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MANAGING THE RISKS IN THE VADOSE ZONE ASSOCIATED WITH THE LEAKAGE OF CO_2 FROM A DEEP GEOLOGICAL STORAGE

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1 *INTRODUCTION*

1.1 CCS technology

CO_2 capture and geological storage (denoted CCS) is seen as a promising technology in the portfolio of measures required for decreasing greenhouse gas emissions (IPCC, 2005). CCS involves: (1) the capture of CO_2 stemming from different human activities including coal- or gas-fired power plants and industrial facilities (such as refineries, steel mills, etc.); (2) the transport to a storage location; (3) the injection into a suitable geological formation for long-term storage (depleted natural gas and oil fields, deep aquifers and unmineable coal seams). CO_2 is injected in its supercritical state to achieve a higher density, hence occupying less volume underground. This supercritical state is reached at pressures greater than 7.4 Mpa and temperatures higher than 31.1 °C, which correspond to a storage reservoir depth of about 800 m (Law et al., 1996). Since the 1990's, the CCS technology has given rise to major research programs throughout the world (in Europe, the USA, Canada, Australia, Japan, etc.). A number of storage operations are currently underway including pilot projects (Frio in the USA, Nagaoka in Japan, Ketzin in Germany characterized by an injection rate >10kt/y and a life time of weeks to few years, Michael et al., 2010) and large scale industrial projects (Sleipner in the North Sea, Snohvit in Norway, In Salah in Algeria characterized by an injection rate >1Mt/y and a life time of more than 10 years, Michael et al., 2010). The International Energy Agency (IEA) recently outlined that one fifth of the emissions reduction should be carried out by CCS by 2050 (IEA, 2009), hence corresponding to an objective of 100 projects in 2020, and more than 3000 in 2050, and implying an annual amount of stored CO_2 of 10 Gt/y.

1.2 Safety of the CO_2 geological storage

A prerequisite to the wide scale implementation of the CCS technology is demonstrating its safety (IEA, 2007). In this view, an integrated safety strategy should rely on site specific risk assessment and on appropriate monitoring plans. Nevertheless, any industrial activity is confronted with residual risk and the need to know "what can be done" in case of "abnormal behaviour" of the reservoir has been outlined by the European directive on geological storage operations (directive 2009/31/EC, April 2009[1]): *Article 16* "Measures in case of leakages or significant irregularities": "[...] the operator immediately notifies the competent authority, and takes the necessary corrective measures, including measures related to the protection of human health. [...]". Besides this directive states that "Liability for environmental damage (damage to protected species and natural habitats, water and land) is regulated by Directive 2004/35/EC of the European Parliament and of the Council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage, [...]". Therefore, a proper risk management scheme should also be completed with a remediation plan to demonstrate that any undesired consequences can be simply and effectively corrected in the case the safety criteria are not met. Furthermore, such intervention protocols will help to build confidence and public acceptance in the merging technology of CCS.
One major concern is the risk of CO_2 escape from the deep reservoir containment. Such an event might occur through different potential leakage pathways (Figure 1) either man-made (such as operational or abandoned wells) or geological (high-permeable flaws within the caprock overlying the storage reservoir, existing or induced fractured zones, geological faults, etc.) This process is referred as "leakage" (Oldenburg and Unger, 2003). In the present study, we consider the risk event that a CO_2

[1] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0114:0135:EN:PDF

leakage from deep geologic CO_2 sequestration sites reaches the unsaturated shallow subsurface corresponding to the vadose zone, leading to high CO_2 concentrations (either locally in case of leakage through the micro-annulus of an abandoned well for instance, or on much larger spatial scale in case of migration through fractured zones for instance). This might pose severe health and environment risks in the near surface environment or at the ground surface if the CO_2 migration continues through the vadose zone (process referred as “seepage”, Oldenburg and Unger, 2003).

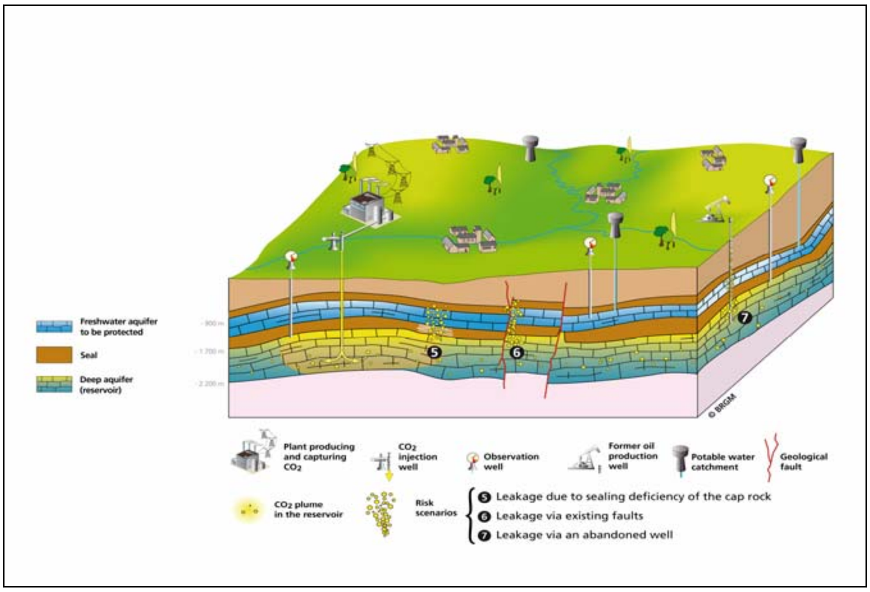


Figure 1: Potential leakage pathways from a CO_2 storage reservoir (adapted from Bouc et al., 2009)

1.3 Consequences of a potential CO2-related pollution

The human exposure to CO_2 is a well-known subject. Regulatory thresholds exist in many countries (IPCC, 2005). In France, these thresholds on CO_2 atmospheric content are as follows (Commission Directive 2006/15/EC of 7 February 2006 establishing a second list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Directives 91/322/EEC and 2000/39/EC”, 9.2.2006): 0.5% for occupational exposure (time-weighted 8 hour average); a 5% short-term exposure limit corresponds to irreversible effects; a 10% short-term exposure limit corresponds to first lethal effects and a 20% short-term exposure limit leads to significant lethal effects.

Impacts of elevated CO_2 exposure of ecosystems remain much less understood, as the responses of individual species are highly variable (IEA GHG, 2007). The consequences of CO_2 intrusion (and possible impurities initially present in the injected CO_2 streams) on surface targets and groundwater still remain an on-going research area. Recent studies include analysis of natural analogues (e.g. naturally occurring gas vent located within a Mediterranean pasture ecosystem in Latera geothermal field, central Italy, Beaubien et al., 2008), in-site CO_2 injection within the vadose zone (e.g. ZERT CO_2 Release Test in Montana (USA), Kharaka et al., 2010, Oldenburg et al., 2009), and various research efforts at both experimental and modelling level (e.g. Zheng et al., 2009). In this context, we can define the characteristics a CO_2-related pollution in the unsaturated shallow subsurface as follows:

- The CO_2 pollution is of gaseous form (in near-ambient conditions acting in the vadose zone);
- The CO_2 pollution is potentially diffuse i.e. affecting large spatial scale especially in case of leakage through fractured zones for instance;
- The CO_2 pollution potentially affects population at surface in case of mixing with indoor environments or accumulation at the ground surface in topographic depressions or confined environments;
- The CO_2 pollution is of acidic nature as CO_2 interacts with the interstitial water, forming the acid H_2CO_3 through dissolution;
- The CO_2 pollution is potentially of poly-metallic nature as it may cause mineral acid attack leading to the release of metal trace elements.

1.4 Methodology

In this study, we will focus on the unsaturated shallow subsurface (also named vadose zone). This zone represents the "last" underground compartment, which might be impacted in case of CO_2 from deep reservoir (depth > 800m). Furthermore, this zone may become a secondary source of pollution for the shallow subsurface or surface targets (especially considering indoor environment).
The objective of this article is to define guidelines for an intervention strategy in case of CO_2 pollution in the vadose zone. In this view, we choose to adopt an analogy-based approach considering the similarities that can be found with the nature and characteristics of other cases of pollution, which are related with other substances. Lessons can be drawn from the risk management strategies of these complex remediation real cases. Note that the analogy has not been carried out regarding the health and environmental effects of other substances.

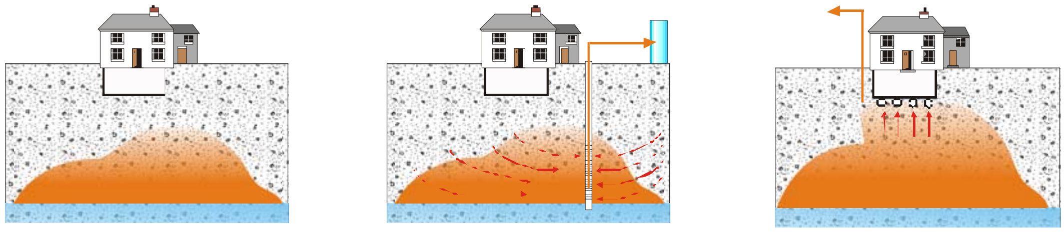
2 *HOW TO CONTROL THE TRANSFER OF THE CO_2 LEAK WITHIN THE VADOSE ZONE ?*

In this section, we focus on the migration of the CO_2 leak through the vadose zone and the possible remediation options for removing the CO_2 gas plume and preventing the potential emission of the CO_2 into ambient air.

2.1 Analogy with VOC remediation: case of a limited impacted area

Considering the migration of the CO_2 at the near-ambient pressures and temperatures within the vadose zone, the CO_2 presents several similarities with Volatil Organic Compounds (VOC) with a density of the same order of magnitude (1.81 kg/m^3 at 25°C and 1 bar, Falta et al., 1989) and a dynamic viscosity reaching intermediate values between those of air and of water. The vapour pressure of the CO_2 gas reaches 58.5×10^5 Pa and the Henry's law constant reaches 1.41 (at 20°C). Nevertheless, two main differences should be outlined : (1) CO_2 gas is relatively harmless to humans and other animals at low concentration, whereas various VOC, such as Methylene chloride, Benzene, Xylene, present a high level of toxicity at very low concentrations (order of magnitude of a few µg/m^3) ; (2) the « source » of pollution is situated within the storage reservoir at a great depth (> 800m) so that in case of a potential leakage from the reservoir, the CO_2 mainly migrates upwards (Figure 1), whereas most of the VOC present a source at the subsurface (comparatively less deeper) so that their migration is mainly lateral or downwards.
Various remediation techniques have been developed for the last 20 years to restore a vadose zone contaminated by VOC. These strategies can be divided into three main categories as depicted in Figure 2:

- natural attenuation (also named "passive remediation"). This relies on natural processes (biological transformation, dispersion, dilution, sorption, volatilisation and chemical or biological stabilisation, transformation or destruction of pollutants) , which allow to reduce the mass, toxicity mobility, volume or concentration of contaminants in soil and groundwater (e.g. as defined by the US EPA, 1997). This means that contaminants are left in place while natural processes act without human intervention to destroy or neutralize contamination. The main advantage is the financial aspect in comparison to other active methods. This method should be combined with active monitoring techniques to ensure that the natural processes capability is in agreement with the prediction (as advocated by US EPA, 1997) ;
- active extraction techniques such as "Soil Vapour Extraction" SVE, which is an appealing technique because of the relatively low costs associated with installation and operation, effectiveness of remediation, and widespread use at contaminated sites (e.g. Lehr, 2004);
- protection of targets through techniques aiming at stopping the vertical migration of CO_2 (using impermeable cover at the surface for instance). On these aspects, further details are given in the section 5 of this article.



A) B) C)

Figure 2: intervention strategy for managing the transfer of CO_2 within the vadose zone : A) monitored natural attenuation ; B) active extraction techniques such as SVE; C) protection of targets through techniques aiming at stopping the vertical migration of CO_2

We assess the feasibility of removing a CO_2 plume from a 35 m thick sandy homogeneous soil after 1 year of leakage at a constant rate of 2 kg/day/m² (which is equivalent to the leakage rate observed at the natural analogue in Latera, Beaubien et al., 2008). The CO_2 leakage occurs over a circular surface of 66m radius, so that the total amount of CO_2 leak reaches 10 000 t/y (equivalent to 1% of leakage of a large scale storage of 1 Mt/y). We define a remediation scenario considering a starting-time after which the irregularity (i.e. formation of the CO_2 leakage plume) has been detected through the monitoring plan and after which appropriate corrective measures have been undertaken at the reservoir depth to control and to cut off the source of the CO_2 leakage. A three dimensional model is constructed using the multiphase and multi-component TOUGH2/EOS7CA, which models the Darcy flow and Fickian diffusive transport of five components (water, brine,CO_2, a gas tracer, and air) in gaseous and aqueous phases at near-ambient pressures and temperatures (Oldenburg et al., 2009). TOUGH2/EOS7CA is designed for near-surface applications where the pseudo component air is present (Oldenburg and Unger 2003). The solubility is modelled by means of the Henry's Law.
Four remediation options are investigated (Figure 3): (A) natural attenuation of the CO_2 plume after 6 months; extraction of the CO_2 plume during 6 months using an applied vacuum to draw pore gas: (B) toward a single vertical well (mass rate extraction of 0.03 kg/s); (C) toward three vertical wells (mass rate extraction of 0.01 kg/s/well) with a distance between them of 75m and (D) toward a single vertical well and two 150 m long horizontal conduits (mass rate extraction of 0.01 kg/s/well).
After 6 months of operation more than 70% of initially leaked CO_2 still remain within the system for the natural attenuation strategy, more than 50 % still remains for the extraction strategy B), about 25 % for strategy C) and about 15 % for strategy D). These results emphasize the good effectiveness of standard extraction techniques in case of CO_2 leakage source characterized by either limited spatial extent or moderate flux rate. More detailed investigations can be found in Zhang et al., 2004.
It should be underlined that the performance of such extraction techniques is strongly linked with the ability of the CO_2 to migrate toward the extraction wells (Bradner and Murdoch, 2005), which depends on the vadose zone properties, such as the presence of high water saturation zone, of very low intrinsic permeability regions or of high permeability conduits, which can lead to much longer extraction times due to the diffusion of the gaseous pollutant from lower permeability regions to these regions (Pruess and Wang, 2001). An additional limitation may be due to the ability of CO_2 to interact through dissolution with the interstitial water of the vadose zone.

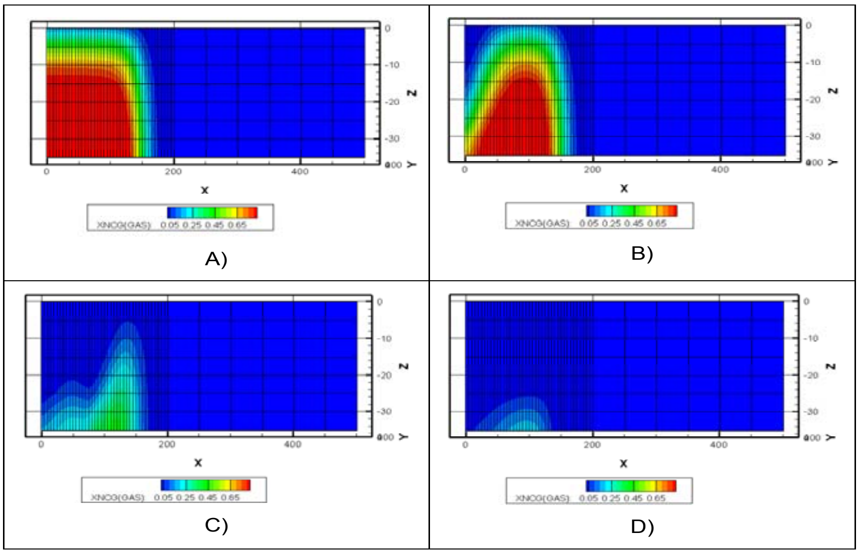


Figure 3 : CO_2 mass fraction in the vadose after 6 months of operation for four remediation strategies: A) natural attenuation; B) extraction through a single vertical well; C) extraction through three vertical wells and D) extraction through one vertical well and two horizontal conduits.

3 *WHAT IS THE INTERVENTION STRATEGY IN CASE OF A DIFFUSE POLLUTION ?*

One major concern is the potential impact of the gaseous CO_2 over a large soil area, which may likely to occur in case of leakage through a large fractured zone for instance.

3.1 Analogy with the pesticide case : case of a diffuse pollution

To deal with such a “diffuse” pollution, lessons can be drawn from the pesticide contamination cases with a special attention paid to the chlordecone case. This chlorinated insecticide, is one of the 17 chemicals currently regulated by the Stockholm convention on persistent organic pollutants. It was used from early 1970 until 1993 in the French West Indies in banana plantations for the control of banana root borer.
The measurements revealed a significant chlordecone contamination of the natural environments of French West Indies, including soils, river waters, spring waters, vegetables and animal local food resources. The total impacted surface area represents roughly 52 km² for Guadeloupe and 62 km² for Martinique (more details can be found in Cabidoche et al., 2005). To compare, the surface area of Paris city is about 105 km².
CO2 and pesticide present great differences regarding their behaviour in the environment and their health effect. The pesticide case is only interesting in the way the environmental issue is managed.

3.2 Lessons drawn from the pesticide case

Since the surface areas in question are quite substantial, the pollution management methodology (under-development for the French authorities) advocates the need to study the issue as a whole (i.e. global approach) and arrive at a set of priorities and shared rules. Regarding treatment, the quantities of material are so large that the cost of traditional techniques (i.e. confinement, stabilization, washing, etc.) is expected to be prohibitive. Therefore, the remediation techniques should be reserved for targeted sectors. The prioritization of zones affected by the contamination can be based on the following criteria:

- identification of vulnerable elements such as cultivation zones, habitation area, potable water catchments, playing areas, protected areas of importance for wildlife, flora, fauna such as nature reserves i.e. zones where populations are directly threatened;
- identification of zones, where the pollutant could potentially accumulate (highly concentrated soils), corresponding, in case of CO_2 leakage to the near zones of abandoned wells, to faulted (or fractured) zones, to confined spaces or buildings located in topographic depressions for instance. Note that the identification of such vulnerable elements is fully integrated in the

phase of site selection for CO_2 geological storage (Grataloup et al., 2009).

4 *HOW TO PREVENT THE MIGRATION OF THE CASEOUS CO2 FROM THE SOIL TO THE INDOOR ENVIRONMENTS?*

In case of diffuse pollution, one major concern is the release of gaseous CO_2 into buildings (mainly through advective and diffusive flow transport mechanisms). Once mixed with indoor air, it may cause health hazards, the first irreversible effects begin at a 5% in volume short-term exposure limit. To protect indoor environments from the gaseous intrusion of CO_2, guidelines can be drawn from the radon case. Like the previously-mentioned pollutant substances, CO_2 and radon can not be compared regarding the sanitary risks.

4.1 Analogy with the Radon case

Radon is a natural radioactive gas that is formed from the radium decay issued from uranium contained in the earth's crust and particularly in granitic and volcanic soils. Radon may enter buildings from the ground and rises upwards through cracks in the construction and accumulate at high concentration levels in the confined indoor atmosphere of the buildings. When radon mixes with indoor air, part of it will be inhaled and expose the airways to α-radiation and may eventually cause lung cancer. In France, nearly 300 000 individual dwellings are considered to present radon concentrations greater than the French reference level of 400 bq.m-3 (Gambard et al., 2000).

4.2 Preliminary phase: prediction of potential zones of leakage

Like the radon case, a preliminary screening phase can be undertaken in a preventive approach to identify the potential zones of leakage. In the CO_2 case, this phase can be based on the risk-oriented site selection (see section 3.2) during a CO_2 storage project (Grataloup et al., 2009). It should be mentioned that the implementation of such a procedure could be integrated within the management of building permits.

4.3 Monitoring plans in indoors environments

Monitoring plans can be defined for the measurement of CO_2 at the surface. Within indoor environments, cost-friendly techniques can be proposed based on infrared spectroscopic tools (detection threshold of 10 ppm) for instance. Such measurements could be undertaken: (1) in the regions identified in the first step; (2) in case of events indicating possible CO_2 leakage (such as reports of respiratory troubles in the building basements); (3) in case the “deep” sub-surface monitoring plan has detected such an irregularity (e.g. through an observation well located in an aquifer formation overlying the storage reservoir, Benson and Hepple, 2005).
It should be underlined that the objective is not the early detection of such an intrusion, rather the protection of the populations. A special attention should be paid to ascertaining the origin of abnormal CO_2 concentration in the building atmosphere, as the source of CO_2 emission can be of various kinds including industrial sources and natural sources (degradation of organic matter for instance).
Defining robust and cost-friendly protocols represents a subject of various research studies (for instance the SENTINELLE research project aiming at developing CO_2 storage monitoring techniques and funded under the CO_2 program of the French National Research Agency).

4.4 Remediation measures

Defining remediation measures in case of CO_2 within indoor environment requires a good diagnostic of the building aiming at accurately identifying CO_2 intrusion pathways (e.g. presence of cracks within the construction). On this basis, different strategies can be proposed aiming at:

- cutting off or reducing the transfer at the soil - building interface by means of sealing techniques;
- decreasing the air pressure at the interface by means of naturally-enhanced or man-made techniques (Soil Depressurization System, denoted S.D.S., Collignan and Sullerot, 2008, Figure 4);
- increasing the dilution of the CO_2 directly within the indoor environment by means of naturally-enhanced or active ventilation systems (through vents).

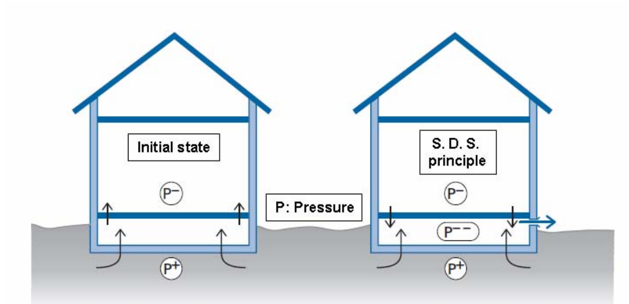


Figure 4: Soil Depressurization System S.D.S. principle: the air flow direction between the basement and the indoor environement is inverted by the pressure decrease at the interface (denoted P^{--}), hence preventing the gaseous pollutant advective upwards migration (adapted from Collignan and Sullerot, 2008)

Over the last few years, the implementation of such measures has shown that an effective protection can be achieved at a moderate cost, ranging from thousands of euros for individual housings to tens of thousands of euros for sensitive buildings such as schools (e.g. Collignan et Sullerot, 2008).

5 *HOW TO MANAGE THE POTENTIAL GEOCHEMICAL IMPACT OF CO2 WITHIN THE VADOSE ZONE ?*

The gaseous CO_2 can interact with the interstitial water contained within the pore space of the vadose zone system forming the acid H_2CO_3 dissociating in the water ($CO_2 + H_2O \rightarrow H^+ + HCO_3^-$). This will cause a drop in pH (increase in acidity) and may cause a mineral acid attack (of carbonate, sulfide and iron oxyhydroxide minerals for instance). Dissolution of these minerals and desorption/ion exchange could lead to the potential release of trace elements, which might lead to two major undesired consequences: (i) adding Fe, Pb, U, As, Cd, and other toxic metals to groundwater, which may exceed the regulatory quality limits for water consumption, as established in the European Union (Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, 5.12.1998) and (ii) increasing metal bioavailability for plants and animals in soils and surface water. The evidence of the geochemical impacts in groundwater has been outlined by the recent field determinations at the ZERT in-site experiment (Kharaka et al., 2010). A rapid and systematic changes in pH (7.0–5.6), alkalinity (400–1330 mg/l as HCO_3), and electrical conductance (600–1,800 µS/cm) have been reported following CO_2 injection (300 kg/day) in samples collected from the 1.5 m-deep wells. CO_2 injection appears to be responsible for mobilization of metals (but still under the maximum contaminant levels mandated by U.S. Environmental Protection Agency). The mobilization of BTEX (e.g. Benzene, 0–0.8 ppb) has been reported as well.

5.1 Analogy with acidic mine drainage and industry contamination

To deal with such a complex environmental issue, lessons can be drawn from the pollution real cases implying poly-metallic contamination either due to mining or industrial activities. A review of the largest contamination cases can be found in NATO, 2005 for instance.

A special attention is paid to the acid mine drainage phenomenon (denoted AMD), which is a much documented problem afflicting mining regions (e.g. Younger et al., 2002). When rock surfaces are exposed to water (either stemming from rain or water table changes due to the pumping cease in case of mine abandonment), a reaction can occur with the elements in the rock which results in a change in the characteristics of the water that drains off. If the rock contains sulphides, a natural oxidation process can acidify the water. As the water becomes more acidic, its capacity to leach out other elements from the rock, such as metals, increases. The resulting drainage can become very acidic and contain a number of harmful constituents.

We recall that the geochemical consequences of CO_2 intrusion in groundwater and in the vadose zone is still an on-going research subject. In this context, we draw lessons from the AMD case keeping in mind this case can be considered a worst-case regarding the order of magnitude of pH drop (in a Californian mine near Redding[2], it reaches -3.6) and regarding the concentrations of released trace elements.

[2] http://ca.water.usgs.gov/issues/water_quality/acid/,

5.2 Preliminary phase: identification of zones characterized with high potential of metals release

In a preliminary phase, the zones, where the phenomenon of acidification and metal elements release is likely to occur should be identified. Ahead of the CO_2 injection and storage, a particular attention should be paid to (i) soils, which naturally present high metal concentrations (for instance the lead-rich Triassic soils in the French region Jura); (ii) to polluted sites and (iii) to zones where pollution has been removed (as these zones may still present residual metal concentration).
In a second step, the sensitivity of these zones to release metals (initially contained in soils) and to transfer them to the targets identified such as groundwater, surface water or the vegetation following CO_2 leakage should be assessed. In this view, several data should be collected: mineral composition of the solid phase, geochemical composition of groundwater, the neutralization and buffering capacity of soils, etc. further detailed guidelines are described by the PIRAMID consortium[3] for instance.

5.3 Vulnerable elements inventory

Following the methodology to tackle large scale diffuse pollution (see section 3), the vulnerable elements in the expected impacted area should be identified. These may correspond to cultivation zones or potable water catchments or domestic kitchen gardens, playing areas, protected areas of importance for wildlife, flora, fauna such as nature reserves. Such an approach can easily be integrated within the screening phase of site selection (Grataloup et al., 2009). In relation to the vulnerable elements, an environmental monitoring and an intervention/remediation plan should be defined.

5.4 Environmental monitoring

Though such a procedure is highly site specific, key parameters of the soil can be outlined: soil pH, Cation Exchange Capacity CEC (combined with the pH, it provides an indicator of soil quality agronomy), presence of leachable trace elements contained in soils, trace element concentrations in cultivated vegetables, etc. Like the radon case, such a monitoring plan should take into account the natural variability in order to accurately determine the origin of trace element anomalies.

5.5 Remediation measures

The methodologies and techniques (e.g. Mulligan et al., 2001), which are currently undertaken (or under development) for remediation of acidic-induced pollution (mainly in the field of acidic mine drainage and poly-metallic contamination on industrial plants) may be deployed in case of acidification and potential metal release due to CO_2 leakage. Such techniques aim at:

- treating the acidity perturbation (i.e. controlling the pH drop) by means of amendments or additives-based techniques (using for instance substances such as $Ca(OH)_2$, CaO, $CaCO_3$, Na_2CO_3, …), constructed basins (wetlands), phyto-remediation, etc.
- controlling the metal-related pollution by acting on the source (through isolation and containment); on the transfer by means of permeable walls treatments or directly on the targets through chemical treatments based on precipitation, adsorption or ion exchange (for instance iron precipitation by phosphate), biochemical treatments (for instance sulphate-reducer bacteria), electrically-based methods (for instance electrolyse or simply restrictions for land use, etc.

To illustrate one of these methods, the case of the spoil heap leachate at Shilbottle, Northumberland, can be used (Bowden et al., 2005). At this site, a 170 m long PRB (permeable reactive barrier) was installed in summer 2002, in two sections, for the treatment of acidic (pH≈4.0), metal-rich (≈700 mg/l of Fe, ≈300 mg/l of Al and ≈240 mg/l of Mn). The barrier is 3 m deep and 2 m wide, with a nominal hydraulic retention time of 48 hours. After 2.5 years of operation, the extent of removal of metals was particularly encouraging (with approximate removal efficiencies of 96% for Fe, 78% for Zn, 71% for Ni, 52% for Mn, and 59% for SO_4). The study outlined that the implemntation of such technique requires maintenance. The Shilbottle case demonstrates that restoring AMD-induced pollution can be achieved effectively at a moderate financial cost. Nevertheless, this case can not be generalized and it should be kept in mind that the cost and the restoration time of complex sites polluted (mega-) sites polluted by metals or metalloid is highly site specific and depend on the spatial scale of the pollution.

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[3] http://www.ncl.ac.uk/environment/research/PIRAMID.htm

The case of La Combe du Saut (France) provides order of magnitude of costs for pollution management of a so-called “Mega site”. For one century, 15 million tonnes of ore were treated at this site to produce gold and arsenic trioxide (the activity ceased in 2004). This caused large contamination (arsenic concentration in soils up to 100000 mg/kg are reported). In order to significantly reduce the transfer of pollution, to restore satisfactory water quality and to avoid the accumulation of polluted sediments in the river, a combination of techniques are used: evacuation of highly polluted waste, confinement of the polluted material exhibited concentrations above 3 g/kg, and phytostabilisation of excavated zones (12 ha). The programme was accompanied by a specific long term monitoring plan (1999 – 2006). The total cost of such a restoration plan reaches 23.3 millions of euros (including 11 millions for the excavation, containment, management of run-off water and phytostabilization). Further details can be found in the research project DIFPOLMINE – LIFE ENVIRONMENT website[4].

6 *CONCLUDING REMARKS*

In case of leakage of CO_2 from deep geological storage into the unsaturated shallow subsurface environment (vadose zone), a number of guidelines for possible intervention and remediation plans can be drawn based on the similarities that can be found between the expected characteristics of a CO_2-related pollution and complex environmental cases related with other contaminants.

- In case of limited spatial impact, standard extraction strategies (based on SVE techniques for instance) as developed in the VOC case can be deployed (as demonstrated by the numerical simulations carried out in this article and in Zhang et al., 2004). But, we have to keep in mind the limitations of such techniques in heterogeneous soils;
- In case of much larger spatial impact (i.e. diffuse pollution), guidelines can be based on the currently-developed methodologies for the pesticide-related pollution case, which advocate the need to study the issue as a whole (i.e. global approach) and to define a set of priorities for remediation actions, focusing on vulnerable elements and highly concentrated zones ;
- In case of diffuse pollution, one major concern is the release of gaseous CO_2 into buildings; the radon case demonstrates that simple remediation techniques can be cost-effectively deployed for the protection of existing or future buildings. The key aspect will be to ascertain the origin of the CO_2 anomaly;
- The experience gained in the pollution related to acidic mine drainage activities can be used in case of potential metal release due to CO_2 dissolution, but treating such a complex environmental problem remains strongly site specific and dependent on the spatial scale of the pollution. To define precise guidelines, better insights in the impact assessment of a CO_2 leakage should be acquired (on this issue several research programme are currently underway).

This article has focused on the pollution of soil and vadose zone. Further works are currently undertaken to formulate guidelines for the CO_2 -related pollution considering the groundwater issue (confined and phreatic aquifers).

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REFERENCES

Beaubien S.E., Ciotoli, G., Coombs P. Dictor M.C., Kruger M., Lombardi S., Pearce J., West J., 2008. The impact of a naturally occurring CO_2 gas vent on the shallow ecosystem and soil chemistry of a Mediterranean pasture (Latera, Italy). Int. J. Greenhouse Gas Control 2(3), 373-387.

Benson, S. and Hepple, R., 2005. Prospects for early detection and options for remediation of leakage from CO_2 storage projects. In: D.C. Thomas and S.M. Benson (Eds.) Carbon Dioxide Capture for Storage in Deep Geologic Formations-Results from the CO2 Capture Project, vol. 2. Elsevier, London, UK (2005).

Bouc O., Audigane P., Bellenfant G., Fabriol H., Gastine M., Rohmer J., Seyedi D., 2009. Determining safety criteria for CO2 geological storage. Energy Procedia 1(1), 2439-2446.

Bowden L.I., Jarvis A., orme P., Moustfa M., Younger P.L., 2005. Construction of a novel Permeable

[4] http://www.difpolmine.org/servlet/KBaseShow?m=3&cid=10264&catid=10265&id=10265&sort=-1

Reactive Barrier (PRB) at Shilbottle, Northumberland, UK: engineering design considerations and preliminary performance assessment. INWA 2005, Oviedo (Spain), 5-7 September 2005.

Bradner G.C., and Murdoch L.C., 2005. Effects of skin and hydraulic fractures on SVE wells, J. of Contaminant Hydrology 774:271-297.

EC (European Commission), 2009. Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009 on the geological storage of carbon dioxide and amending Council Directive 85/337/EEC, European Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12,EC, 2008/1/EC and Regulation (EC) No 1013/2006.

Cabidoche YM., Jannoyer M. et Vannière H. (2005), Atelier du 3 au 7 octobre ; Dossier « pollution par les organochlorés aux Antilles », CIRAD –INRA, 19p, in French.

Collignan B. and Sullerot B., 2008. Le radon dans les bâtiments : guide pour la remédiation dans les constructions existantes et la prévention dans les constructions neuves, collection Guide technique, CSTB, in French.

Falta R.W., Javandel I., Pruess K., Witherspoon P.A., 1989. Density-driven flow of gas in the unsaturated zone due to the evaporation of volatile organic compounds. Water Resour. Res. 25, 2159–2169.

Gambard J.., Mitton N., and Pirard Ph., 2000. Campagne nationale de mesure de l'exposition domestique au radon IPSN/DGS. Bilan et représentation cartographique des mesures au 1er janvier 2000. Note technique SEGR-LEADS-2000-14, IPSN, France.

Grataloup, S., Bonijoly, D., Brosse, E., Garcia., D., Hasanov., V., Lescanne, M., Renoux., P., Rigollet C., Thoraval., A., 2009. PICOREF: A site selection methodology for saline aquifer in Paris Basin. Energy Procedia 1(1), 2929-2936.

IEA GHG, 2007. International Energy Agency (IEA). “Role of Risk Assessment in Regulatory Framework for Geological Storage of CO_2: Feedback from Regulators and Implementers”, Report 2007/2, 88 p.

IEA GHG, 2009. International Energy Agency (IEA) “Technology Roadmap – CCS”, IEA, Paris, 46 p.

IPCC, 2005. Intergovernmental Panel on Climate Change (IPCC) Special Report on Carbon Dioxide Capture and Storage. In: Metz, B., Davidson, O., de Connick, H., Loos, M., Meyer, L. (Eds.), Cambridge University Press, New York.

Kharaka Y.K., Thordsen J.J., Hovorka S.D., Nance H.S., Cole D.R., Phelps T.J., Knauss K.G., 2009. Potential environmental issues of CO2 storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA, Applied Geochemistry 24, 1106–1112.

Law D.H.S., Bachu S., 1996. Hydrogeological and numerical analysis of CO2 disposal in deep aquifers in the Alberta sedimentary basin. Energy. Convers. Manag. 37, 1167–1174.

Lehr J.H., 2004. Wiley’s Remediation Technologies Handbook, Major Contaminant Chemicals and Chemical Groups, John Wiley and Sons, Hoboken NJ.

Michael K., Golab A., Shulakova V., Ennis-King J., Allinson G., Sharma S., Aiken T., 2010. Geological storage of CO2 in saline aquifers—A review of the experience from existing storage operations. Int. J. Greenhouse Gas Control (2010), doi:10.1016/j.ijggc.2009.12.011

Mulligan C.N., and Yong R.N., Gibbs B.F., 2001. Remediation technologies for metal-contaminated soils and groundwater : an evaluation. Engineering Geology. 60, 193-207.

NATO, 2005. North Atlantic Treaty Organization, NATO/CCMS Pilot Study, Prevention and Remediation Issues in Selected Industrial Sectors: Mega-Sites 2005 Annual Report N273.

Oldenburg, C.M., and A.J.A. Unger. 2003. On leakage and seepage from geologic carbon sequestration sites: Unsaturated zone attenuation, Vadose Zone J., 2:287–296.

Oldenburg C.M., Lewicki J.L., Dobeck L., Spangler L., 2009. Modeling gas transport in the shallow subsurface during the ZERT CO2 release test, Transport in Porous Media 82, 77–92.

Pruess K., and Wang J.S.Y., 2001. Numerical Modeling of Isothermal and Nonisothermal Flow in Unsaturated Fractured Rock: A Review, in Flow and Transport Through Unsaturated Fractured Rock, Second Edition, Geophysical Monograph 42, eds. D.D. Evans, T.J. Nicholson, and T.C. Rasmussen, AGU, Washington D.C.

U.S. EPA Directive 9200.4-17 (1997). Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.

Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. Mine Water: Hydrology, Pollution, Remediation. Kluwer Academic Publishers, London.

Zhang Y., Oldenburg C., Benson S., 2004. Vadose Zone Remediation of Carbon Dioxide Leakage from Geologic Carbon Dioxide Sequestration Sites. Vadose Zone Journal, 858-866.

Zheng L., Apps J. A., Zhang Y., Xu T., Birkholzer J.T., 2009. On mobilization of lead and arsenic in groundwater in response to CO2 leakage from deep geological storage. Chemical Geology 268(3-4), 281-297.