

CHAT QUESTIONS AND ANSWERS
CL:AIRE Dense Non-Aqueous Phase Liquids (DNAPLs)
Site Remediation: Technologies and their Applicability Webinar
29th September 2011 at 13:00-14:30 BST

1. Q: Slide 16 can we have some numbers against what highly permeable and lower permeability means - seems like the middle ground is best for VER?
A: The optimum hydraulic conductivity range for VER is typically 10^{-8} to 10^{-5} m/s.
2. Q: Why is MNA not considered suitable and establish
A: It is agreed that MNA (monitored natural attenuation) is an established practice which may be suitable for DNAPL sites. There are various options for including MNA as part of the full solution. For example active treatment of a source area may be combined with an MNA approach for the associated plume, where full or even partial treatment of the source will control plume migration and eventually cause the plume to diminish. Whether MNA could be appropriate for a DNAPL site without any other remedial action is a site-specific matter dependant on site conditions, location sensitivity and the applicable regulatory regime. In general, reliance on MNA alone for a DNAPL source will involve very extended monitoring periods.
3. Q: Slide 23 ISB - is there any issue of mobilised/ dissolved DNAPL being lost before it is degraded? Is some form of containment or at least sentinel monitoring essential to demonstrate control is being maintained? Mass balance of source reduction against chloride ion generation perhaps?
A: In principle, some ISB applications could mobilise DNAPL if not properly controlled. Enhancing dissolution of DNAPL is generally one of the objectives of ISB because otherwise the treatment timescale will be limited by the pre-treatment dissolution rate. Monitoring should be carried out during ISB operations for several reasons: (i) to provide data on which to base process control actions (for example when to inject more electron donor), (ii) to measure treatment performance and (iii) to ensure that unacceptable contaminant concentrations are not generated at the treatment zone boundary and/or other applicable locations. Hydraulic controls may be required during treatment according to site-specific conditions. Chloride ion generation can provide a useful indication of treatment performance, although this is generally a less useful parameter where background chloride concentrations are high.
4. Q: Slide 24 can you expand on EVO? What does it stand for? Thanks.
A: EVO – emulsified vegetable oil.
5. Q: Slide 29 why does TCE mass removal and cDCE mass enhancement (at SABRE site) constitute net mass removal?
A: Based on analysis of multiple soil core samples (>200) prior to treatment the test cell contained of the order of 2,000 kg of TCE, of which >95% was DNAPL. Measurement of abstraction volumes and regular sampling and analysis of the influent groundwater and the groundwater abstracted from the test cell allowed an accurate contaminant mass balance to be determined, Allowing for inflow mass, the combined net mass of chlorinated ethenes abstracted as dissolved phase in groundwater from the test cell during treatment was approximately

1000 kg expressed as TCE equivalent. Virtually all of the chlorinated ethene mass removed during the treatment period was derived from TCE DNAPL. Therefore significant TCE DNAPL mass removal was demonstrated.

6. Q: Are the cost comparisons corrected for % mass contaminant removal? A: Yes, they are based on the same mass removal performance.

7. Q: Which technologies are suitable for fractured bedrock at approx 40m depth DNAPL remediation?

A: Any technology involving injection of treatment fluids will be more challenging in fractured bedrock compared to shallow unconsolidated formations. ISB may be effective under these conditions, subject to desk study, bench testing and/or pilot trials. DNAPL remediation in fractured bedrock at this depth would require extensive feasibility study, almost certainly including field pilot trials.

8. Q: How effective are the thermal technologies in treating DNAPL below the water table? Is a lot of the energy lost to the water?

A: Thermal technologies are often applied beneath the water table, but groundwater is a significant heat sink that can lead to increased power consumption and costs. Often flow control systems (pumping, sheet piling, etc.) are used to minimize or reduce the influx of groundwater.

9. Q: For ISB, how did you define the source zone? My feeling is ISB is suitable mainly for dissolved plume as high contaminate concentration and DNAPL will be toxic to bioactivities.

A: The source is nominally the zone where DNAPL is present, because the mass of contaminant per unit volume of aquifer is typically 10 to 100 times greater in the DNAPL zone compared to areas where only dissolved and adsorbed phases are present. Of course, other definitions for the source zone could be made. As outlined in the answer to Question 5, during the SABRE field trial significant TCE DNAPL mass removal was demonstrated from the DNAPL source using ISB.

10. Q: Also to achieve the remediation objectives in source zone by ISB will take considerably longer time and hence may not be economically viable?

A: Treatment time scales will be longer with ISB than, for example, thermal or chemical oxidation alternatives. When treatment time is taken into consideration, total treatment costs for ISB are competitive with thermal and chemical oxidation technologies.

11. Q: Does heating the ground to 1000 degrees Celsius as in the STAR technology cause any unwanted side effects such as minerals melting or causing the ground to expand?

A: Technically, the ground isn't heated to 1000 degrees Celsius in STAR. The combustion temperatures can reach 1000 degrees Celsius, but it isn't due to external heating, but only due to the temperatures of the exothermic smouldering reaction. Regardless, to answer your question, there is no evidence to date to suggest that these temperatures significantly impact the properties of silicate materials, but clay particles can be affected (like clay placed in a kiln to make pottery). There has been no soil expansion observed, but it is possible to have some subsidence of soils due to the destruction of natural organic matter.

12. Q: Two comments: the limitation of reagent distribution can be effectively mapped by tracer testing and also in your case study, leaving significant VC beneath the site may be more problematic than leaving TCE. In ERD, I think, the

major issue is to achieve the degradation of VC as pCE to TCE and TCE to DCE are fairly quick and VC may be more toxic than TCE. Thanks.

A: Tracer tests can be useful and were included in the SABRE field studies. It is agreed that VC is an undesirable end point and that treatment performance with respect to VC is a critical success factor. In general, the best treatment performance, including effective removal of VC, is achieved by engineering sufficiently low redox potentials – an indicative guideline redox target is lower than -300mV.

13. Q: Re Star below water table, what happens to combustion gases? Do they dissolve in groundwater and is there any evidence of incomplete combustion creating unwanted by-products?

A: The combustion gases formed are CO₂ and CO. There will be some dissolution into the groundwater, but for the most part the combustion gases will rise to ground surface (through convective and buoyancy forces). Incomplete combustion is not an issue, but the heating front in advance of the combustion front can lead to the volatilization of constituents that may require capture and treatment.

14. Q: Question for Dr Grant. At what stage do you decide that DNAPL remediation /*in situ* bioremediation is not working sufficiently and therefore should stop?

A: That is a very difficult question to answer. I think such a thing needs to be negotiated with all stake-holders - regulators, site owner(s), etc. To come to some sort of agreement. In my experience, it isn't that remediation technologies can't work, but that maybe they are not being applied in the optimal manner. Data collection and proper characterisation is key to understanding technology performance.

15. Q: Dr Grants *in situ* bioremediation technology example was for unconsolidated alluvium. Are there any examples of treatment in more complex ideologies, such as fractured rock/chalk? Or is this technology not considered suitable for remediation in these geological strata?

[note, this should be a question for LH]

16. Q: STAR - does the composition of the DNAPL significantly influence the performance of STAR – e.g. coal tar versus chlorinated solvents that are near lab grade or used containing significant hydrocarbon. Also, what is the fate of the chlorine from solvents in STAR treatment?

A: The composition of the DNAPL does indeed significantly influence the STAR process. The ignition protocol can be significantly affected by the volatility of the DNAPL, and each DNAPL will have different combustion characteristics (for example, coal tars are generally more energetic than chlorinated solvents and can tolerate lower concentration limits for self-sustaining behaviour and will result in high combustion temperatures). Chlorine will not be combusted, and will likely form minerals on soil grains.

17. Q: What has been the reaction from regulators to implementation of the STAR technique, given that it is effectively setting fire to the subsurface? How are the vapours controlled from this process? How sustainable is this technique compared to comparative thermal approaches such as steam injection?

A: All regulators approached about the technology have been very supportive to date. STAR is very controllable through the injection of air, so it is a very safe technology that is easily monitored. Vapours can be collected through trenches, shallow extraction wells, or with a surface vapour cover and can be treated if required. In broad terms, STAR uses the energy of the DNAPL to 'fuel' the

process, and doesn't use external energy to heat a large block of material (contaminants, soil, groundwater). Therefore, the energy requirements for this technique are minimal and are primarily associated with the operation of compressors and blowers for air injection.

18. Q: How is combustion initiated with star?

A: Combustion is initiated with a one time, burst of energy per ignition location. A standard-construction carbon steel well is installed in the target treatment zone. A heating element is lowered into the well to heat the soil and DNAPL in the immediate vicinity of the ignition well to the Target Ignition Temperature. Once attained (typically 250 to 400 degrees Celsius), the heating element is turned off, and air is injected to ignite the DNAPL. Because the heated volume of material is so small (a few inches around a well), the energy requirements to raise the DNAPL to the target ignition temperature is small. Once ignited, the combustion continues as long as air is supplied and sufficient DNAPL remains in the subsurface.

19. Q: Can chlorinated solvent source zones be treated with STAR?

A: Yes. Recently a master's student at the University of Western Ontario completed a thesis examining this application.

20. Q: What is soil gas composition (methane, carbon dioxide) post STAR?

A: Significant air is injected into the subsurface during the process, so the gases in the pore spaces are largely replaced with injected air.

21. Q: Does STAR treatment not burn the soil also? The photo of the soil core post treatment seemed to show unburned soil?

A: The temperatures are not hot enough to combust soil, although some transformation of clay particles may occur.

22. Q: What is the energy input of these thermal treatment methods and the resultant impact through energy costs and carbon footprint?

A: The energy costs can be on the order of 30% of remediation costs for ERH and ISTD, but are negligible for STAR. As expected, the carbon footprint is related to the energy requirements

23. Q: Has there been a parallel bio-stimulation only study?

A: The SABRE project involved construction and operation of a single field test cell. Laboratory microcosm studies used to assist with the design of the field programme indicated that bioaugmentation was statistically more effective than biostimulation alone, and therefore the test cell field testing programme included bioaugmentation. There was no parallel biostimulation study in a contained field test cell, largely due to the high cost of multiple field cells. Separate field tests were also carried out at the SABRE site at locations close to the test cell. These "uncontained area" tests evaluated two electron donors (EVO and cheese whey and also a mixture of these), but did not include bioaugmentation and therefore were biostimulation only. Performance in the uncontained area was broadly similar to that measured in the test cell. However, the onset of significant VC and ethene enhancement above baseline occurred earlier in the test cell (approximately 16 to 20 weeks) than in the uncontained area (20 weeks and to 50 weeks). This may be a result of bioaugmentation but could be due to or complicated by dissimilarities between the experimental conditions.

24. Q: Please provide more details of the STAR technique - how is the contamination ignited and is oxygen/air pumped into the ground? I assume that this technique is seriously limited by below ground services, such as gas mains!
A: See response to Q18. Air is injected through the ignition well via an above ground compressor or blower. Subsurface utilities and surface features must be considered during the design of a STAR application - physical separation (i.e., sheet pile walls) may be required by utility companies to protect underground utility corridors.
25. Q: With STAR what are the impacts on soil structure and on groundwater flows in the area with such high temps?
A: See response to Q11. Groundwater flow is temporarily affected by the injection of high-pressure air, but should return to 'normal' following treatment.
26. Q: How did you initiate ignition in the STAR?
A: See response to Q18
27. Q: I would like to know how you would initiate ignition as well?
A: See response to Q18
28. Q: Has regulatory approval for STAR been tested in the UK context?
Not as of yet, although we are working towards our first UK application in the very near future.
A: As a general comment, more information on the STAR technology can be found at www.siremlab.com/STAR