"Is ISCO Right for Your Site?"

*In Situ Chemical Oxidation (ISCO)

RITS Fall 2010

Presentation Overview

- Introduction to ISCO
- ISCO Technology Practices Manual (TPM): ESTCP Project Background and Overview of Results
- ISCO Screening
- ISCO Conceptual Design
- ISCO Detailed Design, Implementation, and Monitoring
- Case Studies
- Summary and Conclusions

Review presentation outline

Definitions and ISCO Fundamentals

- ISCO: In situ chemical oxidation (formerly ChemOx)
  - Delivery of oxidants into the subsurface to destroy contaminants in groundwater
  - Chemical reactions occur primarily in aqueous phase though some treatment of NAPL and sorbed phases may occur
- COCs: Contaminants of concern
- NAPL (DNAPL): non-aqueous phase liquid (dense)
- NOD/SOD: natural or soil oxidant demand
  - Mass of oxidant consumed per mass of media contacted

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Use definitions to introduce ISCO Fundamentals: define AND describe each

Definitions and ISCO Fundamentals (cont.)

- Chemical oxidants can rapidly destroy many contaminants of concern (COCs)
  - Chlorinated hydrocarbons, fuel related compounds, phenols and PAHs, energetics, pesticides, etc.
  - Electron transfer $C_2HCl_3 + 2MnO_4^- \rightarrow 2MnO_2 + 3Cl^- + 2CO_2 + H^+$
  - Free radical oxidation $Fe_2^+ + H_2O_2 \rightarrow Fe_3^+ + OH^- + OH^\bullet$
- Common oxidants
  - Permanganate (electron transfer)
  - Activated persulfate (free radical)
  - Catalyzed hydrogen peroxide (CHP or Modified Fenton's reagent) (free radical)
  - Ozone (both electron transfer and free radical)

Use definitions to introduce ISCO Fundamentals: define AND describe each

Definitions and ISCO Fundamentals (cont.)

- **Oxidant Dose: ISCO design parameter**
  - Ratio of mass of oxidant delivered to mass of geologic media in treatment zone, typically reported in units g oxidant/kg of treatment zone
- **Pore Volumes Delivered: ISCO design parameter**
  - Ratio of volume of oxidant solution injected to volume of pore space in treatment zone, unitless parameter
- **Treatment goals**
  - MCLs: Maximum contaminant levels (EPA or state regulatory levels)
  - ACLs: Alternative Concentration Limits (risk-based)
  - Mass flux: Rate of contaminant release from a source zone (mass discharge)
  - Percent concentration or mass reduction

Use definitions to introduce ISCO Fundamentals: define AND describe each

Definitions and ISCO Fundamentals (cont.)

- TPM: Technology Practices Manual
  - Funded by ESTCP to enable more predictable, cost-effective application of ISCO
  - Available at SERDP/ESTCP Web site
- DISCO: Database for ISCO
- ISCO Protocol components
  - ISCO Screening
  - ISCO Conceptual Design
  - ISCO Detailed Design and Planning
  - ISCO Implementation and Performance Monitoring

Use definitions to introduce ISCO Fundamentals: define AND describe each. Describe availability of TPM.

Definitions and ISCO Fundamentals (cont.)

- **Application of ISCO requires delivery of oxidants into and throughout a target treatment zone (TTZ)**
  - **Delivery methods**
    - Direct-push probes, drilled wells, or specialized injectors, with some use of fracturing or mixing techniques; Reactive barriers, recirculation schemes, multiple delivery modes, or other strategies
  - **Viability of a given delivery method depends on the oxidant used and site-specific conditions**
- **Remedial action objectives and site cleanup goals have varied**
  - **Reduce the concentration or mass by some percentage (e.g., ≤90%)**
  - **Achieve a target concentration (e.g., ≤100 µg/L or ≤1 mg/kg)**
  - **Achieve a concentration in a plume at some compliance plane downgradient from a source zone**

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Key points: Not only do we need the right chemistry for treating COCs, we need the right delivery approach for oxidant and site conditions. When the right approach is used, an array of treatment goals can be achieved, when the treatment goals are APPROPRIATE for the site.

ISCO Performance

- At some sites, clean up goals have been met in a predictable, cost-effective and timely manner using ISCO
- At other sites, ISCO performance has not met expectations
  - Inability to achieve site cleanup goals based on predictions for the ISCO system that was designed and implemented
  - So-called "rebound" in groundwater concentrations following the end of active ISCO operations

However, sometimes ISCO doesn't work – treatment goals aren't met or rebound is observed post-treatment.

Reasons for Poor Performance

- Poor performance is often attributed to…
  - Site heterogeneities and low permeability zones
  - Excessive oxidant consumption by soil and aquifer media
  - Presence of large masses of contaminants (e.g., NAPLs)
  - Poor design: Insufficient oxidant DOSE or VOLUME
- Example regulator comments on ISCO case study
  - "Residual DNAPL in the soil appears to inhibit the success of the injected solutions."
  - "The source has not been removed and continues as a source for groundwater contamination."
  - "Insufficient quantities of [ISCO product trade name] may limit the success of the treatment."

Actual Injection Conditions:

Injected Volume = 0.00012 PV
Dose = 0.002 g/kg

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Review most common reasons for poor performance and example of poor design. (It isn't always the site's fault when it fails)

Reasons for Poor Performance (cont.)

- **Common mistakes**
  - **Not fully identifying or understanding site conditions**
    - Geochemistry, geology, contaminant mass distribution, etc.
  - **Underestimating interaction of oxidants with natural media**
    - Not conducting oxidant demand or oxidant persistence evaluations
  - **Trying to achieve unrealistic goals**
    - For example: treatment of NAPL sites to MCLs
  - **Assuming a single application will do the job**
  - **Not delivering enough mass of oxidant**
    - This does not mean increasing concentration will necessarily do the job!
  - **Not delivering enough volume of oxidant**

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Review common mistakes in designing and applying ISCO systems that lead to failure

ISCO's Sweet Spot

- **ISCO performs well when adequate contact with contaminants occurs**
  - **Hydrogeology**
    - Permeable media
    - Homogeneous media
      - Heterogeneous media meets treatment goals less frequently, costs more, and experiences more frequent rebound
  - **Contaminant characteristics**
    - Dissolved phase and low sorbed mass
  - **Adequate design**
    - Oxidant volume and mass
    - Delivery frequency and duration

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These are the conditions under which ISCO performs best – this does NOT mean that ISCO isn't applicable under other conditions… just that they are more challenging for ISCO (and most technologies)

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Transition to ISCO TPM.

ISCO Technology Practices Manual (TPM)

- ESTCP funded development of a TPM including protocols and tools to enable site-specific engineering of ISCO (ER-0623)
  - "In Situ Chemical Oxidation for Groundwater Remediation – Technology Practices Manual", available at SERDP/ESTCP Web site
- Project focus and overall goal
  - The goal is to enable more predictable, cost-effective application at DoD sites by providing knowledge and know-how within an ISCO TPM

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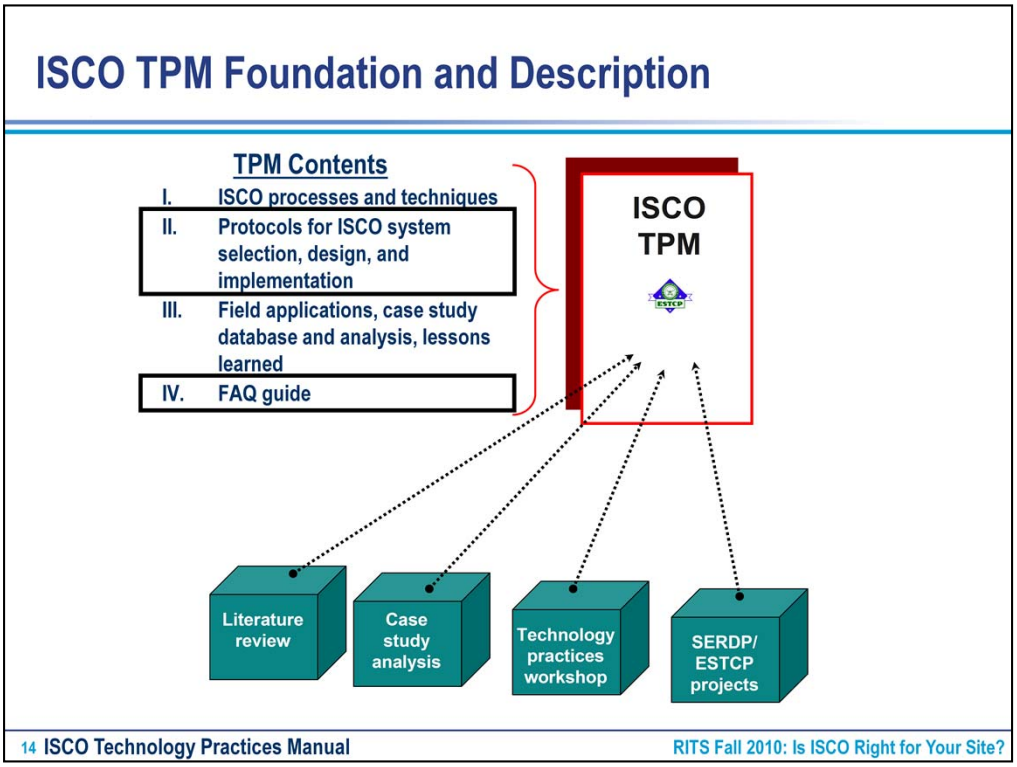
Funded by ESTCP to improve predictability and success of ISCO and develop a standard of practice for the technology.



Introduce building blocks of TPM briefly. Introduce components of TPM. Today's discussion will highlight and integrate the protocol and FAQ.

ISCO Literature

- Critical review of the literature relevant to ISCO science and technology
  - Extensive search of published literature revealed about 600 ISCO-relevant publications
  - Search limited to common oxidants
    - Permanganate
    - Persulfate
    - Hydrogen Peroxide
    - Ozone
  - Sources initially characterized and classified and then thoroughly reviewed for key findings
  - Literature review forms the basis for part of the Technology Practices Manual

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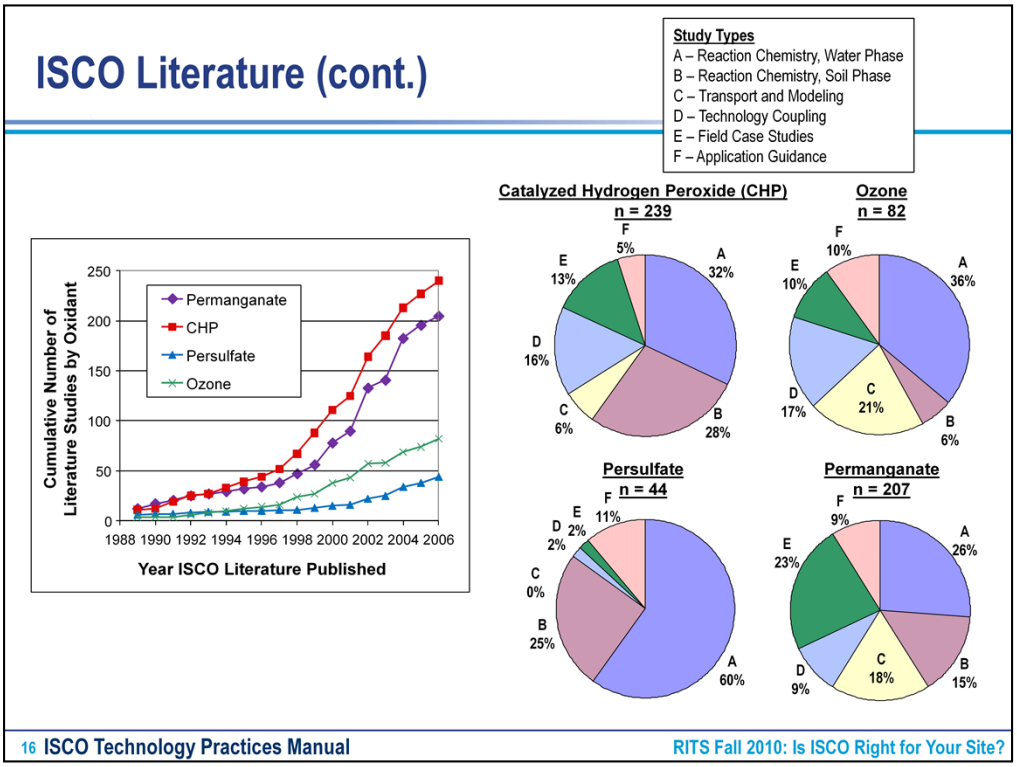
Building Block 1: Introduce approach of literature review (focus on > 600 refs)



Introduce “demographics” of ISCO literature.

ISCO Case Studies

- **Critical analysis of ISCO case studies**
  - **Design of the ISCO database, obtain and extract project information, populate database and analyze information**
  - **ISCO database includes 242 ISCO projects (42 states, 7 nations)**
    - Federal sites (46)
    - Manufacturing/Industrial facilities (45)
    - Dry cleaners (45)
    - Service stations (25)
    - Former MGPs (11)
    - Others
  - **Database available as "DISCO"**
    - ISCO design vs. site conditions vs. cost and performance…

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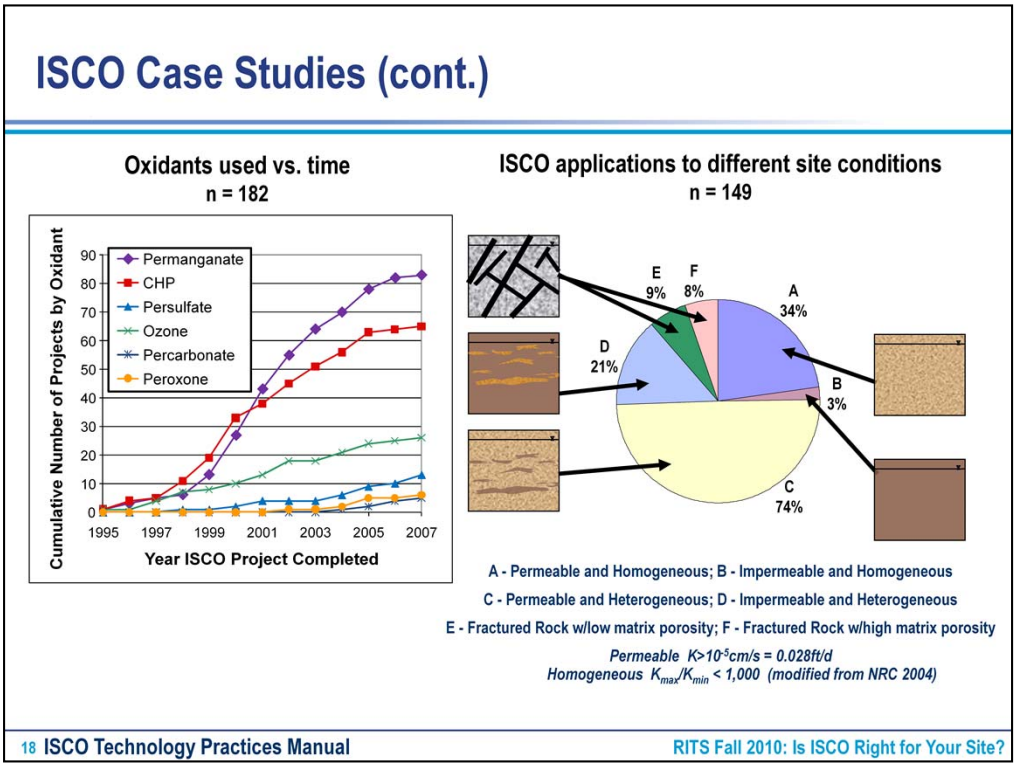
Building Block 2: Introduce approach of case history review. Introduce DISCO. Mention DISCO availability.



Introduce “demographics” of case histories.

Workshop of ISCO Professionals

- **Technology practices workshop convened at Colorado School of Mines**
  - **2-day workshop included 43 participants representing chemical companies, technology vendors, environmental consultants, academics, RPMs**
    - Presentations, panel sessions, and breakout sessions
    - Exercise where 6 scenarios were used to obtain views regarding ISCO design and performance
    - A proceedings document has been published

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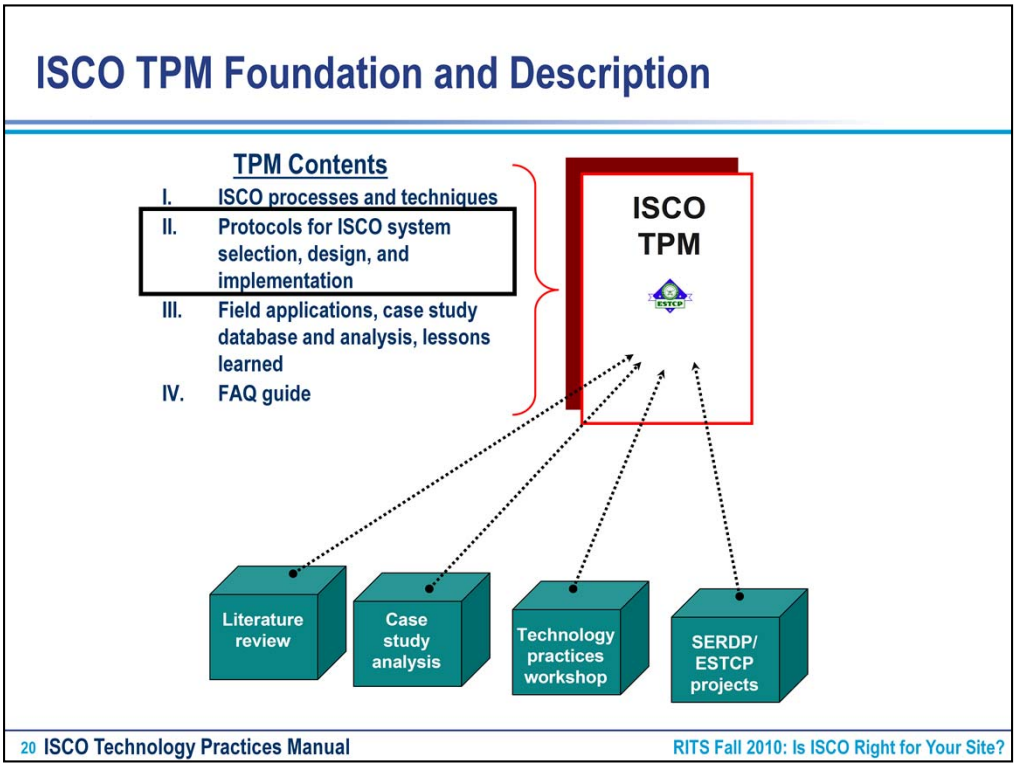
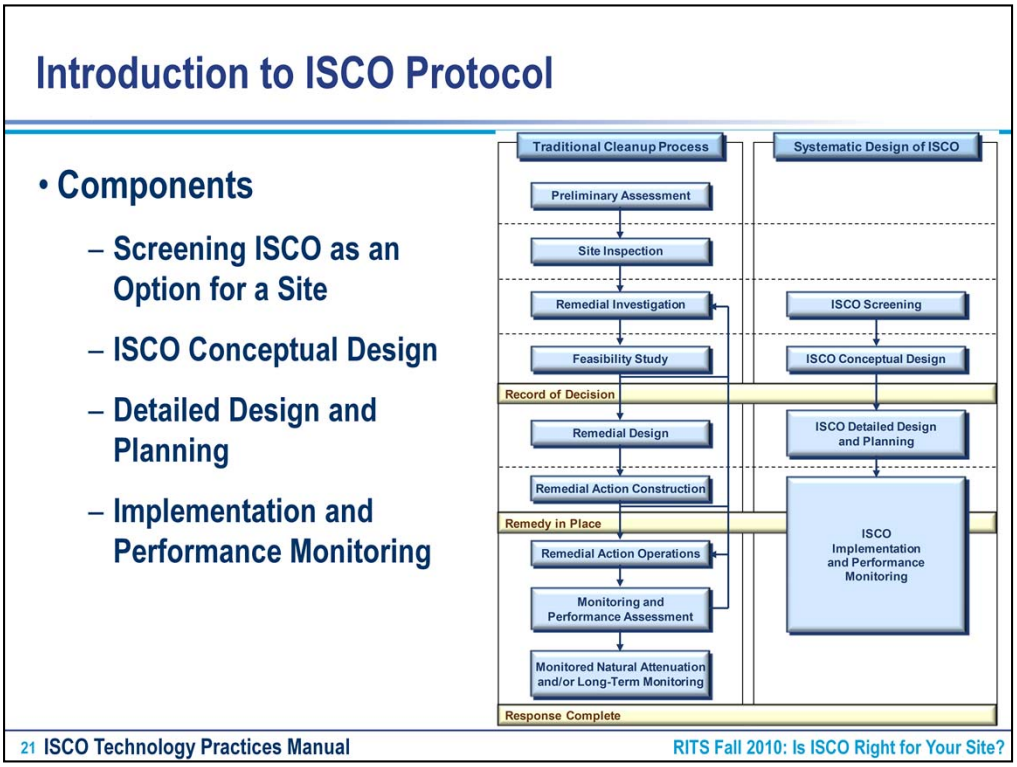
Building Block 3: Introduce ISCO workshop. Mention availability of proceedings document.



Remind audience of focus on protocol to lead into next slide.



Introduce four components of the ISCO protocol. Protocol follows traditional cleanup process.

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Transition to next slide. Will first review frequently asked questions within the Screening component context, then will review the protocol and introduce example tools to see how key factors are considered when screening ISCO's applicability to a site.

How does ISCO work?

- *Electron transfer*

Oxidant + Contaminant → Innocuous Byproducts

  – Simpler chemistry, more predictable, less powerful

- *Free radical oxidation*

Oxidant + Activator → Radicals
Radicals + Contaminant → Innocuous Byproducts

  – More complex chemistry, less predictable, more powerful

CONTACT CONTACT CONTACT!

Matching the oxidant and delivery system to the contaminants of concern and site conditions is critical to achieving performance goals

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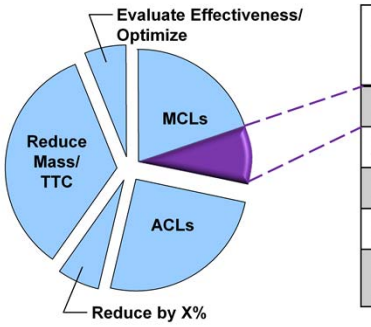
Review points from ISCO fundamentals slides. Emphasize the need for contact… the right oxidant using the right delivery approach for site contaminants and conditions.

What goals can ISCO achieve?

- Large concentration reductions (e.g., 90-99%+) are achievable
- Significant risk reduction and mass flux reduction goals are achievable
- Ability to meet goals depends on
  - Contaminant mass and distribution
  - Hydrogeology
  - Proper design

Frequency of Goals SET for Sites



Goal	% Meeting Goal n = 122
MCLs	21%
ACLs	44%
Reduce by X%	33%
Reduce Mass/TTC	82%
Eval. Effectiveness/ Optimize	100%

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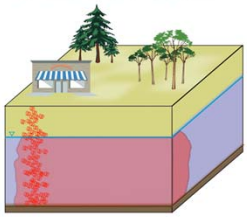
Review achievable goals, dependent factors, data in pie chart from database. Pie = goals set for sites… values on right = % of sites meeting goal within each category.

When does ISCO work best?

- Hydrogeology
  - Permeable media with range of distribution approaches; lower heterogeneity
- Contaminant characteristics
  - Dissolved phase and low sorbed mass
- Proper design
  - Correct reagent at adequate mass and volume
  - Adequate number and frequency of delivery events

When appropriate delivery and contact occur!



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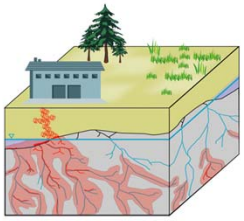
Reiterate from ISCO fundamentals… emphasize that these are the conditions where appropriate contact is most likely.

What conditions are challenging for ISCO?

- **Significant NAPL mass**
  - **Particularly trapped in fractured rock**
    - HOWEVER reduction of mass flux is feasible
  - **Particularly when present as highly saturated pools**
    - HOWEVER ISCO is a viable polishing step following source removal
- **Treatment to MCLs in source areas**
- **Large, diffuse plumes**
- **Presence of natural materials that are highly reactive with oxidants**



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Review most challenging conditions. These do not preclude applying ISCO in these settings… just that expectations must be reasonable or other options may be more appropriate.

Is pre- or post-ISCO treatment beneficial?

- Pre-ISCO mass recovery or Post-ISCO polishing
  ↑ probability of meeting goals; ↓ costs; ↓ time
- Examples from case histories
  - Pre-ISCO excavation, pump & treat, and soil-vapor extraction are most common (in that order)
  - Post-ISCO enhanced bio and Monitored Natural Attenuation (MNA) are most common
    - MNA used post-ISCO at 19% of sites in database, likely an underestimate
  - Post-ISCO coupling more common at DNAPL sites

Present DISCO evidence of value of pre- and post-ISCO treatment

What ISCO chemistry options are out there?

- Permanganate
- Catalyzed hydrogen peroxide (CHP, or Modified Fenton's reagent)
  - Natural iron
  - Chelated-iron (wide range of chelating agents)
  - Iron + low pH
- Persulfate/Activated Persulfate
  - Heat
  - Hydrogen peroxide (H_2O_2)
  - Chelated-iron
  - Alkaline pH
- Ozone
- Others (e.g., Peroxone, Percarbonate)

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Review the array of options. Presented oxidants earlier… here the focus is activation. Different approaches work better at different sites and with different contaminants.

What ISCO delivery options are out there?

- **Most common**
  - **Vertical well injection**
  - **Direct push probe**
- **Others**
  - **Often due to CONTACT limitations**

Delivery Method (n=148)	Count	Percent
Injection Wells	53	35.8
Direct Push	35	23.6
Sparge Points	24	16.2
Infiltration	17	11.5
Injectors	11	7.4
Recirculation	9	6.1
Fracturing	8	5.4
Mechanical Mixing	3	2.0
Horizontal Wells	2	1.4

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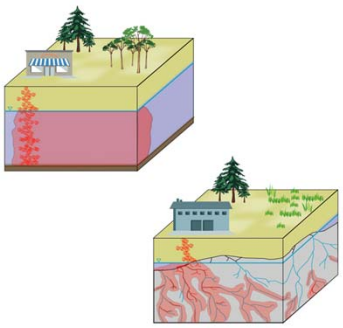
Review the most common delivery approaches and statistics from DISCO of frequency of use (table).

How do I choose the best option?

- Understand site conditions!
  - Ability to degrade COCs
  - Deliverability with respect to site-specific hydrogeology and geochemistry
  - Appropriate treatment goals for site conditions



There is no one oxidant and/or delivery approach that works for all contaminant, hydrogeology, & geochemical conditions!

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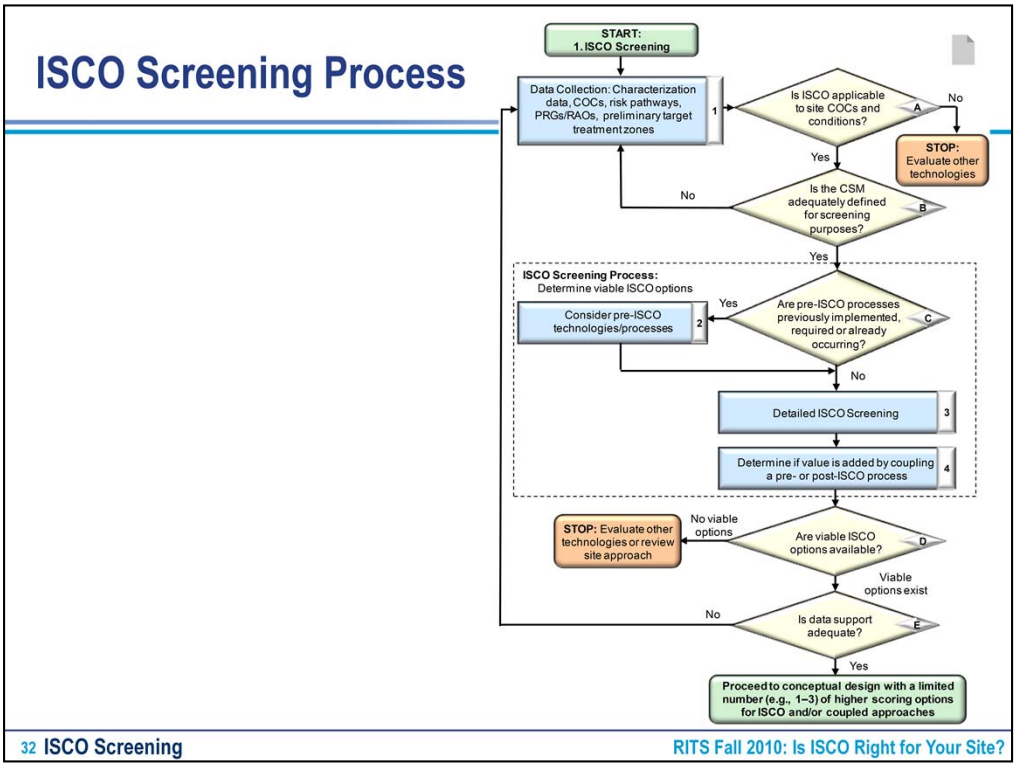
Summary slide (this is the trick… choosing the best option). Focus on selecting the right oxidant for the contaminant and site geochemistry, the right delivery approach for the oxidant and geology, having appropriate goals, and having appropriate expectations for ISCO meeting goals.

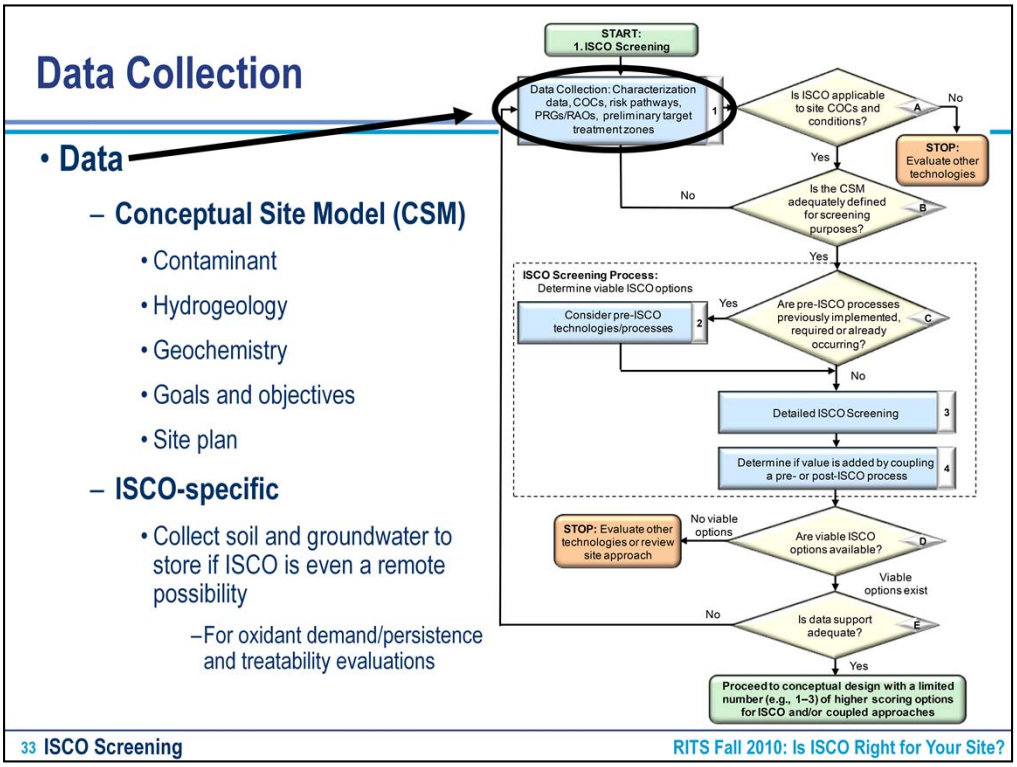
ISCO Screening: Lessons Learned

- **Successful ISCO depends on:**
  - **Understanding site conditions**
    - Basic geology, geochemistry, contaminant mass and its distribution
  - **Selecting the correct oxidant for the site contaminants and geochemical conditions**
  - **Selecting the correct delivery approach for the oxidant and site hydrogeological conditions**
  - **Appropriate treatment goals for site conditions**
    - Understanding ISCO's ability to meet these goals
  - **Coupling ISCO with other pre- or post-ISCO conditions appropriately**
  - **Appropriate design: mass, volume, frequency, duration**

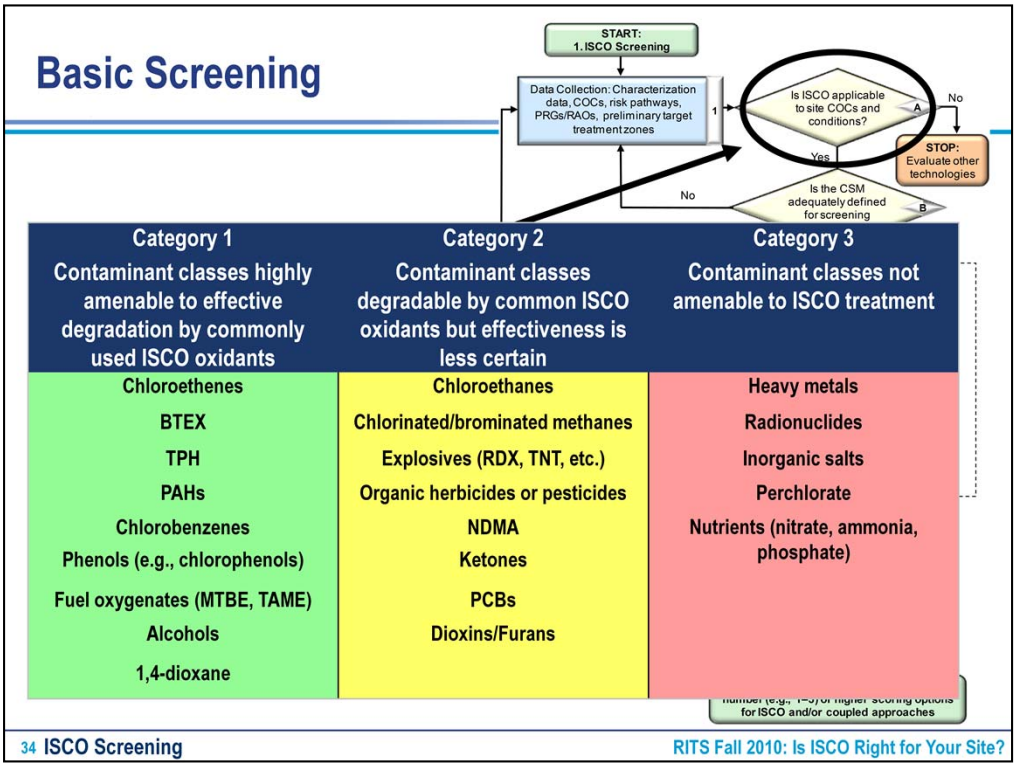
Summary of FAQ lessons learned… lead in to protocol.



Introduce Screening component of protocol. The initial part of the screening process is to collect the right data, then consider very basic site characteristics to consider viability of ISCO in general… then move to a higher level of screening looking in detail at site geology and geochemistry toward selecting an oxidant and delivery approach (or range of options thereof). The protocol finishes with a review of data adequacy toward conceptual design. Underlying each “process” (box) or “decision point” (diamond) there is guidance… text-based guidance, checklists, excel-based tools, etc.



The majority of data to collect is data typical of the RI process toward building a CSM with high certainty. It is advised to collect soil and groundwater toward treatability evaluations now if ISCO is even a remote possibility to save costs associated with later mobilizations to meet data needs.

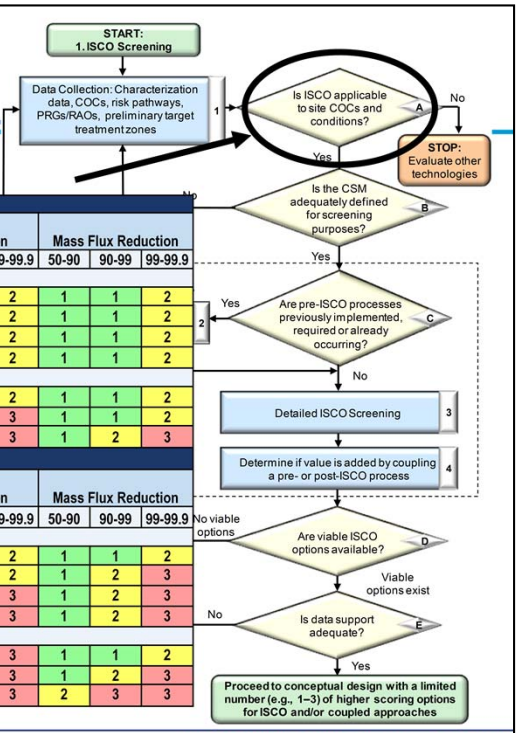


The first level of initial screening is to evaluate if ISCO is a possibility for the contaminants at the site. Green = yes and lots of data support, Yellow = contaminants are oxidizable but either slowly or with little data support; red = not amenable. Important to consider co-contaminants or naturally present materials with “red” category characteristics as well.

Basic Screening (cont.)

Low Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	2	1	1	2	1	1	2
Homogeneous low permeability	1	2	2	1	1	2	1	1	2
Heterogeneous low permeability	1	2	2	1	1	2	1	1	2
Consolidated media (fractured)									
Sedimentary	1	2	2	1	1	2	1	1	2
Igneous/metamorphic	1	2	3	1	2	3	1	1	2
Karst	1	2	3	2	2	3	1	2	3

High Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	3	1	1	2	1	2	3
Homogeneous low permeability	1	2	3	1	2	3	1	2	3
Heterogeneous low permeability	1	2	3	1	2	3	1	2	3
Consolidated media (fractured)									
Sedimentary	1	2	3	1	2	3	1	1	2
Igneous/metamorphic	2	2	3	2	3	3	1	2	3
Karst	2	3	3	3	3	3	2	3	3



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Next we move to the next level of screening, considering contaminant concentration/mass (upper/lower table portions), basic geology (left-hand column), and treatment goals (columns across top). Using the same green, yellow, red designation… (transition to next slide)

Basic Screening (cont.)

Low Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
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Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
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Homogeneous permeable	1	1	2	1	1	2	1	1	2
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Homogeneous low permeability	1	2	3	1	2	3	1	2	3
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Consolidated media (fractured)									
Sedimentary	1	2	3	1	2	3	1	1	2
Igneous/metamorphic	2	2	3	2	3	3	1	2	3
Karst	2	3	3	3	3	3	2	3	3

High Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
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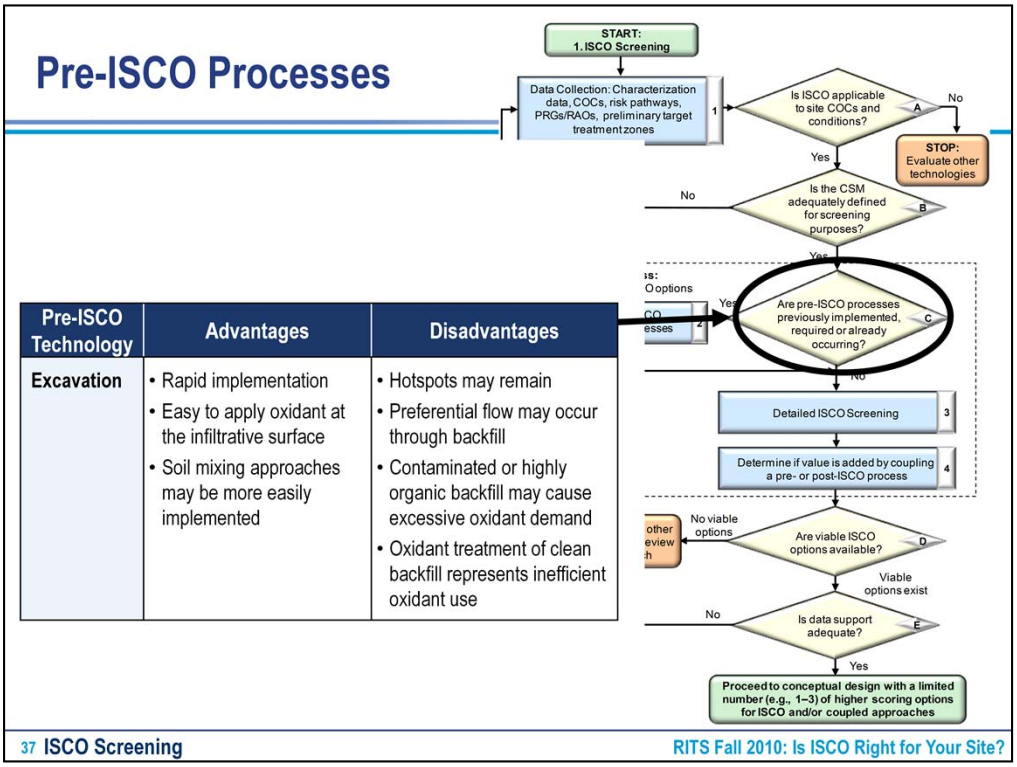
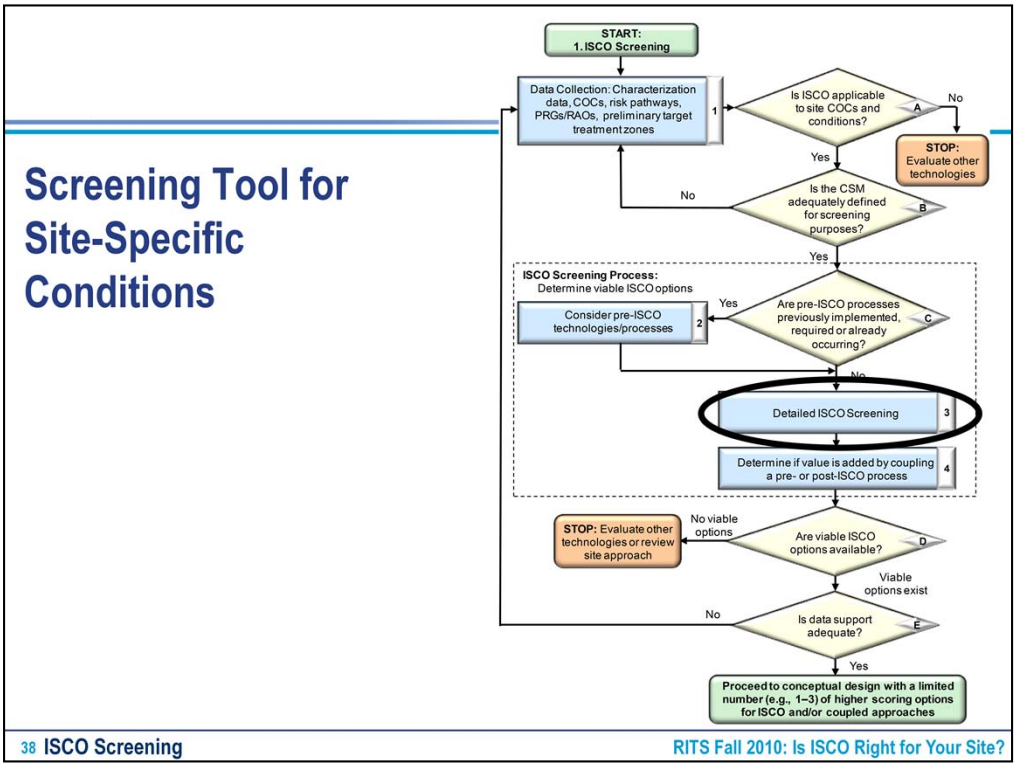
Homogeneous low permeability	1	2	3	1	2	3	1	2	3
Heterogeneous low permeability	1	2	3	1	2	3	1	2	3

We can look at an example. Focus on the fact that stringent goals with high contaminant mass density are very challenging to meet (for any technology, really). More complex geology is harder to treat.



Pre-ISCO Technology	Advantages	Disadvantages
Excavation	• Rapid implementation • Easy to apply oxidant at the infiltrative surface • Soil mixing approaches may be more easily implemented	• Hotspots may remain • Preferential flow may occur through backfill • Contaminated or highly organic backfill may cause excessive oxidant demand • Oxidant treatment of clean backfill represents inefficient oxidant use

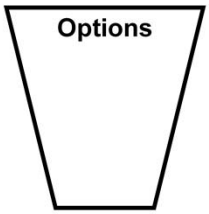
Another step in the screening process is to consider what has happened previously at the site and how they may impact ISCO viability. The TPM contains a set of look-up tables that capture advantages and disadvantages of other approaches occurring before ISCO. For example, excavation can remove high contaminant mass density (beneficial), but we need to think about the materials used to backfill and how it may interact with oxidant.



Next we move to a higher level of screening, where we consider in more detail site geology and geochemistry. The goal is to narrow the oxidant and delivery options for the site based on these site characteristics.

Screening Tool for Site-Specific Conditions (cont.)

- Site factors
  - Basic geology
  - Contaminants and co-contaminants
  - Geochemistry (e.g., pH, alkalinity, chloride, organic carbon content)
  - Aquifer hydrology parameters (e.g., permeability and heterogeneity)
- Lookup categories
  - Appropriate oxidant and activation approaches for contaminant(s)
  - Appropriate oxidant and activation approaches for geochemistry
  - Appropriate delivery approach for viable oxidants
  - Appropriate delivery approach for geology



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The TPM includes an excel-based tool to help with this. The tool captures the key site considerations (review list). The tool then refers to a series of look-up tables that help to select the oxidant, oxidant activation approach, and oxidant delivery approach. (Review list of lookup tables) In this way we narrow the options for the site and sort out those that are most viable.

Screening Tool for Site-Specific Conditions (cont.)

- **Output**
  - **Narrower range of viable options for the site based on site-specific factors**
  - **These are the options that can be carried to the Conceptual Design phase**
- **NOTE**
  - **There is room for practitioner experience and expertise in the process!**
  - **Other key considerations in selecting the oxidant and delivery approach**
    - Issues of implementability
      - Are there operations/activities or structures that cannot be disrupted?
      - Are there subsurface utilities that must be considered?

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The output is a “scored” range of viable approaches for the site to being Conceptual Design process. It is important to note that practitioner experience is valued in the process… if a preferred option is one of several viable options, then it is appropriate to move forward with that preferred approach. There are other considerations, too, that lookup tables don’t capture… for example site disruption.

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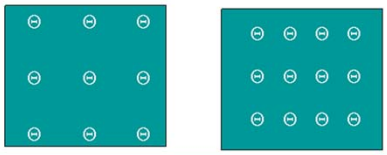
Transition to Conceptual Design FAQs

How many injection points?

- Function of
  - Oxidant characteristics – reaction and/or decomposition
  - Oxidant depletion/decomposition rate
  - Delivery duration and rate
  - Delivery volume
  - Porosity
  - Contaminant mass and mass distribution

TO WHAT EXTENT ARE THESE VALUES WELL UNDERSTOOD WHEN INITIATING ISCO DESIGN?



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There are many site-specific and design factors that will influence the number and spacing of ISCO injection points. We may start off having a low degree of certainty about some of these conditions. Conceptual design occurs in two tiers – first a design estimate based on known or assumed values (or range thereof). This may be done with several ISCO options (to compare oxidants or delivery methods, perhaps). When we start to get close to an effective or cost-effective design, then we reduce uncertainty about these parameters and others through data collection (Tier 2).

How many injection events?

- Typical number of injections is 2-3
  - Average number of injection events in case study database is ~3
  - Survey of professionals: 78% said 2 or more injection rounds was their average experience of ISCO for dissolved plumes in sandy media
  - Will not know exact number of events before project start
- Observational approach is critical component of execution
  - Forms basis for decision based on site-specific experiences

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The probability of success with one injection alone is very low. To treat sorbed or NAPL contaminant, the contaminant must first desorb or dissolve. This re-equilibration of contaminant mass in the more densely contaminated areas isn't always predictable and is monitored real-time. The observational approach (will review this in a moment) is a critical component of ISCO implementation.

What volume of oxidant?

- More successful sites tend to have longer injection duration per injection event AND greater total volume of oxidant delivered
- Review of case histories
  - PCE sites with >90% reduction = 0.51 PV
  - PCE sites with <90% reduction = 0.24 PV
  - TCE sites with >90% reduction = 0.49 PV
  - TCE sites with <90% reduction = 0.24 PV
- Survey of professionals
  - 10-30% of PV is average injected volume specified in design

Review stats from DISCO. Average current practice may not reflect the design factors associated with success.

What are treatability and pilot tests?

- Treatability tests are:
  - Laboratory-scale ISCO simulations
  - Also called “bench tests”
  - Batch reactors or flow-through columns/tanks
  - Used to evaluate ISCO chemistry issues
- Pilot tests are:
  - Initial ISCO application performed at field site
  - Generally smaller scale than anticipated full scale application
  - Used to evaluate oxidant delivery issues

Briefly explain what bench and pilot studies are.

Why perform lab treatability tests?

- Improve understanding of system chemistry
  - Contaminant destruction extent and rate under idealized conditions
  - Oxidant depletion extent and rate
  - NAPL destruction
  - Byproducts/intermediates and other geochemical impacts (e.g., metals mobilization)

Basic oxidant demand test and contaminant treatability test: typically under $10-20K
Duration: 1 week to 2 months
More complexity = greater cost and longer duration

- Byproducts/intermediates analysis, transport evaluations, complex contaminant mixtures, extensive number of reaction conditions

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The goal of treatability tests is to reduce the uncertainty associated with reaction chemistry.

Why perform lab treatability tests? (cont.)

- Will the oxidant sterilize the soil and prevent future microbial degradation of contaminants?

  NO!

- Can ISCO byproducts inhibit or enhance bioprocesses?

  BOTH!

- Does ISCO mobilize metals?

  Be aware of and prepare for possibility

- What other effects does ISCO have?

  pH, solids, gas, temperature, DO, specific conductance
  THESE ARE GREAT MARKERS OF DELIVERY…

Some additional related FAQs…

Why perform field pilot-scale tests?

- To assess
  - Ability of formation to accept volume of oxidant and/or rate of delivery
  - Impact of heterogeneities on oxidant distribution
  - Radius or zone of influence of oxidant
  - Design certainty
  - Treatment effectiveness
  - Rebound potential
  - BONUS: initial contaminant mass destruction
- Example from case histories
  - In heterogeneous media with DNAPL, the percentage reduction of chlorinated VOCs was greater at full-scale sites that performed pilot tests

The purpose of pilot tests is to reduce the uncertainty associated with oxidant deliverability

What does ISCO cost?

- **What are typical or expected costs?**
  - **Median: $94/yd^3 (n=33)**
  - **Median total project cost: $220,000 (n=55)**
- **What are the primary determinants of cost?**
  - **COC group**
    - Contaminant solubility and hydrophobicity
    - Amenability to biodegradation
  - **Geology**
    - Permeability and heterogeneity
  - **Contaminant mass density**
    - DNAPL treated at higher cost

Median number of delivery events = 2 (n=27)

Median duration of delivery events = 8 days (n=19)

Median PVs = 0.2 (n=21)

(above includes only sites with unit cost data, and omits ozone projects, which typically last longer but are automated systems)

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Median costs from DISCO and factors that impact cost (statistically). “Cost” is also resources and time (call out box)

What does ISCO cost relative to other technologies?

- Median costs of treatment at DNAPL source zones:
  - Bioremediation $29/yd^3
  - Thermal $88/yd^3
  - ISCO $125/yd^3
  - Surfactant/Cosolvent Flushing $385/yd^3
- Industry thinking is that total costs are

  Bioremediation < ISCO < Thermal
- Industry thinking is that total time required to achieve treatment is

  Thermal < ISCO < Bioremediation

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Note that costs shown are for DNAPL sites.

Costs are in ballpark of other technologies.

NOTE: What is the cost associated with choosing the WRONG technology?

What do ISCO reagents cost relative to other options?

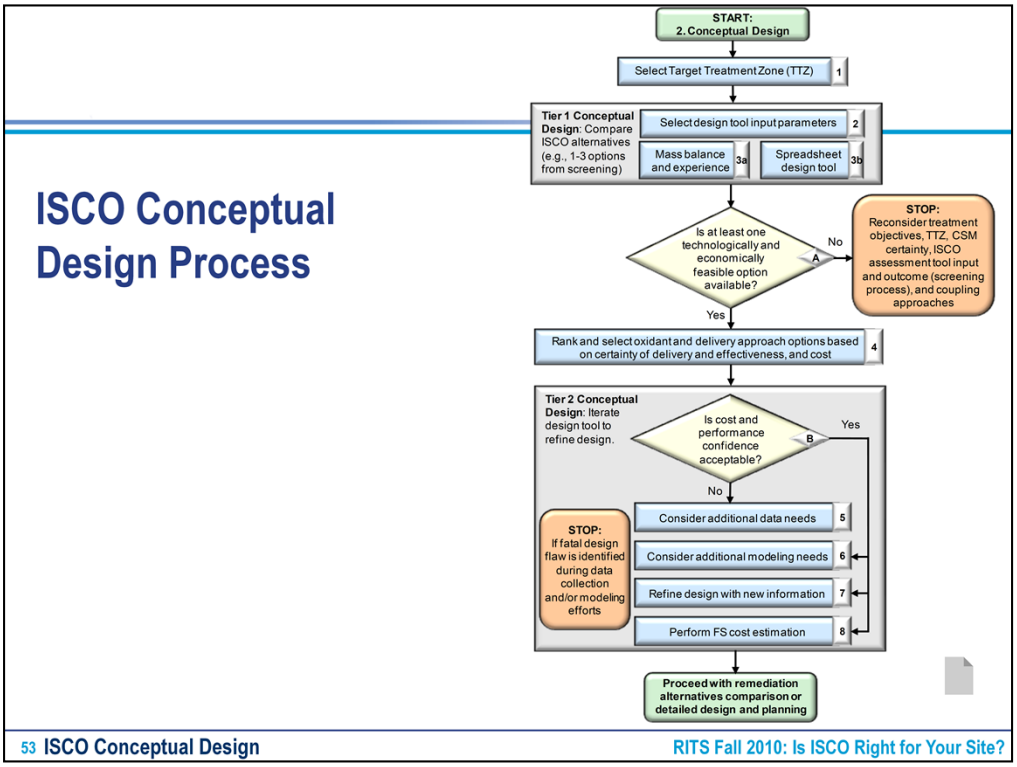
- Approximate ISCO Reagent Costs
  - Permanganate $2/lb
  - Persulfate $2/lb
  - Hydrogen Peroxide $0.5/lb (50% to 67% water)
  - Ozone costs depend on generator
- Approximate Bioremediation Reagent Costs
  - Molasses $0.4/lb
  - Sodium Lactate $1/lb
  - Emulsified Oils $1 to $2/lb (~50% water)

Costs of oxidants and other amendments… but the costs aren't necessarily comparable… a pound of one amendment does not do the same amount of work as a pound of another. More appropriate to compare options at Feasibility Study stage AFTER sending the options through the conceptual design process.

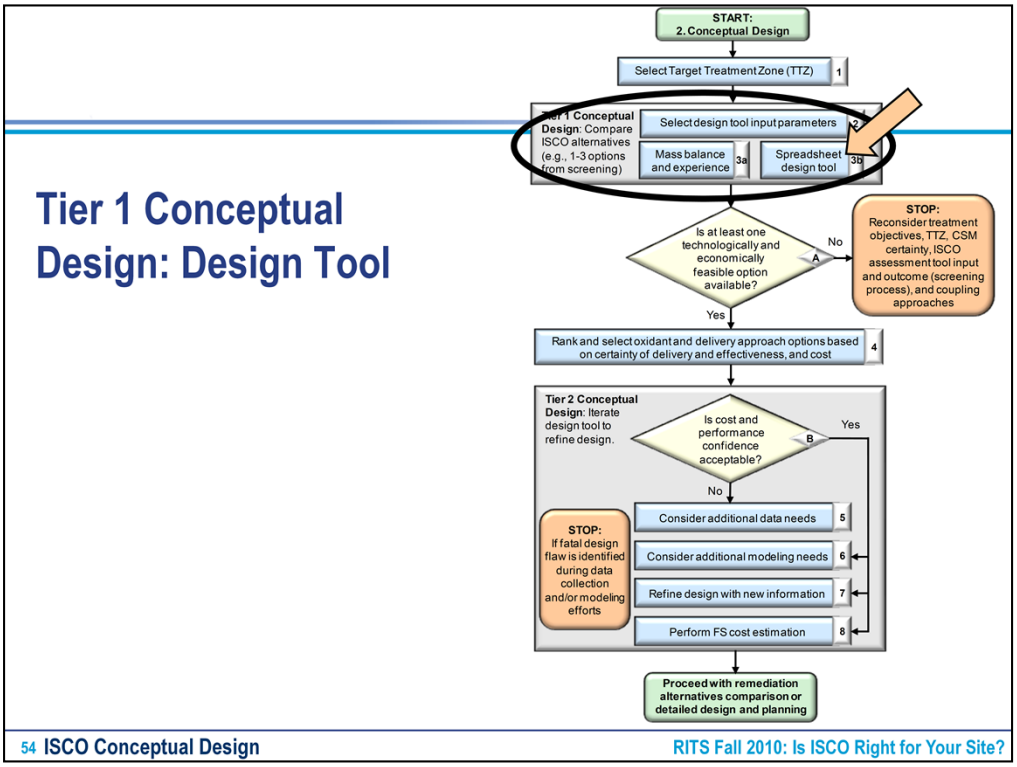
ISCO Conceptual Design: Lessons Learned

- **Successful ISCO depends on:**
  - **Understanding interaction of oxidants with natural media**
    - Relationship of rate of oxidant depletion to rate of oxidant delivery
  - **Applying the appropriate mass, concentration, and volume**
    - Increasing delivery volume has been associated with success
  - **Planning for multiple delivery events**
  - **Understanding design uncertainty**
    - If focused on chemistry/geochemistry, reduce uncertainty with lab tests
    - If focused on issues of deliverability, reduce uncertainty with pilot tests
  - **Understanding cost variables and appropriately reducing cost uncertainty**
    - Costs are minimized through solid design and real-time decision making

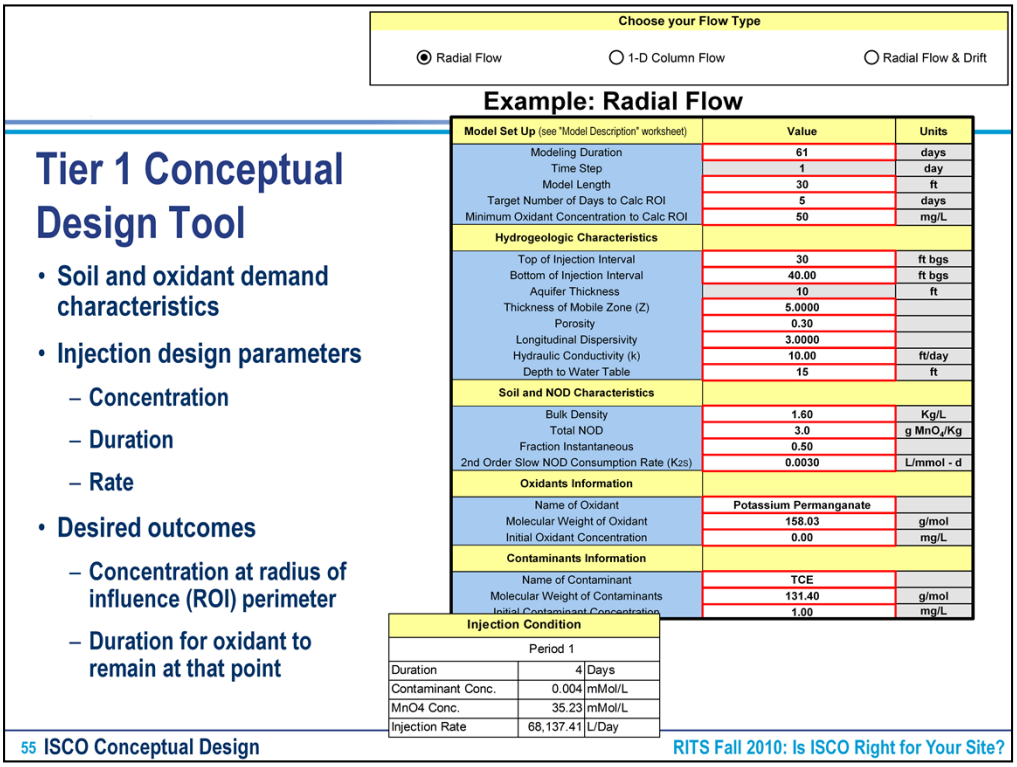
Lessons learned… leading to the Conceptual design process



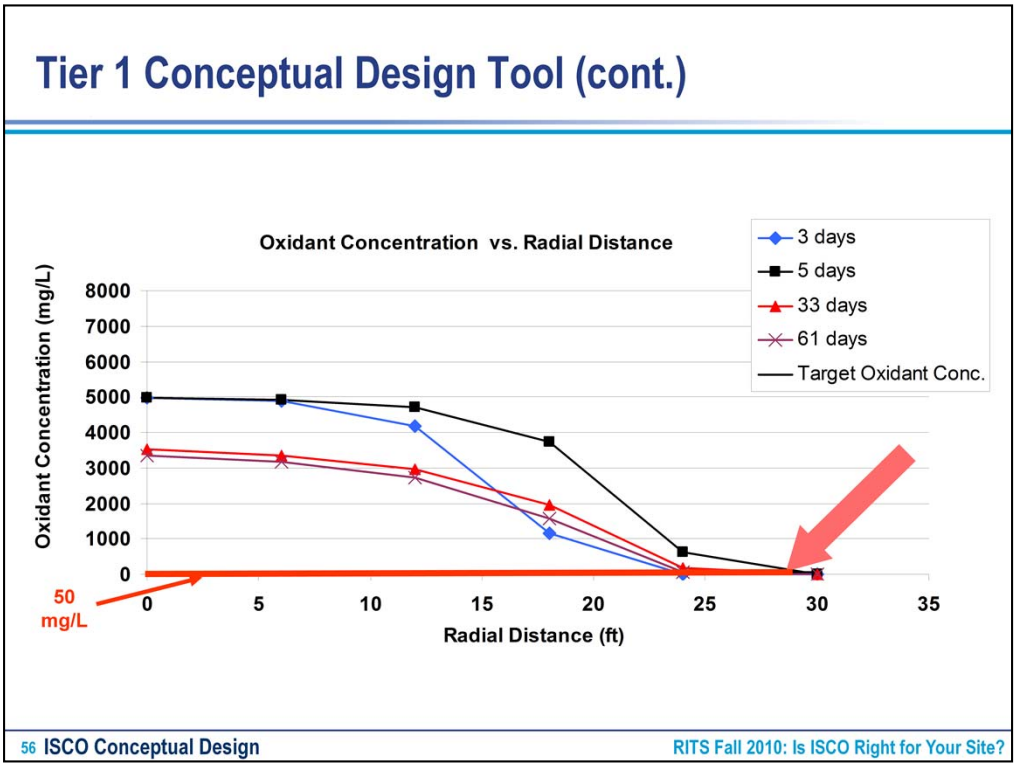
Note: Tier 1 – you may have low certainty of input values, but a valuable process to compare options you leave ISCO Screening process with. The most viable (technical/cost) option is carried to Tier 2 design, where data collection occurs toward reducing uncertainty (cost and effectiveness).



Will be showing an example of Tier 1 design using a tool developed for permanganate delivery, focusing on the key factors that must be considered for a good conceptual design.



The design tool estimates the oxidant's radius of influence for a given set of input conditions (site and design characteristics). This is what the input page of the tool looks like. The input parameters that are most critical include: (1) rate and extent of natural oxidant demand, (2) injection concentration, duration, and rate, and (3) the outcomes desired, including the concentration desired at the ROI and the duration you want that concentration to last. The tools runs quickly and efficiently to evaluate a range of these key parameters. Next, you enter info about the size of the site and the tool estimates the total number of injection points needed to cover the site. These values, along with a selection of how you will inject (well, direct push) are integrated with a cost estimation tool that captures capital, O&M, and post-closure costs associated with the particular design.



The output includes concentration vs. distance from injection. It shows these data for a range of time points based on model input. From these data, the tool then estimates an ROI. This is the desired concentration for the duration of interest. In this example, we are looking for 50 mg/L for 5 days. The ROI = 28 ft.

Tier 1 Conceptual Design Tool: Examples

- **Base case**
  - **60 day model duration; minimum oxidant concentration to achieve = 50 mg/L**
  - **Treatment area = 50' x 75'**
  - **Injecting into 10' thickness at 30-40' depth interval**
    - 5 foot mobile zone within the 10 foot thickness
  - **Longitudinal dispersivity = 3 ft**
  - **Hydraulic conductivity = 10 ft/day**
  - **Natural oxidant demand = 1 g MnO_4^-/kg porous media**
    - Fraction instantaneous = 0.5
    - 2nd order rate for slower fraction = 0.003 L/mmol-d
  - **Radius of influence (ROI) overlap desired = 20%**
  - **Five days of injection (2 injection events)**
  - **5,000 mg/L oxidant concentration**

WELL DELIVERY
- 2" well
- 25 psi inj. pressure
- 10 hours/day

= 6,000 gpd/well

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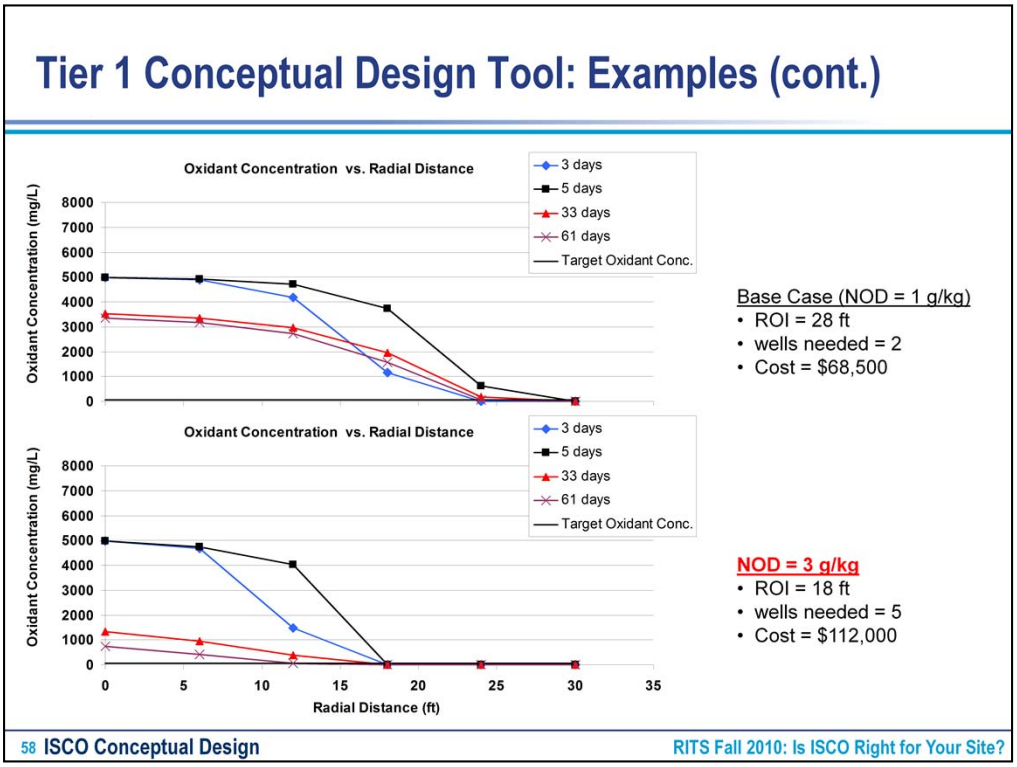
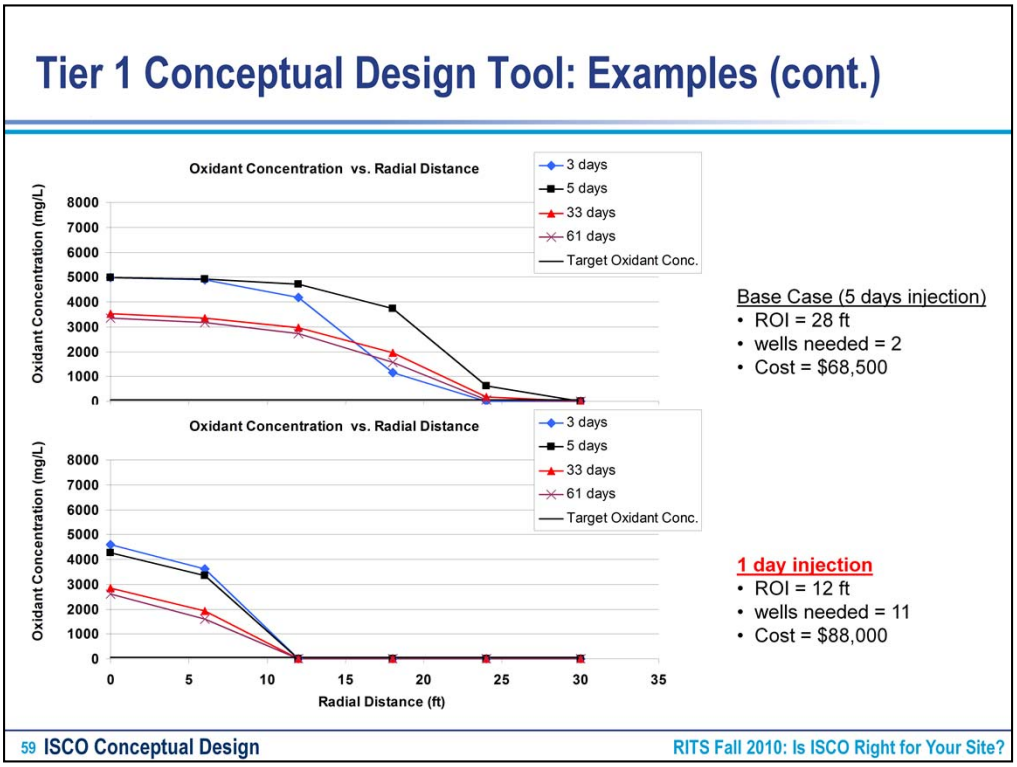
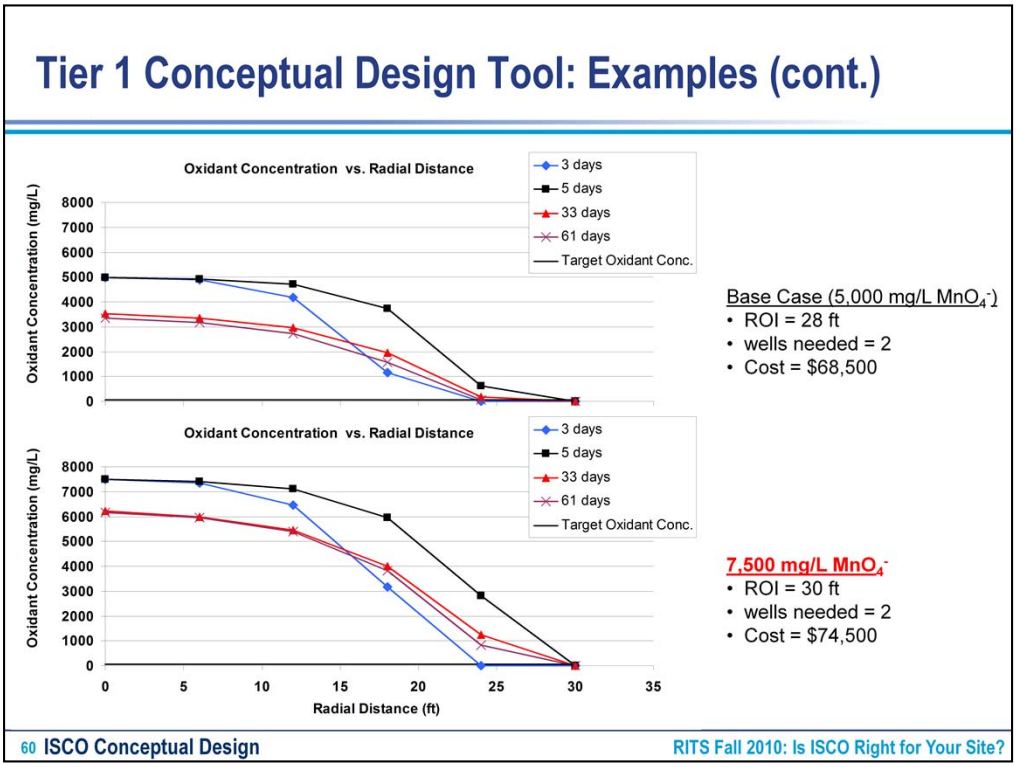
An example to see how a range of site and design characteristics for the site can be examined, as well as the influence of uncertainty of values on cost uncertainty. Review base conditions for the model run. The values in RED will be varied in the next sets of runs.



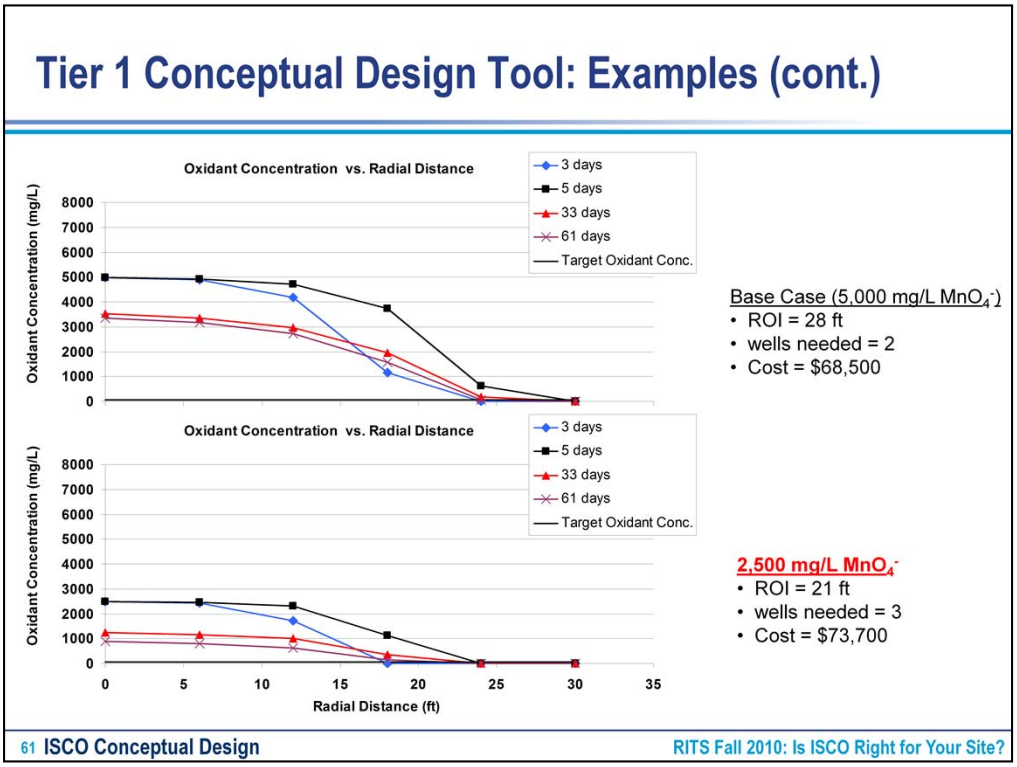
Top = output of base case (this is the output we saw in earlier slide). For our 50 x 75' site, we need two wells at a cost of $68,500. What if we are uncertain of NOD value? Outcome if NOD is really higher (3 g/kg)… ROI = 18 ft, 6 wells needed, cost = $112K. Is this acceptable cost and performance uncertainty? NOD test costs around $5-$10K… worth it?



Example injecting one day vs. 5 days…

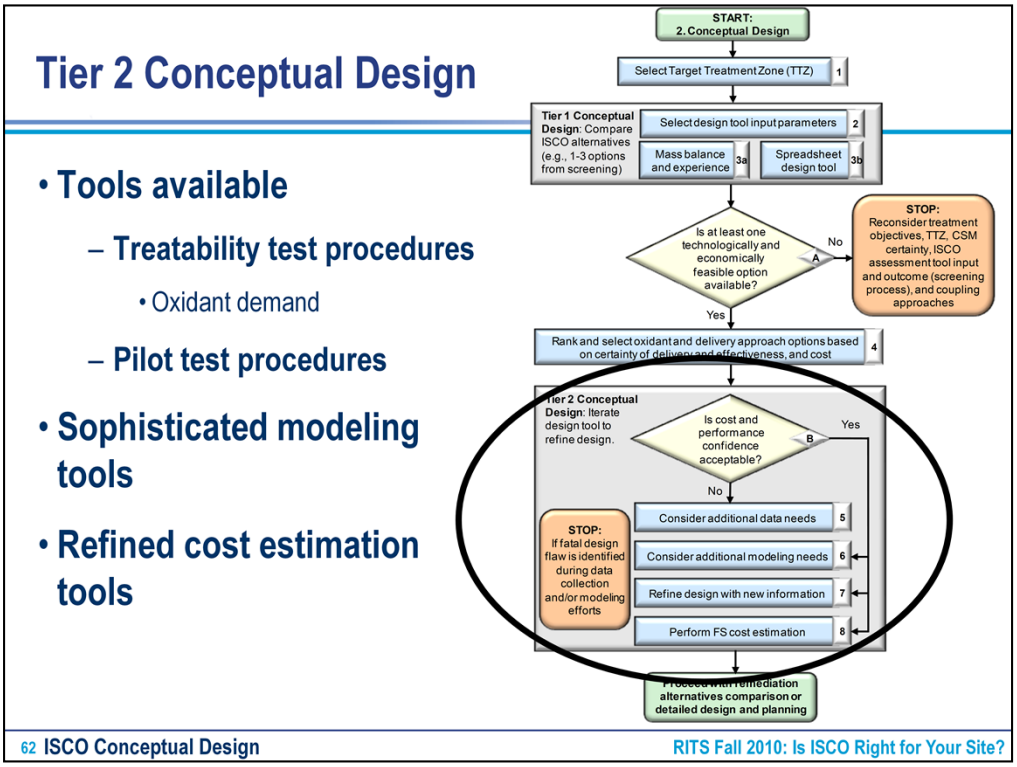


Example with higher concentration… does it add value? NO (costs more)



Does lower concentration add value? NO… need another well. Costs more.

IMPORTANT POINT: Outcome estimates are specific to base case values!! Changing variables will have an impact that is site-specific and design-specific. This depends on factors such as rate of delivery, rate of NOD, desired oxidant concentration, etc.



Tier 1 can be used to hone in on an appropriate site-specific design. Tier 2 focuses on reducing uncertainty associated with the “best” design. Treatability or pilot tests may be conducted to capture issues associated with chemistry or delivery uncertainty. More sophisticated modeling tools may be applied for more complex sites. And costing is conducted with a higher level of detail. After leaving Tier 2 design, we are ready to compare ISCO to other technologies at the FS stage.

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Transition to FAQs associated with both of last two components: Detailed Design and Planning; Implementation and Performance Monitoring

Are there regulatory issues for ISCO?

- Similar for all oxidants
- Regulatory Programs
  - RCRA Hazardous Waste RSD for ex-situ systems
  - CERCLA "release" or "process" definition
  - EPCRA reporting
- State approval for materials (variances have been granted)
- Underground injection control (UIC)
- Homeland Security Top-Screen
- Secondary containment
- Occupational Safety Health Administration (OSHA)
- Potential for exacerbation of indoor air exposure
- Impacts to secondary water quality standards
  - Taste and odor
    - Manganese, sulfate, etc.
- Metals residuals after ISCO

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Review typical regulatory considerations

What are the important safety precautions?

- Careful health and safety planning, training, and monitoring is mandatory
- Common hazards
  - Chemical potential energy
  - Exothermic reaction heat and gases
  - Chemical incompatibility
  - High pressure
  - Acids/bases
  - Electrical
  - Dust hazards
  - Leak potentials

Review common hazards. Stress the importance of planning, preparing, and training for these hazards.

What should be monitored?

- **Dynamic, adaptive, flexible**
- **Real-time (optimization)**
- **Baseline, routine, closure**

- **Two phases**
  - **Delivery/Operational**
    - Many of the products of ISCO (e.g., pH, gas, dissolved oxygen, solids, etc.) are excellent indicators of successful delivery
    - Delivery should be confirmed BEFORE treatment monitoring is initiated
  - **Treatment/Performance**
    - Verification of desired COC treatment
    - Can include sampling of groundwater and/or soil phases

Monitoring should allow for real-time decision making based on outcomes measured in the field.

How is design optimized real time?

- **Triad Approach**
- **Observational Method**
  - **Integrate performance monitoring results and decision logic REAL-TIME**
    - Operation/injection can be adapted "as you go"
  - **Relies on understanding of and planning for uncertainties**
    - Reasonable bounds of conditions and response plans
- **Techniques**
  - **Direct push technologies (DPT)**
  - **In situ sensors with data loggers (e.g., temperature, conductivity)**

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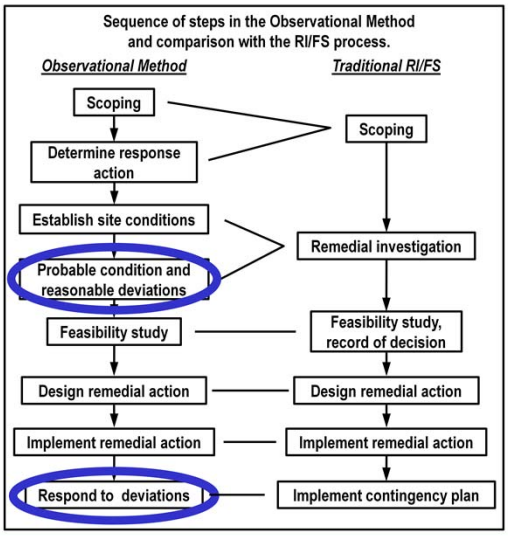

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The observational method calls for estimating a range probable conditions for the site and for delivery performance, along with contingency plans to adapt to actual measured conditions real-time in the field. Field techniques that facilitate this include in situ sensors and direct push technologies… can really be worth the added cost!

Is rebound a problem?

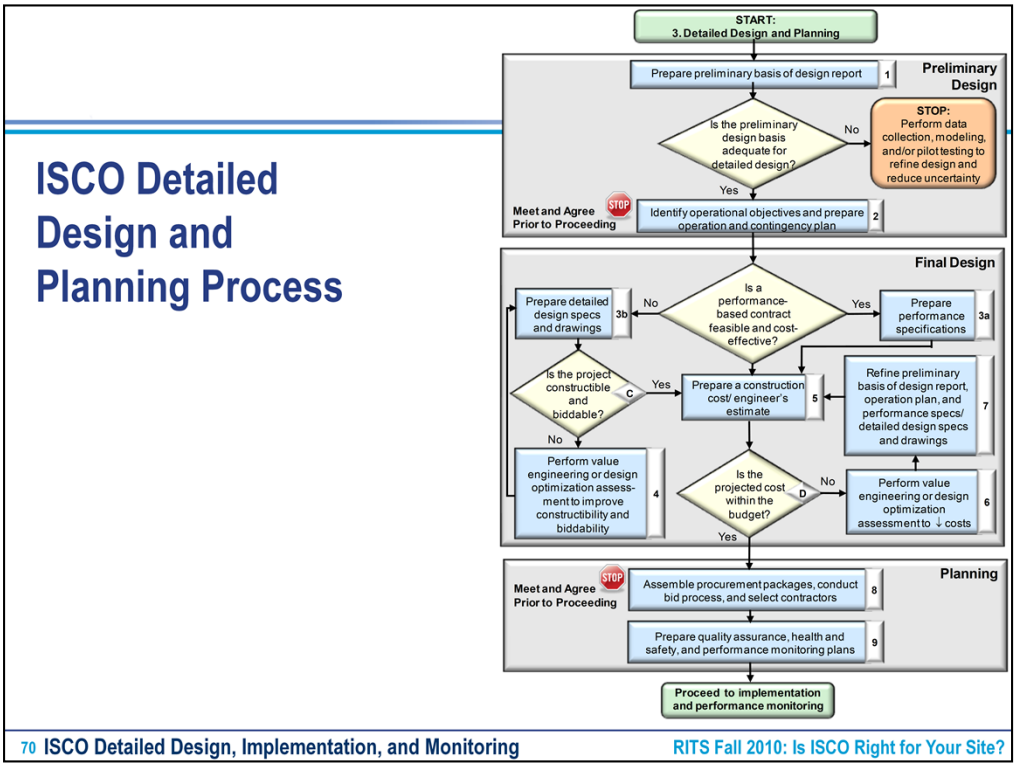
- **Rebound defined**
  - **Increase in aqueous phase COC concentrations that occur after ISCO following an initial reduction in concentration that resulted from the ISCO application: NOT influx**
- **Causes**
  - **Contaminant mass remains untreated**
    - Post-ISCO equilibration/partitioning
- **ATTRIBUTES**
  - **Marking transfer of contaminants to more treatable aqueous phase**
  - **Can help locate unknown NAPL/sorbed**

Rebound is NOT influx from upgradient. It is to be expected as sites re-equilibrate from ISCO treatment. It helps site contaminant moving into a more mobile and treatable phase. It can help find specific source zones. Used to plan subsequent injections.

ISCO Detailed Design, Planning, Implementation and Monitoring: Lessons Learned

- **Successful ISCO depends on:**
  - **Regulatory compliance**
  - **Understanding and planning for hazards associated with handling oxidants**
  - **Real-time, dynamic monitoring**
    - Delivery and treatment performance considered independently
  - **Applying the Observational Method or Triad Approach**
    - Real-time decision making and optimization
    - Contingency planning
  - **Planning for and exploiting "rebound" or contaminant re-equilibration**

Review key lessons learned and transition to protocol components. Protocol components will be very briefly touched on. These last two components are not necessarily unique to ISCO.



Present diagram. Focus in on stages… Preliminary Design, Final Design, Planning.

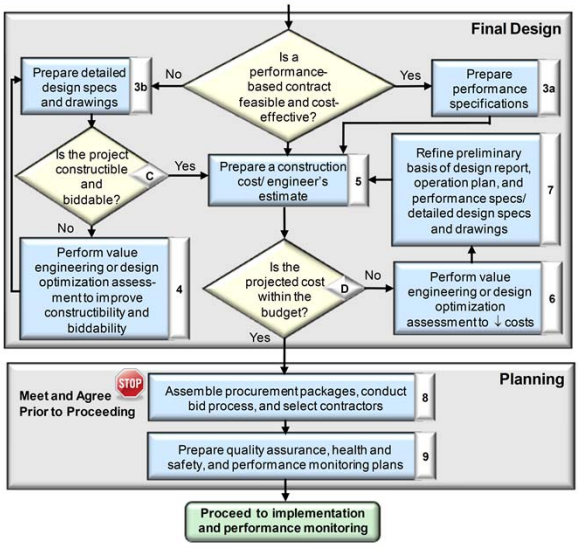
ISCO Detailed Design and Planning Process (cont.)

- **Key features**
  - **Preliminary design**
    - Refine conceptual design
      - Rerun design tools with new data
      - Detailed evaluation of logistics of well locations, oxidant delivery, etc.
    - Document design in Design Basis Report
    - Reassess adequacy of information
    - Prepare contingency plans

Review key features of preliminary design.

ISCO Detailed Design and Planning Process (cont.)

- **Key features (cont.)**
  - **Final design and planning**
    - Decide on contracting approach
    - Evaluate constructability and cost
    - Prepare contracting packages and plans



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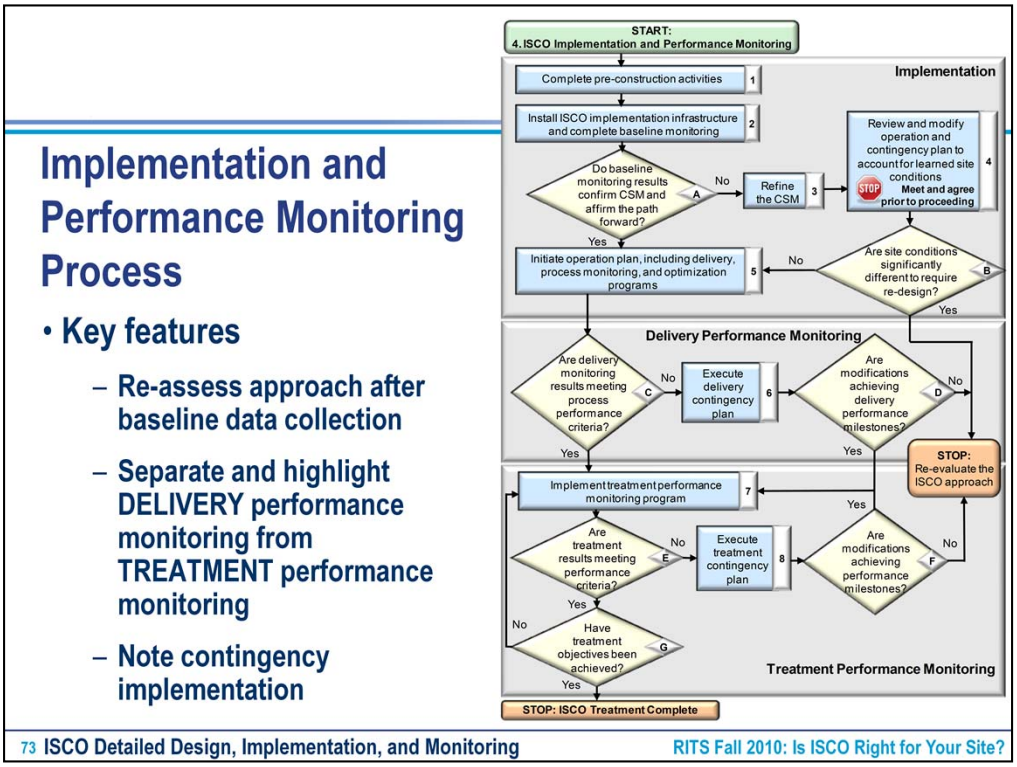
Review key features of final design and planning.



Present diagram. Review key features listed.

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Case Study 1 – NTC Orlando OU-4 (2000 to 2003)

- **COC Conditions**
  - PCE and degradation products, maximum concentrations in GW: PCE 26,000 µg/L, TCE 13,000 µg/L, 3,900 µg/L *cis*-DCE, DNAPL assumed to be present
- **Geologic Conditions**
  - Fine to medium sand, average hydraulic conductivity (K) = 30 ft/day
- **Project Goals**
  - Attain Florida MCLs of 3 µg/L PCE and TCE, 70 µg/L *cis*-DCE in groundwater
  - Up to 99.99% concentration reduction required
- **ISCO Full Scale Design**
  - Permanganate recirculation
  - 5-minute NOD bench test, pilot, and MODFLOW

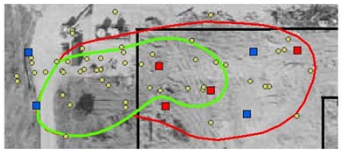

Photo courtesy of M. Singletary, NAVFAC Southeast

75 Case Study 1 RITS Fall 2010: Is ISCO Right for Your Site?

Brief overview of COCs (amendable to oxidation but high concentrations and DNAPL), geology (seems reasonably amenable to ISCO), project goals (very large % reductions), and ISCO design. ** Use language that mirrors screening language. ** Comment that relatively old case study.

Project Results

- Injection and extraction rates declined significantly over time
  - Attributed to solid manganese dioxide (MnO_2) precipitation
  - Well rehabilitation and alternative filtration efforts unsuccessful
  - Resulted in fewer than expected PVs recirculated
  - Outcome significantly different than that predicted by MODFLOW
- Project goals not achieved, and COCs persisted at concentrations above MCLs
- Bioremediation with emulsified oil used in source area after ISCO
- Subsequent 5-day NOD testing indicated high NOD (0.5 to 7 mg/kg) and reactive transport modeling indicated short to very short permanganate transport distances

Considerable precipitation fouled up the works, with the ultimate result being that goals were not achieved and an additional source area technology was required. Additional work showed that NOD was very much higher than design team thought

Key Lessons Learned

- **Results highlight the importance of NOD**
  - Significant amount of oxidant consumed due to non-target reactions
- **Traditional groundwater models (e.g., MODFLOW) may not predict ISCO result**
  - Groundwater flow ≠ Oxidant flow because oxidant reacts during transport
  - ISCO can change aquifer hydraulic properties
- **Project goals were very aggressive, and unrealistic in most situations**

Photos courtesy of M. Singletary NAVFAC Southeast

77 Case Study 1 – NTC Orlando OU-4 RITS Fall 2010: Is ISCO Right for Your Site?

Project executed before importance of NOD really understood. Non-target reactions were key to technology failure in this case. Groundwater models that do not consider reactive transport or how ISCO may impact aquifer properties may not accurate predict ISCO results. 99.99% reductions in concentration to MCLs in DNAPL source zone are highly unlikely.

Case Study 2 – NAS South Weymouth Bldg. 81 (2000)

- **COC Conditions**
  - Commingled PCE and BTEX from UST and solvent use, maximum concentrations in GW: PCE 1,000 µg/L, 850 µg/L BTEX, DNAPL likely present
- **Geologic Conditions**
  - Fractured granite bedrock, average K = 0.4 ft/day
  - Fractures spacing generally less than 1 ft, though borehole geophysics indicate that hydraulically significant fractures are more widely spaced
- **Project Goals**
  - Reduce COC concentrations in GW by 90%
- **ISCO Pilot Design**
  - 2 events of CHP into vertical wells, 1 PV of 50% H_2O_2 mixed with iron catalyst

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Both PCE and BTEX, so permanganate was not favorable, though other oxidants could have been used. Fractured rock site. Goal is 90% (one order magnitude) reduction in GW concentrations. ** Again, use language from ISCO Screening section. ** Project implemented as pilot, used CHP and fairly robust design

Project Results

- Significant COC reductions observed in GW, followed by rebound
  - 90% reductions only achieved for short time
  - Rebound occurred within approximately 2 months of injection
  - Rebound occurred in only one third of monitoring wells
- Project goals not achieved as COC reductions were not permanent
- Monitoring data indicated that oxidant solution may have flowed preferentially through larger fractures
- Another source zone remedy to be selected in 2011

Some reductions observed in short term, followed by rebound. Project goals not met in longer term.

Key Lessons Learned

- ISCO can be performed in fractured rock, but significant challenges exist
  - Preferential flow through fractures
  - Diffusion of COCs out of rock matrix ("back-diffusion") leading to rebound
  - Very difficult to assess mass of COCs in non-aqueous phases, so mass reduction calculations also very difficult
- Rebound was limited to small portion (~33%) of treatment zone
  - Similar observations at other ISCO fractured rock applications in DISCO
  - May suggest that ISCO rebound data can help refine location of subsurface hot spots

Fractured rock poses challenges to ISCO, as it does to other technologies. In particular, oxidant goes almost entirely to fractures while significant portion of COCs may be in rock matrix. Mass reduction is difficult to assess because sampling media other than aqueous contents of fractures is very difficult.

Rebound occurred, as might be expected. BUT, it occurred in only 1/3 of MWs. This has been observed at other fractured rock ISCO sites, and suggests that rebound data may help refine CSM.

Case Study 3 – Allegheny Ballistics Lab., WV (2005)

- COC Conditions
  - 1,000 lbs TCE disposed of each month in unlined pits from 1970 to 1978 (96,00 lbs total?), GW concentrations up to 50,000 µg/L, DNAPL presence very likely
- Geologic Conditions
  - Heterogeneous sand and gravel alluvial deposits
- Project goals
  - Evaluation of ISCO as potential mass reduction technology
- ISCO Pilot Design
  - Persulfate injected into vertical wells, activated by iron first, followed by heat
  - 0.4 g/kg oxidant dose, 0.007 PVs

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Significant concentrations of TCE, and likely DNAPL. Geology is permeable, which is good, but heterogeneous, which is challenging. Goal is simply to evaluate ISCO as possible mass reduction technology. Persulfate pilot implemented with design parameters shown below.

Project Results

- Modest reductions observed 3 weeks post-ISCO
- Significant rebound from 6 weeks post-ISCO onwards, in some cases to concentrations equal to or greater than pre-ISCO concentrations
- No soil sampling performed, groundwater concentrations didn't decline, how to assess mass reduction?
  - "…it may have been useful to evaluate removal efficiency by measuring concentrations of COCs in both soil and groundwater… it is possible that removal efficiency achieved by pilot test was underreported based solely on analytical results of groundwater samples." (NAVFAC 2010)
  - Mass reductions generally greater, sometimes significantly greater, in soil phase relative to groundwater phase based on sites in DISCO
- Total cost $407,000, or $58/yd^3 (NAVFAC 2010)

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Performance monitoring indicated that COC reductions were modest and transient. Change in COC mass not reported. No soil sampling was performed. Among DISCO sites with both mass and aqueous phase concentration reductions reported, mass reductions generally greater than GW phase reductions.

Key Lessons Learned

- **Performance monitoring program not ideal for project goals because only aqueous phase was sampled**
  - **Aqueous phase COC concentrations only tell a small part of the story**
  - **Soil sampling can provide more comprehensive data, including:**
    - Assessment of DNAPL, sorbed, and other phases
    - Much stronger basis from which to perform mass reduction calculations
- **ISCO project may have been under-designed**
  - **Known DNAPL disposal and very high TCE concentrations in GW**
  - **Low oxidant dose and very low number of PVs delivered**

Project highlights importance of collection of soil samples as performance verification technique, in particular when significant non-aqueous phases are present and targeted by ISCO.

Project was likely under-designed (low oxidant dose delivered over very low percentage of pore space in DNAPL situation)

Case Study 4 – NAS Alameda Point Site 14 (2007 to 2009)

- **COC Conditions**
  - Vinyl chloride (VC) resulting from solvent storage followed by partial reductive dechlorination, maximum concentrations in GW: VC 390 µg/L, no DNAPL
- **Geologic Conditions**
  - Heterogeneous fine to medium sand Fill materials, average K = 8 ft/day
- **Project Goals**
  - Risk-based VC concentration 15 µg/L in GW
- **ISCO Full Scale Design**
  - Persulfate recirculation, 3 injection events
  - 1 to 3 g/kg oxidant dose, 1 to 2 PVs
  - Bench and pilot studies implemented

Photo courtesy of T. Chaudhry, NAVFAC ESC

COCs are modest concentrations of VC, with no indication of DNAPL presence. Geology is permeable, which is good, but heterogeneity may pose challenge. Goal 15 µg/L risk-based standard, requiring ~ 95% reduction (contrast with previous case study, where 4 orders magnitude needed while 1 to 2 required here). Design was recirculation using robust dose and volume, informed by bench and pilot results

Project Results

- Maximum VC concentration in groundwater reduced from 300 to <40 µg/L
- 70% reduction in VC mass
- Remedial goal of 15 µg/L met in 20 of 25 MWs, monitoring ongoing
- Total cost $1,850,000, or $54/yd^3 (NAVFAC 2010)

Photo courtesy of T. Chaudhry, NAVFAC ESC

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90+% reduction in most highly impacted area, 70% overall. Goal met across most of site. Total cost fairly high, but unit costs quite low (contrast to median of 94 $/yd3 form DISCO).

Key Lessons Learned

- ISCO design incorporated health & safety concerns
  - Iron activation selected over base activation after verification of comparable performance in bench study
- Attempted to reduce risk to nearby Oakland Inner Harbor
  - Clear persulfate solution chosen over dark purple permanganate after both oxidants performed similarly in pilot study
- Observational Method used to guide ISCO application
  - GW sampling in between ISCO events helped target next phase of work
  - Recirculation rates modified based on field observations
  - Extraction wells retrofitted with vacuum to enhance flow rates
- Cost data provide good example of "economies of scale" when treating large sites

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Several non-technical, but important, factors impacted design, such as H&S and risk of obvious impact to adjacent water body. Observational method used to refine design: improve result and likely lower cost. Unit cost data demonstrate that unit costs get lower as treatment zones get larger.

Presentation Overview

- Introduction to ISCO
- ISCO Technology Practices Manual (TPM): ESTCP Project Background and Overview of Results
- ISCO Screening
- ISCO Conceptual Design
- ISCO Detailed Design, Implementation, and Monitoring
- Case Studies
- Summary and Conclusions

Take-Home Messages

1. One or more oxidants can destroy most, if not all, of the common organic COCs
2. Effective in situ delivery is essential
3. ISCO can successfully achieve treatment goals
4. ISCO has great potential for successful use at some, but not all sites
5. ISCO can be, and often must be, synergized with other remedies
6. ISCO will normally require two or more delivery events
7. ISCO can temporarily perturb subsurface conditions
8. Monitoring program must be consistent with project objectives
9. So-called "rebound" will often occur, more so at some sites than others
10. The cost of ISCO varies widely

References

- NAVFAC ESC 2010. Technical Report TR-2333-ENV: Cost and Performance Report for Persulfate Treatability Studies, June.