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Public abstract
While strenuous efforts will be made to minimise the risk of the leakage of CO_2 from engineered storage sites, there will always remain a residual risk that CO_2 could migrate from the storage site into the shallow subsurface along permeable pathways such as faults or wells. This report provides a comprehensive review of the available techniques for CO_2 leakage remediation in the near surface environment considering relevant experience and expertise from pilot scale CCS projects and natural analogues, as well as CO_2-EOR operations, natural gas storage, the geothermal industry, groundwater pollution remediation, industrial waste remediation and dam construction. The applicability of each method to remediate CO_2 leakage in the near surface environment, the ease of implementation of the method and the associated costs were compiled

to produce a summary table of the probable roles of the available remediation techniques, to assess the relative merits of near-surface CO_2 leakage remediation methods. The review carried out and summarised in this report suggests that a wide range of techniques are available for near surface CO_2 remediation, and that any remediation strategy will need to be site specific to be effective.

Public introduction (*)

This report provides a comprehensive summary of near-surface CO_2 leakage remediation methods, including their effectiveness and approximate costs. The near surface environment is defined as the depth range of typical remediation techniques used by the pollution clean-up industry, rather than by the hydrocarbon industry. The techniques considered suitable to remediate a leak of CO_2 are used in relevant fields of experience including pilot scale CCS projects and natural analogues, CO_2-EOR operations, natural gas storage sites, the geothermal industry, groundwater pollution remediation, industrial waste remediation and dam construction, as there is relatively little experience of the remediation of shallow CO_2 leaks. These relevant fields provide analogues for the CO_2 storage industry and facilitate the evaluation of mitigation and remediation procedures.

CO_2 dissolves in water to form a weak acid which can potentially mobilise toxic metals. Remediation must be implemented when established standards, e.g. the maximum allowable concentrations of metals in groundwater and drinking water, are exceeded. High levels CO_2 contamination at ground level can reduce crop yields; impair/kill vegetation locally; render buildings unsafe for human habitation and return the stored CO_2 back to the atmosphere, and hence should be prevented where possible.

The emphasis should be on achieving the earliest possible detection of CO_2 migration outside the storage reservoir, to maximise the time available for suitable mitigation actions to be implemented.

This document provides initially a brief review of current industry best practises for the monitoring of CO_2 leakage in the near surface and the reporting required to aid the design of a risk-based remediation and reporting protocol. The report also presents a classification of sites that may require remediation intervention. The assessment that follows in the case of an incident involves an iterative process where the site characterisation / baseline data and the ongoing monitoring data feed into the risk assessment, which in turn informs the remediation action, and prompts further tailored monitoring and risk analysis. CO_2 leakages from known naturally occurring CO_2 reservoirs are also reviewed to inform the reader on the spatial and temporal character of CO_2 leakage episodes at such sites.

The report discusses the aims and objectives of any remediation plan and presents a review of the currently available remediation technologies and methodologies including the use of: fluid control measures; cut off walls; permeable reactive barriers; soil zone remediation; bioremediation and methods appropriate to remediate buildings affected by CO_2 leakage. It then provides a summary of the applicability of the different methods for CO_2 remediation and a summary of the pros and cons for each method reviewed. A screening approach that may be used to identify relevant remediation methods for a given setting on the basis of the effectiveness and associated costs is also discussed.

The report also presents a summary of the monitoring and remediation steps undertaken following a well blowout that took place in 1968 at the naturally occurring CO_2 reservoir at the Bečej field in Serbia. The effectiveness of different remediation methods and associated costs are also discussed.

The applicability of each CO_2 leakage remediation method in the near surface environment, the ease of implementation and the associated costs for each method were compiled to produce a summary table to indicate the probable role different remediation techniques could play in the near-surface environment. The results indicate that a wide range of remediation techniques may be used for near surface CO_2 remediation and that any remediation strategy will need to be site specific to be effective.

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1 INTRODUCTION

The objective of this report is to provide a comprehensive review of the available approaches to remediation of CO_2 leakage in the near surface environment, and of the plans implemented to remediate any leakage from engineered CO_2 storage sites, including criteria used to assess the effectiveness of the methods and the costs of mitigation.

While strenuous efforts will be made to minimise the risk of the leakage of CO_2 from engineered storage sites, there will always remain a residual risk that CO_2 could migrate outside the storage site into the shallow subsurface along permeable pathways such as faults or wells. CO_2 leakage from geological storage will not necessarily negate the net reduction in CO_2 emissions as it is physically impossible that all of the injected CO_2 would be returned to the atmosphere during leakage due to the various trapping mechanisms operating within the subsurface. However, the leakage must be controlled as it could ultimately result in the closure of the storage project; fining of the operator by the relevant authorities; the return of credits for carbon storage; and damage to the reputation of the site operator. Regardless of the style of leakage there may be adverse health, safety and environmental risks associated with elevated levels of CO_2 in the near surface. The impact of CO_2 leakage will vary on a site by site basis; in some cases the effect may be negligible, where as in other cases it may cause serious human, agricultural, environmental or economic impacts. Recently completed projects such as QICS (Quantifying and monitoring potential ecosystem impacts of geological carbon storage; http://www.bgs.ac.uk/qics/home.html) and the EU funded ECO2 project (Sub-seabed CO_2 Storage: Impact on Marine Ecosystems; http://www.eco2-project.eu/) helped to define the changes in selected environments, in this case the marine realm, through experimental and modelling work.

In May 2009, the EU directive on the geological storage of CO_2 included the requirement for a corrective measures plan to be submitted with any storage permit application (EU Directive, 2009). The directive defines leakage as any release of CO_2 from the ‘storage complex’ and states that measures must be taken to protect human health, along with other measures deemed necessary by the national authority, as a remediation plan.

Examples of CO_2 and other leakage into the near surface from natural sources, groundwater remediation, industrial waste, geothermal, CO_2-EOR and oil and gas operations provide analogues for the CO_2 storage industry and facilitate the evaluation of mitigation and remediation procedures. They provide valuable insights into the nature of the leakage and the impact of elevated CO_2 levels on human health, biodiversity, ecology, agriculture, surface water, and ground water quality in the near surface. They also allow to assess the effectiveness and suitability of the remedial measures.

The next section defines what is considered near surface environment in the context of this work and discusses the potential CO_2 leakage routes. The remediation techniques considered suitable for CO_2 leakage remediation originate in other relevant fields, as there is relatively little experience of remediation of shallow CO_2 leaks. Such fields are:

1) The control of groundwater pollution, especially potable water – in near surface environments. CO_2 in the gas phase has a similar density to some volatile organic compound (VOC) vapours, which are a common pollutant that is considered in remediation. However, it should be noted that CO_2 is non- toxic at low concentrations and is generally sourced from below the rock / soil matrix that requires remediation (Zhang et al., 2004);
2) Oil / gas operations (including EOR / CO_2 EOR) including both routine and acute incident scenarios – there are no recorded instances of leakage to the surface that did not involve boreholes;
3) Natural gas storage projects (review in Benson and Hepple, 2005);
4) CO_2 production for EOR (e.g. the blow-out at Sheep mountain, Colorado, USA; IEA GHG, 2007 p. 38);
5) Natural analogues for surface leakage (e.g. Crystal Geyser, Utah, USA);
6) Geothermal power in high-CO_2 regions (e.g. Torre Alfina, Italy);
7) The grouting of the foundations of dams (for water storage);

8) Pilot-scale and proposed industrial-scale carbon capture and storage (CCS).

1.1 Definition of near surface

The primary focus of this report is leakage that is ‘near surface’, which is a term that should be clearly defined in the context of this report. Near surface could be defined in relation to the following criteria:

1) The top of the storage complex (Figure. 1; i.e. everything above the storage complex is deemed to be near surface);
2) The phase change boundary for CO_2, so that the CO_2 is in the gas phase, usually cited to be at c. 800m for a ‘normal’ geothermal gradient;
3) The maximum depth for meteoric / potable water zone which is at c. 500 m depth, but may not exist at all in an offshore setting;
4) The depth of the shallowest aquifer, though this could be the storage reservoir in some cases;
5) The top of the sediment consolidation zone (>c. 60 – 70 ^{o}C for the onset of significant cementation by quartz overgrowth; the cementation of limestones begins at much shallower depths, effectively at the sea floor; mudrocks are cohesive so this definition is difficult to apply);
6) The lower limit of the biological zone (c. 60 – 70^{o} C);
7) An arbitrary depth below the ground surface, seafloor or sea surface;
8) The depth range of typical remediation techniques used by the pollution clean-up industry rather than by the hydrocarbon industry.

Here we adopt the last of the above approaches. This is partly to avoid overlap with the other work packages of the MiReCOL project, which will consider the remediation of leakage using many of the techniques developed and implemented in the field by the hydrocarbon industry. The techniques considered here will not be examined by any other part of the project, and are (at least sometimes) not covered in detail by recent reviews of techniques for the remediation of CO_2 leakage.

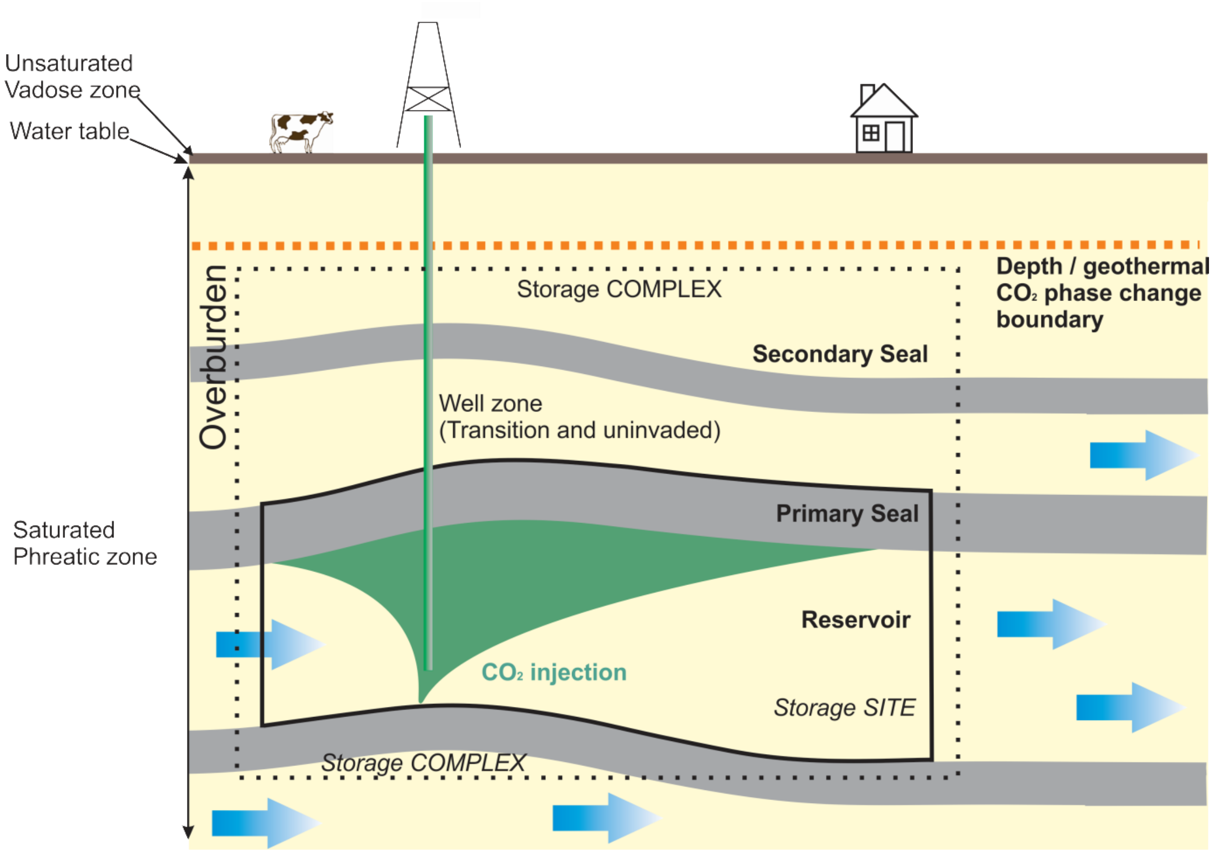


Figure 1 *The CO_2 storage complex.*

Given that the focus of this review is the near surface environment, then there are a number of factors which make this environment different from that being considered for the deeper subsurface, which is the realm of the hydrocarbon industry:

1) Low to very low water salinity (typically << 35 ppt NaCl, i.e. seawater equivalent);
2) Higher water flow rates;
3) CO_2 in gas phase, possibly present as hydrates;
4) Natural fractures may be open due to low confining pressure (e.g. Becker and Lynds, 2012);
5) In an active sedimentary basin:
    a. unconsolidated, uncemented sediments;
    b. very high porosity and permeability (> 20 % and Darcy scale permeability);
    c. low capillary entry pressure;

d. biological activity including:
   i. biodegradation of hydrocarbons;
   ii. formation of kerogen and biogenic methane;
e. lack of structures (traps) to collect leaked CO_2;
f. lack of (active) faults as pathways for leakage;
g. presence of polygonal clay shrinkage cracks (Cartwright et al., 2003).

The possible pathways for the leakage of CO_2 in the near surface are similar to those associated with leakage at typical hydrocarbon depths:

1) Boreholes – both abandoned and active;
2) Faults and fractures, including both those sufficiently large for resolution using seismic imaging, and those too small for seismic resolution;
3) Matrix rock porosity within lithologies such as sandstones and limestones.

1.2 Trade names and proprietary products

No proprietary products are identified in this report, and consequently no recommendations or endorsements (or otherwise) of commercial products are made. The remediation techniques described in this report require the use of many products and services that are available commercially, many of which have been developed by the pollution remediation industry. It is the responsibility of the user of this report to identify suitable products and service providers for the techniques described herein.

1.3 Near surface impacts that are considered as requiring mitigation intervention

Elevated CO_2 concentrations in the near surface environment can impact upon resources both within the subsurface, and above. Onshore, the major resource located within the near surface environment is potable water. In the USA, a volume of the subsurface surrounding an area from which ground water is abstracted is defined as a wellhead protection area, which is "the surface and subsurface area surrounding a water well or well field, supplying a public water system, through which contaminants are reasonably likely to move toward and reach such water well or well field" (US EPA, 1987). Many

States within the USA have defined wellhead protection areas on the basis of the time taken for contaminants to flow from the boundary of the area to the point of abstraction of the groundwater (Bai et al., 2000, p.42). As such, any contamination of groundwater within such a wellhead protection area would require remediation, or at least an assessment of the likely consequences of the contamination.

It should be noted that the addition of CO_2 to subsurface groundwater resources is not, in itself, necessarily a problem – ironically, carbonated water is sold for a premium price on Western World markets, and water carbonated from subsurface sources has the highest premium of all. However, as has been well documented, CO_2 dissolves in water to form a weak acid. This can then mobilise toxic metals e.g. Li, Mg, Ca, Rb, Sr, Mn, Fe, Co, Ni, Zn (Little and Jackson, 2010) including arsenic (As) and lead (Pb) (Benson and Hepple, 2005). Standards for groundwater and drinking water composition, in this case maximum allowable concentrations of metals, for the EU, UK and USA are listed in Table 1.

The ground surface itself is also a valuable resource, used for virtually every activity in which humans are involved. The monetary value of the land surface is highly variable – land in a city centre may be worth literally millions of dollars per square metre, whereas desert or other 'waste' land has little or no monetary value.

High levels of CO_2 contamination can reduce crop yields; impair/kill vegetation entirely as at Mammoth Lake, USA (Lewicki et al, 2008); or render buildings unsafe for human habitation.The ingress of CO_2-rich ground gas into buildings within Arkwright Town in Derbyshire, UK, caused the demolition of the entire village, and its relocation to a safe location at a reported cost of 15 M GBP (value in 1990's; Independent, 1994). The leakage of CO_2 to the surface in any inhabited area is likely to require some form of remediation, which could be as varied as subsurface intervention or the education of the local inhabitants to avoid highly contaminated areas. Potentially, leakage to an agricultural area may have to be remediated also, though with relatively low value agricultural land the cost of remediation may well exceed the value of any lost productivity of the land.

Table 1 Standards for groundwater and drinking water composition, in this case maximum allowable concentrations of metals, for the EU, UK and USA. References: (1) SEPA (2010); (2) Scottish Government (2010); (3) US EPA (2009); (4) European Council (1998) (Based on table compiled by Kit Carruthers of the University of Edinburgh).

Metal	Water Quality Standards				
	Marine	Fresh	Drinking Water		
	SEPA EQS (µg/l) (1)	SEPA EQS (µg/l) (1)	Scottish Water (µg/l) (2)	US EPA (µg/l) (3)	EU (4) (µg/l)
Aluminium	15	15	200	200	200
Antimony	-	-	5	6	5
Arsenic	25	50	10	10	10
Barium	-	-	-	2000	
Boron (5)	7	2	1	-	1
Cadmium	0.20	0.25	5	5	5
Calcium	-	-	-	-	
Cobalt	3	3	-	-	
Copper	5,000	28	2000	1,300	2000
Chromium	0.6	3.4	50	100	50
Iron	1,000	1,000	200	300 (4)	200
Lead	7.2	7.2	25	15	10
Magnesium	-	-	-	-	
Manganese	-	30	50	50 (4)	50
Mercury	0.05	0.05	1	2	1
Nickel	20	20	20	-	20
Potassium	-	-	-	-	
Selenium	-	-	10	50	10
Sodium	-	-	-	-	200
Titanium	-	-	-	-	
Uranium	-	-	-	30	
Vanadium	100	60	-	-	
Zinc	40	125	-	5,000 (4)	

The leakage of CO_2 to the seafloor is a possible consequence of migration from an offshore storage site (e.g. Kirk, 2011). While the seafloor may not have monetary value as such (in the sense that it cannot be bought or sold), it is extensively used for many activities, including the siting of facilities for the production of oil and gas; the siting of wind farms; the anchorage of aquiculture facilities such as fish farms; and the harvesting of naturally growing marine food sources such as fish and sand eels. Some areas benefit from legal protection, such as Special Areas of Conservation (SAC) within the UK territorial waters, as defined under the UK Habitats Directive. They are areas of international importance for either or both threatened habitats and species. The leakage of CO_2 to the seabed and the overlying water column would possibly require remediation if the area were protected, or was utilised in one of the ways described below. The consequences of leakage will depend upon the nature of the leakage site – a site with strong tidal currents, for example, may have little impact compared to an area with little water flow or exchange. Consequently, the need for remediation will have to be assessed on a site-by-site basis.

An impact of leakage which is not related to the site of leakage as such is that of return of the stored CO_2 back to the atmosphere. Since the aim of CCS is to prevent the addition of CO_2 to the atmosphere and oceans, migration outside the storage complex into the near surface environment (and hence through time possibly into the oceans and atmosphere) should be prevented where possible. Equally, if financial reward has been accepted for the avoidance of CO_2 emissions to the atmosphere, for example through the European Emissions Trading Scheme (EU ETS), then emitting CO_2 into the atmosphere will engender a financial penalty and hence encourage remediation. However, it should be noted that the cure can be worse than the disease, in that the carbon footprint of remediation schemes can be very high (Ellis and Hadley, 2009). These authors cite a proposed scheme from the USA in which it was estimated that the *difference* between two proposed remedies could be as high as 2 percent of the annual greenhouse gas emissions of the state of New Jersey. Care should be taken that the remediation of a leak does not actually increase net CO_2 emissions compared to allowing the leak to continue unabated.

1.4 Natural analogues for surface leakage

Natural analogues for the remediation of CO_2 leakage are locations where naturally-occurring CO_2 is leaking into the near surface, many of which have been studied either because of environmental effects such as vegetation die-off, or because of interest in geological carbon storage. It is unusual to attempt to remediate a natural leak, as they are either simply avoided or, in some cases, are exploited for naturally-carbonated water, which is sold for a premium price as in the Eifel region of Germany (Ulrich, 1958). In some countries with large areas of land that are affected by high fluxes of natural CO_2, then avoiding such areas for building has not proved to be practical, and in Italy for example, significant numbers of people live in areas of high natural emissions (e.g. Carapezza et al., 2003). A recent review of leakage rates for the EU-funded QICS project (Kirk, 2011) covered both onshore and offshore sites, but is not comprehensive. As an example, there only 2 Italian sites in the Kirk (2011) review, but 286 natural CO_2 seeps in Italy and Sicily listed in a database of such sites (Googas Catalogue, 2009). A further compilation of non-volcanic CO_2 leakage sites is in Mörner and Etiope (2002), with c. 25 diffuse sites, and c. 30 vents listed worldwide. A comprehensive compilation of natural CO_2 leakage sites is beyond the scope of this project, and in any case sites of leakage directly from volcanoes is here considered to be less valuable as analogues than leakage from natural accumulations of CO_2 from sedimentary basins which mimic the likely conditions of engineered CO_2 storage more closely. Tables 2 and 3 summarise the sites from Kirk (2011) and others. Sub-sea sites are included, although the present authors consider that the difficulty of implementing most of the remediation techniques described in this report make shallow intervention in an offshore setting an unlikely option.

An important caveat to this review is that, as the topic is near surface leakage, then inevitably all the cases described involve the leakage of CO_2 into the near surface environment. It would be misleading to give the impression that all, or even many, sites of natural subsurface CO_2 accumulation are leaking – many do not have any surface expression. Sites such as the high-CO_2 province in the Northern North Sea that includes the well-known Sleipner and Miller fields (Lu et al., 2009; 2010), and the less well-known CO_2 province in the Southern North Sea that includes the Fizzy prospect (Wilkinson et al., 2009) have no known surface expression and give confidence that carefully chosen storage sites will hold CO_2 for geological periods of time. The above indicate that the majority of known sub-sea leakage sites are from vents, which may occur either singly or in clusters.

Table 2 Offshore natural analogue sites.

Site	Flux rate	Surface expression	Water depth (m)	References
Panarea Southern Tyrrhenian Sea (Italy)	1670 – 8500 t/m^2/year	Linear faults and vents aligned on faults	up to 30m	Tassi et al. (2009); Caramanna (2010); Lombardi (2010); Etiope et al. (2007)
Ischia, Italy	12.8 t/m^2/year	Vents, <5 per m^2	<5	Lombardi (2010); Hall-spencer et al. (2008);
Champagne area, Mariana arc	35000 t/year as liquid drops	Vents	1600	Lupton et al., 2006
Hatoma Knoll, Okinawa Trough	-	Vents	700 - 1400	Shitashima et al., 2008
Salt Dome Juist, German North Sea	1 – 10 t/day	Point source above dome	-	McGinnis et al. (2011)

Table 3 Onshore natural analogue sites.

Site	Flux rate (t/m^2/year)	Surface expression and area	References
Laacher See caldera, Germany	variable, 0.0084 – 0.020 diffuse; 500 – 1200 close to vent; background 0.011	2 vents; diffuse; bubbles in the lake water; area c. 2 by 1 km	Jones et al. (2009); Krüger et al. (2009); Aeschbach-Hertig et al. (1996); Gal et al. (2011)
Ukinrek Maars, Alaska	0.25 – 0.43	diffuse with 4 zones of plant kill, 30,000 – 50,000 m^2; 2 vents 3 km away	Evans et al. (2009)
Furnas and Fogo volcanoes, Azores	0 – 1.7	diffuse near fumarole fields	Viveiros et al. (2008)
Horseshoe Lake, Mammoth Mountain, California USA	0.08 – 1.3	diffuse, 6 tree-kill areas, largest 120,000 m^2	Lewicki et al. (2008)
Pululhua caldera, Ecuador	detection limit – 0.052	linear trend	Padrón et al. (2008)
Rekjanes geothermal field, Iceland	2.5	diffuse (soil gas), steam vents, mud pools	Fridriksson et al. (2006)
Rapolano fault	52560	vents, production wells	Mörner and Etiope (2002); Rogie et al. (2000)
Little Grand Wash Fault, Utah, USA	0.3 – 1.0	carbonates springs; abandoned exploration well	Burnside (2010); Han et al. (2013)
Northern Fault, Salt Wash Graben, Utah, USA	0.04 – 0.12; 12,000 t/year from Crystal Geyser	springs and abandoned exploration well	Burnside (2010); Gouveia et al., 2005
Pannonian Basin, Hungary	1100 – 3670 (total)	bubbling wells, streams, springs	Pearce et al (2010); Sherwood Lollar et al (1997)
Mefite d'Ansanto, Italy	338,000 – 730,000 (estimates vary)	numerous gas vents	Chiodini et al. (2010); Rogie et al. (2000); Italiano et al. (2000)
Latera Caldera, Italy	0.0012 – 1.3, background <0.008	4 vents on faults	Annunziatellis et al. (2008)
Italy (other)	< 1 to > 100 ton / day	Bubbling water; diffuse; vent; spring; well; fumarole	Roberts et al (2011); Googas Catalogue (2009)
Springerville, Arizona, USA	~63 kTon/year	high CO_2 groundwater, travertine	Keating et al. (2014); Allis et al. (2005)

The nature of natural CO_2 seeps is very variable (bubbling water, diffuse, vent, spring, well, fumarole; Roberts et al. 2011), and the area over which leakage occurs is also variable. Some implications for the remediation of engineered CO_2 storage sites can be made.

Firstly, the total area over which CO_2 can leak at a single site can be substantial. For example both the modern and the paleo-leakage zone along the Little Grand Wash Fault, Utah, USA are approximately 3 km long (Shipton et al., 2004, 2005; Burnside, 2010; Jung et al, 2014; Figure 2), though leakage is apparently restricted to the fault trace. In contrast, in the nearby Salt Wash Graben there is evidence of paleo-leakage (travertine mounds) at least 500m into the footwall of the fault (Burnside, 2010).

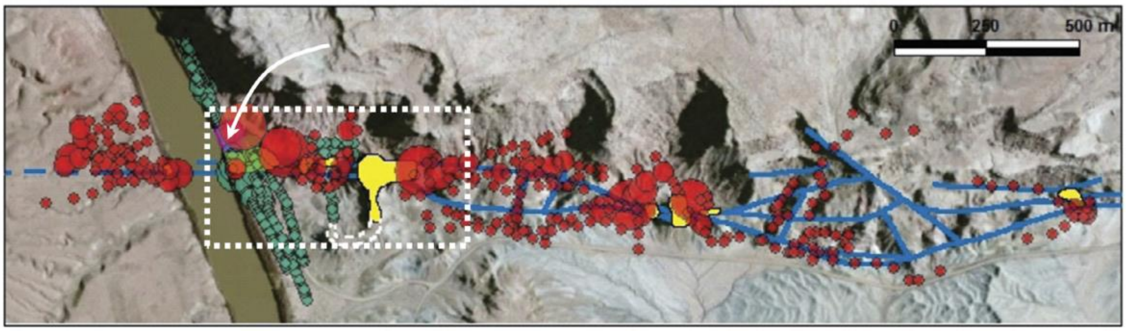


Figure 2 *The distribution of modern CO_2 leakage along the Little Grand Wash Fault, Utah, USA (Jung et al., 2014). Small circles 0 – 20 g/m2/day, largest circles are >1500 g/m2/day. Note detectable leakage over c. 3km of the fault.*

At Laacher See, Germany, high CO_2 concentrations have been recorded over an area of approximately 2 by 1 km (Gal et al., 2011), some of which are easily visible such as bubbles in the lake and surface vents, but others have been detected only by gas monitoring (Figure 3). At Mammoth Mountain, California, there are 6 distinct areas of tree-kill due to high CO_2 concentrations, the largest is c. 120,000 m^2 (Lewicki et al., 2008).

At Springerville, Arizona, USA, 49 individual travertine mounds associated with a natural deep CO_2 reservoir are found over approximately 20km^2, they are spatially associated with fold axes and faults (Embid et al., 2006; Figure 4).

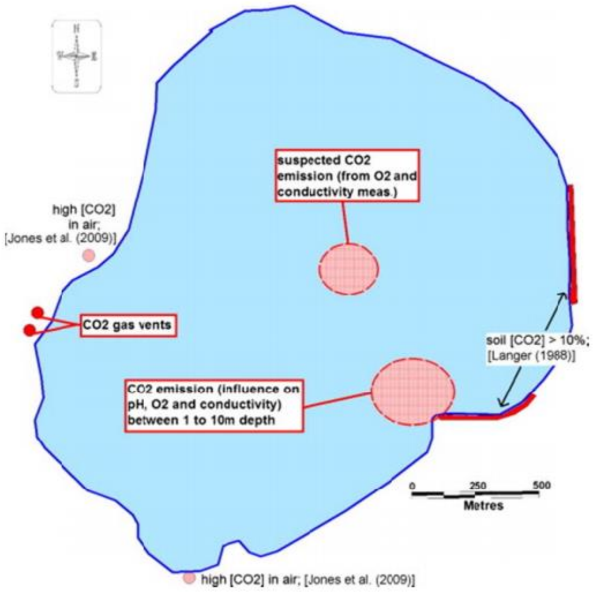


Figure 3 *At Lacher See, Germany, high CO_2 concentrations have been recorded over an area of approximately 2 by1 km (Gal et al., 2011, their Fig. 11).*

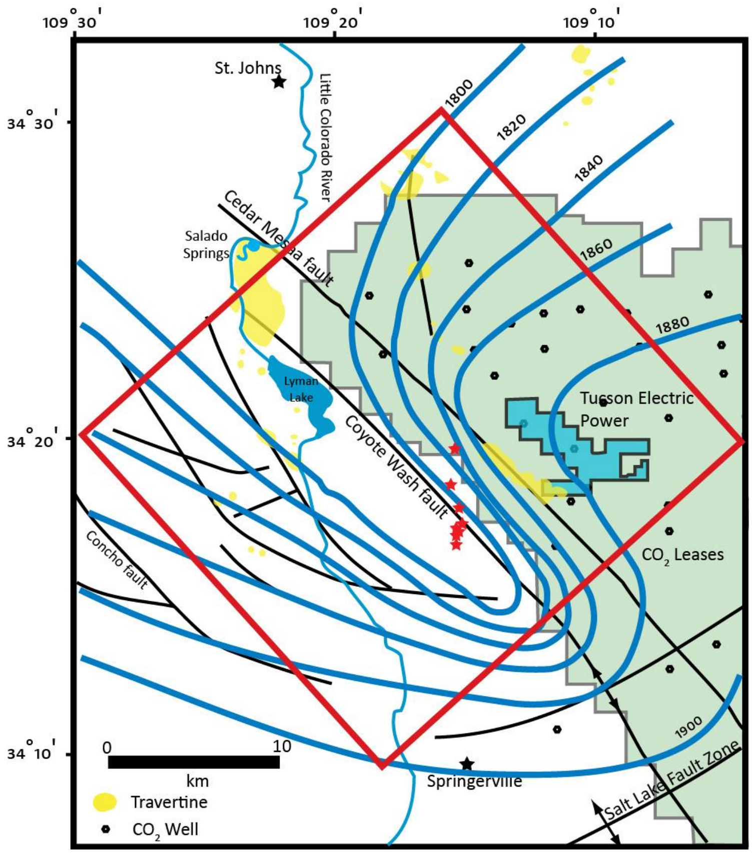


Figure 4 *Travertine (yellow) as an indicator of paleo-leakage of CO_2 around Springerville, Arizona, USA. From Keating et al., 2014).*

The travertines at the both the Little Grand Wash Fault, and Springerville, both suggest leakage from a large number (49 in the case of Springerville; Embid et al., 2006) of distinct leakage sites. It is not known for certain why an individual leakage point is abandoned in favour of another, but a reasonable assumption is that the sub-surface fractures that are carrying the fluids (both CO_2 and water) to the surface become cemented up. In the case of the Little Grand Wash Fault, then modern-day erosion has dissected some of the older travertines, showing extensive veins of calcite and aragonite (Shipton et al., 2004, 2005; Burnside, 2010) which are presumably the paleo-fluid conduits. Once an individual leakage point (travertine mound) becomes sealed, then leakage moves to a nearby alternative site.

The volcanic craters of Ukinrek Maars, Alaska date from only 1977. Between 30,000 and 50,000 m^2 of ground area has conspicuous plant damage or death (Evans et al., 2009). Geographically separate gas vents, linked geochemically to the same source, lie some 3 km from the damaged vegetation (Evans et al., 2009).

On the assumption that leakage from an engineered storage site followed similar patterns, then it might be deduced that leakage, if prevented at a localised high flux site (for example by grouting the fluid-conduit fractures), will move to another site nearby. Furthermore, a single underground source can supply CO_2 to a large area – certainly measured in square kilometres, or kilometres in length if following a fault trace. Larger areas can be affected by CO_2 emissions, e.g. 25 km^2 in the case of a 1995 event in the Alban Hills of Rome, Italy (Quattrocchi et al., 1998, cited in Pizzino et al., 2002) though whether this comes from a single underground source, as would be the case with a leaking storage reservoir, is uncertain.

The rate at which CO_2 concentrations build up during natural release events can be very rapid, though release events can be short (days). Annunziatelli et al. (2003) describe a sudden release of CO_2 from the ground in the Italian town of Cava dei Selci. Groundwater pH decreased from 6.0 to 5.5, and pCO_2 increased from 0.7 to 2.5 bars. The affected area was about 10,000 m^2. In separate events in October 1999 and in

March 2000, 30 cows and some sheep died due to asphyxiation by CO_2 (Annunziatelli et al., 2003). Faulting has been implicated in at least some release events (Quattrocchi and Venanzi, 1989; Quattrocchi and Calcara, 1994; Calcara et al., 1995; Quattrocchi and Calcara, 1998). Another control of release events is the weather – monitoring of CO_2 levels on São Miguel Island in the Azores shows that soil water content, barometric pressure, wind speed and rainfall explain much of the observed variation in soil gas concentrations (Viveiros et al., 2008). Rapid decreases in barometric pressure are especially associated with sudden increases in CO_2 concentration in residential buildings, with detected levels in the Azores exceeding 20 % - though the studied house lies within a volcanic caldera! (Viveiros et al.,2008). Similar results were obtained at Mammoth Mountain, California, where average daily CO_2 fluxes were correlated with both average daily wind speed and atmospheric pressure, the degree of correlation depended on the magnitude of the fluctuations in the atmospheric parameters (Lewicki et al., 2008). The authors noted that any genuine change in the CO_2 supply from depth would be at least partly obscured by the meteorological effects.

A further lesson from natural analogues is that CO_2 can lie undetected at shallow depths within the crust, both within unconsolidated high porosity sediments but also within consolidated bedrock (Carapezza and Tarchini, 2007) The CO_2 can then be released to the surface by routine engineering activities such as the drilling of shallow groundwater boreholes, or the removal of low permeability cover during excavation (Carapezza and Tarchini, 2007; Barberi et al., 2007). The remediation of such a case is described below.

Natural analogues also enable study of the effects of the CO_2 on the flora and fauna of the leakage site. At Laacher See, Germany, an investigation of microbial communities in the soil showed significant differences between CO_2-rich (>90 % soil gas), medium CO_2 (20%), and a control site with background CO_2 concentrations (Krùger et al., 2009). The ecosystem was interpreted to have adapted to the different conditions through species substitution or adaptation, with a shift towards anaerobic and acidophilic species under elevated CO_2 concentrations. Krùger et al. (2009) suggested that it might be possible to identify botanical and microbial species whose presence or absence provide easily detectable indicators for the leakage of CO_2.

The infamous lethal release of CO_2-rich gas from Lake Nyos, Cameroon, in 1986 is cited as an example of the potential dangers of CCS. Studies of other naturally-CO_2 rich lakes enable a more balanced view to be taken. The Laacher See in Germany has a flux of CO_2-rich gases into the deep water, but seasonal overturning allows the release of the CO_2 without concentrations building to dangerous levels (Aeschbach-Hertig et al., 1996). The Cuicocha caldera lake in Ecudor also has an overturn period from June to August, again allowing volcanically-derived CO_2 to escape (Padrón et al., 2008). The physical and climatic conditions of a lake are hence crucial in determining the extent to which a CO_2 leak might be dangerous to life, and seasonal overturning (or stable stratification) is the most important factor. Natural analogues can also be used to assess the risks to life associated with natural (and presumably engineered) CO_2 leakage. Roberts et al. (2011) calculated that the risk of accidental human death from CO_2 seeps in Italy to be 10^{-8} year^{-1} to the exposed population, note not to the population at large. Roberts et al. (2011) pointed out that the CO_2 risk is significantly lower than that of many socially accepted activities, such as driving a car for which the risk of death is reported as $1.8x10^{-4}$ per year.

In summary, natural leakage from known single reservoirs can cover large areas at the surface (> 10 km^2), and commonly follows the traces of faults. Gas release can be either steady state or episodic, sometimes with an obvious control by tectonic activity. Undetected CO_2 can exist in high concentrations at shallow depths, and be released by the drilling of boreholes, or by excavation though a low permeability caprock.

2 MONITORING AND REPORTING PROTOCOLS

Emphasis should be on achieving the earliest possible detection of CO_2 migration from the reservoir, to maximise the time available for suitable mitigation actions to be implemented before leakage (migration of CO_2 out of the storage complex) occurs, and also to provide sufficient time for full remediation prior to any planned transfer of liability from the operator to the competent authority (CO_2CARE, 2013). This review of industry best practises concluded that the design of a risk-based remediation plan would be an essential step in abandoning a storage site. Bai et al. (2000) describe a network of 'sentinel' wells that surround a sensitive resource, in this case a drinking water supply, that allow sufficient time after the detection of contaminants in one of the wells to plan and implement remediation methods.

The adoption of an incident response protocol in advance of a CCS project is vitally important (IEA GHG, 2007). Lack of a protocol for responding to CO_2 leakage allegations can lead to years of complaints to government and industry from landowners, with landowners eventually seeking answers from unqualified sources. Wrong conclusions and inaccurate information will then distribute in the international press, affecting public perception of CCS.

An example of this is the Weyburn-Midale CO_2 monitoring and storage project (LaFleur, 2010; 2011). In January 2011, farmers living near the IEAGHG Weyburn-Midale CO_2 Monitoring and Storage Project (Saskatchewan Canada) announced to the press that leaking CO_2 from the storage reservoir was reaching ground surface and impacting their land. The story of leakage originated from an independent study commissioned by the landowners after years of complaints that government and industry officials had not addressed to their satisfaction (LaFleur, 2010; 2011). CCS experts questioned the technical merit of the independent study. To address the uncertainty in the source of the CO_2 on the Kerr farm, and in keeping with its mission to advance best practices and performance verification for geologic carbon storage, the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide (IPAC-CO_2) commissioned a scientific study at the Kerr farm, with the Bureau of

Economic Geology's Gulf Coast Carbon Center as the technical lead. One important finding of the study was that soil CO_2 on the land was natural and not the result of a CO_2 storage leak (Sherk et al., 2011; Romanak et. al, 2014).

Guidelines from the IEAGHG state that "Under EU regulations, requirements for leaked emissions falls under the EU Emissions Trading Scheme (EU ETS) (Directive 2003/87/EC)" which, operating since 2005, builds upon the Kyoto Protocol, the Clean Development Mechanism (CDM) and Joint Implementation (JI) (EC, 2008); and for geological storage of CO_2 would now be triggered by the EU CCS Directive which entered into force in 2009. Article 16 of the EU CCS Directive 2009/31/EC lays out requirements in the event of leakages or significant irregularities, dictating that should any leakage occur then there would be a surrender of allowances under the EU ETS. In June 2010, Decision 2007/589/EC (establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC) was amended to say leakage 'may be excluded as an emission source subject to the approval of the competent authority, when corrective measures pursuant to Article 16 of Directive 2009/31/EC have been taken and emissions or release into the water column from that leakage can no longer be detected.' A further amendment to Decision 2007/589/EC under Annex XVIII adds 'Monitoring shall start in the case that any leakage results in emissions or release to the water column. Emissions resulting from a release of CO_2 into the water column shall be deemed equal to the amount released to the water column' and defines an approach for quantification, stating 'The amount of emissions leaked from the storage complex shall be quantified for each of the leakage events with a maximum overall uncertainty over the reporting period of ± 7.5%. In case the overall uncertainty of the applied quantification approach exceeds ± 7.5%, an adjustment shall be applied'

2.1 Existing monitoring and reporting protocols

The principles of the existing CO_2 surface leakage monitoring and reporting protocols are drawn from authoritative international guidance produced by the Intergovernmental Panel on Climate Change (IPCC) in its Revised 1996 IPCC Guidelines for National

Greenhouse Gas Inventories (IPCC Guidelines) and related Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (Good Practice Guidance). These documents can be accessed from the web at:

- http://www.ipcc-nggip.iges.or.jp/public/gl/invs1.htm and,
- http://www.ipcc-nggip.iges.or.jp/public/gp/gpgaum.htm respectively.

The current CO_2 monitoring and reporting protocols are discussed briefly in the following paragraphs:

1) EU Environmental Liabilities Directive;
2) London Convention and protocol;
3) EU Emissions Trading System;
4) IPCC Guidelines and good practice reports;
5) UNFCCC Kyoto protocol committee for developed countries;
6) UNFCCC Kyoto protocol CDM for developing countries;
7) US EPA GHG Emissions.

EU Environmental Liabilities Directive

Any damage to the environment - such as groundwater pollution caused by CO_2 leakage could be covered by the EU Environmental Liabilities Directive (which focuses on habitats, water and land pollution). Under this directive an operator is liable for damage up to 30 years after an incident takes place, irrespective of the time the facility closes. In the UK, the Environment Agency is able to order companies to restore polluted environments through this directive, although it is unclear how this would apply to the sea, (EU Directive, 2004).

The London Protocol to the London Convention

An international framework governing the disposal (dumping) of industrial waste at sea which was amended in 2006 to allow "CO_2 from capture processes" to be stored under the seabed. This amendment came into force in 2007, but a further amendment is necessary to allow for the storage of CO_2 that has crossed an international border (transborder CO_2). In 2007, the Convention for the Protection of the Marine Environment of the North-East Atlantic (“OSPAR Convention”) was also amended to allow CO_2 storage in geological formations under the seabed. This amendment has yet to be ratified, and so is not in force.

EU Emissions Trading System (ETS)

An EU ETS operator must propose a monitoring plan when applying for a greenhouse gas emissions permit (or emissions plan for aviation operators). The monitoring plan provides information on how the EU ETS operator’s emissions will be measured and reported. A monitoring plan must be developed in accordance with the European Commission’s Monitoring and Reporting Regulation and be approved by an EU ETS Regulator. The reporting year runs from 1 January to 31 December each year.

http://ec.europa.eu/clima/policies/ets/monitoring/index_en.htm

The EU ETS requires all annual emissions reports and monitoring to be verified by an independent verifier in accordance with the Accreditation and Verification Regulation. A verifier will check for inconsistencies in monitoring with the approved plan and whether the data in the emissions report is complete and reliable. Annual emissions are reported in accordance with two Commission Regulations: the Monitoring and Reporting Regulation (MRR); and the Accreditation and Verification Regulation (AVR).

IPCC permit

The IPCC Guidelines and good practice reports give guidance on monitoring, verification and estimation of uncertainties, as well as on quality assurance and quality control measures (IPCC, 2006, v.2 Chapter 5). General guidance is given on how to plan a monitoring programme; what to monitor; and how to report on results. The purpose of verifying national inventories is to establish their reliability and to check the accuracy of the reported numbers by independent means. The guidelines work on the principle that with good site characterisation, risk assessment of leakage, monitoring and reporting, then zero leakage can be assumed unless monitoring indicates otherwise.

Monitoring includes: measurement of background CO_2 flux; continuous measurement of CO_2 injected; monitoring of injection emissions; periodic monitoring of CO_2; and monitoring of CO_2 fluxes to surface.

Kyoto Protocols

A series of ratifications from 2008 - 2012 (Kyoto 1st Period) for:

- Developed country emission commitments;
- CCS included in KP Art 2.1;
- IPCC GHG Guidelines (2006) allows CCS to be included;
- CDM – Policy mechanism for rewarding CO_2 reduction in developing countries. Project-based carbon credits.

US EPA - GHG Emissions

The US Environmental Protection Agency (EPA) mandates for the reporting of the injection of greenhouse gasses and the geological sequestration of CO_2 (Final rule federal register Vol 75 p75060 Dec 1 2010 http://www.epa.gov/ghgreporting/reporters/subpart/rr.html).

The requirement is to report GHG data to the EPA annually, including:

- EPA approved site specific monitoring reporting and verification plan;
- Quantify and report amount of CO_2 stored;
- Detect and quantify emissions to surface;
- Verify whether leakage and distinguish from baseline.

2.2 Reporting protocols

Under the Clean Air Act, the US EPA Office of Air specified rules for the mandatory reporting of greenhouse gases (MRR) from upstream suppliers of fossil fuels and industrial gasses as well as downstream emitters of GHG's. The rule covers many activities associated with CCS and EOR. It requires the monitoring, measurement and reporting of GHG emissions. The EPA estimate that facility level GHG emission reporting will cover 90% of emissions from electricity generation, 85% of total oil and gas industry emissions and 60% of emissions from ethanol production (Granger Morgan, 2012). Any facility that captures and exports CO_2 must report the mass of CO_2 so captured and exported. The reporting protocol also requires the development of a site specific monitoring, reporting and verification plan (MRV) that must include, Figure 5:

1) Leakage risk assessment – the identification of all potential leakage pathways;
2) Monitoring strategy – a site specific plan that may include a combination of subsurface, vadose, surface water and / or atmospheric monitoring – leakage must be quantified if CO_2 is detected at the surface;
3) Pre-injection environmental baselines – site specific establishment of pre-injection CO_2 levels;
4) Site specific mass balance equations to calculate the net amount of CO_2 sequestered.

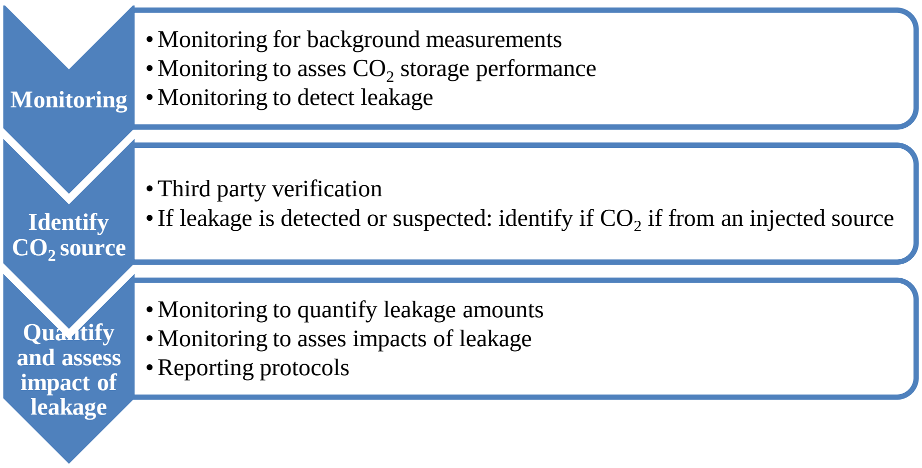


Figure 5 Shallow surface monitoring and reporting (Figueiredo el al. 2012).

2.3 CO_2 leakage monitoring

The crucial factor for monitoring and reporting protocols is that: the leakage of CO_2 must be distinguished from variable natural background CO_2 levels.

Benson (2004) stated that a site with a storage rate of ~4 MT /year, with a homogenous (i.e. diffusive) leakage of 0.1 % per year of the stored CO_2 within an area of 10 km × 10 km, would produce a CO_2 flux two to three orders of magnitude less than that of a typical ecosystem, and four to five orders less than fluxes found in some geothermal areas. However, if the same flux is localised in a restricted area, (small surface site, well bore, fault etc.) the CO_2 flux will locally far exceed the background level and will be easy to detect through monitoring to produce an early warning.

There are a number of considerations that must be taken into account when undertaking the monitoring of potential leakage, including:

1) variation in background levels;
2) the risk of false positives;
3) the need for wide spatial coverage – hence low resolution;
4) the need for high sensitivity and low uncertainty;
5) the definition of the area to be monitored;
6) the uncertainty in measurements may exceed accuracy requirements;
7) cost.

In particular, it is crucial to quantify the background CO_2 fluxes and concentrations which are dependent on CO_2 production in the soil; the movement of CO_2 from sub-soil sources into the soil; and the exchange of CO_2 with the atmosphere as controlled by concentration (diffusion) and pressure (advection) gradients.

Biologically produced CO_2 in soils (i.e., soil respiration) is derived from root respiration and the decay of organic matter. While many factors may influence soil respiration rates, changes in atmospheric and soil temperature and soil moisture have been shown to strongly affect these rates and related concentrations and fluxes (Lewicki and Oldenburg, 2004). CO_2 that enters soil from sub-soil sources can be derived from groundwater degassing of CO_2 derived from respiration, atmospheric, and carbonate mineral sources. Also, production of CO_2 at sub-soil depths can occur by oxidative decay of relatively young or ancient (e.g., peat, lignite, kerogen) organic matter in the vadose zone (Lewicki and Oldenburg, 2004). Exchange of soil CO_2 from subsurface sources with the atmosphere can occur by diffusion and/or advection, (Baldocchi et al 2001). Diffusive flux depends on the gas production rate and soil temperature, moisture and properties such as porosity, with each of these factors varying in both space and time. Advective flow can be driven by fluctuations in atmospheric pressure, wind, temperature, and rainfall (Lewicki and Oldenburg, 2004).

There are a variety of methods available to detect and monitor shallow surface CO_2 leakage including (for sources see below):

1) Surface gas laser monitoring;
2) Remote sensing;
3) Ecosystem monitoring;
4) Soil gas flux;
5) Gas concentration / geochemistry / isotopes;
6) Soil geochemistry;
7) Fluid chemistry of shallow groundwater.

Surface gas laser monitoring

Surface gas monitoring was carried out at the In Salah Gas project in 2009 using a Boreal Laser open path laser CO_2 detector, linked to a gasFinder FC analyser and mounted at a height of 38 cm above ground on a Toyota Landcruiser (Jones *et al.*, 2011). The detector used a wavelength of 2 μm and had a sensitivity of around 5-10 ppm for CO_2.

Remote Sensing

Direct detection of CO_2 can be undertaken using high resolution hyperspectral imagery to detect and map the effects of elevated CO_2 soil concentrations on the roots of plants. It can also detect hidden faults which may localize CO_2 leakage. Elevated CO_2 levels deprive the plant root system of oxygen, which will degrade plant health and species distribution (Pickles and Cover, 2005).

Ecosystem monitoring

Ecosystem monitoring is based upon a detailed analysis of the non-mobile organisms, i.e. plants, meiofauna and the microbial populations inhabiting the soil at a suspected leak. These are then compared with control sites representing the background ecosystem to be expected without disturbances.

Soil gas flux monitoring

Recent advances in cone penetrometer and sensor technology have enabled contaminated sites to be rapidly characterised using vehicle-mounted direct push probes. Probes are available for directly measuring contaminant concentrations in-situ, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, groundwater, and soil gas samples for subsequent laboratory analysis (Sara, 2003).

A range of technologies exists to measure CO_2 concentrations and fluxes in the shallow subsurface and the atmospheric surface layer (Lewicki and Oldenburg 2004; IEA GHG, 2012). These technologies include:

1) The infrared gas analyser (IRGA) for measurement of point CO_2 concentrations;
2) The accumulation chamber (AC) technique to measure point soil CO_2 fluxes;
3) The eddy covariance (EC) method4 to measure net CO_2 flux over a given area;
4) Light distancing and ranging (LIDAR) to measure CO_2 concentrations over an integrated path.

Gas concentrations / geochemistry / isotopes

A combination of concentrations and isotopic ratios of gases is frequently combined with soil gas flux measurements. Soil gas samples are most typically collected using small, lightweight soil probes. The method involves driving a hollow steel tube into the ground, typically to a depth of 0.5 - 1.0 m, and drawing soil air to the surface for analysis. Analysis can be conducted in the field using portable equipment or the samples stored in pre-evacuated airtight containers for laboratory analysis. In addition to CO_2, other gas species can be targeted: due to their association with the reservoir (e.g. CH_4 or H_2S in CO_2-EOR projects); man-made tracers that are added to the injected stream (e.g.

fluorocarbons); or natural tracer gases (e.g. helium or radon). Isotopic analyses can also be conducted such as carbon in CO_2 ($^{\delta 13}C$ to determine origin and ^{14}C to determine age).

Soil geochemistry

Mineralogical studies of the clay-rich soils of the natural CO_2 leakage site at Latera, Italy, have indicated variations in soil geochemistry associated with increased acidity and anoxic conditions (Beaubien *et al.*, 2008; Pettinelli *et al.*, 2008). In particular, the results showed an increase in the concentration of K-feldspar with an associated decrease in albite, and a decline in the occurrence of oxides such as MgO, CaO, Fe_2O_3 and Mn_3O_4 in the region of the gas vent compared with the surrounding soils. However, soil geochemistry analyses related to mineralogy may be unsuitable for CO_2 leakage monitoring due to the slow reaction rates involved.

Fluid chemistry of shallow groundwater

CO_2 is a natural constituent of groundwater. Depending on the pH and chemical composition of the groundwater, CO_2 will form various chemical species. The concentrations of these species can be measured with established hydrochemical methods reasonably accurately. The quantification of leakage requires the integration of groundwater volumes and fluxes multiplied by the concentrations of carbon species that originate from the CO_2 ascending from the storage reservoir (IEA GHG 2007).

2.4 CO_2 leakage characterisation

Quantification of CO_2 leakage

Four steps are necessary to quantify leakage (IEAGHG, 2012):

1) Detection of leakage through implementation of an appropriate monitoring strategy;
2) Sampling of phases and analysing concentrations of carbon species – i.e. whether the CO_2 represents leakage from storage or a natural background flux;
3) Volume or flux measurements – although, it may be difficult to measure all the leakage mechanisms, such as free phase gas or dissolved gas;

4) Calculation of leakage mass or flux – however, along with measurement accuracy, flux calculations are further complicated by the natural variability in background values.

Measurement uncertainties

Given the specific requirement in the EU for defining the level of uncertainty in quantification of leakage, it is important to consider the current knowledge of the uncertainties associated with measurement instrumentation and techniques. The level of uncertainty will decrease with further refinement through increased application; however, the natural system will always impose some level of uncertainty. For example, in surface water chemistry techniques, Mau et al. (2006) estimated 10 to 20% of their uncertainty was due to variations in the local background with over 50% due to variations in flow velocity. From reported research there is evidence to suggest some technologies in their current level of development may have uncertainty ranges exceeding the required range of ±7.5%, i.e. Trotta et al. (2010) estimated the largest uncertainties can range from 10 to 40% for different set-ups of eddy-covariance-based estimates of net ecosystem exchange; and uncertainty of CO_2 flux increases with increasing absolute magnitude of the flux (Hollinger & Richardson, 2005).

Attribution of CO2 source

Techniques to attribute the origin of potential leakage of CO_2 include:

1) Stable carbon isotopic ratio – not always definitive;
2) Noble gas abundance and isotopic ratios;
3) Tracer gas signature – may give false positives;
4) Process based soil gas – using simple gas ratios (CO_2, CH_4, N_2 and O_2).

2.5 Monitoring costs

IEA GHG (2007, p.140) give a table of costs associated with monitoring and leak detection for 3 scenarios:

- A CO_2-EOR scheme with additional CO_2 storage;

- A saline aquifer with high residual gas saturation as the CO_2 plume is fairly static after injection;
- A saline aquifer with low residual gas saturation as the CO_2 plume is mobile after injection.

In both cases a ‘basic’ and ‘enhanced’ cost was calculated, which ranged from c. 1 – 40 M USD (2007 prices). Additional costs were estimated for well integrity logging, of 12 – 18 M USD for 10 CO_2 injection wells over 50 years.

3 CLASSIFICATION OF SITES REQUIRING MITIGATION

Mitigation planning involves an iterative process where the site characterisation / baseline data and the ongoing monitoring of the site feed into the risk assessment, which in turn informs the remediation action which then required further monitoring and risk analysis (Oldenburg, 2008; Figure 6).

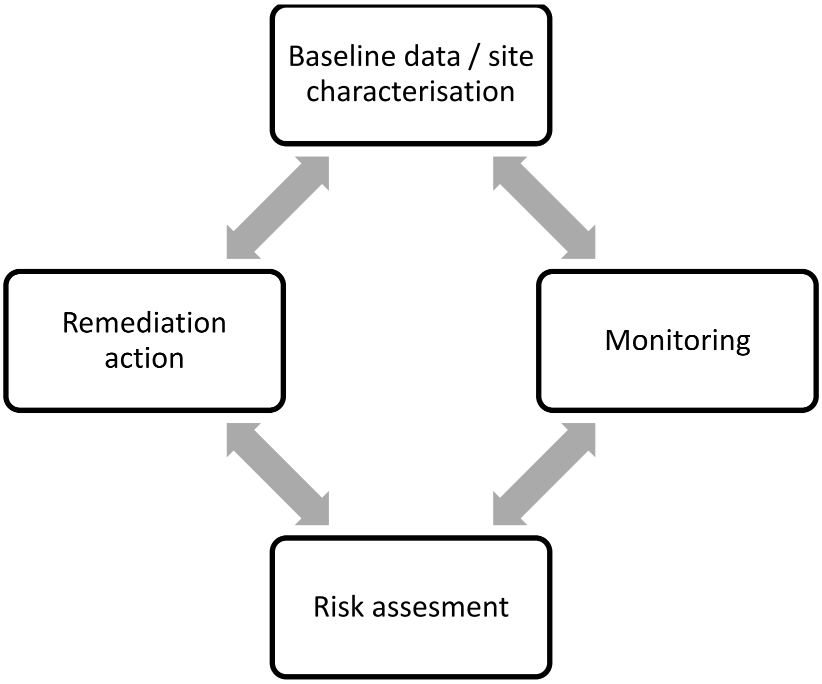


Figure 6 Classification of sites requiring remediation (Oldenburg, 2008).

3.1 Site Characterisation – Baseline data

Baseline data of the storage site should be acquired during the initial appraisal phase of a project. Relevant data should be collected in an efficient and cost-effective manner. This provides a baseline from which monitoring can identify any changes in the shallow subsurface.

The best case remediation plans are implemented at initial site characterisation (IEA GHG, 2007), where:

1) favourable storage sites with low risks of CO_2 leakage are selected during site characterisation;

2) emphasis is placed on well integrity, both active and abandoned;
3) comprehensive monitoring systems for the CO_2 storage site are installed and maintained;
4) a phased series of reservoir simulation-based modelling is undertaken to track and predict the location of the CO_2 plume;
5) a "Ready-to-Use" contingency plan/strategy for remediation is established.

Recent advances in cone penetrometer and sensor technology have enabled contaminated sites to be rapidly characterised using vehicle-mounted direct push probes. Probes are available for directly measuring contaminant concentrations in-situ, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, groundwater, and soil gas samples for subsequent laboratory analysis (Sara, 2003)

Non-invasive geophysical techniques such as ground-penetrating radar; cross-well radar; electrical resistance tomography; vertical induction profiling; and high resolution seismic reflection produce computer-generated images of subsurface geological conditions and are qualitative at best. Other approaches, such as chemical tracers, are used to identify and quantify contaminated zones, based on their affinity for a particular contaminant and the measured change in tracer concentration between wells employing a combination of conservative and partitioning tracers (Darnault, 2008).

3.2 Risk Assessment

Once site contamination has been confirmed by a programme of thorough site characterisation and monitoring, a risk assessment is performed. A risk assessment is a systematic evaluation used to determine the potential risk posed by the detected contamination to human health and the environment under present and possible future conditions (Darnault, 2008). If the risk assessment reveals that an unacceptable risk exists due to the contamination, a remediation strategy must be developed to assess the problem. If corrective action is deemed necessary, the risk assessment will assist in the development of remedial strategies necessary to reduce the potential risks posed by CO_2 contamination of the shallow subsurface (Sara, 2003).

The USEPA and the American Society for Testing and Materials (ASTM) have developed comprehensive risk assessment procedures. The USEPA procedure was originally developed by the United States Academy of Sciences in 1983. It was adopted with modifications by the USEPA for use in Superfund feasibility studies and RCRA corrective measure studies (USEPA, 1989). This procedure provides a general, comprehensive approach for performing risk assessments at contaminated sites. It consists of four steps:

1) hazard identification;
2) exposure assessment;
3) toxicity assessment;
4) risk characterisation.

The ASTM Standard E 1739-95, known as the Guide for Risk-Based Corrective Action (RBCA), is a tiered assessment originally developed to help assess sites that contained leaking underground storage tanks containing petroleum (ASTM, 2002).

A flow chart of severity / risk is based on:

1) depth (minimum);
2) onshore / offshore setting;
3) well description, completion, age, cement character;
4) matrix (soil vadose, soil phreatic, alluvium, ‘solid’ rock);
5) leakage rate;
6) quantity already leaked;
7) existing impacts including human impact;
8) land use (urban, agriculture, undeveloped);
9) geometry of the leak (diffuse, focussed, along a well);
10) hydrology (regional water flow rate / direction).

3.3 Remediation action

When the results of the risk assessment reveal that a site does not pose risks to human health or the environment, then no remedial action is required, but often further monitoring of a site may be required to validate the results of the risk assessment. Corrective action is required when risks posed are deemed unacceptable in the risk assessment. When action is required, a remediation plan must be developed to ensure that the intended remedial method complies with all technological, economic, and regulatory considerations.

The costs and benefits of various remedial alternatives are often weighed by comparing the flexibility, compatibility, speed, and cost of each method (Reddy, 1999). A remedial method must be flexible in its application to ensure that it is adaptable to site-specific soil and groundwater characteristics. The selected method must be able to address site contamination while offering compatibility with the geology and hydrogeology of the site.

The remediation objectives are to:

1) Bring contaminant levels to below environmental standard limits ;
2) Reduce mobile separate phase CO_2 to limit growth of the leakage plume;
3) Remove CO_2 from the aquifer in both gas and liquid phase;
4) Reduce the aqueous phase concentration of CO_2 – minimising decrease in pH.

The efficacy of the remediation technique will depend on (Hamby, 1996):

1) The size of the aquifer;
2) The size, shape and distribution of the CO_2 plume;
3) The leakage rate (possibly by multiple flow processes);
4) Whether there is two zone saturation gradient within the leak, i.e. a cone shaped plume with high gas saturation at top and a gravity tongue at bottom;
5) The total leakage amount;
6) Well orientation, horizontal or vertical;
7) Well depth in relation to aquifer;

8) well spacing.

Generally, remediation methods are divided into two categories: in-situ remediation methods and ex-situ remediation methods. In-situ methods treat contaminated groundwater in-place, eliminating the need to extract groundwater. In-situ methods are advantageous because they often provide economic treatment, little site disruption, and increased safety due to lessened risk of accidental contamination exposure to both on-site workers and the general public within the vicinity of the remedial project (Darnault, 2008). Successful implementation of in-situ methods, however, requires a thorough understanding of subsurface conditions. Ex-situ methods are used to treat extracted groundwater. Surface treatment may be performed either on-site or off-site, depending on site-specific conditions. Ex-situ treatment methods are attractive because consideration does not need to be given to subsurface conditions. Ex-situ treatment also offers easier control and monitoring during remedial activity implementation (Reddy, 1999).

4 REMEDIATION AIMS AND IMPLEMENTATION

4.1 The aims and objectives of remediation

The aims and objectives of remediation of leaked CO_2 will vary from site to site, according to the likely impacts and consequences. Generally, the aims will include:

1) To stop the source of the leakage – in the context of the near surface, the leak is almost certainly sourced from a much a deeper storage reservoir, and mitigation at depth is probably more appropriate;
2) To reduce the mobile free phase CO_2, to limit the continued growth of the leakage plume, i.e. to prevent the spread of the contamination (Esposito and Benson, 2012);
3) To delay the spread of a plume or dissolved CO_2, either while plans are drawn up for permanent remediation, or while legal action takes place to determine who is going to pay for remediation;
4) To remove CO_2 from the aquifer in both gas and aqueous phase, both to recover the CO_2 for disposal and to restore the aquifer back to pre-contamination conditions (Esposito and Benson, 2012);
5) To minimise the decrease in pH from the formation of carbonic acid. Minimising the drop in pH may indirectly decrease the amount of secondary contamination from the CO_2 leakage caused by the mobilisation of heavy metal ions (e.g. Esposito and Benson, 2012; Keating et al., 2014);
6) To directly reduce the concentration of mobilised toxic metals to either background levels, or to levels acceptable to relevant legislation.
7) To reduce the concentration of hydrocarbons that may be mixed with, or dissolved in, the leaking CO_2, especially if the primary storage reservoir is a depleted gas or field, or a depleted oil field with a high proportion of light oil that can volatilise into the free CO_2 phase;
8) Prevent the CO_2 from reaching the surface, to avoid payment of fines or the return of credits for the avoidance of CO_2 emissions;
9) Prevent the CO_2 from reaching habitations or other sensitive locations (‘receptor’ in pollution control terminology).

4.2 Published remediation or leakage plans

For CO_2 storage schemes, a small number of emergency plans have been published worldwide, that describe the actions to be taken in the event of an unplanned release or irregularity in the movement of the CO_2.

4.2.1 Decatur CO_2 injection project emergency plan

For the Decatur CO_2 injection project, Illinois, USA, the Emergency and Remedial Response Plan (ERRP) describes actions that the owner / operator (Archer Daniels Midland; ADM) shall take to address movement of the injection fluid or formation fluid in a manner that may endanger an underground source of drinking water (USDW) during the construction, operation, or post-injection periods. The ERRP includes the effects of both the direct movement of the injected CO_2, and also the associated pressure front. The plan summary has the following actions (Decatur, unknown date):

1) Initiate shutdown plan for the injection well, i.e. cease the injection of CO_2;
2) Take all steps reasonably necessary to identify and characterise any release;
3) Notify the permitting agency (UIC Program Director) of the emergency event within 24 hours;
4) Implement applicable portions of the approved ERRP.

In the event of evidence of contamination of groundwater by the CO_2, directly or indirectly, then the following remediation is planned (Decatur, unknown date):

1) Arrange for an alternate potable water supply, if the USDW was being utilised and has been caused to exceed drinking water standards;
2) Proceed with efforts to remediate USDW to mitigate any unsafe conditions (e.g., install system to intercept/extract brine or CO_2 or "pump and treat" to aerate CO_2-laden water);
3) Continue groundwater remediation and monitoring on a frequent basis (frequency to be determined by ADM and the UIC Program Director) until unacceptable adverse USDW impact has been fully addressed.

4.2.2 FEED study for Shell Goldeneye (UK) project

The Shell Goldeneye project, a component part of the Scottish Power CCS Consortium, involves the storage of CO_2 in the Goldeneye field, a soon-to-be depleted gas field approximately 100 km offshore in the UK North Sea. Although the original project was abandoned in October 2011, the product of a Government-funded FEED (Front-end engineering design) study is published in the UK National Archives (http://webarchive.nationalarchives.gov.uk/). The Goldeneye field is the storage site for the Peterhead CCS Project which in March 2013 was chosen as one of two CCS demonstration projects to progress to the next stage of the UK Government's CCS Commercialisation Competition funding.

The 'Corrective Measures Plan' is described in Scottish Power CCS Consortium (2011). Section 7.5 covers the scenario that 'CO_2 Flows Up To Near Seabed / At Seabed', which is considered to be 'not possible' without the CO_2 following a problematic well, so that remediation interventions would be focussed on that well (p. 38). Moreover, the flow of CO_2 to the seabed would inevitably involve the flow through, or the bypassing of, the primary seal. Hence, the mitigation measures considered for this scenario would be deployed. However, 'No remedial actions can remove CO_2 that has already migrated above the primary seal and therefore following consultations with the regulator, an additional storage license will be sought.' (p. 28). The principal remediation method considered for failure of the primary seal (away from a borehole) appears to be the reduction in pressure close to the leak by changing the pattern of CO_2 injection, in the expectation that the seal has failed by stress fracturing or the opening of existing fractures by excessive fluid pressure within the reservoir. The possibility of drilling a relief well is discussed, though whether this is to reduce pressures close to the primary seal; to inject sealants; or for some other purpose is not specified. The problems of locating a leak with sufficient precision to make remediation a realistic possibility, and the questionable likelihood of successful remediation are highlighted.

Under certain circumstances (e.g. migration through the primary seal via a diffuse fracture network), it was considered that may have been be easier to fix a leak path where this passes through the secondary seal. Again, this was considered to be most likely along a borehole. In the event that migration occurred through both the primary and secondary seals, and none of this migration path was related to boreholes, then it was considered that remedial interventions were unlikely to be successful. It was suggested that, in consultation with the regulator, the decision to intervene or not would be considered taking into account the likely effectiveness of intervention alternatives (relief wells).

In the event of leakage from an abandoned well, then re-entry directly from the surface is impossible (p.65) as the wells are severed below the surface of the seabed sediment. Therefore, a relief well must be drilled, with the advantage that casing can be set and cemented prior to entry into the leaking well. *This re-entry has to be performed at a depth such that there is sufficient integrity (strength) in the formation (i.e. the formation will not fracture as the leaking well is entered) to withstand the pressure within the affected borehole, as the casing is milled away to gain entry (p.65).* It is noted that milling through casing is not without its hazards; it is entirely possible to mill into the well, and back out the other side, leaving the well casing badly damaged.

It is considered very difficult or near impossible to enter an uncased section of a borehole, as it is conventional to use the magnetic or / conductive nature of casing to locate the borehole – this is not a problem at shallow depths where casing will be present. If there is magnetic material in the uncased section (e.g. a jammed drill string or production tubing) then it is possible to locate that instead. Past attempts at re-entry via a relief well show that 10+ attempts may be needed to locate the well, using successive sidetracks. The detection technique used to locate the leaking well, magnetic ranging, works at c. 60m distance. The time estimated for drilling a relief well into a cased hole target is around 55 days. Sourcing and mobilising a rig would be additional to this.

In the event of a CO_2 blow-out (p.74), the suggested remediation consists of:

1) injecting kill fluid (hazards are toxic gases and low temperatures) – this may not be possible;

2) drilling a relief well, sufficiently deviated to place the drill rig a safe distance from the affected platform (i.e. several km).

In the event of a blow out that is not at a well – the only suggested mitigation technique is to expect that the leakage path self-seals (!) as the pressure drops and the fractures close.

4.2.3 FEED study for EON Kingsnorth (UK) project:

The FEED study for the EON Kingsnorth project appears not to include a plan for the remediation of any CO_2 leakage. In EON (2010) there are numerous references to FEED2, which was presumably a planned follow-on to the published FEED study. However, this is not available. Regarding the effect of "Generation of potential migration/leak paths along well bores", 'Further Action' is described as "Further review and remedial actions to be addressed in the final design and procedures in FEED2" (EON, 2010, section 2.3, p. 6).

4.2.4 Rotterdam Capture and Storage Demonstration Project (ROAD), Netherlands

The ROAD project aims to capture 1.1 Mt of CO_2 per year from the Rotterdam area, and store it in a depleted offshore gas field. The corrective measures plan is available (http://www.rvo.nl/sites/default/files/sn_bijlagen/bep/70-Opslagprojecten/ROAD-project/Fase1/4_Aanvragen/A-06-2-Aanvulling-opslagvergunning-kl-354540.pdf; from p.437) in the Dutch language but is summarised by Steeghs et al. (2014). The plan is based on three principles:

- Corrective measures are site and risk specific, and linked to the risk management plan;
- The implementation of corrective measures is triggered by pre-defined monitoring outcomes;
- Corrective measures will take place in the event of a leak which is considered a significant irregularity.

The plan is structured as: the contingency scenario; consequences; and the corresponding corrective measures. A traffic light system is used to describe the conformance of the site, with ‘red’ triggering the implementation of the corrective measures. The part of the corrective measures plan which is most relevant to the shallow leakage described in this report is the scenario of CO_2 leakage from the reservoir into the biosphere. The suggested measures are: additional monitoring, and the cessation of injection, either temporarily or permanently. Communication, for example with the competent authority, and information sharing are also considered to be important, regardless of the nature of the irregularity or leakage. Back production of injected CO_2, followed by alternative storage or controlled release into the atmosphere would take place after the cessation of injection, with the aim of returning the storage complex back into a stable state.

4.2.5 Sleipner, North Sea, monitoring and remediation plans

Sleipner is an off shore storage site and as such a series of 3D seismic surveys have been carried out over the storage area to monitor the evolution of the site in relation to the baseline survey taken before injection started and to feed into the reservoir modelling. As such, the monitoring data generated are also used in long term simulations (IEA 2005). No published remediation plan have been located found by the present study.

4.2.6 In-Salah, Algeria, monitoring and remediation plans

A 5-6 year \$30 million “In Salah Gas CO_2 storage Assurance Joint Industry Project” has been proposed and taken place in the Algerian Sahara. For both commercial and technical reasons, the CO_2 gas is separated from the natural gas in the same manner as on Sleipner. In Salah is the first geological CO_2 storage site in the deep saline formation of an active gas reservoir. Since the start-up in 2004, more than three million tonnes of CO_2 have been stored below ground. Near surface environmental monitoring was designed to monitor the CO_2 levels in the soils, at ground surface and in the atmosphere just above ground surface. Extensive field investigations, carried out in 2009–2010, consisted of near-ground atmospheric CO_2 measurements with a mobile open-path laser system; soil gas pressure and flux measurements; botanical and microbiological surveys; initiation of longer-term subsurface monitoring of radon and other gases (Jones et al., 2011). Independent of these studies, due to preliminary conclusions regarding the reservoir properties (mainly related to capacity), the injection of CO_2 was reduced in mid-2010 and stopped in June of 2011 as a safety measure (http://www.statoil.com/en/TechnologyInnovation/NewEnergy/Co2CaptureStorage/Pages/InSalah.aspx, updated 17 Dec 2013). No published remediation plan has been located in the present study.

4.2.7 Weyburn, Canada monitoring and remediation plans

Soil gas studies were undertaken to establish background concentrations of CO_2 and other gasses. Three periods of sampling occurred over a 360 point grid, there is also continued comparison with a control site 10km away. An alleged surface leakage at the Weyburn project was reported by Petro-Find Geochem, a company commissioned by local landowners to investigate surface emissions at their property, who undertook geochemical soil gas surveys and concluded that the anomalous levels of CO_2 were the result of leakage of CO2 injected at Weyburn (LaFleur, 2010). This conclusion sparked contrasting perceptions between the experts and public (and the media) regarding the risks of CO_2 storage (Boyd et al., 2013). Subsequently, three separate studies for the Weyburn-Midale project, the International Performance Assessment Centre for Geological Storage of CO2 (IPAC-CO2) and Cenovus Energy, who operated the Weyburn project, independently monitored, investigated, and reassured that it was a false positive detection (Sherk et al., 2011; Trium and Chemistry Matters, 2011; Beaubien et al., 2013; Romanak et al, 2014). No published remediation plan has been located in the present study.

4.2.8 Rangely, Colerado, US, monitoring and remediation plans

CO_2 has been stored as a by-product of EOR, and soil gas and soil atmosphere flux measurements have been made at the site along with a hyperspectral survey. Seasonal variations in the desert location means there are strong fluctuations in natural CO_2 flux, and leakage CO_2 is easier to detect in the winter (IEA, 2005). No published remediation plan has been located in the present study.

5 REMEDIATION TECHNOLOGIES

5.1 Previous reviews of remediation technologies and methodologies

The most recent review of the remediation of the leakage of CO_2 from a CO_2 storage site is that of Manceau et al. (2014). It is broad in scope, but includes the remediation of near surface leakage as part of a wider review. Other relevant reviews include:

- Zhang et al. (2004) – vadose zone remediation;
- Benson and Hepple (2005): early detection of CO_2 leakage and remediation;
- IPCC (2005);
- Oldenburg and Unger (2005) present a model of CO_2 leakage specifically designed for the near-surface;
- IEA GHG (2007), very comprehensive review;
- Kirk (2011), a very useful review of natural CO2 emissions sites, as a part of the UK QICS project;
- Rǜtters et al. (2013), from CGS Europe, State of the art monitoring methods to evaluate CO_2 storage site performance.

Outside the fledgling CCS literature, there is little or nothing published concerning the remediation of CO_2 leakage. The journal 'Remediation' which, as the title suggests, is dedicated to environmental clean-up technologies, techniques and costs, appears to have no papers specifically concerning the remediation of leaks of CO_2. No text book appears to consider the problem. Given that text books are generally considered to be some 10 years behind journals this is unsurprising.

5.2 Classification of remediation techniques

There are a number of different remediation technologies suitable for the near surface remediation of CO_2 leakage, which can be classified by:

1) Objective of the technology (containment or treatment);
2) Process involved in the remediation (physical, chemical, biological or thermal);
3) Location of the remediation process (in situ or ex-situ).

Containment versus treatment

Containment prevents the spread of the CO_2 without necessarily removing or degrading the contamination. Treatment transforms the CO_2 into less toxic, or non-toxic concentrations. Containment is typically cheaper, can be used until a more efficient clean up technology becomes available, can provide a means of evaluating the potential for natural attenuation processes to degrade the CO_2 and can present a lower overall risk as CO_2 exposure can be minimised (Oldenburg; 2008). Many remediation technologies will involve both containment and treatment.

In-situ or ex-situ remediation

Here it is important to highlight the distinction between the application of the remediation technology versus the location of the remediation treatment, for example in pump and treat the pumping is in-situ but the treatment of the CO_2 contamination is ex-situ (Sara, 2003).

Active or passive technologies

Passive containment refers to treatment systems that clean up the CO_2 contamination without the need for energy input for the treatment process to be effective. In contrast, active technologies require further enhancements or energy inputs to achieve the required level of clean up (Reddy, 1997). Active systems are generally more expensive than passive systems.

These are a number of remediation techniques available for the shallow surface clean-up of CO_2 which are now presented and a summary of their remediation technologies are given in Table 4.

Table 4 Summary of the shallow surface CO_2 remediation technologies available.

Remediation	Remediation Technique	Containment or treatment	in-situ or ex-situ	Active or passive
Fluid control measures	Pump and treat	Treatment	In-situ technology, ex-situ treatment	Active
	Pump and treat with cap	Containment and treatment	In-situ technology, ex-situ treatment	Active
	Water injection	Treatment	In-situ technology, ex-situ treatment	Active
	Hydrodynamic isolation	Treatment	In-situ	Active
	Air stripping	Treatment		Active
	Hydraulic barrier	Containment and treatment	In-situ	Active
Cut off wall (unconfined aquifer)	Cut-off wall / slurry wall	Containment	In-situ	Passive
	Two-phase diaphragm wall	Containment	In-situ	Passive
	Composite diaphragm wall	Containment	In-situ	Passive
	Interlocking bored-pile diaphragm wall	Containment	In-situ	Passive
	Installation of thin wall and sheet pile into the soil	Containment	In-situ	Passive
	Injection permeation grouting	Containment	In-situ	Passive
	Jet grouting	Containment	In-situ	Passive
	Frozen wall	Containment	In-situ	Passive
	Bio barrier	Containment	In-situ	Passive
	Water control agent	Containment	In-situ	Passive
	High strength rigid set material	Containment	In-situ	Passive
	Organic polymer sealant	Containment	In-situ	Passive
	Super absorbent crystals	Containment	In-situ	Passive
	Granular activated carbon	Treatment	In-situ technology, ex-situ treatment	Active
Cut off wall - Fractured aquifer	Grout curtain	Containment	In-situ	Passive
Permeable reactive barriers (treatment walls)	Sorption barriers	Treatment	In-situ	Passive
	Ionic species removal	Treatment	In-situ	Passive
	Microbes	Treatment	In-situ	Passive
	Carbonation stabilisation	Treatment	In-situ	Passive
	De-acidisation	Treatment	In-situ	Passive
Soil Zone remediation	Soil vapour extraction	Treatment	In-situ technology, ex-situ treatment	Active
	Air sparging	Treatment	In-situ technology, ex-situ treatment	Active
	Bioslurping	Treatment	In-situ technology, ex-situ treatment	Active
	De-acidise soil	Treatment	In-situ	Passive
	Thermal treatment	In-situ technology, ex-situ treatment	In-situ technology, ex-situ treatment	Active
	Capping	Containment	In-situ	Passive
	Gas collection trench	Treatment	In-situ	Passive
	Ecosystem restoration	Treatment	In-situ	Active
Bioremediation	Bioremediation of low pH groundwaters	Treatment	In-situ	Passive
	Bioremediation of CO_2	Treatment	In-situ	Passive
	Bioremediation of toxic metals	Treatment	In-situ	Passive
	Bioremediation of hydrocarbons	Treatment	In-situ	Passive
	Natural attenuation	Containment	In-situ	Passive
Buildings	Passive vapour intrusion mitigation	Treatment	In-situ	Passive
	Passive / active sub slab venting	Treatment	In-situ	Passive
	Active vapour intrusion mitigation – subsurface pressurisation	Treatment	In-situ	Active
	Block wall depressurisation	Treatment	In-situ	Passive
	Active ventilation	Treatment	In-situ	Active
	Passive ventilation	Treatment	In-situ	Passive
	Demolish and rebuild to suitable standards.	Treatment	In-situ	Active

5.3 Remediation techniques (1): Fluid control measures

5.3.1 Pump-and-treat

Pump and treat is probably the most common technique used in pollution control. The idea is simple – the contaminated groundwater is brought to the surface through a number of purpose-drilled boreholes, and is treated at the surface. After treatment, it may be re-injected into the aquifer, or used for other purposes. IEA GHG (2007) suggest that horizontal pinnate (leaf-vein pattern) drilling described by von Shoenfeeldt et al. (2004) could access and extract near-surface accumulations of CO_2. Esposito and Benson (2012) model both vertical and horizontal extraction wells to remove the CO_2 in both the gas and aqueous phase. They conclude that small plumes of CO_2 with no gravity tongue can be remediated effectively through a single vertical well located in the middle, with a time span of several years. Large plumes of free-phase CO_2 where a gravity tongue has formed will require horizontal wells, and in excess of 10 years for effective remediation. In this scenario, Esposito and Benson (2012) suggest that injecting water to quickly immobilize and dissolve the CO_2 may be as effective in the short term. For larger plumes, a combination of sequential and/or simultaneous injection and extraction from multiple wells is likely to be required. However, Esposito and Benson (2012) conclude overall, that even a large plume of CO_2 can be contained and remediated effectively using the methods described.

If CO_2-rich water is brought to the surface, then it must be treated to remove the CO_2 before it can be re-injected. Both Benson and Hepple (2005) and IEA GHG (2007) suggest aerating the water to remove the CO_2. Given the low solubility of CO_2 in water at atmospheric pressure, and the likely resulting low concentrations of CO_2 in the air that is used in the aeration process, it seems highly unlikely that the CO_2 removed from the water could be collected for re-injection, and certainly not within any probable budgetary constraints. It is, therefore, highly likely that the CO_2 will be vented to the atmosphere.

If toxic metals are present within the CO_2-rich water at concentrations above background levels, or above statutory levels for potable water, then these must be removed before the water can be re-injected.

Pump-and-treat can be done is conjunction with a treatment wall, or PRD (Figure 7; Fetter, 1990). The contaminated groundwater is extracted from one side of the wall, treated and injected back into the aquifer on the uncontaminated side.

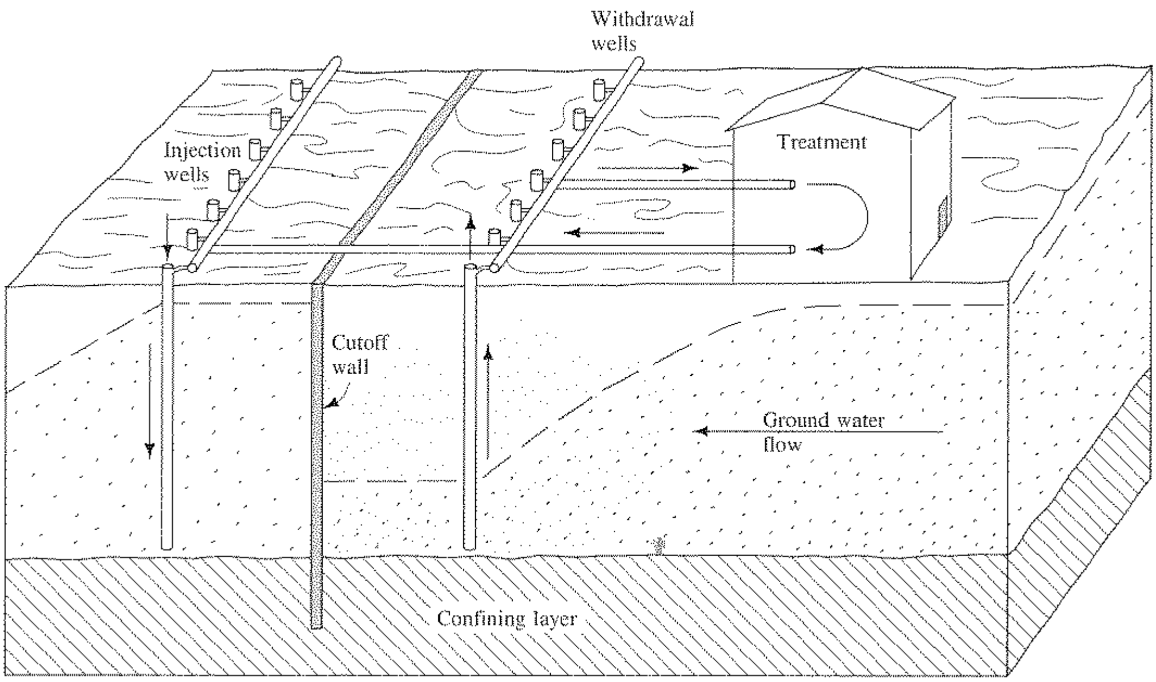


Figure 7 Pump-and-treat in association with a treatment wall (Fetter, 1999).

5.3.1.1 Pump and treat with a cap or vapour barrier

IEAGHG (2007, p.132) after Benson and Hepple (2005) suggested that the flux of CO_2 from a subsurface leak to the atmosphere could be halted, or at least slowed, by an impermeable cap or vapour barrier. The CO_2 could be pumped from below the barrier to reduce the concentration, or presumably for recovery and re-injection. Similar technology is used in land-fill sites, to prevent rain water for seeping into the landfill, and hence to prevent the contaminants from leaching from the site (CPEO, 2014). This is not especially similar to the case of a CO_2 leak, where the aim is (presumably) to prevent the CO_2 from reaching the atmosphere. The USA Resource Conservation and

Recovery Act (RCRA) established standards for landfill caps. For non-hazardous waste landfills a cap consists of three layers:

1) An upper vegetative (topsoil) layer;
2) A drainage layer; and
3) A low permeability layer made of a synthetic material (geomembrane, synonym: flexible membrane liner or FML; Daniel and Koerner, 2007) covering c. 0.6 m of compacted clay.

For hazardous waste landfills the standard is more onerous (Daniel and Koerner, 2007). The performance of the caps varies, for example drying of the clay layer can lead to cracking and loss of integrity (CPEO, 2014). The caps function most effectively where most of the waste is above the water table, and only have a design life of 50 – 100 years. They require monitoring to ensure that parameters such as soil moisture are not changing, and that earthquakes or subsidence have not compromised the cap (CPEO, 2014). Caps have been built for radon gas and may provide a better analogue for CO_2 leakage than do non-radioactive waste repositories, unfortunately there seems to be very little description of such systems in the literature. Costs for barrier components are given in Daniel and Koerner (2007), but are taken from Shepherd et al. (1993) and so are substantially out of date.

5.3.1.2 Hydrodynamic isolation

This is a variant of pump-and-treat, whereby one or more boreholes are used to extract porewater from an aquifer, and the boreholes are so placed that all the porewater which flows through the contaminated zone is extracted to the surface (Fetter, 1999; Figure 7). The advantage of this approach is that the contaminant plume is stabilised, preventing the plume from reaching the uncontaminated parts of the aquifer. The contaminated water may require to be treated, after which it can be re-injected into the subsurface if desired, usually down-flow from the contaminated zone.

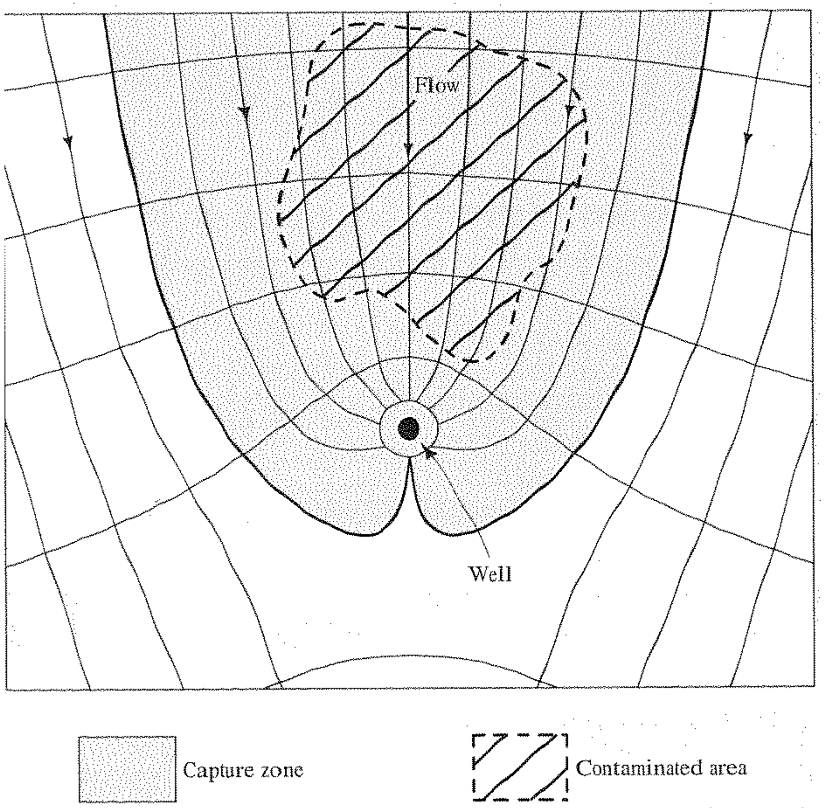


Figure 8 *Hydrodynamic isolation of the contaminated portion of an aquifer, plan view. From Fetter (1999)*

The technique has been developed for sparingly soluble pollutants, which remain in largely in place while a portion dissolves and is removed by groundwater flow. As such, this technique could be applicable to the remediation of CO_2 leakage. For example, if free phase CO_2 had accumulated in a shallow pericline (dome) within an aquifer (so that the CO_2 was trapped by buoyancy within the dome) but the flow of ground water was taking dissolved CO_2 from the free-phase accumulation, and transporting it along the aquifer, then hydraulic isolation would prevent the spread of the dissolved CO_2. The isolation technique is especially useful if a delay is anticipated in implementing a more permanent remediation solution, either while a study is undertaken, or because legal action over the costs of remediation is anticipated to delay the implementation of any more costly techniques.

In the event that the surface treatment plant must shut down temporarily, perhaps for routine maintenance, then Fetter (1999) suggests that the pumping and re-injection of untreated water may be preferable to the cessation of pumping, as the latter option may allow the plume to spread beyond the limits of the stabilised zone. With multiple well systems, there is the possibility of shutting one well periodically for maintenance, while maintaining effective isolation.

5.3.1.3 Air stripping

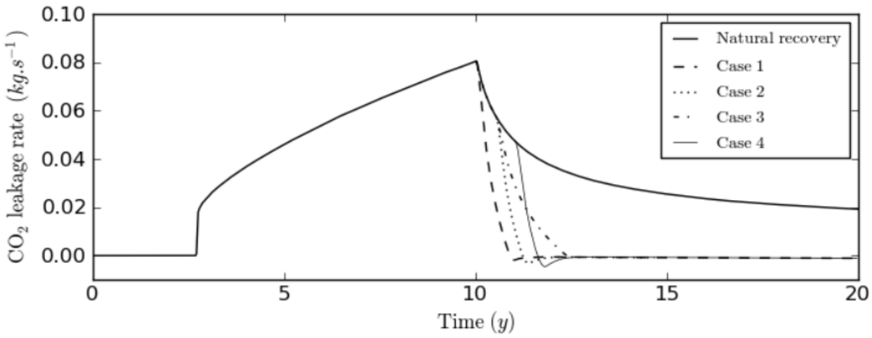
A pump and treat method. The contaminated water is pumped for surface treatment, where air is pumped through CO_2 saturated water and the CO_2 is removed through evaporation. The contaminated water is sprayed into a packing material designed to increase surface area, air is blown over the water at the base of the tank, the CO_2 vapours collected by accumulation and the separated clean water collected. The process is relatively quick and cheap but will depend on CO_2 concentration or volume (Khan et al., 2004). The method does not remove the residually trapped CO_2 in the formation so this may need additional treatment.

5.3.2 Water injection

The purpose of water injection is to dissolve the gaseous CO_2 and increase capillary trapping (Esposito and Benson, 2012). The treatment differs from a pump and treat method in that it does not involve bringing either water or CO_2 to the surface. Instead the free-phase CO_2 is immobilized as residual saturation falls below the critical saturation, isolating 'bubbles' of CO_2 within the pore spaces with an relative (effective) permeability of zero.

5.3.3 Hydraulic barrier

A hydraulic (or pressure) barrier is a remediation technique that can be used for the scenario that a storage reservoir is leaking into an overlying aquifer via a previously undetected leak path, such as a fault or borehole. Water is injected into the aquifer, with the objective of raising the pore fluid pressure of the aquifer sufficiently to counter the buoyancy force that is driving the vertical migration of the CO_2.



Case	Brine injection design			CO2 in the shallower aquifer after 1000 years	
	Delay (month)	Flow-rate (m3/h)	Duration (month)	in tons	Part having leaked after 10 years
Natural recovery	0	0	0	166250	96%
1	0	30	12	6640	4%
2	6	30	10	7141	11%
3	6	15	18	7359	14%
4	12	30	8	7351	14%

Figure 9 *Remediation using the hydraulic barrier method after CO_2 injection stops at 10 years and at a time when 6342 tons of CO_2 were in the shallower aquifer. From Réveillère and Rohmer (2011).*

Similar results are presented in Réveillère et al. (2012; Figure 9). Both papers conclude that the pressure barrier method is very successful where leakage is into an overlying aquifer, and where intervention begins fairly quickly. Highly permeable aquifers can present problems where water injection rates would have to be unrealistically high. Correctly locating the point of leakage is also important, as an injection well even 1 km from the leak point is significantly less effective, taking almost 3 years to prevent flow in the modelled case, as opposed to less than 6 months for a well within a few metres of the leak.

5.3.4 Summary of fluid control remediation measures

Table 5 presents a summary of the fluid control remediation methods. The table presents a short summary of the principals of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 5 Summary of the fluid control remediation methods

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Pump and Treat	Ground water is pumped from wells to an above ground treatment system that removes the CO_2. Pump and treat can also be used to contain the contaminant plume to stop it spreading by pumping the contaminated water towards the wells.	CO_2-rich water is brought to the surface, and then it must be treated to remove the CO_2 before it can be re-injected. Toxic metals must also be removed before re-injection.	IEA GHG (2007) suggests aerating the water to remove the CO_2. Given the low solubility of CO_2 in water and the likely low concentrations of CO_2 in the air that is used in the aeration process. It is therefore highly likely that the CO_2 will be vented to the atmosphere.	Esposito and Benson (2012) conclude that small plumes of CO_2 can be remediated effectively through a single vertical well located in the middle of the contaminated zone over a time scale of a few years. Larger plumes require horizontal wells and timescales in excess of 10 years.
Pump and treat with cap or vapour barrier - Impermeable barrier	The flux of CO_2 from a subsurface leak could be halted by an impermeable cap or vapour barrier. CO_2 would be pumped from below the barrier and treated using pump and treat.	Caps are useful to prevent rain leaching from the surface. The caps work best where most of the CO_2 is above the water table and tend to have a design life of 50-100 years.	Caps have been built for Radon gas capping so indicate that they may be suitable for CO_2 applications. If caps are combined with pump and treat it should be an effective technology.	Caps require monitoring as they may be compromised by earthquakes or subsidence. Cost will depend on extent of barrier and barrier material.
Water injection to dissolve the CO_2	Residually trapped as immobile gas phase CO_2 can be removed by dissolving it in injected water and extracting it as dissolved phase for surface treatment and possible re-injection.	A pump and treat method.	Does not remove CO_2 from the aquifer, so if remediation goal is to remove CO_2 additional measures required	May be a useful short term method to reduce the concentration of CO_2; however it will not remove all the residually trapped CO_2.
Hydrodynamic isolation	This is a variant of pump-and-treat, whereby one or more boreholes are used to extract porewater from an aquifer, and the boreholes are so placed that all the porewater which flows through the contaminated zone is extracted to the surface for treatment and possible re-injection.	The CO_2 contaminated water may require to be treated, after which it can be re-injected into the subsurface if desired, usually down-flow from the contaminated zone.	If the flow of ground water was taking dissolved CO_2 from the free-phase co2 accumulation, and transporting it along the aquifer, then hydraulic isolation would prevent the spread of the dissolved CO_2.	It stabilises the CO_2 plume, preventing its spread into the uncontaminated reservoir.
Air stripping	Air is pumped through CO_2 saturated water and the CO_2 is removed through evaporation	A pump and treat method – contaminated water is sprayed into a packing material designed to increase surface are, air is blown over the water at the base of the tank, the CO_2 vapours collected by accumulation and the separated clean water collected.	Does not remove the residually trapped CO_2 in the formation so may still need additional treatment	Process is relatively quick and cheap but will depend on CO_2 concentration or volume.
Hydraulic barrier	Water is injected into the aquifer, with the objective of raising the pore fluid pressure of the aquifer sufficiently to counter the buoyancy force that is driving the vertical migration of the CO_2.	Effective when a storage reservoir is leaking into an overlying aquifer via a previously undetected leak path, such as a fault or borehole.	Réveillère et al. (2012) conclude that the pressure barrier method is effective if there is quick intervention, the aquifer is not very highly permeable and the source of leakage is accurately located.	Effective if there is quick intervention, the aquifer is not very highly permeable and the source of leakage is accurately located.

5.4 Remediation techniques (2) – Cut-off Wall in an unconfined (surface) aquifer

The aim of a cut-off wall is to isolate one portion of an aquifer from another portion, for example to isolate the contaminated portion of an aquifer from an uncontaminated portion, or to interrupt a flow path that would carry CO_2 or mobilised toxic metals towards, for example, a residential area. Experience in this field is from the landfill industry; the remediation of contaminated land; and hydraulic and foundation engineering particularly for dams (e.g. Weaver and Bruce, 2007). Imperfections in the wall can reduce effectiveness considerably: a 1 m^2 hole can allow as much water bypass as 100,000 m^2 of good quality wall (Dűllmann, 1999 in Meggyes, 2005). Walls can be either single, or a chamber geometry can be adopted, where by 2 parallel walls are linked at c. 50 m intervals by cross walls. The porewaters within the chambers can be individually pumped, and monitored for leakage. The scale of cut-off walls can be large – a 3.7 km long cut-off wall chamber system was constructed to contain the landfill in Vorketzin, near Berlin, where waste from the former West Berlin had been deposited (Kellner and Scheibel, 2004, cited in Meggyes, 2005). Costs are substantial too, specimen outline economic estimates by Hiebert (1998, in Meggyes, 2005) are a cost range of US$ 6.5 - 10.7 million for a biobarrier and US$ 9.8-13.5 million for a grout curtain 3200 m long and 30 m deep. A sheet-pile wall only 12 m depth but of the same length would cost US$15-17 million (2005 prices).

Meggyes (2005) summarises the available construction methods for cut-off walls, including a summary table from Jessberger (1992, translated from German) and an example cost calculation. The techniques described in Meggyes (2005) allow the construction of cut-off walls to more than 100 m below the ground surface:

5.4.1 Excavation and replacement, the traditional method:

For a single phase diaphragm wall, individual panels 0.4 – 1.0 m thick are constructed in a trench which is typically 0.6 – 1 m wide and up to 18 m deep if dug with backhoe, or up to 36 m deep, if dug with clam-shell shovel (Need and Costello, 1984). A self-hardening slurry is pumped into the trench, e.g. bentonite-cement mix. In the ‘Pilgrim’s

Pace' method (Meggyes, 2005), the wall in made of panels, of which alternating ones are formed in the first phase (i.e. panels 1, 3, 5 etc). When the filler has hardened after 36 – 48 hours, the intermediate panels (2, 4, 6 etc) are dug out, removing 0.3 – 0.6 m of the ends of the primary panels leaving clean surfaces. As the primary panels are not yet hardened, infilling the gaps results in a seamless wall.

5.4.2 Two-phase diaphragm wall (> 50 m depth).

In this construction method, the trench is held open during digging by a slurry of bentonite and water, which acts in a similar way to drilling mud during the drilling of a borehole. The fluid in the slurry penetrates the permeable formation of the trench walls leaving a filter cake (Fetter, 1999, p.434). In the second phase, the bentonite slurry is replaced by the final barrier material using tremie pipes. The wall is constructed in panels bounded by stop-end tubes, which can cause imperfections in the final wall once removed. To ensure efficient replacement of the initial bentonite slurry, the density of the cut-off slurry must exceed that of the bentonite slurry by at least 500 kg/m^3.

5.4.3 Composite diaphragm wall (c. 30 m depth)

In both the above methods, additional elements can be inserted into the wall, such as sheet plies, glass walls or tiles, and geomembranes (the most common). The aim is to improve strength and / or water tightness.

5.4.4 Interlocking bored-pile diaphragm wall (c. 20 m depth)

An interlocking bored-pile diaphragm wall is constructed with secant piles, which are overlapping holes filled with concrete. One pile cuts into the next so that they are in direct contact, along an arc of the intact pile. The piles are constructed in a sequence of 1,3, 5 followed by the overlapping 2, 4, 6 etc.

5.4.5 Displacement of soil and installation of sealing material

Thin wall (18 – 23 m depth) - firstly sheet piles, then heavier steel beams are vibrated into the ground and a clay-cement-water mix is injected into the void as the beams are retracted. The panels are cut into the adjacent ones, so ensuring that there is an overlap and water-tightness. A high density slurry of c. 16000 kg/m^3 is required to prevent closure of the hole while the pile is being retracted. A well-proven mixture is 25 kg bentonite; 175 kg Portland cement; 800 kg rock flour and 640L water (Arz, 1988).

For a sheet-pile wall, sheet plies are manufactured from steel, or less commonly aluminium, concrete or wood. These are driven into the ground. There is minimal disposal of soil or other contaminated material, and with modern ‘labyrinth’ joints or sealing pastes and plastic sealants there is little leakage.

5.4.6 In-situ permeability reduction

5.4.6.1 Injection

A cement-suspension, artificial resin or water glass-based material is injected through boreholes. The separation between boreholes depends upon the rock permeability, the viscosity of the injected fluid, and the maximum pressure of injection.

5.4.6.2 Jet grouting

Soilcrete columns are constructed using a rotary drilling technique, with a high density mud for both cutting medium and sealant.

5.4.6.3 Frozen wall

Pore water is converted into ice by the continuous circulation of a cryogenic fluid within a system of small diameter closed ended pipes installed in a pattern to match the contaminated area. The frozen water acts as a bonding agent fusing together particles of soil or rock to significantly increase strength and decrease permeability. The technique is most probably of no value over geological timescales as it requires the active (powered) circulation of refrigerant or liquid nitrogen. However, the technique could be of use in the short term (e.g. for temporary containment) for example if the source of the CO_2 contamination was sealed, leaving only shallow contamination to be remediated.

5.4.6.4 Bio-barrier.

The injection of bacteria to form biofilm barriers or bio-barriers in permeable formations which plug, clog or foul the pore network to contain or reduce the migration of the CO_2. Reductions in the hydraulic conductivity of one to three orders of magnitude have been reported (Denis and Turner, 1998). For bio-barriers to be effective the temperature must be suitable, and nutrients and food must be present; if conditions are not ideal the technique will not work. The resulting biofilm must also be resistant to CO_2.

5.4.6.5 Water control agent.

This technique utilises the injection of water control agents into the pore network to block the flow of CO_2 contaminated water. Utilises technology developed in the hydrocarbon industry to plug high permeability thief zones (Halliburton, 2014). Work is needed into the resistance of proprietary water control agents to CO_2.

5.4.6.6 High strength rigid set material

This technique utilises the injection of a rigid setting polymer into the pore network to block the flow of CO_2 contaminated water. Utilises technology developed in the hydrocarbon industry (Halliburton, 2014). Work is needed into resistance of proprietary high strength rigid set materials to CO_2.

5.4.6.7 Organic polymer sealant

This technique utilises the injection of an organic cross-linked polymer into the pore network to block the flow of CO_2 contaminated water. Utilises technology developed in the hydrocarbon industry (Halliburton, 2014). Work is needed into resistance of proprietary organic polymer sealant materials to CO_2 on the timescale relevant to CO_2 storage.

5.4.6.8 Super absorbent crystals

This technique utilises the injection of super absordant crystals into the pore network to block the flow of CO_2 contaminated water. It utilises technology developed in the hydrocarbon industry, Halliburton (2014). Work is needed into resistance of proprietary super absorbent crystals to CO_2.

5.4.7 Summary of cut-off wall in unconfined surface aquifer remediation measures

Table 6 presents a summary of the cut-off wall in unconfined surface aquifer remediation methods. The table presents a short summary of the principles of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 6 Summary of the cut-off wall in unconfined surface aquifer remediation methods

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Cut-off wall / Slurry wall: Excavation and replacement	The aim of a cut-off wall is to isolate one portion of an aquifer from another portion, for example to isolate the contaminated portion of an aquifer from an uncontaminated portion, or to interrupt a flow path that would carry CO_2 or mobilised toxic metals towards, for example, a residential area	Single phase diaphragm wall (up to 35 m depth). A trench is excavated and filled with stabilising slurry typically bentonite cement and water. The slurry forms a filter cake with low hydraulic conductivity on the side walls of the trench and the remaining cement slurry then sets.	Important considerations in the slurry are solid content, type of bentonite and type of cement and care should be taken to ensure these materials are CO_2 resistant.	Requires a full excavation trench over what could be considerable distances and depths. Imperfections in the wall can reduce effectiveness considerably. Although cut-off walls are not used extensively for long-term containment, they may be used in conjunction with other remediation technologies to aid in temporary, partial containment
Excavation and replacement: Two-phase diaphragm wall	The first phase is the same as a single phase wall described above. In addition the bentonite slurry is replaced with a different final barrier material that has a higher density than the bentonite slurry	Two-phase diaphragm wall facilitates walls >50m depth.	The inner core material can be of a material with enhanced CO_2 resistant properties.	As above
Excavation and replacement: Composite diaphragm wall	In addition to the two phases of slurry and final barrier material further elements can be inserted into the wall such as sheet piles or geo-membranes.	The aim of the additions to the wall structure is to enhance strength and / or water tightness.	The addition of a geo-membrane can enhance the CO_2 resistant properties of the cut-off wall.	As above
Excavation and replacement: Interlocking bored-pile diaphragm wall	In addition to the two phases of slurry and final barrier material interlocking piles are inserted.	The aim of the addition of interlocking piles into the wall structure is to enhance strength and / or water tightness.	The addition of interlocking piles into the wall structure can enhance the CO_2 resistant properties of the cut-off wall.	As above
Installation of thin wall and sheet pile into the soil	Piles are vibrated into the ground and a clay-cement-water mix is injected. The piles are cut into the adjacent ones, so ensuring that there is an overlap and water-tightness	There is minimal disposal of soil or other contaminated material, and with modern 'labyrinth' joints or sealing pastes and plastic sealants there is little leakage	Impermeable CO_2 resistant materials can be used.	There is a significant reduction in amount of soil excavated. However corrosion is a problem with respect to the use of sheet-pile walls.
In-situ permeability reduction: injection permeation grouting	Permeation grouting is the injection of a liquid grout that fills the natural porosity and then gels to form a solid void-filling material A cement-suspension, artificial resin or water glass-based material is injected through	There is concern over the integrity of the containment system and potential leakage of CO_2 through gaps in the barriers, such as high permeability zones between the grout. The	Care should be taken to ensure that the cement-suspension, artificial resin or water glass-based material is CO_2 resistant.	Concern over the integrity of the containment system and potential leakage of CO_2 through gaps in the barriers, such as high permeability zones between the grout. Although jet grouting barriers do not provide long-term containment, they

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
	boreholes into the porous soil.	separation between boreholes depends upon the rock permeability, the viscosity of the injected fluid, and the maximum pressure of injection.		could be used in conjunction with other remediation technologies to aid in temporary, partial containment.
In-situ permeability reduction: jet grouting (deep soil mixing)	Jet grouting uses high-energy emplacement of cement or chemical grout materials whereby the sediment is displaced and mixed with the grouting material.	There is concern over the integrity of the containment system and potential leakage of CO_2 through gaps in the barriers, such as high permeability zones between the grout.	Jet grouting cement, biofilms, foam, gels must be CO_2 resistant	Although jet grouting barriers do not provide long-term containment, they could be used in conjunction with other remediation technologies to aid in temporary, partial containment.
In-situ permeability reduction: frozen wall	A coolant is continuously circulated through refrigeration pipes which are embedded in the ground. The coolant will be at around -20°C which will freeze the surrounding soil and create the wall.	The entire system is closed; no materials are injected into the ground	Requires the active (powered) circulation of refrigerant coolant or liquid nitrogen.	Most probably of no value over geological timescales as requires the active (powered) circulation of refrigerant or liquid nitrogen. Though could be of use in the short term (e.g. for temporary containment) for example if the source of the CO_2 contamination was sealed, leaving only shallow contamination to be remediated
Bio-barrier	The injection of bacteria to form biofilm barriers or bio-barriers in permeable formations which plug, clog or foul the pore network to contain or reduce the migration of the CO_2	Reductions in the hydraulic conductivity from one to three orders of magnitude have been reported using many types of bacteria including stimulation of indigenous bacteria (biostimulation), and injection of full-sized living and dead bacteria (Dennis and Turner 1998).	For bio-barriers to be effective the right temperature, nutrients and food must be present, if conditions are not ideal it won't work. The resulting biofilm must also be resistant to CO_2	Possibly unlikely to be suitable for CO_2 remediation as to get ideal concentrations for biofilm generation require very specific conditions, the biofilm must be CO_2 resistant of the bacteria use the CO_2 as food plus the timescales will be long.
Water control agent	Utilises the injection of very capable water control agents into the pore network to block the flow of CO_2 contaminated water.	Utilises technology developed in the hydrocarbon industry to plug high permeability thief zones.	Work needed into resistance of proprietary water control agents to CO_2.	Technology available and low cost. Resistance to CO_2 untested.
High strength rigid set material	Utilises the injection of rigid set polymer to block matrix to flow	Utilises technology developed in the hydrocarbon industry.	Work needed into resistance of proprietary rigid set polymer to CO_2.	Technology available and low cost. Resistance to CO_2 untested.
Organic polymer sealant	Utilises the injection of Organic cross-linked polymer blocks matrix to flow	Utilises technology developed in the hydrocarbon industry.	Work needed into resistance of proprietary Organic cross-linked polymer to CO_2.	Technology available and low cost. Resistance to CO_2 untested.
Super absorbent crystals	Utilises the injection of Cross-linked polyacrylamide superabsorbent crystals for flow barrier	Utilises technology developed in the hydrocarbon industry.	Work needed into resistance of proprietary Cross-linked polyacrylamide superabsorbent crystals to CO_2. Works Best in fractures	Technology available and low cost. Resistance to CO_2 untested.

5.5 Remediation techniques (3) – Cut-off walls in fractured rock (Grout curtains)

The migration of naturally occurring CO_2 along faults and fractures has been documented at several sites worldwide, e.g. Keating et al. (2014); Wilkinson et al. (2009). In any inverted sedimentary basin, which will include many basins that are currently onshore, there is the possibility that the surficial rock will have been buried to substantial depths prior to uplift and erosion. This burial causes compaction of the rock, lithification or induration, and the reduction in porosity and permeability. Many such rocks have been subjected to tectonic forces, for example during basin inversion and uplift, and are now fractured. The resulting bulk properties of the rock, with respect to fluid flow, may be dominated by the fractures if the rock matrix is effectively impermeable, or a by the dual-porosity network of fractures plus matrix porosity if the latter is significant. In either case, a substantial body of expertise exists that has been developed associated with the engineering of the foundations of dams, which must be made effectively impermeable to water flow (e.g. Weaver and Bruce, 2007).

The technologies used for remediation in fractured rock may be the same as those used in the remediation of pollution in porous media (Bruell and Inyang, 2000), or these techniques may not be appropriate. However, the engineering properties of highly indurated but fractured rock are not the same as less indurated but porous rock, so that there are important differences. Natural fracture systems are extremely heterogeneous, with highly variable number, density, size, and direction of fractures. A potential problem is that of very low bulk permeability, so that a pollutant may be very difficult to extract from the fracture system using the standard shallow remediation techniques (soil vapour extraction; air sparging; bioremediation). In the case of contamination by highly toxic organic chemicals, standard practise has involves fracturing the low permeability rock, to increase bulk permeability (Bruell and Inyang, 2000). Both hydrofracturing and pneumatic fracturing are used, the latter is identical in principle to the procedure used for ‘fracking’ in shales associated with the production of shale oil and gas. In this case, the ‘fracking’ fluid needs to be sufficiently viscous so that it will not flow into the formation, so that a biodegradable gel (e.g. cross-linked food grade guar gum) and sand are used. An enzyme is also added, which later degrades the biodegradable gel, leaving the fractures open to fluid flow. The sand acts as a 'proppant', preventing the fractures from closing when the pressure is reduced. Pneumatic fracturing relies upon self- propping as a proppant cannot be added to the injected air, an example of self-propping mechanisms include block shift. While fracturing is a rapidly moving field, the reported spatial extents of fracture propagation for remediation are rather limited, only mm-scale fractures extending less than 10 m for pneumatic fracturing and up to 1.0 cm fractures extending only 10 m for fluid fracturing (Suthersan 1997; Nyer et al. 1996).

The following investigative techniques are used to characterise fractured rock sites (Paillet 1991; Shapiro and Hsieh, 1991; Bruell and Inyang, 2000; Weaver and Bruce, 2007):

1) Surface and regional geology including mapping if not available at a suitable resolution or if fractures are not well mapped;
2) Trenching for enhanced geological mapping;
3) Photointerpretation (for regional fracture patterns);
4) Exploratory drilling;
5) Surface geophysics including refraction seismic surveys;
6) Borehole geophysics;
7) Cross-hole tomographic imaging using seismic or electromagnetic sources;
8) Geochemical analysis,
9) Tracer testing;
10) Acoustic televiewers to produce a photo-like image of borehole walls (using a scanning ultrasonic beam) for characterising fractures with respect to position, strike, dip, and relative aperture (Paillet 1991);
11) Cross-hole flow logging utilising packers to isolate individual fractures intersecting boreholes, by positioning packers above and below the fracture of interest. Pumping of individual fractures can be used to reveal interconnectivity and hydraulic properties of selected fracture groups.

The aim is to predict the fluid and chemical movement at a site. Bruell and Inyang (2000) note that, in fractured rock, site characterization can be expensive due to the cost of boreholes and the often complex and lengthy field testing. Weaver and Bruce (2007) emphasise that the site geology and hydrogeology must be understood before any plan of remediation can be drawn up. Important aspects of the hydrogeology include (Weaver and Bruce, 2007):

1) Any surface streams feeding the groundwater table;
2) Any shallow perched groundwater;
3) The relationship between the piezometric surface and the ground surface;
4) The lowest pietzometric level;
5) Seasonal variations in the pietzometric level;
6) The direction and flow of the groundwater.

The bedrock type influences grouting procedures and the likelihood of success (Weaver and Bruce, 2007), with the following common rock types:

1) Shales and mudrocks – very variable in character, and often with poor bonding vertically, so that grout separates and penetrates bedding planes, but achieves little penetration into either pre-existing fractures or matrix porosity;
2) Interbedded sands and mudstones – the more brittle sandstones are commonly jointed due to unloading, and may require elaborate curtain grouting;
3) Weakly cemented sandstones – joints and fractures filled with weakly consolidated sand may be impossible to grout successfully;
4) Conglomerate – performance depends on the degree of cementation of the matrix;
5) Limestones – solution caverns present obvious problems;
6) Gypsum and anhydrite – may be impossible to grout;
7) Volcanic and pyroclastic rocks – lava tubes and cooling joints are challenging;
8) Granite and metamorphic rocks – it is unlikely that the remediation of a CO_2 leak would involve these rock types.

The permeability of the fractured rock is crucial to the design of a grouting programme as conventional grouting materials will not penetrate the very fine fractures associated with low permeabilities (Weaver and Bruce, 2007). In-situ bulk rock permeability is conventionally measured using flow tests in boreholes, on 3 – 5 m length sections of the borehole. Longer test intervals are not recommended, on grounds that the results cannot be adequately tied to the subsurface geology. If high permeabilities are detected at low test pressures (10^{-3} cm/s; Waever and Bruce, 2007) then tests at higher pressures are not required. With lower permeabilities ($1 - 5 \times 10^{-4}$ cm/s) then flow tests at higher pressures (500 – 1500 kPa) should be run for 5 or 10 minute intervals. The Lugeon unit, which is defined as a water pumping rate of 1 L/m of hole per minute of test at a pressure of 10 atmospheres, is the permeability unit most commonly used in connection with grouting. Because application of water at a pressure of 10 atm at shallow depth would be potentially damaging to many foundations, testing of permeability is commonly conducted at a lower pressure, and the permeability under 10 atmospheres is calculated. This is referred to as the modified Lugeon test (Weaver and Bruce, 2007, p.382).

Unless very high quality data is available from an analogue site, it is considered to be prudent to conduct a test grouting programme (Weaver and Bruce, 2007, p. 67). This will determine:

1) The residual permeability after grouting (otherwise expressed as the coefficient of permeability reduction), a parameter that cannot be determined by any other method;
2) The average grout consumption for each step;
3) The maximum allowable spacing between the centres of the boreholes for the final grouting stage.

Grout curtains are constructed by injecting grout into one or more rows of boreholes drilled for that purpose. The initial (primary) holes are relatively widely spaced (6 – 12 m apart; Weaver and Bruce, 2007, p. 72), so that the grout is unlikely to flow from one hole to another. The spacing between these holes is then split midway by secondary holes. This split-spacing sequence is repeated with tertiary holes, quaternary holes, and so on until the progressive reduction in the volume of grout injected into the holes or, more significantly, the results of permeability tests made in the final holes indicate that the design criterion for permeability reduction has been achieved. Note that Weaver and Bruce (2007, p.72) recommend that the predicted number of boreholes should be deliberately over-estimated, and suggest that 50 % is a suitable safety margin. In the event that the initial estimate is too low, then both time and cost over-runs are unavoidable, with predictable consequences.

Boreholes for grouting are traditionally drilled perpendicular to the landscape, with the aim of building as curtain of constant thickness, or to drill vertically for a constant length. Ideally, boreholes would be oriented so that all likely orientations of fractures are intercepted and sealed, with the specific aim of avoiding drilling parallel to the orientation of any significant fracture set (Weaver and Bruce, 2007, p. 72). Although single-row configurations of boreholes has been used, because of the possibility of incomplete grout penetration, then Weaver and Bruce (2007, p. 73) recommend the multiple-row curtains. In the USA, a three row configuration (for dam foundations) is commonly adopted, though the outer rows are not grouted to be independently sealing. If two rows are used, they can be drilled at opposing angles rather than parallel to each other.

Injection of grout into each hole is done in a series of stages of selected length that may vary with the depth of the stage and the geological conditions encountered. Depending principally on the condition of the rock related to its mechanical competence, either descending stage grouting (downward stages) as the hole is being drilled may be required, or grouting may take place as a series of ascending stages (ascending stage grouting) temporarily sealed off with a packer after the hole has been drilled and remains open and stable to the final planned depth.

Grouting materials can be classified as follows (Weaver and Bruce, 2007; p. 87):

1) Particulate (suspension or cementitious) grouts. Mixtures of water and cement plus other particulate solids such as fly ash, clays, or sand, and chemical additives. They may be stable (i.e., have minimal bleeding) or unstable when left at rest;
2) Colloidal solutions, in which viscosity progressively increases with time. Often sodium silicate-based;
3) Pure solutions, in which viscosity is essentially constant until setting. Often resin-based;
4) Others, used relatively infrequently and only in certain applications requiring special performance characteristics.

The composition water used in the grout mix can have significant effects upon grout performance, for example suspended solids or dissolved sulphates are to be generally avoided (Weaver and Bruce, 2007). This may be a significant consideration for the construction of grout curtains in areas with an arid or semi-arid climate. The composition of cements (both Portland and otherwise) and other components of grout is considered in great detail by Weaver and Bruce (2007). Important factors of the final grout mix are the rheology; viscosity; cohesion; specific gravity; settlement (i.e. the tendency for water to escape from the grout while at rest); filtration pressure (i.e. the ease with which filter cake builds up on the walls of the boreholes); grain size and water-repellence (and hence resistance to washing out when injected below the water table; Weaver and Bruce, 2007).

The penetration of the grout is controlled by the following properties of the rock fractures: aperture dimensions; surface roughness; hydraulic routing (hydraulic percolation pathways within the fracture network); tortuosity; porosity; and permeability (Weaver and Bruce, 2007). The effectiveness of the grouting is affected by procedural factors including: drilling methods and procedures; borehole deviation; the choice of circulating medium within the borehole (the drilling mud in oil industry terminology); the staging of the drilling and the protection of the open boreholes from the ingress of contaminants and detritus (Weaver and Bruce, 2007). Factors which influence the durability of the grout curtain, which may be crucial in the case of a long-term leak of CO_2, include:

1) The geochemical environment, i.e. presence or absence of deleterious minerals in the host rock (Osende, 1985, and Mielenz, 1962, present a list which includes minerals abundant in virtually every common rock type!);
2) The nature of the groundwater, whether aggressive or not to the grout;
3) The hydraulic gradient, a high gradient may shear the grout; will exacerbate dissolution; and will enhance mechanical erosion rates;
4) The erodability or solubility of the host rock, especially if minerals such as gypsum or anhydrite are present.

In the specific case of the remediation of a leak of CO_2, then a grout that is reactive to CO_2 could be used (Ito et al., 2014). Reaction between the silicate solution and CO_2 causes the precipitation of amorphous silica. Laboratory experiments show a 99% reduction in permeability in a glass-bead artificial rock with an initially high permeability of several Darcy's.

5.5.1 Summary of cut-off wall in fractured rock remediation measures

Table 7 presents a summary of the cut-off wall in fractured rock remediation methods. The table presents a short summary of the principles of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 7 Summary of the cut-off wall in fractured rock remediation methods.

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Hydrofracking	Natural fracture systems are extremely heterogeneous and a potential problem is that of very low bulk permeability. Fracturing the low permeability rock, to increase bulk permeability. Both hydro-fracturing and pneumatic fracturing are used. This facilitates and more thorough deployment of the grout material.	The 'fracking' fluid needs to be sufficiently viscous so that is will not flow into the formation, so that a biodegradable gel (e.g. cross-linked good grade guar gum) and sand are used. An enzyme is also added, which later degrades the biodegradable gel, leaving the fractures open to fluid flow. The sand acts as a 'propant', preventing the fractures from closing when the pressure is reduced.	The hydrofracking simply facilitates the application of the sealing material into the fractured rock more effectively and must be used in conjunction with a filling and clogging grout material.	Facilitates greater dispersion of the clogging grout material, but risks increasing the CO_2 leakage.

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Grout curtain	Grout curtains are constructed by injecting grout into one or more rows of boreholes. Ideally, boreholes would be oriented so that all likely orientations of fractures are intercepted and sealed. Injection of grout into each hole is done in a series of stages of selected length that may vary with the depth of the stage and the geological conditions encountered. Depending principally on the condition of the rock related to its mechanical competence	The permeability of the fractured rock is crucial to the design of a grouting programme as conventional grouting materials will not penetrate the very fine fractures associated with low permeabilities. Bedrock type influences grouting procedures and the likelihood of success. The penetration of the grout is controlled by the following properties of the rock fractures: aperture dimensions; surface roughness; hydraulic routing (hydraulic percolation pathways within the fracture network); tortuosity; porosity; and permeability	Important factors of the final grout mix are the rheology; viscosity; cohesion; specific gravity; settlement (i.e. the tendency for water to escape from the grout while at rest); filtration pressure (i.e. the ease with which filter cake builds up on the walls of the boreholes); grain size and water-repellence. In the specific case of the remediation of a leak of CO_2, then a grout that is reactive to CO_2 could be used. Reaction between the silicate solution and CO_2 causes the precipitation of amorphous silica.	Boreholes ideally orientated to intersect as many fractures as possible, fracture permeability important and can be enhanced through hydrofracking. Grout material must be compatible with CO_2.

5.6 Remediation techniques (4) - Treatment walls (or Permeable Reactive Barriers, PRB's)

Treatment walls (or permeable reactive barriers, PRB's) are structures installed in the shallow subsurface that trap or alter pollutants that are carried though the wall by natural groundwater flow (EPA, 1996), Figure 10. Treatment walls work best with a porous and permeable aquifer with a 'high' rate of water flow (EPA, 1996). The pollutants are either:

1) Adsorbed onto the porous and permeable fill of the wall, involving some or all of chemical adsorption; ion exchange, co-precipitation, solid-solution formation (Roehl et al., 2005). Usually there is no change in the oxidation state of the contaminant metal. The specific surface area of the absorbant is critical;
2) Precipitated as an insoluble salt by reacting with the fill of the wall;
3) Degraded into harmless by-products by biologically mediated reactions.

Barrier fills typically include activated charcoal and iron fillings, numerous examples of experiences with both fill types are described by Roehl et al. (2005). The flow of water can be directed towards the wall by impermeable barriers installed within the aquifer, the so-called 'funnel and gate' system, (Figure 11), see sections on grouting and cutoff walls for the construction and other details of impermeable barriers within aquifers. The cost of the barrier will be an important factor in determining whether a continuous or funnel-and-gate configuration is used – a cheap fill material favours the continuous geometry. The cost of replacing spent reactive material is one of the factors that limit the utility of treatment walls (Freethey et al., 2005). Treatment walls can be permanent, semi-permanent or replaceable (Roehl et al., 2005, p.2).

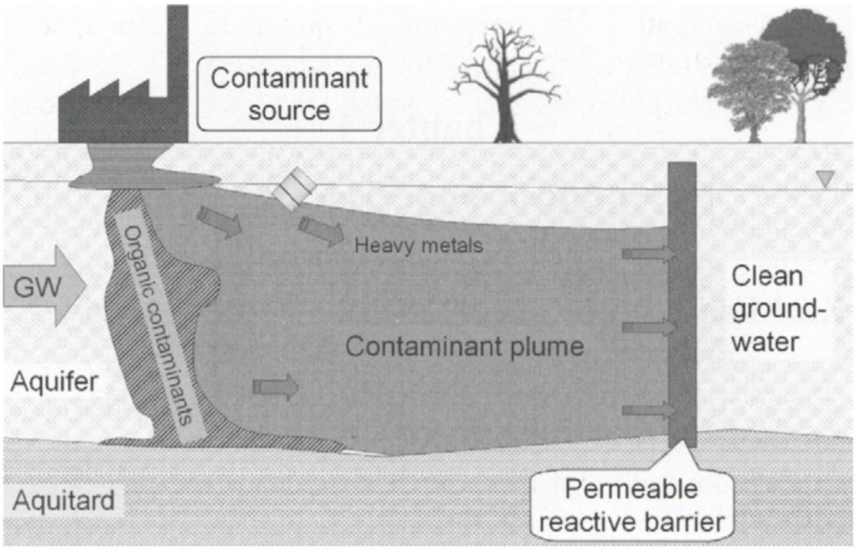


Figure 10 The treatment wall, or permeable-reactive barrier (PRB) concept as applied to conventional surface pollution. From Roehl et al. (2005)

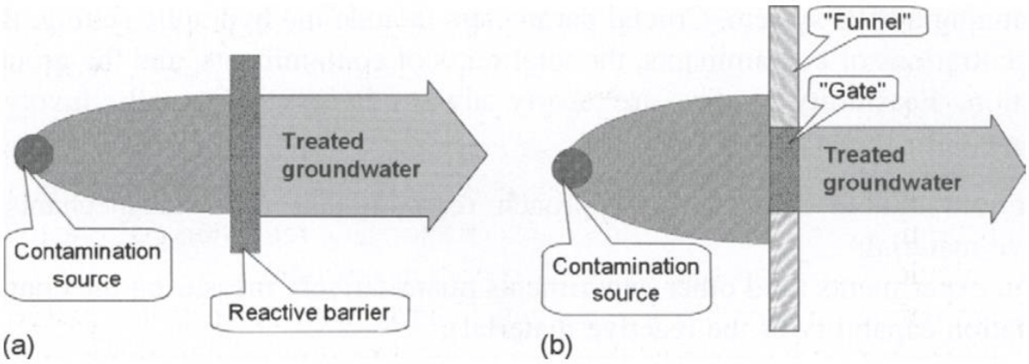


Figure 11 A continuous treatment wall (left) and the 'funnel and gate' configuration. From Roehl et al. (2005).

Because treatment walls are low maintenance and have no ancillary equipment such as tanks, pumps or containers, they can be used not only in industrial settings, but at least in principle in urban areas. Treatment walls offer several advantages over other remediation technologies (Carey et al., 2001):

1) Demonstrated as effective, but mostly for e.g. chlorinated solvents;
2) Below ground, so unobtrusive;
3) Passive, low environmental impact;
4) Retain the groundwater resource;
5) Minimal volume of soil and water to be handled;
6) Potentially low cost, with possible exception of monitoring operations;
7) Potential design lives of decades.

There are also disadvantages (Carey et al., 2001):

1) Decades may be needed to deal with a persistent source of pollution;
2) Long-term monitoring is required;
3) Site characterisation is often complex and costly;
4) Sub-surface structures can be problematic;
5) Deeper plumes (i.e. anything not in the top m or at most 10's m) problematic for construction and design;
6) Possible need to remove after use, or to renew reactive material;
7) Use is constrained by geological conditions, including fractured rocks.

Factors to be considered when planning and installing a treatment wall include (Roehl et al., 2005):

1) Property boundaries;
2) The position of underground utilities e.g. pipes, gas lines;
3) The disruption to existing site activities during the construction phase;
4) The need to dewater the construction pit, and the disposal of the water;
5) Logistics and management of material placement (e.g. quality control; homogeneous filing of the reactors; dust prevention etc.);
6) H&S issues;
7) Unforeseen ground conditions such as undetected subsurface structures such as old foundation walls.

Planning of the treatment wall should take into account at least the following factors (Roehl et al., 2005):

1) Choice of removal mechanism and the material itself;
2) Relevant experiments to determine the attenuation properties of the reactive material (column experiments, e.g. Banasiak and Indraratna, 2012);
3) The likely time the treatment wall will be required for;
4) The thickness of the barrier which must be sufficiently thick so that the pore water is in contact with the reactive material for sufficiently long to reduce contamination to acceptable levels.

The performance requirements for a treatment wall are (Meggyes, 2005):

1) Replaceability of the reactive materials;
2) Higher permeability than the surrounding reservoir (50 – 200 times higher);
3) Resistance to fines washed in from the reservoir;
4) Long life span.

The selection of a construction technique mainly depends on the character of the site (Gavaskar, 1999 in Meggyes, 2005):

1) Most importantly: depth. The deeper the target reservoir, the more specialist are the methods of construction re required, and the higher the costs;
2) Geotechnical character of the site: soil or rock strength; any subsurface obstacles;
3) Soil excavation, disposal of contaminated soil;
4) H&S during construction, e.g. entry of personnel into the excavation.

Although very shallow barriers (< 8 m, Meggyes, 2005) may consist only of the reactive fill, deeper barriers typically have a layered construction with a layer of gravel to filter fines from the inflowing pore water, to prevent entry to the reactive core. The top of the barrier is usually covered by a low permeability material, i.e. clay, to prevent contact with oxygen in the overlying air. Pumping and 'treatability' tests may have to be conducted prior to the onset of construction. Column tests are the standard technique used to assess the reactive material to be used for a given site (Meggyes, 2005).

The techniques used for the construction of treatment walls are similar to those described above for cut-off walls (Maggyes, 2005). To date, the majority of treatment walls have been installed by conventional excavation techniques – i.e. a trench is dug with an excavator, and simply filled from the surface with the reactive material (Freethey et al., 2005). The relatively shallow depth of operation (15 m) lead Manceau et al., (2014), in a review of techniques for the remediation of CO_2 leakage, to reject treatment walls as a viable technique. However, in a situation with CO_2 contamination in a thin surficial aquifer, perhaps fluvial or alluvial sediments resting on relatively impermeable basement, then the technique might have potential. Note that Freethey et al. (2005) suggest that 21 m is a more realistic depth limit assuming the availability of 'modified' excavators. Techniques for deeper installation include (Freethey et al., 2005 and refs therein):

1) Tremie tube (http://www.tremiepipe.com/) / mandrel;
2) Deep soil mixing within individual circular casings (caisson) using multiple augers with the reactive material injected through the hollow kelly bar of the mixing tools (Meggyes, 2005);
3) High-pressure jetting and milling – in low strength rocks, a slurry jet excavates the aquifer between vertical stop end tubes, while in stronger rocks, a milling head is driven by a hydraulic motor;
4) Vertical hydraulic fracturing - similar to the techniques developed for 'fracking' shale for oil and gas. A fluid with a 'proppant' such as sand is injected at high pressure. Can be used to place reactive material into an aquifer, or to generate zones of high permeability to direct fluids towards reactive gates (Meggyes, 2005). The reactive material cannot be recovered, placing limitations upon the nature of the material;
5) Deep well injection – reactive material is injected into a series of closely-spaced boreholes with no geometrical boundaries, merging to form a continuous wall. Ensuring that there are no significant gaps within the wall, allowing flow to

bypass the wall, is a problem. Injection can be into either induced fractures (as above) or into the natural porosity of the reservoir (Meggyes, 2005). With low permeability reservoirs, the injected material may be limited to liquids (i.e. not suspensions or slurries);

6) Deep aquifer remediation tools (DARTs): Freethey et al. (2005) and Maggyes (2005) describe this method for installing treatment walls in so-called 'deep' aquifers (deep in the context of groundwater treatment means that the aquifer is confined, i.e. is not immediately at the surface, and / or that the depth to the base of the aquifer exceeds c. 21 m). DARTs consist of a series of closely-spaced boreholes with rigid polyvinyl chloride shells, each with high-capacity flow channels that contains the permeable reactive material and flexible wings to direct the flow of groundwater into the reactive material. The reactive material used in a DART should be chosen to have a hydraulic conductivity 50 to 200 times greater than the hydraulic conductivity of the host aquifer material (Freethey et al., 2005). Configurations of DARTs are shown in Figures 12 and 13.

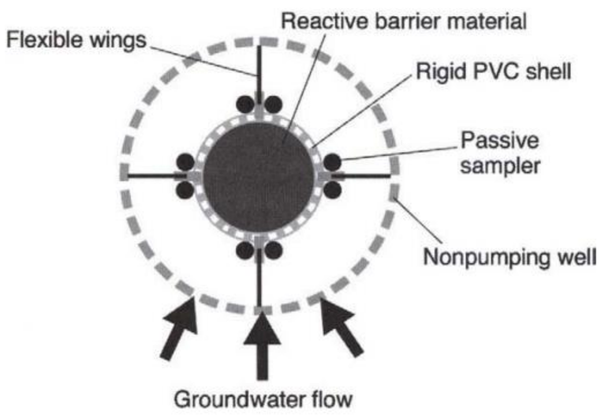


Figure 12 Schematic diagram of a deep aquifer remediation tool (DART), plan view. From Freethey et al. (2005).

Indicative cost estimates for treatment walls are given in Meggyes (2005, his Table 2.5). Regulatory and economic aspects of the use and construction of treatment walls are discussed in detail by Simon et al. (2005). The UK situation for regulation is summarised by the Environment Agency (Carey et al., 2002), who include screening criteria for the feasibility of a project.

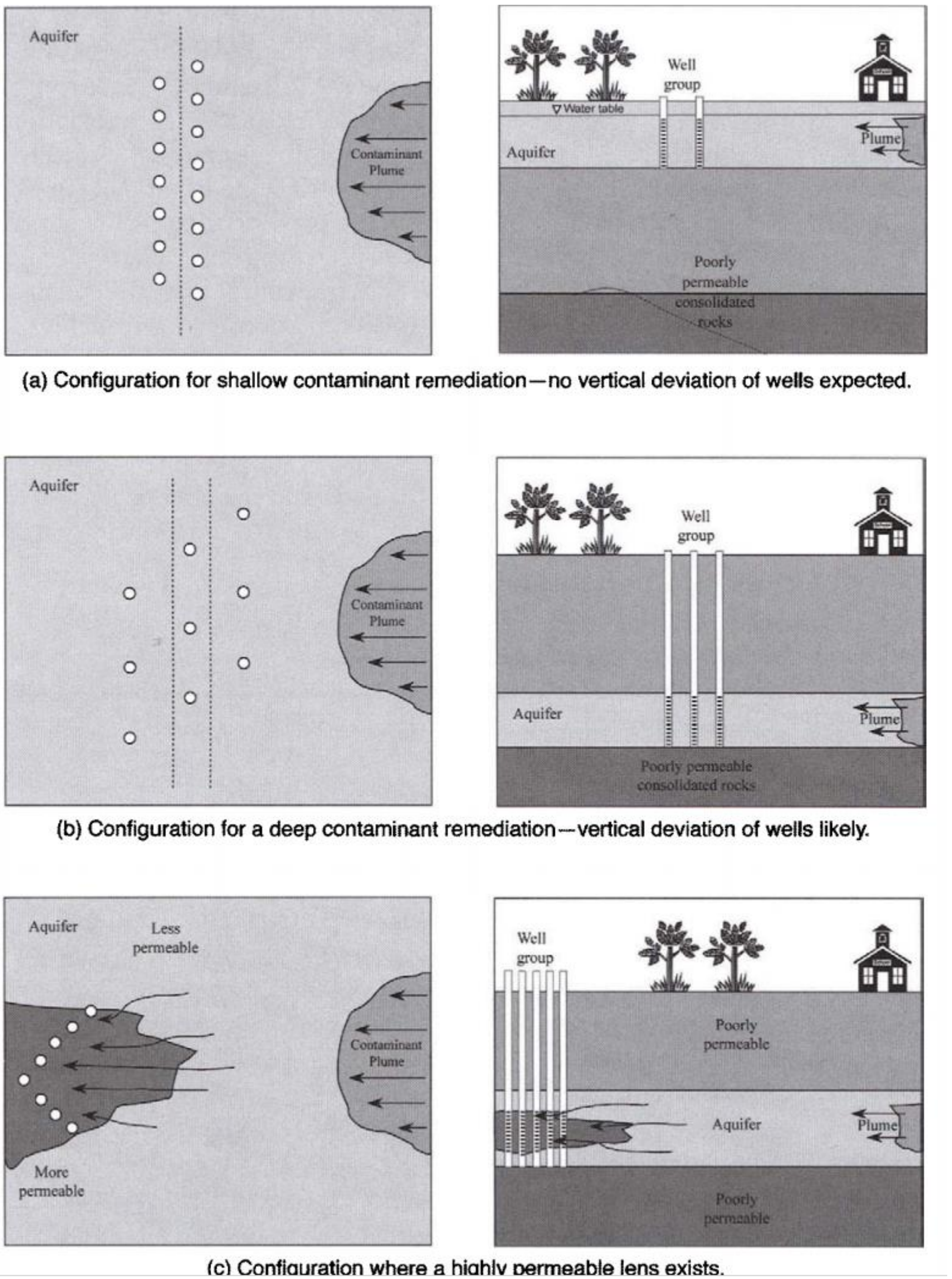


Figure 13 Three configurations for 'deep' aquifer remediation tools (DARTs). Plan on left, and cross-section on the right. From Freethey et al. (2005).

5.6.1 Ionic species removal

Some ionic species can be removed by reductive immobilisation, such as chromium, nickel, lead, uranium, sulphate, nitrate, phosphate, arsenic and molybdenum (Roehl et al, 2005). For example, chromate - a carcinogen - can be removed from groundwater using elemental iron as the reactive material, through a coupled reduction/precipitation mechanism (Blowes et al., 2000):

$$Fe^0_{(solid)} + CrO_4^{2-} + 8H^+ \text{->} Fe^{3+} + Cr^{3+} + 4H_2O$$
$$(1 - x)Fe^{3+} + xCr^{3+} + 4H_20 \text{->} Fe_{(1\_x)}Cr_xOOH_{(solid)} + 3H^+$$

Reohl et al. (2005) list a series of possible reactions that can be employed, including the use of bacterial sulphate reduction fed by compost or wood chips, to produce alkalinity and raise pH. Dissolved metals precipitate as hydroxides as a consequence. Mercury can be removed by reaction with elemental copper shavings derived from scrap, though the released copper must then be removed from the pore water through the use of a zeolite filter.

5.6.2 Sorption barriers

For sorption barriers, a wide range of reactive materials have been utilised. These include (Roehl et al., 2005):

1) Activated carbon in granular form derived from coal, wood, nutshells and other carbon rich materials for a wide range of both organic and inorganic contaminants (the most common material used to date);
2) Phosphate minerals such as hydroxyapatite and biogenic apatite such as fishbones (for the removal of Pb, Sb, U);
3) Others tailored for specific applications e.g. diatomite with silane surfaces.

Factors that must be taken into account when selecting a reactive material include (Roehl et al., 2005):

1) Reactivity - high reactivity enables a barrier to achieve the desired reaction with minimal thickness;

2) Stability – as replacement may be difficult, the material should remain reactive for long periods of time. Stability to changes in pH, temperature and pressure are also desirable;
3) Availability and cost – low bulk cost is desirable as the volume of reactant required may be large;
4) Hydraulic performance – the bulk permeability must exceed that of the surrounding soil or aquifer;
5) Environmental compatibility – there should be no unwanted by-products;
6) Safety – the material should be safe to handle during installation, and during any replacement operations.

5.6.3 Treatment walls – de-acidisation

For the remediation of aquifer water that is contaminated with CO_2, there are two remediation tasks:

1) Remove the CO_2 and raise the pH of the water;
2) Remove any toxic metals that have been mobilised by the reduced pH of the water – clearly the suite of metals that have been mobilised is crucial here in the design of the reactive material.

In the case of contamination of an aquifer by CO_2, then the material within the barrier must react with, or otherwise immobilise the CO_2, and must be sufficiently abundant and cheap to make deployment practical. It is not clear if a treatment wall has ever been used for the remediation of a CO_2-contaminated aquifer. A relatively recent book on the subject of treatment walls (Roehl et al., 2005) does not explicitly discuss CO_2 amongst the pollutants covered. However, treatment walls have been used to remediate acid mine drainage, which is a common pollution problem worldwide and which can be considered to be a useable analogue for the remediation of groundwater acidified by the addition CO_2. In Australia, Banasiak and Indraratna (2012) describe the construction of a treatment wall successfully neutralised the acidic groundwater from c. pH 3 to c. pH 7.3 and removed around 95 % of dissolved Al and Fe. Twenty five alkaline materials were tested (as batch experiments) as candidates for the reactive core of the treatment wall, including recycled concretes, limestone, oyster shells, calcite-bearing zeolitic breccias, air-cooled blast furnace slag (ACBFS), lime and fly ash. Drain water collected from the remediation site was used for the tests. Column tests were conducted on the best performing materials (recycled concrete and oyster shells) and the recycled concrete was selected as having the longest life times and resistance to clogging by precipitates. The dimensions of the barrier are not analogous to probable remediation of a CO_2 leak – the barrier was only 18 m by 3 m. Any CO_2 leak might be expected to be rather larger unless the leak is highly constrained laterally.

Calcite has been used as a reactive barrier (along with CO_2 injection to improve the removal efficiency of fluoride – hardly applicable here; Turner et al., 2008) and could perhaps be used, if not to remove the CO_2, then to moderate the pH of the acidified CO_2-rich groundwater (Naftz et al., 2003) as has been used for the treatment of acid mine drainage. Limestone is a cheap and readily available source of calcite, however problems encountered are the low solubility of calcite (Morel and Hering, 1993), and armouring. The latter occurs when iron is dissolved in oxic groundwater, as is common with acid mine drainage for example, and the iron reacts with bicarbonate in solution to produce iron (III) oxyhydroxides which precipitate on the surface of the limestone particles, effectively isolating the reactive calcite from the groundwater (Sun et al., 2000; Waite et al., 2002). A high slope of the ground (> 20 %) prevents armouring (Ziemkiewicz et al., 1997), as does periodic disturbance (Rose and Laurenso, 2000 in Waite et al., 2002). Neither of these conditions is likely to be appropriate for the remediation of a significant CO_2 leak.

5.6.4 Carbonation stabilisation

In this technique, contaminated groundwater and soil is mixed with binding agents that cause a chemical reaction with the CO_2 to trap it and reduce environmental release. Carbonation is a strongly exothermic reaction and calcium carbonate ($CaCO_3$) is formed by the reaction between cementitious materials and CO_2. Mineral carbonation is one of technologies utilising CO_2, and is used to form carbonated materials by the reaction between CO_2 and Ca or Mg-bound compounds such as wollastonite ($CaSiO_3$), olivine (Mg_2SiO_4), and serpentine.

5.6.5 Microbes

Microbes are used to clean up CO_2 contaminated soil and groundwater. Bioremediation uses microbes that use the CO_2 for food and energy. Work is undergoing with Chlorella Microalgaen. Also coccolithophorid algae can sequester carbon by photosynthesis as well as in calcium carbonate scales known as coccoliths. There are a number of high CO_2 tolerant micro algae:

- Cyanidium caldarium - Seckbach et al. (1970);
- Scenedesmus sp. - Hanagata et al. (1992);
- Chlorococcum littorale - Kodama et al. (1993);
- Synechococcus elongatus - Miyairi (1995);
- Euglena gracilis - Nakano et al. (1996);
- Chlorella sp. - Hanagata et al. (1992);
- Eudorina spp. - Hanagata et al. (1992).

For bioremediation to be effective the temperature must be appropriate, and nutrients and food must be present; if conditions are not suitable then the technique will not work.

5.6.6 Summary of permeable reactive barriers (treatment walls) remediation measures

1) Treatment walls (PRB’s) offer the potential to remediate both low pH and toxic metal mobilisation as a consequence of a shallow CO_2 leak;
2) The technology is well established from remediating other types of pollution, but has probably never been applied to the contamination of an aquifer by CO_2;
3) Costs may be substantial (millions of pounds) assuming that a barrier of km length needs to be constructed;
4) The choice of reactive material depends upon the toxic metals that have been mobilised, and is site-specific. The most suitable reactive material can be determined by experiment.

Table 8 presents a summary of the Permeable Reactive Barriers (treatment walls) remediation methods. The table presents a short summary of the principles of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 8 Summary of the permeable reactive barriers (treatment walls) remediation methods.

Remediation technique	**Principles**	**Information**	**CO_2 applicability considerations**	**Pros / cons**
Treatment walls (permeable reactive barriers PRB)	Treatment walls (or permeable reactive barriers, PRB's) are structures installed in the shallow subsurface that trap or alter pollutants that are carried though the wall by natural groundwater flow. Treatment walls work best with a porous and permeable aquifer with a 'high' rate of water flow. There are numerous methods to install treatment walls which are covered in the full report.	The CO_2 pollutants are adsorbed, precipitated, react to form less harmful material or are degraded.	There are many applications that will be suitable for CO_2 application and they are presented below.	They are effective, unobtrusive, passive, retain groundwater resources, minimal soil volumes handled, lower cost and long design lives. But long term monitoring required, site characterisation is complex and costly, deeper plumes difficult to handle and use is geologically constrained to porous media. Over time reactive materials become less effective at removing CO_2 and the contaminated reactive material needs to be removed and replaced with fresh material.
PRB – sorption barriers	The CO_2 pollutants are adsorbed by the core material within the permeable barrier.	Suitable materials for sorption barriers include activated carbon, phosphate minerals and other site specific materials such as diatomite with silane surfaces.	CO_2 is readily sorbed onto coal so the technology should be applicable to CO_2 remediation.	Factors to consider are: reactivity, stability, availability, cost, environmental compatibility, safety and hydraulic performance.
PRB – Ionic species removal	Ionic removal can be achieved by electrical currents through inert electrodes, reactive materials and ion exchange resin.	Some ionic species can be removed by reductive immobilisation, such as chromium, nickel, lead, uranium, sulphate, nitrate, phosphate, arsenic and molybdenum	Will remove trace elements mobilised by the CO_2 – rather than the CO_2 itself.	Cost and effectiveness will be important factors and cleans up trace elements rather than the CO_2.
PRB - Microbes	Microbes are used to clean up CO_2 contaminated soil and groundwater. Bioremediation uses microbes that use the CO_2 for food and energy.	Work is undergoing with Chlorella Microalgaen. Also coccolithophorid algae can carbon by photosynthesis as well as in calcium carbonate scales known as coccoliths.	There are a number of high CO_2 tolerant micro algae. Cyanidium caldarium - Seckbach et al. (1970); Scenedesmus sp. - Hanagata et al. (1992); Chlorococcum littorale -Kodama et al. (1993); Synechococcus elongatus -Miyairi (1995); Euglena gracilis - Nakano et al. (1996); Chlorella sp. -Hanagata et al. (1992); Eudorina spp. -Hanagata et al.	For bioremediation to be effective the right temperature, nutrients and food must be present, if conditions are not ideal it won't work

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
			(1992)	
PRB - Carbonation stabilisation	Contaminated groundwater and soil is mixed with binding agents that cause a chemical reaction with the CO_2 to trap it and reduce environmental release.	Carbonation is a strongly exothermic reaction and calcium carbonate ($CaCO_3$) is formed by the reaction between cementitious materials and CO_2	Mineral carbonation is one of technologies utilizing CO_2, and is used to form carbonated materials by the reaction between CO_2 and Ca or Mg-bound compounds such as wollastonite ($CaSiO_3$), olivine (Mg_2SiO_4), and serpentine	Reaction rates will determine effectiveness.
PRB – de-acidisation	Alkali materials are used as the reactive core in the permeable barrier such as; recycled concretes, limestone, oyster shells, calcite-bearing zeolitic breccias.	Banasiak and Indraratna (2012) describe the construction of a treatment wall which successfully neutralized the acidic groundwater from c. pH 3 to c. pH 7.3.	Treatment walls have been used to remediate acid mine drainage. and which can be considered to be a useable analogue for the remediation of groundwater acidified by the addition CO_2	Choice of reactive material will be site specific. Technology is established but needs further investigation for CO_2 remediation.

5.7 Remediation techniques (5) – Soil zone contamination

A number of techniques have been developed to treat contamination in the vadose or soil zone, and technologies can be considered to be mature with a 35 year history (Benson and Hepple, 2005; Zhang et al., 2004). Soil-vapour extraction and air sparging are the most common. IEA GHG (2007) suggest that large amounts of CO_2 could be removed with these technologies.

5.7.1 Soil-vapour extraction

Published models of soil-vapour extraction (SVE) with both analytical and numerical results enable good use of resources (Zhang et al., 2004 and refs. therein). Both active and passive methods (i.e. with and without powered pumping of the air, respectively) have been modelled (Zhang et al., 2004). Factors determining the effectiveness are (Zhang et al., 2004):

1) The intrinsic permeability of the porous medium – a high permeability is required to allow for a reasonable flow of air;
2) Soil water content – water saturation must be sufficiently low to allow the flow of air;
3) Henry's Law coefficient of the target compound – high solubility and low vapour pressure require higher (or longer duration) flow of air;

4) The ratio of horizontal to vertical permeability (k_v/k_h). A high ratio enhances the effective horizontal radius of a single well (Shan et al., 1992);
5) The anisotropy of the porous medium (Shan et al., 1992).

Where the water table is more than 3 m deep, then shallow boreholes are drilled into the very shallow subsurface (Fetter, 1999). The wells are completed with a slotted plastic well screen, but with a solid plastic casing for the top 1.5 m or so. The completed sections of the borehole are filled with course gravel backfill, to maximise air flow. The top portion of the borehole must be cemented with grout, so that the annular space is filled and air cannot be sucked down directly from the surface. Ground gas is pumped from the boreholes, and in the case of CO_2 would be vented to air as CO_2 capture would be prohibitively expensive. If very high concentrations of CO_2 were being remediated, then the CO_2-contaminated ground gas could be mixed with clean air, to reduce the CO_2 concentration, before the air is vented. Passive boreholes are also drilled, to enable the inflow of air from the atmosphere; these are also completed (perforated) only below c. 1.5 m depth (Figure 14).

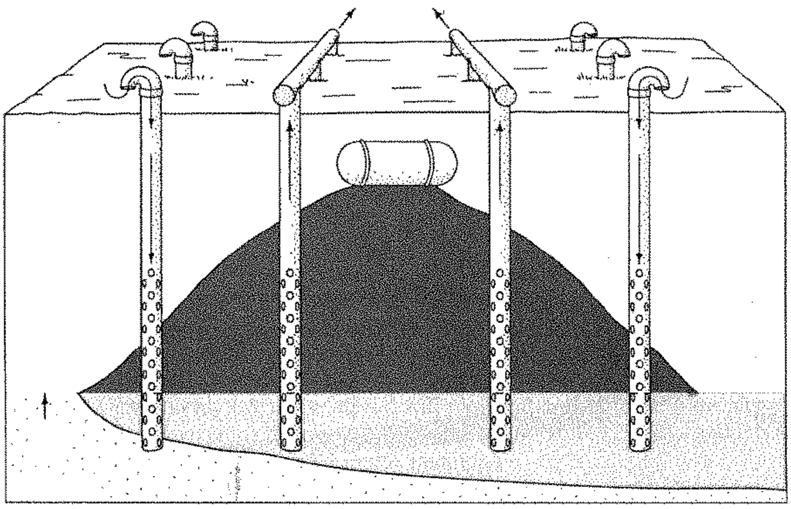


Figure 14 Soil-vapour extraction by boreholes for a groundwater table more than 3 m below the surface. From Fetter (1999).

If the water table is less than c. 3 m below the ground surface, then the borehole technique is not practical, and trenches can be used instead (Fetter, 1999). The trenches are excavated to just above the highest point that the ground water table is expected to reach, allowing for seasonal variation. A layer of gravel is laid in the excavated trench, followed by a perforated plastic pipe which is covered with gravel. The remainder of the trench is filled with a low permeability material, such as clay, to prevent air ingress direct from the atmosphere. Ground gas is actively pumped from the pipes. Passive trenches are also constructed, with a surface connection but no active pumping (see Figure 15), these allow the ingress of atmospheric air. If the CO_2 is contaminated with hydrocarbons (for example if the storage is in a depleted gas field) then the extracted vapours could be explosive when mixed with air. Suitable precautions must be taken in this circumstance.

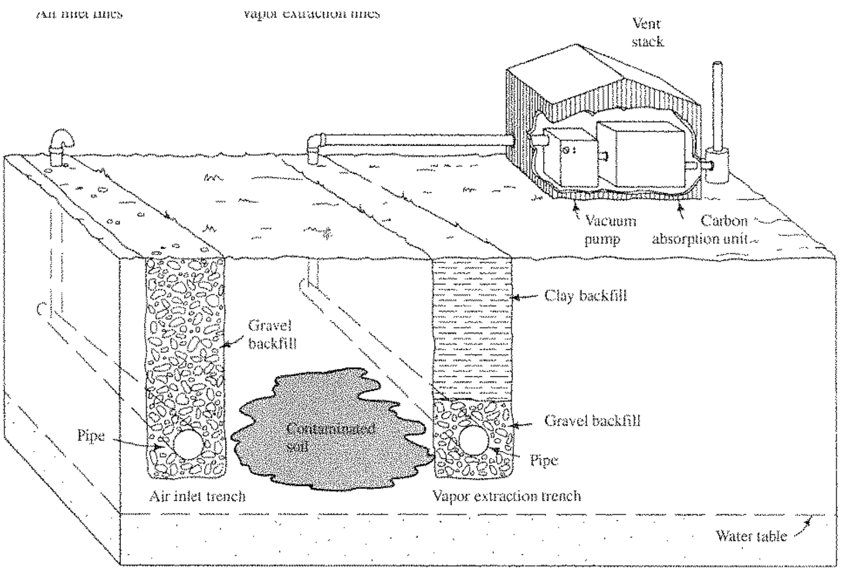


Figure 15 Trenches for the extraction of ground gas for shallow water tables. From Fetter (1999).

Zhang et al. (2004) concluded, from modelling CO_2 leakage scenarios, that standard passive and active soil vapour extraction will be effective for remediating potential CO_2 leakage plumes in the vadose zone. They found that:

1) In the scenarios modelled (Figure 16) the time required to half the concentration of CO_2 in the ground gas was from 0.27 – 2.5 years;
2) Movements of ground gas induced by natural variations in air pressure (barometric pumping) enhanced the modelled rate of removal compared to models with no barometric pumping;

3) Passive removal of CO_2 from high water saturation regions near the water table is limited by low gas saturation and high solubility in groundwater;
4) For vertical wells, the screen should not be too close to the water table;
5) An impermeable cover improves the removal rate;
6) A combination of both vertical and horizontal wells is more effective than either type alone;
7) High k_v/k_h results in a high rate of removal early on, but a lower rate in the letter stages.

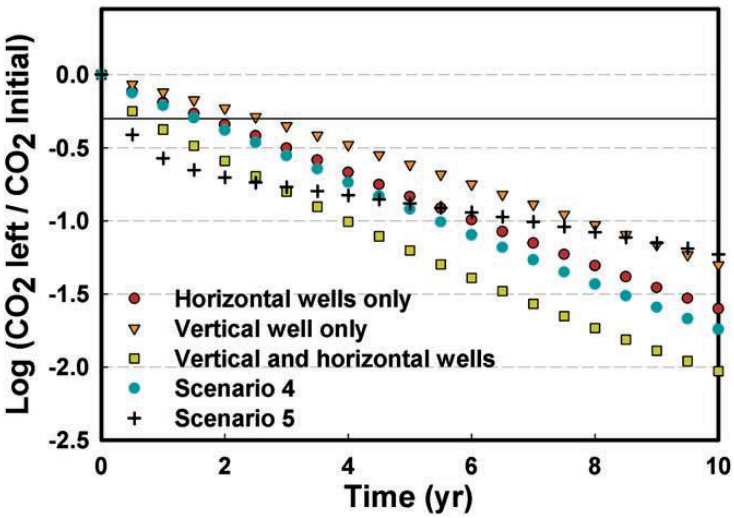


Figure 16 *Remaining CO_2 vs. time, for soil-vapour extraction scenarios modelled scenarios by Zhang et al. (2004). Scenario 4 = longer horizontal well length; scenario 5 = higher kv/kh than scenarios 1 – 4.*

5.7.2 Air sparging and bioslurping

Air sparging consists of injecting air below the water table. CO_2 dissolves in rising bubbles of air, as the two gases (mixtures) are fully miscible at the pressures and temperatures of interest. The volumes of air injected are 'small', and 2.5 cm diameter wells are sufficient. The system must be designed to avoid the air rising up the borehole casing (Fetter, 1999), instead an inverted cone of bubbles should be produced. In practise, the air bubbles follow pathways of high permeability, so that initial recovery rates are high, and quickly fall as the recovery becomes limited to diffusion. Air sparging can be used in conjunction with a vadose zone extraction system.

Vacuum-enhanced recovery, or bioslurping, uses both air and water to remove the CO_2. The well is designed so that the level of the water table can be depressed to close to the bottom of the well by groundwater removal, followed by pumping of the ground gas. The aquifer below the level of the depressed water table is remediated only by the extraction of the porewater (Fetter, 1999).

5.7.3 Addition of alkali to soil

If soil has become acidified from contact with leaked CO_2, then IEA GHG (2007, p. 132) suggest remediation by irrigation and drainage, or the addition of agricultural supplements such as lime.

5.7.4 In-situ thermal treatments

Thermal treatments mobilise CO_2 through heat towards wells where it is collected, (EPA 2012). There are three methods to generate heat:

1) Electrical resistance heating, where an electrical current passes between electrodes generating heat as the current meets resistance from the soil, converting groundwater into steam;
2) Steam enhanced extraction, where steam is injected underground by pumping;
3) Thermal conduction heating, where heaters in underground pipes heat the contaminated area.

CO_2-rich vapour is brought to the surface, and then it must be treated to remove the CO_2 before it can be re-injected. Toxic metals must also be removed before re-injection. Thermal treatments can take a few months to a few years to clean up a site. The clean-up time depends on the CO_2 concentration, area of contamination, depth of contamination variety of soil causing uneven heating and organic content of the soil which can cause the CO_2 to sorb rather than evaporate.

5.7.5 Gas collection trench

As CO_2 is a dense gas, a gas collection trench could collect the CO_2 if the trench is filled with crushed rock and lined with a vapour barrier. The method is widely used in landfill sites for methane gas collection, and should be applicable to CO_2, Darnault (2008).

5.7.6 Capping

A cover is placed over the CO_2 contaminated soil. Concrete, vegetation, drainage layers, geomembranes or clay can be used as a cap material. Capping does not remove or destroy the CO_2 but isolates it and keeps it in place to avoid or minimise contamination effects on the surface (Oldenburg, 2008).

5.7.7 Ecosystem restoration

The process of returning a contaminated site to a natural environment, similar to that that existed before the leakage. Done through fertilisers, nutrients and other soil amendments, restoring watercourses, planting native trees, shrubs etc and re-establishing wildlife. The final step in the remediation process.

5.7.8 Summary of soil zone remediation measures

Table 9 presents a summary of the soil zone remediation methods. The table presents a short summary of the principles of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 9 Summary of the soil zone remediation methods.

Remediation technique	**Principals**	**Information**	**CO_2 applicability considerations**	**Pros / cons**
Soil vapour extraction (SVE)	Contaminated vapours are removed from soil above the water table for treatment above ground by applying a vacuum to pull the vapours out. Vapours can be collected in boreholes if the water table is more than 3m deep and trenches if the water table is less than 3m deep.	One or more extraction wells are drilled above the water table which must be deeper than 3 feet below the ground surface. A vacuum pump creates a vacuum which pulls the air and vapours through the soil and up the well for surface treatment. Effectiveness is determined by permeability, soil water content and anisotropy of the porous medium.	Process is relatively quick and cheap but will depend on CO_2 concentration or volume. Does not trap the CO_2 as it is captured as a gas so will still need additional treatment.	Zhang et al. (2004) concluded, from modelling CO_2 leakage scenarios, that standard passive and active soil vapour extraction will be effective for remediating potential CO_2 leakage plumes in the vadose zone
Air sparging	Contaminated vapours are removed from below ground for treatment	Needs one or more injection well into the groundwater soil as air bubbles through	Process is relatively quick and cheap but will depend on CO_2	In practise, the CO_2 and air bubbles follow pathways of high permeability, so that

Remediation technique	Principals	Information	CO_2 applicability considerations	Pros / cons
	above ground. Air is pumped underground to help extract the CO_2 from groundwater and wet soil beneath the water table. Air facilitates the evaporation of CO_2.	the soil it carries the CO_2 vapour upwards into the soil above the water table – this mixture of air and vapour can be extracted for treatment using soil vapour extraction (SVE)	concentration or volume. Does not trap the CO_2 as it is captured as a gas so will still need additional treatment.	initial recovery rates are high, and quickly fall as the recovery becomes limited to diffusion. Air sparging can be used in conjunction with a vadose zone extraction system.
Bioslurping / vacuum enhanced recovery	Uses similar techniques to air sparging, except it uses both air and water to remove the CO_2.	The well is designed so that the level of the water table can be depressed to close to the bottom of the well by groundwater removal, followed by pumping of the ground gas.	The aquifer below the level of the depressed water table is remediated only by the extraction of the porewater	In practise, the CO_2 and air bubbles follow pathways of high permeability, so that initial recovery rates are high, and quickly fall as the recovery becomes limited to diffusion. Biooslurping can be used in conjunction with a vadose zone extraction system.
Alkali to de-acidise soil / pH buffering	Soil that have been acidized by CO_2 could be remediated with irrigation, drainage and an alkali such as lime.	Irrigation, drainage and agricultural methods can deliver the alkali materials	IEA GHG (2007, p. 132) suggest remediation by irrigation and drainage, or the addition of agricultural supplements such as lime.	Including lime into the soil is a cheap and effective well tested method to de-acidise the soil.
In situ thermal treatment (steam)	Thermal treatments mobilise CO_2 through heat towards wells where it is collected. There are three methods to generate heat: Electrical resistance heating, steam enhanced extraction and thermal conduction heating.	Contaminated soil is heated to vaporise the CO_2 and water which means the gas CO_2 can move easily through the soil. Heat is generated by electrical resistance heating (electrical currents), steam enhanced extraction or thermal conduction heating (heaters)	CO_2-rich vapour is brought to the surface, and then it must be treated to remove the CO_2 before it can be re-injected. Toxic metals must also be removed before re-injection.	Thermal treatments can take a few months to a few years to clean up a site. The clean up time depends on CO_2 concentrations, area of contamination, depth of contamination variety of soil causing uneven heating and organic content of the soil which can cause the CO_2 to sorb rather than evaporate.
Capping	A cover is placed over the CO_2 contaminated soil	Concrete, vegetation, drainage layers, geomembranes or clay can be used as a cap material.	Capping does not remove or destroy the CO_2 but isolates it and keeps it in place to avoid or minimise contamination effects on the surface	A short term solution to prevent surface leakage.
Gas collection trench	As CO_2 is a dense gas, a gas collection trench could collect the CO_2	Trench is filled with crushed rock and lined with a vapour barrier.	Widely used in landfill sites for methane gas collection, and should be applicable to CO_2.	Cheap and basic method to collect soil CO_2.
Ecosystem restoration	The process of returning a contaminated site to a natural environment, similar to that that existed before the leakage.	Done through fertilisers, nutrients and other soil amendments, restoring watercourses, planting native trees, shrubs etc and re-establishing wildlife.	Standard practise in mining remediation.	The final step in the remediation process.

5.8 Remediation techniques (6) – Bioremediation

Bioremediation is the process where a biological agent (bacteria, fungi, plant, enzyme) is used to reduce contamination mass and toxicity in the soil, groundwater and air. It is typically low cost, but bioremediation of CO_2 is yet to be fully tested. The factors affecting bio-remediation are (Shackelford and Jefferis 2000):

1) Microorganisms: Natural organisms are best as introduced organism may need acclimatised and suitable environmental conditions may need to be provided;
2) Toxicity: need non-toxic conditions;
3) Water: 25-85% water holding capacity desirable in the soil;
4) Oxygen: Aerobic conditions required, which may be a problem if CO_2 concentrations are too high and oxygen may need to be added;
5) Electron acceptors: O_2 (aerobic conditions); NO^{3-}, Fe^{3+}, Mn^{2+}, and SO_4^{2-} otherwise;
6) pH: 5.5 – 8.5 is optimum;
7) Nutrients: N, P and other nutrients required for microbial growth;
8) Temperature: affects degradation rates.

5.8.1 Bioremediation of hydrocarbon contamination

If the leaking CO_2 has encountered high concentrations of hydrocarbons, then these may have mixed or evaporated into the CO_2 phase. This is perhaps most likely where the primary storage reservoir of a CCS scheme is a depleted hydrocarbon field, especially a gas field or an oil field with a light (volatile) oil. Bioremediation generally uses in-situ microbes, the majority of which are bacteria that are absorbed onto the surfaces of rock and soil particles (Fetter, 1999). Bacteria that can degrade hydrocarbons are thought to be ubiquitous in the subsurface (Atlas, 1975). The principle is to add ‘food’ i.e. nutrients for the bacteria, to speed up what are otherwise natural biodegradation processes. The nutrient requirements of the native bacteria must be determined by culturing in a laboratory, and the experiments should attempt to reproduce the conditions of the subsurface as accurately as possible. Nutrients are added in varying proportions and concentrations to different cultures, and the rate of degradation of the contaminant is measured. Carbon can be added as methanol or molasses for example (Fetter, 1999).

If the hydrocarbons are in the soil zone, then the nutrients must be injected below the root zone of any plants growing on the site, otherwise the main effect will be to fertilise the plants! An infiltration gallery (a structure to contain water and direct it into the soil) is built above the contaminated zone, and periodically filled with water in which the optimum nutrients are dissolved, along with oxygen. Additional oxygen is allowed to diffuse into the soil when the infiltration gallery dries out between flooding events; or can be added by sparging with air or pure oxygen; or through the use of hydrogen peroxide. The latter can be toxic to micro-organisms so cannot always be utilised. Active recovery of ground water from shallow boreholes can be used to encourage the circulation of pore water in the remediation zone. In many cases, the only nutrient that need be added is oxygen, which can be circulated by soil-vapour extraction. If the soil is dry, then humid air may be used (Fetter, 1999).

5.8.2 Bioremediation of low pH groundwaters

Bacterial activity within groundwater could be artificially increased by the injection of urea, which can increase pH (Dupraz et al. (2009) and potentially remediate the effects of dissolved CO_2. Calcite may be precipitated as a by-product, though in a real aquifer the supply of calcium ions would presumably limit this process. It is unknown whether this technique has ever been tested outside of a laboratory. Ménez et al. (2007) list several mechanisms by which bacteria may alter pH:

1) Remove CO_2 by e.g. photosynthesis, clearly restricted to the very shallow subsurface and is involved in the precipitation of travertine and tufa;
2) Generate CO_2 by aerobic or anaerobic oxidation of organic matter, allegedly resulting in the precipitation of calcite;
3) Generate CO_2 and ammonia by aerobic or anaerobic oxidation of nitrogen compounds, increasing pH and triggering the precipitation of calcite;
4) Generate CH_4 or acetate from CO_2, an important process in the subsurface;
5) Reduce sulphate anaerobically, promoting calcite precipitation.

5.8.3 Bioremediation of dissolved toxic metals

Several studies have suggested that it may be possible to remove toxic metals that are in solution in porewaters by incorporating the metals into calcite precipitated through bacterial action (Fujita et al., 2000; Warren et al., 2001; Mitchell and Ferris, 2005). The technique is likely to be effective only for divalent ions (e.g. Pb, Zn, Ba, and Cd) and radionuclides (e.g., ^{90}Sr and ^{60}Co). The technique may be more effective than precipitation by redox reactions, whereby previously co-precipitated species may be inadvertently liberated into pore waters (Mitchell and Ferris, 2005). Bacterial precipitation of calcite through ureolysis (the hydrolysis of urea to ammonium and carbon dioxide) has also been proposed as a method of selectively reducing porosity and permeability in the subsurface (Ferris et al., 1996; Stocks-Fischer et al., 1999) and for the removal of calcium from industrial wastewater (Hammes et al., 2003).

5.8.4 Natural attenuation

Natural attenuation can be defined as the process of immobilizing, retarding, or degrading the CO_2 contaminants in the soil or ground water that results from geochemical interactions between the natural geological material and chemical constituents in the ground water (Rouse and Pyrith 1993). Natural geochemical attenuation mechanisms can include cation and anion exchange with clays, adsorption of cations and anions on hydrous metal oxides (e.g., iron and manganese oxides), sorption on organic matter or organic carbon, precipitation of metals from solution, and co-precipitation by adsorption. With regards to CO_2, it has a high propensity to adsorb onto organic carbon.

An assessment of the extent to which geological materials will attenuate the migration of CO_2 in the soil or ground water requires knowledge of:

1) The properties and mineralogy of the geological material (porous medium);
2) The properties of the contaminated ground water; and
3) The chemical conditions (e.g., pH and Eh) that are established during contact of the contaminated groundwater with the geological material.

Natural attenuation has high costs associated with monitoring as the site needs to be monitored to determine whether or not natural attenuation processes will remediate the site, or whether enhanced remediation steps need to be taken.

5.8.5 Summary of bioremediation measures

Table 10 presents a summary of the bio-remediation methods. The table presents a short summary of the principles of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 10 Summary of the bioremediation methods.

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Bioremediation of low pH groundwaters	CO_2 acidises the soil and bacteria activity can be used to remediate this acidisation.	Bacterial activity within groundwater could be artificially increased by the injection of urea, which can increase pH (Dupraz et al. (2009) and potentially remediate the effects of dissolved $_{CO2}$	Bacteria may alter pH by removal of CO_2 by photosynthesis, generate CO_2 by aerobic oxidation of organic matter, generate CO_2 and ammonia by aerobic oxidation of nitrogen compounds, generate CH_4 from CO_2, reduce sulphate anaerobically promoting calcite precipitation.	Small area of effect and long time scale inhibits effectiveness.
Bioremediation of CO_2	Microbes are used to clean up CO_2 contaminated soil and groundwater. Bioremediation uses microbes that use the CO_2 for food and energy.	Work is undergoing with Chlorella Microalgaen. Also coccolithophorid algae can carbon by photosynthesis as well as in calcium carbonate scales known as coccoliths.	There are a number of high CO_2 tolerant micro algae. Cyanidium caldarium - Seckbach et al. (1970); Scenedesmus sp. - Hanagata et al. (1992); Chlorococcum littorale -Kodama et al. (1993); Synechococcus elongatus -Miyairi (1995); Euglena gracilis - Nakano et al. (1996); Chlorella sp. -Hanagata et al. (1992); Eudorina spp. -Hanagata et al. (1992)	For bioremediation to be effective the right temperature, nutrients and food must be present, if conditions are not ideal it won't work.
Bioremediation of toxic metals	Studies have suggested that it may be possible to remove toxic metals that are in solution in pore waters by incorporating the metals into calcite precipitated through bacterial action.	The technique is likely to be effective only for divalent ions (e.g. Pb, Zn, Ba, and Cd) and radionuclides (e.g., ^{90}Sr and ^{60}Co).	The technique is likely to be effective only for divalent ions (e.g. Pb, Zn, Ba, and Cd) and radionuclides (e.g., ^{90}Sr and ^{60}Co).	Small area of effect and long time scale inhibits effectiveness.
Bioremediation of hydrocarbons	If the leaking CO_2 has encountered high concentrations of hydrocarbons, then these may have mixed or evaporated into the CO_2 phase.	Bacteria that can degrade hydrocarbons are thought to be ubiquitous in the subsurface. Bacteria that can degrade hydrocarbons are thought to be ubiquitous in the subsurface.	The nutrient requirements of the native bacteria must be determined by culturing in a laboratory, and the experiments should attempt to reproduce the conditions of the subsurface as accurately as possible. If the hydrocarbons are in the soil zone, then the nutrients must be injected below the root. In many cases, the only nutrient that need be added is oxygen, which can be circulated by soil-vapour extraction. If the soil is dry, then humid air may be used	Tested method within hydrocarbon clean-up.
Natural attenuation	The process of immobilizing, retarding, or degrading the CO_2 contaminants in the soil or ground water that results from geochemical	Natural geochemical attenuation mechanisms can include cation and anion exchange with clays, adsorption of cations and anions on hydrous metal oxides	CO_2 has a high propensity to adsorb onto organic carbon.	Natural attenuation has high costs associated with monitoring as the site needs to be monitored to determine whether

Remediation technique	Principles	Information	CO_2 applicability considerations	Pros / cons
	interactions between the natural geological material and chemical constituents in the ground water.	(e.g., iron and manganese oxides), sorption on organic matter or organic carbon, precipitation of metals from solution, and co-precipitation by adsorption.		or not natural attenuation processes will remediate the site, or whether enhanced remediation steps need to be taken.

5.9 Remediation techniques (7) - Residential buildings

The problem of ground gas entering residential and other buildings has a long history, which has in extreme cases caused entire settlements to be demolished and rebuilt in safer areas at high cost, e.g. Arkwright Town in Derbyshire, UK, at a reported cost of 15 M GBP (value in 1990's; Independent, 1994) . The main gases of concern are methane, radon and CO_2, all of which can be ultimately fatal to humans. It is the case that the majority of experience of ground gas remediation (at least in the UK) concerns radon gas, and to a lesser extent, methane. There seems to be no accessible literature (at least in English) concerning CO_2 ingress into buildings in Italy for example, which is well known as the location of numerous natural CO_2 leakage sites. In the UK, the remediation of ground gas penetration into buildings is covered by British Standard BS 8485:2007 (BSI, 2007), though it is clear that the code is designed for gas generated at shallow depths of burial such as methane from landfill, rather than CO_2 escaping from a deep source. Ground gas enters a house or other building by a variety of pathways, Figure 17.

The process of characterisation and remediation is summarised as follows, with comments regarding the applicability to CO_2 remediation from a leaking deep storage site (BSI, 2007):

1) Desk study to construct a conceptual model of the gas sources and likely migration pathways. This should include the history and current use of the site; the geology and hydrogeology of the site; and the buildings (receptors) that are or could be affected;

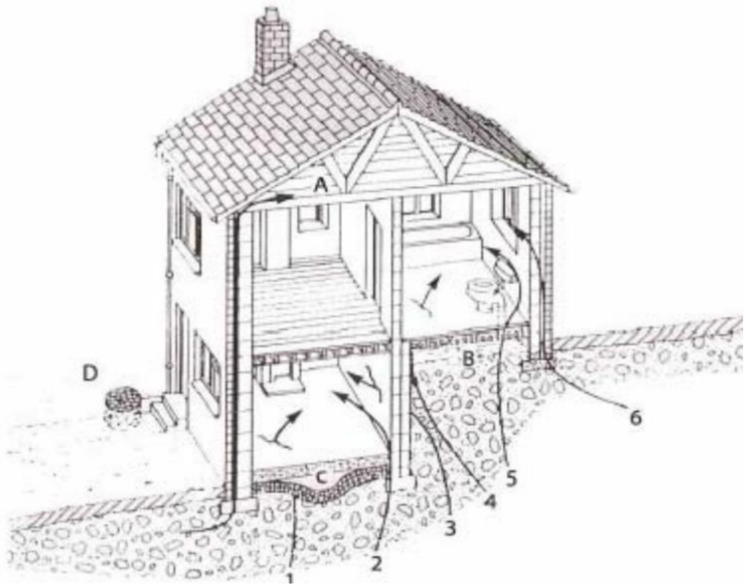


Figure 17 *Typical pathways for ground gas to enter a house or other building. From CIRIA 149 (1995) in NHBC (2007).*

2) A site walk-over study or reconnaissance;
3) Site investigation;
4) Geology and hydrogeology; made-ground; contamination; source of gas. Boreholes and trial pits are suggested though these may be more appropriate to shallow gas sources than to a leaking deep CO_2 source;
5) Install monitoring installations adequate to determine gas source and migration pathways, and likely receptors. Frequency and duration of monitoring must be sufficient to characterise changes in the gas regime due to changes in ambient conditions;
6) Gas flow rate and concentration must be assessed adequately, including measurements when atmospheric pressure is falling;
7) Estimation of an indicative gas flow rate for the entire site, or rates for each section of the site if division if required (known as 'site characteristic hazardous gas flow rate' or 'gas screening value'). This is ranked on a scale of 1 – 7 which implies a level of assessed hazard.
8) Choice of remediation solution. The factors involved are:
    a. Characteristic gas situation;
    b. Construction of foundations and ground slab (if any);

c. Size (especially width) of building;
d. Use of building (e.g. domestic or industrial, room size and degree of control over utilisation);
e. Management of gas control facilities and service provision;
f. Views of client or building owner.

The process of selection should be transparent. BS8485:2007 recognises that off-site remediation may be the most appropriate, i.e. it may be possible to intercept the leaking gas between the source and the affected buildings (see remainder of this report for appropriate technologies) rather than intervene at the buildings themselves.

Robinson (2010) reports on attempts to prevent CO_2 ingress into a home from subsurface sources, in this case from the reclaimed coal-mine spoil upon which the house was built. The CO_2 concentrations within the building were found to correlate with external weather-related conditions, with the first two being the strongest predictors:

1) Rapid drops in barometric pressure;
2) Rainfall;
3) Windy conditions;
4) Cold weather;

There are at least ten different systems that might be adopted to prevent the build-up of CO_2 in a basement or other parts of a building, at least some of which consist of simply increasing the amount of ventilation within the utilised space of the building (as opposed to non-utilised space e.g. crawl ways, wall cavities). Some of these are taken from the literature concerning the ingress of radon into houses as experience with CO_2 ingress is relatively limited. These remediation techniques must all be used in conjunction with a programme of sealing of all likely joints, cracks and surfaces whereby CO_2 might enter a building; the installation of gas-proof floor drains and sump-pit covers (Robinson, 2010) and, at least in some cases, the sealing of the loft hatch to reduce the upward flow of air within the house (Hodgson et al., 2011). Note that, in the case described by Robinson (2010), none of the techniques successfully prevented the ingress of CO_2 during adverse weather conditions, and that the analysis of Hodgson et al. (2011) gave success rates for radon remediation of 35 – 74 % (to below the legal safety limit). Indicative costs vary from 200 – 800 GBP per installation guideline (excluding the demolition option 8, below), with a maximum of 2,000 GBP for an actively pumped radon sump (UKRadon, 2014). The size of the building, the complexity of the floor construction, and the surface upon which the building is cited are presumably factors determining cost. The techniques are briefly described:

5.9.1 Passive sub-slab or sub-membrane depressurization system

Passive sub-slab (Figure 18 left) or sub-membrane (Figure 18 right) depressurization system (EPA, 2001) are also known as a ‘passive sump’ (Hodgson, 2011). This should reduce the gas concentration below the floor slab to acceptable levels, i.e. not just in the occupied volume of the building (BSI, 2007). The vented layer can be open void, or constructed from gravel, geocomposites, polystyrene or other materials (BSI, 2007).

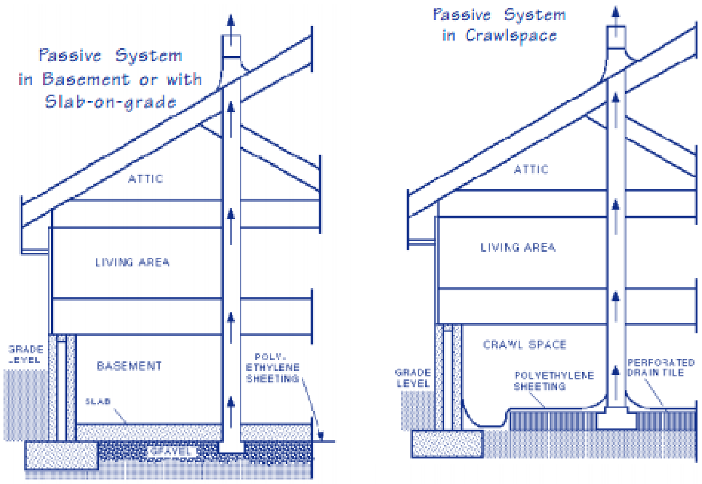


Figure 18 Passive sub-slab (left diagram) or sub-membrane (right diagram) depressurization system (Hodgson, 2011).

5.9.2 Active sub-slab or sub-membrane depressurisation system

This method is also known as an ‘active sump’ Figure 19 ((EPA, 2001; Hodgson, 2011). This should reduce the gas concentration below the floor slab to acceptable levels, i.e. not just in the occupied volume of the building (BSI, 2007). The effectiveness of membranes is crucially dependant on the design of the installation, the resistance to damage after installation, and the quality of any seals (BSI, 2007):

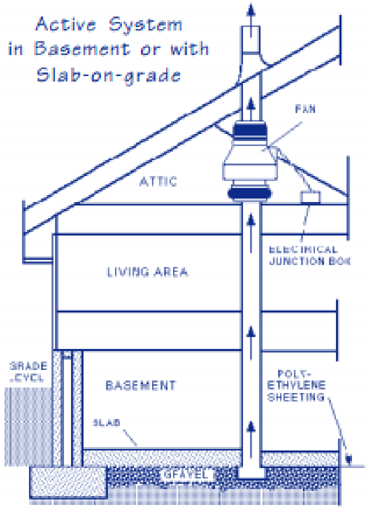


Figure 19 Active sub-slab or sub-membrane depressurisation system (Hodgson, 2011).

5.9.3 Block-wall depressurisation

A hole is drilled into the wall surrounding the basement (which must be of the cavity type), and a pipe and fan attached, venting the air at a safe height above the basement (Robinson, 2010).

5.9.4 Block-wall and sub-slab pressurisation

Similar to the above (3) but with the air flow reversed, and with a further pipe allowing the air access to below the basement slab (Robinson, 2010).

5.9.5 Positive ventilation

A fan in the roof space blows air into the living space, increasing ventilation, and presumably slightly increases the air pressure within the house so reducing the flow of CO_2 into the dwelling (Hodgson et al., 2011).

5.9.6 Natural under-floor ventilation

Under-floor ventilation is increased by clearing or replacing airbricks with modern vents and / or increasing the number of vents (Hodgson et al., 2011).

5.9.7 Passive ventilation

Trickle vents in windows increase ventilation (Hodgson et al., 2011).

5.9.8 Positive pressure

A fan blows air into the basement, increasing the air pressure and preventing the ingress of external CO_2 (Fetter, 1999). Not suitable for climates where the outside air is below freezing in winter, otherwise the cold air can cause water pipes within the basement to freeze. Probably for this reason the technique is absent from current USA and UK sources of information. Ventilation installed in a car park located in a basement or undercroft is likely to be both adequate and highly effective (BSI, 2007).

5.9.9 Demolish the buildings and rebuild

If all other options fail, then the only option may be to demolish the buildings and rebuild to a standard to prevent CO_2 ingress following standards set by for example Scivyer (2007) and other reports by the UK's Building Research Establishment (BRE, http://www.bre.co.uk/), or by the National House-Building Council (NHBC, 2007). This option has recently been adopted for a group of houses affected by CO_2 ingress in Gorebridge, Scotland (BBC News, 2014). The cost of rebuilding the houses has been reported as being 12 M GBP (June 2014). The removal of the village of Arkwright town (UK), in the 1990's was of comparable cost as described above. The inflation-adjusted cost would presumable be substantially higher than the Gorebridge case.

For many of the techniques described above, as with some other domestic building work, it is possible to 'Do It Yourself' to some extent, and that the work could potentially be conducted by contractors with varying levels of relevant experience. The Radon Council (UK) note that 'Some techniques, such as the use of extract fans to increase ventilation can in fact exacerbate the problem and cause greater volumes of the gas to be drawn into the property. It would therefore be unwise to place such responsibility in the hands of an unskilled contractor.' (http://www.radoncouncil.org/testing.html). An analysis of the effectiveness of a variety of techniques, in the context of radon, did not attempt to distinguish between DIY or professional installation, or of the competence of the professional contractors (Hodgson et al., 2011). In the context of CO_2 remediation, the DIY issue is probably not relevant. However, the experience of any contractors, most probably gained in the field of radon or methane gas remediation rather than CO_2, might be a factor in deciding effectiveness and ultimately, costs. It is here assumed that ineffective remediation will require further work, and ultimately, further costs.

Monitoring of CO_2 levels after remediation can be achieved using hand-held equipment at suitable intervals, though BSI (2007) regards this as a low-effectiveness strategy. They suggest permanent monitoring and alarm systems should be installed in the building, and preferably in the venting or diluting system itself (BSI, 2007).

5.9.10 Summary of building remediation measures

1) The cost of remediation for a home is small on the scale of the other costs in a CCS scheme, unless demolition and rebuilding is the only effective option;
2) Based on very limited experience with CO_2, and much more experience with radon gas, the success rate of remediation is only around 50 %;
3) Monitoring of CO_2 levels must be over a protracted period of time (weeks or months), as concentration depends upon external factors such as temperature and rainfall;
4) Remediation can be a lengthy process, as different (and progressively more expensive) techniques are employed;
5) Contractors with relevant experience are preferred.

Table 11 presents a summary of the building remediation methods. The table presents a short summary of the principles of each technique, additional information, CO_2 applicability considerations and the technical pros and cons.

Table 11 Summary of the building remediation methods

Technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Passive vapour intrusion mitigation	Prevents the entry of CO_2 vapours into buildings.	Sealing of all openings or vapour entry points. Installing vapour barriers of geomembrane or plastic beneath buildings to prevent vapour entry.	Applicable to CO_2 vapour intrusion. Permanent monitoring and alarm systems should be installed in the building	Cheap

Technique	Principles	Information	CO_2 applicability considerations	Pros / cons
Passive / active sub slab venting	A venting layer is built beneath a building so vapours move through the venting layer towards the sides and vented outside.	Passive venting can be by passive sub slab or sub membrane with porous sub base vented to the outside. Active sub slab or sub membrane with fan extraction venting from below the sub slab	Applicable to CO_2 vapour intrusion. Permanent monitoring and alarm systems should be installed in the building	Cheap
Active vapour intrusion mitigation - Subsurface pressurisation	The pressure difference between the subsurface and inside of the building keeps the CO_2 vapours out.	Subslab depressurisation involves linking a fan to a small pit dug into the basement to vent the vapours outside. Building overpressurisation involves adjusting the heating, ventilation and air conditioning to increase the pressure indoors relative to that of the basement area.	Applicable to CO_2 vapour intrusion. Permanent monitoring and alarm systems should be installed in the building	Effective
Block wall depressurisation	A hole is drilled into the wall surrounding the basement (which must be of the cavity type), and a pipe and fan attached, venting the air at a safe height above the basement	This can be combined with sub slab pressurisation but with air flow reversed and a further pipe allowing the air access to below the sub slab.	Applicable to CO_2 vapour intrusion. Permanent monitoring and alarm systems should be installed in the building	Effective
Positive ventilation / pressure	Air is blown into the living space increasing ventilation and air pressure in the house, reducing the flow of CO_2 into the house.	Ventilation and air pressure is increased, reducing CO_2 ingress.	Applicable to CO_2 vapour intrusion. Permanent monitoring and alarm systems should be installed in the building	Effective
Natural underfloor ventilation / passive ventilation	Trickle vents in windows and air vents in the building base walls increase ventilation	Ventilation is increased, reducing CO_2 ingress.	Applicable to CO_2 vapour intrusion. Permanent monitoring and alarm systems should be installed in the building	Effective
Demolish building and rebuild to a standard preventing CO_2 ingress.	This option has recently been adopted for a group of houses affected by CO_2 ingress in Gorebridge, Scotland (BBC News, 2014). The cost of rebuilding the houses has been reported as being 12 M GBP (June 2014).	Re-build to standards set by UK's building research Establishment or National House Building Council.	Prevents future CO_2 intrusion.	Expensive

5.10 Principles for remediation technologies screening and costs analysis

In order to propose a realistic approach for the selection of appropriate CO_2 leakage remediation technologies, analogue approaches from the contaminated land remediation field have been reviewed. The most comprehensive approach is the Remediation Technologies Screening Matrix and Reference Guide, 4th Edition which has been developed by the Federal Remediation Technologies Roundtable (FRTR) in the USA (http://www.frtr.gov/matrix2/top_page.html).

This concept will be further investigated and refined for CO_2 leakage remediation during the Mirecol project using the treatment technologies screening matrix proposed by the FRTR and the Remedial Action Cost Engineering and Requirements (RACER) software as a starting point. RACER was developed under the direction of the U.S. Air Force for estimating environmental investigation and cleanup costs. The most recent version 11.2 was released in October 2014 by AECOM (the company maintaining the software, http://www.aecomassetmanagement.com/index.php/racer/) and is available for download.

Similar to contaminated land remediation, the characteristics of the CO_2 leakage remediation site and the specific operating conditions are expected to affect significantly the performance of each technology as well as the costs of implementation. In addition, the relevant factors to each remediation technology-are specific to the technique. Therefore, it is difficult to estimate the costs accurately.

For this reason, it is proposed that technology costs to be estimated in Mirecol may be classified in coarse relative cost categories (above average, average and below average) using the expected technology specific capital costs and the operating/maintenance costs. Technology performance will likely be evaluated in terms of remediation reliability and maintainability, time to implementation, availability and the technology development status (maturity).

6 REMEDIATION AND MONITORING OF CO_2 LEAKAGE FROM THE BEČEJ FIELD, SERBIA

The Bečej field is located in the northern part of Serbia, about 130 km north of Belgrade. The field was discovered in 1951 and named after Bečej, a city located nearby. The field is located in the southeastern part of the Pannonian basin and its geologic structure is complex. The reservoir fluid consists of CO_2 (87-94 mol %), hydrocarbons C_1-C_7 (3.80 - 7.54 mol %) and nitrogen (1.83 - 5.31 mol %). At the surface, the total dissolved salt content of the formation water is 4.4 g/l; the water is slightly acidic (pH=6.6) because of the residual dissolved carbon dioxide. Under reservoir conditions, the CO_2-saturated water is much more acidic; chemical analysis of those samples indicated 58.2 g/l TDS and presence of high amount of free and dissolved CO_2. The CO_2 pool of the Bečej field is in the heterogeneous massive reservoir of Upper Cretaceous flysch and Badennian sedimentary deposits. The reservoir is located along a regional fault zone, along which felsic igneous rock was intruded, which generated carbon dioxide during metamorphism of the country rock. The lower part of the reservoir is formed of Upper Cretaceous siltstones, marlstones and very fine grained sandstones which lay transgressively over Paleozoic basement of metamorphic and igneous rocks. The upper part of the reservoir consists of shallow marine Badennian (middle Miocene) facies such as fine to medium grained sandstones composed of mineral, rarely rock or organic detritus with calcite cement and organic limestones.

The Badennian rocks are overlain unconformably boundary by the Lower Pontian (uppermost Miocene) marlstones, clayey and marly sandstones and clays deposited in caspi-brackish condition. Sedimentation continued throughout the Upper Pontian and during that period the caspi-brackish depositional environment gradually altered to lacustrine. The sediments are alternating poorly cemented sandstones and clayey sandstones and marlstones in the lower part of the unit, while sands and clays dominate in upper part. Laminae of coal and coaly clays are very frequent. Over the course of the Pliocene and Quaternary the depositional environment changed from lacustrine to fluvio-lacustrine, fluvial and aeolian environment. During these periods layers of alternating sands and clays and their varieties were deposited. Geological cross sections of the Bečej area are shown in Figure 20.

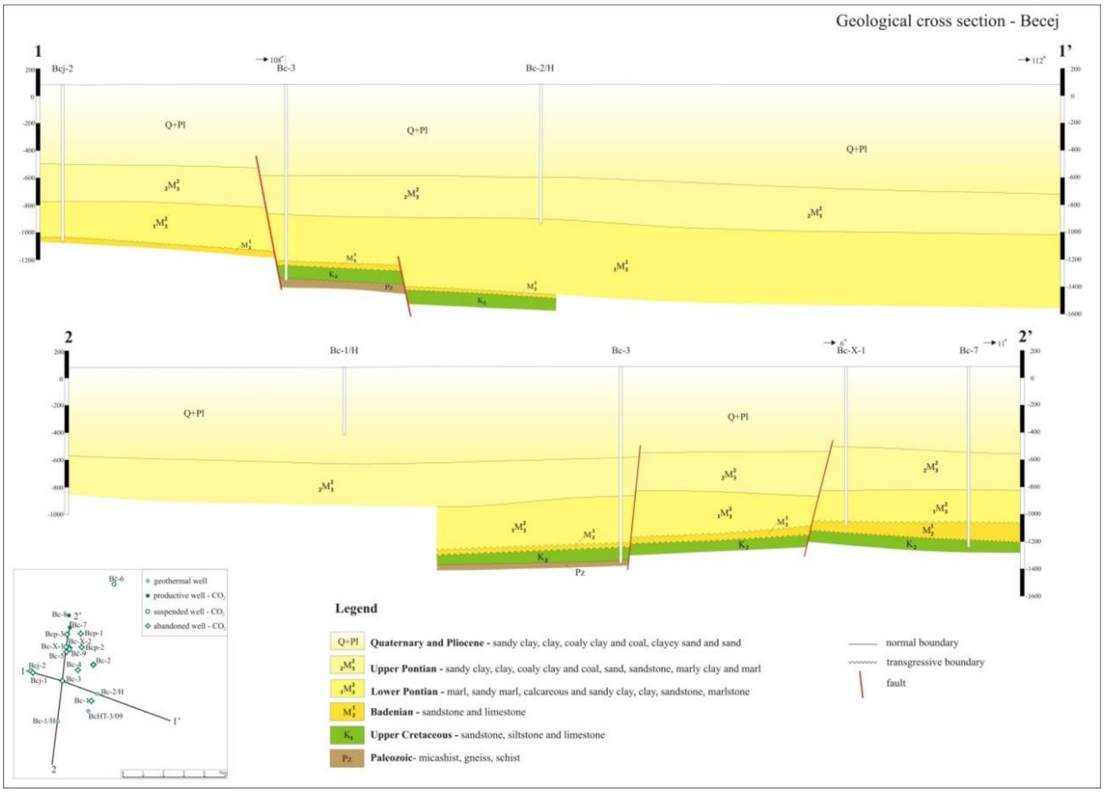


Figure 20 Geological cross-sections of the Bečej field.

The Upper Pontian and Pliocene sandstones and sands have great significance as very porous and permeable rocks saturated with hydrocarbon gasses and geothermal groundwater. Small reservoirs of methane were also explored through the drilling of several wells, these gave positive results but all the wells were abandoned after the CO_2 of the gas increased. On the basis of seismic surveying, a total of eight small hydrocarbon reservoirs are defined with a depth range from 450 to 900 m.

Beside the hydrocarbon reservoirs, geothermal groundwater is an important mineral resource, with a long history of exploitation. All the geothermal wells are artesian flowing wells because they are tapping confined aquifers saturated with water and gas, dominantly methane. Water from aquifers at 400 m depth has a temperature of 35 °C and it has been used for drinking and bathing in Bečej spa more than hundred years. The deep wells provide waters of 60 to 65 °C used for space heating of the hotel and sport center in Bečej.

A blowout of CO_2 in the Bečej field happened during the drilling of well Bc-5 at a depth of 1093.25 m and uncontrolled leakage lasted from 10.11.1968 until 06.06.1969. Carbon dioxide leaked to the surface; however, the total amount of gas leaked from the reservoir was estimated to be tens of times larger than the surface emissions. The borehole collapse, which caused the self-killing of the well and the cessation of leakage to the atmosphere, but the process of gas migration from the reservoir was not stopped. The seepage of CO_2 gas continued into the shallower aquifers above the CO_2 reservoir.

The impact was closely monitored because of the vicinity of a populated area and with special attention to gas migration in groundwater reservoirs, especially in an unconfined aquifer. The monitoring objectives involved more than 30 wells with depths in the range from 10 to 300 with a radius of 1000 m around well Bc-5. The new remediation wells Bc-X-1 and Bc-X-2 were drilled in 1969 for pressure measurements in the reservoirs at depths from 740-850 m.

6.1 Blowout of CO_2 from well Bc-5 and applied methods of remediation and monitoring

Based on the analysis of collected data, the event was divided into seven phases:

1. 1st phase - 10.11.1968 up to 17.05.1969

A concentration of 10 % CO_2 in gas was measured in an unconfined aquifer with decreasing concentrations as the distance from the source of leakage increased. The cause of the high concentration was spilling of gas on the surface covering an area of 3 km × 0.3 km toward the channel Mrtva Tise. In this area the CO_2 concentration in the air was up to 50 %. The leakage of gas was primarily through a surface crater formed at the location of well Bc-5 (Figure 21). The impact on the confined aquifers, subartesian or artesian, was not known at this stage.

Figure 21 The blowout of CO_2 on well Bc-5.

2. 2nd phase - 17.05.1969 to 06.06.1969

The process of the seepage of CO_2 into the shallow aquifers resulted in the bubbling and raising of water levels in monitored water wells, while the intensity of leakage to the atmosphere reduced. Higher concentrations of CO_2 caused the formation of small ponds on the surface around the crater during this stage.

This period can be divided into four stages:

- **Stage 1**. – The main characteristics of this stage are bridging of the borehole by produced formation solids, the suppression of eruptions within the crater and the highest rate of gas seepage into the unconfined aquifer. The gas intrusion was progressing toward the drilling sites of two new remediation wells Bc-X-1 and Bc-X-2. To prevent further advancement of the gas a line consisting of 32 shallow boreholes for the degassing of groundwater and vadose zone was installed. The boreholes were at a distance of 135 m in the north and east direction from the damaged well Bc-5 (depth of boreholes range from 10 to 15 m). The degassing processes manifested in intensive venting and eruptions of gasified water. Since the method of degassing through shallow wells was successful and enough to stop the flow path that carried the CO_2, additional measures such as the idea of creating a grout curtain was abandoned (Figure 21). The end of the seepage into the unconfined aquifer was registered on 02-03.06.1969.
- **Stage 2**. – The bridging in the wellbore happened at a depth of 50 m that had influence on the confined aquifers laying between 50 and 130 m. The frequency

of great eruptions reduced and was gradually replaced with bubbles that often occurred on the surface of the pond formed on the site of the well.

- **Stage 3**. – The bridging in the wellbore happened at a depth below 150 m that caused a sudden decrease of water level in subartesian water wells on 04-05.06.1969.
- **Stage 4**. – The wellbore collapse stopped the eruption on 06.06.1969. Since there was no record of increase of the capacity of the monitored artesian water wells up to 300 m depth the conclusion was that collapse probably occurred in wellbore at depths between 320 and 825 m.

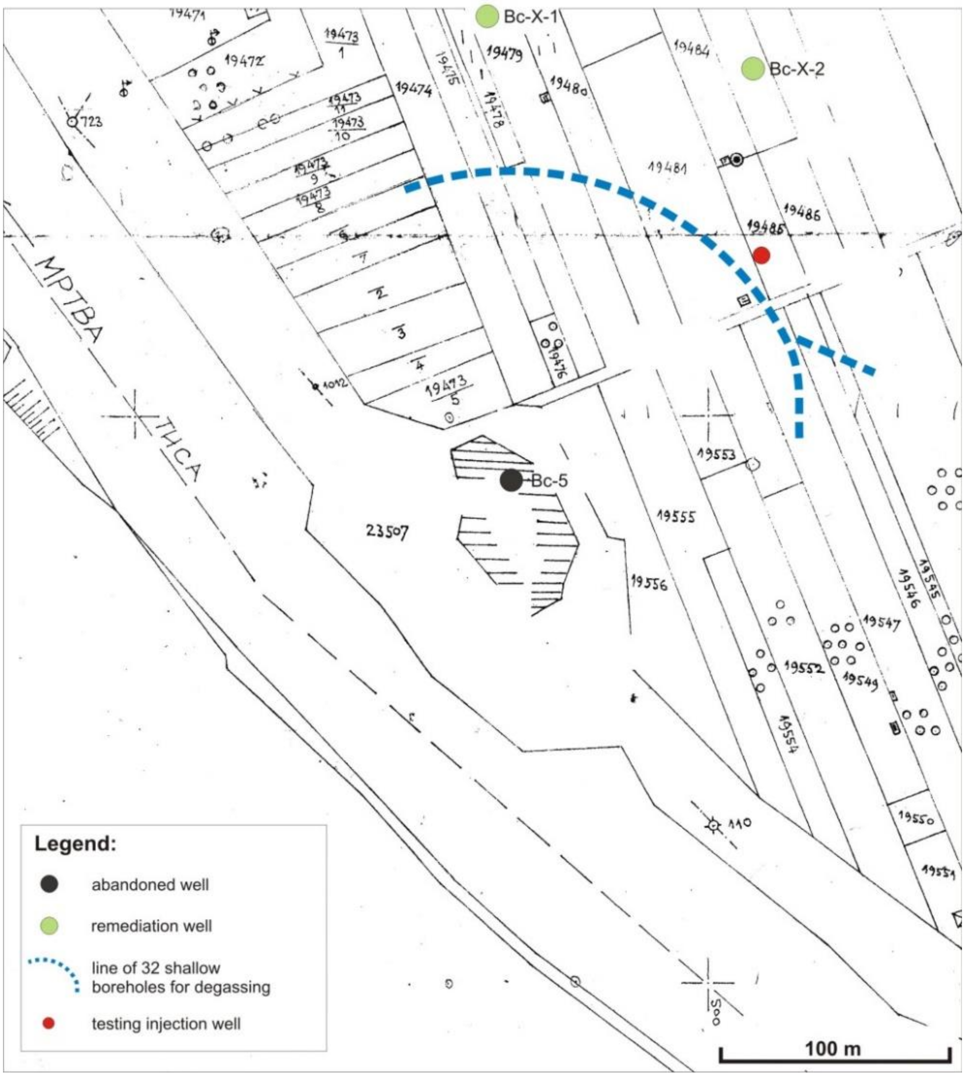


Figure 22 The position of boreholes for degassing of groundwater and soil.

3. III phase - period from 06.06.1969 to 03.08.1969

During this period no influences on aquifers up to 300 m were recorded.

4. IV phase - period from 03.08.1969 to 08.05.1970

Pressure monitoring started at the newly drilled wells Bc-X-2 and Bcp-2 and a significant increase of pressure was measured in the "hydrocarbon reservoir I" at 825-832 m in well Bc-X-2. The well produced periodically at different production rates during the beginning stage of monitoring period and the CO_2 content in the gas composition increased from 1.2 to 22 mole% in three weeks.

5. V phase - period from 08.05.1970 to 08.12.1970

The monitoring of CO_2 migration from the reservoir into the hydrocarbon reservoir I and hydrocarbon reservoir II above it continued and included a new well Bcp-3 (Table 12). The pressure data from this period indicated that the migration processes from the CO_2 reservoir into the hydrocarbon reservoir I had almost finished along with a stop in migration from reservoir I into reservoir II (Figure 23). The gathered data of static pressures led to conclusion that the wellbore collapsed at depths between the reservoir of carbon-dioxide and the hydrocarbon reservoirs.

Table 12 Basic data of static pressure measurements at wells Bc-X-2, Bcp-2 and Bcp-3.

Well	Interval (m)	Hydrocarbon reservoir	Start of measurement	End of measurement
Bc-X-2	825 - 832	I reservoir	26.08.1969	28.02.1973
Bcp-2	746.5 - 750.5	II reservoir	02.04.1970	28.02.1973
Bcp-3	838 - 842 846.5 - 849	I reservoir	01.09.1970	28.02.1973

6. VI phase - period from the 08.12.1970 to 04.05.1971

The monitoring of CO_2 continued. The gas migrations were evaluated as processes in stagnation, because no indications of gas migration was evidenced either between reservoirs I and II or from reservoir II into shallower confined layers saturated with hydrocarbons and groundwater.

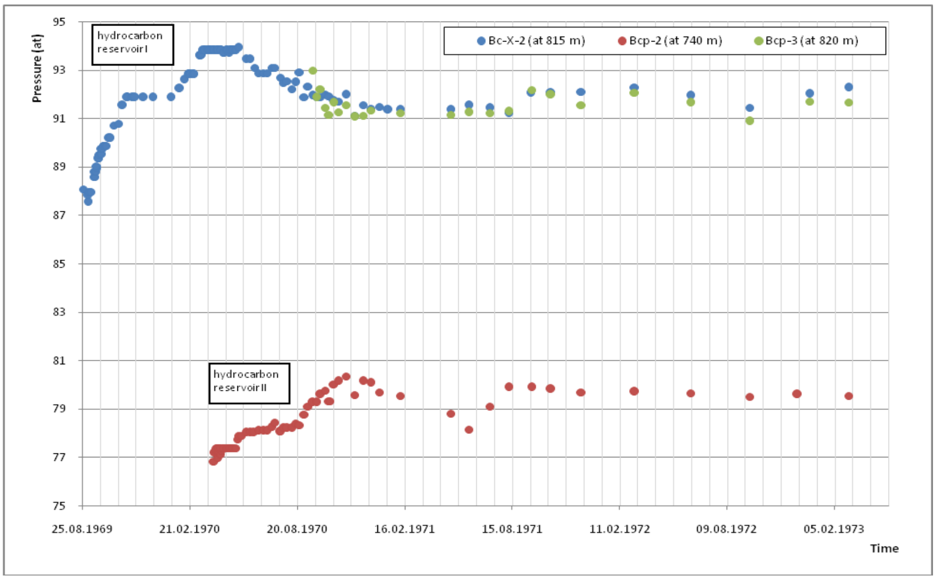


Figure 23 The static pressure measured at wells Bc-X-2, Bcp-2 and Bcp-3 from1969-1973.

7. VII phase - period from 04.05.1971 to 28.02.1973

At the end of the monitoring period the final conclusion was that leakage of CO_2 stopped.

6.2 Monitoring and remediation of CO_2 leakage

During 1980's NIS conducted the periodical control of water quality and no evidence of any increase of CO_2 concentration was detected in groundwater samples from aquifers up to 400 m depth.

At the same time the continuing decline of pressure in the CO_2 reservoir indicated that the collapsed wellbore, Bc-5 represented the flow path to leakage in above layers of the Pontian and Pliocene age. This assumption was confirmed by the results of geophysical well logging conducted in Bc-X-1 in 1982, 1986 and 1991 and by drilling of Bcj-1 in 1996 (gas sample from layer at 893-911 m - 15.19 mole % CH_4, 79.8 mole % CO_2) and Bcj-2 in 2002 (gas sample from layer at 658.43-672 m - 44.41 mole % CH_4, 51.33 mole % CO_2, gas sample from layer at 428-440 m – gas composition not analysed, test on field gas did not support burning). All these layers have increased static pressures 27.6 to 34.3 % higher than hydrostatic pressure.

The accumulations of carbon-dioxide in layers above the CO_2 reservoir were registered by earlier explorations in the Becej area (e.g. reservoirs of the Lower Pontian age on well Bc-2 tested in 1952) but the blowout in 1968 and linked processes that followed afterward caused intensive migration and leakage of CO_2. The leaked gas was trapped in the layers represented by sandstones of the Pontian and Pliocene age and the collapsed wellbore was identified as a prime source of leakage. This knowledge led to conclusion that some further measures of remediation should be conducted to seal wellbore Bc-5. The method of injecting of silica solution was chosen and the operation carried out in 2007.

The monitoring plan of effects of injection included:

- Monitoring of the pressure of CO_2 reservoir in well Bc-X-1;
- Monitoring of CO_2 flux in soil;
- Monitoring of the quality of water from pond formed on the site of destroyed well Bc-5; and
- Monitoring of the quality and gas composition of groundwater from shallow aquifers up to 70 m depth.

The monitoring started a year before the remediation method was applied so it was not possible to determine exact natural concentrations of CO_2 in soil and water and the frequency of measuring was once a month. The effects of blowout had disturbed the natural conditions on site so the data were gathered to establish the reference values for the analyses of deviation during the monitoring of remediation in the period July 2006-May 2007. The samples of groundwater taken from 4 observation wells that had been drilled in the period June-July 2006 enabled the monitoring of the water quality and CO_2 flux in soil to start a year before the injection of sealant was performed. The drilling of the injection well Bc-9 and subsequently the sealing of wellbore of Bc-5 was conducted in 2007 after which the monitoring was carried on for 5 years after finishing the remediation.

6.2.1 Monitoring of the pressure of CO_2 reservoir in well Bc-X-1

The static pressure was monitored within the CO_2 reservoir in production interval 1135.7-1150.5 m. Given the results of the pressure measurements when compared with previous measurements (including those from the other production wells) it indicated that the repair of the collapsed wellbore resulted in ceasing the constant pressure decline (Figure 23). This indicates that the leakage of CO_2 was significantly reduced if not completely stopped and remediation had been successful.

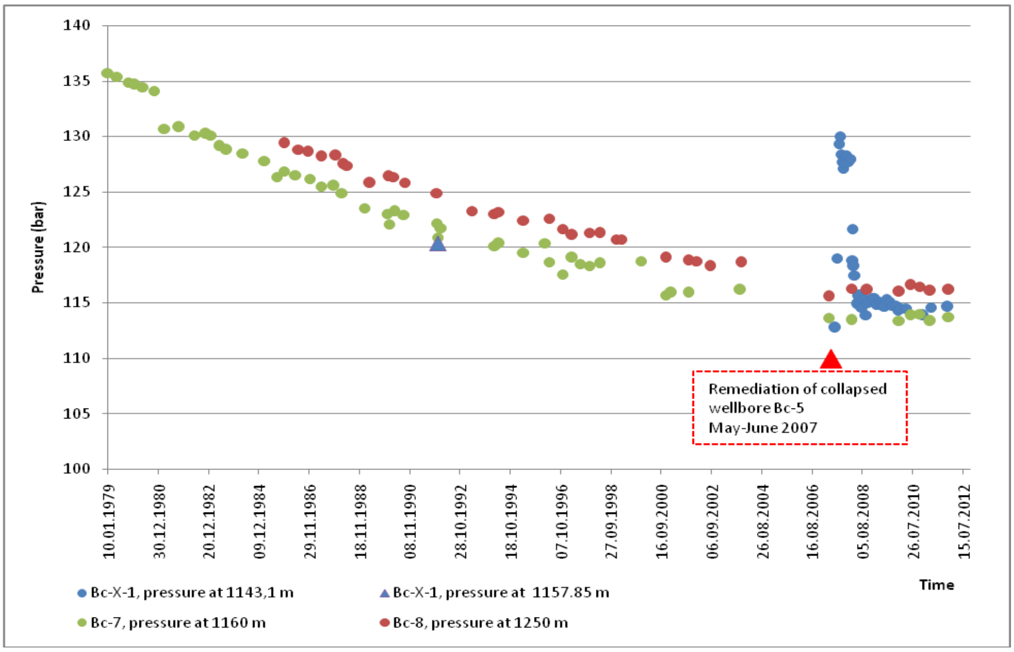


Figure 24 Monitoring pressure of CO_2 reservoir in well Bc-X-1 (1979-2011).

6.2.2 Monitoring of CO_2 flux in soil

CO_2 flux in soil was measured at 22 points by apparatus LI-6400 Portable Photosynthesis System (LICOR Inc., Lincoln, Nebraska). Along with the flux measurements, values of pH and soil moisture were also collected as well as the meteorological parameters that lasted during measuring (air temperature and pressure, humidity, wind, insolation).

6.2.3 Monitoring of the quality of water in the pond formed on the site of destroyed well Bc-5

During monitoring the signs of degassing on the pond surface were constantly visible on several locations, CO_2 content was in the range of 4.62 to 66.8 g/l with pH values from 6.99 up to 9.31 (in some samples no CO_2 were measured).

6.2.4 Monitoring of the quality and gas composition of groundwater from shallow aquifers up to 70 m depth

The positions and technical characteristics of the monitoring wells are given in Figure 24 and Table 13.

Table 13 The technical characteristics of monitoring wells.

Well	Screen (m)	Distance from Bc-5 (m)	Construction
Bc-5-1/P	13-19	21.08	PVC d 75 mm
Bc-5-2/P	61-67	42.40	PVC d 125/75 mm
Bc-5-3/P	55.5-61.5	84.54	PVC d 125/75 mm
Bc-5-4/P	13-19	59.90	PVC d 125/75 mm

The following set of parameters were analysed: sample temperature, groundwater level, pH value, alkalinity, hardness, CO_2 content, consumption $KMnO_4$, dry residue, major cations (Na, K, Ca, Mg) and anions (bicarbonates, carbonates, sulphates, chlorides and nitrates).

After five years of monitoring of groundwater quality it was concluded that the measured concentrations of CO_2 did not exceed usual values for groundwater in shallow confined and unconfined aquifers except in samples taken from well Bc-5-1/P. This monitoring well is the closest to the former location of well Bc-5 and remarkable deviations are recorded especially in comparison to results of water samples from well Bc-5-4/P since both screened the unconfined aquifer at the same depth (the concentration of CO_2 in Bc-5-1/P is several times higher than in well Bc-5-4/P). Beside CO_2, the other measured parameters that deviated are pH, content of carbonates and bicarbonates, hardness, dry residue and consumption $KMnO_4$.

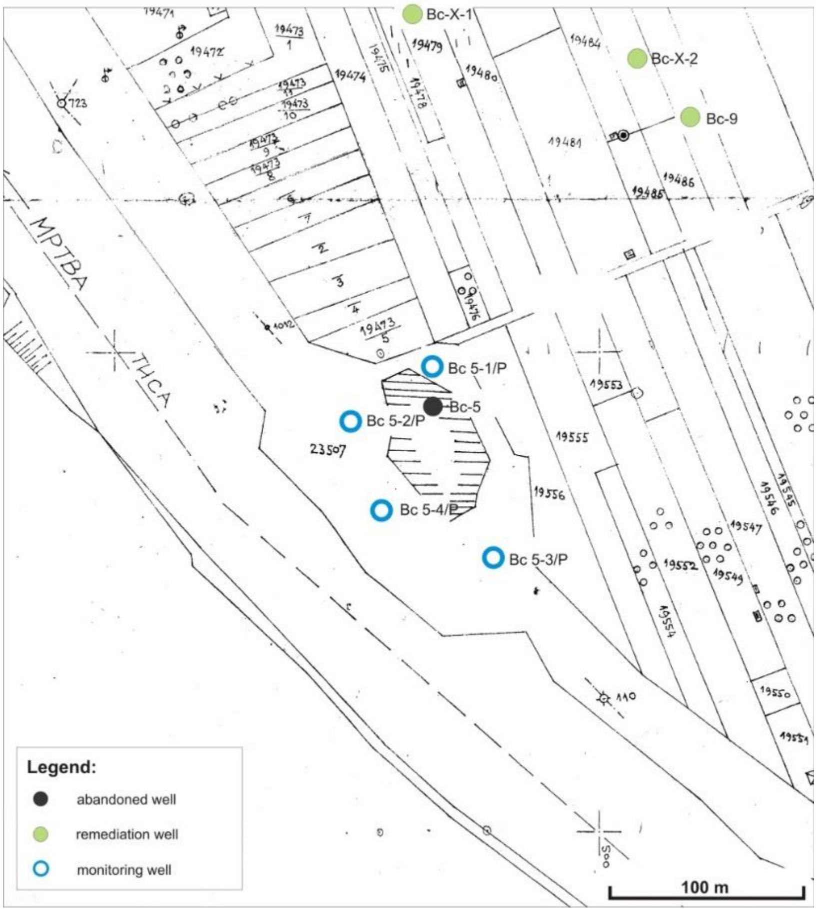


Figure 25 The positions of the monitoring wells in shallow aquifers up to 70 m depth.

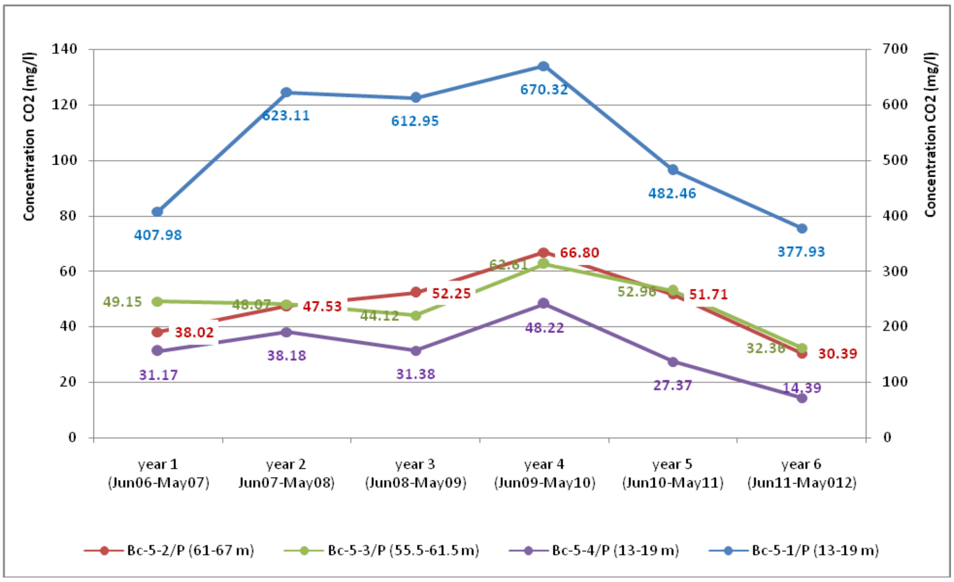


Figure 26 The average annual concentration of CO_2 in groundwater on site of Bc-5 (2006-2012).

Figure 26 shows the graph of average annual concentrations that content of CO_2 reaches its maximum value in the fourth year of monitoring and then has a trend of decline in all monitored wells. During monitoring the smallest values were registered in the last year and these results pointed out that remediation of well Bc-5 had been carried out successfully.

6.3 Cost summaries

6.3.1 Costs of remediation and monitoring operations at the Bečej field

The costs of remediation and monitoring operations are calculated on the base of 2014 prices in NIS and given in Table 14.

Table 14 Costs of remediation and monitoring operations in Bečej field.

Stage	**Scope of work**	**Estimated costs** (million EUR)
Blowout and monitoring the effects (1968-1972)		**2.50**
Monitoring of the quality of groundwater	Wells - depth from 10 to 400 m, approximately 300 analyses, mainly analyses of gas composition	0.02
Drilling of shallow boreholes	32 shallow boreholes for degassing of groundwater and vadose zone	0.05
Drilling of injecting boreholes	3 shallow boreholes and testing for forming an injection curtain	0.02
Drilling of remediation well Bc-X-1	Drilling and completion of well - 1150 m	1.15
Drilling of remediation well Bc-X-2	Drilling and completion of well - 860 m	0.86
Pressure measurement	Conducting measurement on three wells (1969-1972)	0.18
Consulting services	Design of project, interpretation of collected data, etc.	0.23
Monitoring of the quality of groundwater (1979 and 1988)		**0.01**
Monitoring of the quality of groundwater	Wells - depth from 80 to 400 m, approximately 100 analyses, mainly analyses of gas composition	0.01
Monitoring the effects of CO_2 leakage (1982, 1986 and 1991)		**0.25**
Workover on well Bc-X-1	Geophysical well logging, well cementing (1982, 1986, 1991), hydrodynamic measurements, test of injection (1991)	0.25
Monitoring of CO_2 leakage and remediation of well Bc-5 (2006-2012)		**2.00**
Drilling and injection on well Bc-9	Drilling and completion of well - 1150 m, injection operation	1.65
Workover on well Bc-X-1	Preparation for pressure measurement	0.01
Pressure measurement	Conducting measurement (2007-2011)	0.08
Drilling of monitoring wells	Drilling of 4 wells	0.04
Monitoring the effects of remediation	Monitoring of CO_2 flux in soil, monitoring of the quality of water from pond formed on site of destroyed well Bc-5, monitoring of the quality and gas composition of groundwater from shallow aquifers up to 70 m depth	0.04
Consulting services	Design of project, interpretation of collected data, etc.	0.18
	Total	**4.76**

6.3.2 Costs of remediation and monitoring operations in the literature

IEA GHG (2007, p.140) give a table of costs associated with remediation. Shackelford and Jefferis (2000) indicate the following two cost comparisons of remediation technologies in the US. Tables 15 are costs in the context of remediation of dense non aqueous phase liquids and Table 16 are costs in respect to Brownfields remediation, regardless of type of contaminant with only treatment technologies included. Neither is specifically to CO_2 contamination.

Table 15 Cost comparison of selected in situ technologies (modified after Grubb and Sitar 1995).

Technology (C = containment; T = treatment)	**Approx. Cost ($US/m^3) (from 2000)**
Bioremediation (T)	20–80
Shallow Soil Mixing (T)	35- 85
Permeable Reactive Walls (T)	65-130
Water Flooding (T)	65-130
Soil Vapour Extraction (T)	65-130
Steam Injection (T)	65-160
Slurry Walls (C)	75-140/m^2
Grouting (C)	80-130
Radio Frequency Heating (T)	85-210
Soil Flushing (T)	100-160
Air Sparging (T)	100-160
Electro-osmosis (T)	100-200
Electrokinetics (T)	> $17/Mg
Deep Soil Mixing (T)	170-340

Table 16 Cost comparison of in situ treatment technologies (after Reddy et al. 1999).

Technology	**Approx. Cost ($US/m^3)**
Bioremediation	30-340
Soil Heating	55-110
Electrokinetics	100-140
Soil Vapor Extraction	< 110
Phytoremediation	< 110
Soil Flushing	105-215/m^2
Stabilization/Solidification	130-200/m^2

The costs estimated will always be a ball park figure as each costing will be site specific, but for comparative purposes the Bečej costs and the quoted costs from sections 19.1 and 19.2 indicate that:

1) Bioremediation tends to be the cheapest technology;
2) Stabilisation/solidification, especially with respect to deep soil mixing, is relatively expensive;
3) Slurry walls are expensive and depend on the length of the wall required;
4) Active soil zone remediation techniques are relatively equal in cost;
5) Containment is the cheapest technology for metals remediation; and
6) The costs associated with most of the *in situ* enhanced removal technologies vary by only a factor of ~ 2;
7) Drilling a new well is expensive, workover of existing wells is much cheaper (approximately one sixth of the cost of a new well);
8) Monitoring costs are very small in comparison with treatment costs (approximately one tenth).

7 CONCLUSIONS

7.1 Remediation techniques summary

An assessment by one of the authors, Edlmann, of the probable role each of the remediation techniques with regards to CO_2 remediation was undertaken. The assessment is based upon the information presented in this report and is the opinion of the investigator.

The probable role was assessed in terms of:

1) Practicality of application to CO_2 contamination. Is there an established CO_2 remediation application (or at least a reasonable expectation that the application would successfully remediate CO_2) or is it a potential but untested possibility;
2) Ease of implementation of the remediation technology – is it an easy deployed in-situ technology with passive maintenance or a technology that requires significant ground works and implementation infrastructure and active maintenance;
3) Cost – reasonable or so expensive it prohibits the use of the technology.

A summary of the probable role grading process can be seen in Table 17.

The results are presented in Table 18. The table also includes information on what improvements or further research is required to increase its likelihood of applicability of CO_2 contamination remediation.

The results from Table 18 indicate that there are a wide range of remediation techniques available for near surface CO_2 remediation and that any remediation strategy will be site specific.

Table 17 Summary of the probable role grading

Probable role	CO_2 applicability	Ease of technology implementation	Costs
Likely	Proven / established CO_2 applicability	Relatively straightforward technology application	Reasonable
High intermediate	Potentially applicable to CO_2 contamination	Relatively straightforward technology application	Reasonable
Intermediate	Potentially applicable to CO_2 contamination	Complex technology application	High
Minor	Potentially applicable to CO_2 contamination	Complex technology application	Very high
Unlikely	not directly applicable to CO_2 contaminations	Complex technology application	Very high

Table 18 Summary assessment of the probable role each of the remediation techniques with regards to CO_2 remediation.

Remediation	Remediation Technique	Probable role	Improvements / comments
Fluid control measures	Pump and treat	**Likely**	Larger plumes may require horizontal wells and longer remediation times.
	Pump and treat with cap	**Likely**	Cost will depend on extent of cap
	Water injection	**High Intermediate**	Useful short term to reduce concentration of CO_2, but residually trapped CO_2 remains.
	Hydrodynamic isolation	**Likely**	Stabilises CO_2 plume
	Air stripping	**Likely**	Process is quick and relatively cheap
	Hydraulic barrier	**High Intermediate**	Works if aquifer is not very permeable and location of leak is known
Cut off wall (unconfined aquifer)	Cut-off wall / slurry wall	**Intermediate**	High costs depending on length of wall, risk of wall leakage and degradation. Only provide partial containment and further clean up technologies needed
	Two-phase diaphragm wall	**Intermediate**	High costs depending on length of wall, risk of wall leakage and degradation. Only provide partial containment and further clean up technologies needed
	Composite diaphragm wall	**Intermediate**	High costs depending on length of wall, risk of wall leakage and degradation. Only provide partial containment and further clean up technologies needed
	Interlocking bored-pile diaphragm wall	**Intermediate**	High costs depending on length of wall, risk of wall leakage and degradation. Only provide partial containment and further clean up technologies needed
	Installation of thin wall and sheet pile into the soil	**Intermediate**	High costs depending on length of wall and risk of sheet material corrosion
	Injection permeation grouting	**Intermediate**	Leakage risk through permeability gaps. Only provide partial containment and further clean up technologies needed
	Jet grouting	**Intermediate**	Leakage risk through permeability gaps. Only provide partial containment and further clean up technologies needed
	Frozen wall	**Unlikely**	Requires the active (powered) circulation of refrigerant coolant or liquid nitrogen
	Bio barrier	**Intermediate**	Technology untested in situ for CO_2, costs and application low.
	Water control agent	**High intermediate**	Technology available and low cost. Resistance to CO_2 untested.
	High strength rigid set material	**High intermediate**	Technology available and low cost. Resistance to CO_2 untested.
	Organic polymer sealant	**High intermediate**	Technology available and low cost. Resistance

Remediation	Remediation Technique	Probable role	Improvements / comments
			to CO_2 untested.
	Super absorbent crystals	**High intermediate**	Technology available and low cost. Resistance to CO_2 untested.
	Granular activated carbon	**Likely**	Process is relatively quick and cheap but will depend on CO_2 concentration or volume
Cut off wall - Fractured aquifer	Grout curtain	**Likely**	Boreholes ideally orientated to intersect as many fractures as possible, fracture permeability important and can be enhanced through hydrofracking. Grouting materials need to be CO_2 resistant
Permeable reactive barriers (treatment walls)	Sorption barriers	**Likely**	Sorption materials need to be CO_2 specific. Over time reactive materials become less effective at removing CO_2 and the contaminated reactive material needs to be removed and replaced with fresh material.
	Ionic species removal	**High Intermediate**	Established procedure to clean up the trace elements potentially mobilised by the CO_2 contamination
	Microbes	**Intermediate / minor**	A cheap option but CO_2 specific microbes that will be in optimum conditions are hard to establish
	Carbonation stabilisation	**Intermediate / minor**	A cheap option but carbonation rates are hard to establish
	De-acidisation	**Likely**	Established cheap technology
Soil Zone remediation	Soil vapour extraction	**Likely**	Potential to be used in conjunction with containment treatments.
	Air sparging	**High Intermediate**	CO_2 will follow high permeability pathways so initial recovery rates high but will fall off as recovery is limited to diffusion. Potential to be used in conjunction with containment treatments
	Bioslurping	**High Intermediate**	CO_2 will follow high permeability pathways so initial recovery rates high but will fall off as recovery is limited to diffusion. Potential to be used in conjunction with containment treatments
	De-acidise soil	**Likely**	Established cheap technology
	Thermal treatment	**Intermediate**	Costs high and not for CO_2 plume but clean-up of the trace elements potentially mobilised by the CO_2 contamination
	Capping	**Likely**	Cost will depend on extent of cap and most likely to be used in conjunction with a treatment.
	Gas collection trench	**Likely**	Cheap and established method to collect soil gas.
	Ecosystem restoration	**Likely**	Final result of any contamination clean up.
Bioremediation	Bioremediation of low pH groundwaters	**Intermediate**	Cheap established option, but extent controlled by ideal biological condition.
	Bioremediation of CO_2	**Minor**	Cheap, extent controlled by ideal biological condition. But CO_2 specific microbes sill to be field tested.
	Bioremediation of toxic metals	**Intermediate**	Cheap established option, but extent controlled by ideal biological condition.
	Bioremediation of hydrocarbons	**Intermediate**	Cheap established option, but extent controlled by ideal biological condition.
	Natural attenuation	**Likely / Intermediate**	May be first step in the risk assessment procedure, however high costs associated with monitoring.
Buildings	Passive vapour intrusion mitigation	**Likely**	Established cheap technology
	Passive / active sub slab venting	**Likely**	Established cheap technology
	Active vapour intrusion mitigation – subsurface pressurisation	**Likely**	Established cheap technology

Remediation	Remediation Technique	Probable role	Improvements / comments
	Block wall depressurisation	**Likely**	Established cheap technology
	Active ventilation	**Likely**	Established cheap technology
	Passive ventilation	**Likely**	Established cheap technology
	Demolish and rebuild to suitable standards.	**Minor**	Final resort if other building remediation technologies are unsatisfactory.

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