Katsaus In Situ Chemical Oxidation (ISCO) tekniikiikan sovellutuksiin

Mutku – päivät

Hämeenlinna 22.3.2010

Tuula Tuhkanen

TAMPERE UNIVERSITY OF TECHNOLOGY
Bio- and environmental engineering

Esityksen sisältö

- Pilaantuneet maa-alueet; yleistä
- Katsaus ISCO tekniikoihin
- ISCO tekniikat meillä ja varsinkin muualla
- Täyden mittakaavan kunnostus vs. tutkimuksen haasteet
  - Soveltuvuus kunnostuskohteelle ja ko. aineelle
  - (Maa-) matriisin vaikutus kemikaalitarpeeseen
  - Käytettävän kemikaalin määrän minimointi → esikäsittelynä biologiselle hajotukselle?
  - Vai toisin päin?
  - Kemikaalin ja hapetuskemikaalin kontakti maaperässä → ROI; kunnostettavan kohteen hydrogeologisten ominaisuuksien tutkiminen
  - Mahdolliset riskit

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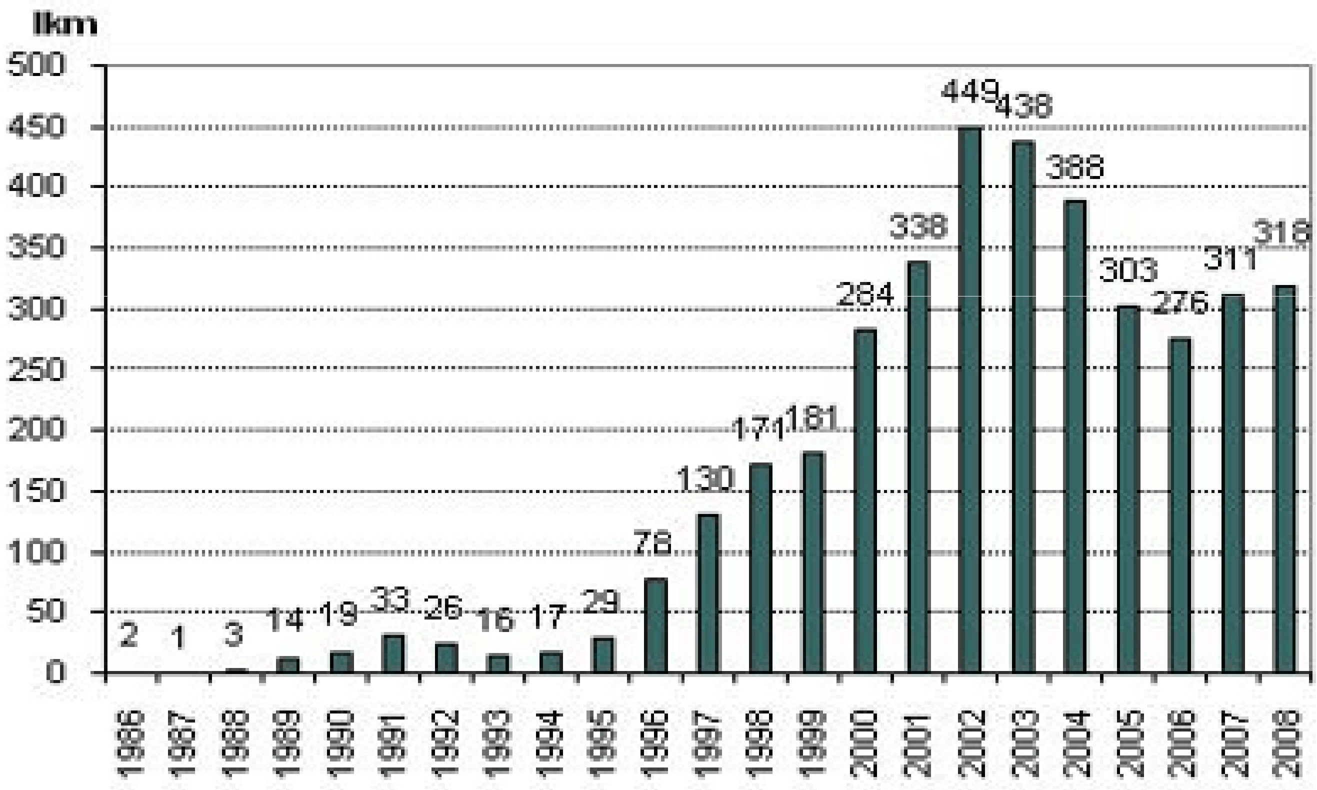
Pilaantuneiden maa-alueiden kunnostuspäätösten lukumäärät vuosina 1986-2008.

http://www.ymparisto.fi/default.asp?contentid=341490&lan=fi&clan=fi



Kunnostustustekniikat

- Vuonna 2008
  - 91 prosentissa massanvaihto
  - 4 % massanvaihto + muu tekniikka
  - Muut: eristys, kemiallinen hapetus, huokosilmakäsittely

Pilaantumisen syyt

- 55 % öljyhiilivedyt
- 2,3 % öljyhiilivedeyt + metallit
- 12,5 % öljyhiilivedyt + monipilaantuneet
- 2,2 kloorifenolit + PCDD/F
- Metallit

- Tuhansia pilaantuneita kohteita vedenhankinnan kannalta tärkeillä alueilla

Advanced oxidation processes (AOPs)

- = *kehittyneet hapetustekniikat*
- *In situ* generation of highly reactive intermediate oxidants such as the hydroxyl radical (OH·)” Glaze and Kang 1987, Ozone Sci&Eng
- OH· is a very powerful, non-selective oxidant and very short-lived
- H_2O_2 with a metal catalyst, UV or O_3
- O_3 with UV or at alkaline conditions
- ”AOPs are widely studied, promising techniqies”

Chemical oxidation

Species	Oxidation potential (V)
Hydroxyl radical	2.8
Sulfate radical	2.5
Ozone	2.1
Sodium persulfate	2.0
Hydrogen peroxide	1.8
Permanganate	1.7
Chlorine	1.4
Oxygen	1.2

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situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming ground-water or soil contaminants into less harmful chemical species.”

Fenton reaktio

- H_2O_2 katalyyttinen hajoaminen Fe^{2+} ionin vaikutuksesta happamissa olosuhteissa aloittaa hajoamisen ketjureaktion

- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot$ (chain initiation)
- $OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$ (chain propagation)
- $HO_2\cdot + H_2O_2 \rightarrow O_2 + H_2O + OH\cdot$ (chain propagation)
- $Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + H_2O$ (chain termination)

- “alternative theory including the formation of FeO^{2+}, which acts as the key intermediate in the reaction”

Fenton's reaction

- $Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + HO_2^-$ (ferrous iron reduction)
- $Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2$ (ferric iron oxidation)
- $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+$ (ferric iron oxidation)

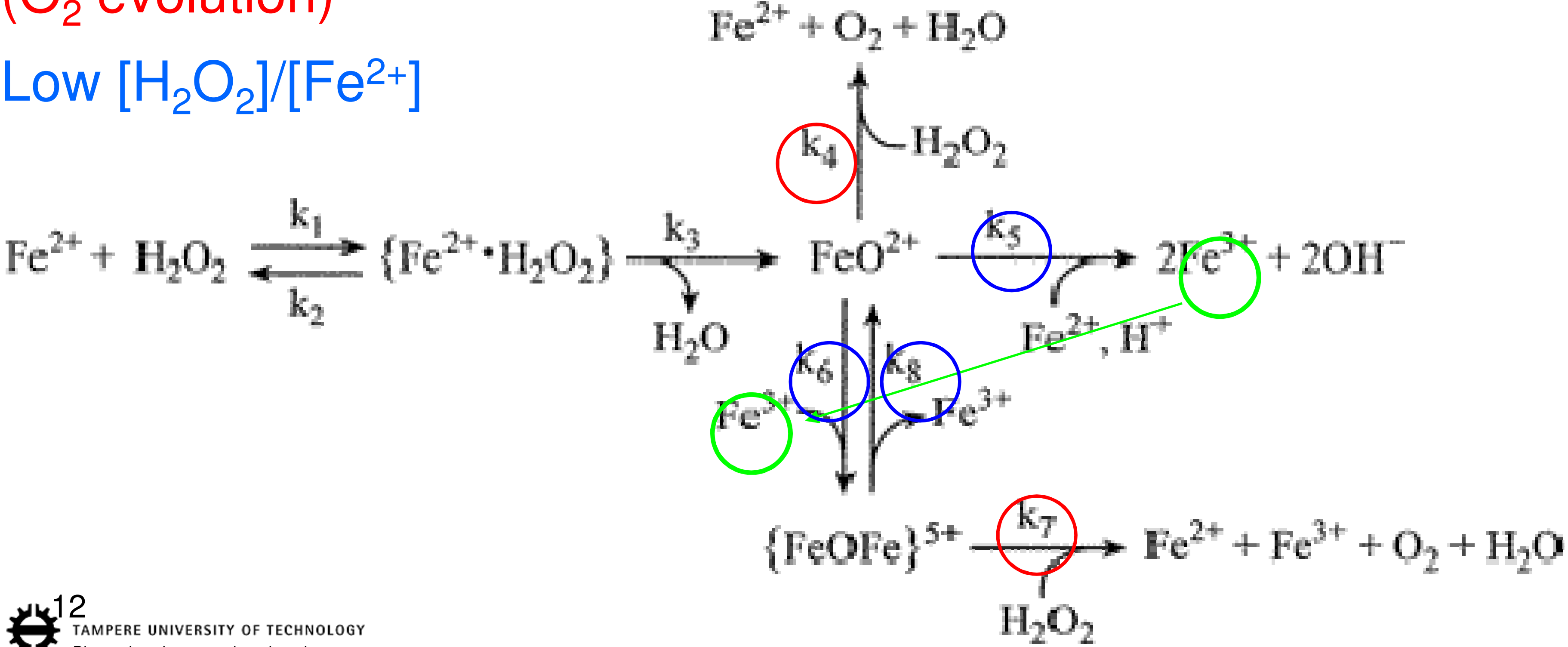
- Low $[H_2O_2]/[Fe^{2+}]$:
  - $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$
- High $[H_2O_2]/[Fe^{2+}]$:
  - $2H_2O_2 \rightarrow O_2 + 2H_2O$

Fenton's reaction

Mechanism, in which FeO^{2+} acts as the key intermediate:

High $[H_2O_2]/[Fe^{2+}]$ (O_2 evolution)

Low $[H_2O_2]/[Fe^{2+}]$



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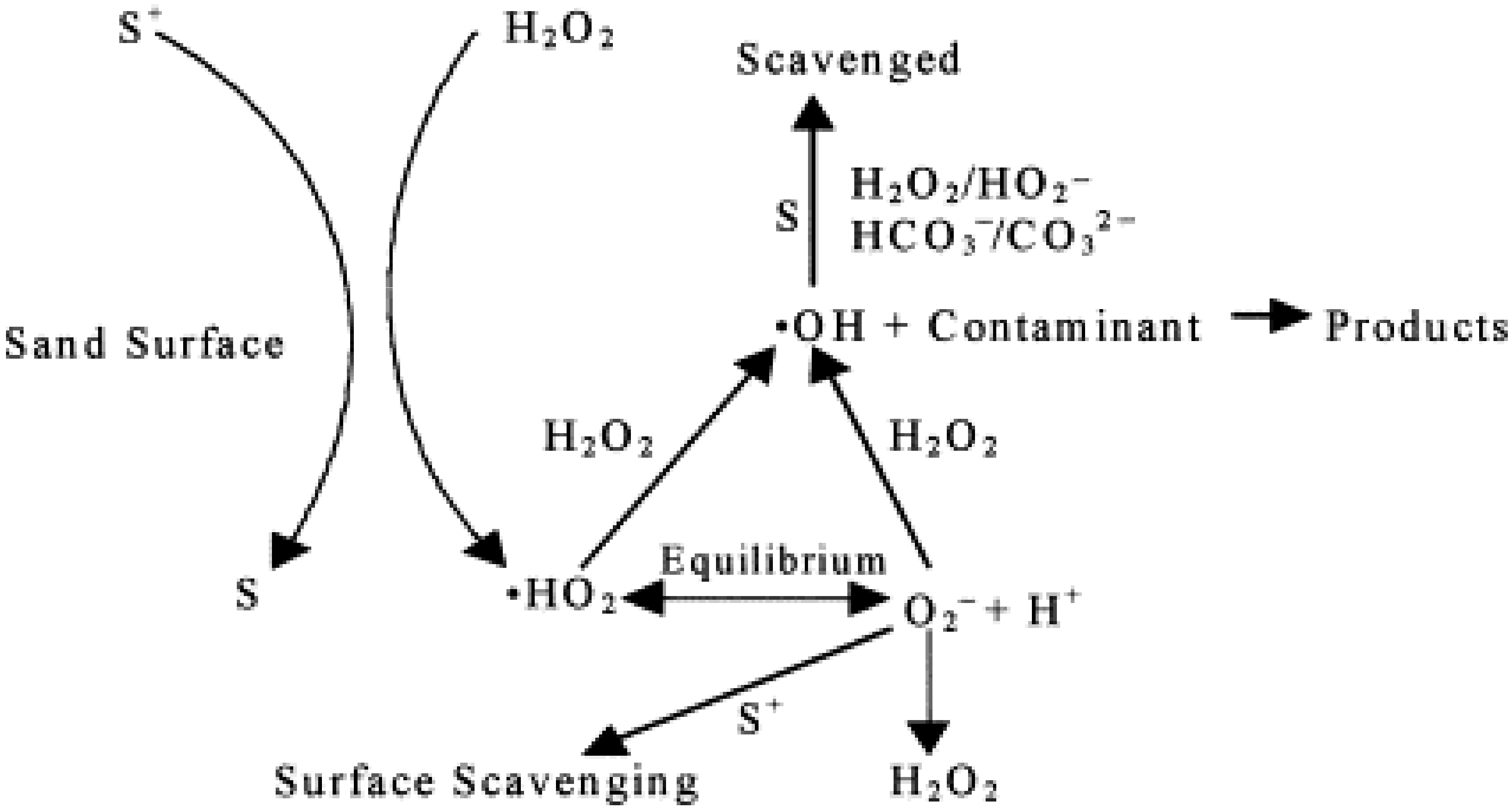
Reaction mechanism for H_2O_2 decomposition

echanistic studies of surface catalyzed H2O2 decomposition and contaminant degradation in the presence of sand" (1999) *Water Research*, 33 (12), pp. 2805-2816.

ntine (1999)



Fenton käsittely

- Happamissa olpsuhteissa (pH optimi noin 3)

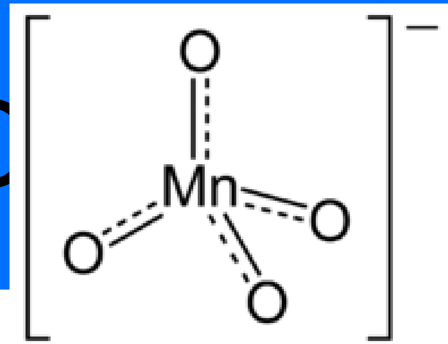
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO° + OH^-$$

- Hydroksyyliradikaalien muodostuminen **OH•**
- “Fast, simple, inexpensive (?)”
- **Mutta!**
  - Hydroksyyli -radikaalit kuluvat epäselektiiviseen matriisin hapettamiseen
  - Käytännön kohteissa “Rebound effect”
  - Eksoterminen reaktio

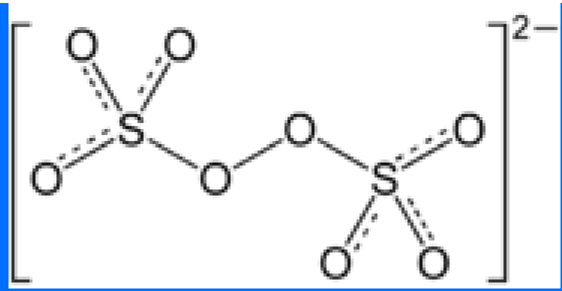
Modifoiutu Fenton käsittely

- Maaperän luontaiset rautayhdisteet (ja muut metallit) riittävät vetyperoksidin hajomisen katalysoimiseen
- Goethite yleisn mineraali
- Maaperän luontainen pH ilman hapon lisäystä
- Kelatoivien yhdisteiden käyttö raudan sitomiseen ja vetyperoksidin stabiloimiseen

Permanganate, MnO



- Releases oxygen and forms MnO_2(s)
- High potential, wide pH (3-12), cheap
- Slow process – allows diffusion to low permeable mediums
- $KMnO_4$ or $NaMnO_4$

Persulfate, 

- Sulphate radicals, $SO_4^{-\cdot}$, catalyzed
- Sodium persulphate salt, $Na_2S_2O_8$
- Not effective for ethanes
- Alkaline conditions with thermal activation

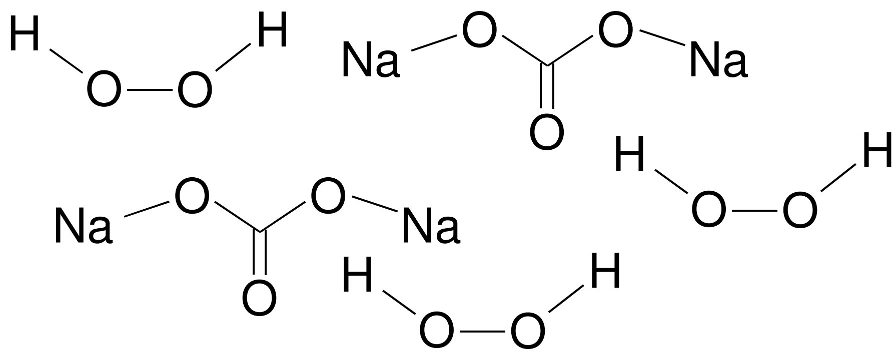
$$SO_4^{-\bullet} + RH \rightarrow R^{\bullet} + HSO_4^{-}$$
$$SO_4^{-\bullet} + H_2O \rightarrow OH^{\bullet} + HSO_4^{-}$$
$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$$
$$R^{\bullet} + S_2O_8^{2-} \rightarrow SO_4^{-\bullet} + HSO_4^{-} + R$$
$$SO_4^{-\bullet} + OH^{-} \rightarrow OH^{\bullet} + SO_4^{2-}$$

Magnesium and calcium peroxide

- $CaO_2(s) + H_2O \rightarrow Ca(OH)_2(s) + H_2O_2$
- [illegible] ORC, alkaline conditions
- Stable H_2O_2 concentration
- pH control important
- Solid product
- Good bioremediation base

RegenOx

- Hydrogen peroxide confined in sodium percarbonate, $[Na_2CO_3]_2{\cdot}[H_2O_2]_3$
- Slow dissolution in alkaline conditions
- $FeSO_4$ as a catalyst
- Perhydroxyl radicals, $HO_2{\cdot}$



Regenesis

- "Regenesis, an American company specialized in remediation of contaminated aquifers, produces a Fenton chemistry based RegenOx[tm] –product. It comprises of two components, an oxidizer complex and an activator complex. The oxidizer complex is a white powder consisting of sodium percarbonate confined hydrogen peroxide, $2Na_2CO_3 \cdot 3H_2O_2$, sodium carbonate, Na_2CO_3, sodium silicate, Na_2SiO_3, and silica gel, mainly SiO_2. The activator is a blue and green liquid consisting of ferrous sulphate, $FeSO_4$, sodium silicate, silica gel and water. (Regenesis 2005b, Regenesis 2005c) "

RegenOx – case in Atlanta

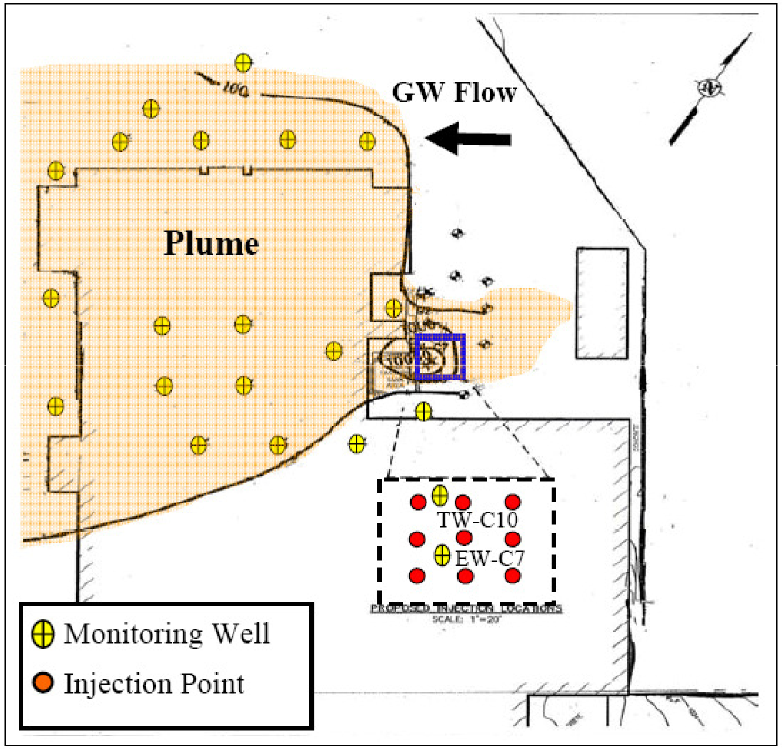


Figure 1. Site Map with RegenOx Injection layout

- $40m_2$, chemical packaging
- 500kg RegenOx
- Soil saprolite rock
- TCA: 23µg → ND
- 1,1-DCA: 21µg → 11 µg

Table 1. RegenOx Application Results – Well TW-C10 (ug/L)

Contaminant	Baseline	48 Hrs.	72 Hrs.	1 Week	4 Weeks	8 Weeks	11 Weeks	% Reduction
1,1,1-TCA	23	12	9	6	ND	ND	ND	99 %
1,1- DCA	21	18	16	13	9	7	11	47 %

ORC-Advanced™

- Product

Advanced Formula Oxygen Release Compound (ORC-A) is a proprietary formulation of calcium oxy-hydroxide ($CaO(OH)_2$) that produces a controlled release of oxygen for period of up to 12 months when hydrated.

- Purpose

To supply oxygen to accelerate the rate of naturally occurring aerobic contaminant biodegradation in groundwater and saturated soils.

http://www.regenesis.com/products/enhAer/orcadv/default.aspx

ORC-Advanced™

- **Specification**
  - ✓ (Hydrated) Calcium Oxide Peroxide [$CaO(OH)_2$] - **60%** by weight, minimum
  - ✓ Other inorganic calcium compounds : $Ca(OH)_2$ and $CaCO_3$ - **35%** by weight, minimum
  - ✓ Active Oxygen - 17%

$$\mathbf{CaO(OH)_2 + H_2O \rightarrow Ca(OH)_2 + 1/2\ O_2}$$

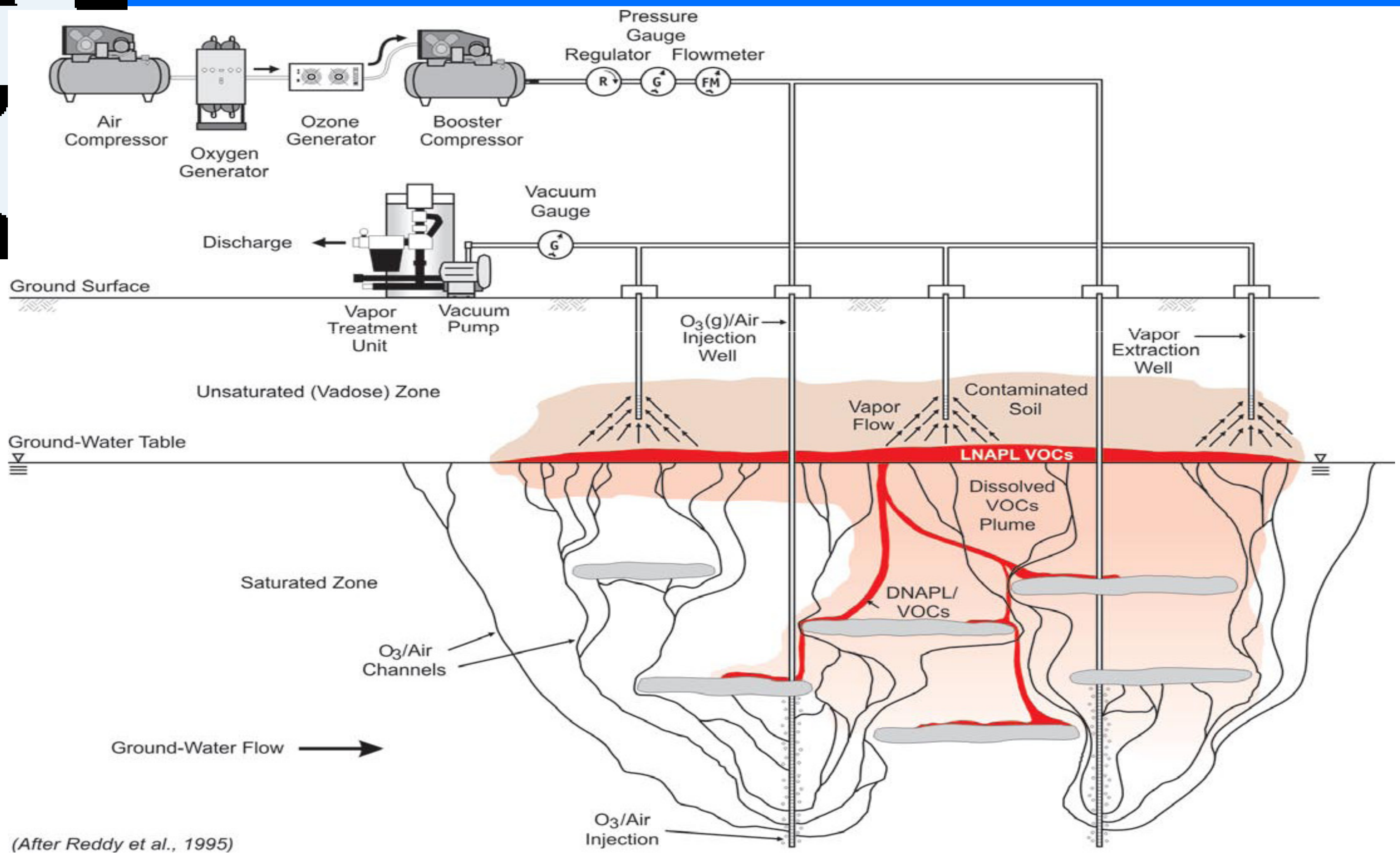
http://www.regenesis.com/products/enhAer/orcadv/default.aspx

Performed works by VentEko
ORC-Advanced™ injection

Performed works by VentEko
ORC-Advanced™ injection

Performed works by VentEko
Barriers with ORC-Advanced™ socks

General conceptual model of in-situ ozonation in the [redacted]turated zone with soil vacuum extraction to capture volatile emissions and O3(g).



(After Reddy et al., 1995)

Otsonin reaktiomekanismit

Direct Oxidation

$O_3 + C_2HCl_3 + H_2O \rightarrow 2\ CO_2 + 3\ H^+ + 3\ Cl^-$

OH-radical formation

$O_3 + H_2O \rightarrow O_2 + 2\ \cdot OH$ (Slow)

$2\ O_3 + 3\ H_2O_2 \rightarrow 4\ O_2 + 2\ \cdot OH + 2\ H_2O$ (Fast)

Menetelmien soveltuvuuden arviointi on tehtävä tapauskohtaisiesti

- Hapettimien luontainen tarve; orgaaninen ja epäorgaaninen matriisi, kilpailevat haitta-aineet
- Matriisin määrä ja reaktiivisuus (org.aineet)
- Hapetettavan yhdisteen konsentraatio ja reaktiivisuus
- Kohteen ominaisuudet , hydrogeolologia
- Haitta-aineiden ja matriisin mobilosoitumisen aiheuttama riski ympäristölle ja mahdollisuudet riskin minimoimiseen

Target contaminants

COCs	Fenton's	Ozone	$KMnO_4$	S_2O_8
Petroleum hydrocarbons	E	E	P	G-E
Benzene	E	E	P	G
Phenol	E	E	G	P-G
PAHs	E	E	G	G
MTBE	G	G-E	P-G	P-G
Carbon tetrachloride	P-G	P-G	P	P
Ethene: PCE, TCE, DCE, VC	E	E	E	G
Ethane: TCA, DCA	G-E	G	P	P
PCBs	P	G	P	P
Pesticides	P-G	P-G	P	P

By Eric Bergeron

P = poor G = good E = excellent

Selecting the chemical/geology

Permeability

Oxidant / permeability	High	Low	Medium
MnO_4	E	G	G-E
S_2O_8	E	G	G-E
Fenton	E	P	P
$SO_4^{-\cdot}$	E	P	P
O_3	E	P	P

By Eric Bergeron

P = poor **G = good** **E = excellent**

electing the chemical/geology

NOD = Natural Oxidant Demand

Affects the dosage of chemical

Oxidant / NOD	Carbonate	Metals	Organic matter
MnO_4	L	H	H
S_2O_8	L	L	L
Fenton	H	M	H
$SO_4^{-\cdot}$	H	M	M
O_3	H-M	M	M

By Eric Bergeron

H : high **M : medium** **L : low**

Matriisin vaikutus

Tarvittavan annoksen määrittäminen kokeellisesti laboratoriossa

Determination of Natural Oxidant Demand and optimal dose of oxidant Huom. Myös H2O2:Fe suhde

Fenton treatment

Shaking procedure

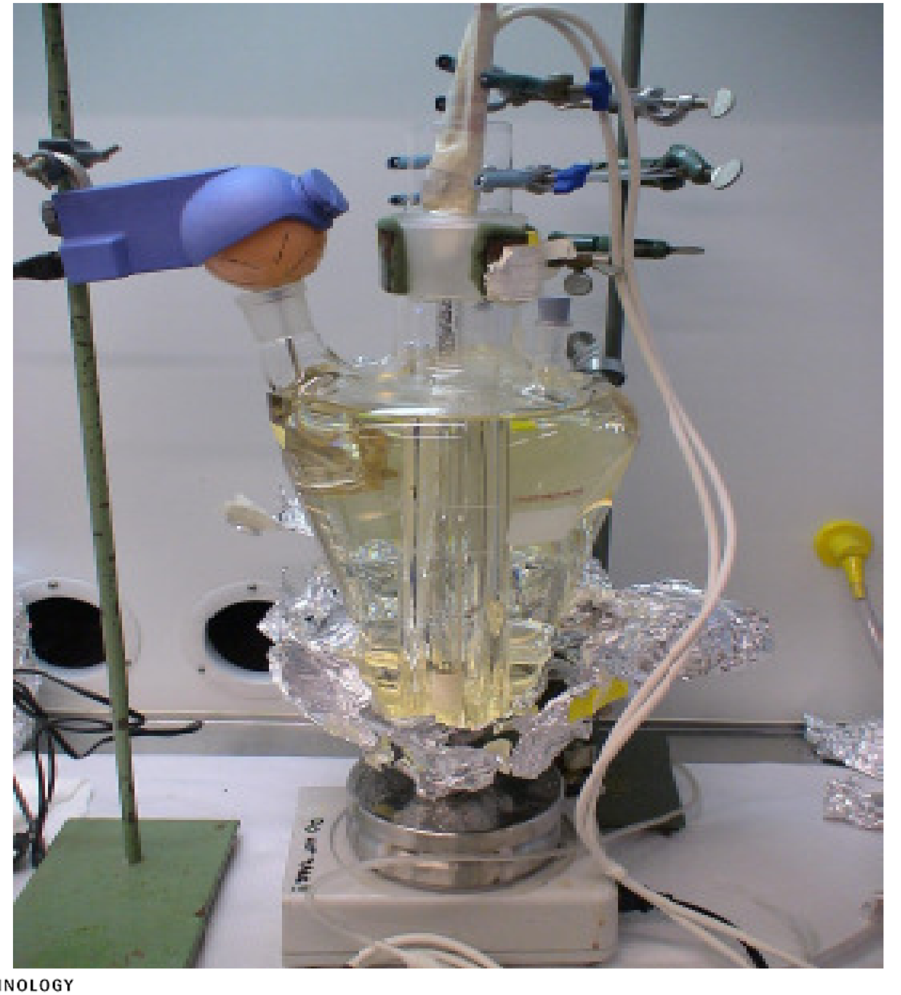
Reaction time: 72 hours

H_2O_2 concentrations: 0.005 mol/l
0.012 mol/l
0.024 mol/l
0.073 mol/l
0.050 mol/l
0.500 mol/L

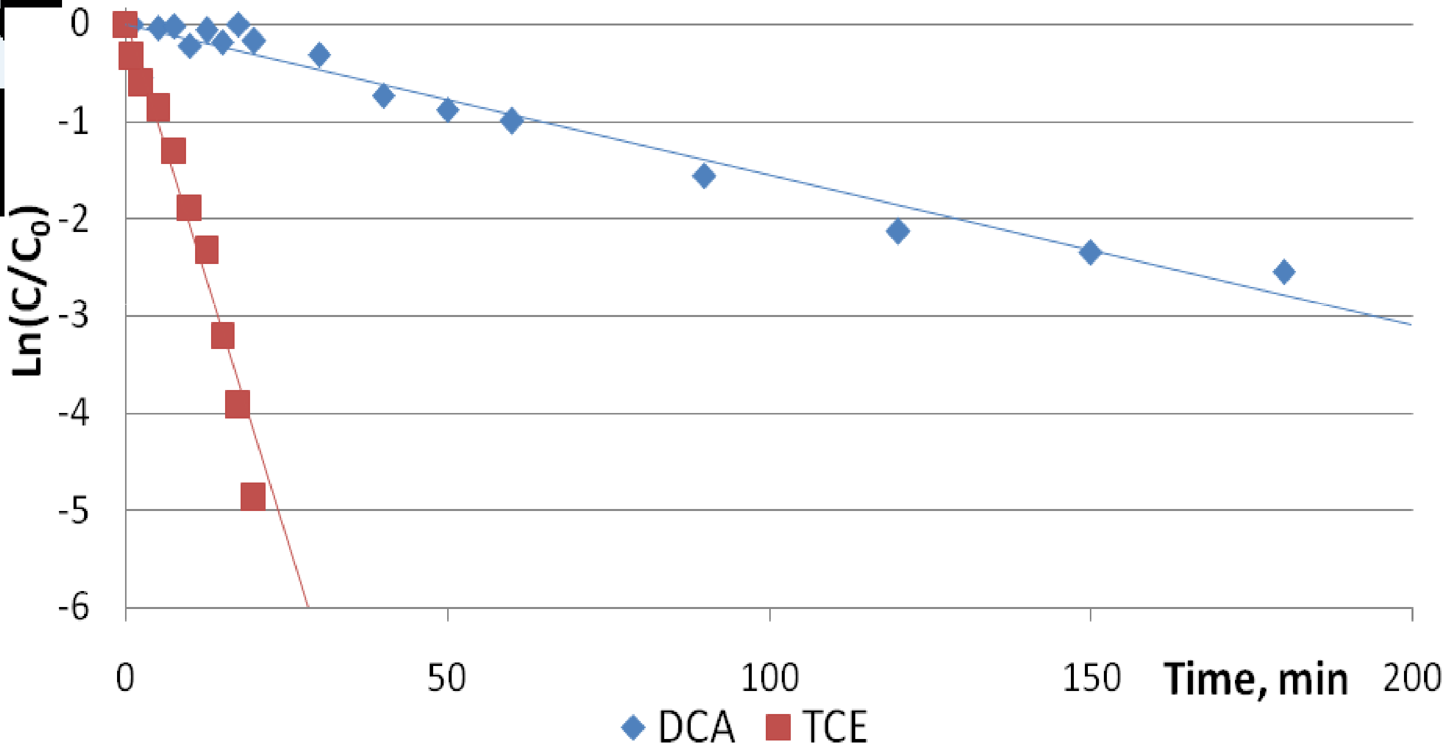
No iron addition

pH adjustment: in selected samples

Pohjaveden kunnostus talousvedeksi

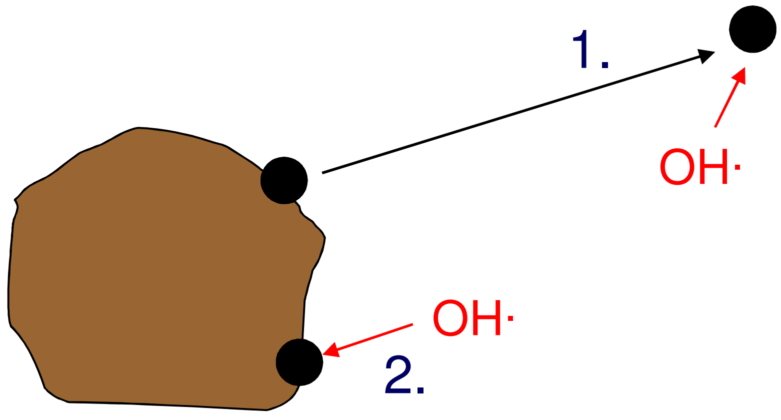


Ultraviolet light induced hydrogen peroxide DCA and TCE degradation results on a logarithmic scale



Reaktiot yhdisteiden kanssa voivat tapahtua

- Kaasufaasissa (VOC huokosilmassa)
- Nestefaasissa
- Kiinteän faasin pinnalla
  1. Desorptio → hapetus
- Esim NAPL pinnalla
  - Fassin väheneminen →
  - Mass reduction

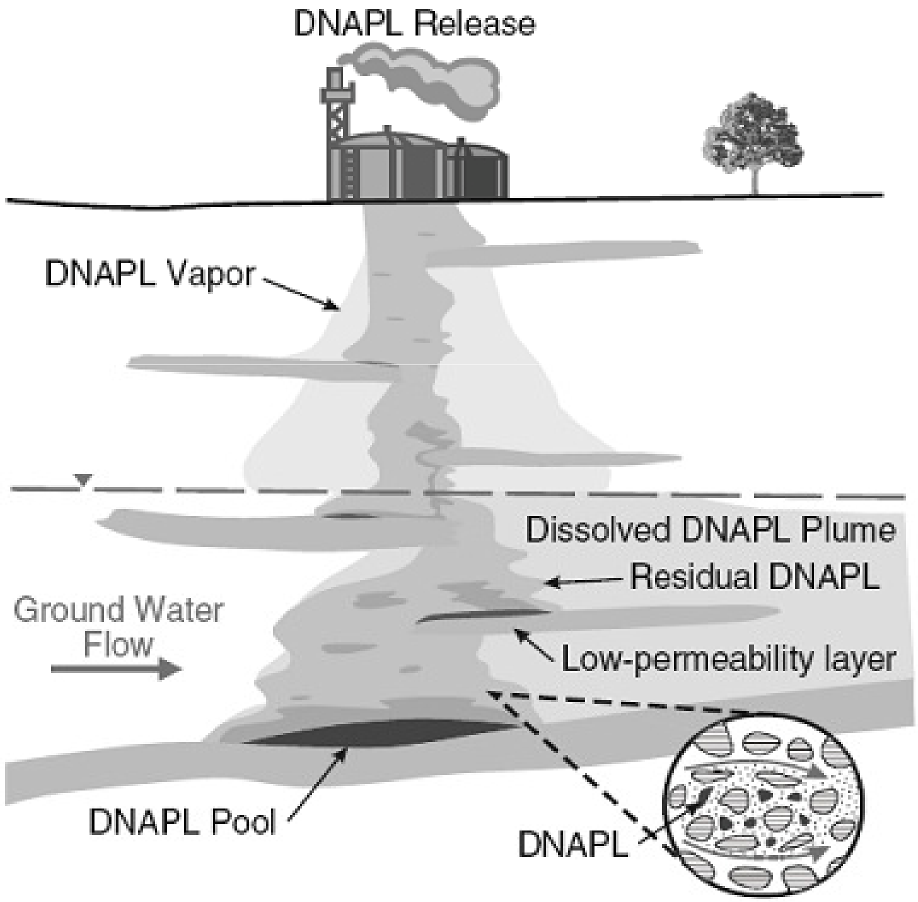


Maaperän ominaisuudet, hydrogeologia

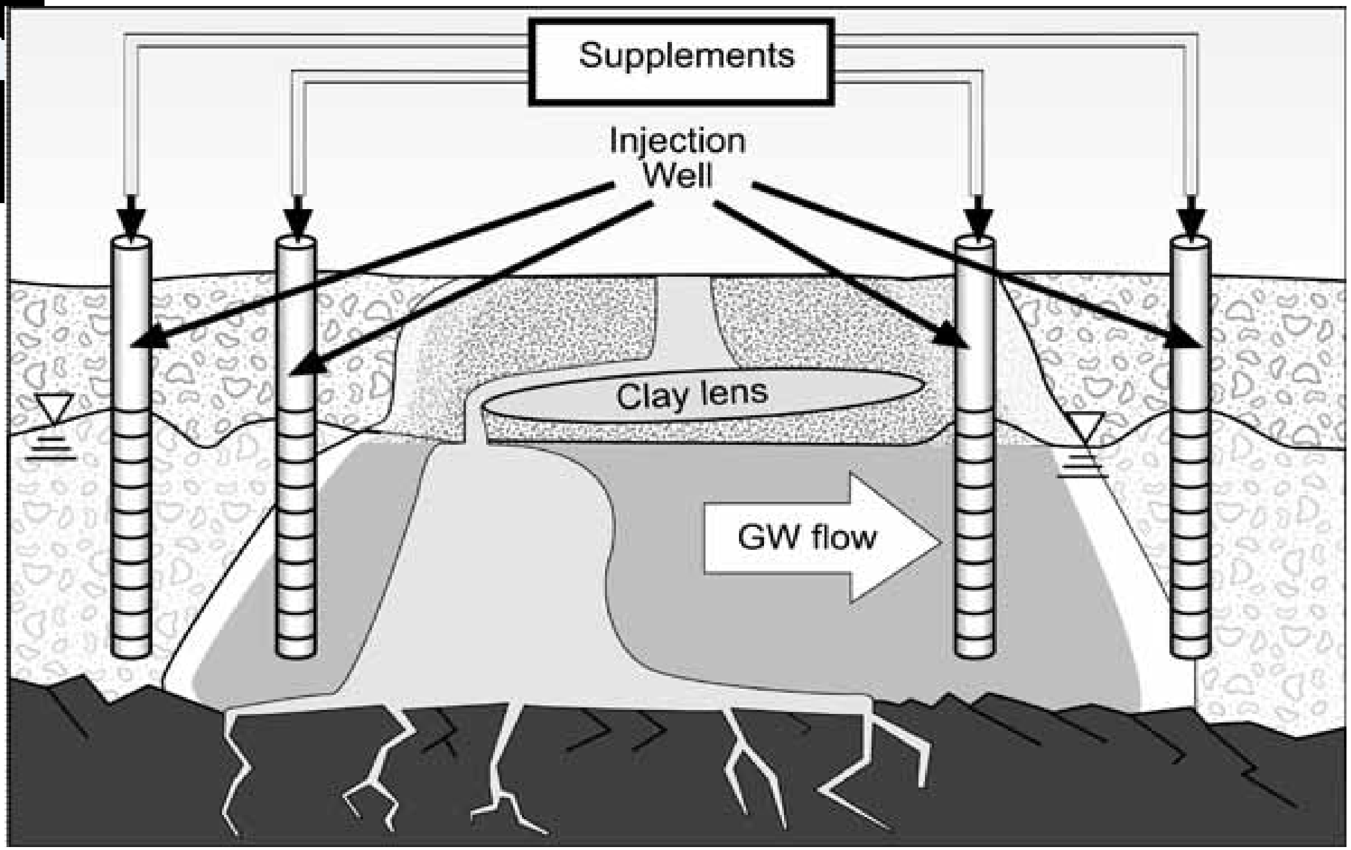
Tontin entinen ja tuleva käyttötarkoitus

Menetelmän hyväksyttävyys

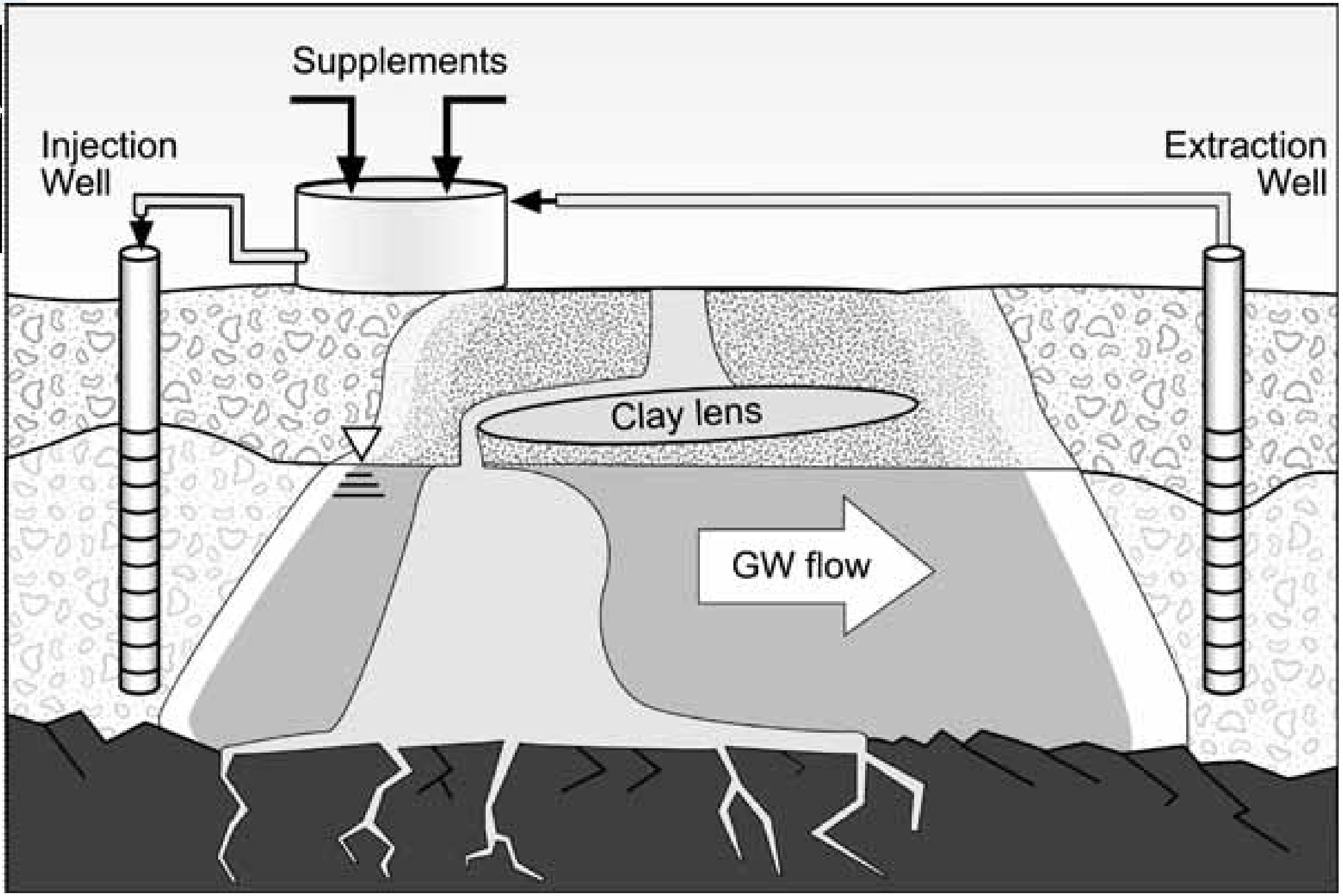
Fate and transport of chlorinated organic compound …ses in the subsurface (Sleep;ym., 2004)



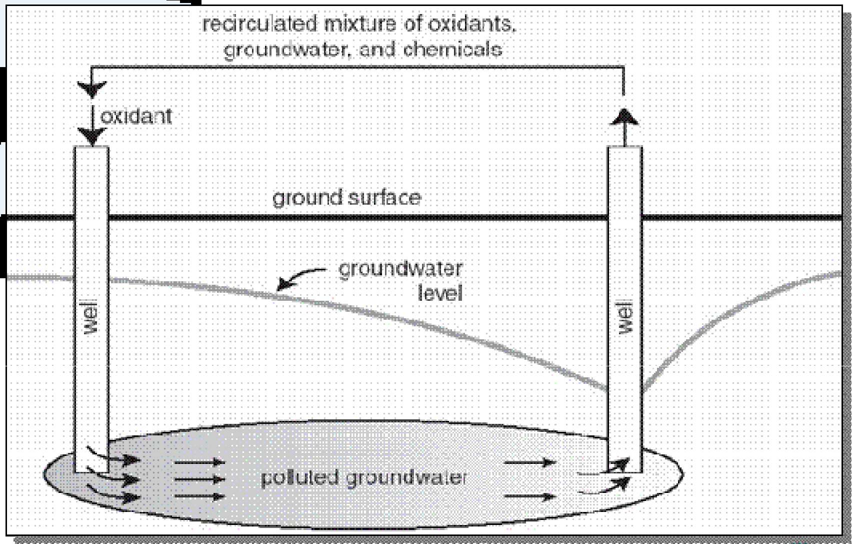
Direct injection system for DNAPL contaminated soil (EPA 2000) **EPA,** gineered approaches to in situ ioremediation of chlorinated solvents: fu entals and field applications [Journal]. - Washington DC : United States nvironmental Protection Agency, July 2000. - EPA 542-R-00-008.

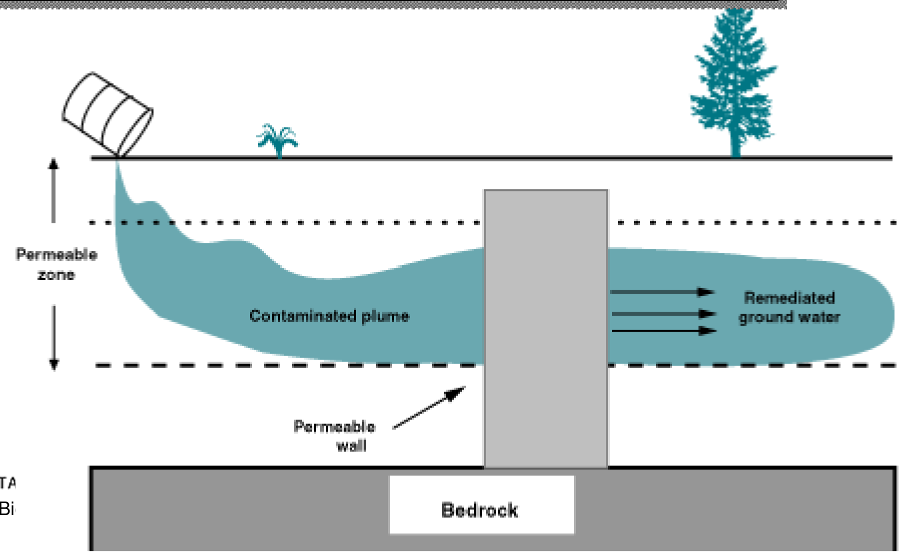


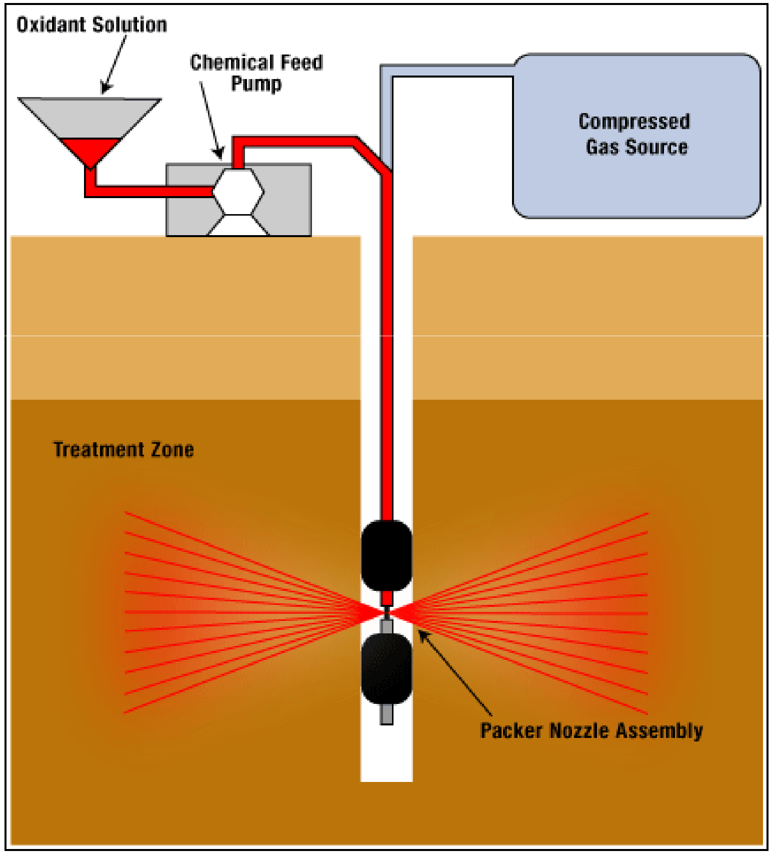
Recirculation system for DNAPL contaminated soil (EPA 2000)



Chemical oxidation methods







Oxidation in slurry

- Treatment procedure
  - Batch conditions
  - 40 g of soil and 40 mL of liquid phase (H_2O + H_2O_2)
  - Mixing on rotary shaker (160 rpm)
  - 72 hours of oxidation
  - with/without Fe^{2+} addition
  - with/without pH adjustment
  - Room temperature

Materials and methods

Fenton treatment

Shaking procedure

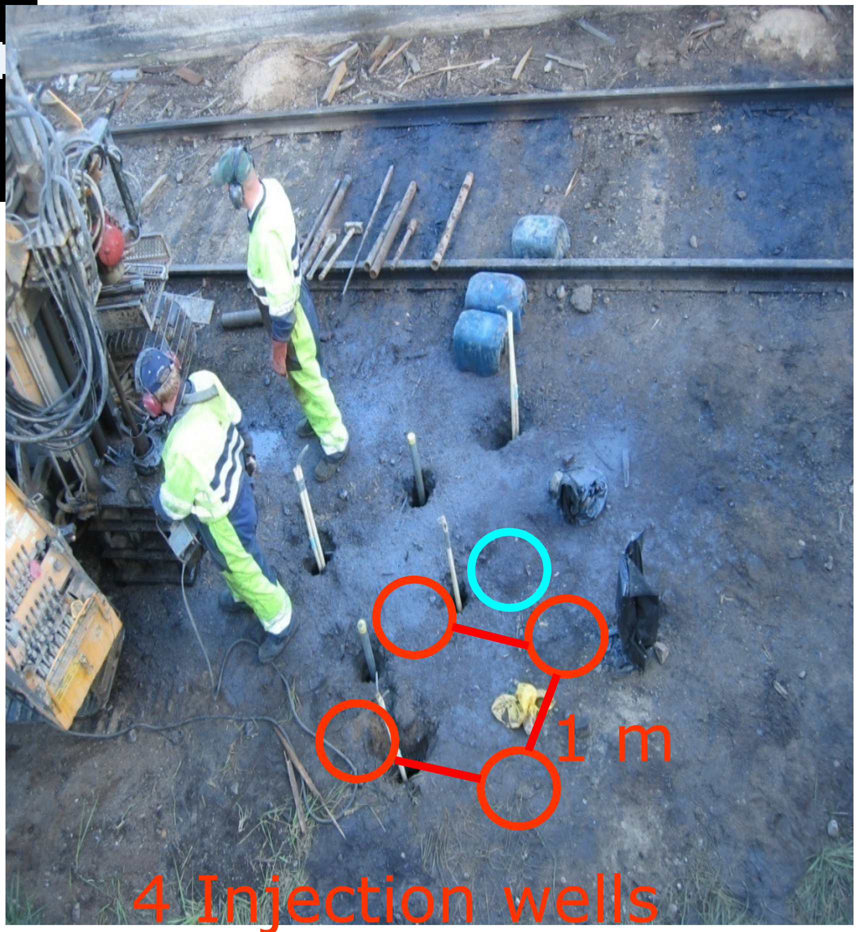
Reaction time: 72 hours

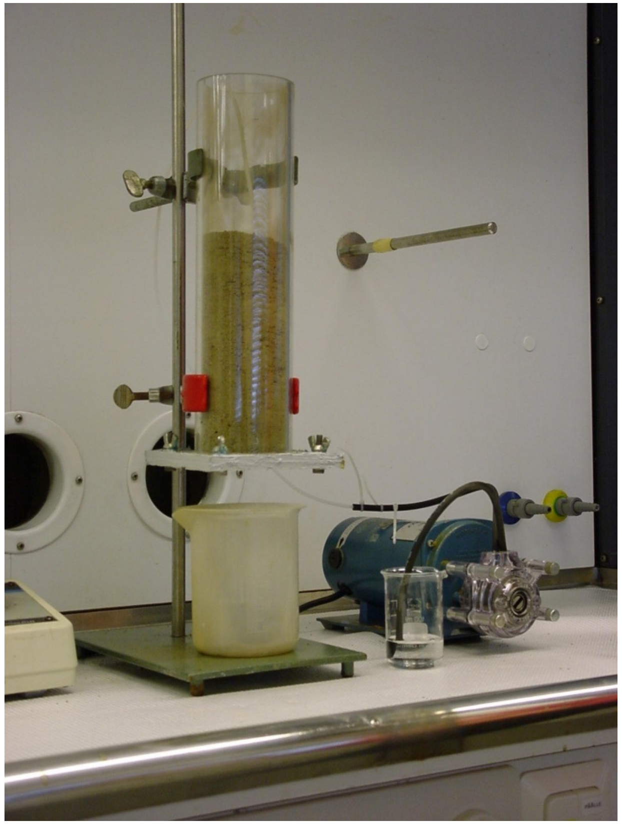
H_2O_2 concentrations: 0.005 mol/l
0.012 mol/l
0.024 mol/l
0.073 mol/l
0.050 mol/l
0.500 mol/L

No iron addition

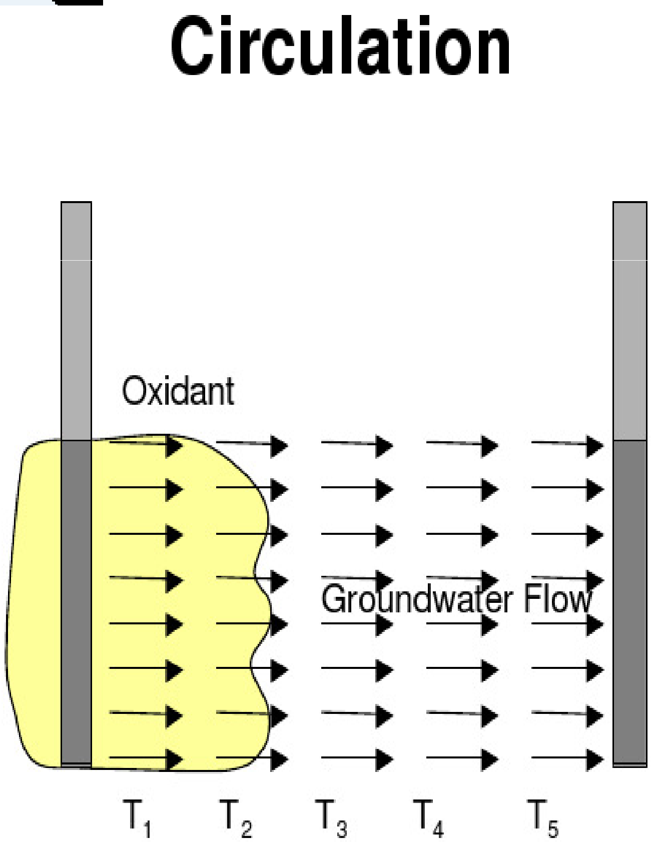
pH adjustment: in selected samples

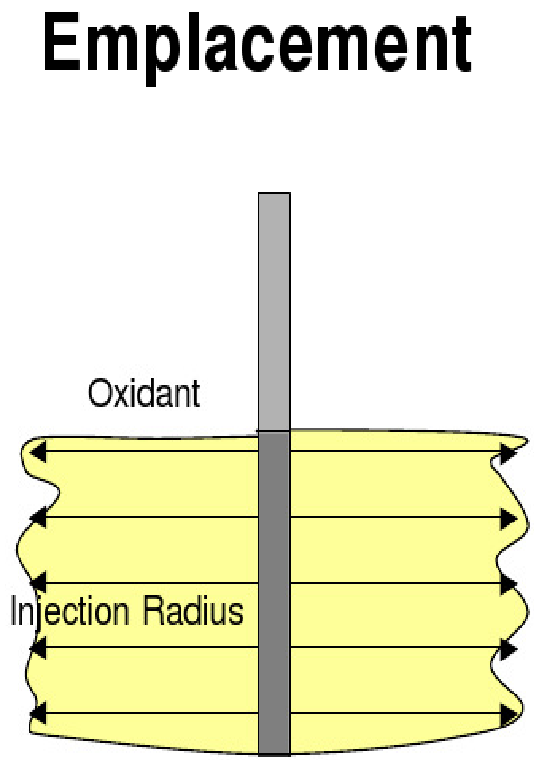
Remediation of PAH containing soil in sity and in lab (Tuomo Aunola)



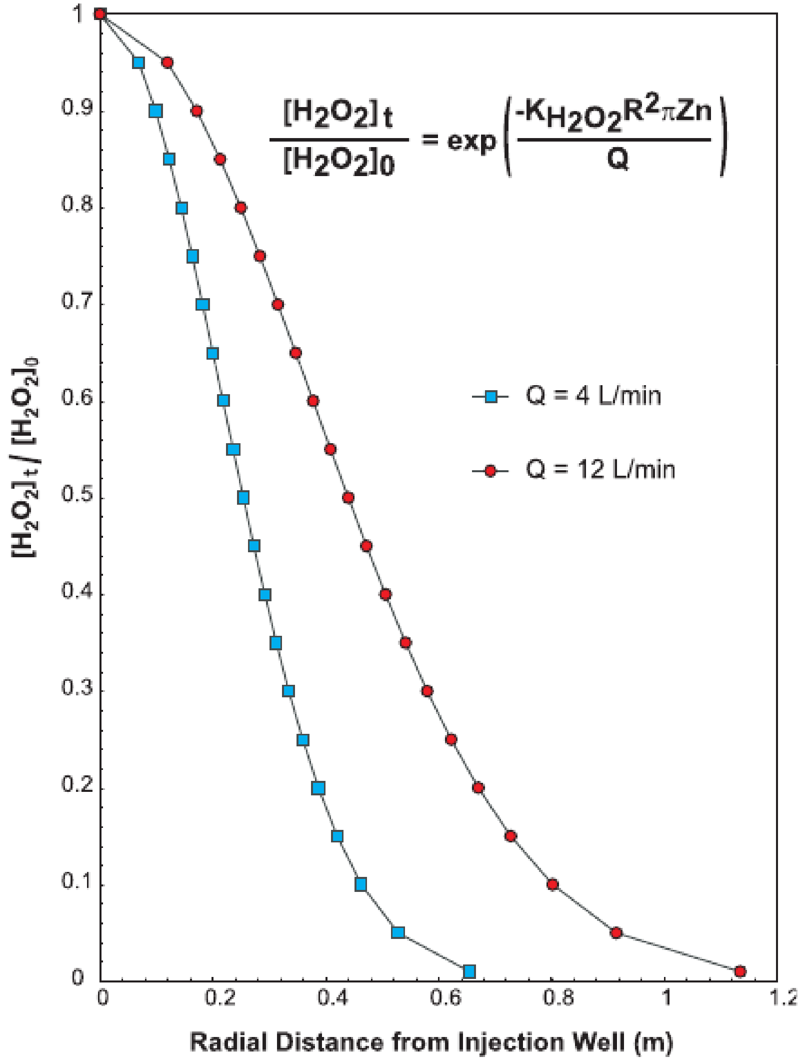


Hapetin maaperään tai pohjaveteen





Radius of H_2O_2 propagations from source Huling, S.G. and B. Pivetz. **"In-Situ Chemical Oxidation - Engineering Issue".** (2006) US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center, Ada, OK. EPA/600/R-06/072.



$k = 0.91\ h^{-1}$
$Z = 3m$
$n_f = 0.3$
R [m]
Q [L/min]

Huling and Pivetz, 2006

Government Degree an Assessment of Soil Contamination and Remediation Needs 1.12.2007

Threshold and lower and upper guideline values in Finland

Compound	Treshold value	Lower guideline value	Higherquaideline value
PAHs, mg/kg	**15**	**30 (e)**	**100 (e)**
PCDD/F, mg/kg[1]	**0.00001**	**0.0001 (h)**	**0.0015 (e)**

1) WHO – TEQ including dioxin like PCBs
e = environment, h = health

SWEDEN: 10 and 250 pg-TEQ/g sensitive and less sensitive land use

Drivers and pressures

- How clean is clean enough?

- Initial concentration vs. required / accepter concentration in the treated waste stream?

- How much it can cost compared to alternative, conventional techniques

- Indented use of site after treatment → risk based remediation?

References

- www.**redox**tech.com:

Huling, S.G. and B. Pivetz. **"In-Situ Chemical Oxidation - Engineering Issue".** (2006) US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center, Ada, OK. EPA/600/R-06/072