICAL REMEDIATION OF CRUDE OIL-POLLUTED SOIL USING HYDROGEN PEROXIDE AND ITS MODELLING

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ABSTRACT

In-situ chemical oxidation (ISCO) process was used to effectively remediate a sandy clay soil polluted with crude oil. H₂O₂ in the absence of Fenton's reagent was the remediating agent. 500ml of crude oil was used to pollute two plots of land 1m² each. Hydrogen peroxide application was observed to be faster than natural attenuation. The experiment was conducted for fifteen (15) weeks during which, 37.5mg/100g concentration of crude oil was reduced to 4.5mg/100g. A regression model was developed for this method.

Keywords: In-situ, ISCO, THC, Remediation, Polluted, Crude oil.

1. INTRODUCTION

There is every need to remove anthropogenic contaminants like crude oil from the soil. Crude oil exposure even at very low concentrations can cause deleterious effects, whether lethal or sub-lethal, to an organism or community [1]. In-situ chemical oxidation [ISCO] is an environmental remediation technique used for soil and/or ground water remediation to reduce the concentration of targeted environmental contaminants to acceptable levels. The *In-situ* ISCO is just Latin for "in place", signifying that ISCO is a chemical oxidation reaction that occurs at the site of the contamination [2].

Different researchers have listed and disclosed the various methods of ISCO. In [2], it was asserted that the remediation of certain organic substances such as chlorinated solvents [trichloroethene and tetrachloroethane] and gasoline-related compounds [benzene, toluene, ethylbenzene, MTBE and xylenes] by ISCO is possible. Common Oxidants used in ISCO as identified by researchers are listed and discussed below:

i) **Hydrogen peroxide and Fenton's Reagent:** Hydrogen Peroxide [H₂O₂] is one of the most powerful oxidizers known. In the presence of a transition metal such as iron or copper, hydrogen peroxide reacts much more vigorously and aggressively than without the metal [acting as a catalyst]. The reaction of iron - catalyzed hydrogen peroxide oxidation is called a "Fenton Reagent". According to [3], soil treatment with hydrogen peroxide has a potential for both ex-situ and in-situ applications. For In-situ remedial applications, naturally occurring iron in the soil or fill materials dramatically increases the oxidative strength of hydrogen peroxide [4]. This increase in oxidation power is attributed to the production of hydroxyl radicals [OH^o]. This can further be explained by the chemical equation below:



Residual hydrogen peroxide not used in the oxidation process breaks down to water and oxygen in a matter of hours. After the Fenton's Reagent has been completely depleted, the breakdown products of the spent hydrogen peroxide can serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants [4].

In [2] was identified an advantage of this method stating that hydroxyl radicals are very strong oxidants and react very rapidly with contaminants and impurities. Disadvantages of this method as reported in [3] are: the cost of hydrogen peroxide and the ability of the hydroxyl radical to react with many other substances other than the targeted contaminants making it ineffective in soils containing carbonate, bicarbonate and organic matter.

ii) **Permanganate:** Permanganate salts are well-known oxidizing agents as they are commonly used in many water treatment applications at low concentrations. As an oxidizer, permanganate has a unique affinity for destroying organic compounds containing carbon-carbon double bonds. In [4] was stated that potassium permanganate [KMnO₄] lasts longer and can react in an environment with much higher pH compared to hydrogen peroxide. Permanganate was described as an oxidizer weaker than hydrogen peroxide [3]. This statement was buttressed by the fact that permanganate is unable to oxidize benzene claiming that this quality can lead to the early elimination of permanganate as candidate for oxidation technology at petroleum cleanup sites [3]. The solubility of potassium permanganate is strongly influenced by temperature. At 30°C, the solubility is more than 8% [4]. The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. The chemical equation below summarizes the permanganate reaction:



iii) **Ozone:** Ozone is a strong oxidant and can oxidize contaminants directly or through the formation of hydroxyl radicals. Ozone is about 12 times more soluble than O₂ [2], although it is still comparably insoluble. Contaminants in the soil that can be easily eradicated by Ozone were identified as MTBE [Methyl Tertiary-Butyl-Ester], hydrocarbons, diesel, pesticides, VOCs [Volatile Organic Compounds], Benzene, Toluene, Ethyl benzene, Xylene, trichloroethylene and Aromatics [5]. It was claimed that Ozone is an effective agent for at least the partial oxidation of simple ions and species containing multiple bonds [6]. The innovative in-situ remedial technology using ozone is a form of chemical oxidation which destroys organic contaminants leaving behind harmless end products. Ozone is generated on site because the gas is very difficult to store; therefore, all the ozone gas that is generated must be injected into the sub-surface or destroyed using an ozone destruction unit on the Ozone generator [4]. The advantages as its reactivity and the wide range of substances which can be treated; the disadvantages are the complications during its application as a result of high reactivity and its distribution in soil after injection were identified [3]. Peroxone, a type of advanced oxidative process [AOP] uses hydrogen peroxide activated ozone to create the hydroxyl and perhydroxyl radicals [Aquazone, 2011]. Ozone and peroxone can mineralize most petroleum hydrocarbons and chlorinated solvents into water and carbon dioxide by the equation below [4].



iv) **Sodium Persulphate (Na₂S₂O₈):** It was reported that persulphate oxidation commonly uses sodium persulphate (Na₂S₂O₈) catalyzed by a chelated iron complex such as iron (II) EDTA at a neutral pH to produce sulfate radicals (SO₄^{•-}) that attack most petroleum hydrocarbons and selected chlorinated solvents [7]. It was claimed that field pilot or full-scale application of activated persulphate has been performed at over sixty (60) sites in more than twenty [20] states in Ukraine treating effectively chlorinated ethenes, chlorinated ethanes, chlorinated methanes, polyaromatic hydrocarbons, petroleum hydrocarbons, BTEX, MTBE, etc. [3]. The advantage of using persulphate is that persulphate is much more stable than either hydrogen peroxide or Ozone above the surface and it does not react quickly by nature [2]. It can be injected into the site of contamination at high concentrations and can be transported through porous media by density driven diffusion.

Having studied the different oxidants that can be used for chemical remediation, weighing their advantages and disadvantages, there was need to select an oxidant that will be readily available, affordable and has high reactivity. This suggested the selection of H₂O₂ [without Fenton].

It was claimed that Fenton's reagent should be used with caution because it has been found to be detrimental to the microbes in the soil and can also rapidly degrade the soil [2]. Based on this fact, H₂O₂ without Fenton's reagent was used in ISCO of crude oil in a soil to achieve rapid cleanup of the soil and conservation of the soil after remediation process.

2. MATERIALS AND METHOD

MATERIALS

The following materials were used in the research:

- i) Hydrogen Peroxide [H₂O₂]
- ii) Crude Oil
- iii) 500ml measuring cylinder
- iv) 2m² piece of land

METHOD

Two square meters was marked out on a sandy clay soil piece of land. The land was divided into two plots 1m² each with a trench of about 15cm wide and 10cm deep separating the two plots. Soil samples from the two plots were collected and tested for total hydrocarbon content. The two plots were polluted with 500ml Crude oil. Plot A was treated with 400ml of Hydrogen peroxide daily. Plot B was not treated, therefore, it served as a control. Soil samples from the two plots were collected weekly and tested for total Hydrocarbon content. The experiment lasted for fifteen (15) weeks

3. RESULTS AND DISCUSSION

Total Hydrogen Content of soil before pollution was 3.0mg/100g soil.

Table 1, shows the readings obtained from the weekly measure of THC of the soil samples in the two plots for fifteen (15) weeks.

Table 1: Total Hydrocarbon content of the two plots after pollution, measured weekly.

WEEKS	PLOT A [mg/100g]	PLOT B [mg/100g]
1	37.5	150.0
2	37.5	112.5
3	30.5	90.5

4	22.5	67.5
5	22.5	51.0
6	2.5	49.5
7	15.0	51.0
8	15.0	50.0
9	13.0	49.0
10	10.0	48.5
11	8.5	46.0
12	7.0	44.0
13	7.00	41.0
14	5.5	40.5
15	4.5	38.0

Mathematical Modelling:

The readings obtained were modelled with regression analysis using LINEST software In Microsoft Excel. The analysis is shown in Table 2 below:

Table 2: Data for Chemical Remediation modeling

WEEKS	CONCENTRATION [mg/100g]	H ₂ O ₂ APPLIED WEEKLY
0	45	400
1	37.5	2800
2	37.5	2800
3	30.5	2800
4	22.5	2800
5	22.5	2800
6	20.5	2800
7	15	2800
8	15	2800
9	13	2800
10	10	2800
11	8.5	2800
12	7	2800
13	7	2800
14	5.5	2800
15	4.5	2800

-82.61832658	-160.1047583	5407.624779
34.67826079	93.25769898	1344.487316
0.426755519	487.9722721	#N/A
4.838966554	13	#N/A
2304479.801	3095520.199	#N/A
#N/A	#N/A	#N/A
#N/A	#N/A	#N/A
#N/A	#N/A	#N/A

Using the regression Model:

$$Y = a_0 + a_1X_1 + a_2 X_2 \tag{1}$$

Where: Y – Amount of remediating agent needed for clean-up

X₁ = time in weeks

X₂ = Concentration of pollutant after time, X₁.

Substituting values in equation 1;

$$Y = 5407.6 - 160.1X_1 - 82.6X_2 \quad (2)$$

4. DISCUSSION

The experiment was conducted for fifteen (15) weeks. Table 1 shows the Total Hydrocarbon Content of the two plots [A & B]. There was significant reduction in THC in PLOT A. This is not evident in PLOT B as the THC decreased slowly. Due to the high instability of hydrogen peroxide, not all the quantity applied went into the oxidation of hydrocarbons. Also, the values obtained in PLOT A were, at times, constant over two weeks. This can be attributed to the slow reactivity of hydrogen peroxide in the absence of Fenton's reagent. Another consideration may be environmental factors like rainfall which can cause deep percolation of the pollutant as against the days without rainfall. The regression model developed can aid in the cleaning of pollutants with hydrogen peroxide.

5. CONCLUSION

H₂O₂ was used to clean-up a sandy clay soil polluted with crude oil. H₂O₂ (in the absence of Fenton's reagent) was found to be faster than natural attenuation. A regression model was developed for this ISCO method of remediation.

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