ATTACHMENT 2: ISCO Relevance to COCs, Geology, and Goals

ISCO can be an effective remediation technology capable of degrading organic contaminants of concern (COCs) in the subsurface environment and meeting risk-based or performance-based remediation goals. However, it is important to note that ISCO cannot be applied universally to all remediation sites, and that the ease and effectiveness of ISCO depends significantly upon site-specific conditions. The following sections provide guidance and precautions to support the decision of whether or not to consider ISCO during the preliminary technology screening process. More detailed screening is provided in subsequent sections of the ISCO Screening Component.

DETERMINE ISCO APPLICABILITY FOR COCs

ISCO should be considered for sites where groundwater and/or soil are contaminated with organic COCs that are degradable by common ISCO oxidants in a cost-effective manner. Table A2-1 divides a list of major contaminant classes into 3 categories. Please note that these findings are based upon the cumulative experience with all ISCO oxidants, but specific contaminants and site conditions may be much more amenable to one oxidant versus another, necessitating additional screening beyond this process. It should also be noted that this table is based on the information available at the time of this writing. Additional research continues on many of these oxidants, so new information is likely to be learned in the future. This table is only to help establish whether or not ISCO should be considered, and to give some answer to the level of experience of ISCO with specific contaminant types.

Table A2-1. Categorization of Contaminant Classes by ISCO Treatability*

Category 1 Contaminant classes highly amenable to effective degradation by currently used ISCO oxidants	Category 2 Contaminant classes degradable by common ISCO oxidants but effectiveness is less certain	Category 3 Contaminant classes not at all amenable to ISCO treatment
Chloroethenes	Chloroethanes	Heavy metals
BTEX	Chlorinated or brominated methanes	Radionuclides
TPH	Explosives (RDX, TNT, etc.)	Inorganic salts
Other halogenated 2 or more carbon alkanes	Organic herbicides or pesticides	Perchlorate
PAHs	NDMA	Nutrients (nitrate, ammonia, phosphate)
Chlorobenzenes	Ketones	
Phenols (cresols, chlorophenols, nitrophenols)	PCBs	
Fuel oxygenates (MTBE, TAME)	Dioxins / Furans	
Alcohols		
1,4-dioxane		

*It should be noted that the degradability of contaminants will vary by the oxidant used, so additional evaluation is required to select the most appropriate oxidant. Sources: (Hoigné and Bader 1983b; Hoigné and Bader 1983a; Huang et al. 2005; ITRC 2005; Huling and Pivetz 2006; Waldemer and Tratnyek 2006).

Category 1 contains organic contaminant classes that common ISCO oxidants readily degrade. In general, the bulk of ISCO applications and experience have been in treating sites with Category 1 contaminants. Proceed with consideration of ISCO if the site COCs are included in this category.

Category 2 contains organic contaminants that are degradable by ISCO oxidants, but their degradability is much more site- and process-specific. These contaminants will often either exhibit more resistance to oxidation and reduced degradation efficiency, or their degradability and cost-effective treatment by ISCO oxidants is less proven and more uncertain. If the site's primary risk-driving COCs are in Category 2 contaminant classes, more caution should be exercised by the user in screening these contaminants because the science and engineering knowledge base regarding ISCO application to these COCs is less defined. In particular, compared to Category 1, Category 2 contaminants are more sensitive to oxidant selection, activation methods, concentrations of reagents, scavengers, pH, etc., so more attention should be paid to the geochemistry and effectiveness aspects of the screening protocol rather than just on hydrology.

Category 3 contains contaminant classes for which ISCO should NOT be considered for COC treatment. Generally, these are inorganic contaminants where ISCO will be either ineffective, or potentially worsen a situation by altering contaminant behavior in the subsurface. Furthermore, if redox-sensitive heavy metals or radionuclides are present as co-contaminants at a site where target COCs are in Categories 1 or 2, ISCO screening should consider the potential for affecting risk due to impacts of ISCO on co-contaminant concentrations and/or mobility. Site conceptual model uncertainty should be low at such sites before proceeding with ISCO screening.

DETERMINE ISCO APPLICABILITY FOR SITE GEOLOGY, CONTAMINANT MASS, AND ISCO TREATMENT GOALS

Even when the contaminants are amenable to oxidation, ISCO may prove challenging and ISCO treatment goals may be unachievable in certain geologic settings because of the difficulty in delivering the oxidant to the contaminants. Furthermore, ISCO is often utilized as part of an overall monitored natural attenuation (MNA) strategy. During this screening phase, a first-cut contaminant mass balance estimate can be made to support MNA or confirm treatment goals. The probability that ISCO can achieve ISCO treatment goals as a stand-alone technology must be weighed against coupled ISCO treatment trains or other technologies in such situations.

Table A2-2 presents a matrix of the relative probability of ISCO effectiveness for different ISCO treatment goals for different generic geologic conditions and contaminant mass densities. It presents qualitative effectiveness ratings for various removal efficiencies, with a red, yellow, or green flag depending on relative assessments regarding whether or not ISCO alone can achieve these desired endpoints after the completion of remedial activities.

The information in Table A2-2 has been assembled based on results from a survey of ISCO experts, experiences documented in case studies, findings from scientific literature, and the experience of the authors. It should be noted that the contaminant treatment at a site will vary, depending on oxidant and delivery system approach, ISCO system design, and site-specific factors, with possible performance either higher or lower than indicated in this table. It should also be noted that this table was developed with the idea of site-wide reductions in concentration, mass, or flux in mind; better treatment than indicated in the tables could be anticipated in localized areas like hot spots.

Table A2-2. Matrix of Probability of Stand-Alone ISCO Effectiveness Versus Site Hydrogeology, Remediation Goal Type, and Contaminant Mass Density

Low contaminant mass density									
Type of ISCO Treatment Goal:	**Concentration reduction**			**Mass reduction**			**Mass flux reduction**		
Removal magnitude (percent):	**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	Feasible	Feasible	Possible	Feasible	Feasible	Possible	Feasible	Feasible	Possible
Heterogeneous permeable	Feasible	Possible	Possible	Feasible	Feasible	Possible	Feasible	Feasible	Possible
Homogeneous impermeable	Feasible	Possible	Possible	Feasible	Feasible	Possible	Feasible	Feasible	Possible
Heterogeneous impermeable	Feasible	Possible	Possible	Feasible	Feasible	Possible	Feasible	Feasible	Possible
Consolidated media (fractured):									
Sedimentary	Feasible	Possible	Possible	Feasible	Feasible	Possible	Feasible	Feasible	Possible
Igneous / metamorphic	Feasible	Possible	Doubtful	Feasible	Possible	Doubtful	Feasible	Feasible	Possible
Karst	Feasible	Possible	Doubtful	Possible	Possible	Doubtful	Feasible	Possible	Doubtful
High contaminant mass density									
Type of ISCO Treatment Goal:	**Concentration reduction**			**Mass reduction**			**Mass flux reduction**		
Removal magnitude (percent):	**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	Feasible	Feasible	Possible	Feasible	Feasible	Possible	Feasible	Feasible	Possible
Heterogeneous permeable	Feasible	Possible	Doubtful	Feasible	Feasible	Possible	Feasible	Possible	Doubtful
Homogeneous impermeable	Feasible	Possible	Doubtful	Feasible	Possible	Doubtful	Feasible	Possible	Doubtful
Heterogeneous impermeable	Feasible	Possible	Doubtful	Feasible	Possible	Doubtful	Feasible	Possible	Doubtful
Consolidated media (fractured):									
Sedimentary	Feasible	Possible	Doubtful	Feasible	Possible	Doubtful	Feasible	Feasible	Possible
Igneous / metamorphic	Possible	Possible	Doubtful	Possible	Doubtful	Doubtful	Feasible	Possible	Doubtful
Karst	Possible	Doubtful	Doubtful	Doubtful	Doubtful	Doubtful	Possible	Doubtful	Doubtful

Definitions for key terms are included below.

Several key terms must be defined to use Table A2-2.

- **Low Contaminant Mass Density** – Represents target treatment zones where COCs are present in dissolved phases significantly below contaminant solubility limits (e.g., < 1% solubility) or where low levels of sorbed contaminant mass are present in soil, such as conditions often found in groundwater plumes.

- **High Contaminant Mass Density** – Represents target treatment zones where COCs are present in dissolved phase concentrations indicative of large sorbed masses or where residual NAPL contamination is present in soil. Typically, high contaminant mass densities are found in or near contaminant source zones. Pooled NAPL falls under this category as well, though NAPL pools should be pretreated to reduce contaminant mass before ISCO application. As such, the values in Table A2-2 do not apply to pooled DNAPL or LNAPL unless these pools are removed or reduced to residual-phase levels prior to ISCO treatment.

- **Type of ISCO Treatment Goal** – Represents the type of groundwater remediation goal being pursued as the desired post-ISCO endpoint at a given site. Three types are presented in this table.

    - **Concentration Reduction Goals** – This category represents sites where the remediation goal being pursued is either a specific soil or groundwater contaminant concentration reduction (e.g. 95%), or a target concentration value. Performance is assessed by either comparing pre- and post-treatment concentrations in groundwater or whether the post-treatment concentration exceeds a threshold concentration (e.g. MCL or risk-assessment based concentration) *after* oxidant has been depleted in the subsurface. Success or failure of meeting concentration-based goals may be determined by whether the set reduction or threshold concentration is met or exceeded at a point, at a boundary, or site-wide. Values in the table are based on literature review, field experience and case studies evaluated by the authors.

- **Mass Reduction Goals** – This category represents sites where the goal is to reduce contaminant mass (e.g., by reducing source or plume longevity). Performance is assessed based on an estimate of the amount of contaminant mass in the subsurface before and after treatment. In some cases mass reduction goals are the target, but no performance estimate is made (e.g., remediation is only applied to facilitate a follow-up treatment such as MNA or bioremediation). Typically, these type of goals are applied across an entire site or source zone and use geospatial methods and routine monitoring data for estimation. Values in the table are based on literature review, field experience and case studies evaluated by the authors.

- **Mass Flux Reduction Goals** – This category represents an emerging type of remediation goal that has been the subject of increased research and discussion. Mass flux reduction considers the flow of groundwater contaminant mass across a two-dimensional compliance plane. Mass flux-based goals account for reductions in concentrations across this two-dimensional plane, as well as impacts to the groundwater flow field that may result from remediation. Although recent research has indicated that mass flux reductions may be more easily achievable at challenging sites than concentration or mass reduction based goals, and mass flux reductions may generate scientifically valid improvements to groundwater quality, regulatory acceptance of this type of goal has lagged. As such, the experience base with these goals at the time of the ISCO Protocol's development is small, but this type of goal is included here because the authors anticipate that mass flux reduction goals may become more prevalent in the future. The performance probability values for ISCO treatment included in Table A2-2 are thus based on the authors' judgment, research and experience, rather than actual case study performance, which is currently lacking for this goal.

- **Unconsolidated Media** – This category represents all sites where contaminant target treatment zones are located within unconsolidated porous media (e.g., uncemented sands, silts, clays, tills, etc.). This category is divided into four subcategories based on the site permeability and heterogeneity.

  - **Permeability** – for the purposes of this tool, a site is permeable if the average hydraulic conductivity is greater than 10^{-4} cm/s and low permeability if it is less than 10^{-4} cm/s.

  - **Heterogeneity** – A site is considered heterogeneous if the hydraulic conductivity varies spatially by more than a factor of 1000, and homogeneous if it varies by less than a factor of 1000. Determination of such a factor is often based on idealized estimates based on the presence of sands, silts and clays rather than measured K values.

- **Consolidated Media** – This category represents all sites where the contaminant target treatment zone is in consolidated fractured rock formations. Divisions are made based upon the standard geologic definitions of sedimentary, igneous and metamorphic rock formations, with the sole exception of karst formations. Karst formations pose unique problems to groundwater remediation using ISCO and thus must be evaluated separately.

To use Table A2-2, the user must first assess contaminant mass density for a site. Often, low contaminant mass density is assumed if concentrations are < 1% of contaminant solubility, and high mass density if greater than this value (this value corresponds to the standard rule of thumb used in assessing DNAPL presence based on aqueous-phase COC concentrations (EPA 1992)). It is important to consider that sites with high organic carbon content will likely have significant sorbed contaminant mass, yet concentrations may be below this 1% threshold. Low mass density is addressed in the top portion of the table, and high mass density in the lower portion.

Next, the reduction needed to meet a remediation goal is determined. For example, if a site contains PCE concentrations of 5 mg/L, and the remediation goal is to meet the MCL for PCE at 5 μg/L, then a

99.9% concentration reduction is needed. The percent reduction is located across the top row of each portion of the tables for high and low contaminant mass density.

Once the percent reduction needed is determined, the site characteristics that most closely match actual site conditions are considered (left-hand column of Table A2-2). The box corresponding with the appropriate goal and site characteristics in the table provides the probability of ISCO effectiveness for these conditions. There are three color coded assessments of the probability that ISCO will be effective in meeting the desired goal, and each is explained below.

- If the value given is **Feasible** in green, proceed to screening for ISCO considering it as a stand-alone. Coupling with other technologies may not be necessary unless another remediation technology or process has been previously applied at the site, is currently ongoing, or if the user perceives a value would be added by including coupled approaches.

- If the value given is **Possible** in yellow, it is conceivable that ISCO may succeed as a stand-alone, albeit with a higher degree of uncertainty than for “feasible” conditions. The user should proceed to screening for ISCO, but is encouraged to also consider a coupled approach in addition to considering ISCO as a stand-alone technology.

- If the value given is **Doubtful** in red, then the user should not expect ISCO as a stand-alone to meet their remediation goal. In such cases, coupling with other remediation technologies is probably necessary to meet site goals. Coupling may strongly improve the likelihood of success, as additional remediation technologies either before or after ISCO may add to the percent reduction to meet the required goal. The user is encouraged to proceed with ISCO screening, but should realize that their goals likely fall out of reach of ISCO stand-alone approaches.

For users requiring a greater than 99.9% reduction, ISCO should not be counted on to achieve such reductions as a stand-alone technology. Based on a collection of field-scale case studies, concentration reductions greater that 99.9% have been achieved in some situations, but they are the exception rather than the rule. Should users desire to achieve such reductions, it is recommended that a particularly robust ISCO design (e.g., several delivery events, multiple pore volumes of ISCO reagents) be developed, and that a contingency plan including a post-ISCO polishing coupled technology (e.g., enhanced bioremediation or MNA) be carried forward with the design.

Consider, for example, an unconsolidated homogeneous permeable site with residual TCE DNAPL, groundwater TCE concentrations measured at 200 mg/L, and a risk-based concentration goal of 20 µg/L site wide as the remediation objective. A 99.99% concentration reduction is required, but is unlikely with ISCO alone based on the values in Table A2-2. However, a 99-99.9% removal is “Possible”, and a 90-99% removal is “Feasible”, for this site's geology and contaminant mass density. In such an instance, ISCO could be applied to achieve an initial 99% removal, followed by either enhanced bioremediation or monitored natural attenuation to achieve an additional 99% removal (of the remaining concentration) and meet the remediation goal.

ADDITIONAL CONSIDERATIONS FOR SITES WITH CONTAMINATED FRACTURED ROCK

Sites with contaminated fractured rock matrices generally pose tremendous difficulties to all remediation technologies that require introduction of amendments to treat contaminant source zones or plumes. ISCO is no different, as it relies on solid, liquid or gas phase oxidant injection to achieve effective contact with contaminants in order to degrade them. In fractured rock matrices, this oxidant-contaminant contact can be very difficult to achieve. Nonetheless, fractured rock sites frequently require remedial action, and because these sites often pose enormous challenges to all possible remedial technologies, ISCO may be considered as it may yield benefit to site owners and RPMs. However, before considering or applying ISCO to these sites, it is vital for fractured rock site RPMs and site owners to understand the nature of the challenge posed by their site, to anticipate that difficulties may arise during remediation, and to have realistic performance expectations.

From a survey of ISCO professionals conducted at a workshop convened in March of 2007 at the Colorado School of Mines (see S3. ISCO 2007 Workshop Proceedings), the following trends about fractured rock sites were noted:

- More regular fracture patterns are more easily treated than irregular fracture patterns
- Sites with more extensive fracture continuity are more treatable
- Mass flux reduction and risk-assessment based cleanup goals are more achievable for fractured rock sites than contaminant mass reduction.
- For most organic contaminants, MCLs are unrealistic remediation goals for fractured rock sites unless contaminant mass densities are very low.
- Distribution methods will be limited to well injection, recirculation, density-driven delivery, and fracturing to assist distribution.

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