ATTACHMENT 17:
Laboratory Bench Testing for
Contaminant Treatability and Byproducts

INTRODUCTION

While ISCO Screening assists with identifying viable oxidants and appropriate oxidant activation approaches, the ultimate effectiveness is site-specific. It may be necessary to compare or optimize these approaches using site media to improve design and treatment effectiveness certainty. The data collected using these tests may be used to further compare ISCO options where certainty in oxidant distribution, treatment effectiveness, and cost differences between options are unclear, even after Tier 1 Conceptual Design evaluation.

Additionally, while the A11. ISCO Spreadsheet Design Tool run in Conceptual Design Process 3 captures primary reaction and transport processes dictating ISCO effectiveness for dissolved contaminant treatment, there are additional reaction processes to consider for sites with extensive NAPL or sorbed phase contaminant, co-contaminants, or potential for reaction byproducts or intermediates that may be of concern. These processes affect contaminant destruction efficiency and effectiveness, and include:

- Oxidant activation optimization (critical to catalyzed hydrogen peroxide (CHP) and persulfate oxidants)
- NAPL dissolution
- Contaminant desorption
- Impact of co-contaminants on contaminant dissolution, desorption, and destruction and the associated rates thereof
- Metals solubilization/mobilization

The following procedures have been developed to assist ISCO remediation practitioners with the collection of data using site-specific media to consider additional appropriate reaction processes and to optimize the system reaction chemistry for improved oxidant distribution, treatment effectiveness, risk reduction, and cost certainty. These procedures will: (1) further guide the decision of the optimum oxidant activation approach, as necessary for CHP and persulfate oxidants; (2) provide refined input to the ISCO Conceptual design tool; (3) clarify the ability to meet treatment objectives (e.g., extent of contaminant mass destruction with NAPL or highly sorbed contaminant); and (4) guide during and post-ISCO monitoring approaches (e.g., based on byproducts or metals "red flags" that may be outcomes of the procedures). It is important to note that these procedures are offered as guidance and there may be a variety of means of meeting the objectives of the procedures.

CONTAMINANT TREATABILITY AND BYPRODUCTS TEST PROCEDURE 1:
Optimize Oxidation Chemistry

The goal of this procedure is to determine the most efficient and effective approach for ISCO with respect to: (1) the ranges of oxidant activation approaches; (2) the ratio of oxidant to contaminant; and (3) the ratio of activator(s) to oxidant. NOTE: These evaluations are deemed critical for CHP and persulfate oxidants, and the A16. Laboratory Bench Testing for Oxidant Persistence can be conducted concurrent with this procedure (i.e., it is not necessary to conduct both procedures separately).

Based on the results of ISCO Screening, there may be more than one oxidant and more than one activation approach (as appropriate per oxidant) viable for general site conditions. The ISCO Spreadsheet Design Tool was the first step to evaluating appropriate oxidant concentrations as per preliminary conceptual design possibilities given site contaminant and hydrogeological conditions. In support of the Tier I Conceptual Design process, kinetic parameters critical to oxidant distribution are assumed and contaminant destruction rates based on the literature are applied. The values are used in the design tool to assess the most promising injection configuration(s) and oxidant delivery

concentrations to achieve the most extensive and cost-effective oxidant distribution and thus contaminant destruction. The purpose of this procedure is to refine the estimates and literature values employed in the design tool to optimize the system chemistry to achieve oxidant distribution, contaminant treatment, and cost targets. The procedure to evaluate/optimize oxidation chemistry is outlined below:

1. Select oxidants and range of oxidant doses (mg-oxidant/kg-media) to test. Selection should be based on feedback from the Tier 1 conceptual design process (such as the use of the <u>A11. ISCO Spreadsheet Design Tool</u>). It is recommended to evaluate at least three oxidant doses for each oxidant to be evaluated. The following are recommendations for the initial oxidant doses to consider for these tests. NOTE: The recommended doses are the target in situ doses at the maximum oxidant radius of influence distance from injection. Injection concentrations will be later scaled accordingly.

    Permanganate: Recommended test doses include 10, 50, and 100 times the amount (mol) of dissolved contaminant to be treated in the target treatment zone (kg-media). These values reflect those typically targeted for full-scale application, and are typically sufficient to satisfy natural media demand for the oxidant, as well as sorbed or NAPL contaminant under a majority of oxidant delivery conditions. If NAPL or sorbed mass is deemed extensive, it may be appropriate to extend the range of doses to evaluate up to an order of magnitude or greater than these recommended values. An example for determining target doses is included below:

    Maximum site dissolved TCE concentration = 10 mg/L
    Target treatment includes 10,000 kg-media
    Site bulk density = 1.6; porosity (n) = 0.3

    Treatment pore volume = (kg-media)(n) / 1.6 kg/L = (10,000 kg)(0.3) / 1.6 kg/L
    $\qquad\qquad\qquad$ = 1,875 L
    TCE = (10 mg/L)(1875 L) / (131.4 g/mol)(1000 mg/g) = 0.14 mol
    $\qquad$ 0.14 mol-TCE / 10,000 kg-media = 1.4E-05 mol/kg

    Oxidant dose $\quad$ = (10)(1.4E-05 mol/kg) = $\quad$ 1.4E-04 mol/kg
    $\qquad\qquad\qquad$ = (50)(1.4E-05 mol/kg) = $\quad$ 7.0E-04 mol/kg
    $\qquad\qquad\qquad$ = (100)(1.4E-05 mol/kg) = 1.4E-03 mol/kg

    1.4E-04 mol/kg = approx. 16.6 mg-MnO_4^-/kg-media
    7.0E-04 mol/kg = approx. 83.2 mg-MnO_4^-/kg-media
    1.4E-03 mol/kg = approx. 166.5 mg-MnO_4^-/kg-media

    Hydrogen Peroxide: Recommended test oxidant doses include 1,875 mg-oxidant/kg-media, 5,625 mg/kg, and 18,750 mg/kg. These values translate to concentrations of 1 wt%, 3 wt%, and 10 wt% hydrogen peroxide solutions under the example field conditions presented above for permanganate. These values provide molar ratios of oxidant to contaminant for the 10 mg/L TCE example presented above of approximately 4,000, 12,000, and 40,000 (mol-oxidant/mol-TCE), respectively.

    Persulfate: Recommended test oxidant doses include 937.5 mg-oxidant/kg-media, 2,810 mg/kg, and 5625 mg/kg. These values translate to concentrations of 5.0, 15, and 30.0 g/L of sodium persulfate solution under the example field conditions presented above for permanganate. These values provide molar ratios of oxidant to contaminant for the 10 mg/L TCE example presented above of approximately 281.5, 843, and 1,689 (mol-oxidant/mol-TCE), respectively.

2. Select range of conditions for oxidant activation, as necessary. This step may be omitted where permanganate is the test oxidant.

    Hydrogen Peroxide: General test conditions should be based on the outcome of the ISCO Screening process, and may include:
    - No activation (relying on catalysis by metals naturally present at site)
    - Dissolved iron addition (typically ferrous or ferric)

- Dissolved iron plus acid addition
- Chelated iron addition (typically $FeSO_4$ plus EDTA or citrate)

For low pH activation, a pH of 3 is the optimum value. However, acid addition requirements may be great, and metals may be mobilized by this low of a pH, and thus many employing pH adjustments may not try to depress pH to this low of a value. The amount of acid to add to achieve the desired pH must be determined on a case-by-case basis for the site media prior to beginning testing. It is important to note that pH may drift during experimentation, so in determining the target acid volume to add in a screening test, it is critical to monitor pH of the system over at least 24 hours to ensure the low pH condition is maintained.

Ranges of iron to evaluate typically span ~0.001 to 0.1 times the molar concentration of hydrogen peroxide (for CHP) to be tested, and ~0.1 to 10 times the molar concentration of sodium persulfate to be tested. In determining the specific concentration of iron to add, it is important to evaluate dissolved iron concentrations naturally present at the site. If it is anticipated that the natural site media (soil and groundwater) contain high iron concentrations, then it is likely that very little to no additional iron will be necessary to catalyze hydrogen peroxide decomposition to generate oxidative free radicals.

Ranges of chelating agent to evaluate typically span 0.1 to 10 times the molar concentration of iron to be tested (naturally present or added iron).

Persulfate: General test conditions should be based on the outcome of the ISCO Screening process, and may include:
- No activation (relying on catalysis by metals naturally present at site)
- Chelated iron addition (typically $FeSO_4$ plus EDTA or citrate)
- Base addition for elevated pH activation
- Heat activation
- Addition of hydrogen peroxide

Ranges of iron to evaluate typically span 0.1 to 1.0 times the molar concentration of oxidant to be tested. In determining the specific concentration of iron to add, it is important to evaluate dissolved iron concentrations naturally present at the site. If it is anticipated that the natural site media (soil and groundwater) contain high iron concentrations, then it is likely that very little to no additional iron will be necessary to catalyze hydrogen peroxide decomposition to generate oxidative free radicals. Ranges of chelating agent to evaluate typically span 0.1 to 10 times the molar concentration of iron to be tested (naturally present or added iron).

For high pH activation, a pH of 10 or greater is typically the target. The amount of base to add to achieve this pH must be determined on a case-by-case basis for the site media prior to beginning testing. It is important to note that pH may drift during experimentation, so in determining the target acid volume to add in a screening test, it is critical to monitor pH of the system over at least 24 hours to ensure the high pH condition is maintained.

The appropriate temperature for heat activation is contaminant-specific, although ranges typically span 20^oC (68^oF) to 50^oC (122^oF). It is important to note that typical groundwater temperatures can be well below the typical 20^oC "room temperature". Variations in experimental temperatures can be achieved via use of temperature-control ovens or water baths.

The dual oxidation approach of persulfate plus hydrogen peroxide should be tested at varied molar ratios of the two oxidants, ranging from 10:1 to 1:10 hydrogen peroxide to persulfate. The higher the initial hydrogen peroxide concentration, the faster the contaminant destruction and oxidant depletion (both oxidants) will be.

3. According to the target oxidant and activator conditions selected in Steps 1 and 2 above, samples are prepared according to the general procedure outlined in the A16. Laboratory Bench Testing for Oxidant Persistence procedure, beginning at Step 6 of that procedure, with the following modifications:

- The site's contaminant of concern MUST be included in the systems at a mass/concentration representative of site conditions. This may be achieved using a contaminant spike using purchased chemical, however it is recommended to use contaminated site groundwater and soil, particularly if there are co-contaminants present at the site.
- Oxidant is added LAST to all systems (i.e., oxidant activators other than heat are added before the oxidant is added).
- It may be necessary to prepare a separate reaction vessel for each time point to be assessed depending on the volumes of sample necessary to perform oxidant and contaminant concentration analyses over time.
- Analyses are to be made for both oxidant and contaminant concentrations over time using standard methods, and rates of depletion/destruction of each are characterized.
- It is necessary to perform a final, full-vessel extraction for contaminant, without quenching the oxidant (which may modify system chemistry), to determine if any sorbed or NAPL contaminant remains in the system. Extractants to employ are oxidant- and contaminant-specific. Examples of typical extractants include methanol and hexane.

4. Compare results to select optimal reaction chemistry. The optimal system will result in the most extensive contaminant destruction under the most persistent oxidant conditions. Ideal systems will demonstrate:
    - Maximum contaminant destruction
    - The slowest oxidant depletion rate(s)
    - The fastest contaminant destruction rate(s)
    - Minimum or controlled evolution of off-gas

CONTAMINANT TREATABILITY AND BYPRODUCTS TEST PROCEDURE 2:
Additional System Chemistry Considerations

The goal of this procedure is to determine the impact of the presence of NAPL or sorbed contaminant or the potential generation of reaction intermediates/byproducts on overall contaminant destruction, risk reduction, and cost. The procedure is outlined below:

1. Follow the general sample preparation procedures described in the A16. Laboratory Bench Testing for Oxidant Persistence procedure, beginning at Step 6 of that procedure, with the following modifications:
    - Use optimized reaction chemistry determined in the Chemistry Optimization procedure (above)
    - Adapt preparation according to data objectives. Adaptations for example data objectives include:
        a) NAPL dissolution: add the appropriate mass/volume of site NAPL to the reaction vessel to achieve a representative saturation; allow for 24 hour equilibration period prior to oxidant addition.
        b) Contaminant desorption: add the appropriate mass/volume of contaminated field soil to system with site groundwater (using contaminated media from the field is critical as system aging will impact rate and extent of contaminant desorption); allow for 24 hour equilibration period prior to oxidant addition.
            NOTE: for (a) and (b), it may be necessary to consider use of a fugacity-based partitioning model
        c) Co-contaminant treatment/effects: use contaminated site groundwater having representative mixture constituents and concentrations; scale oxidant concentration to the total molar concentration of all constituents totaled.
        d) Byproducts/intermediates assessment: conduct a thorough review of the literature to understand possible byproducts and intermediates that may be generated; modify analyses accordingly; employ multiple reactors to assess byproducts/intermediates over time (keeping in mind that metals increases noted in the field are typically transient even when laboratory tests show persistent increases in metals concentrations);

    e) Metals solubilization/mobilization: ensure reactors include specific site media of concern (natural or co-contaminant metal sources); conduct a thorough site characterization and review of the literature to understand potential for and implications of metals solubilization/mobilization.

- It may be necessary to prepare a separate reaction vessel for each time point to be assessed depending on the volumes of sample necessary to perform analyses for the analyte of interest over time as per standard methods.

2. Adapt measurements/analytical approaches according to data needs. Adaptations for example data objectives include:

- NAPL dissolution or contaminant desorption: perform a full extraction for contaminant(s) with solvent compatible with contaminant characteristics; include sacrificial vials for each time point to be measured.
- Co-contaminant treatment/effects: assess total contaminant destruction in addition to primary COC destruction.
- Byproducts/intermediates assessment: conduct analyses for potential intermediates / byproducts over time employing standard methods for each analyte of interest and including sacrificial vials for each time point to be measured. The goal initially is to detect any Tentatively Identified Compounds (TICs). Based on findings, further analyses can be conducted to verify and quantify any TICs.
- Metals solubilization/mobilization: in considering analytical results, consider changes as a function of ORP, pH, and ionic strength – longer-term impacts may be estimated as a function of the return of post-ISCO conditions to pre-ISCO conditions. For example, while high Mn^{2+} concentrations may be anticipated during ISCO and immediately post-treatment due to high pH and ORP, if initial site conditions include moderate pH and ORP, long-term elevated Mn^{2+} will not likely be a concern (i.e., treatment effects may be short-lived; changes during and post-ISCO may be predictable based on results of lab tests).

3. Consider the implications of results in ISCO design. Example approaches for doing so include:

- For sites with significant NAPL and sorbed contaminant mass:
  - a) Use multiple delivery events. This calls for revisiting the Conceptual Site Model between each delivery event and allowing time between events for significant contaminant desportion/dissolution.
  - b) Maximize oxidant persistence by modifying system chemistry, employing a combination of Contaminant Treatability and Byproducts Procedures 1 and 2 above to evaluate impacts on oxidant depletion and contaminant destruction.
  - c) Modify the planned delivery approach as appropriate to consider a recirculation delivery scheme to provide a continuous supply of oxidant via multiple pore volumes of oxidant delivery. Viability will depend significantly on site hydrogeological conditions as described in the ISCO Screening process.
- For sites where byproducts/intermediates, including metals, may be a concern:
  - a) Consider implications of the return to pre-ISCO site conditions (e.g., ORP and pH) to determine if the issue may be short-lived.
  - b) Evaluate the risk implications of the presence of the byproduct/intermediate or metal(s). Weigh the overall risk reduction benefit of implementing ISCO.
  - c) Consider modifications to system chemistry to avoid undesirable byproducts/intermediates of metals. For example, increasing oxidant concentrations may facilitate complete transformation of harmful intermediates to harmless byproducts. Also, decreasing oxidant concentrations may decrease concentrations or the accumulation of byproducts or metals of concern.
  - d) Consider coupled ISCO processes for managing byproducts/ intermediates and/or metals.

GENERAL GUIDANCE

The procedural guidance offered here provides a general framework for conducting treatability tests and acknowledges that a range of approaches may be used to meet the goals of these procedures. There are some general precautions, however, that must be taken into consideration when conducting treatability tests regardless of the approach. These include:

1. Initial range-finding experiments over a shorter-duration may be appropriate with respect to optimizing oxidation chemistry (Contaminant Treatability and Byproducts Procedure 1) prior to conducting kinetic evaluations of oxidant depletion and contaminant destruction rates. To do so, samples are prepared as described above; however, measurements are made at only one time period (e.g., 8, 24, 48 hr) to provide data to compare activation approaches or ratios of oxidant to activator and/or contaminant. Following this approach, at the time point of interest, a measurement is made of an aliquot of the aqueous-phase of the sample for oxidant concentration, then a full extraction of the reaction vessel is performed to measure contaminant concentration(s) at this time point. The "best" approach will provide the greatest extent of contaminant destruction with the least amount of oxidant depleted. The more expensive and extensive kinetic evaluations may then be focused on the approach that offers the most favorable results. Selection of the time period of interest must be based on general oxidant characteristics. For example, CHP is a faster-reacting oxidant and would call for a shorter reaction period than the more persistent persulfate and permanganate oxidants.

2. Quenching the oxidant to halt the oxidation reaction for later measurement of contaminant concentrations at a given reaction period is not recommended. Quenching can alter system chemistry in a way that impacts other measurements that may be of interest (e.g., pH, ORP, metals concentrations, byproducts/intermediates, etc.). Impacts of quenching are not well understood, therefore it is best avoided. A better approach is to extract contaminant from the dissolved phase sample (where oxidant is maintained) to halt the reaction. It is important to use an extractant that: (1) will not react, or react minimally, with the oxidant; (2) is compatible with the planned analytical approach (e.g., gas chromatograph detector); and (3) will fully extract the contaminant(s) of interest.

Results of both Contaminant Treatability and Byproducts Procedures 1 and 2 must be considered as the "best case" or "worst case" scenarios, as appropriate, when extrapolating to anticipated effects at the full scale. For example, when considering the extent of contaminant treated in laboratory studies, results must be considered "best case" due to the complete contact, complete mixing, and idealized opportunity for contaminant mass transfer. The extent of treatment observed at the field-scale is often less than predicted in the laboratory. Results of oxidant depletion must be considered "worst case" also due to complete contact, complete mixing, and idealized opportunity for mass transfer. Rates of oxidant depletion in the field are often slower than predicted in the laboratory. Also, when examining intermediates/byproducts and/or metals mobilization, results must be considered "worst case", primarily due to the lack of important processes that occur in the field that minimize these effects, including dilution, return to pre-ISCO equilibrium conditions (via reaction completion or flow from upgradient), or other natural attenuation processes. These results are intended to guide monitoring approaches and are not to be considered *pro forma* indicators that ISCO is not appropriate for a site.