

# ATTACHMENT 16:

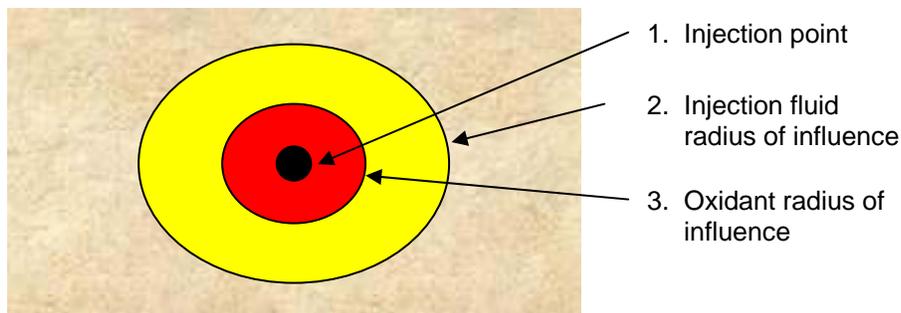
## Laboratory Bench Testing for Oxidant Persistence

### INTRODUCTION

When oxidizing agents are delivered into the subsurface (e.g., by probe injection or well delivery), they can react nonproductively through interactions with porous media and groundwater constituents. The reactions that occur and their rates are site-specific, depending on the type and concentration of oxidizing agent employed and the media characteristics (e.g., presence of reactive minerals, organic carbon, etc.). Due to contaminant degradation and nonproductive reactions, the transport of the oxidizing agents will typically be retarded compared to the transport of the injected solution during injection and transport. For example, Figure A16-1 presents a highly simplified comparison of the radius of influence (ROI) of the total volume of injection solution delivered to that of the oxidizing agent itself for an example scenario where oxidant depletion may be relatively rapid.

The extent of the transport of the injection solution is dependent on injection rate and hydrogeologic conditions in the zone to which delivery is occurring (e.g., thickness of mobile zone). The transport of the oxidizing agent away from the injection location is a function of the delivery rate compared to the oxidant depletion rate. A higher transport distance can be anticipated under rapid oxidant delivery conditions and slow rate of nonproductive oxidant depletion conditions (e.g., very persistent oxidant). An exception is the potential for enhanced delivery of hydrogen peroxide that can result due to gas generation, which can facilitate movement beyond the estimated injection solution delivery radius. While the rate of oxidizing agent delivery is controlled by system design, the rate of oxidant depletion is site-specific and must be evaluated and quantified to improve certainty associated with the design ROI.

The following procedures have been developed to assist ISCO remediation practitioners with the collection of data for site-specific media to determine the rate and extent of oxidant depletion. These procedures capture what is commonly referred to as “natural oxidant demand” (NOD) for permanganate, or oxidant persistence for free radical-based oxidants catalyzed hydrogen peroxide (CHP) and persulfate. The data can be used to estimate the oxidant radius of influence when data are incorporated into design tools such as CDISCO, described in Chapter 9. It is important to note that these procedures are offered as guidance and there may be a variety of means to meet the objectives of this process. The procedures outlined in this document are based on a simplified “1 pore volume (PV)” plug-flow approach and is provided herein for illustration purposes, assuming the target oxidant delivery volume is equal to 1 PV of the Target Treatment Zone (TTZ). The test procedures can be modified as necessary for more/less than 1 PV.



**Figure A16-1. ROI of Delivery Fluid and of Oxidant with Subsurface Injection.** [The ratio of the oxidant ROI to fluid ROI is a function of the rate of reaction of oxidant with naturally-present media.]

## SAMPLE COLLECTION, PRESERVATION, AND STORAGE

The number of samples to be collected for a given site is a function of the extent of heterogeneity of the site, particularly with respect to the design TTZ. At least one sample of field porous media is necessary from each distinct lithologic zone to be contacted with oxidant, and at least three samples from each zone are recommended. Even within a given lithologic zone, there can be high variability in oxidant persistence measurements for a media. The number of samples collected should be a function of the degree of certainty in the oxidant persistence measurement necessary to have sufficient certainty in cost and delivery effectiveness. The number of samples to collect, along with their collection procedure(s), handling, and storage should be guided by publications [EPA 600/8-89/046, Soil Sampling Quality Assurance Users Guide, 2<sup>nd</sup> Edition](#); and [EPA 625/4-91-026, Site Characterization for Subsurface Remediation](#) and references therein.

In general, uncontaminated, background samples of the site media and groundwater are preferred. The procedure can be conducted with contaminated media; however consideration must be made in extrapolating results across the site where contaminant water and soil concentrations may vary by several orders of magnitude. The mass of media and volume of sample to collect should be decided based on the outcome of calculations made in the procedures below, and allow for appropriate sample replication. Media should be collected in a manner that most approximately represents in-place field conditions (e.g., field moist soil cores, etc.), with minimum handling until ready for test preparations.

## OXIDANT PERSISTENCE TEST PROCEDURE

1. Determine the maximum achievable fluid radius of influence ( $R_{max}$ ) for the intended system design. This value is assumed to be the MAXIMUM possible oxidant ROI ( $R_{ox}$ ). If the  $R_{max}$  is unknown or uncertain, based on field experiences, a reasonable default value may be 15 ft. (4.6 m) for probe injection and 30 ft. (9.2 m) for well delivery (the two most commonly used delivery approaches).
2. Calculate the total bulk treatment volume ( $V_b$ ).

$$\text{Area} = \pi(R_{max})^2 \quad [1]$$

Thickness = treatment depth/thickness

$$V_b = \text{Area} \times \text{Thickness} \quad [2]$$

Note that the volume that will be contacted at the site is less than this maximum value because heterogeneities will cause preferential flow through more mobile zones. If the mobile porosity can be accounted for based on tracer tests or other site characterization information, then a correction can be applied here (i.e., use mobile volume instead of total volume).

3. Calculate the mass of porous media ( $M_{media}$ ) associated with this volume using the media dry bulk density, typically in the range of 1.6 to 2.0 g/mL (99.9 to 124.9 lb/ft<sup>3</sup>).
4. Calculate the volume of oxidant solution to be delivered (1 PV) that is associated with the ROI ( $V_{fi}$ ). If an approach using less than 1 PV is desirable, modify  $V_{fi}$  accordingly.

$$V_{fi} = \text{Porosity of site media} \times V_b \quad [3]$$

5. Select the maximum desirable oxidant concentration ( $C_{max}$ ) that may be chosen for the site. (Note that oxidant concentrations are conventionally expressed as mg-MnO<sub>4</sub><sup>-</sup>/L, mg-H<sub>2</sub>O<sub>2</sub>/L, or mg-S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/L for permanganate, catalyzed hydrogen peroxide, and persulfate, respectively.) This concentration may be based on a variety of factors including:
  - Oxidant solubility
  - Site contaminants – type, concentration, mass, mass distribution
  - Potential for anticipated undesirable byproducts (e.g., gas, oxidant impurities, solids, pH, etc.)
  - Outcome/output of Tier 1 Conceptual Design (see Chapter 9)
  - Hazards associated with the oxidant
  - Practitioner experience

Alternatively,  $C_{\max}$  may be determined using the [A11. ISCO Spreadsheet Design Tool](#).

6. Calculate the maximum oxidant dose anticipated (mg-oxidant/kg-media (dry wt.) initial condition ( $D_o$ ) (Eqn. 3):

$$D_o = (C_{\max} \times V_{fl}) / M_{\text{media}} \quad [4]$$

Units:  $D_o = \text{mg-oxidant} / \text{kg-media (dry wt.)}$

$C_{\max} = \text{mg-oxidant} / \text{L-solution}$

$V_{fl} = \text{L-solution}$

$M_{\text{media}} = \text{kg-media (dry wt.)}$

7. Select 2 fractions of  $D_o$  that span the range of desirable conditions to evaluate (e.g.,  $0.5 D_o$ ,  $0.1D_o$ ), designated  $D_1$  and  $D_2$ .
8. For a reaction vessel size of at least 40 mL, calculate the mass of media ( $M_{rx}$ ) (Eqn. 5) and volume ( $V_{rx}$ ) (Eqn. 6) of solution to use to achieve a 1:1 (v/v) solids to solution ratio with minimal resulting headspace. These are the values that will be employed in the tests for EACH dose and EACH replicate (20% replication of all samples is a standard approach). An example calculation is provided below assuming use of a 40 mL reaction vessel and a media particle density of 2.65 g/mL (NOTE: a larger volume reactor vessel may be needed to handle a representative sample volume obtained at sites with heterogeneous subsurface conditions (e.g., samples of very low bulk density soils or fractured bedrock).

$$M_{rx} = 40 \text{ mL} \times 0.5 \times 2.65 \text{ g/mL} = 53 \text{ g of media (dry wt.)} \quad [5]$$

$$V_{rx} = 40 \text{ mL} \times 0.5 = 20 \text{ mL} \quad [6]$$

NOTE: where field moist solids are employed,  $M_{rx}$  and  $V_{rx}$  must be corrected for water content, where  $V_{rx}$  is decreased by the water content associated with the solids and  $M_{rx}$  is increased by this value (applying water density of 1.0 g/mL). For example, if field moist soil solids having a water content of 0.25 v/v are used, then  $V_{rx}$  must be decreased by 5 mL ( $5 \text{ mL} = 0.25 \times 20$ ) which accounts for the volume "space" the water in the field moist solids will occupy, and  $M_{rx}$  (dry wt.) must be increased by 13.25 g ( $13.25 \text{ g} = 0.25 \times 20 \text{ mL} \times 2.65 \text{ g/mL}$ ) to obtain a new  $M_{rx}$  (field moist wt.), which accounts for the weight of the water in the field moist sample.

9. Calculate the concentration of oxidant ( $C_o$ ) (Eqn. 6) that will result in the  $D_o$  dose value. (Note: while  $D_o$  was based on an initial high concentration value that may be desirable for the site ( $C_{\max}$ ), it is the resulting dose (mg-oxidant/kg-media [dry wt.]) from the application of this concentration to the target media ( $M_{\text{media}}$ ) that must be evaluated in these studies. This may result in using a different concentration in the lab tests than  $C_{\max}$  because of the predetermined mass of media ( $M_{rx}$ ) used in the tests.) Perform the same calculation to achieve  $C_1$  and  $C_2$  values. An example calculation for  $C_o$  is provided below.  $C_1$  and  $C_2$  will be the same resulting fractions of  $C_o$  as the  $D_1$  and  $D_2$  values selected in Step 5.

$$C_o = (M_{rx} \times D_o) / V_{rx} \quad [7]$$

Units:  $C_o = \text{mg-oxidant} / \text{L-solution}$

$M_{rx} = \text{kg-media (dry wt.)}$

$D_o = \text{mg-oxidant} / \text{kg-media (dry wt.)}$

$V_{rx} = \text{L-solution}$

10. Choose a reaction vessel compatible with the oxidant of interest and contaminants of concern for the site. Amber or colored glass vials are recommended due to the photosensitivity of some oxidants. NOTE: for gas-producing oxidant, it may be necessary to choose a vessel that will allow for gas release (i.e., venting) during reaction.
11. Weigh the appropriate mass of media into the replicate reaction vessels. Field moist soil is recommended to mitigate potential porous media property changes that can result with air or oven drying. It is best to use field moist soil that has been properly preserved to avoid oxidation

by atmospheric oxygen while drying. However if field moist soil is used, the  $M_{rx}$  and  $V_{rx}$  calculations must be adjusted for water content as described in Step 8.

12. Add the appropriate concentrations of oxidant as per Step 9 calculations. NOTE: if volumes lower than  $V_{rx}$  of stock oxidant are used, the additional make-up solution to achieve  $V_{rx}$  may be provided as site groundwater or deionized water. Use of site groundwater is recommended for those sites anticipated to have a high concentration of reduced constituents or oxidant scavengers in groundwater. In this case, it is recommended that at least 75% of  $V_{rx}$  be composed of groundwater and 25% or less of oxidant solution. Typically the reaction of oxidant with groundwater constituents at most sites is a small fraction of the loss of oxidant from reaction with the porous media. An exception may be sites with high total dissolved solids (TDS) concentrations, the constituents of which may have significant oxidant scavenging capacity.
13. Completely mix the reaction vessels throughout the reaction period. NOTE: it may be necessary to release gas from reaction vessels for gas-producing oxidants. If contaminated porous media is used and VOCs are present, they may be released. If this is the case, the vented gas needs to be captured and properly handled for safety reasons. If contaminant degradation is being measured the VOCs in the vented gas need to be quantified (e.g., by using a solvent trap).
14. Sample each reaction vessel and measure oxidant concentration at multiple time points (at least 4) within the initial 48 hours of reaction and daily thereafter (at least three additional days) until there is minimal change (e.g., < 5-10% decline) in oxidant concentration over 3 sampling events. For rapidly reacting oxidants, such as peroxygen oxidants, a more condensed sampling timeframe is recommended, with multiple sample time points within the first several hours and additional samples every several hours thereafter. It is recommended to take the minimum volume of sample as possible while remaining within the oxidant's detection limit if dilution is necessary. This is to avoid significant loss of volume from the system, development of headspace, and/or leakage from septa if applicable. For example, it is often reasonable to remove 0.1 mL of sample per measured time point, then to dilute the sample to the volume necessary for oxidant measurement procedures. If it is necessary or desirable to use a larger sample volume for analysis, then it may be prudent to use a reaction vessel larger than 40 mL or use a separate 40-mL reaction vessel for each time point measurement. [A summary of analytical techniques](#) for various oxidants is included for convenience.
15. Characterize reaction rates for each oxidant dose ( $D_o$ ,  $0.5D_o$ ,  $0.1D_o$ ) evaluated. For hydrogen peroxide and persulfate, it is appropriate to determine a pseudo-first order rate for oxidant decomposition for the duration of the test. For permanganate, a range of values for NOD can be collected as defined below and illustrated in Figure A16-2:
  - Ultimate NOD ( $NOD_{ult}$ ) is the total demand exerted over the entire test duration in (mg-oxidant / kg-media (dry wt.)).
  - Instantaneous fraction of NOD ( $NOD_{if}$ ) is the initial fast reaction of permanganate with natural media constituents. This is the fraction of the  $NOD_{ult}$  that is exerted typically within the first 8-12 hours of the test.  $NOD_{if}$  is unitless and < 1.0.
  - The pseudo-first order or the second-order, slower rate of NOD ( $NOD_{slow}$ ) is the rate at which the remainder of the oxidant reacts with the media ( $NOD_{ult} - NOD_{if}$ ).  $NOD_{slow}$  is determined using at least four data points as any pseudo-first order or 2<sup>nd</sup> order reaction rate is determined.
16. Plot initial oxidant dose vs. depletion rate (or all three terms for permanganate) to generate a curve (i.e., model) of dose vs. rate of oxidant depletion (Figure A16-3). From this curve, an estimate of oxidant depletion rate can be made for a range of oxidant doses falling within the three test values ( $D_o$ ,  $0.5D_o$ , and  $0.1D_o$ ).
17. Manage materials and wastes appropriately upon test completion.

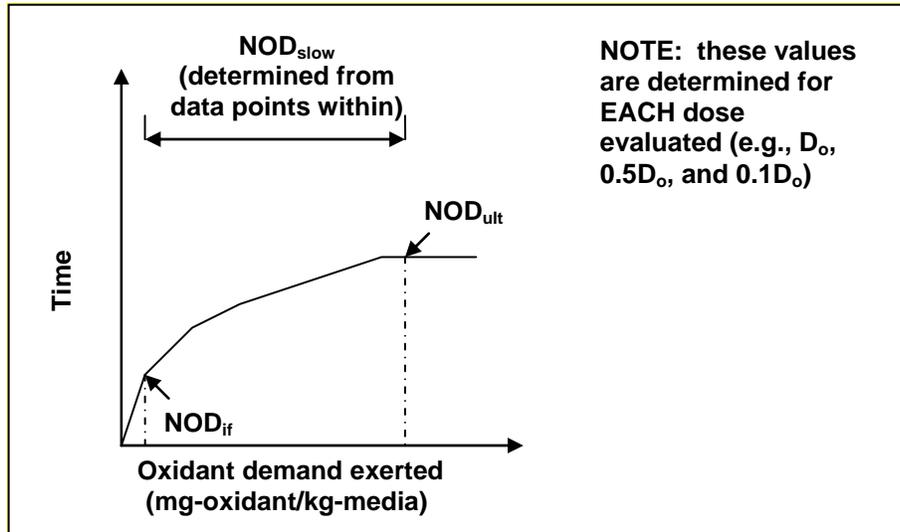


Figure A16-2. Illustration of NOD terms for permanganate laboratory tests

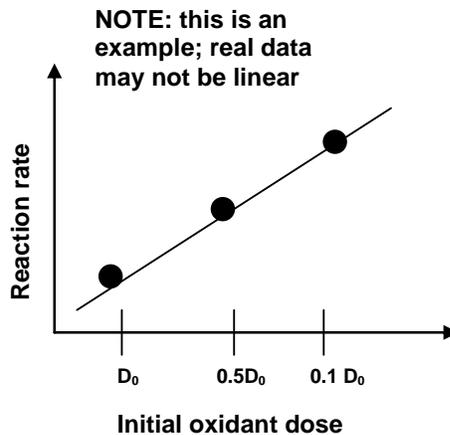


Figure A16-3 Illustration of oxidant dose vs. rate of oxidant depletion assessment

## SUMMARY OF ANALYTICAL TECHNIQUES

[Table A16-1](#) below summarizes some of the more common analytical methods that have been used to analyze for the major ISCO oxidants. These generally represent methods that involve simple equipment and less intensive sample preparation and preservation because often they may be used to monitor ISCO in the field or for use in treatability studies. Undoubtedly there are other analytical methods that are not included in this table that may either reduce the interferences or provide more certainty in results, but they are also more likely to be equipment and preparation intensive. However, an exception to this may include ozone where many real-time ozone monitors for both gas and aqueous phase concentrations are available, but are not reviewed here.

It is worth pointing out that the most common analysis method for persulfate and hydrogen peroxide are virtually identical, with the exception of the catalyst (ammonium molybdate). Furthermore, although the indigo method is more common for ozone, iodometric titration will also quantify ozone (Eaton et al. 2005). If only one of these oxidants is present, then good agreement between this titration and the actual oxidant concentration can be expected. This agreement between iodometric titration and oxidant concentration

allows for the establishment of a calibration curve to determine oxidant concentration. However, some ISCO approaches involve the injection of multiple oxidants into the subsurface, such as hydrogen peroxide and persulfate, or hydrogen peroxide and ozone. In these instances, the iodometric method is incapable of distinguishing between the oxidants. Hence this method is not an oxidant specific test but rather measures the bulk oxidizing potential of a sample. The indigo method with ozone is more oxidant specific, as ozone rapidly decolorizes indigo, whereas hydrogen peroxide, the most likely oxidant to be coupled with ozone, decolorizes indigo much slower. Thus prompt measurement may minimize this interference. One general interference that can impact any of the methods results from any natural color, turbidity or absorbance in the sample background that may interfere with the spectrophotometer reading, or the ability of the lab user to view colorimetric endpoints.

It is also worth noting that most of these methods, especially those with colorimetric or spectrophotometric readings, perform optimally (e.g. linear calibration) when low oxidant concentrations are measured (e.g., 1-100 mg/L). As this is generally far below the range of concentrations applied to the field during ISCO, samples must often be diluted by a factor of 100 or more to bring them down to the optimal range, and a source of dilution water will be required.

Virtually all of these methods involve some degree of wet chemistry to determine the oxidant concentration. Some methods, including those for hydrogen peroxide and ozone, have commercially available test kits that spare the user the work of having to prepare and measure reagents. However, others may not be available and may require the user to prepare their own reagents. Technology vendors will often be able to provide additional expertise for oxidant analysis.

## REFERENCES

Eaton, A.D.; Clesceri, L.S.; Rice, E.W.; Greenberg, A.S. (2005). "Standard Methods for the Examination of Water and Wastewater." American Public Health Association, Washington, DC.

Huang, K.C.; Couttenye, R.A.; Hoag, G.E. (2002). "Kinetics of Heat-Assisted Persulfate Oxidation of Methyl-*Tert*-Butyl Ether (MTBE)." *Chemosphere*, 49, 413-420.

Kolthoff, I.M.; Carr, E.M. (1953). "Volumetric Determination of Persulfate in the Presence of Organic Solutes." *Anal. Chem.*, 25, 298-301.

Kolthoff, I.M.; Sandell, E.B. (1969). *Quantitative Chemical Analysis*, Macmillan, New York.

Liang, C.; Huang, C.F.; Mohanty, N.; Kurakalva, R.M. (2008). "A Rapid Spectrophotometric Determination of Persulfate Anion in ISCO." *Chemosphere*, 73, 1540-1543.

*Soil Sampling Quality Assurance User's Guide*, 2nd edition. EPA 600/8-89/046, NTIS PB89-189864. 1989.

*Site Characterization for Subsurface Remediation; Seminar Publication*. EPA 625/4-91/026. 1991.

**Table A16-1: Summary of Analytical Methods for Major ISCO Oxidants.**

Oxidant	Citation	Necessary Equipment	Available as test kit?	Reagents	Synopsis	Interferences	Estimated time per sample <sup>3</sup>
Persulfate	Kolthoff and Carr 1953	Glassware only	No	Potassium iodide Sodium bicarbonate Sodium thiosulfate Starch (indicator)	Iodometric titration with back-titration to the starch endpoint	Other oxidants	~5 min prep 15 min rxn
	Liang et al. 2008	Spectrophotometer, glassware	No	Potassium iodide sodium bicarbonate sodium thiosulfate	Iodometric titration with absorbance read at 352 nm	Other oxidants,	~5 min prep 15 min rxn
	Huang et al. 2002	Spectrophotometer, glassware	No	Sulfuric acid Ferrous ammonium sulfate Ammonium thiocyanate	Persulfate is reacted with ferrous iron in acidic solution, thiocyanate added and read at 450 nm	Other oxidants, possibly organics <sup>2</sup> , background absorbance at 450 nm	~5 min prep 40 min rxn
Ozone	Standard Method <sup>1</sup> 4500-O <sub>3</sub>	Spectrophotometer or filter colorimeter, glassware	Yes	Phosphoric acid Monobasic sodium phosphate Indigo (potassium indigo trisulfonate)	Indigo colorimetric method. Ozone rapidly decolorizes indigo in acidic solution and is read at 600 nm or compared to a color wheel	Manganese and other oxidants. H <sub>2</sub> O <sub>2</sub> is okay if samples are read promptly	~5 min prep
Permanganate	Standard Method <sup>1</sup> 4500-KMnO <sub>4</sub>	Spectrophotometer, filtration apparatus (e.g. 0.2 micron), glassware	No	None	Direct measurement of permanganate at 525 nm	Manganese dioxide. Any turbidity or color that absorbs at 525 nm	~2 min prep
Hydrogen Peroxide	Kolthoff and Sandell 1969	Glassware only	Yes	Potassium iodide Sodium thiosulfate Ammonium molybdate Sulfuric acid Starch (indicator)	Iodometric titration with back titration to the starch endpoint	Other oxidants	~5 min prep 5 min rxn

<sup>1</sup> See Eaton et al. 2005<sup>2</sup> Kolthoff and Carr 1953 reported that organics interfered with the iron(III) reaction yield due to propagation reactions involved with persulfate free radical chemistry. This interference may be overcome by the addition of a significant scavenger, such as potassium bromide.<sup>3</sup> "prep" indicates the estimated preparation time per sample, "rxn" indicates the estimated reaction time (if any) per sample.