

## Best Scientific (or verification) advancement

### Carbon Dioxide (CO<sub>2</sub>) Supersaturated Water Injection (SWI) to Enhance Hydrocarbon Recovery: First UK Field Trial

#### Summary

The remediation of non-aqueous phase hydrocarbon is a persistent problem that challenges the remediation industry. Since residual hydrocarbon acts as a source for dissolved phase hydrocarbon the importance of recovering the largest possible volume of separate phase hydrocarbon is critical at most sites. CO<sub>2</sub> SWI is a new and innovative in-situ enhancement technology which can yield significant increases in the recovery of NAPL and associated organic contaminant phases. The first UK pilot trial of this patented technology has successfully demonstrated its potential.

The pilot trial has indicated that CO<sub>2</sub> SWI can enhance mass recovery rates by 394% compared to HVE treatment alone and therefore has the potential to reduce remediation programmes by similar factors, thereby reducing the overall project and environmental costs. The estimated CO<sub>2</sub> emission for a HVE system enhanced by CO<sub>2</sub> SWI will be more than 40% less than just HVE treatment alone powered by a portable diesel generator. In addition, the relative simplicity of the equipment involved, the ready availability of bottled CO<sub>2</sub> and the likely regulator acceptance of the technique due to its low environmental risk should

#### Introduction

The remediation of non-aqueous phase hydrocarbon is a persistent problem that challenges the remediation industry. Since residual hydrocarbon acts as a source for dissolved phase hydrocarbon the importance of recovering the largest possible volume of separate phase hydrocarbon is critical at most sites. Recovery enhancement techniques are desirable not only due to the potential for increased overall mass recovery, by liberating mass which may not be recoverable through conventional techniques, but also provides the opportunity to shorten remediation timescales by achieving the site target levels much sooner than through conventional recovery techniques alone. In addition, successful development of enhancement techniques will mean that sites which may not have been considered treatable due to gross contamination or likely lengthy remediation timescales may become viable for remediation and re-use, widening the market and creating new opportunities for brownfield redevelopment.

With this principle in mind, Celtic and Cornelsen undertake the first UK field pilot trial of carbon dioxide Supersaturated Water Injection (SWI) in February 2013 with the aim of enhancing mass recovery from a site contaminated with chlorinated solvents. This new technology had previously been trialled successfully at the Canadian Forces Base Borden field research site, which involved the use of SWI in a test cell artificially spiked with pentane and hexane. The Celtic-Cornelsen pilot trial is believed to be the first application of the technology in real site conditions involving a complex mixture of contaminants.

The trialled site is a former chemical test site and located in the north west of England. Historical land use had left a legacy of ground and groundwater impacted with a mixtures of chlorinated hydrocarbons including dichloroethenes (DCE), trichloroethene (TCE), tetrachloroethene (PCE), dichloroethanes (DCE), trichloroethanes (TCA) and tetrachloroethanes (PCA). Site geology comprises made ground with an underlying alluvial deposits layer and glacial despoits. The alluvial deposits within the trialled area consists of two layers, a cohesive soft to firm sandy clay layer and a less cohesive silty medium to fine sand layer. The glacial deposits consist of firm to very stiff red brown sandy gravelly clay with inter-bedded medium to dense brown gravelly sand. The groundwater in the alluvial layer is a confined aquifer due to the overlying cohesive sandy clay layer. A schematic diagram of the site geology is illustrated in Figure 1.

Dense non-aqueous phase liquid (DNAPL), predominately 1,1 DCA, 1,1,1 TCA, TCE, 1,1,2 TCE, PCE and 1,1,1,2 PCA, was present in the trial area.

Plate 1— Recovered DNAPL Sample



Plate 2—CO<sub>2</sub> SWI Pilot Plant



Plate 3—CO<sub>2</sub> Micro Bubbles



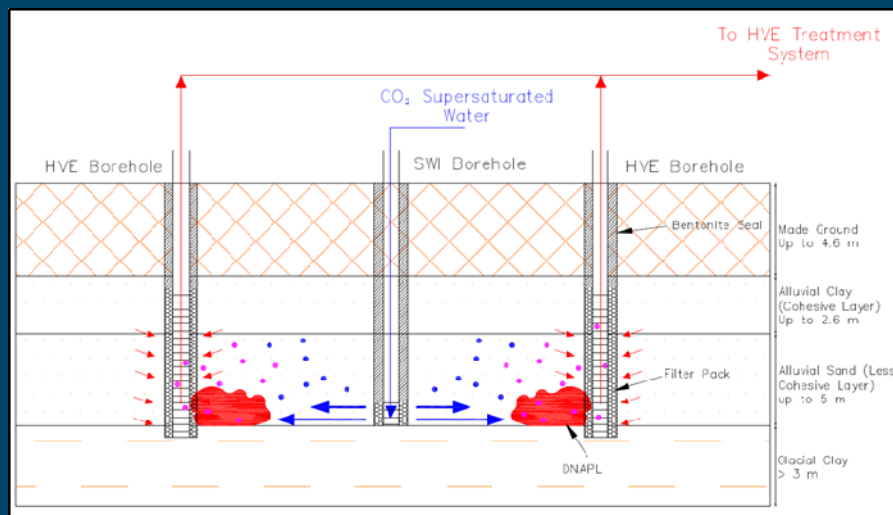
**The principle of SWI**

Carbon dioxide (CO<sub>2</sub>) supersaturated water injected into the subsurface results in the nucleation of CO<sub>2</sub> bubbles at and away from the injection point. Following injection, carbonated water moves out from the injection well through the porous medium and begins to release dissolved gas, forming a treatment zone. Discrete volumes of gaseous CO<sub>2</sub> grow due to the pressure reduction. Because of the volatility of (the majority) of hydrocarbons, some of the hydrocarbon contacted by gas immediately dissolves into it and is mobilised. This NAPL can then be recovered by conventional vapour extraction systems. Volatile NAPLs, such as separate phase hydrocarbon gasoline or chlorinated solvents, are transferred to the gas phase during the SWI process and mobilised, enabling vapour phase recovery. The technology offers the following benefits:

- LNAPL and DNAPL recovery enhancement for trapped and immobile NAPL mass
- CO<sub>2</sub> strips volatile NAPL component enabling capture in the unsaturated zone
- Mobilises liquid NAPL trapped in aquifer matrix for recovery

A simplified conceptual model for CO<sub>2</sub> SWI technology is illustrated in Figure 1. When rising CO<sub>2</sub> bubbles contact hydrocarbons they cause volatilisation. Groundwater and soil vapour (including CO<sub>2</sub> and volatilised hydrocarbons) are removed through recovery wells.

**Figure 1 —Conceptual Site Model of SWI Field Trial**



CO<sub>2</sub> SWI works on the same principle as conventional air sparging (AS) where bubbles are introduced into the subsurface to mobilise and volatise hydrocarbons for recovery. However, conventional AS is only applicable for light non-aqueous phase liquid (LNAPL) in an unconfined aquifer. The SWI on the other hand is more effective at mobilising residual NAPL than conventional AS because gas saturation develops in-situ, leading to greater microscopic sweep efficiency. The CO<sub>2</sub> gas phase becomes mobile when the gas saturation reaches approximately 12%, at which point advective gas flow is initiated. Considerable lateral, and therefore uniform, expansion of the gas phase occurs prior to the onset of upward mobilisation of growing gas clusters under the action of buoyancy forces.

Gas mobilisation is accompanied by fragmentation and stranding of the gas clusters, which prevents fingering of the gas phase as is commonly observed in air sparging systems. This meant SWI would be equally effective in a confined aquifer containing DNAPL.

**Celtic-Cornelsen Field Trial**

Following consultation and approval from the site-owner and the Environment Agency (EA), the CO<sub>2</sub> SWI system was mobilised to a site in the North West to conduct a field scale pilot trial. Previous investigation indicated that the site was contaminated with a mixture of chlorinated compounds, primarily within the saturated zone comprising less cohesive granular alluvial deposits. Contamination was identified in dissolved and vapour phases, in addition to localised DNAPL. The aims of the trial were to:

- Assess CO<sub>2</sub> supersaturated water injection as a contaminant recovery enhancement technique.
- Compare CO<sub>2</sub> SWI enhancement technique with enhancement via conventional air sparging.

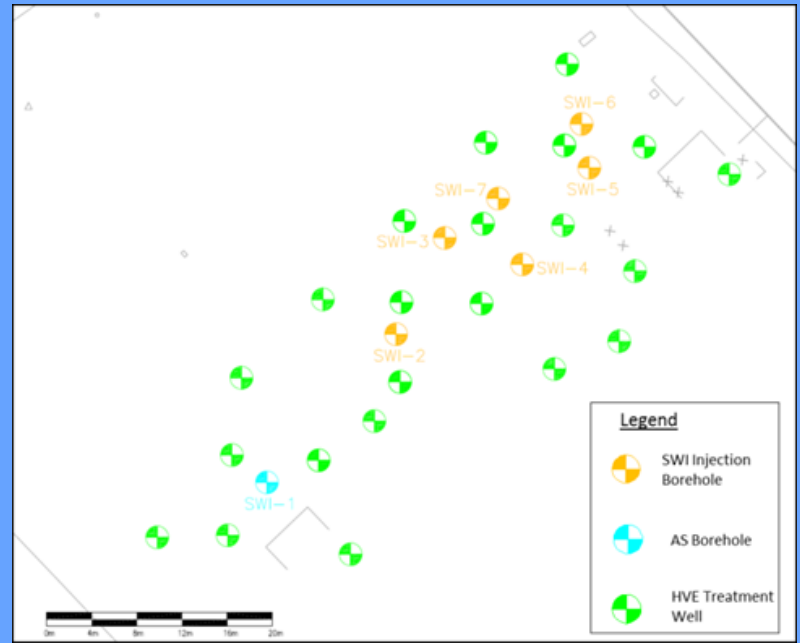
A total of seven CO<sub>2</sub> SWI injection wells were installed with an associated network of High Vacuum Extraction (HVE) treatment wells in an area known to contain DNAPL. The borehole layout within the trial area is illustrated in Figure 2. To ensure the trials were undertaken in a controlled environment, the extraction rate of the HVE system (up to 5000 m<sup>3</sup>/hr) was significantly greater than the CO<sub>2</sub> (up to 2.5 m<sup>3</sup>/hr) and AS (up to 6 m<sup>3</sup>/hr) injection rates in order to prevent fugitive release of mobilised hydrocarbons from the trial area. Secondary capture wells surrounding the primary network of extraction boreholes provided an additional safety net. During the field trial, the HVE system was operated for 24 hours to collect baseline contaminant mass recovery rate prior to the CO<sub>2</sub> SWI trial and air sparging comparison trial.

A Flame Ionisation Detector (FID) was utilised to measure the concentration of recovered vapour phase contaminants. This

was chosen as the primary means of performance assessment for the field trial due to high resolution real-time measurement. Dissolved and free-phase contaminant recovery was also measured during the trial.

**CO<sub>2</sub> SWI Trial Methodology** – CO<sub>2</sub> supersaturated water was injected in one of the designated CO<sub>2</sub> injection wells (SWI-4). This injection well was selected because DNAPL was noted in this borehole and some of the adjacent treatment well. The CO<sub>2</sub> supersaturated water initial starting concentration was at 1.5 g of CO<sub>2</sub> per litre of water and this was subsequently increased to 2.8 g of CO<sub>2</sub> per litre of water. Each CO<sub>2</sub> injection concentration test was repeated at least two to three time over a two to three day period to ensure the data collected were repeatable. Each injection period ranged from 2 to 6 hours. Total fluid including vapour and DNAPL was recovered by the surrounding treatment wells via the HVE system. The hydrocarbon vapour mass recovered by the treatment system was recorded via flame ionisation detector every 5 minutes.

Figure 5 Actual Groundwater Elevation (mAOD)

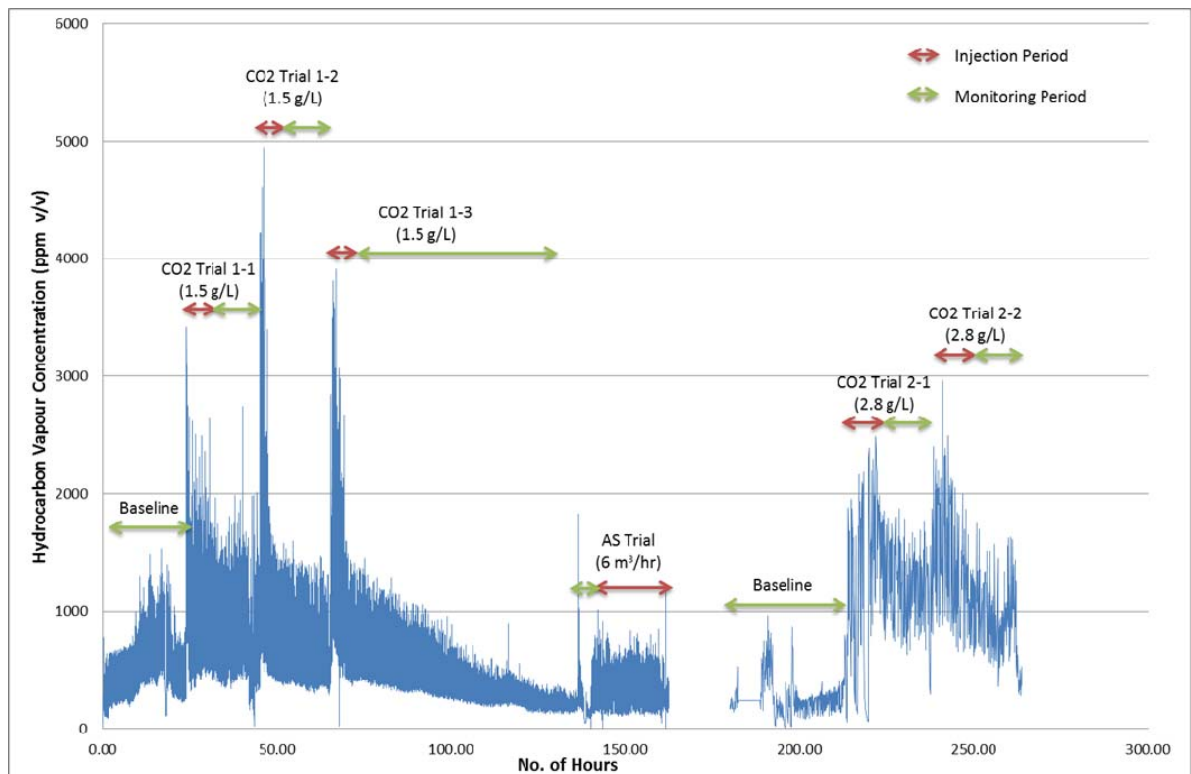


**AS Trial Methodology** – To compare air sparging and CO<sub>2</sub> SWI as mass recovery enhancement techniques, a dedicated air sparging borehole (SWI-1) was installed and a small quantity of compressed air (up to 6 cu.m/ hr) was injected at the base of alluvial layer for a duration of 20 hours. Total fluids including vapour and DNAPL were recovered from the surrounding treatment wells via the HVE system. The hydrocarbon vapour mass recovered by the treatment system was recorded via flame ionisation detector every 5 minutes.

**Hydrocarbon Mass Recovery** - The vapour mass recovery during baseline, SWI and AS trial phases is presented in Figure 3 and the calculated hydrocarbon vapour mass recovery rate is summarised in Table 1. The calculated hydrocarbon mass recovery rate illustrated that both AS and SWI increased the hydrocarbon vapour mass recovery rate. However, the AS method only increased the vapour mass recovery rate by 35% against the baseline, whereas the SWI trials significantly increased the hydrocarbon vapour mass recovery rate by up to 394%.

Groundwater samples were collected before and during the trials for laboratory analysis. The volume of DNAPL accumulated in the oil water separator was also quantified before and after the trials. No significant changes in dissolved phase or NAPL recovery were observed throughout the trials; however, a longer term trial would be necessary to accurately assess recovery of these contaminant phases.

**Figure 3—  
Recorded  
Hydrocarbon Vapour  
Concentration**



**Table 1 – Calculated Hydrocarbon Vapour Mass Recovery Rate**

| Trial                            | Test Borehole | Baseline (kg/day) | Test A (kg/day) | Test B (kg/day) | Test C (kg/day) |
|----------------------------------|---------------|-------------------|-----------------|-----------------|-----------------|
| CO2 Injection Trial 1 (1.5 g/ L) | SWI 4         | 6.94              | 18.27           | 19.78           | 15.98           |
| CO2 Injection Trial 2 (2.8 g/ L) | SWI 4         | 4.19              | 13.68           | 20.69           | N/A             |
| Air Sparging (6 m3/hr)           | SWI 1         | 8.17              | 11.02           | N/A             | N/A             |

The successful deployment of the technology and the observed increases in mass recovery indicate that SWI is a viable technique to mobilise residual separate phase hydrocarbons yielding significant improvement in recovery compared to conventional techniques.

#### **Financial and Environmental Cost-effectiveness**

The financial viability of enhancement techniques will always vary according to specific site conditions including the nature, location and extent of contamination, the remediation objectives and available timescale. The Celtic-Cornelsen pilot trial has indicated that SWI can enhance mass recovery rates by a factor of three compared to HVE as a standalone remediation technique and therefore has the potential to reduce remediation programmes by similar factors, reducing overall project costs. Furthermore, the environmental cost, in the form of CO<sub>2</sub> emissions, is significantly reduced by reduction in operating timescale. For example, the estimated CO<sub>2</sub> emission for a HVE system enhanced by CO<sub>2</sub> SWI will be more than 40% less than just HVE treatment alone powered by a portable diesel generator. This is calculated based on the assumption that the remedial programme will be reduced by almost 75% with the CO<sub>2</sub> enhancement method (typically 6 months treatment programme); the full scale CO<sub>2</sub> SWI plant will be 10 times bigger than the pilot plant (injection capacity of 25 m<sup>3</sup>/hr at 2.8 g of CO<sub>2</sub>/ litre), and a diesel consumption rate of 15 litres/ hour for the portable generator. It must be noted that CO<sub>2</sub> is normally produced as a by-product of other manufacturing processes such as production of hydrogen or ammonia from natural gas and therefore the above comparison is conservative given that the actual CO<sub>2</sub> emission by the SWI plant excluding the actual quantity of CO<sub>2</sub> injected into the ground is negligible.

#### **Future use of the Technology**

The Celtic-Cornelsen field trial has demonstrated the effectiveness of CO<sub>2</sub> SWI as a technology in the mobilisation of residual separate phase hydrocarbon and as a recovery enhancement technique in real site conditions. In addition, the relative simplicity of the equipment required, the ready availability of bottled CO<sub>2</sub> and the likely regulator acceptance of the technique, due to its low environmental risk, should present no barriers to the widespread application of the technology in the UK and further afield.