Conducting Persulfate Chemical Oxidation in Soil and Groundwater while limiting the Sodium and Sulfate Outtake in the Subsurface Aquifer

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Presentation summary

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- Excess Salt Issue in soil and groundwater
- Persulfate Oxidation Chemistries
- Alternative Salt Option
- Lab Scale Validation Study
- Additional Testing Phase
- Conclusion

Excess Salt Issue

Typical environmental impacts associated with excess salt in soil, surface water or groundwater are:

- Degradation of soil chemical properties and impaired vegetative growth;
- Degradation of soil physical properties caused by excess sodium concentrations;
- Degraded surface water or groundwater quality.
- **In-situ remediation, on-site soil washing or other treatments must not result in additional adverse effects on or off the site through transfer of contaminants to other media (e.g., groundwater).**

Source: Alberta Environnement –
Salt Contamination Assessment and Remediation Guideline – May 2001

Excess Salt Issue

In-situ remediation of saline-sodic soils involves:

1) Replacement of exchangeable sodium with calcium while maintaining sufficient EC in the soil solution to prevent swelling and dispersion;

2) Subsequent removal of salts (including sodium) in the soil solution by leaching with natural precipitation or irrigation. This step may involve collection and proper disposal of leachate.

Source: Alberta Environnement –
Salt Contamination Assessment and Remediation Guideline – May 2001

Typical Selected Ion Concentration

Table A.1 Selected Properties and Ions of Formation Waters from the Alberta Basin

Parameter	Minimum	Maximum	No. Of Samples
Depth (m)	104.3	3,632.3	689
Temperature (°C)	10	118	689
Na (mg/l)	390	100,800	694
K (mg/l)	5.6	8,800	694
Mg (mg/l)	0	7,800	694
Ca (mg/l)	4	38,700	694
Sr (mg/l)	0.2	1,320	690
Ba (mg/l)	0.04	680	564
F (mg/l)	0.01	22	465
Cl (mg/l)	305	199,510	694
Br (mg/l)	0.5	1,313	662
I (mg/l)	0.3	66	619
SO4 (mg/l)	1	6,444	680
HCO3 (mg/l)	10	7,750	694
pH***	4.29	8.1	666

***calculated at formation temperature and in equilibrium with calcite using SOLMINEQ.88 (computer model)

Table A.2 Selected Ion Concentrations from Seawater, River Water, and Brines

Parameter	River Water[a]	Seawater[a]	Formation Water[a] (Western Canada Basin)	Viking Formation (Swan Hills Field)[b]	Gilwood Formation (Swan Hills Field)[b]	Brine Water From Oil Battery[c]
Cl^{-1} (mg/l)	7.6	19,500	26,920	24,800	132,000	125,000
Na^{+1} (mg/l)	7.0	10,800	14,340	15,00	62,800	47,250
Ca^{+2} (mg/l)	36.0	413	2,210	570	16,100	20,434
Mg^{+2} (mg/l)	7.8	1,300	317	300	2,300	3,687
SO_4^{-2} (mg/l)	31.4	2,700	350	12	150	<3
HCO_3^{-1} (mg/l)	106	-	1,500	300	75	394
Salinity (mg/l)	203	35,334	46,400	-	-	201,567
Electrical Conductivity (dS/m)	<1[d]	-	-	19.6	-	187

a Hitchon et al, 1998
b Innes & Webster, 1978
c CAPP, 1996
d Aqualta, North Saskatchewan River, Rossdale (pers. comm. 1998)

Source: Alberta Environnement – Salt Contamination Assessment and Remediation Guideline – May 2001

Soil & Water Quality Guideline

Table 2.2 Soil Quality Guidelines for Unrestricted Land Use

Parameter		Rating Categories			
		Good	Fair	Poor	Unsuitable
Topsoil[c]	EC dS/m (salinity)	<2[a]	2 to 4	4 to 8	>8
	SAR (sodicity)	<4	4 to 8	8 to 12	>12[b]
Subsoil[c]	EC dS/m (salinity)	<3	3 to 5	5 to 10	>10
	SAR (sodicity)	<4	4 to 8	8 to 12	>12

a Some plants are sensitive to salts at EC < 2 dS/m (e.g., flax, clover, beans, wheat, peas, some garden crops).

b Material characterized by SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.

c Topsoil: surface A horizons on the control area, or the equivalent surface soil on the reclaimed site.
Subsoil: B and C horizons and the upper portion of the parent material.

Table 2.3 Commercial/ Industrial Soil Quality Guidelines

Parameter	CCME C/I Soil Criteria
EC	4 dS/m
SAR	12

Table 2.4 Selected Canadian Water Quality Guidelines

Water Use	Parameter
Drinking Water	• Chloride – 250 mg/l • Total dissolved solids – 500 mg/l • Nitrate (as N) – 10 mg/l • Nitrite (as N) – 1 mg/l (where nitrates and nitrites are both present, the total acceptable concentration is 10 mg/l)
Livestock Watering	Total dissolved solids – 3000 mg/l[a] 100 mg/l for nitrate plus nitrite, and 10 mg/l for nitrite alone

a Water with higher TDS concentrations can be used but other factors should be taken into consideration (e.g., type of livestock, age, reproductive state). See CCME (1999).

Source: Alberta Environnement – Salt Contamination Assessment and Remediation Guideline – May 2001

Chemical Oxidation Principles

- Oxidants are introduced or mixed into the soil and groundwater to react with the organic contaminants
- Chemical oxidation treatments are commonly used in potable and wastewater applications
- Oxidants are non-specific and will react with the targeted contaminants AND with the soil organic and mineral content.
- Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds
- Water is the carrier for the oxidants used in chemical oxidation (except for ozone)

Oxidation – Reduction Potentials of Various Chemistries

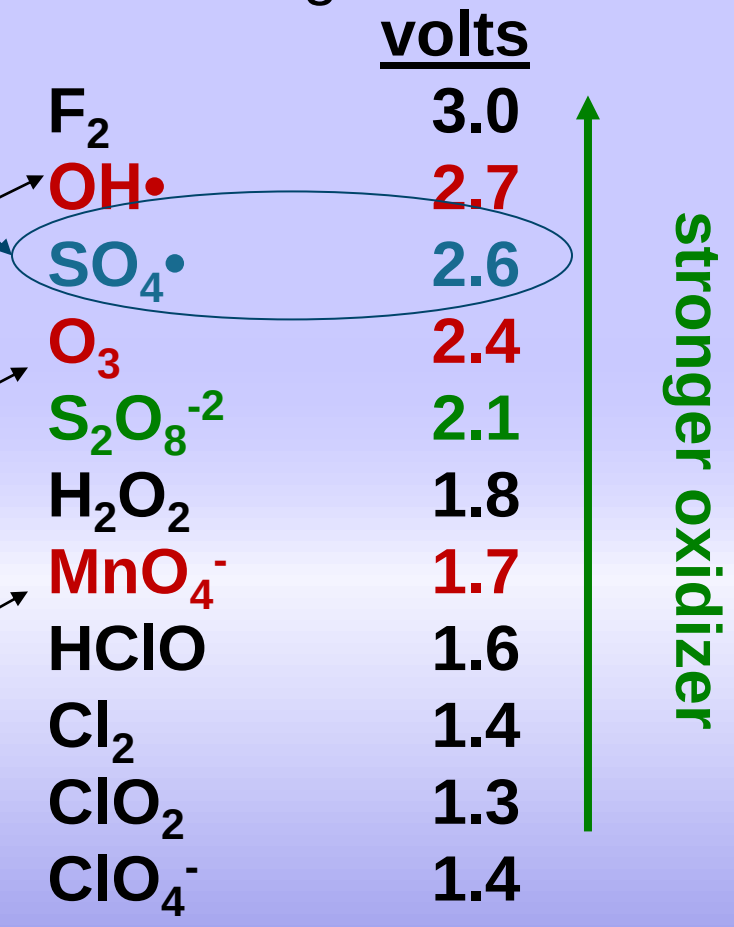
Higher the oxidation potential the stronger the oxidizer

Klozur® Activated Persulfate
- Treats wide range of contaminants
- Sulfate radical forms slower than the hydroxyl radical, allowing a larger radius of influence

Fenton's
- Treats wide range of contaminants
- Short subsurface lifetime
- Difficult to apply in reactive soils

Ozone
- Treats wide range of contaminants
- Short subsurface lifetime
- Limited use in saturated zone

Permanganate
- Treats limited range of contaminants
- Long subsurface lifetime
- Potential effects on hydrogeology



Persulfate Chemistries for the Remediation of Soil and Groundwater

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Strong Oxidizer

Persulfate anion:

$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-2}$ $E^0 = 2.12$ v

Persulfate radical:

$SO_4^{\bullet -} + e^- \rightarrow SO_4^{-2}$ $E^0 = \sim 2.6$ v

In Comparison:

H_2O_2	$E^0 = 1.8$ v
$OH^{\bullet -}$	$E^0 = 2.7$ v
MnO_4^-	$E^0 = 1.7$ v

Persulfate Activation Chemistries for the Remediation of Soil and Groundwater

- **Heat**
- **Divalent metals and zero valent iron (Fe^{+2})**
- **Chelated metals**
- **Hydrogen peroxide activation**
- **Alkaline activation**
- **Combination persulfate/permanganate for soil and groundwater**

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(United Technologies and U. Conn)
Purchase of FMC's Klozur® Persulfate includes rights
to practice the inventions covered by the patents in the purchase price of the product.

- **One key to success: Proper activation for your contaminant and site lithology and hydrogeology**

Sodium Persulfate for the Remediation of Soil and Groundwater

TECHNOLOGY	BTEX	chlorinated ethane's	chlorinated ethane's	oxygenates (MTBE)	PCB	dioxins
PERSULFATES						
NON ACTIVATED PERSULFATE	Y	N	N	N	N	N
NON CHELATED METAL ACTIVATION	Y	Y	N	Y	?	Y
HEAT ACTIVATION	Y	Y	Y	Y	Y	?
CHELATED METALS ACTIVATIONS	**Y**	**Y**	**N**	**Y**	**?**	**Y**
HYDROGEN PEROXIDE ACTIVATION	**Y**	**Y**	**?**	**?**	**?**	**?**
ALKALINE ACTIVATION	**Y**	**Y**	**Y**	**?**	**?**	**Y**

Sodium Persulfate for the Remediation of Soil and GroundWater

Stability

Sodium persulfate is a safe to handle, stable crystal.

Persulfate radicals have a significantly longer life *in situ* than the hydroxyl radicals, allowing for greater penetration into the contamination zone.

Soluble

The solubility of sodium persulfate is 73 g / 100 g H_2O at 25 C.

Easy to mix and dilute.

Low Soil Oxidant Demand

Less than permanganate (sodium or potassium) or hydroxyl radical (hydrogen peroxide, percarbonate)

Other Persulfate salt (potassium or ammoniu comparative properties

Stability

Sodium persulfate is a safe to handle, stable crystal as with potassium and ammonium,

ALL Persulfate radicals have a significantly longer life *in situ* than peroxide radicals, allowing for greater penetration into the contamination zone.

Solubility

Ammonium persulfate 85 g / 100 g H_2O at 25 C
Potassium persulfate 6 g / 100 g H_2O at 25 C
Sodium persulfate 73 g / 100 g H_2O at 25 C

Targeted groundwater concentration above 5 g of persulfate per litre

Nitrogen content in ammonium persulfate could help Bioremedation processes after the oxidation phase

Soil Oxidant Demand (SOD)

- Any oxidant will react and be consumed by the organic material contained in the soil and by some minerals.
- Bench scale testing and/or pilot testing are recommended for better and more exact SOD evaluation

Proof of Concept – Soil oxidant Demand Comparison

- Typical SOD value for sodium persulfate 100 % ranges from 1 to 5 g per kg of soil
- Lab analysis have shown that ammonium persulfate and potassium persulfate have similar value than sodium persulfate showing the same reactivity with the same soil matrix.

Proof of Concept – Contaminant Removal Rate (persulfate alkaline activation)

Contaminant	Test soil A (sandy silt) DRO C10-C50 Initial Soil contaminant concentration (mg/kg)	Test soil B (silty-clay) DRO C10-C50 Initial Soil contaminant concentration (mg/kg)	Test B (silty-clay) PAH Initial Soil contaminant concentration (mg/kg)
Untreated Blank	C10-C50 PHC 5650 mg/kg	C10-C50 PHC 2100 mg/kg	PAH 26.9 mg/kg
Sodium Persulfate	C10-C50 PHC 2900 mg/kg	C10-C50 PHC 1440 mg/kg	PAH 1.5 mg/kg
Potassium Persulfate	C10-C50 PHC 3200 mg/kg	C10-C50 PHC 1020 mg/kg	PAH 0.6 mg/kg
Ammonium Persulfate	C10-C50 PHC 4100 mg/kg	C10-C50 PHC 1450 mg/kg	PAH 0.7 mg/kg

Additional Testing Phase

- Alternative Activation Methods to be validated with potassium and ammonium persulfate (heat, chelated metals, hydrogen peroxide at various mol ratios)
- Sulphate anion fate, Electrical Conductivity (EC) and SAR impact when using various activator package (lime, potassium hydroxide, calcium peroxide)

Additional Testing Phase

Soil and Groundwater Chemistry

- Salinity (most laboratories have a detailed salinity analysis which includes relevant ions such as chloride)
- Sodium adsorption ratio (SAR)
- Electrical conductivity (EC)
- pH
- Soluble Na, Ca, Mg, K, SO4, Cl, and HCO3;
- % saturation;
- Theoretical gypsum requirement (TGR) (optional).
- Carbonate content of soils
- Background groundwater chemistry (pH, EC, N, Ca, K, Mg, Na, Cl)

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- **Training and Education:** technical transfer session, health and safety training;
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- **Products supply, logistic and storage**: nutrients, bacterial preparations strains, oxidants, reducing agents, catalysts, oxygen and hydrogen release compounds, co solvent-surfactant blends
- **Laboratory Services and Analysis**: Groundwater Parameter Analysis, Tracer Study, Soil and Groundwater Oxidant Demand Evaluation (SOD), Bench Scale Treatability testing in saturated and unsaturated conditions.

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Thank you for your attention !

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