Key factors for a successful ISCO application with Permanganate

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Program Manager

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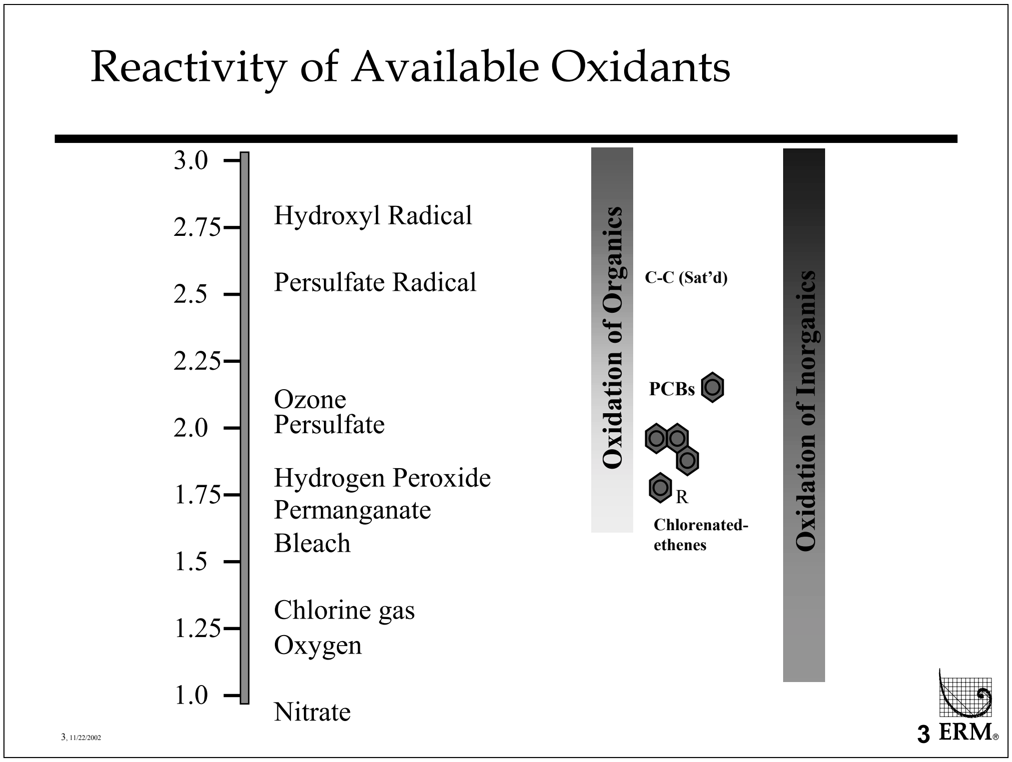
ISCO Treatment

- **Two key issues**
  - **Does the reaction take place?**
    - Competing reactions
  - **Can the reagent contact the contaminant?**
    - The most critical part of the application

Chemical oxidation is a direct chemical reaction involving the application or injection of oxidants into soil matrixes to destroy or chemically transform the contaminant.

When a material is oxidized it is converted to a higher valence state. Typically with organics (carbon) this results in the conversion of the organic to carbon dioxide (CO_2).

There are two key issues that must be addressed with in situ chemical oxidation. The first is whether or not the oxidant being used will react with the contaminant being treated. Whether the reaction will take place is a function of the electrode potential and of the activation energy of the oxidant. These will be discussed latter. The second issue is, assuming that the reaction will occur, whether the oxidant can be brought into contact with the contaminant. One of the innovations in in situ treatment that has helped in the application of oxidants is the use of push tools. These will be discussed latter.



Reactivity of Available Oxidants

3.0
2.75 Hydroxyl Radical
2.5 Persulfate Radical
2.25
Ozone
2.0 Persulfate
1.75 Hydrogen Peroxide
Permanganate
Bleach
1.5
Chlorine gas
1.25 Oxygen
1.0
Nitrate

Oxidation of Organics

C-C (Sat'd)

PCBs

R

Chlorenated-ethenes

Oxidation of Inorganics

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In summary, There are a wide range of chemical oxidants They can be used both for oxidizing organics and inorganics. Roughly, organic oxidation occurs at potentials greater than 1.5 eV. Inorganic oxidations occur at potentials above 1.2 eV.

The electrode potential necessary will vary with vary with individual compounds. Ethenes are the easiest to oxidize. Simple aromatics are next, then PAHS and finally highly recalcitrant contaminants such as PCBs. Because the electrode potential varies with different compounds, the choice of oxidant will also vary.

Oxidant Usage

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

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

+ [Soil Matrix Demand]
- **[Metals]**
- **$[\text{Organic Carbon}]_{\text{Oxidizable}}$**

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

The amount of oxidant that is needed to oxidize a contaminant in situ is a function of a number of things. First, obviously, is the amount of contaminant. The stoichiometric demand is determined by writing out a balanced equation to determine the mole ratio of oxidant to contaminant. The weight ration is calculated by multiplying the mole ratio by the ratio of molecular weights. In addition to the stoichiometric demand there may be another reduced species present that will react with and consume the oxidant. These include metals and other oxidizable carbon.

In addition to the consumption of the oxidant by reactions with the contaminant and other reduced species, the oxidant demand may be increased by the decomposition of the oxidant. This, as will be discussed, is a particular problem with hydrogen peroxide.

Soil Matrix Demand

- **Range of Values, Kg ($KMnO_4$)/m^3 Soil, US Soils**
  - **Low - 0.07 -0.2**
  - **Average - 1 - 2**
  - **High - 4 - 10+**
- **Importance of SOD**
  - **Stoichiometric Demand - TCE (for comparison)**
    - 100 PPM Dissolved - 0.05 Kg/m^3
    - 100 PPM Adsorbed - 0.25 Kg/m^3
  - **Kg $KMnO_4$ for 30m x 30m x 7m Site**
    - Low - 1680 Total - 0.26 Kg/m^3
    - Average - 16,800 Total - 2.6 Kg/m^3
    - High - 67,200 Total - 10.6 Kg/m^3

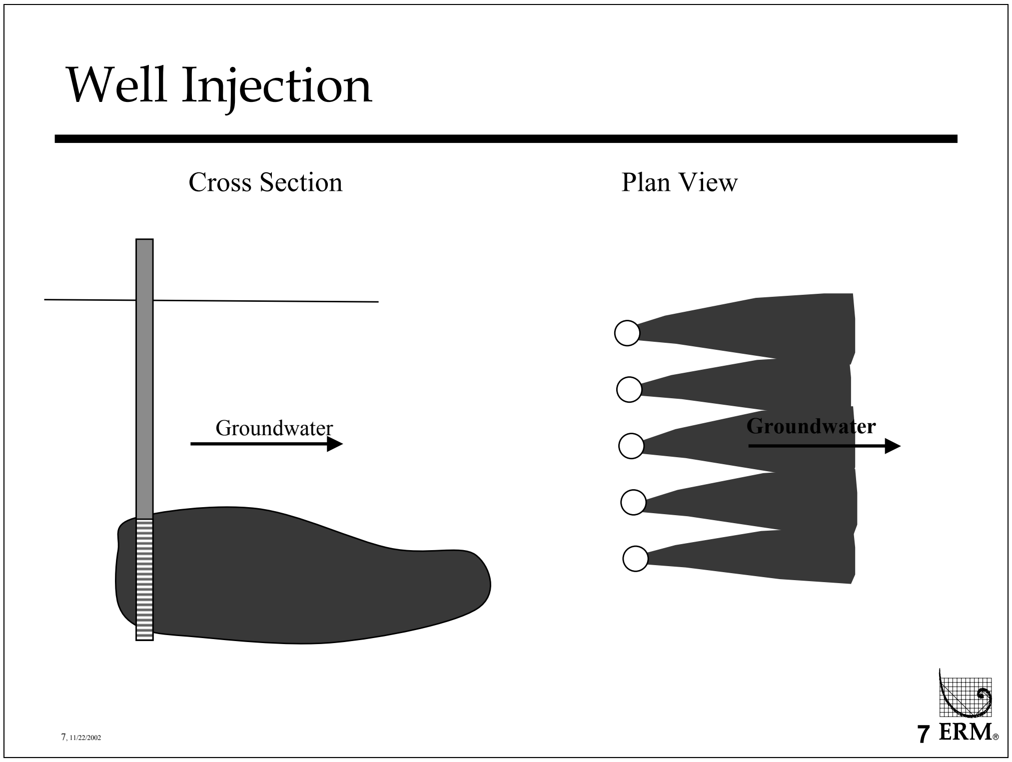
Application Methods

- **Wells (Single Injection)**
  - **Existing SVE, Monitoring, Pumping Wells**
  - **1000 - 2000 gal/well**
  - **20-40’ Radius**
  - **No Depth Limit**
- **Push Tool Injection (Pressure)**
  - **50-200 gal per 5’ Interval**
  - **Limited to < 70’**
  - **5 - 15’ Radius**
  - **3-6/Day/Rig**
- **Recirculation Wells**
  - **Single or Dual**
  - **Limited by Lithology**
  - **Limited by Sat’d Thickness**
- **Liquid Atomization**
  - **Pneumatic Fracturing**
    - High Pressure N_2
  - **Atomized injection**
  - **20-40’ Radius**
- **Hydraulic Fracturing**
  - **20-40’ Radius**

There are two general methods of applying permanganate, addition to wells or push tool injection.

Application through wells consists of adding 1-2000 gal of permanganate per well. Wells have no depth limitation. In permeable soils the injection radius may be 20-40’; less in lower permeability soils. Existing wells can be used or special wells may be installed. Using wells typically requires several applications.

Push tool (e.g., Geoprobe) injection involves the injection of 50-100 gallons of permanganate every ~5 feet. Push tool injection is depth limited. Most rigs can get to ~70 feet. The injection radius is ~5-10’. Depending on depth and soil type a push tool rig can do 3-6 points in a day. The permanganate is injected under pressure, using a grout pump or other pressure injectors. Injection pressures are ~100 psi.



Well Injection

Cross Section

Plan View

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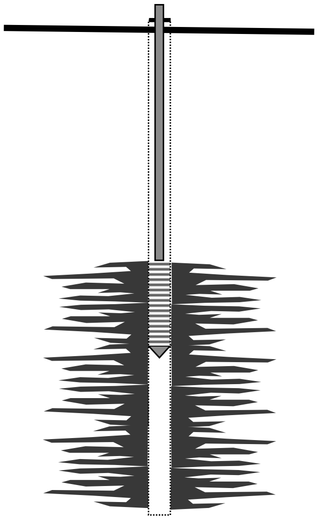
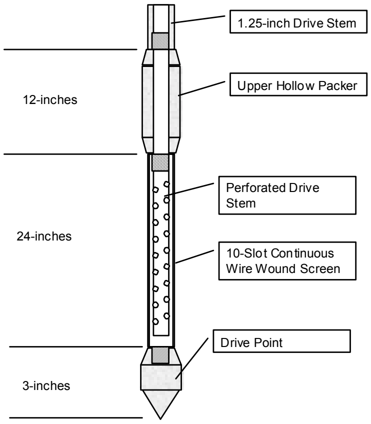
Injection through wells is much more tied to groundwater conditions than is push tool injection. Most of the permanganate added will follow groundwater flow. Thus to get complete coverage wells have to be spaced so that dispersion will cause the individual permanganate “plumes” to overlap. The spacing of wells can be determined through groundwater modeling.

Push Tool Injection

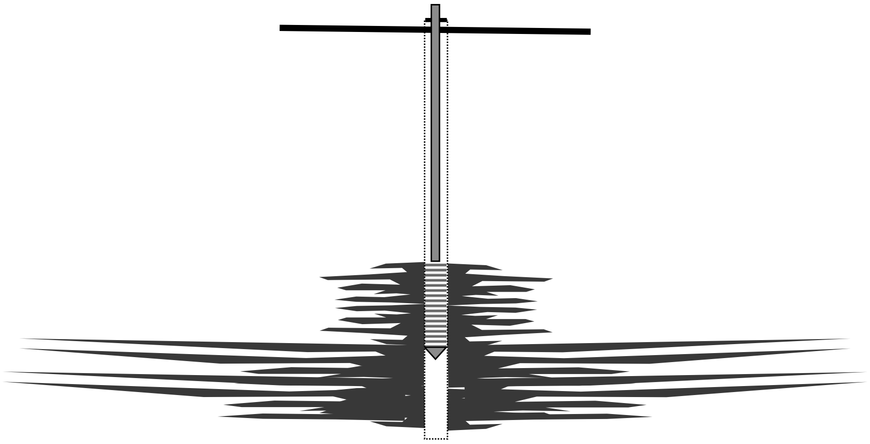
Injection Tip Detail

Sequential Injection





Liquid Atomized Injection



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Liquid Atomization

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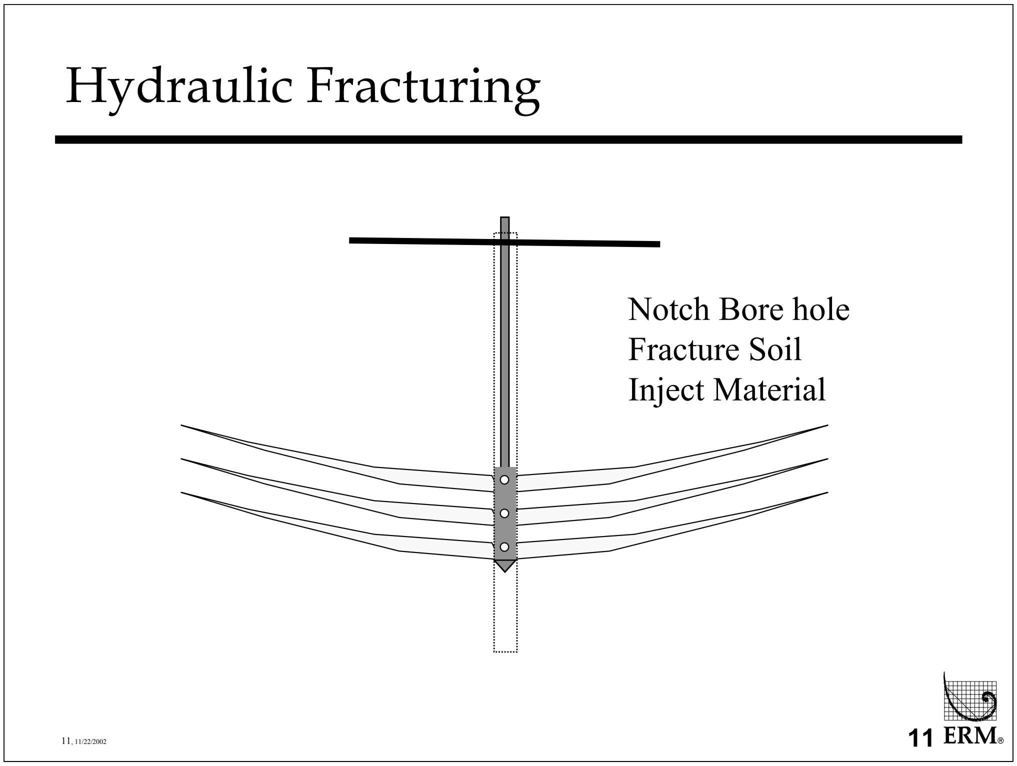
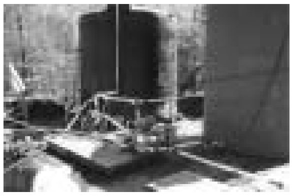
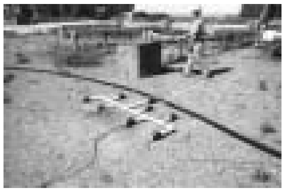


Hydraulic Fracturing

Notch Bore hole
Fracture Soil
Inject Material

Union Chemical Superfund Site



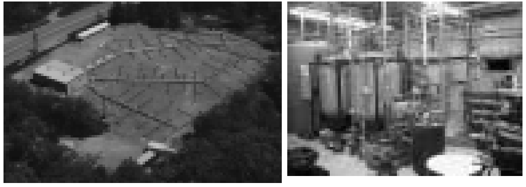


- ISCO
  - Pre-Treatment: CVOCs and T,X (5 – 115 mg/L)
  - Pilot test 1997
  - Application 1998 (3,500 pounds)
  - Application 1999 (29,000 pounds)
  - Application 2000 (10,500 pounds)
  - Post-Treatment: CVOCs (0 – 4 mg/L)
  - 85-95% reduction
- Allowed deactivation of P&T component
- Facilitated transition to enhanced anaerobic biologic remediation
- Used $KMnO_4$ (site wide) and targeted $NaMnO_4$
- Flow rate ~ 3 gpm @15 psi [11 l/min @ 103 kpal]

Union Chemical Superfund Site

Project History

1997 (Pre ISCO)

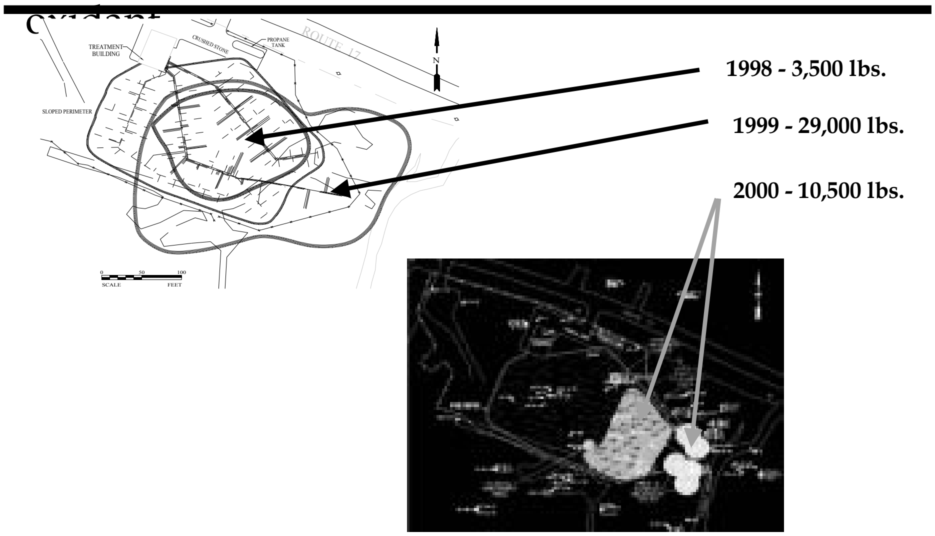


1999 (During ISCO)

2000 (Post Treatment)

Chemical Oxidation Treatment Areas

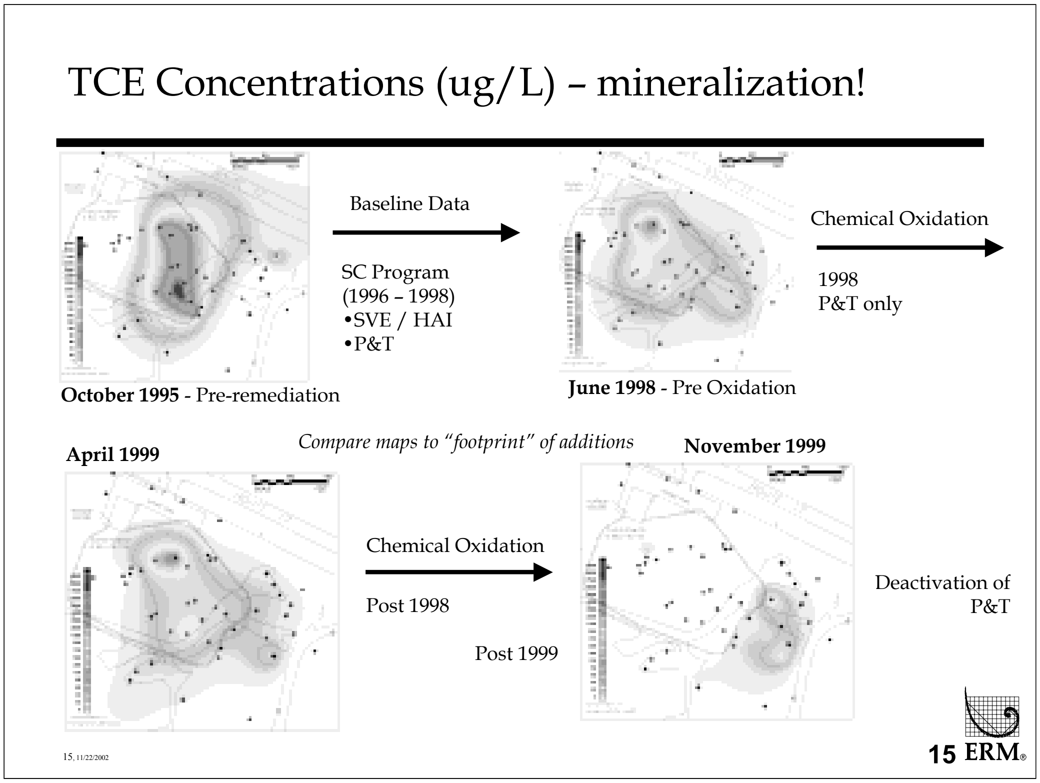
(1998, 1999 and 2000) – pounds listed is pounds of oxidant



1998 - 3,500 lbs.

1999 - 29,000 lbs.

2000 - 10,500 lbs.



TCE Concentrations (ug/L) – mineralization!

October 1995 - Pre-remediation

Baseline Data

SC Program
(1996 – 1998)
- SVE / HAI
- P&T

June 1998 - Pre Oxidation

Chemical Oxidation

1998
P&T only

Compare maps to "footprint" of additions

April 1999

Chemical Oxidation

Post 1998

Post 1999

November 1999

Deactivation of
P&T

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Former Industrial Site, Quincy, MA

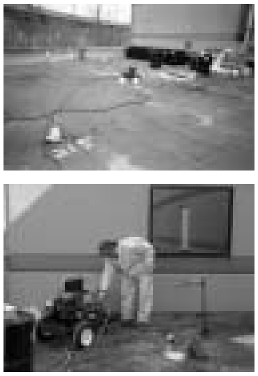
- ISCO
  - Pilot tests
    - 2000 (6,500 lbs.) multiple wells and
    - 2001 (1,100 lbs.) various well types
    - Oxidant demand 1 –2 g/kg (field tests)
  - Full scale application 2001
    - 44,700 lbs. of oxidant (as $KMnO_4$ and $NaMnO_4$)
    - Flow Rates 5 gpm @ 15 psi
  - Residual Targeted areas 2002
    - Trench additions - 12,500 pounds
    - Two MWs 2002 - 1,980 pounds
- Allowed deactivation of P&T component
- Allowed sale of property (redevelopment)
- Cost savings > $1.5M

Pre Full-Scale – Summer 2001

Post Full-Scale – Winter /Spring 2002

Former Industrial Site, Quincy, MA

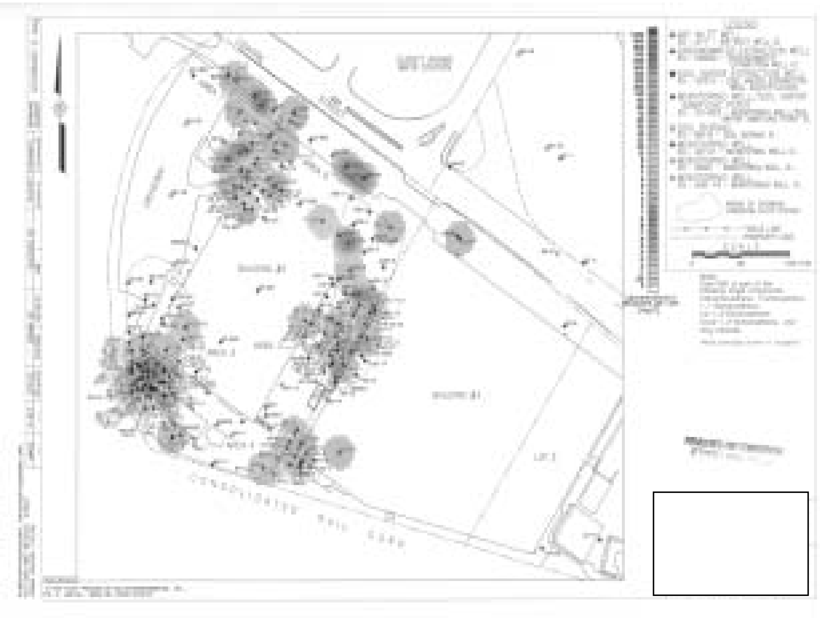
From Pilot (2000 and 2001)

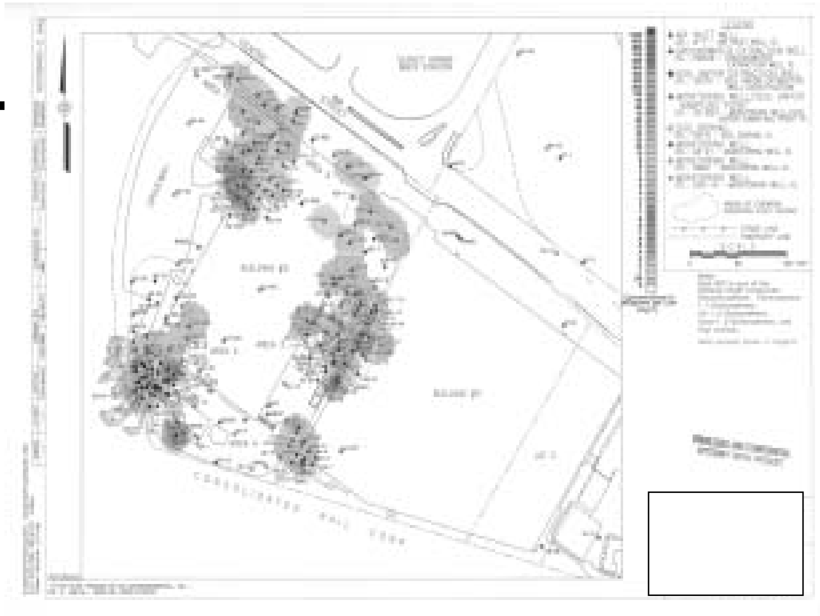


To Full Scale (2002)

To Residual Treatment (2002)


CONSOLIDATED RAIL CORP


CONSOLIDATED RAIL CORP



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