In Situ Chemical Oxidation:

Performance, Practice, and Pitfalls

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ISCO Presentation Topics

Overview of ISCO (In Situ Chemical Oxidation)

- What oxidants are available
- How are they applied

How to decide which to use

- Cost
- Performance

Designing an ISCO Project

Available Oxidants

- Ozone
- Hydrogen Peroxide
- Calcium Peroxide
- Sodium Persulfate
- Sodium/Potassium Permanganate

Ozone

Molecular Weight - 48g   Equiv. Weight - 24g

Solubility - 600 mg/L

Availability – On site generation

- **3-5% Air**
- **8-12% O_2**

Reactions

- **Oxidation**
  - $O_3 + 2H^+ + 2e^-$ ® $O_2 + H_2O$ $E^o = 2.07v$
  - $2OH\cdot + 2H^+ + 2e^-$ ® $2H_2O$ $E^o = 2.76v$
- **Hydroxyl Radical Formation**
  - $O_3 + H_2O$ ® $O_2 + 2OH\cdot$ (Slow)
  - $2O_3 + 3H_2O_2$ ® $4O_2 + 2OH\cdot + 2H_2O$ (Fast)
- **Decomposition**
  - $2O_3$ ® $3O_2$ $4HO\cdot$ ® $2H_2O + O_2$

Hydrogen Peroxide

Molecular Weight- 34g Equiv. Weight - 17g, 34g ($OH^{\bullet}$)

Solubility - Miscible

Availability - 30%, 50% Solutions

Reactions

Oxidation

$2OH^{\cdot} + 2H^{+} + 2e^{-}$ ® $2H_2O$ $E^{o} = 2.76v$

$H_2O_2 + 2H^{+} + 2e^{-}$ ® $2H_2O$ $E^{o} = 1.77v$

$HO_2^{-} + H_2O + 2e^{-}$ ® $3OH^{-}$ $E^{o} = 0.88v$

Hydroxyl Radical Formation

$H_2O_2 + Fe^{+2}$ ® $Fe^{+3} + OH^{\cdot} + OH^{-}$

$2O_3 + 3H_2O_2$ ® $4O_2 + 2OH^{\cdot} + 2H_2O$

Decomposition

$2H_2O_2$ ® $2H_2O + O_2 +$ D (Above 11% steam is formed)

$4HO^{\cdot}$ ® $2H_2O + O_2$

Calcium Peroxide

Molecular Weight- 72g Equiv. Weight - 36g

Solubility – Slightly Soluble

Availability – Powder 75% Purity

Reactions

Oxidation

$CaO_2 + 2H_2O + 2e^-$ ® $Ca(OH)_2 + 2OH^-$ $E^o = 0.9$

$HO_2^- + H_2O + 2e^-$ ® $3OH^-$ $E^o = 0.88v$

Reduction:

$HO_2^- + OH^-$ ® $O_2 + H_2O + 2e^-$

Hydrolysis

$CaO_2 + H_2O + OH^-$ ® $Ca(OH)_2 + HO_2^-$

Decomposition

$2CaO_2 + 2H_2O$ ® $2Ca(OH)_2 + O_2$ + D

Sodium Persulfate

Molecular Weight- 238.05g Equiv. Weight - 119.02g

Solubility - 56 g/100 mL

Availability – Crystalline Solid

Reactions

- **Oxidation**
  - $S_2O_8^{=} + 2e^{-} \circledR 2SO_4^{=} \quad E^{o}\ 2.01v$
  - $HSO_5^{-} + 2H^{+} + 2e^{-} \circledR HSO_4^{-} + H_2O \quad E^{o}\ 1.8v_{EST}$
- **Sulfate Radical Formation**
  - $SO_4^{-\cdot} + e^{-} \circledR SO_4^{=} \quad E_o = 2.5v_{EST}$
  - $S_2O_8^{=} \circledR 2SO_4^{-\cdot}$
- **Decomposition**
  - $2Na_2S_2O_8 + 2H_2O \circledR O_2 + 2H_2SO_4 + 2Na_2SO_4$
- **Hydrolysis**
  - $Na_2S_2O_8 + H_2O \circledR NaHSO_4 + NaHSO_5$

Permanganate (Na/K)

Molecular Weight- 158.04g K; 141.9 Na

Equivalent Weight - 52.6g K; 47.3 Na

Solubility -   K 64g/l @ 20^{o}C; Na >400 g/L @ 20^{o}C

Availability   K Purple Crystalline Solid;

Na – 40% Solution

Reactions

Oxidation

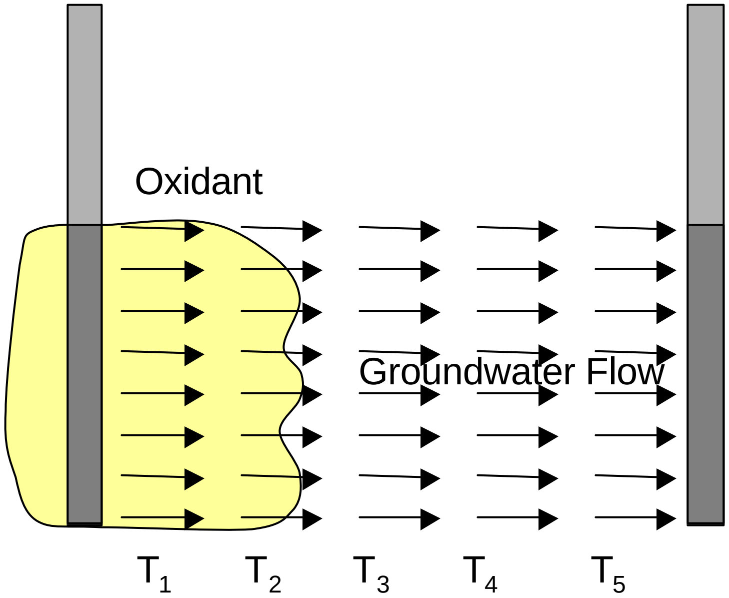
MnO_4^- + $4H^+$ + $3e^-$ ® MnO_2 + $2H_2O$ E_o = 1.695v

Decomposition

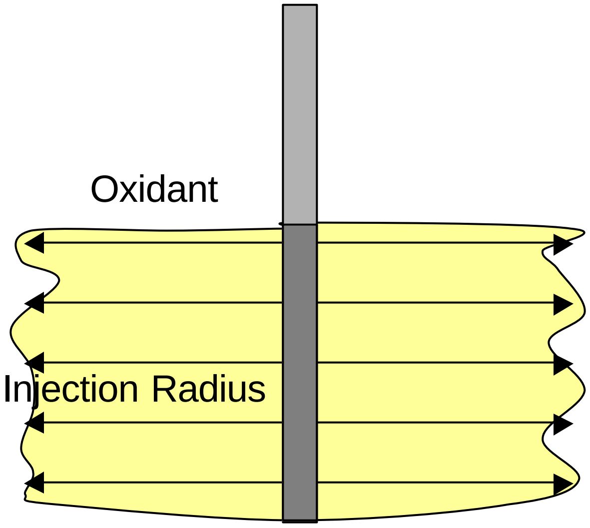
$4KMnO_4$ + $4H^+$ ® $3O_2$ +$2H_2O$ + $4MnO_2$ + $4K^+$

Application Methods

Circulation



Emplacement



Circulation Methods

Injection Only

- Galleries
- Wells
  - Vertical
  - Horizontal
- Trenches
- Direct injection

Injection & Recovery

- Galleries & Wells
- Trenches
- Conventional Wells
  - Vertical
  - Horizontal
- Recirculation Wells

Emplacement Methods

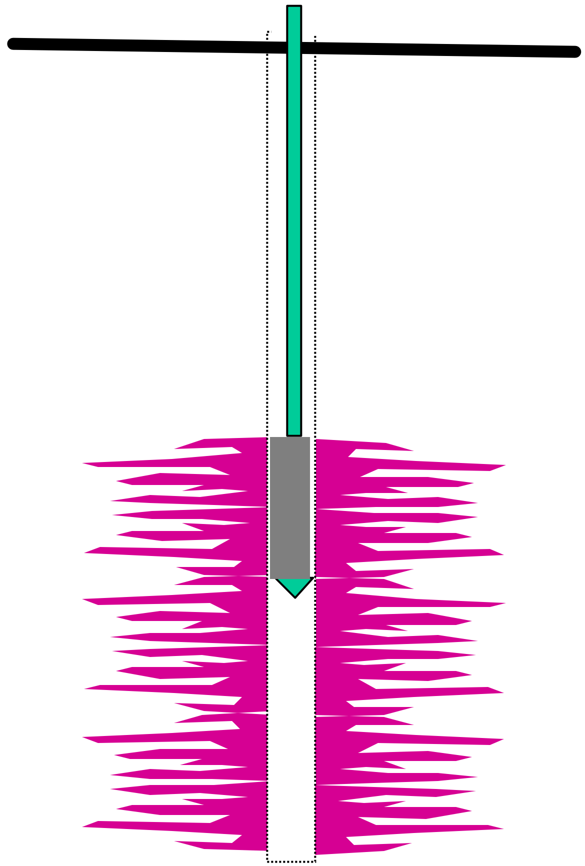
- **Soil mixing**
  - **Back-hoe, Excavator**
  - **MITU (Trencher)**
  - **Augers**

Power

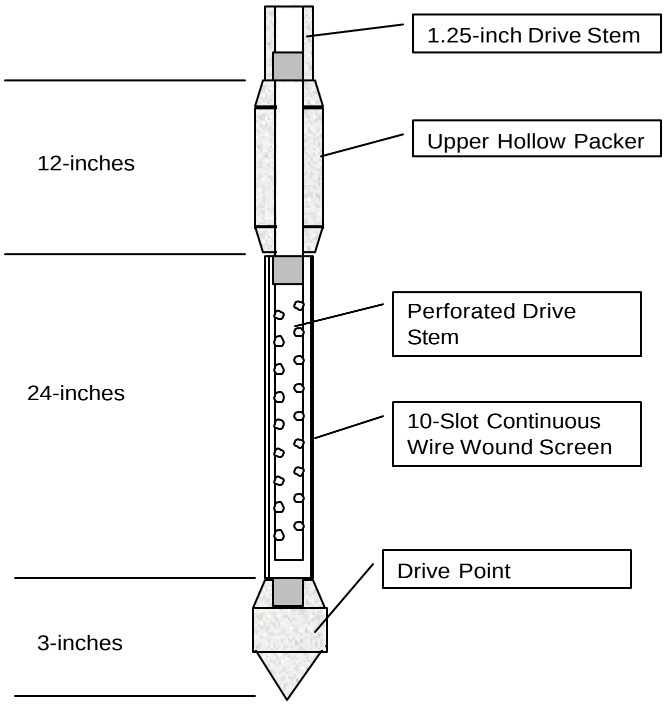
- **Pressurized well injection**
- **Geoprobe injection**
- **Pneumatic fracturing**
  - **Channel creation**
  - **Direct injection**
- **Hydraulic fracturing**
  - **Channel creation**
  - **Direct injection**
- **Jet grouting**

Push Tool Injection

Sequential Injection



Injection Tip Detail



Reactivity of Oxidants

Oxidant	Amenable CVOC's	Reluctant CVOCs	Recalcitrant CVOCs
Peroxide, Old Fenton's	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2	TCA, CT, $CHCl_3$
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2	TCA, CT, $CHCl_3$
Calcium Peroxide	PCE,TCE, DCE, VC, CB	TCA, CH_2Cl_2	CT, $CHCl_3$
Potassium Permanganate	PCE, TCE, DCE, VC,		TCA, CT, $CHCl_3$, DCA, CB, CH_2Cl_2
Sodium Permanganate	PCE, TCE, DCE, VC,		TCA, CT, $CHCl_3$, DCA, CB, CH_2Cl_2
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2, $CHCl_3$	TCA, CT
Sodium Persulfate, Heat	All CVOCs		

Reactivity of Oxidants

	B	TEX	PAHs	Phenols	Explosives	PCBs	Pesticides
Peroxide, Old Fenton's	H	H	M	H	M	L	L
Peroxide, New Fenton's	H	H	M	H	M	L	L
Potassium Permanganate	NR	H	H	H	H	L	M
Sodium Permanganate	NR	H	H	H	H	L	M
Sodium Persulfate, Fe	H	H	M	H	M	L	M
Sodium Persulfate, Heat	H	H	H	H	H	H	H
Ozone	M	M	H	H	H	H	H

Heated Persulfate is the most reactive oxidant

Oxidant Usage

$[\text{Oxidant}]_{\text{Required}}$ =

$[\text{Stoichiometric Demand}]_{\text{Contaminant}}$ +

[Soil Oxidant Demand] +

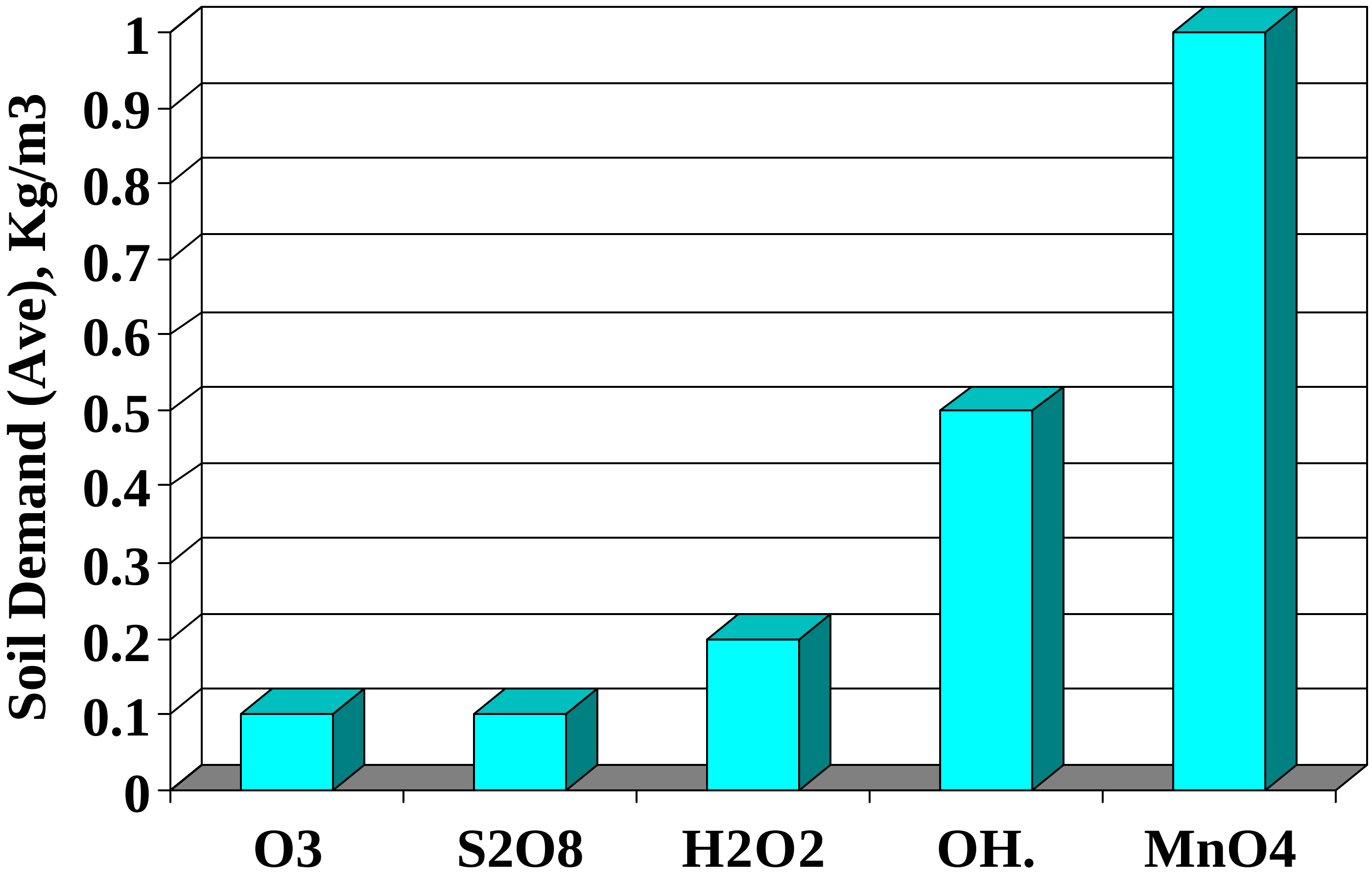
$[\text{Metals}]_{\text{Red}}$

$[\text{Organic Carbon}]_{\text{Oxidizable}}$

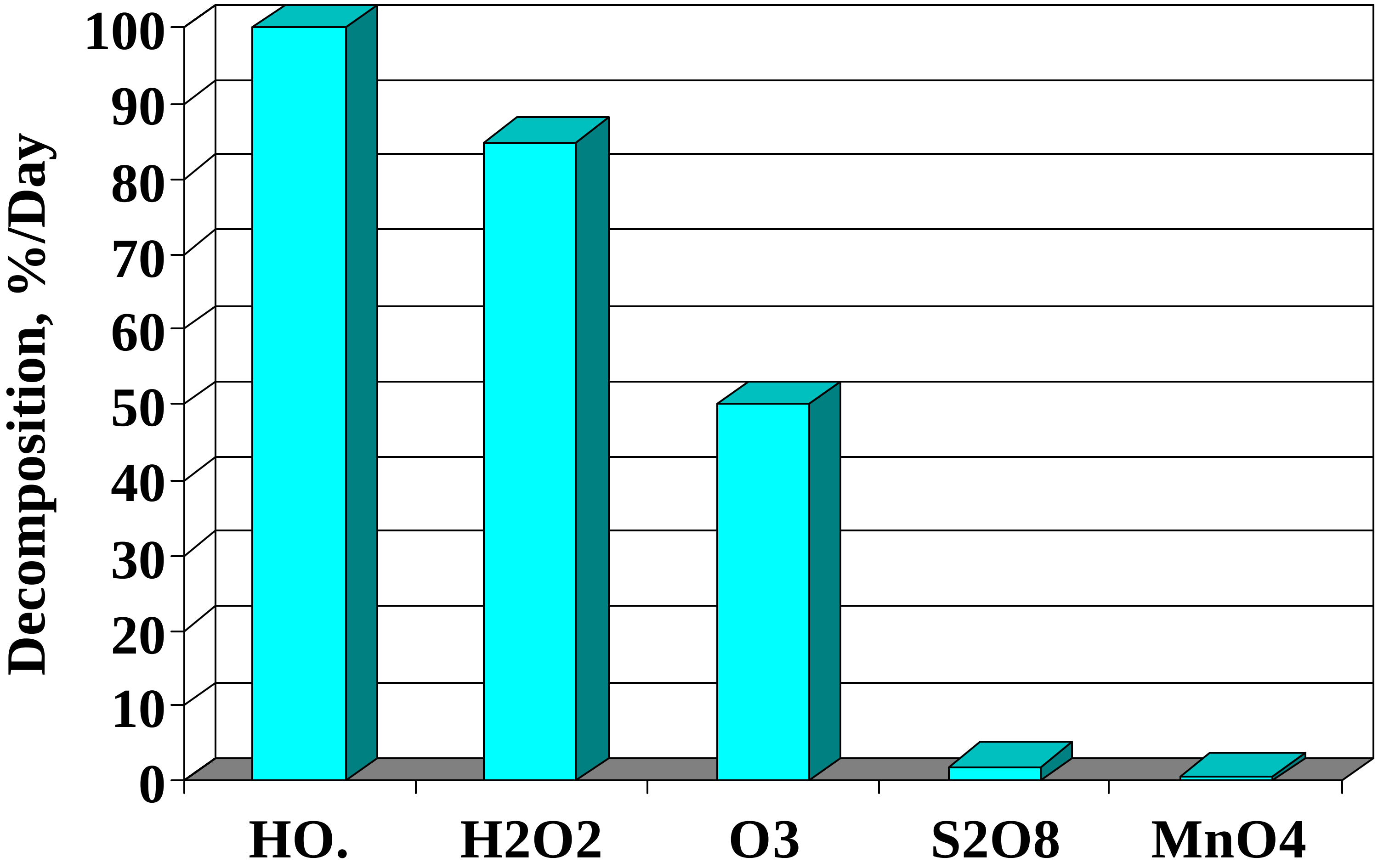
$[\text{Decomposition}]_{\text{Oxidant}}$

Decomposition and SOD are critical and often overlooked factors

SOD Soil Oxidant Demand



Decomposition Rates



Comparison of Oxidants

Oxidant	Limitations	Equivalent Weight	Oxidant Cost $/Lb	Oxidant Cost $/1000Equiv	Wt of 1000 Equiv, Lb	Chief Advavantage
Peroxide, Old Fenton's	Stability (10-95% decomp/hr), low pH	34	$0.75	$56	75	Reactivity, costs
Peroxide, New Fenton's	Stability (10-50% decomp/hr)	34	$0.75	$56	75	Reactivity, costs, pH
Calcium Peroxide	Not Soluble, Reaction Speed	36	$3.00	$237	105.7	Stability
Potassium Permanganate	Soil oxidant demand	52.6	$1.40	$162	115.8	Ease of use,
Sodium Permanganate	Soil oxidant demand	47.3	$5.95	$620	104.2	Ease of use,
Sodium Persulfate, Fe	Stability (10-25% decomp/wk), low pH	119	$1.08	$283	262	No SOD, reactivity
Sodium Persulfate, Heat	Stability (20-50% decomp/wk), low pH, heating costs	119	$1.08	$283	262	Reactivity

Comparison of Oxidants

Oxidant	Cost/1000 Equivalents	Cost @ Max Decomp	Cost @ Min Decomp
Hydrogen Peroxide	$56	$1,120	$70
Potassium Permanganate	$162	$165	$162
Sodium Permaganate	$619	$625	$619
Sodium Persulfate	$262	$350	$284
Calcium Peroxide	$237	$249	$239
Ozone	$42	$55	$45

Peroxide is cheapest oxidant <u>if it is stable</u>.

Comparison of Oxidants

Impact of SOD on Costs

Oxidant	Cost $/Lb.	Chemical Cost, $/yd^3 (Xylene)		
		10 mg/L	50 mg/Kg	1000 mg/Kg
Sodium Persulfate, Low SOD	1.10	0.58	8.70	164
Sodium Persulfate, High SOD	1.10	0.58	8.70	164
Potassium Permanganate, Low SOD	1.50	0.40	3.59	92.1
Potassium Permanganate, High SOD	1.50	6.00	9.19	97.2

Notes: Low SOD 0.1 g/kg, High SOD 3 g/kg

High SOD affects Permanganate economics

Comparison of Oxidants

Oxidant	Solubility	Maxium Mass Delivery, Kg/1000 L	Maxium Mass Delivery, K Eq/1000 L
Hydrogen Peroxide	Miscible	100 (11%)	3
Potassium Permanganate	6.40%	64	1.2
Sodium Permaganate	40%	400	9.36
Sodium Persulfate	56%	560	4.7
Calcium Peroxide	Insol.	100 (Slurry)	2.7
Ozone	600 mg/L	0.6	0.025

Mass delivery is a function of solubility and equivalent weight

Comparison of Oxidants

Oxidant	Stability, % Loss/day	Speed of Reaction	$T_{1/2}$ @ Max Decomp	Max Travel Distance, m Max Decomp, GW Flow @ 0.5 m/day
Hydrogen Peroxide*	10 - 95+	6-12 Hrs	10 Hrs	1.2
Calcium Peroxide	1 - 5	2 - 7 Days	10 Days	NA - Solid
Potassium Permanganate	0.1 - 1.0	1 - 3 Days	50 Days	125
Sodium Permaganate	0.1 - 1.0	1 - 3 Days	50 Days	125
Sodium Persulfate	1 - 3	2 - 7 Days	17 Days	42.5
Ozone	1 - 5	1 - 2 Hours	10 Days	NA - Depends on gas Flow

Oxidant	$T_{1/2}$ @ Min Decomp	Max Travel Distance, m Min Decomp, GW Flow @ 0.5 m/day
Hydrogen Peroxide	5 Days	12.5
Calcium Peroxide	50 Days	NA - Solid
Potassium Permanganate	500 Days	1250
Sodium Permaganate	500 Days	1250
Sodium Persulfate	50 Days	125
Ozone	50 Days	NA - Depends on gas Flow

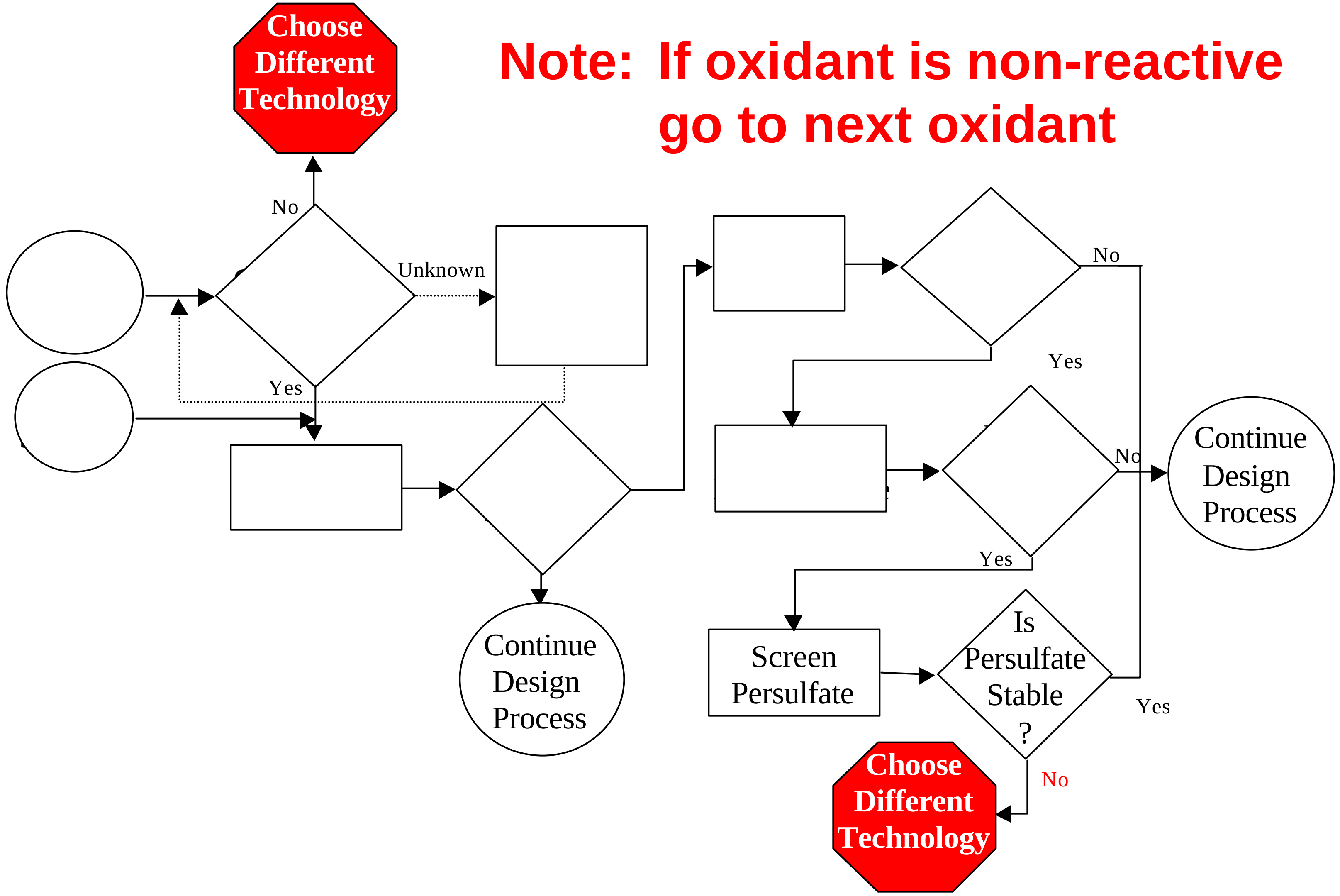
Permanganate is the most stable oxidant

Design Approach

- Select an oxidant
  - Reactivity
  - Cost
  - Speed
- Select application method
  - Circulation
  - Emplacement

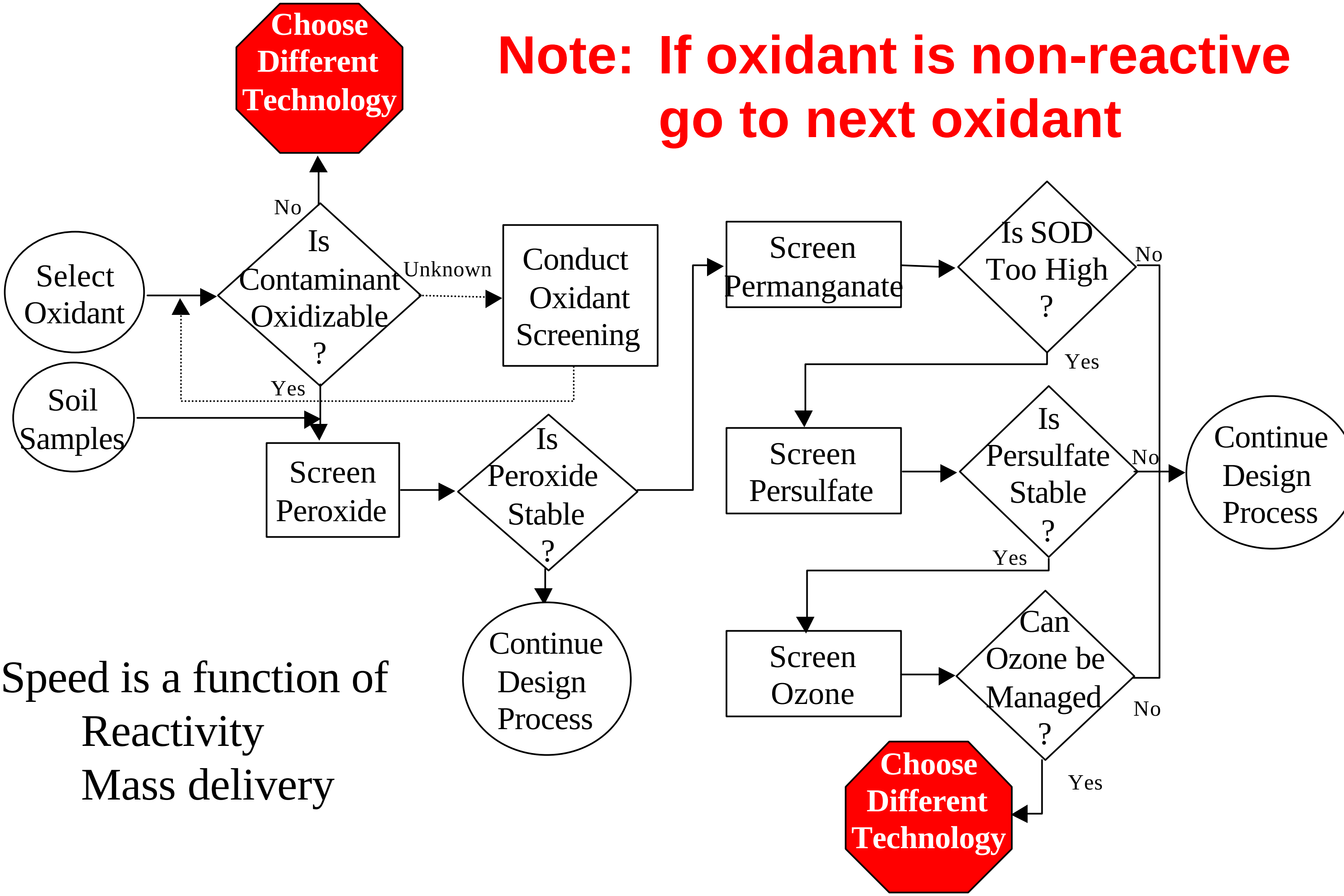
Oxidant Selection – Cost

Note: If oxidant is non-reactive go to next oxidant



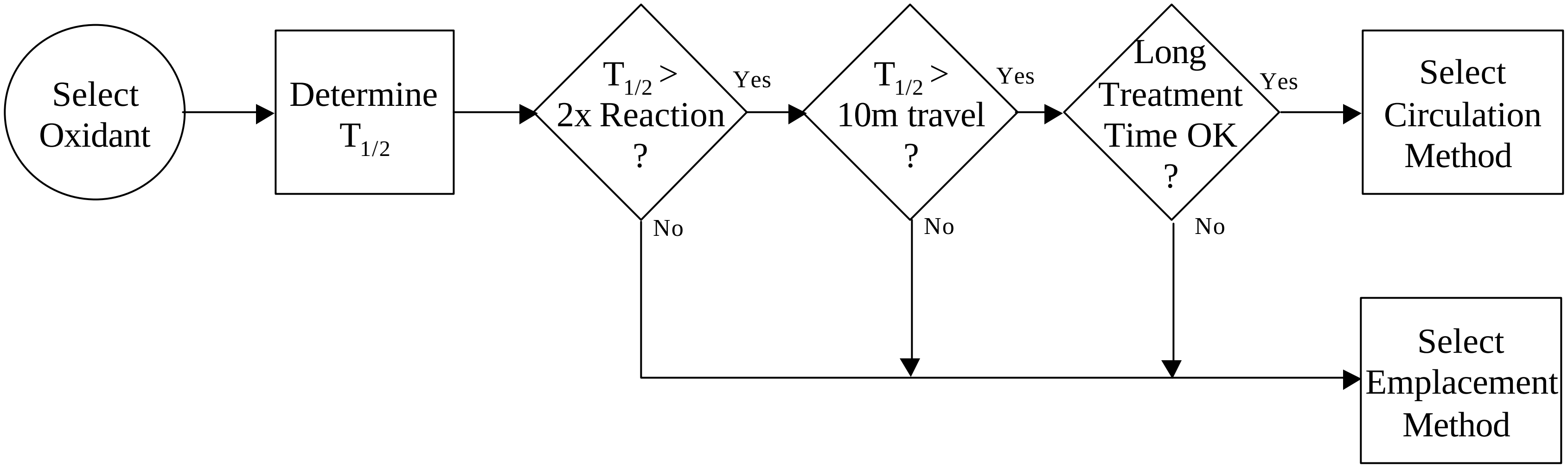
Oxidant Selection – Speed

Note: If oxidant is non-reactive go to next oxidant

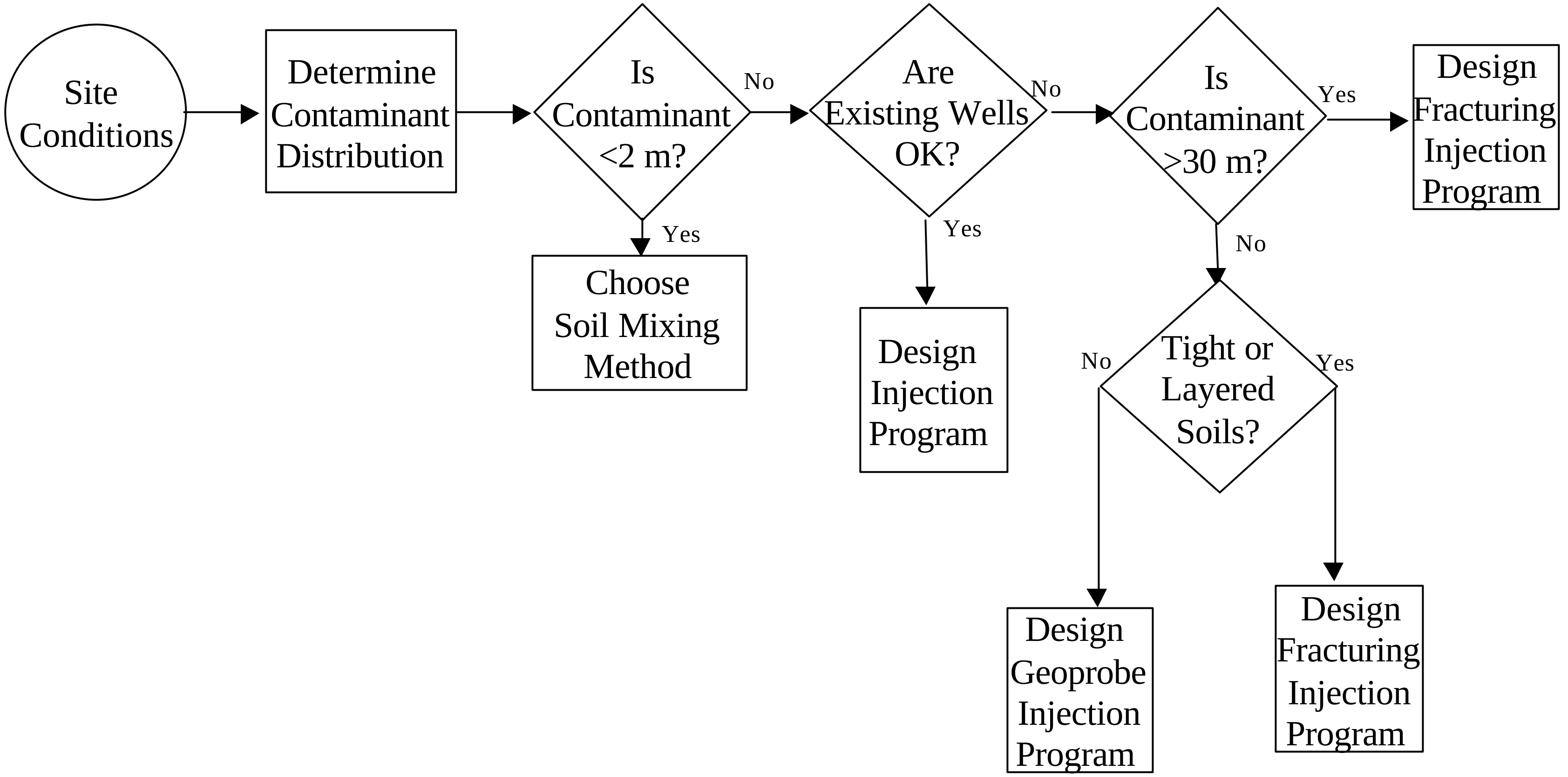


Speed is a function of
Reactivity
Mass delivery

Application Method Selection

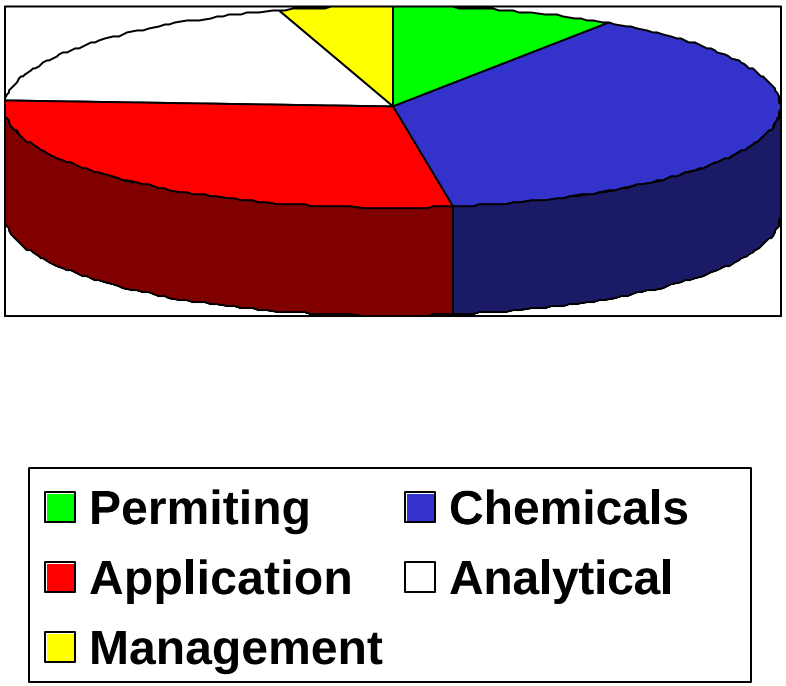


Selecting an Emplacement Method

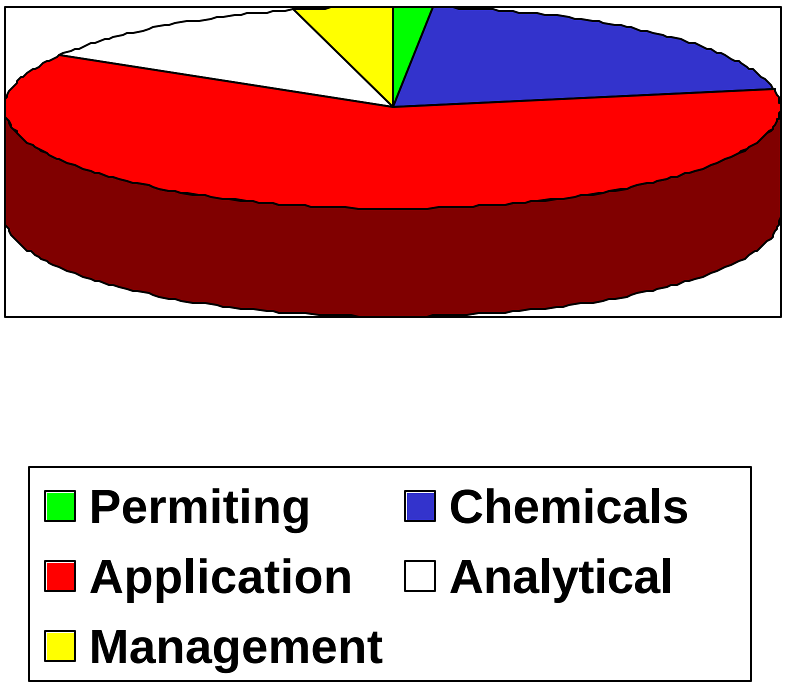


Overview of ISCO

ISCO Costs



ISCO Success



ISCO Summary

- Many oxidants are available
- A wide range of contaminants are treatable
- Selecting the right oxidant is important
  - Reactivity
  - Cost
    - Competing reactions
- Good design ensures success
  - Choose the best application method
    - Push Tools are an important application method
- There is still room for development