treatability bulletin

CL:AIRE Treatability Bulletins describe the key factors to be considered in the early stages of designing a remediation project. Treatability studies provide a means of determining, through laboratory- or pilot-scale tests, the practicability and likely effectiveness of remediation, and can be an essential part of a remediation options appraisal.

Chemical Oxidation

Technology Description

In situ chemical oxidation (ISCO) involves the injection of liquid or gaseous oxidising agents (or oxidants) into the subsurface to bring about the rapid degradation primarily of organic contaminants. Some organic compounds will undergo complete degradation whilst others may only be partially degraded, although these breakdown products are generally amenable to treatment by other methods, such as bioremediation. In some cases these breakdown products may require further consideration as contaminants themselves.

Inorganic compounds may also be oxidised, for example, arsenic (As) from As(III) to As(V), or chromium (Cr) from Cr (III) to Cr (VI). In both cases, the latter species is more harmful, and these additional reactions must be considered and managed.

Oxidation is a chemical process in which the oxidation state of a target substance is increased and in which the oxidant is reduced by accepting electrons from both target contaminants and non-target reactive species.

The most typical oxidants are listed below:

- Ozone (O_3)
- Catalysed hydrogen peroxide (e.g. Fenton's reagent)
- Activated persulphate (gives $SO_4^{\cdot}$ etc)
- Persulphate ($S_2O_8^{2-}$)
- Permanganate (MnO_4^-)
- Percarbonate ($Na_2CO_3.1.5H_2O_2$)

Table 1 provides a general applicability matrix of ISCO to different contaminant groups and ground materials.

It should be noted that the ability to oxidise these contaminants effectively will vary depending upon the selected oxidant or combination of oxidants as well as various site-specific factors. Treatability testing should be carried out in addition to desk-based assessment on a case by case basis.

Table 1: Generic applicability of ISCO technology to contaminants and ground materials (adapted from Defra, 2010). Key: Usually or potentially applicable Y; May be applicable ?; Not applicable N.

Organic		Inorganic		Materials	
Halogenated VOCs	Y	Metals	?	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	N	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	?	Silt 2-60µm	Y
Non-halogenated SVOCs	Y	Cyanides	?	Clay <2µm	?
Organic corrosives	N	Asbestos	N	Peat	N
Organic cyanides	N				
PCBs	?*	**Miscellaneous**			
Pesticides/herbicides	?	Explosives	?	* amended from Y to ?	
Dioxins/furans	N				

Notes:
VOC - Volatile organic compound
SVOC - Semi-volatile organic compound
PCB - Polychlorinated biphenyl

Treatability Testing

There are three types of treatability tests: simple laboratory tests; bench-scale tests; and pilot tests, all of which are required for the successful implementation of full-scale ISCO projects. It should be noted that variable subsurface conditions make it difficult for laboratory and bench-scale treatability tests to predict what will occur in field-scale projects, which is why the results of these studies must be validated in an on-site pilot study prior to full-scale applications.

Laboratory and bench-scale treatability tests

Laboratory and bench-scale treatability tests provide useful design information regarding remediation potential and assist in oxidant selection which should be viewed as contaminant and site specific. They are the first stage of testing before scaling up ISCO to pilot- and/or full-scale.

The main objective of these ISCO treatability tests is to establish proof of concept that the target compound(s) can be transformed into less harmful species. Another primary aim of the bench-scale work is to establish an overall oxidant demand and as such a likely rate of oxidant injection. As well as providing an understanding of technical suitability, these tests will also allow an assessment of the commercial suitability of the treatment; too high an oxidant demand may increase the cost of reagent applications to unaffordable levels.

Table 2 highlights the key factors to consider in developing ISCO laboratory and bench-scale treatability tests. The tests should assess various oxidants at various dosing rates (or concentrations) on soils, aquifer material and groundwater recovered from the site since they are likely to contain the majority of the contaminant(s) and other parameters that will largely influence oxidant demand and the success or failure of the treatment process. The tests will measure natural oxidant demand, degradation rates, the level of residual oxidant and contaminant concentrations before and after treatment. A thorough approach will also consider the creation of other reaction products. The treatability tests may consist of batch tests and column tests.

Table 2: Key factors to consider when developing ISCO laboratory and bench-scale treatability tests.

Optimising the oxidation process	Managing concerns
Oxidant selection Dose optimisation Oxidant/stabiliser concentration Soil oxidant demand or natural oxidant demand Contaminant oxidant demand	pH changes Mobilisation of metals (e.g. Cr (VI)) Contaminant desorption Formation of reaction by-products
Catalyst selection (if one is required) Oxidant stability / gas evolution Soil buffering capacity	When estimating costs, significant contaminant reduction should be demonstrated using reasonable quantities of oxidant and reagents under reasonable simulated conditions.

Some of the limitations of treatability testing at this scale include difficulty in simulating heterogeneity in a test column, the tests involve a small sample volume compared to site volume to be treated, and it is a well mixed system with good contaminant/oxidant contact which may give the results a positive bias. It is also not possible to assess the oxidant delivery process, which is why pilot-scale treatability tests are recommended.

Pilot-scale treatability tests

Pilot-scale treatability tests provide design parameters for full-scale ISCO implementation and require extensive monitoring. They are typically performed on more than one area of the site and may be an immediate precursor to full-scale treatment. Table 3 highlights the key factors to consider in developing ISCO pilot-scale treatability tests.

Multiple injections of oxidant and/or reagents under different conditions can be used to accomplish different treatment and testing objectives.

As mentioned above, monitoring of the pilot tests is key. Recommended monitoring parameters that are a direct indicator of oxidative treatment include the target compounds, reaction byproducts, metals, and the oxidant. Indirect indicators such as CO_2, dissolved oxygen, total organic carbon, chemical oxidant demand, and temperature are sometimes used but can be unreliable alone. Control reactors can be used to help quantify non-oxidation losses and are recommended. Measuring pre- and post-oxidation concentrations of the target compound in the aqueous, solid, and gaseous phases allows mass balance calculations which serve as the basis for performance evaluation. Monitoring and observation of rebound post treatment should also be considered as a factor in assessing treatability.

Box 1. Health and safety

As always, health and safety issues need to be carefully considered particularly if the treatability studies are at pilot-scale. Specific health and safety considerations should include storage and handling of hazardous materials (oxidants), appropriate dosing and delivery pipework, material selection and use of appropriate PPE when carrying out tests. Heat generation and gaseous by-products and their potential effects are also an important consideration that should be addressed.

Table 3: Key factors to consider when developing ISCO pilot-scale tests.

Optimising the delivery process	Managing concerns
Radius of influence Rate of application Field-scale inefficiencies Field oxidant volume estimates Injection strategies; injection rate; injection pressure Assess travel times, distribution (vertical/horizontal), and persistence of the oxidant and reagents (Fe, acid, stabilisers, chelators) Determine whether groundwater contaminants are mobilised or volatilised Assess the mobilisation of metals Assess contaminant rebound Determine reaction byproducts Potential and actual preferential pathways	An opportunity to revise cost estimate from bench-scale tests before a decision is made on whether to proceed to full-scale implementation Assess the adequacy of the monitoring programme Anticipate well fouling problems Assess potential difficulties in scaling up Finding or creating preferential pathways Assess how oxidation changes fundamental fate and transport characteristics and whether there is loss of adsorption capacity or impact on microbial communities

References and Suggested Reading

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