# ATTACHMENT 26: Elements of a Performance Monitoring Program

An adequately designed delivery and treatment performance monitoring program is essential to provide data that are consistent with operation and performance. The Performance Monitoring Plan should cover the three primary stages of ISCO implementation: baseline monitoring, delivery performance monitoring, and treatment performance monitoring. Typical Performance Monitoring Plan components include:

- Clearly defined data needs and objectives (including measurements for contingency assessment)
- Baseline monitoring program
- Delivery performance monitoring program
- Treatment performance monitoring program
- Number and location of monitoring points
- Frequency of monitoring
- Field and laboratory analytical methods

Additional components may be added to the Performance Monitoring Plan based on site-specific needs, oxidant-specific issues, or as negotiated as part of regulatory requirements. Common additional components include data quality objectives, QA/QC sampling procedures, a general data analysis plan, and reference to a Contingency Plan for decision logic.

## CLEARLY DEFINED DATA NEEDS AND OBJECTIVES

Performance monitoring is performed to:

- Collect the necessary data to measure achievement of the operational objectives and treatment milestones,
- Monitor the ISCO process to continually confirm that the design is performing as designed and is being optimized as prescribed by the Contingency Plan, and
- To document whether the implementation was a success or failure with respect to the ISCO treatment goals as prescribed by the Treatment Cessation Plan.

ISCO Detailed Design and Planning Process 2 contains details on each of these activities and documents and instruction on how to define data needs and objectives.

## BASELINE SAMPLING

Baseline sampling is conducted to establish pre-ISCO conditions, and can include analysis of:

- soil and groundwater samples from the site for target contaminant(s);
- potential biological or abiotic degradation by-products;
- occurrence of metals; and
- general water quality parameters that may affect oxidant performance, or can be used as a surrogate tracer for oxidant migration and distribution.

Ideally, groundwater baseline monitoring should be conducted more than once over a period of approximately a year to gain an understanding of the ambient variability (including seasonality) inherent in many aquifer settings. The baseline data set will be particularly important as a database of comparison to post-ISCO treatment performance monitoring data. The magnitude of rebound can be more accurately estimated after accounting for the ambient variability in groundwater contaminant concentrations.

The baseline sampling plan should include:

1.) locations upgradient of the contaminated zone of a site for establishing ambient background conditions,

2.) locations within the TTZ for establishing baseline conditions for delivery performance monitoring, and
3.) locations downgradient of the TTZ for treatment performance monitoring (e.g., if downgradient migration of oxidants is expected, or if mass flux evaluations will be conducted as a treatment cessation criterion).

Typical ISCO baseline monitoring programs include the laboratory and field parameters presented in Table A26-1, based on the oxidant(s) being delivered.

**Table A26-1. Baseline Monitoring Parameters.**

| Parameter | $MnO_4^-$ | CHP | $S_2O_8^{-2}$ | Ozone |
|---|---|---|---|---|
| pH | | FI, FK | FI, FK | FI, FK |
| ORP | FI | FI | FI | FI |
| Temperature | | FI | | FI |
| Alkalinity | | L, FK | | |
| Vadose Zone Gas ($CO_2$, $O_2$, VOC) | | FI | | FI |
| Dissolved Oxygen | | FI | | FI |
| Specific Conductance | FI | | FI | |
| Sodium | | | L, FK | |
| Sulfate | | | L, FK | |
| Contaminants of concern (soil and groundwater) | DPT, L | DPT, L | DPT, L | DPT, L |
| Chloride | L, FI, FK | L, FI, FK | L, FI, FK | L, FI, FK |
| Manganese | L, FK | | | |
| Redox Sensitive Metals (e.g., As, Ba, Cd, Cr, Cu, Fe, Pb, Se) | L, FK | L, FK | L, FK | L, FK |
| Iron | | L, FK | L, FK | |
| Water level | FI | FI | FI | FI |

L = laboratory analysis
DPT = direct-push deployed sensor (e.g., membrane interface probe (MIP) for VOCs, conductivity probe for specific conductance)
FS = field spectrophotometer
FI = field instrument (e.g., meter, gauge, thermometer)
FK = field kit (e.g., colorimeter, color wheel, test strips)

## DELIVERY PERFORMANCE MONITORING

Delivery performance monitoring is performed during and immediately after oxidant delivery to:

- Monitor injection flow rates and volume,
- Ensure adequate distribution of the oxidants,
- Monitor and manage aquifer conditions that affect oxidant chemistry, and
- Monitor migration/displacement of COCs during injection.

For some oxidants (i.e., CHP and ozone) it also includes the measurement of oxidant impact on groundwater temperature and off-gas generation in the vadose zone and well headspace. As such, delivery performance monitoring is also an important component of a comprehensive ISCO health and safety program. Typically, delivery performance monitoring only includes well locations within the TTZ, however upgradient locations may be included if natural fluctuations in ambient groundwater geochemistry is expected to vary significantly such that they would need to be monitored and screened out from the data collected from the TTZ. Typical ISCO delivery performance monitoring programs include the laboratory and field parameters presented in Table A26-2, based on the oxidant(s) being delivered.

**Table A26-2. Delivery Performance Monitoring Parameters.**

| Parameter | $MnO_4^-$ | CHP | $S_2O_8^{-2}$ | Ozone | Example Monitoring Frequency* |
|---|---|---|---|---|---|
| Oxidant | FS, V | FK | FK | FI, FK | baseline and end of injection |
| Color | V | | | | daily during injection |
| pH | | FI, FK | FI, FK | FI, FK | daily during injection (or real-time monitoring with datalogger) |
| ORP | FI | FI | FI | FI | daily during injection (or real-time monitoring with datalogger) |
| Temperature | | FI | | FI | daily during injection (or real-time monitoring with datalogger) |
| Alkalinity | | L, FK | | | daily during injection |
| Vadose Zone Offgas ($CO_2$, $O_2$, VOC, ozone) | | FI | | FI | daily during injection |
| Dissolved oxygen | | FI | | FI | daily during injection (or real-time monitoring with datalogger) |
| Specific conductance | DPT, FI | | DPT, FI | | daily during injection (or real-time monitoring with datalogger), or once the day after injection |
| Sodium | | | L, FK | | daily during injection |
| Sulfate | | | L, FK | | daily during injection |
| Iron | | L, FK | L, FK | | daily during injection |
| Injection pressure | FI | FI | FI | FI | constant |
| Injection flow rate | FI | FI | FI | FI | constant |
| Water level | FI | FI | FI | FI | daily during injection (or real-time monitoring with datalogger) |
| Injectate concentration | C | C | C | C | daily during injection |
| Fluid pressure | FI | FI | FI | FI | daily during injection |
| Tracers | L, FI | L, FI | L, FI | L, FI | daily during injection (or real-time monitoring with datalogger) |

* Actual monitoring frequency should be determined on a site-specific and oxidant-specific basis, or negotiated as part of regulatory requirements.
L = laboratory analysis
DPT = direct-push deployed sensor (e.g., MIP for VOCs, conductivity probe for specific conductance)
FS = field spectrophotometer
FI = field instrument (e.g., meter, gauge, thermometer)
FK = field kit (e.g., colorimeter, color wheel, test strips)
V = visual
C = calculated

The frequency of monitoring parameters during delivery performance monitoring will be highly dependent on the oxidant, injection design, and the site-specific hydrogeology. Monitoring frequency during oxidant delivery will typically be more frequent than during treatment performance monitoring, and may range from weekly to more than once a day for certain parameters, depending on the ISCO design and site characteristics. For example, for a long-term ozonation delivery approach, monitoring may only occur weekly to monthly. It is also important to understand the differences in oxidant distribution and injection fluid distribution when using indicators of oxidant distribution. Due to chemical reaction during injection, the oxidant will not move as far as the bulk injectate. This should be accounted for in the monitoring frequency and the time elapsed between measurements. The ROI, determined using the A11. ISCO Spreadsheet Design Tool during the ISCO Conceptual Design Process, reflects the oxidant travel distance and can be used to plan monitoring frequency/duration.

Another consideration during delivery performance monitoring is that the injected oxidant solution's lateral and vertical distribution will not be completely uniform due to subsurface heterogeneities. For this reason, observing the oxidant at a monitoring location does not necessarily mean that the oxidant has contacted the entire thickness of the injection zone, and/or radially uniform from the injection point. Therefore, it's important to have an adequate, radially-variable monitoring network and robust monitoring program to be able to capture the non-uniformity of delivery. Vertically nested monitoring wells can also be employed to provide a means of monitoring the vertical distribution of oxidant during injection.

All effort should be made to optimize the monitoring program as it progresses and data value changes. For example, there may be no need for additional metals measurement if the initial measurements taken during the strongest oxidation reaction are negligible.

## TREATMENT PERFORMANCE MONITORING

Treatment performance monitoring is conducted after ISCO delivery to determine if the specific treatment goals and milestones established by stakeholders during the Preliminary Design phase are being met. In general, treatment performance metrics of an ISCO design will include:

- Extent and uniformity of COC treatment within the target treatment zone
- Degree of source removal or source mass flux reduction
- Progress towards achieving remedial cleanup goals.

Treatment performance monitoring typically includes well locations within the TTZ and locations downgradient of the TTZ (e.g., if downgradient migration of oxidants is expected, or if mass flux evaluations will be conducted), however upgradient locations may be included if natural fluctuations in ambient groundwater geochemistry is expected to vary significantly such that they would need to be monitored and screened out from the data collected from actively treated areas of the site. Typical ISCO treatment performance monitoring programs include the laboratory and field parameters presented in Table A26-3, based on the oxidant(s) being delivered.

Treatment performance monitoring is typically conducted on a less frequent basis than delivery performance monitoring, but will vary depending on the longevity of the oxidant and time for re-equilibration, site-specific hydrogeology, and/or regulatory monitoring requirements for ISCO by-products (e.g., redox sensitive metals).

The ultimate objective of treatment performance monitoring is to collect data that will demonstrate progress towards or achievement of ISCO treatment milestones as prescribed in the Operation and Contingency Plan. Evaluating and interpreting monitoring data towards this objective should be conducted with several important considerations:

- Depending on the location of monitoring wells, post-injection decreases in dissolved COC concentrations may be a result of groundwater displacement rather than actual contaminant mass destruction. The results of monitoring at all locations in and outside of the TTZ should show a decline after injections if displacement was minimized. Field parameters and tracer can be used to understand the effects of dilution. Ideally, groundwater samples are only collected after hydraulic re-equilibration occurs.

- As discussed in Detailed Design and Planning Process 2, a concern inherent in remediation performance assessment is the potential for rebound of contaminant concentrations in the source area as a result of residual DNAPL dissolution, or back-diffusion of COCs from low-permeability layers that were not contacted by oxidant during injections. Historically, rebound has occurred in 60 percent of ISCO sites (see DISCO). Therefore, it makes sense to account for the occurrence of some degree of contaminant rebound in the treatment performance monitoring program.
- Analysis for COCs in both soil and groundwater is critical for ISCO treatment performance monitoring. Analysis of groundwater alone does not enable determination of the mass of contaminant desorbed from saturated soil.

**Table A26-3. Treatment Performance Monitoring Parameters.**

| Parameter | $MnO_4^-$ | CHP | $S_2O_8^{-2}$ | Ozone | Example Monitoring Frequency* |
|---|---|---|---|---|---|
| Oxidant | FS, V | FK | FK | | weekly to monthly |
| pH | FI, FK | FI, FK | FI, FK | | weekly to monthly |
| ORP | FI | FI | FI | FI | weekly to monthly |
| Alkalinity | | | | L, FK | weekly to monthly |
| Dissolved Oxygen | | FI | | FI | weekly to monthly |
| Specific Conductance | DPT, FI | | DPT, FI | | weekly to monthly |
| Sulfate | | | L, FK | | weekly to monthly |
| Contaminants of concern (groundwater) | DPT, L | DPT, L | DPT, L | DPT, L | monthly to quarterly or as needed to document treatment efficiency |
| Contaminants of concern (soil) | DPT, L | DPT, L | DPT, L | DPT, L | Post-ISCO, any time after the oxidant is consumed |
| Chloride | L, FI, FK | L, FI, FK | L, FI, FK | L, FI, FK | monthly and/or at end of treatment performance monitoring |
| Manganese | L, FK | | | | monthly for the first quarter |
| Redox Sensitive Metals (e.g., As, Ba, Cd, Cr, Cu, Fe, Pb, Se) | L, FK | L, FK | L, FK | L, FK | at the end of treatment performance monitoring |
| Geochemical indicators for NA (e.g., nitrate, $CO_2$)[1] | L, FK | L, FK | L, FK | L, FK | at end of treatment performance monitoring |

* Actual monitoring frequency should be determined on a site-specific and oxidant-specific basis, or negotiated as part of regulatory requirements.
L = laboratory analysis
DPT = direct-push deployed sensor (e.g., MIP for VOCs, conductivity probe for specific conductance)
FS = field spectrophotometer
FI = field instrument (e.g., meter, gauge, thermometer)
FK = field kit (e.g., colorimeter, color wheel, test strips)
V = visual
C = calculated
1 – Appropriate for systems utilizing a coupled approach with a biological component

## NUMBER AND LOCATION OF MONITORING POINTS

The appropriate number and spacing of wells for the monitoring network depends on site-specific treatment goals and regulatory requirements. The monitoring network should be designed to achieve the data objectives for both operations monitoring (e.g., delivery effectiveness) and demonstration of treatment efficiency. For example, an adequate number of monitoring wells should be sited within and around the TTZ to demonstrate uniform oxidant delivery both near the injection locations and at the farthest reaches of the predicted oxidant radius of influence. Similarly for treatment efficiency demonstration, if statistical methods will be used to determine post-ISCO re-equilibrated conditions, then an adequate number of sample locations should be established to perform a valid analysis. Generally, injection points are not suited for monitoring, since concentrations of target contaminants in an injection well are expected to be lower than in the formation because of the presence of higher concentration of oxidant, and therefore such measurements are not representative of site conditions. However, if sufficient time is allowed for the hydrogeologic conditions to re-equilibrate after an oxidant is consumed, monitoring at the injection points may be useful. Temporary direct-push wells may be an inexpensive way to augment an existing monitoring well network for post-ISCO treatment monitoring.

## FIELD AND LABORATORY ANALYTICAL METHODS

Data collection methods should be carefully considered with respect to data quality and cost-effectiveness. For example, the method of data collection can range from simple sampling of dedicated wells, to direct push continuous core soil sampling, to real-time continuous data logging using down-hole sensors for off-gas monitoring. The method chosen is typically based strongly on site-specific field and management conditions. Therefore, no additional method selection guidelines are provided herein.

The Performance Monitoring Plan is designed ultimately to verify if the ISCO system can meet the performance specifications. However, it also requires a dynamic component to allow real-time optimization by project stakeholders after review of performance monitoring results. It must allow for adjustments to monitoring parameters, locations, frequency, and durations as appropriate to obtain the necessary data to achieve the data objectives. Due to the short duration and rapid subsurface reactions typically associated with ISCO applications, a flexible Performance Monitoring Plan is essential for efficiently obtaining stakeholder concurrence on field decisions, accurately assessing the delivery and treatment performance, and maximizing the value of field and analytical resources invested into the project.

The use of real-time measurement techniques such as direct push technologies (e.g., MIP for evaluating the distribution of volatile contaminants, and electrical resistivity imaging (ERI) and conductivity probes for evaluating the distribution of injected oxidants) and down-well in situ sensors with redox data loggers have dramatically improved the ability to optimize ISCO treatment processes during implementation. Careful planning should be performed when employing direct-push methods for real-time monitoring, as the drilled probe holes can create preferential pathways for any future oxidant injections.