In-situ and Ex-situ Soil and Groundwater Remediation using Chemical Oxidation Technologies

RPIC-FCS,

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Chemco Inc.

CHEMCO inc.

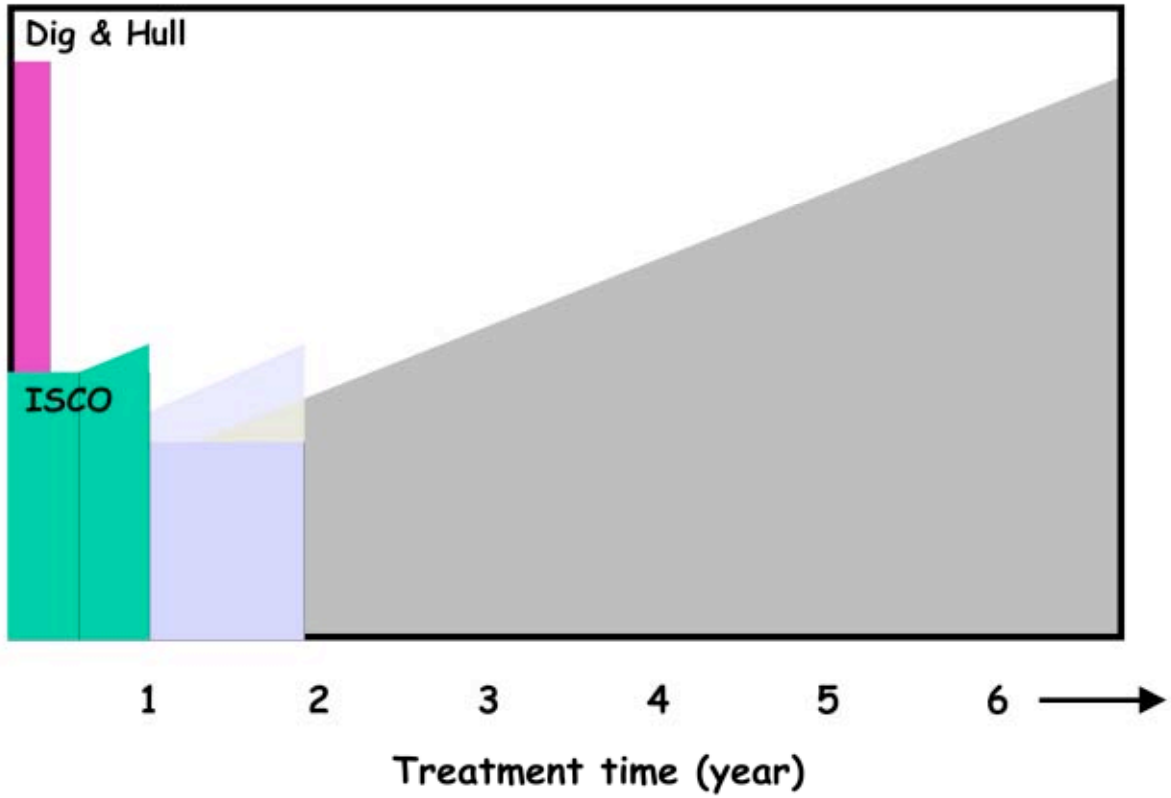
SOLUTIONS AND ENVIRONMENTAL PRODUCTS

WATERS - SOILS - AIR

Typical decontamination techniques

- Dig and Haul
- Pump and Treat
- Soil Vapour Extraction under vacuum with or without air/steam injection
- Chemical Oxidation In-situ//Ex-situ
- Monitored Natural Attenuation
- Reactive Barriers
- Thermal degradation

Remediation time and cost



Chemical Oxidation In-situ//Ex-situ

- Oxidants are introduced or mixed into the soil and groundwater to attack 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 content.
- Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds
- Water is the carrier and where the chemical reaction occur for the oxidants used in chemical oxidation (except for ozone)

Common Chemical Oxidants

- **Potassium or sodium permanganate**
- **Hydrogen Peroxide alone**
- **Catalyzed Hydrogen Peroxide**
  - Hydrogen Peroxide with iron (regular Fenton reagent reaction)
  - Need to establish acidic conditions (ideal pH between 4 and 6)
  - Modified Fenton Reagent with chelated species (neutral pH)
- **Ozone**
  - Ozone is a gas and must be produced on site
  - The gas must be injected into the soil
- **Persulfate**
  - Requires activation to generate free sulfate radicals.
  - Heat, chelated metal, high pH or hydrogen peroxide can be used to activate the persulfate. Activation method can be adapted to site conditions.
  - New Self activated persulfate with calcium peroxide now available combining chem-oc with bio
- **Percarbonate**
  - Requires activation with iron embedded into a silica matrix (high viscosity system) to generate free radicals (perhydroxyl and some hydroxyl)

- **NOTES: 1. ALL THESE PRODUCTS REQUIRE ADEQUATE HANDLING PRATICES AND SAFETY EQUIPMENT.**
  2. Chemical oxidation can slow down the biological activity but will NOT sterilize the soil completely (benefit because of lower toxicity after the Chem-Ox).
  3. Rebound typical with Chemical Oxidation especially with low persistence oxydant. Need to sequence the injection (60-40 or 40-30-30) to minimize Rebound effect.

Oxidant	Potential (V)	Form	Persistence in soil
Fenton Reagent OH*	2.8	Liquid	Low 2 to 5 days
Perozone (O_3 + OH*)	2.8	gas/Liquid	Very Low 20 min to 2 days
Persulfate activé (SO_4^-)	2.6	Liquid/ suspension	Medium 10 to 30 days
Ozone (O_3)	2.42 2.07	gas	Very Low 20 min to 2 days
Persulfate (S_2O_8 2-)	2.01	Liquid/ suspension	Medium 10 to 30 days
Hydrogen Peroxide (H_2O_2)	1.78	Liquid	Low 2 to 5 days
Perhydroxyl (Percarbonate)	1.70	Liquid/ suspension	Medium 10 to 30 days
Permanganate (MnO_4^-)	1.68	Salt/Liquid	High More than 3 month

Ref. John Cherry & M. Marley, U. of Waterloo Workshop, 2003

Conditions for Selecting Chemical Oxidation

	Chemical Oxidation Applicability	Limitation / Disadvantages	Possible Alternative Options
Mobile NAPL	Probably not the best choice	High oxidant requirement ($)	Liquid Extraction Thermal degradation
Residual NAPL (10,000's mg/kg)	Yes, but difficult	High oxidant requirement ($)	Extraction with air/steam injection Thermal degradation
High conc. in soil/groudwater (10's – 1,000's mg/kg)	Yes, good conditions	Normal considerations	Extraction with air/steam injection Bioremediation
Dissolved plume (< 1 mg/kg)	Yes, but could be costly	Higher cost due to SOD	Bioremediation, Reactive barriers

Source : ITRC 2004

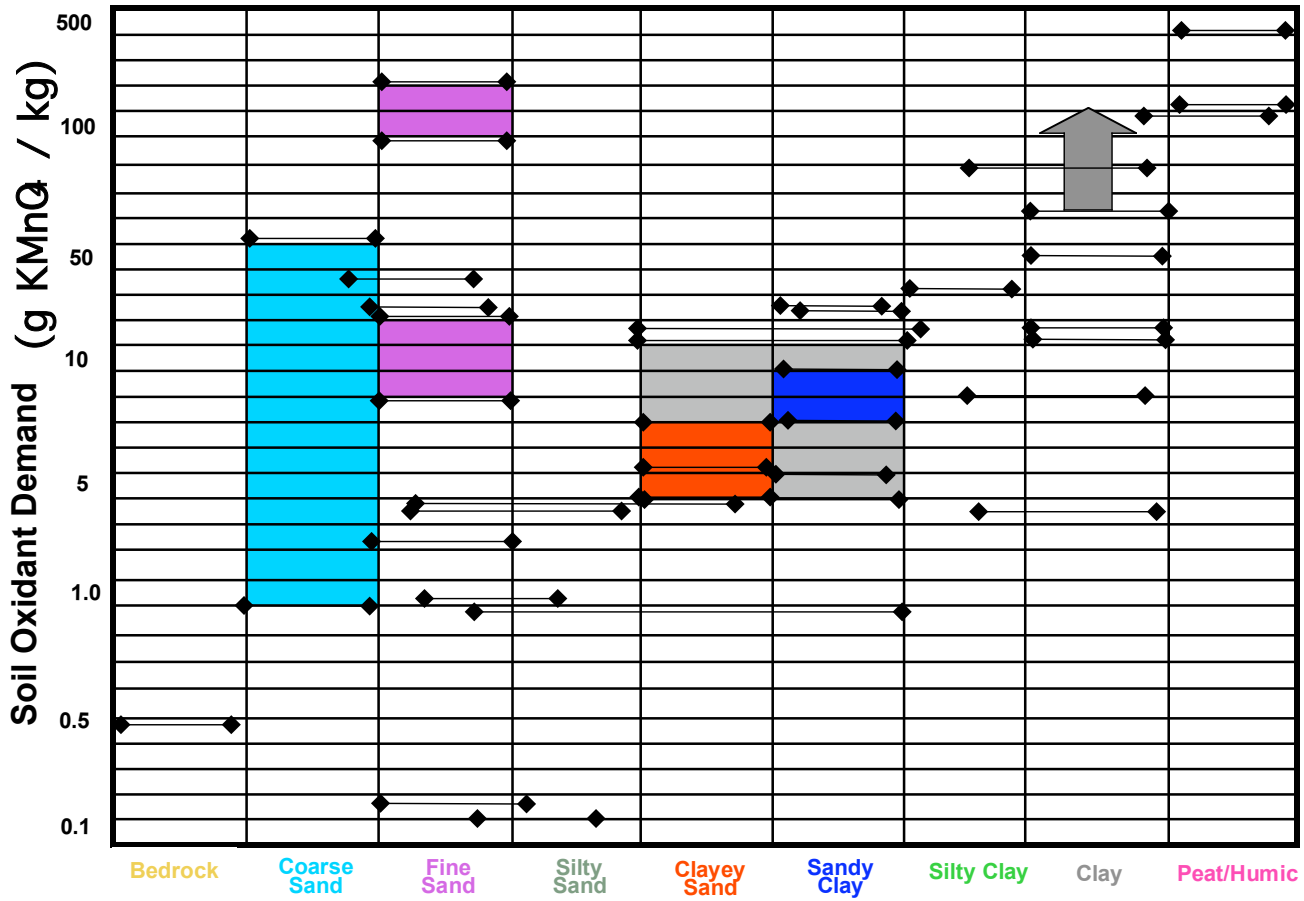
NAPL: Non-Aqueous Phase Liquid

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

Soil Oxidant Demand (SOD)

(adapted from Shaw E & I presentation - 2003)

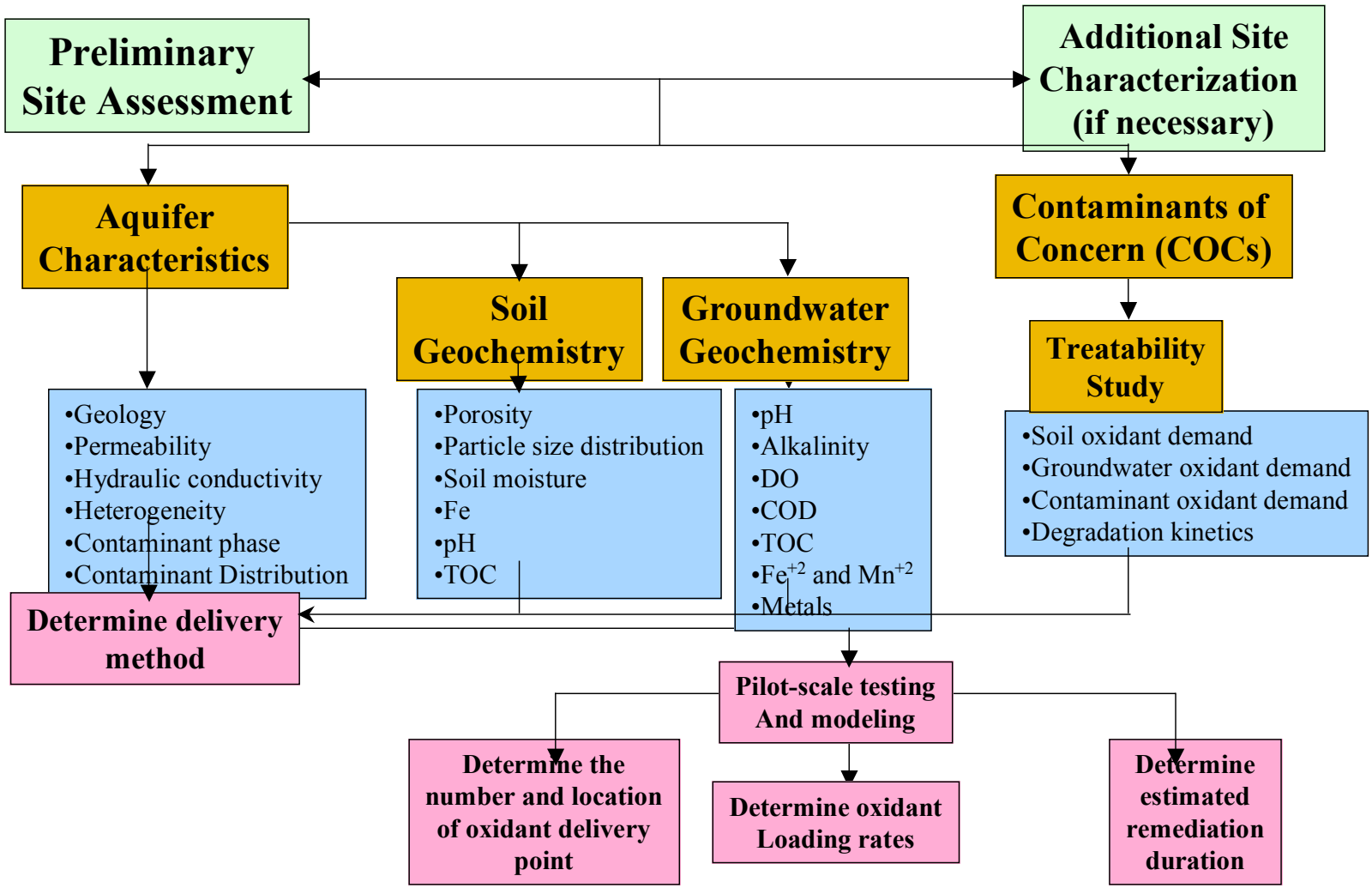


Typical SOD value per oxidant

- **Potassium or sodium permanganate – 10 to 30 g/kg**
- **Hydrogen Peroxide alone – 25 to 50 g/kg**
- **Catalyzed Hydrogen Peroxide – 50 to 100 g/kg**
- **Ozone**
- **Persulfate – 1 to 5 g/kg**
- **Percarbonate - 10 to 25 g/kg**

NOTE: ALL these values need to be CONFIRMED before using them into a specific site.

Carus Haz Rem Assessment Process



(Adapted from R. L. Siegrist et al., "Principles and Practices of In Situ Chemical Oxidation Using Permanganate", p. 202.)

Compatibility oxidant/contaminant

Contaminant/Oxydant	MnO_4	S_2O_8	SO_4^*	Fenton's	Ozone
Petroleum Hydrocarbon	L	G/E	E	E	E
Benzene	L	G	G/E	E	E
Phenols	G	L/G	G/E	E	E[1]
Polycyclic Aromatic Hydrocarbon (PAH)	L	G	E	E	E
MTBE	L	L/G	E	G	G
Chlorinated Ethenes (PCE, TCE, DCE, VC)	E	G	E	E	E
Carbon Tetrachloride	L	G	L/G	L/G	L/G
Chlorinated Ethanes (TCA, DCA)	L	G	G/E	G/E	G
Polychlorinated Biphenyls (PCB)	L	L	L	G/E	G[1]
Energetics (RDX, HMX)	E	G	E	E	E

L=Low G=Good E=Excellent 1=Perozone

Source: Carus Chemical Company

Geological Considerations

Geological Considerations	MnO_4	S_2O_8	SO_4^*	Fenton's	Ozone
Non-consolidated material					
• **Sand and gravel**	E	E	E	E	E
• **Silty sand**	G/E	G	G	L	L
• **Mixed**	G/E	G/E	G	L	L
Consolidated material					
• **High flow**	E	E	L/G	L/G	L/G
• **Low Flow**	G	G	G	L	L

L=Low G=Good E=Excellent

Source: Carus Chemical Company

Hydrogeological considerations

Hydrogeological considerations	MnO_4	S_2O_8	SO_4^*	Fenton's	Ozone
Saturated Zone	E	E	G	G	G
Non-saturated Zone	G *	L/G	L/G	L/G	G
with groundwater flux:					
• slow	G	G	G	L	L
• fast	G	G	G	G	G

L=Low G=Good E=Excellent * If temporarly flooded.

Source: Carus Chemical Company

Geochemical Considerations

Geochemical Considerations	MnO_4	S_2O_8	SO_4^*	Fenton	Ozone
Presence of carbonates	E	E	G	L	L
High dissolved metal content	L	G	E	E	L
High organic matter content	L	G	G	L	L

L=Low G=Good E=Excellent

Source: Carus Chemical Company

Additional Considerations

Criteria	MnO_4	S_2O_8	SO_4^*	Fenton	Ozone
Gas Production	Low	Low	Low	High	High
Heat Production	Low	Low	Low	High	Low
Fugitive Emissions	Low	Low	Low	High	High
Availability	E	E	E	E	G
Ease of handling	G/E *	E	E	G	G
Impact on water quality	Mod.	Mod.	Mod.	Mod.	Low
Patent Restrictions	Low	High	High	High	High
Technological Development	E	L	G	E	G
Information availability	G	L	G	G	G
Field trial	G	L	G	G	G

L=Low G=Good E=Excellent Mod. = Moderate * Sodium

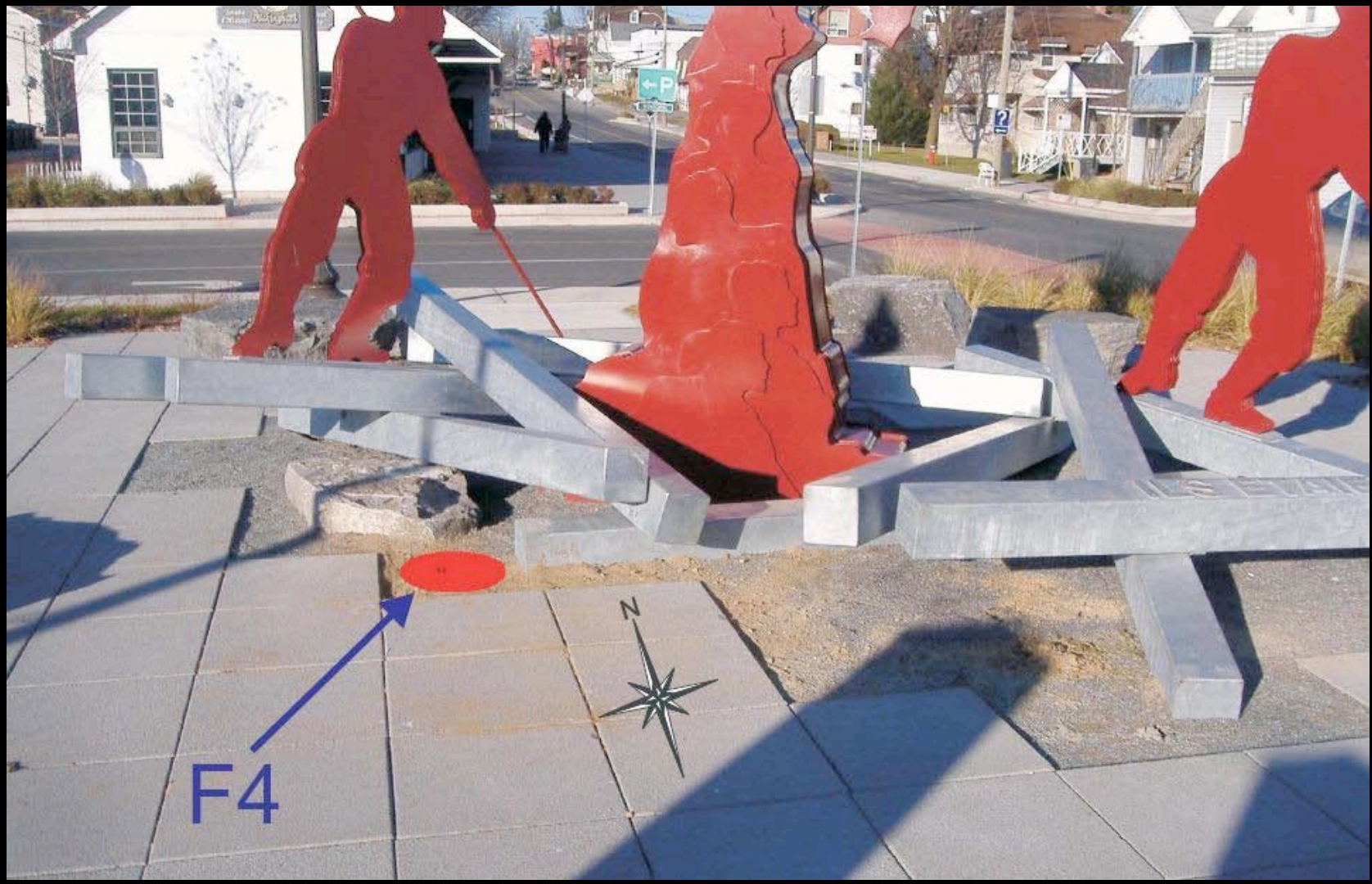
Source: Carus Chemical Company

Additional considerations (2)

- **All oxidants can change the oxidation state of metals and thus increase their solubility and mobility**
- **Metals of particular concern are: chrome, lead, uranium, selenium, vanadium**
- **In most of these cases, the metals will come back in their reduced state once all of the oxidant has been consumed by the environment**
- **Impurities contained in the oxidant must be evaluated**
- **In the case of arsenic, oxidation will help immobilizing the metal by reducing its solubility**

Case Study: Persulphate

- Statue located in Ottawa region
- PHC identified beneath statue
- Fragile construction & high political value
- In-Situ remediation was requested
- PHC C10-C50 – 6,000 mg/kg
- PHC C10-C50 criteria – 3,500 mg/kg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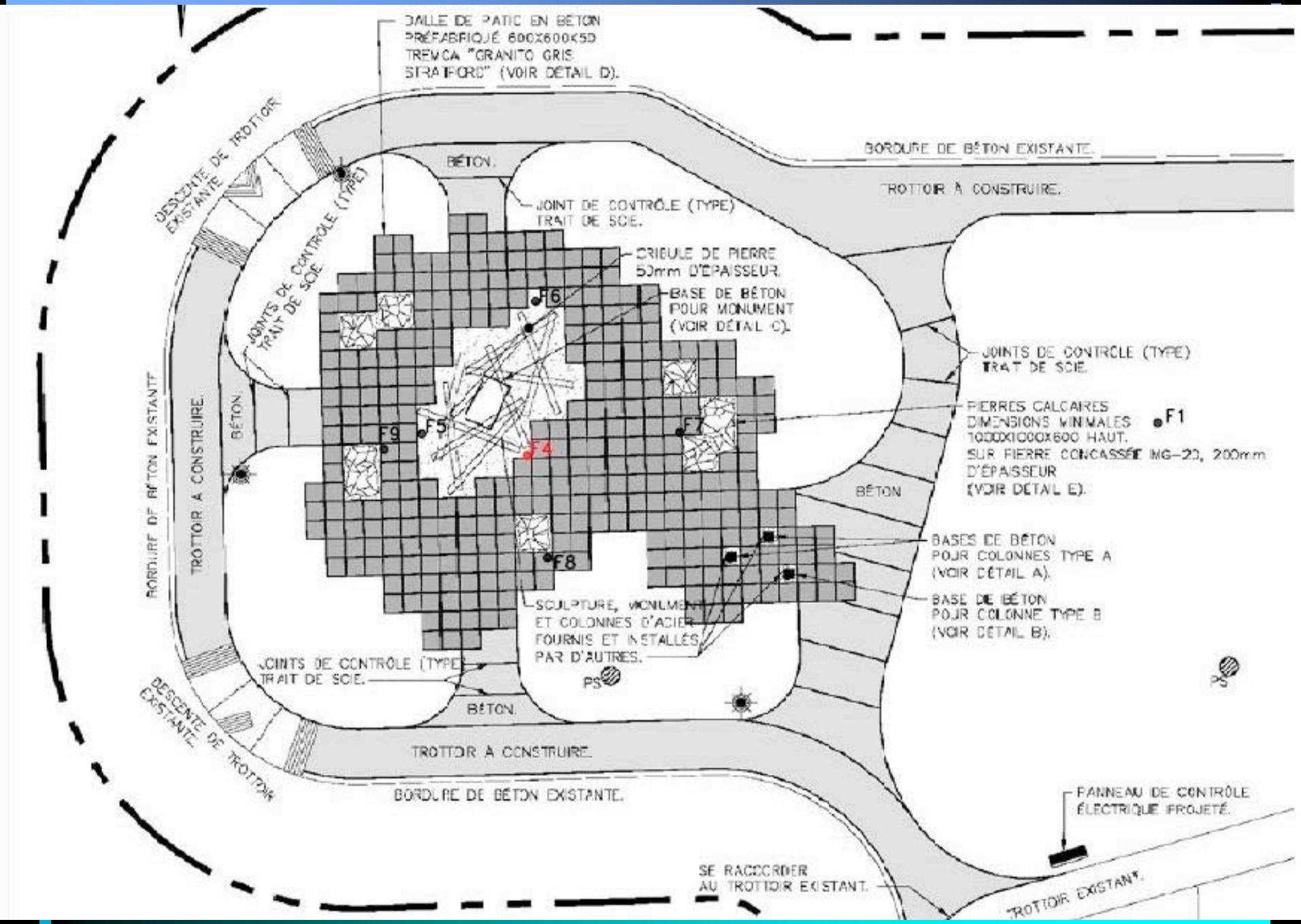
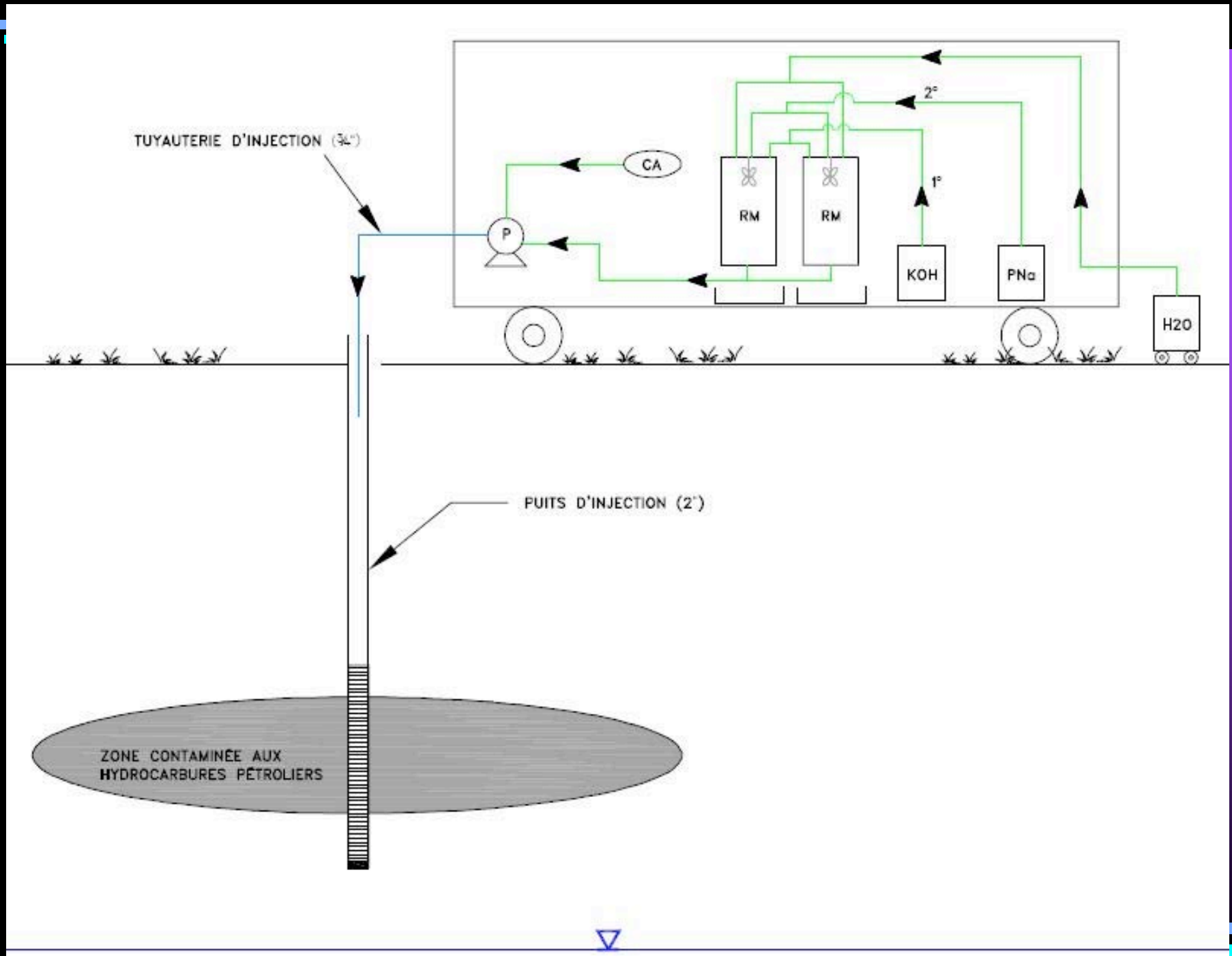
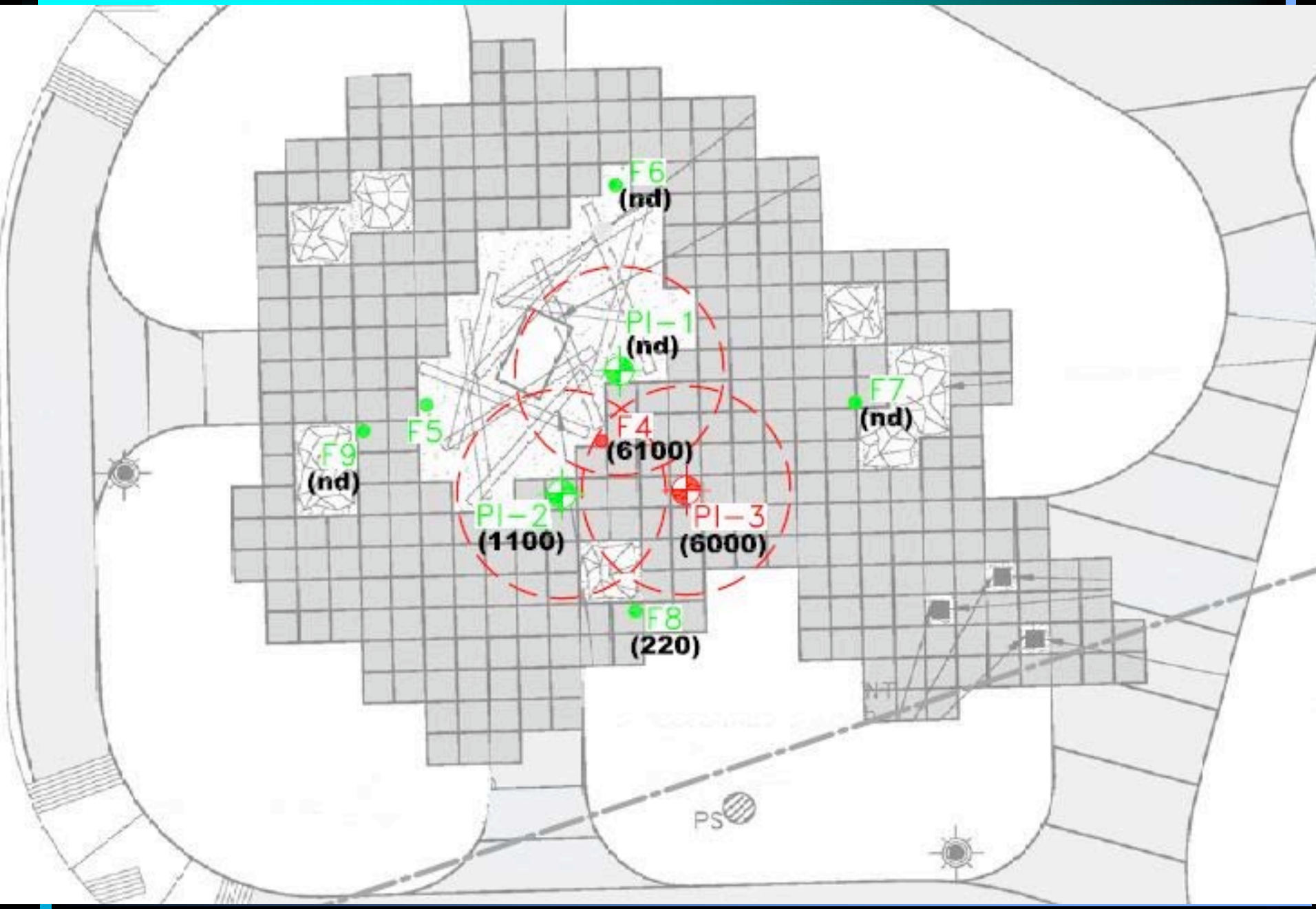

DALLE DE PATIO EN BÉTON PRÉFABRIQUÉ 600X600X50 TREMCA "GRANITO GRIS STRATFORD" (VOIR DÉTAIL D).
DESCENTE DE TROTTOIR EXISTANTE
JOINTS DE CONTRÔLE (TYPE) TRAIT DE SCIE
BÉTON.
JOINT DE CONTRÔLE (TYPE) TRAIT DE SCIE.
BORDURE DE BÉTON EXISTANTE.
TROTTOIR À CONSTRUIRE.
GRIBULE DE PIERRE 50mm D'ÉPAISSEUR.
BASE DE BÉTON POUR MONUMENT (VOIR DÉTAIL C).
F6
F9
F5
F4
F7
F8
JOINTS DE CONTRÔLE (TYPE) TRAIT DE SCIE.
PIERRES CALCAIRES DIMENSIONS MINIMALES 1000X1000X600 HAUT. SUR PIERRE CONCASSÉE MG-20, 200mm D'ÉPAISSEUR (VOIR DÉTAIL E).
F1
BÉTON
BASES DE BÉTON POUR COLONNES TYPE A (VOIR DÉTAIL A).
BASE DE BÉTON POUR COLONNE TYPE B (VOIR DÉTAIL B).
SCULPTURE, MONUMENT ET COLONNES D'ACIER FOURNIS ET INSTALLÉS PAR D'AUTRES.
PS
BORDURE DE BÉTON EXISTANTE.
TROTTOIR À CONSTRUIRE.
BÉTON.
JOINTS DE CONTRÔLE (TYPE) TRAIT DE SCIE.
DESCENTE DE TROTTOIR EXISTANTE
PANNEAU DE CONTRÔLE ÉLECTRIQUE PROJETÉ.
SE RACCORDER AU TROTTOIR EXISTANT.
TROTTOIR EXISTANT.

Case Study: Persulphate

- PHC located in unsaturated zone
- Medium sand underlain by silt
- Impacts identified in 20 cm sand seam above silt layer
- Flood unsaturated zone, persulphate with base (sodium hydroxide) activation
- Titration – no soil buffering capacity
- Oxidant injected every 3 weeks for 3 events (Week 0, Week 3, Week 6)
- Sampled Week 12


TUYAUTERIE D'INJECTION (3/4")
CA
P
RM
RM
2°
1°
KOH
PNa
H2O
PUITS D'INJECTION (2")
ZONE CONTAMINÉE AUX
HYDROCARBURES PÉTROLIERS


F6
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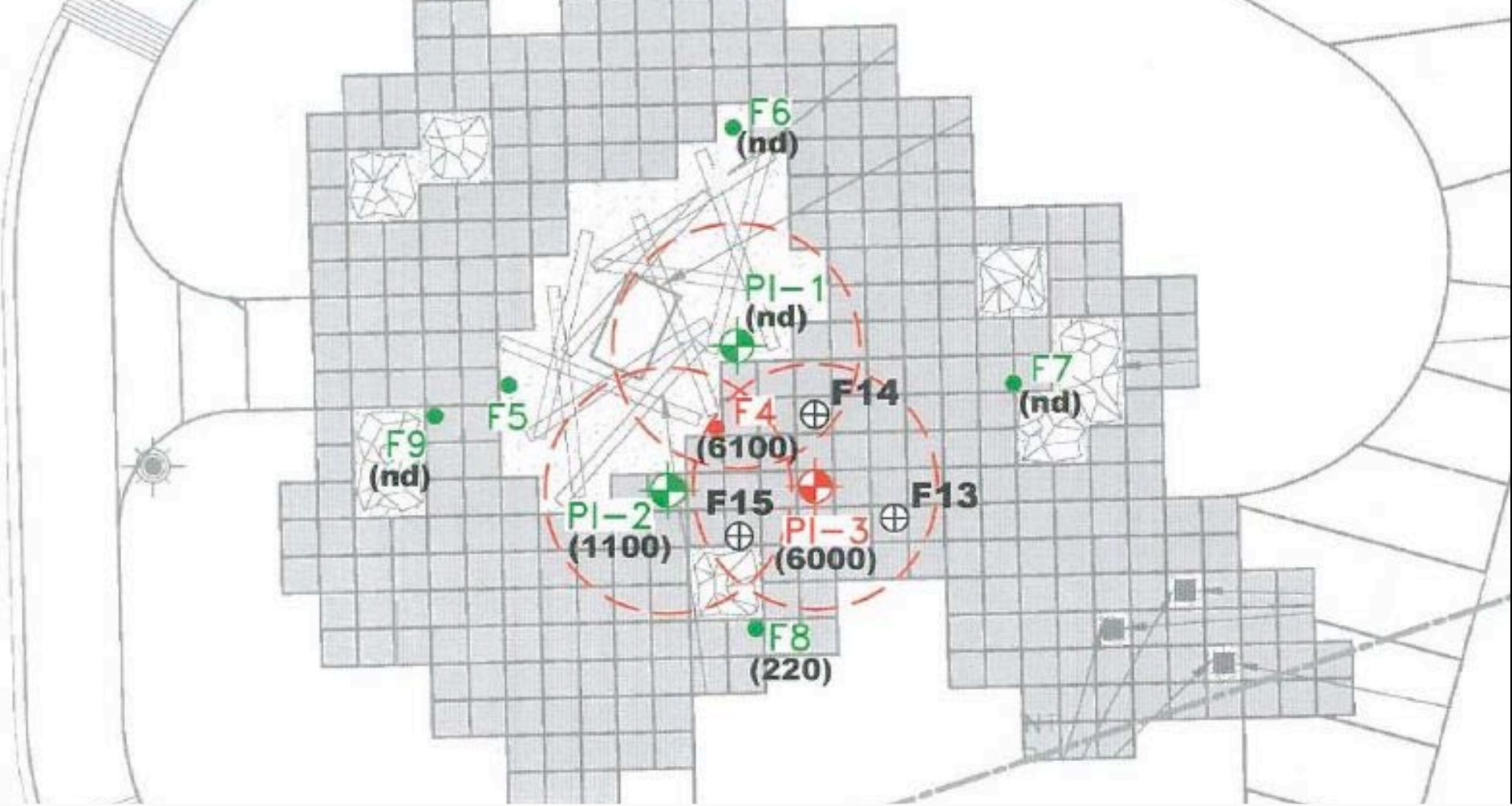

Location	PHC Result	% Reduction	Location
F13	4,000 mg/kg	33%	South IW#3
F14	1,800 mg/kg	70%	Between 2 IWs
F15	1,500 mg/kg	75%	Between 2 IWs

Case Study: Persulphate

Sampling Location	PHC Result	% Reduction	Location
F13	4,000 mg/kg	33%	South IW#3
F14	1,800 mg/kg	70%	Between 2 IWs
F15	1,500 mg/kg	75%	Between 2 IWs

- Reductions noted, with best results in vicinity of injection wells
- One result just over criteria, but far enough from statue that excavation is possible

VERTEX

Who we are

- Canadian Company founded in 1988
- Production and warehouse facilities in Quebec and throughout Canada vs. Strategic Business Alliances
- Sectors of activity
  - Industrial and Municipal Waste Water
  - Contaminated Soil and Groundwater
  - Air, Odours and Atmospheric Emissions
  - Process Water
- Products: coagulants, flocculants, nutrients, preparations of bacterial strains, oxidants, catalysts, oxygen and hydrogen release compounds, odour control agents
- Services: technical support, product supply and sourcing, logistics, laboratories (SOD testing and treatability study), design, and staff training.

Acknowledgements

- Carus Chemical
- ERM Corporation
- FMC Corporation
- Vertex Environmental
- Progressive Engineering & Construction

Thank you for your attention !

Have a good day !!!

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