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The Relevance of Geochemical Tools to Monitor Deep Geological CO₂ Storage Sites

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1. Introduction

Combined with an increase in energy efficiency and production of more renewable energy, Carbon Capture and Storage (CCS) is a promising technological chain that aims to prevent climate change by reducing anthropogenic CO₂ emissions into the atmosphere. The three steps of this technology are (i) capturing large-scale CO₂ emissions produced by industrial activities using fossil fuels (coal-fired power plants, factories, steelworks, refineries), by post or pre-combustion methods, (ii) transporting the captured CO₂ to a storage site through pipelines, (iii) storing the CO₂ deep underground. Potential underground storage targets are (i) deep saline aquifers containing a high concentration of dissolved salts, (ii) depleted oil and gas fields (abandoned or used to perform Enhanced Oil Recovery (EOR) or Enhanced Gas Recovery (EGR)), (iii) coal seams, used to perform Enhanced Coal Bed Methane recovery (ECBM). Another possible solution for CO₂ storage would be to chemically fix CO₂ into the carbonated minerals in mafic and ultramafic rocks. Other geological media proposed as storage for CO₂ are oil or gas rich shales, salt caverns and abandoned mines (IPCC, 2005). According to the International Energy Agency (IEA), CCS could contribute up to 19% in the reduction of global emissions in 2050. Measuring Monitoring and Verification (MMV) is an important part of each CCS project. As stated in the European directive on the geological storage of carbon dioxide, “monitoring is essential in order to assess whether injected CO₂ is behaving as expected, whether any migration or leakage occurs, and whether any identified leakage is damaging the environment or human health....” Various monitoring methods, i.e. geophysics and geochemistry, can be used to fulfil such requirements, assess the efficiency of geological storage and ensure the containment of the storage system. In this chapter, we focus particularly on geochemical methods, and discuss their assets and relevance in monitoring CO₂ geological storage sites. At first, a classification is proposed based on a literature review. The role of geochemical methods to identify fluids sources and physicochemical processes is explained, and some examples of applications to deep geological CO₂ storage monitoring are described. Key elements of a relevant spatial use of geochemical methods during the lifecycle of a CCS project are also given, as well as general guidelines and recommendations for the integration of geochemical tools into a monitoring programme.

2. Assets and relevance of the geochemical methods in the framework of deep geological CO₂ storage

2.1 Geochemical tools classification

Geochemical methods used in the framework of CO₂ geological storage can be classified based on the chemical nature of the measured species and include a broad spectrum of chemical and isotopic parameters. The measurements traditionally performed on liquids, gases or solids are (non-exhaustive list): (i) pH measurements and total alkalinity; (ii) ions concentrations, such as Ca, Mg, Mn, K, Na, Li, Fe, Si, Cl, Sr, Ba, SO₄, NH₃, S₂... and Total Dissolved Solid (TDS); (iii) isotopic compositions ($\delta^2\text{H}$, $\delta^{13}\text{C}(\text{CO}_2)$, $\delta^{13}\text{C}(\text{C}_1\text{-C}_5)$, $\delta^{13}\text{C}(\text{HCO}_3^-)$, $\delta^{13}\text{C}(\text{CO}_3^{2-})$, $\delta^{13}\text{C}(\text{CaCO}_3)$, $\delta^{18}\text{O}(\text{H}_2\text{O})$, $\delta^{18}\text{O}(\text{CaCO}_3)$, $\delta^{34}\text{S}(\text{SO}_4)$, $\delta^{34}\text{S}(\text{H}_2\text{S}(\text{aq}))$, $\delta^{34}\text{S}(\text{H}_2\text{S}(\text{g}))$, $\delta^{15}\text{N}$, $^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, $^{21}\text{Ne}/^{22}\text{Ne}$, $^{38}\text{Ar}/^{36}\text{Ar}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $^{87}\text{Sr}/^{86}\text{Sr}$); (iv) isotopic elementary ratios ($^{20}\text{Ne}/^{36}\text{Ar}$, $^4\text{He}/^{40}\text{Ar}$, $^{84}\text{Kr}/^{20}\text{Ne}$, $^{130}\text{Xe}/^{20}\text{Ne}$...); (v) molar concentrations (CO₂, C₁-C₅, H₂, O₂, Dissolved Inorganic Carbon (DIC) = [H₂CO₃] + [HCO₃⁻] + [CO₃²⁻], noble gases); (vi) measurements of the organic contents and use of organic tracers; (vii) SF₆ and perfluorocarbons concentrations; (viii) ^3H , ^{14}C , CD₄, ^{36}Cl , ^{125}I , ^{129}I , ^{131}I . Tracers and chemical compounds used to measure and verify the presence of the injected CO₂ can be native (indigenous), while others can be exogenous and added as an exotic species.

2.2 Powerful identification of the fluid source

2.2.1 Principles

The identification of crustal-fluid sources is based on knowledge of the isotopic compositions of different end-members (for example, the atmosphere, the crust and the mantle), which could present unique isotopic fingerprints. For example, the isotopic compositions of CO₂ produced by different processes in the geosphere (magma degassing, regional metamorphism of carbonate rocks, contact metamorphism of carbonate rocks, dissolution of marine carbonates, biodegradation of hydrocarbons, maturation and metamorphism of coal) each shows an expected range of $\delta^{13}\text{C}(\text{CO}_2)$ (Figure 1).

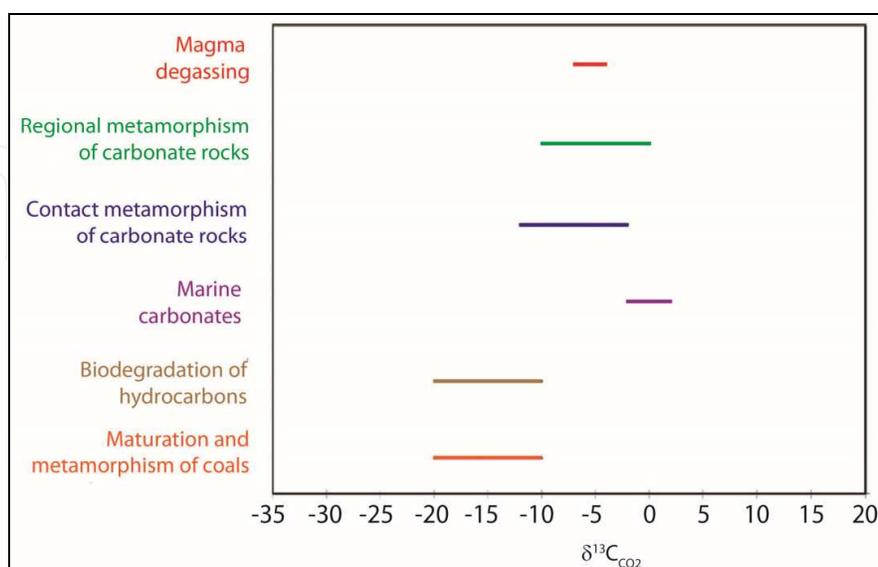


Fig. 1. $\delta^{13}\text{C}(\text{CO}_2)$ values for CO₂ derived from different processes occurring in the geosphere (Holloway et al., 2005).

The source of carbon cannot be unequivocally identified by the $\delta^{13}\text{C}(\text{CO}_2)$ ratios, as there is an overlap in the $\delta^{13}\text{C}(\text{CO}_2)$ of both crustal and mantle origins for CO₂ (e.g. Ballentine, 1997; Jenden et al., 1993; Sherwood Lollar et al., 1994, 1997; Wycherley et al., 1999). Isotopic compositions of mantle-derived carbon are indeed contained between -3 and -8‰ Pee Dee Belemnite (PDB) and isotopic compositions of bulk crustal carbon correspond to a range of -5 to -7‰ PDB. Noble gases can then be used to distinguish between decarbonation/magmatic sources, by comparing for example the measured CO₂/³He ratios in the gas phase with the known values of the crustal and mantle ranges (Sherwood Lollar et al., 1997; Ballentine et al., 2001; Gilfillan et al., 2008; Jeandel et al., 2010).

2.2.2 Applicability to deep geological CO₂ storage monitoring

Isotopic methods can be employed to determine the origin of pre-existing fluids in the reservoir, identify the injected CO₂ based on its isotopic fingerprint and resolve the origin of potentially leaking CO₂.

2.2.3 Examples

If the isotopic fingerprint of the injected CO₂ is sufficiently distinct from that of the background CO₂ in the reservoir, the injected CO₂ can easily be identified. This is notably the case in the International Energy Agency Greenhouse Gas (IEA GHG) Weyburn-Midale CO₂ Monitoring and Storage Project (Saskatchewan) and the Pembina Cardium CO₂ Monitoring Project (Alberta) (Johnson et al., 2009). Fluid and gas samples were regularly collected and analyzed for geochemical and isotopic compositions ($\delta^{13}\text{C}(\text{CO}_2)$, $\delta^{18}\text{O}(\text{H}_2\text{O})$, CO₂ concentrations, DIC). After the CO₂ injection began, even though only a small increase in the CO₂ concentrations was observed in some wells, the $\delta^{13}\text{C}(\text{CO}_2)$ values began to trend towards the value of the injected CO₂. Isotopic monitoring can thus be used to identify and monitor CO₂ breakthrough migration and behaviour.

2.3 Powerful identification of the physicochemical processes

2.3.1 Principles

Geochemical measurements are particularly suitable tools to identify and quantify the physicochemical processes that occur during CO₂ storage. This methodology is based on the knowledge of the physical properties of geochemical tracers and can be used to quantify CO₂/fluids/rocks interactions and fluids partitioning (gas/liquid and possibly oil). The tracers can be reactive (¹⁴C, for example) and be used to monitor chemical reactions. Or they can be un-reactive and conservative (noble gases, perfluorocarbons) and be used to track physical processes, as they are not involved in chemical and biological reactions. The main methodologies applied are based on isotope and mass balance calculations, and the evolution of the chemical and isotopic compositions, and/or the evolution of elementary ratios over time.

2.3.2 Applicability to deep geological CO₂ storage monitoring

The effectiveness, safety and security of geological CO₂ storage depends on a combination of trapping mechanisms such as (i) stratigraphic trapping; (ii) structural trapping; (iii) residual

trapping; (iv) solubility in brine; and (v) mineral trapping. As previously explained, geochemical tools play a key role in detecting the arrival of CO₂ at the observation wells, and are helpful in the quantification of stratigraphic and structural trapping. Mixing curves allow quantifying the respective percentage of background and injected CO₂ over time. Some quantifications of solubility trapping (formation of H₂CO₃ when CO₂ dissolves into water) and ionic trapping (formation of HCO₃⁻) are also documented in the literature, using carbon and/or noble gas isotopes (Gilfillan et al., 2009; Myrntinen et al., 2010). The quantification of mineral trapping, i.e. the formation of carbonate minerals due to the reaction of the dissolved CO₂ with the host rocks, can be similarly performed.

2.3.3 Example

Raistrick et al. (2006) and Myrntinen et al. (2010) introduced and used the following carbon isotope balance calculation to determine the percentage of DIC from CO₂ dissolution in the water phase, and thus to quantify the geochemical trapping of injected CO₂:

$$\frac{\delta^{13}\text{C}_{\text{DICafterinj.}} - \delta^{13}\text{C}_{\text{DICbaseline}}}{\delta^{13}\text{C}_{\text{CO}_2(\text{g})\text{inj.}} - \delta^{13}\text{C}_{\text{DICbaseline}}} \times 100 = \% \text{DIC} \quad (1)$$

from CO₂ dissolution

The percentage of DIC from CO₂ dissolution was corrected for isotope fractionation (−1‰) between CO₂ (g) and CO₂ (aq) at the given reservoir temperature. It should be noted that the trapping quantification is only feasible if the composition of the injected CO₂ is isotopically constant. Moreover, the newly formed DIC from the injected CO₂ and the pre-existing DIC should have different isotopic compositions. Using the geochemical signatures of gas samples taken from different natural CO₂ reservoirs, Gilfillan et al. (2009) have assessed the coherent change in CO₂/³He ratios and δ¹³C(CO₂), for different pH values and dissolution/precipitation processes. In the case of precipitation, there is zero ³He loss from the CO₂ phase and CO₂/³He changes in proportion to the fraction of the remaining CO₂ phase. In the case of dissolution, the change in the CO₂/³He ratio is calculated following the Rayleigh equation. Changes in δ¹³C(CO₂) are calculated using the Rayleigh fractionation equation. They highlighted that in seven gas fields with carbonated or siliciclastic reservoirs, dissolution at a pH of 5-5.8 is the sole major sink for CO₂. CO₂ loss through precipitation as carbonated minerals cannot be ruled out for two siliciclastic reservoirs, but appears minor. Some examples with oxygen isotopes are also reported in the literature (Mayer et al., 2011). Changes of δ¹⁸O values of produced water are due to oxygen isotope exchange between CO₂ and H₂O following CO₂ injection and allow a quantitative assessment of CO₂ dissolved in the fluids and of free phase CO₂ in the pore space of the reservoir.

2.4 Tracer tests and CO₂ plume spreading

Conservative tracers to be injected are extensively used to monitor migration of the CO₂ plume during the CO₂ injection period. Tracers are required to be “chemically inert, environmentally safe, nontoxic, persistent, and stable for purposes of the desired monitoring time scale” (Stalker et al., 2009a). Examples of noble gas, perfluorocarbons, SF₆ and carbon isotopes usage are reported in the literature. They allow for the identification of

single or multiple CO₂ breakthroughs. Their travel time may also validate subsurface flow paths and directions and strengthen the flow modeling of the field test.

2.4.1 Principles

Tracer tests consist of injecting a tracer, generally gaseous and not already present in the reservoir system, into a hydrological system and monitoring its arrival, over time, at various observation points such as monitoring wells. Phase partitioning tracers (non-condensable gases (O₂, CO₂, CH₄), noble gases, SF₆ and other volatile organic chemical compounds), that are both water soluble and volatile, can also give information on the volume fractions of the different fluid phases along the CO₂ migration paths. Due to partitioning into an immobile phase, tracer migration is slowed relative to the inert tracers. This is governed by the Henry law. The retardation factor, expressed as the local ratio of total tracer inventory to the tracer inventory in the mobile phase, depends on the solubility of the tracer in water. For example, more water-soluble tracers are more retarded than fewer soluble tracers. The use of simplifying assumptions (local equilibrium partitioning, absence of diffusion and sorption on solids...) can result in the interpretation of tracer data not being unique, so using several different tracers can reduce ambiguities and uncertainty (Pruess et al., 2005).

In the field, different types of sequence tests can be performed. Prior to CO₂ injection, dual tracer single-well push-pull tests and dual tracer inter-well circulation tests can be carried out to determine fluid-rock interface densities, the connectivity of the hydrologic system and the presence of reservoir heterogeneities. These tests also assess the fluid residence time (Ghergut et al., 2011). For example, tracers can be injected into the aquifer and pushed away by a continuous injection of water. The tracer is then pulled back into the borehole, where a breakthrough curve is measured which is directly dependent on the residual gas saturation. During the CO₂ injection, single well push-pull experiments and dipole flow experiments can be carried out for a dynamic characterisation of CO₂/brine/rock interfaces, and an assessment of the residual saturation.

2.4.2 Examples

Observations from two monitoring wells at the Ketzin CO₂ injection pilot site (Germany), indicated the arrival of nitrogen and krypton gas tracers prior to CO₂ breakthrough (Figure 2) (Martens et al., 2011; Zimmer et al., 2009, 2011). The gases were detected by high temporal resolution Gas Membrane Sensors (GMS), permanently installed at both observation wells (Ktzi 200 (OW1) and Ktzi 202 (OW2)). The first breakthrough was detected after about 530 tons of injected CO₂ in Ktzi 200, which is 50 m away from the injection well. The arrival of the gas at the second observation well (Ktzi 202, 112 m lateral distance to the injection well) was recorded after about 11,000 tons of CO₂ was injected.

The Frio Brine Pilot test (Texas) was another opportunity to test a combination of tracers (perfluorocarbons, SF₆, Kr) and to compare their transport times and to test the efficiency of anticipating a CO₂ breakthrough (Pruess et al., 2005). Tracer tests have been successfully used to monitor migration of the CO₂ plume, after their introduction at given times alongside the injected CO₂ stream and their movement through the formation (Figure 3).

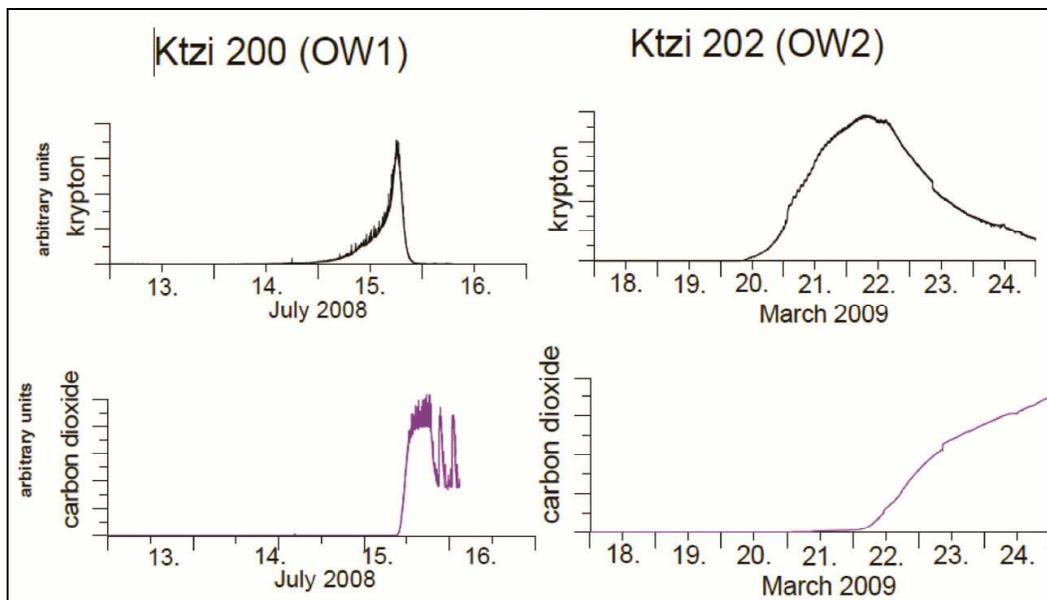


Fig. 2. CO₂ and Kr Arrival in Ktzi 200 (OW1) and Ktzi 202 (OW2). After Zimmer et al., 2011.

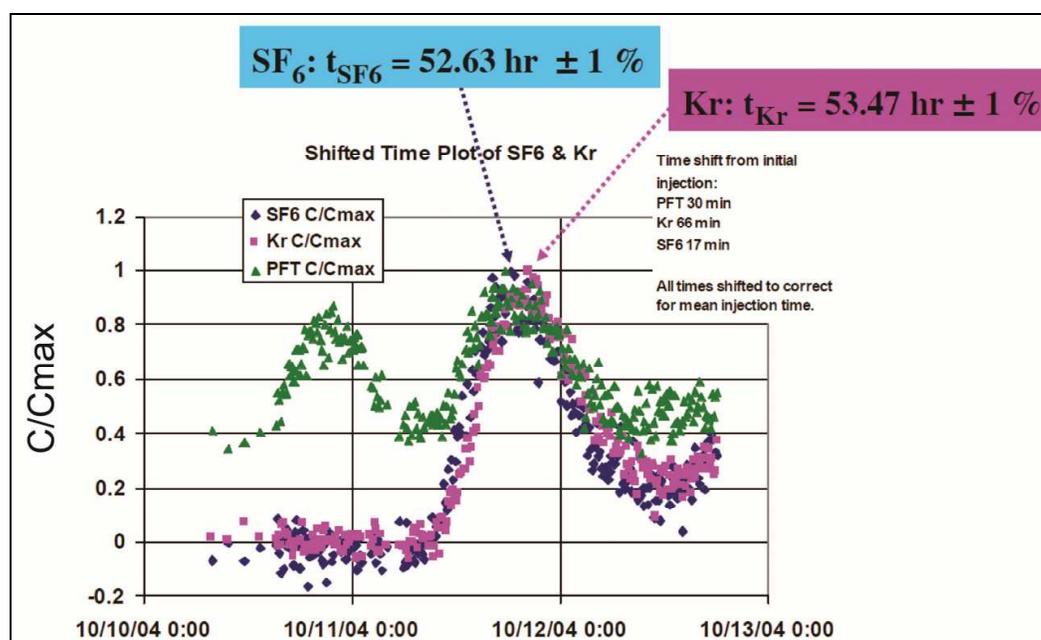


Fig. 3. C/C_{max} of SF₆, Kr and PerFluoroTracers (PFTs) versus time for the Frio brine Pilot test. As Kr is more soluble in water than SF₆, it is retarded relative to less soluble SF₆. After Pruess et al., 2005.

Similar tracer tests (with SF₆ and Kr) were performed at the Cooperative Research Centre for Greenhouse Gas Technologies (CO₂CRC) Otway project (Australia), which was also an opportunity to test perdeuterated methane (CD₄) injection in the depleted Naylor gas field (Stalker et al., 2009b). As the stored gas consists of 75% CO₂ and 20% CH₄, it was hoped that CD₄ would highlight the exchange between native methane (both in the gas cap and the residual gas saturation below) and the injected CO₂/CH₄ gas stream. The new and innovative **Kinetic Interface Sensitive Tracers (KIS-Tracer)** can also be used to assess the interfacial area between supercritical (sc) CO₂ and brine and to survey its development over

time. After the dissolution of the KIS-Tracer in scCO₂, a hydrolysis reaction of the tracer with brine occurs at the scCO₂/brine interface that can be quantified by measuring the concentrations of the reaction products over time at the monitoring wells (Fagerlund et al., 2011).

2.5 Identification and quantification of potential CO₂ leakage from deep geological CO₂ storage sites

Because the detection and quantification of small and diffuse leaks is generally considered to be particularly difficult, the potential role of geochemical methods for such purposes must be scrutinized.

2.5.1 Principles

CO₂ concentrations vary widely in the Earth's crust, so detecting very small releases is difficult. Because of their unique compositions, isotopic fingerprints are particularly useful in identifying and quantifying mixing processes between different sources of CO₂. This geochemical monitoring can be applied to both overlying freshwater aquifers and at the surface.

2.5.2 Examples

Noble gas geochemistry was used to investigate the possible impact of CO₂ migration on groundwater chemistry in the Montmiral natural CO₂ field (France). In plotting the distance between the Montmiral area wells (SL₁, SL₂, VMO₂) and the water sample locations against the measured ⁴He/(²⁰Ne+²²Ne) ratios, an increase in the ⁴He/(²⁰Ne+²²Ne) ratios, associated with a decrease in the distance between SL₁ and the sampling points, was observed. This increase was attributed to a deep gas input (Lafortune et al., 2009), linked to the absence of cement in the abandoned SL1 well. Isotopic compositions can also help to identify the origins of the CO₂ leaks at the surface which were previously detected through flux and concentration measurements. In the Rangely oil field (Colorado), isotopic measurements have shown that loss of injected CO₂ by microseepage into the atmosphere is a fraction of natural biogenic methane seepage (Klusmann 2003). This allowed re-evaluating the deep CO₂ seepage rate.

2.6 Costs and deployment methods

The criteria of an efficient and cost-effective use of tracers should be as follows: sensitivity to detection by analytical methods, low usage volume, and easy handling. For example, Nimz & Hudson (2005) have calculated the quantity of tracers per mass unit of CO₂ needed to detect an increase of 1% of the present natural soil CO₂ (Table 1).

According to Stalker et al. (2009a), application methods (pulsed or continuous injection) also play a role in cost. Analytical costs are seen as the most prohibitive costs overall (specialist tracers, precise measurements by specialized equipment or methods, etc.). Compared to the other methods generally used for CCS monitoring, geochemical methods are by far the least expensive on-site measurements tools to track CO₂ (Benson & Cole, 2008).

Tracer	Atmospheric Concentration (cm ³ /cm ³ air)	Minimum Detectable Variation	Required Tracer Concentration in Stored CO ₂ (cm ³ /cm ³ CO ₂ , STP)	Required Tracer Per 10 ⁶ m ³ CO ₂ (liters, STP)	Tracer Cost (\$US/l)	Tracer Cost/Metric Ton CO ₂ (\$US)	Required Tracer Per Year (liters, STP)
³ He	7.2E-12	300%	2.17E-09	2.2	\$100	\$0.40	1532
²² Ne	1.7E-06	0.1%	1.68E-07	168	\$50	\$15.67	118629
³⁶ Ar	3.2E-05	0.1%	3.16E-06	3161	\$1,000	\$5,904	2234515
¹²⁴ Xe	8.7E-11	0.2%	1.75E-11	0.02	\$20,000	\$0.65	12
¹²⁹ Xe	2.5E-08	0.05%	1.25E-09	1.2	\$1,000	\$2.33	883
¹³⁶ Xe	8.7E-09	0.10%	8.70E-10	0.9	\$300	\$0.49	615
SF ₆	1.0E-11	1000%	1.00E-08	10	\$1	\$0.02	7070
¹⁴ C	1.0E-14	300%	3.00E-12	0.003	\$5,000	\$0.03	2

Table 1. Comparison of different tracers used to detect CO₂ leakage (Nimz & Hudson, 2005).

2.7 Relevance of geochemical methods to fulfill the requirements of the european CCS directive

The European Directive on geological CO₂ storage (Directive 2009/31/EC, 2009), published in 2009, provides a regulatory framework for permanent storage (above 100 kilotonnes of CO₂) and gives details for the practical implementation and permitting of this storage. The Directive recognises that monitoring is essential in assessing whether (i) injected CO₂ is behaving as expected, (ii) whether any migration or leakage occurs, and (iii) whether any identified leakage is damaging the environment or human health. Among the monitoring tasks required by the European Directive, geochemical tools can be relevant for: (i) detecting significant irregularities (Article 13); (ii) detecting migration of CO₂ (Article 13); (iii) detecting leakage of CO₂ (Article 13); (iv) detecting significantly adverse effects on the surrounding environment, particularly drinking water; (v) assessing the effectiveness of any corrective measures; and (vi) updating the short and long term safety and integrity assessment of the storage complex. Geochemical data (mainly dissolution and mineralisation rates) are also included in the list of data collected for the characterisation and assessment of the potential storage complex and its surrounding area (Step I, Annex I). The data are needed to build a three-dimensional static geological earth model of the reservoir and its overburden (Step II, Annex I), and play a key role in assessing the reactive processes and the dissolution rate of CO₂ in water (Step III, Annex I). The characterisation of the storage dynamic behaviour implies a quantification of the trapping rates and an assessment of changes in formations fluid chemistry and subsequent reactions (pH change, mineral formation) (Step III.I, Annex I). A part of the risk assessment (III.III) also concerns the magnitude of leakage in identified leakage pathways (flux rates), and the displacement of formation fluids, as well as the new substances created by CO₂ storage. Consequently, geochemical monitoring methods are central to the monitoring plan (Annex II).

3. Relevant spatial use of geochemical methods in a CCS project

An integrated Measurement Monitoring and Verification (MMV) program must include technologies to track CO₂ through the entire CO₂ storage complex. Benson (2007) schematically describes the different monitoring targets of the bio- and geosphere, for both

offshore and onshore CO₂ storage sites (Figure 4): (i) reservoir rock, (ii) cap rock, (iii) well(s), (iv) overlying aquifers, (v) vadose zone, terrestrial and aquatic ecosystems, (vi) the surface and the atmosphere.

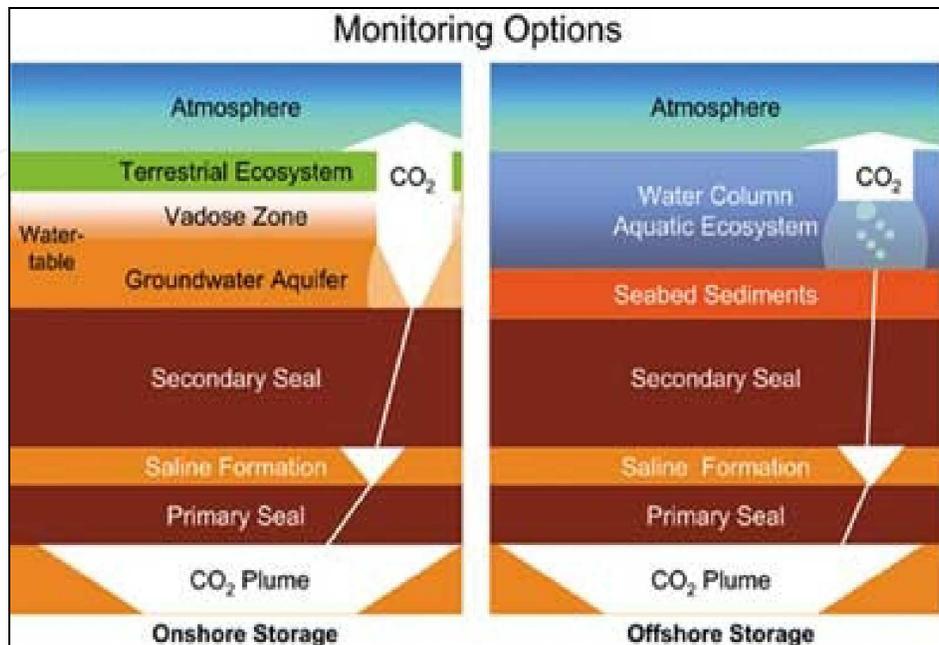


Fig. 4. Main monitoring targets of a CO₂ storage project in the bio- and geosphere (Benson , 2007).

Depending on targeted geological levels, an effective, fully integrated monitoring programme should be implemented, for operational, verification and environmental purposes (Figure 5).

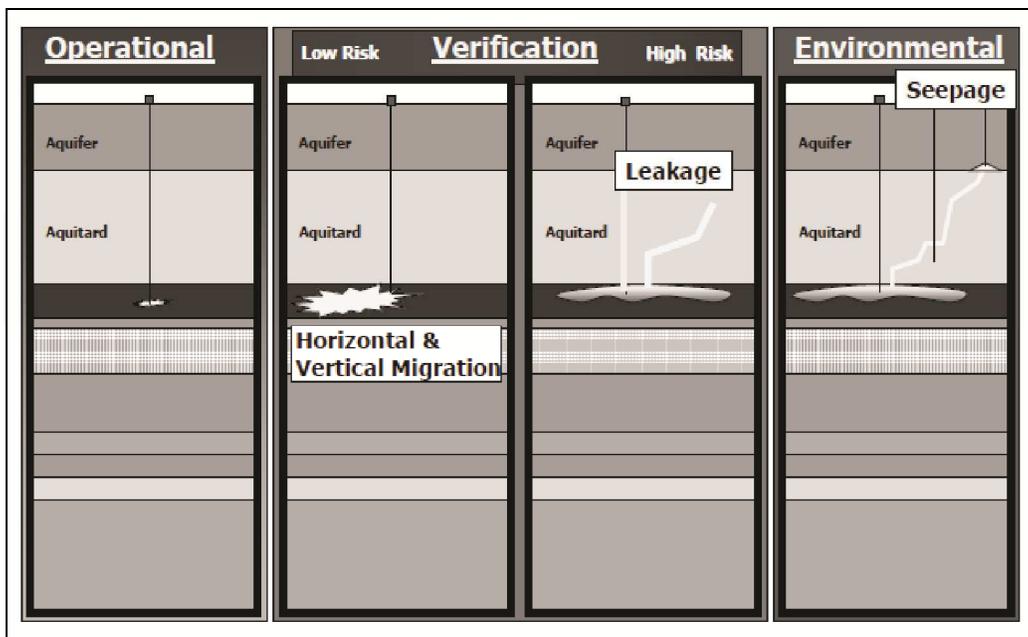


Fig. 5. Monitoring objectives, as a function of the monitored geosphere targets (Chalaturnyk & Gunter, 2005).

3.1 Reservoir monitoring

Produced down-hole fluids sampling and analysis are the main geochemical methods focusing on the CO₂ reservoir. Sampling systems like U-Tube (Freifeld et al., 2005) are of great value in obtaining minimally altered samples of subsurface fluids, preserved from formation contamination and degassing. Different analyses can be performed on the sampled fluid: aqueous chemistry, dissolved gas chemistry, isotopic composition, etc. For instance, geochemical reservoir monitoring of the IEA GHG Weyburn-Midale EOR field (Saskatchewan, Canada) showed that these data are particularly helpful in identifying and quantifying CO₂/fluid/rock interactions, like the dissolution of carbonate minerals and the production of alkalinity (Emberley et al., 2005) (Figure 6).

3.2 Cap rock integrity monitoring

The integrity of long-term cap rock sealing is a critical issue in guaranteeing and demonstrating efficiency, safety and security of CO₂ storage. The following different mechanisms for the loss of cap rock integrity have been identified: (i) reactivated faults in the cap rock: local pressure near a fault during injection reduces effective normal stress and thus reduces the shear strength of the fault; (ii) induced shear failure of cap rock; (iii) hydraulic fracture (prior to injection and during injection); (iv) exceeded capillary membrane seal pressure; and (v) dissolved CO₂ diffusion through cap rock (Shukla et al., 2010). Such processes can lead to concomitant geochemical alteration and geomechanical deformation of the cap rock, as well as to a modification of crucial petrophysical parameters such as porosity and permeability, which play a key role in sealing capacity (Johnson et al., 2004). Both static (batch) and dynamic (flow-through) experiments that permit the reproduction of reservoir conditions (P, T, brine salinity, chemistry, and flow rates in the case of reactive percolation experiments) are performed to investigate the evolution of a fractured cap rock during leakage of CO₂-acidified brine. These experiments also study the geochemical reactivity of cap rocks exposed to CO₂-rich brine injection (Andreani et al., 2008, Ellis et al., 2011). Fluid chemistry (cation concentrations) is monitored during these experiments (which are also applied on reservoir rocks) to identify the dissolution/precipitation reactions occurring in the rock plug and to realize mass-balance calculations (Luquot and Gouze, 2009).

3.3 Well integrity monitoring

One of the main risks identified in geological CO₂ storage is the potential for CO₂ leakage through, or along wells. One of the reasons for the loss of well integrity is the degradation of cement and carbon steel casings through acid attack due to CO₂ dissolution in groundwater and the resulting significant pH decrease (Bachu & Bennion, 2009). Experiments with CO₂-brine-cement and CO₂-cement interactions bring solutions to the problems of understanding and quantifying reactions occurring in the near-well environment. Some authors note that a carbonate layer can be formed at the interface between the CO₂-rich brine and the cement, which forms a barrier to further cement degradation (Kutchko et al., 2007, 2008).

3.4 Overlying aquifer monitoring

In the case of leakage and/or seepage, deep CO₂ storage may potentially impact on the quality and availability of groundwater resources and thus create potential risks for human

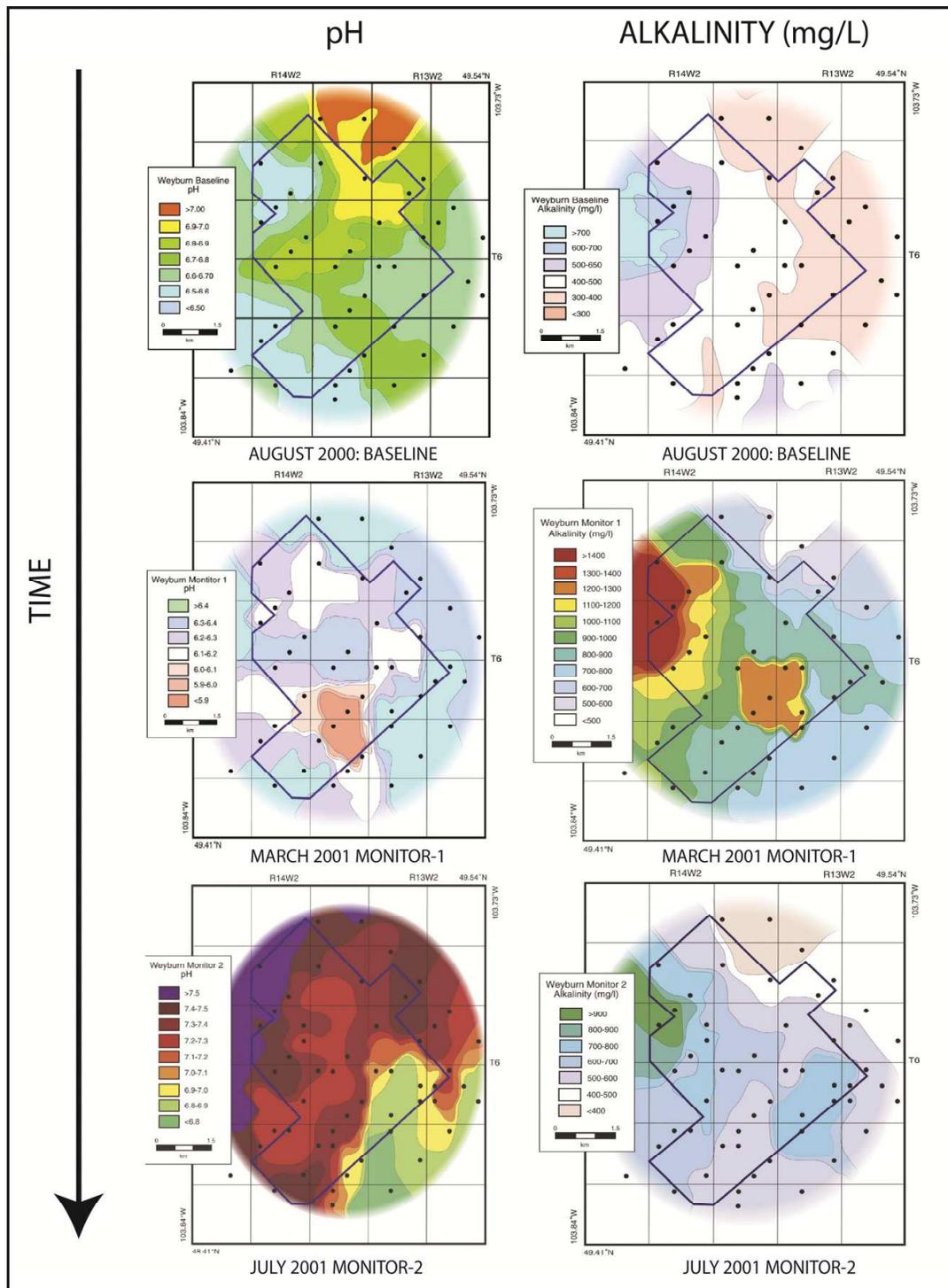


Fig. 6. pH and alkalinity monitoring at the Weyburn CO₂-injection enhanced oil recovery site, Saskatchewan, Canada (modified, after Emberley et al., 2005). AUGUST 2000: Baseline. MARCH 2001: MONITOR-1: the pH has decreased compared to the baseline (between 0.5 and 0.6). Absolute values of alkalinity have increased. JULY 2001: MONITOR-2: the pH has generally increased in comparison to the baseline and Monitor-1 data, indicating reaction with carbonate minerals in the reservoir. The alkalinity is higher than the baseline alkalinity, but has decreased in comparison to the Monitor-1 data, which also suggests a reaction with carbonate minerals in the reservoir.

health and ecosystems. The geochemical effects of CO₂ injection on water quality (for aquifers receiving the CO₂ injection and/or overlying and nearby aquifers that can contain drinking water) have been listed by Norton et al., 2009 as: (i) effects of physical displacement of groundwater by CO₂; (ii) effects of CO₂ injection on pH and alkalinity; (iii) effects of solution and mineral trapping; (iv) effects of CO₂ on soluble organic compounds; (v) effects of CO₂ injection on redox conditions; (vi) effects of CO₂ on microbial populations. Some geochemical clues are indicative of saline water migration into adjacent aquifers, such as an increase of TDS and alkalinity through reactions with host minerals and a possible increase in organic compounds. Furthermore, changes in the relative concentration of cations and anions in drinking water aquifers would occur, depending on the chemistry of the contaminating saline brines (notably through mixing and enrichment in Na-Cl and Na-Cl-SO₄). Saline water and CO₂ migration may also increase some common and trace metals concentrations (Al, Fe, Mn, As, Se, Zn), by leaching due to the pH decrease caused by elevated CO₂ partial pressures (Norton et al., 2009; Wang & Jaffe, 2004). This would depend on the redox conditions, or the buffering capacity of the host rock, that is closely linked to the abundance and type of minerals. Zheng et al. (2009) reported and modelled some secondary effects induced by pH changes. These include the significant mobilization of lead and arsenic, contaminating groundwater both near the CO₂ intrusion and further downstream. Laboratory experiments have also demonstrated that some geochemical parameters (pH, manganese, iron and calcium contents) can serve as early leakage indicators, because their concentrations increase within 2 weeks of exposure to CO₂ (Little and Jackson, 2010). Geochemical parameters can thus act as a warning for potential CO₂ leaks that might affect overlying aquifers.

3.5 The vadose zone and the terrestrial ecosystems

The vadose and soil zone is the final layer underground that could be affected by potential CO₂ leaks from deep reservoirs. Vadose and soil zone monitoring is particularly challenging because it requires the distinction between naturally occurring CO₂ and deep CO₂ leaks. CO₂ is naturally abundant and reactive in the near-surface, and as its concentrations are spatially and temporally variable. Its vulnerability reinforces the importance of soil gases monitoring to protect natural resources and to address landowner concerns. Oldenburg et al. (2003) described the different soil CO₂ sources and sinks, as: (1) exchange with the atmosphere; (2) production from decay of organic matter such as leaf litter; (3) uptake by plants; (4) production by root respiration; (5) deep degassing; (6) release from groundwater due to depressurization; and (7) production by oxidation of organic carbon in groundwater at the water table (Figure 7).

The measurement of natural “background” CO₂ concentrations for at least one year before CO₂ injection is paramount when determining the range of seasonal and diurnal CO₂ variations, which depend on soil temperature, moisture, and soil aeration, substrate quality and pH (Oldenburg et al., 2003). Leak detection is based on changes in soil gases concentration and on the isotopic composition of different CO₂ contributions. One proposed method for identifying deep CO₂ input is to predict gas relationships because an enrichment in deep CO₂ may result in the relative depletion of other existing gases such as CH₄, O₂, N₂ (Romanak et al., 2011). Furthermore, as explained in Yang (2011), carbon isotopes ($\delta^{13}\text{C}$ & $\delta^{14}\text{C}$) in soil gas have been particularly useful in detecting CO₂ leakage in recent years, since the $\delta^{13}\text{C}$ in the gas from fossil-fuel-driven sources is very different from the $\delta^{13}\text{C}$ in shallow soil gas, and $\delta^{14}\text{C}$ is basically absent in fossil CO₂ (Johnson et al., 2009; Klusmann, 2003, Van Alphen et al., 2009).

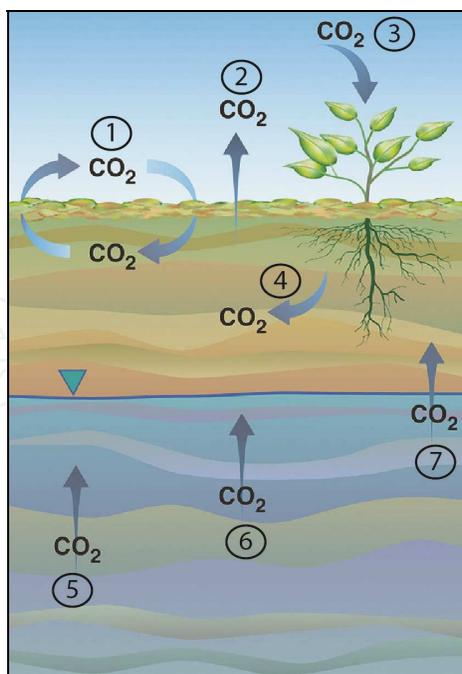


Fig. 7. Soil sources and sinks (modified, after Oldenburg et al., 2003). The significance of the number 1 to 7 is described in the text.

3.6 The aquatic ecosystems

Monitoring techniques for the detection of underwater CO₂ seepage have been recently and extensively developed in parallel with specific underwater methods to identify the CO₂ effects on the marine environment (Caramanna et al., 2005, 2010). These techniques have been notable in the framework of the CO₂GEONET and CO₂Remove projects. PH, dissolved CO₂ and CH₄ concentrations are key geochemical parameters to provide an assessment of water quality. According to Annunziatellis et al., (2009), the corrosive nature of seawater, the potentially high hydrostatic pressures, and the fact that these sites are likely to be isolated and far from the onshore infrastructures or power supplies explain why offshore monitoring is particularly challenging.

3.7 Surface and atmospheric monitoring

The earth's surface and atmosphere offer opportunities to measure gaseous CO₂ concentrations and fluxes; these measurements demonstrate the need for CO₂ to be stored with respect to the atmosphere. One of the most common techniques used for surface measurement is an Infrared Gas Analyser (IRGA) that can be installed on an accumulation chamber to measure CO₂ fluxes. IRGA can also be used with Eddy covariance towers to measure atmospheric CO₂ concentrations at specific heights above the ground, taking into account micrometeorological parameters such as wind speed, humidity and temperature (Oldenburg et al., 2003). Other techniques like Light Detection And Ranging (LIDAR), mobile open path lasers, Fourier Transform InfraRed (FT-IR) spectrometers, and micro gas-chromatographs have also been successfully tested in natural analogues (Gal et al., 2010; Jones et al., 2009; Pironon et al., 2009). However, it seems particularly important to combine the different techniques to increase the possibility of detecting significant anomalies.

Geochemical monitoring at LATERA (Italy) by Jones et al. (2009) showed, for example, that some vents cannot be detected and measured by Eddy covariance tower at heights greater than 10 cm (Figure 8). This indicates that geochemical methods may only be able to sample and analyse at individual locations; very small leaks are particularly difficult to detect and larger leaks can also be missed. The detection capability will thus depend on the coincidence of the leaks and the location of sensors deployed in the area.

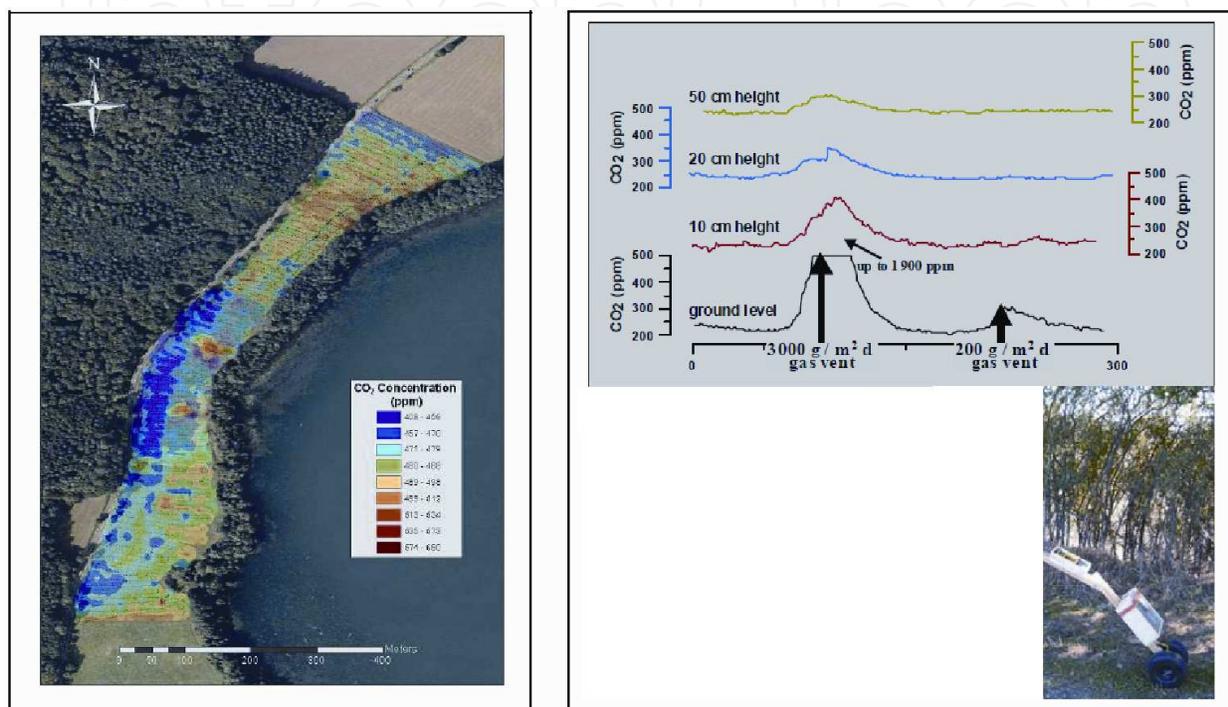


Fig. 8. Ground surface CO_2 concentrations at Latera, obtained using an IRGA measurement system. The weaker CO_2 vent is not seen at heights greater than 10 cm (Jones et al., 2009).

A baseline for soil gas values for CH_4 , N_2 , O_2 , light hydrocarbons, sulphur species, helium, uranium, thorium and radon can also be established by using grid sampling and profiling. This can be used to evaluate natural variations, including seasonal effects. The comparison of the baseline dataset with a dataset obtained after CO_2 injection allows for the identification of anomalies with higher gas fluxes, that may indicate deep gas escape, and for the calculation of upward gas velocity. Such calculation has been performed at Weyburn using long term radon and helium measurements and CO_2 fluxes (Strutt et al., 2002). When CO_2 abundances in soils cannot be distinguished from the biological baseline and when the stable isotopic composition of carbon is insufficient to track CO_2 surface leaks, noble gases measurements can be used as powerful leak detectors and discriminators, as shown by Magnier et al. (2011) in the Buracica EOR- CO_2 field on-shore (Brazil).

4. Relevant use of geochemical methods during the lifetime of a CCS project

Schlumberger distinguishes different parts in a CO_2 storage injection workflow, as the pre-operation phase, the operation phase, and the post-operation phase (Figure 9).

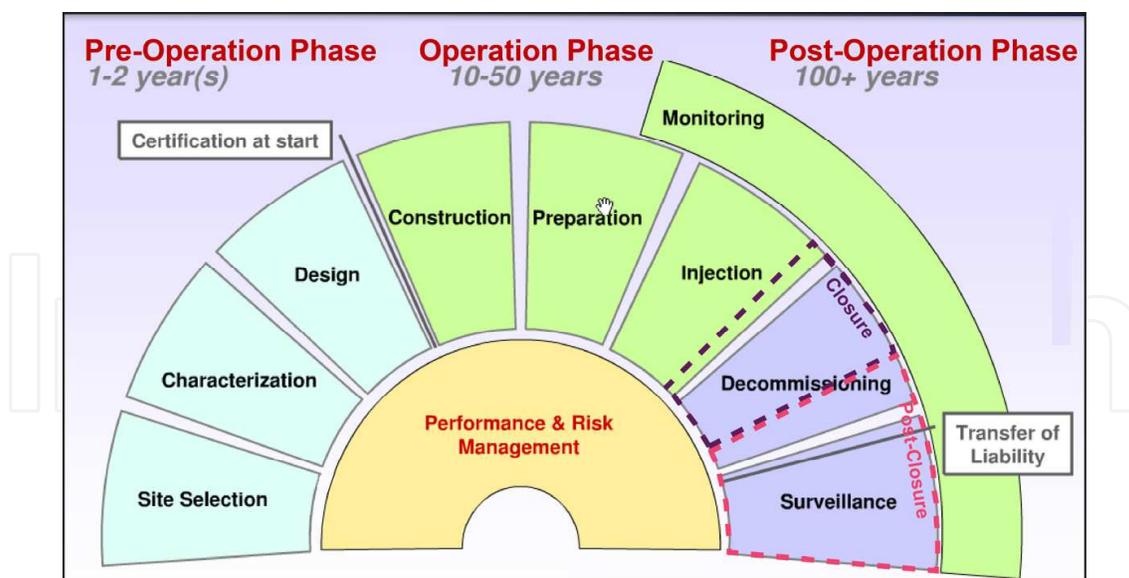


Fig. 9. Life cycle of a CCS project (Modified, after Marquette, 2010).

The pre-operation phase includes site characterization, risk assessment and the establishment of a monitoring baseline. The operation phase deals with verification of the injection rate, tracking the plume location, detection and prevention of any environmental impact. The post operation phase can be divided into two periods: the closure and the post closure. The closure phase implies the end of CO₂ injection, the decommissioning of the injection wells and surface facilities and the confirmation of the long-term storage security. The post closure phase aims to decommission the monitoring wells and complete the records given to regulatory authorities. Long term monitoring may only be needed if long term storage security is not established. During the following steps: (i) site selection and characterisation, as input data for the modelling, (ii) baseline and pre-injection period, (iii) injection period, (iv) post-injection period, (v) abandonment period (closure and post closure phases), geochemical tools can be integrated into the monitoring programmes and applied throughout the lifetime of the CCS project.

4.1 Site selection and characterization

The geochemical properties of the reservoir, the reservoir overburden (cap rock, seals, porous and permeable horizons) and surrounding formations (overlying aquifers) constitute some of the input data required to build both static and dynamic geological models. A simplified geochemical reactivity model is generally associated with building a detailed 2D or 3D fluid flow reservoir model, while a detailed description of the CO₂/fluid/rock interactions with complex mineralogical assemblages and reaction kinetics is required for batch modelling (Gaus et al., 2008). Even though many kinetic data and rate laws are described in the literature (Plummer et al., 1978; Lasaga et al., 1994), the complexity of the system makes it difficult to acquire accurate data. Moreover, kinetics vary widely depending on the minerals and their reactions. For example, the kinetics of aluminosilicate mineral reactions are for instance slower than dissolution kinetics of carbonates and sulphates. The physical and physicochemical properties (density, solubility, viscosity, enthalpy) of the CO₂-brine system are also integrated into the solute transport model. This is achieved via equations of state describing these properties and their P-T evolution (for example, the Equation Of State (EOS) given in Duan et al., 1992).

4.2 Baseline and pre-injection period

Baseline MMV aims to determine the initial hydrological, geochemical and environmental conditions prior to CO₂ injection. For geochemical methods, measuring the baseline consists of analysing fluid properties of the reservoir (fluid and gas compositions, pressures and temperatures), overlying potable aquifers (pH, elemental compositions of the fluid and dissolved gases, isotopic signatures). Soil gas (fluxes, chemical and isotopic fingerprint measurements) and ecosystems properties have also to be determined (Simone et al., 2009). The chemical and isotopic composition of the proposed injected CO₂ should also be measured prior to injection. Chemical analyses of samples must take place in a laboratory, and are labour intensive and time consuming. Therefore, measurements of background concentrations must be limited and cannot be taken from locations throughout the storage complex. A sampling strategy is generally defined, and focuses on high-risk features, such as structural lineaments, that are potential pathways for CO₂ migration and leakage. The monitoring installations can also be deployed along a systematic grid around the injection point. The reliability, resolution, and repeatability of each measurement are key to establishing a high-quality baseline database, which is paramount for detecting and quantifying small rates of leakage. Furthermore, it appears that one year of baseline acquisition is generally not sufficient to capture the full seasonal and annual variation of the natural release of CO₂ from soil. Thus, in every instance, special attention should be paid to baseline acquisition.

4.3 Injection period

After injection has begun, monitoring surveys are repeated at specified time intervals to build up images of site properties and to establish how the geochemical parameters change through time. Hovorka et al. (2005) reported that geochemical monitoring was particularly successful one year after the 2004 injection of 1,600 tons of CO₂ at the Frio field test (Texas). Noteworthy success was achieved in following the evolution of the CO₂ plume, detecting CO₂ breakthrough at the observation well, identifying CO₂/fluid/rocks interactions (a significant pH drop, an increase in alkalinity, dissolved Fe, Mg and Ca contents, indicated dissolution reactions) and quantifying CO₂ saturation and dissolution. Two-phase fluid samples were also obtained during CO₂ injection using a U-Tube. The mobilization of minor amounts of organic compounds was also revealed by an increase in dissolved organic contents concentrations in brine, 20 days after injection.

4.4 Post-injection period

After CO₂ injection is finished, reservoir, groundwater, soil gas, and atmospheric monitoring surveys, continuous or intermittent, should be continued for verification and environmental monitoring and to develop the understanding of long term CO₂ behaviour. For example monitoring results from the Japanese pilot CO₂ injection site of Nagaoka, into which 10,400 tons of CO₂ was injected from July 2003 to January 2005, indicate that solubility and residual trapping are in progress in the reservoir sandstone (Mito & Xue, 2011). Similarly, for the CO₂ CRC Otway project (Australia), geochemical sampling at the Naylor-1 observation well has shown that injected gas migrated into the Naylor structure, as predicted in numerical simulations (Underschultz et al., 2009). Geochemical data obtained during the post-injection period will help to calibrate and update the dynamic model in an

iterative manner, and to calculate the reservoir's trapping mechanisms over time. The observed and predicted results will be compared and any discrepancies should be identified. In case of significant deviation, the model would be recalibrated based on the observed behaviour.

4.5 Abandonment period

The monitoring data obtained during the post-closure period, which can last for decades, should prove that stored CO₂ behaves as predicted. The data should also demonstrate the absence of any detectable leaks. Evolution towards long term stability of the CO₂ plume is also required and is indicated by a small, and declining, rate of change in monitored parameters. Geochemical changes are key parameters for assessing the evolution towards long-term stability and for showing that CO₂ will remain stored within the complex through various trapping processes. All the measured geochemical parameters should be stable and consistent with the results of the CO₂/fluid/rocks interactions models, and should ensure that there is no significant risk of compromising cap rock and well integrity in the future. Geochemical methods play a key role in leakage detection and quantification and in assessing that no sources of drinking water are endangered. These methods can help to increase confidence in the long-term stability of the CO₂ storage complex.

5. Guidelines and recommendations for the integration of geochemical tools into a monitoring programme

5.1 Integration of geochemical data into monitoring programmes

The toolbox available for designing MMV programmes is particularly impressive and comprises geophysical (seismic and non-seismic, electrical), geomechanical, atmospheric, diagraphic, microbiological and geochemical methods. Methodological tools, like the "Monitoring Selection Tool" decision support system from IEA GHG, are particularly useful. The selection of an appropriate multi-disciplinary monitoring package for a particular CO₂ storage project depends on site-specific geological conditions as well as project objectives. The overall monitoring strategy may be improved by using tools of complementary sensitivity, spatial resolution and sampling characteristics, and by combining continuous and/or intermittent, local and/or extended measurements, based on various physical principles. A combined interpretation may lead to a better processes understanding. For instance, geophysical, geochemical monitoring and modelling R&D programmes have been successfully integrated in the IEA GHG Weyburn-Midale monitoring and storage project (Saskatchewan, Canada) (White & Johnson, 2009). According to the authors, the geochemical dataset provides a strong value-added history matching resource for reservoir simulation and reactive transport studies. In the Latera caldera (Italy), a natural analogue site, various geophysical tools were applied to track CO₂ migration from the storage complex and were combined with CO₂ flux measurements and soil gas sampling (Arts et al., 2009). The geochemical data confirmed and validated the geophysical results, reinforcing the conclusion that no single method is sufficient to clearly understand the processes driving CO₂ migration. Jones et al. (2009) have also shown that environmental monitoring can be optimised by combining the use of mobile open path laser measurements and ground surface IRGA measurements over a large area with more detailed

investigations, in order to verify CO₂ migration pathways and leakage extent. When seismic monitoring methods cannot be used for technical and economical reasons, geochemical monitoring can give insights into CO₂ saturation over time. Dissolved CO₂ is unlikely to be detected by any seismic method because of the low acoustic contrast between brine saturated with CO₂ and brine without CO₂. However, geochemical measurements, direct (total inorganic carbon, bicarbonate) and indirect (pH, alkalinity), can be particularly useful. They can also help to identify CO₂ and residual hydrocarbon contact for EOR applications. In fact, seismic monitoring methods are more appropriate for use in deep saline aquifer storage.

5.2 Identification of gaps and research & development perspectives

Future geochemical research into CO₂ storage must touch on different aspects, such as (i) modelling, (ii) experimental studies, (iii) investigations on organic chemistry and on secondary geochemical effects (redox, microbial reaction), (iv) technological development to improve data quality. As the co-injection of impurities (i.e. SO₂) can lead to extremely low pH (Knauss et al., 2005), experimental and modelling studies investigating their geochemical effects could be particularly useful. As pointed out by Gaus et al. (2008), the lack of basic thermodynamic and kinetic data at reservoir temperature and pressure conditions is also a major gap; this is particularly the case for CO₂-brine systems integrating co-injected gases (O₂, N₂, NO, SO₂, H₂S). Coupled reactive transport and geomechanical modelling remain challenging as well. Moreover, few experimental studies have been performed reproducing in situ conditions (P, T, salinity, flow rates). Flow-through experiments are particularly useful in assessing relationships between the chemical changes of the rock and fluids composition, and porosity and permeability evolution induced by mass transfers during percolation (Luquot & Gouze, 2009). Recently, isotopic monitoring has also been performed during flow-through experiments, consolidating the interpretation of cation concentrations evolution and allowing quantification of trapping (Jeandel et al., 2011; Myrntinen et al., 2011). Emissions quantification technologies that measure dissolved CO₂ in the water column and free CO₂ at the surface, are in development, along with specific down-hole and seabed fluid sampling systems. These technologies will require further testing, especially in the marine environment, in which there is a gap in quantification and detection of CO₂. Guidelines for establishing sampling strategies (frequency, spacing, gridding, influence of the climate and meteorological regimes) would also be useful for the environmental monitoring of terrestrial ecosystems. More generally, permanently installed systems with fast-response sensors for monitoring pH, temperature, O₂ and CO₂ would counterbalance the fact that most geochemical measurements are intermittently performed. The coupling of geochemical and microbiological data could also be interesting in assessing the potential environmental CO₂ impact on both aquatic and terrestrial ecosystems.

6. Conclusion

Geochemical methods are extensively used for operational, verification and environmental monitoring because they can be applied to different monitoring targets that could be surveyed in the framework of a CO₂ geological storage project. They play a major role in providing information on fluid sources, which enable a unique identification of injected

CO₂, and on the physicochemical processes occurring within the storage complex. The migration of the CO₂ plume, as well as the distribution of the CO₂ phases (gas or dense versus dissolved), also represent key data that can be provided by geochemical measurements, which complement the other types of data. Geochemical methods provide essential input data for the calibration, validation and development of static and dynamic geological models for characterizing and predicting CO₂/fluid/rocks interaction. Moreover, they are important elements in the risk management process because they can identify the possible contamination of potable groundwater by toxic trace metals and/or organic compounds mobilized by the chemical interactions induced by CO₂ reactivity. Due to their high sensitivity, they also aim to directly detect any CO₂ leakage, which is crucial to ensure that stored CO₂ will be completely and permanently contained. Geochemical methods represent a significant step to improve public and regulatory confidence in geological storage of CO₂.

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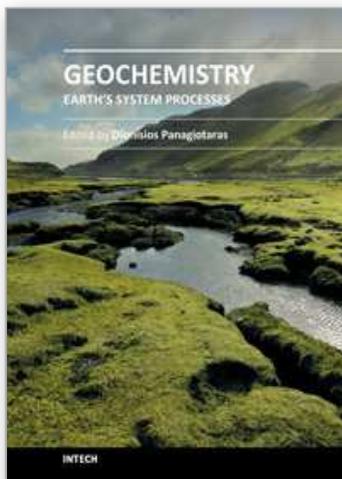
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This book brings together the knowledge from a variety of topics within the field of geochemistry. The audience for this book consists of a multitude of scientists such as physicists, geologists, technologists, petroleum engineers, volcanologists, geochemists and government agencies. The topics represented facilitate as establishing a starting point for new ideas and further contributions. An effective management of geological and environmental issues requires the understanding of recent research in minerals, soil, ores, rocks, water, sediments. The use of geostatistical and geochemical methods relies heavily on the extraction of this book. The research presented was carried out by experts and is therefore highly recommended to scientists, under- and post-graduate students who want to gain knowledge about the recent developments in geochemistry and benefit from an enhanced understanding of the dynamics of the earth's system processes.

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