Injection of Fentons Reagent In-Situ Case studies

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Introduction

The oxidant, known as Fenton's reagent, destroys a variety of industrial wastes and generates innocuous byproducts — water, oxygen and carbon dioxide

Introduction

Background
- – Principles
- – Advantages
- – Disadvantages

Field expirience
- – Brørup, Denmark – Former gas station
- – Sandarne, Sweden – Chemical plant

Summary of results

Background - Principles

The remediation principle is based on chemical oxidation

The oxidating agent are hydroxy radicals, created from hydrogen peroxide in the presence of ferro ions

Background - Principles

Principles

I practice ferro-ions are introduced as a ferro sulphate solution - if nessacery

The injection can either happen in predrilled injection points or during pressing down injection rods

When the neccesary ferro ions are available the hydrogen peroxide solution is injected, resulting in creation of a number og oxidizing and reducing radicals

Background - Principles

Principles

Hydrogen peroxide (H_2O_2) is one of the strongest oxidants known

By a catalytic process a number of radicals are created of which •OH is only surpassed by fluorine as oxidizer

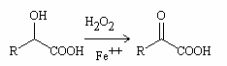
H_2O_2 is between 10^6 and 10^9 times stronger oxidizer than oxygen or ozone

Background - Principles

Principles

Fenton's reagent was invented by H.J.H. Fenton in 1894. But its usefulness as an oxidizing agent that destroys toxic chemicals was not fully recognized until the 1930s. Today, Fenton's chemistry is applied to wastewaters, sludges and contaminated soils.

Fenton Reaction:



H. J. H. Fenton, Proc. Chem. Soc. 9, I, 113 (1893)
J. Chem Soc. 65, 899 (1894); 67, 774 (1895)
H. J. H. Fenton, H. Jackson J Chem. Soc. 75, 1 (1899)

Background - Principles

Principles

Today there are several methods known as "modified" Fenton's reaction where different additives increase the oxidizing efficiancy by increasing the pH tolerance, increasing the reaction time and producing more and more stable radicals.

$H_2O_2 + OH\bullet$ => $HO_2\bullet + H_2O$ (perhydroxyl radical)
$HO_2\bullet$ => $H^+ + O_2\bullet^-$ (superoxide radical anion)
$HO_2\bullet + O_2\bullet^-$ => $HO_2^- + O_2$ (hydroperoxide anion)

The co-existing oxidation-reduction reactions associated with a modified Fenton's process promote enhanced desorption and degradation of recalcitrant compounds. These include compounds such as carbon tetrachloride and chloroform, which were previously considered untreatable by Fenton's chemistry

Background - Advantages

Advantages

- There is a complete mineralization of organic matter
- The breakdown is fast – within days, typically minutes – hours, depending on H_2O_2-concentration
- The process has some effects on residual free phase
- There are no harmfull byproducs
- There is no need for any processing units on the surface

Background - Disadvantages

Disadvantages

- The reactions are only efficient at low pH-levels (<6) – Difficult to maintain in calcarious soils
- The oxidation is not specific to the hazardous substances - organic matter in the sediment like peat will increase the necessary amount af H_2O_2 significantly
- In low permeability soils it can be difficult to distribute the H_2O_2-solution while still reactive
- Metals like chromium and copper can be mobilized and posses a risk to the environment

Field expirience - Brørup, Denmark

Former gas station

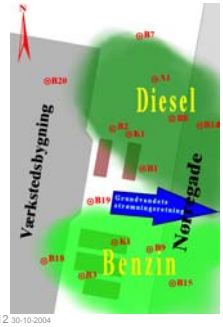
The field tests was conducted at a former gas station heavily polluted with petrol and diesel gasoline in Brørup, Denmark

The purpose of the project was to test the applicability of Fenton's reagent injection in Danish sandy soils

Oliebranchens Miljøpulje financed the project

Site consultant for Oliebranchens Miljøpulje is DGE, Aarhus

Field expirience - Brørup, Denmark



This site was chosen for the testing due to:

A suitable geology – high permeable sands and no carbonates

The ability to extract gases above the groundwater

An intense, well mapped pollution with diesel 5-9 m bg. and petrol 6-9 m bg. in a fairly confined area

Low risk for people and environment by hazardously accidents

Field expirience - Brørup, Denmark

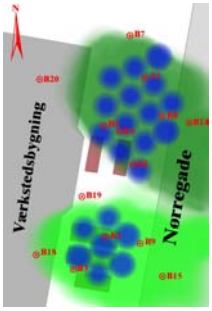
Field Methods

Fenton's reagent was injected as a push/pull technique, where the ferro sulphate solution was injected through a hollow steel rood while it was hammered down though the soil column.

While retracting the rod the hydrogen peroxide solution was injected though the same soil column.

21 injections each covering an area of 7 m^2

Treatet area 150 m^2 or appox. 800 m^3 in volume



DDH

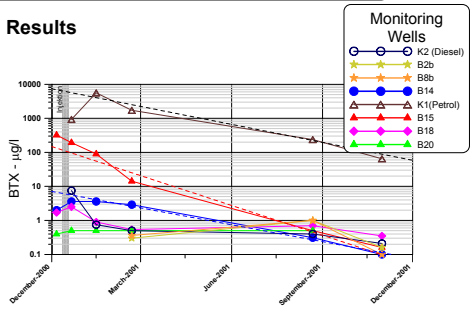
Field expirience - Brørup, Denmark

Field Methods

DDH

Field expirience - Brørup, Denmark

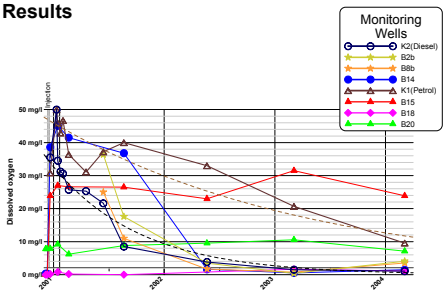
Results



DDH

Field expirience - Brørup, Denmark

Results



DDH

Field expirience - Sandarne, Sweden

Chemical plant

The field tests was conducted at a site heavily polluted with petroleum products near Söderhamn, Sweden

The purpose of the project was to test the applicability of Fenton's reagent injection in Swedish soils

The project is conducted in cooperation between Däldehög AB as contractor and DDH-consulting A/S (Denmark), with GEO (Denmark) as drilling contractor

Statens Geotekniska Institut, Göteborg (Peter Starzec and Lennart Larsson) has been part of the project, compiling all the chemical data and performing the statistical analysis

Svenska Byggbranschens Utvecklingsfond (SBUF) has partly financed the project

Site consultant for the property owner is URS Nordic AB, Stockholm

Field expirience - Sandarne, Sweden

This site was chosen for the testing due to:

A suitable geology – fairly high permeable sands and no carbonates

The ability to extract gases above the groundwater

An intense, well mapped pollution with petroleum products in a fairly confined area

Low risk for people and environment by hazardously accidents

Field expirience - Sandarne, Sweden

Field Methods

The test site had an approximate area of 50m^2 and the injection depth range was 1.5- 5.0 m below grade, where the heaviest pollution was observed.

Prior to the injection 8 vacuum extraction wells where established in and around the test area in order to extract the gas created by the decomposition of hydrogen peroxide and any volatilized hydrocarbons. During the injection a total of 200-300 m^3 gas/h were extracted from the unsaturated zone.

Field expirience - Sandarne, Sweden

Field Methods

The injection of Fenton's reagent took place as a push/pull technique, where the ferro sulphate solution was injected through a hollow steel rood while it was hammered down though the soil column to the desired depth, While retracting the rod the hydrogen peroxide solution was injected though the same soil column.

A total of five injections were carried out, each taking about 1.5 hours to establish.

Field expirience - Sandarne, Sweden

Results

- Significant reduction (approx. 31%) of dissolved hydrocarbon concentrations in groundwater in the test area right after the test
- A further reduction (totally 48%) was observed a month after the injection
- Significant increase in conc. of phenols (16x) and Cr^{6+} (10x) dissolved in groundwater in the test area right after the test. The increase of phenols was reduced to 7.5x after a month
- Slight increase of phenols (1.2x) downstream the test area
- Significant reduction of hydrocarbon concentration (26%) in soil samples after the injection
- Addition of citric acid increased the reaction time and the heat produced during the injection. The results from nearby monitoring wells show a more efficient decomposition of hydrocarbons, where citric acid was added

Summary of Results

The Fenton's Reagent oxidation process was demonstrated to be a simple, safe, fast, and effective in-situ treatment method for petroleum products

For the small, discrete source area, the technology can be very cost-effective

Use of the technology should be evaluated based on site-specific hydrogeologic and geochemical conditions, such as:

- **hydraulic conductivity**
- **carbonate/bicarbonate content**
- **pH**

Acknowledgements

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