Dossier

This paper is a part of the hereunder thematic dossier published in OGST Journal, Vol. 67, No. 2, pp. 187-372 and available online here

Cet article fait partie du dossier thématique ci-dessous publié dans la revue OGST, Vol. 67, n°2, pp. 187-372 et téléchargeable ici

DOSSIER Edited by/Sous la direction de : **F. Roggero**

Monitoring of CO₂ Sequestration and Hydrocarbon Production
Monitoring pour le stockage du CO₂ et la production des hydrocarbures

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D o s s i e r

Monitoring of CO$_2$ Sequestration and Hydrocarbon Production
Monitoring pour le stockage du CO$_2$ et la production des hydrocarbures

A Geochemical Approach for Monitoring a CO$_2$ Pilot Site: Rousse, France. A Major gases, CO$_2$-Carbon Isotopes and Noble Gases Combined Approach

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Résumé — **Une méthode géochimique pour la surveillance d'un site pilote de stockage de CO$_2$: Rousse, France. Approche combinant les gaz majeurs, l'isotopie du carbone du CO$_2$ et les gaz rares** — Ce papier présente la caractérisation géochimique des différents gaz, naturels et anthropogéniques, impliqués dans un pilote de stockage de CO$_2$ en champ de gaz naturel appauvri (Rousse, France). Dans ce pilote, le CO$_2$ est produit par oxycombustion d'un gaz naturel transformé en gaz domestique à l'usine de Lacq. Ce CO$_2$ est transporté dans un pipeline de 30 km de longueur jusqu'au réservoir de gaz appauvri de Rousse. Les gaz produits à Rousse avant injection de CO$_2$, le gaz commercial de Lacq et le CO$_2$ résultant de l'oxycombustion ont été échantillonnés, ainsi que les gaz situés dans un puits de surveillance (à une profondeur de 45 m) et les gaz du sol situés au voisinage de Rousse. Pour tous ces échantillons, la composition en gaz majeurs, la signature isotopique du carbone ainsi que l'abondance et signature isotopique des gaz rares ont été déterminées.

Les compositions gazeuses du gaz naturel de Rousse sont comparables à celle du gaz domestique de Lacq avec le méthane comme composé principal et la fraction C$_2$-C$_5$ et CO$_2$ comme gaz résiduels. Les gaz des sols reflètent typiquement des mélanges entre l'air (pôle pur) et le CO$_2$ d'origine biogénique (avec des teneurs maximales de l'ordre de 9-10 %), tandis que les gaz présents dans le puits de monitoring reflètent typiquement la composition de l'air sans excès de CO$_2$. Le gaz de Rousse et le gaz domestique du site de Lacq ont une composition isotopique $\delta^{13}C_{CH_4}$ égale à $-41,0$ ‰ et $-43,0$ ‰ respectivement. Le CO$_2$ injecté sur Rousse a une composition isotopique $\delta^{13}C_{CO_2}$ égale à $-40,0$ ‰ à la sortie de la chambre d'oxycombustion, tandis que la composition isotopique $\delta^{13}C_{CO_2}$ des gaz des sols est comprise entre -15 et -25 ‰. Le gaz naturel de Rousse et le gaz domestique du site de Lacq sont tous les deux enrichis en hélium, appauvris en néon, argon et krypton par rapport aux valeurs de l'air (standard naturel). Le procédé de combustion produit un CO$_2$ enrichi en hélium, hérité du gaz domestique de Lacq, et une composition en néon, argon et krypton reflétant celle de l'oxygène produit par l'unité de séparation d'air. En effet, le néon est appauvri relativement à l'air, tandis que le krypton est enrichi de 10 fois, résultant de la séparation cryogénique des gaz rares au sein de l'unité de séparation d'air. Les gaz rares des échantillons de sols ont une composition équivalente à celle de l'air.

À partir de ces résultats, les compositions des pôles purs impliqués dans le site pilote de stockage de CO$_2$ montrent que les compositions en gaz rares produits par le procédé d'oxycombustion sont suffisamment

exotiques en comparaison à celles trouvées dans la nature (réservoir, aquifère et air) et peuvent donc être directement utilisées comme traceurs du CO_2 injectés, et donc de détecter et quantifier les fuites au niveau du sol et des aquifères.

Abstract — A Geochemical Approach for Monitoring a CO$_2$ Pilot Site: Rousse, France. A Major Gases, CO$_2$-Carbon Isotopes and Noble Gases Combined Approach — This paper presents the geochemical characterization of various gas end-members involved in a depleted gas field CO$_2$ storage pilot (Rousse, France). In this pilot, CO$_2$ is produced by oxycombustion from natural gas transformed into fuel gas at the Lacq plant, and transported in a pipeline 30 km away to the depleted gas reservoir of Rousse. Gases produced at Rousse before CO$_2$ injection, the Lacq fuel gas and the CO$_2$ resulting from the oxy-fuel combustion were sampled, together with gases from a – 45 m monitoring well and from soils in the vicinity of the Rousse structure. For all samples, the bulk gas composition, the carbon isotopic compositions and the abundance and isotopic signatures of the noble gases were determined.

The bulk gas compositions of the Rousse natural gas are comparable to the Lacq fuel gas with methane as the main compound with residual C$_2$-C$_5$ and CO$_2$. Soil gases are typical mixtures of air with biogenic CO$_2$ (up to 9-10%), while the monitoring well gases display typical air compositions with no excess CO$_2$. The Rousse gas and the Lacq fuel gas have $\delta^{13}C_{CH_4}$ values of – 41.0‰ and – 43.0‰ respectively. The injected CO$_2$ out of the oxycombustion chamber has a $\delta^{13}C_{CO_2}$ of – 40.0‰, whereas $\delta^{13}C_{CO_2}$ value for soils samples is comprised between – 15 and – 25‰. The Rousse natural gas and the Lacq fuel gas are both characterized by a high He enrichment, and depletion in Ne, Ar and Kr compared to the air values. The oxyfuel combustion process provides a CO$_2$ with the He enrichment of the Lacq fuel gas, and a Ne, Ar and Kr composition reflecting that of the oxygen produced at the Air Separation Unit (ASU). Indeed, Ne is depleted relatively to the air, while Kr is enriched up to tenfold, which results from the cryogenic separation of the air noble gases within the ASU. Soil samples noble gas compositions are equivalent to that of the air.

In the light of these results, the compositions of the various end-members involved in this CO$_2$ storage pilot suggest that noble gas compositions produced by oxyfuel process are sufficiently exotic compared to compositions found in nature (reservoir, aquifer and air) to be directly used as tracers of the injected CO$_2$, and to detect and quantify leaks at soil and aquifer levels.

INTRODUCTION

Anthropogenic emissions of CO_2 resulting from the combustion of fossil fuels such as petroleum, gas and coal represent 19 Gt of CO_2 per year. These quantities are one order of magnitude higher than the annual CO_2 production by volcanism or metamorphic processes and one order of magnitude higher than the natural sequestration of CO_2 by geological processes (*e.g.* Kerrick *et al.*, 1995). CO_2 linked to anthropogenic activity is responsible for ca. 64% of the enhanced "greenhouse effect" (Bachu and Adams, 2003).

Although some discrepancies exist on the extent of the consequences, all climate modeling studies predict a significant global climate change in the decades to come (Albritton and Meira Filho, 2001). The large scale efficient technologies for energy supply that prevail up to date are fossil fuel based. Consequently, CO_2 capture and sequestration is envisioned as a strategy to reduce the CO_2 emissions.

Geological storage of CO_2 has been recognized as having significant potential for mitigating increases of atmospheric CO_2 (Holloway, 1997; Gale, 2004; Hepple and Benson, 2005). Saline aquifers offer the largest storage potential of

all of the geological CO_2 storage options and are widely distributed throughout the globe in sedimentary basins. Nevertheless, oil and gas fields are considered to be good potential storage sites as they are well known and well characterized and as the industrial infrastructures needed for CO_2 storage are already installed. Coal beds and flood basalts are also potential storage sites. Geological storage involves injection of supercritical or dense-phase CO_2 into permeable/porous layers in the deep subsurface. The long-term storage of CO_2 can be accomplished by multiple mechanisms:

– structural trapping (CO_2 is trapped by geological structures and buoyant rise); indeed, the first trapping process is the structural. In a case of an anticline structure, the CO_2 will be trapped considering only this form of structure of the reservoir;

– capillary trapping as a residual phase in small pores; indeed, the second is the capillary trapping. In this case, CO_2 gas will be trapped in the porous structure of the reservoir rock by capillary effects after the reservoir overpressure has been dissipated;

– CO_2 dissolution into the brine (solubility trapping) and reaction with the host rock minerals to form ionic species

(ionic trapping); indeed, the third is the dissolution of CO$_2$ into the brine. With time CO$_2$ will be dissolved into the brine and this dissolution is relatively rapid. An equilibrium will exist between the gas phase and the liquid one;

– trapping in a mineral form as CO$_2$ reacts with the rock. Finally, CO$_2$, in the ionic forms, will react with cations to form carbonate minerals as CaCO$_3$, Ca,MgCO$_3$, etc. These reactions are slow but represent the more stable form of CO$_2$ trapping. Indeed, safety trapping increases with these different trapping processes explained.

If a significant impact on atmospheric CO$_2$ levels is expected, CO$_2$ storage must be implemented both on a large scale and in a manner that insures long CO$_2$ residence times (Holloway, 2005). Large-scale injections carry risks not only for migration and leakage of CO$_2$ through conductive pathways (wells and faults), but also for up-dip displacement of brine that may impact fresh-water resources (overlying aquifers) in a domino effect (Bergman *et al.*, 1997; Bentham and Kirby, 2005; Nicot, 2008). This suggests that acceptance of large-scale disposal of CO$_2$ by underground injection will require much more intensive research to minimize the technical uncertainties and risks. This is one of the reason why geological carbon sequestration will require monitoring techniques for storage confirmation and for public assurance. One important feature for communicating and reassuring the general public is near surface detection techniques. In case of a leakage of the injected CO$_2$, it is essential to be able to distinguish the natural CO$_2$ (background, anthropogenic, natural flux of crusted and mantle...) from the injected CO$_2$. A natural respiration and flux of CO$_2$ exist (*e.g.* Daly *et al.*, 2008; Liu *et al.*, 2008). Variations in the surface flux of natural CO$_2$ is likely

taking place on different scales in space and time. It is not realistic to compare natural concentration and flux of CO$_2$ between two different soil samples however, a periodicity exists during the day and the year (*e.g.* Baldini *et al.*, 2008; Fisher *et al.*, 2008). This periodicity can be explained by the biological activity in the soil like photosynthesis (Olchev *et al.*, 2008). Furthermore, organic and mineral carbon present in the soil can influence the CO$_2$ concentration and reciprocally (*e.g.* Paterson *et al.*, 2008; Daly *et al.*, 2008). Moreover, geological target that can be impacted by an eventual contamination is potable aquifer. That's why the communication and general public acceptance are very important in CO$_2$ storage context. A variety of promising techniques have been identified and many have been incorporated into monitoring approaches deployed at existing pilot sites such as Weyburn (Whittaker, 2004), Frio (Hovorka *et al.*, 2006) and Rousse (Aimard *et al.*, 2009).

The TOTAL SA company is conducting the first French pilot, in the South-West of France, to demonstrate the technical feasibility and reliability of an integrated CO$_2$ capture, transportation, injection and storage scheme from a boiler at a 1/10th reduced scale of an industrial project. It entails the conversion of an existing steam boiler into an oxy-fuel combustion unit, oxygen being used for combustion rather than air to obtain a more concentrated CO$_2$ stream easier to capture. The pilot plant, which produces some 40 t/h of steam for use in other facilities, is expected to emit up to 120 000 tons of CO$_2$ over a 2-year period. This produced CO$_2$ is compressed and conveyed via pipeline to a depleted gas field Rousse #1, 30 kilometers away, where it is injected into a deep carbonate reservoir *(Fig. 1)*.
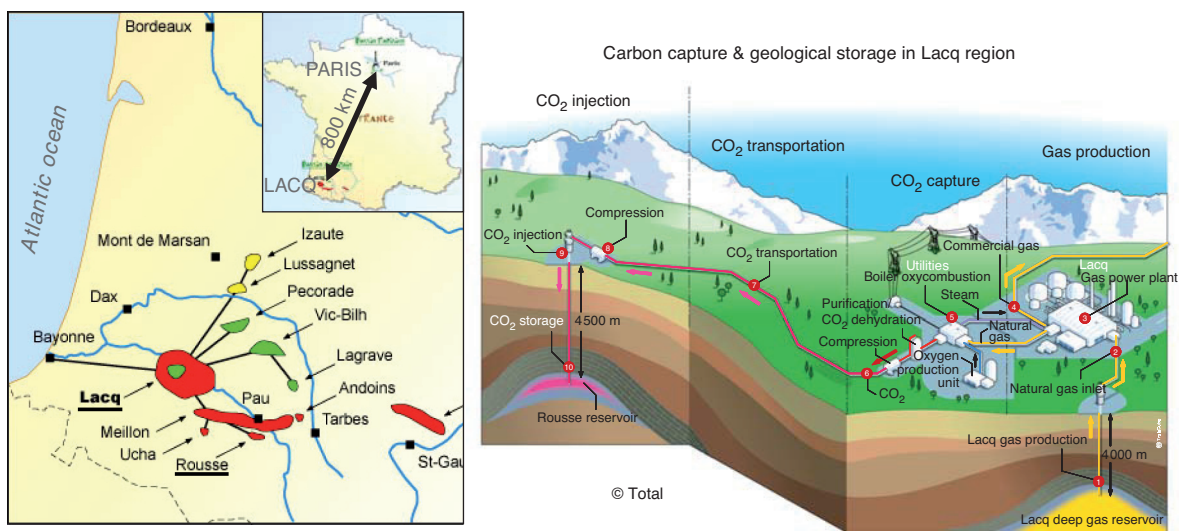

Figure 1

Lacq CO$_2$ pilot location (left) and general scheme with Rousse gas field (right).

CO_2 injection has started at the beginning of year 2010. The main objectives of the pilot plant are:

– to demonstrate the technical feasibility and reliability of an integrated CO_2 capture, transportation, injection and storage scheme for steam production at a reduced scale, typically 1/10th of future larger scale facilities, but within industrial facilities;

– to design and operate a 30 MWth oxy-combustion retrofitted boiler for CO_2 capture in order to confirm the following targets of:
  • 50% reduction of capture cost compared to classical post capture technologies,
  • 50% reduction of overall direct and undirected CO_2 emissions if undirected emissions are not captured;

– to develop and apply geological storage qualification methodologies, monitoring and verification techniques on a real operational case to prepare future larger scale long term storage projects.

A complete official monitoring plan has been defined by the operating company TEPF and consists of:

– mass flowmeters and gas composition analyzers of the CO_2 stream;

– CO_2, methane and H_2S detectors on the Rousse #1 well pad;

– soil gas mapping survey at different surface locations around the site. Started in September 2008, *i.e.* more than one year before the beginning of the injection, this soil monitoring is scheduled every 3 months in the base line phase and at least twice a year during the injection period;

– pressure and temperature measurements by an optical fibre along the well at four different depths to monitor the downhole and reservoir conditions as well as the calibration of the well injectivity and well pressure drop models;

– microseismic monitoring system to identify any effect of the injection on the reservoir and the cap rock. It comprises: seven microseismic sensor arrays installed in seven shallow wells (six at two kilometers around the injector and one on the Rousse well pad) and three microseismic sensors installed downhole slightly above the top of the reservoir (Lescanne *et al.*, 2010).

The primary objectives of this paper are to present geochemical monitoring results of gas characterization combined with CO_2-carbon isotopes and noble gas analyses. This R&D work marks a novel approach to the CO_2 monitoring strategy envisaged in a CCS project. Some of these results (soil major gases composition and soil CO_2-carbon isotopes in March 2009 and 2010) come from monitoring surveys realized in the Sentinelle project (De Donato *et al.*, 2010). All other results obtained (soil major gases and CO_2-carbon isotopes in September 2009, gas fields compositions, fuel gas (PV4410) composition, low depth well results, CO_2 injected composition and all noble gas results) come from R&D project between IFP Energies nouvelles and TOTAL

SA company. This methodology attempts to better understand the dynamic between the gas field, the surface and the atmosphere in order to detect any eventual leakage of the injected CO_2 from the reservoir to the near surface.

An identification of the nature of the CO_2 present in a precise location, at a certain time, can be done with this methodology. Data obtained must then be modelled to predict the evolution of the storage at a large scale.

1 METHODOLOGY

1.1 Injection into the Depleted Upper Jurassic Mano Reservoir of the Rousse Gas Field

1.1.1 Geological Setting

The Rousse reservoir is located in a deep isolated Jurassic horst that was structured during the Early Cretaceous N-S extension phase of the pre-pyrenean rifting *(Fig. 2)*. It is draped and overlaid by a very thick Campanian to Eocene series of marls, shales and silts, namely "Flysch", deposited within the Pyrenean foredeep basin. The stratigraphic column ends with Neogene continental "post-orogenic" Molasses that outcrop in the vicinity of the Rousse site. The gas field has been produced by only two wells: Rousse #1 and #3. It consists of two superimposed but hydrodynamically disconnected Jurassic reservoirs: the upper Mano dolomitic reservoir producing in well #1 and where CO_2 is injected, and the lower Meillon dolomitic reservoir which produces in well #3. Mano reservoir is completely eroded by the Base Cretaceous Unconformity between Rousse #1 and #3.

The Mano reservoir is a fractured dolomitic reservoir lying at around 4 500 m below ground level (4 200 m below MSL). It is 120 m thick, 70 m of which have been cored. The Cretaceous cap rock (shale) has been partly cored. The initial reservoir pressure was 485 bar at 4 500 m. Discovered in 1967, producing between 1972 and 2008, the field is largely depleted with an average downhole pressure of 30 bar in the Mano reservoir before the beginning of the CO_2 injection. The average downhole temperature is 150°C. The initial gas in place contained 4.6% of CO_2 and 0.8% of H_2S and CH_4 essentially (more than 80%) with others HC compounds C_2-C_4 (10% in totality).

1.1.2 Monitoring Strategy

The Rousse site is a depleted gas field which presents many advantages for CO_2 storage, the most important of them being that it is well described in terms of geological and reservoir aspects and it has proven effective seals: it has accumulated and retained acid gases, H_2S and CO_2 for millions of years. Therefore, the loss of integrity can be considered as very unlikely.

B Garcia et al. / *A Geochemical Approach for Monitoring a CO$_2$ Pilot Site: Rousse, France. A Major gases,*
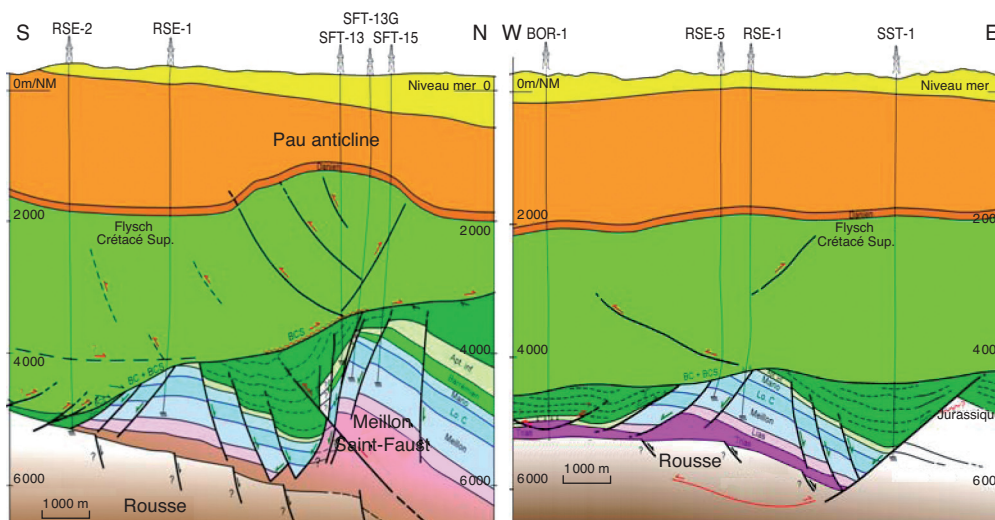*CO$_2$-Carbon Isotopes and Noble Gases Combined Approach*

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Figure 2

N-S and E-W geological cross-sections through Rousse.

The main objectives of the monitoring program of the storage are:

– to measure the flow rate and the injected gas composition;
– to check that the site and the injected CO$_2$ behave as expected;
– to check that there is no loss of integrity, no leakage upward to aquifers and to surface, biosphere and no impact on human health.

The geochemical monitoring approach consists of:

– measuring the concentration of CO$_2$ in soil, at a depth of 1 m on 15 points around Rousse #1, twice a year, with a spatial distribution centered on the injection point;
– measuring the CO$_2$-carbon isotopes composition on these soil points at the same frequency;
– measuring the noble gases composition on 4 soil points at the same frequency;
– measuring the gases chemistry and CO$_2$-carbon isotopes and noble gases composition in: Rousse #1 and Rousse #3 reservoirs before CO$_2$ injection, the CO$_2$ source fuel gas (PV 4410), the CO$_2$ resulting form this gas combustion in the oxy-fuel combustion unit and finally the gas sampled from a Monitoring Well (MW) at a depth of 45 m located in the vicinity of the injection well Rousse #1.

One of the main objectives are to determine the composition of pure end-members represented by Rousse #1 and #3 gases (considered as initial fluids in presence) and to be able to determine mixing processes which can be present between these fluids, the injected CO$_2$ and the surface. Moreover, from this methodology, the amount of dissolved and precipitated CO$_2$ can be determined. Even if this last point is not described in this paper, it is discussed in the summary and conclusion part.

1.2 Experimental Procedure and Analytical Methods

1.2.1 Sampling Procedure

Soil Samples:
For the 15 points of soil that have been analysed, the experimental procedure consists in the *in situ* measurement of the CO$_2$ concentration in soils with different field equipments, a portable GC (also called micro gas chromatograph, with a detection limit equal to 20 ppm) and GA2000+ analyser (with a detection limit equal to 1 000 ppm) and in the sampling of some small amounts of soil gases in order to determine the CO$_2$-carbon isotopes and noble gases compositions back to the laboratory. Sampling (10 mL) are performed with Vacutainers® (initial vacuum of about 10^{-3} mbar) for the CO$_2$-carbon isotope analyses and with stainless steel tubes for the noble gas analysis.

For the CO$_2$ measurements, a hole at one meter depth is drilled and a sampling gas tube is connected to the micro gas chromatograph. Two derivations from the tube are present and allow sampling gas with adapted Vacutainers® and stainless steel tubes.

Atmosphere air serves for the background signal detection and as the external gas standard. Prior to field work, the micro gas chromatograph has been calibrated with a HC/CO$_2$ standard for the response factors of most gas components liable to be present in soils.

The gas analysis in the micro gas chromatograph is repeated 3 to 5 times and a couple of blanks are made before and after analyses in order to bring the background to normal levels.

After *in situ* analysis of the CO_2 concentration, sampling of gas for CO_2-carbon isotope study is performed with Vacutainers®. The experimental procedure consists in filling 2 Vacutainers® (10 mL) for each soil point, (initial vacuum of about 10^{-3} mbar). The carbon isotope analyses are performed at the laboratory with a GC-C-IRMS (Gas Chromatograph – Combustion – Isotopic Ratio Mass Spectrometry) equipment. The procedure for the analysis of a sample is as follows: after 4 standard measurements, 3 injections are made from the first sample Vacutainer®. After that, 2 standard measurements are performed and 1 injection is made from the second Vacutainer® of the same sample. Thus, repeatability and reproducibility of the measurements are determined for each sample. The procedure ends with 2 standard measurements.

Stainless steel tubes are used for the sampling of gas for noble gas. The tubes have two independent volumes and are shut by leak proof valves that isolate gas aliquots very well. The experimental procedure consists in filling 1 tube (20 mL) (which is initially under vacuum) for each soil sample. Analyses are performed at the laboratory with the QUADRAR (Quadripolar Mass Spectrometry).

Samples from the Gas Field:
Gases at the wells are sampled by connecting the stainless steel sampling tubes, linked to a pressure regulator, at the well head. While controlling the exit pressure below 3 bar pressure with a pressure double fold regulator, the well is flushed before sampling for 15 minutes. The sampling is made when the gas is regulated in flow and the tube well flushed. The micro gas chromatograph was used to control the hydrocarbon and CO_2 levels before sampling.

Fuel Gas (PV4410):
This gas is sampled with the same procedure as the one used for the gas field samples.

Low Depth Monitoring Well (MW):
The gas equilibrated with the well atmosphere in the Monitoring Well at a depth of 45 m is sampled using a pump and by flushing through a stainless steel tube.

1.2.2 Analytical Methods

Gas Analyses using a Portable Field Gas Chromatograph (Micro Gas Chromatograph):
The apparatus is a Varian CP4900 gas chromatograph, permitting autonomous high resolution gas analyses because of a set of long enduring batteries (6 h) and two carrier gas reservoirs (here helium). The micro gas chromatograph is equipped for the monitoring and analyses of soils with three columns, detectors and injectors. With the present configuration of columns and detectors (TCD), and in a time span of two minutes, gas is analysed. Compounds separated and quantified are: C_1-C_5 hydrocarbons, CO_2, N_2, O_2 and H_2. The detection limit is 20 ppm. A gas tube is connected to the micro gas chromatograph equipment to perform the gas sampling (see "sampling procedure"). The advantage of this technique is to analyse either in a continuous or in a sequential mode with a good sensibility and a good resolution. The main drawback is the co-elution of water and propane. A regular regeneration of columns (by increase pressure and temperature) is necessary to eliminate residual water, which is performed at night when the equipment is recharged.

GC (Gas Chromatograph) Analyses – Major Gases:
More detailed analyses for a percent relative molecular composition of gases can be performed by a high resolution gas chromatograph (Varian 3 800) in the laboratory on samples contained in Vacutainers® and/or stainless steel tubes. The GC is equipped with several columns in series and three detectors (2 TCD, 1 FID) operating under helium and nitrogen as carrier gas. This allows the quantification of hydrogen and helium (carrier gas nitrogen) by TCD and CO_2, nitrogen, oxygen, methane, ethane, propane and butane on another TCD but with helium as carrier gas. The FID is used for the quantification of low levels of hydrocarbons C_1-C_5. The analyses are given with a precision of $\pm 0.1\%$. The analysis time is much longer than the field GC, but provides better resolution and higher precision with lower gas volumes.

GC-C-IRMS (Gas Chromatograph - Combustion - Isotopic Ratio Mass Spectrometry) Analyses – CO_2-Carbon Isotopes:
The CO_2-carbon isotope compositions were analysed using the gas contained in Vacutainer® or stainless steel tubes. The measurement of the isotopic ratio $^{13}C/^{12}C$ for CO_2 is performed on a triple collection mass spectrometer MAT253 (Finnigan Mat-Thermo Fischer) coupled to a gas chromatograph.

The instrument is calibrated by measuring an internal reference gas (CO_2), calibrated itself with the standard PDB, which has an absolute value of $\delta^{13}C_{PDB} = 0‰$ (the δ notation

$$\text{stands for } \delta^{13}C_{PDB} = 1000 \times \left[\frac{\left(^{13}C/_{12}C\right)_{sample}}{\left(^{13}C/_{12}C\right)_{standard}} - 1 \right]).$$

PDB stands for Pee-Dee Belemnite, an international reference standard. Repeatability and accuracy of the analysis of our internal reference allows us to obtain a relative uncertainty on the $\delta^{13}C$ value of $\pm 0.2‰$ for gases with a CO_2 molar fraction of up to 1%.

QUADRAR Analyses – Noble Gases Composition:
The noble gases elementary composition and the isotopic ratio $^{40}Ar/^{36}Ar$ were determined by quadripolar mass spectrometry after the treatment of the gas sample through an ultra high vacuum (10^{-9} mbar) preparation line. Only samples in stainless steel tubes were analysed in order to guarantee a negligible atmospheric contamination after sampling.

The QUADRAR line allows to determine the compositions in He, Ne, ^{40}Ar, ^{36}Ar and Kr. Prior to the analysis, the ultra high vacuum line is evacuated down to 10^{-9} mbar by the means of three turbomolecular pumps. The inlet part that connects to the sample tube is evacuated under primary vacuum ($< 5 \times 10^{-3}$ mbar) by a primary pump. An aliquot of the sample is admitted inside a volume of about 10 cm³ where the pressure is adjusted and precisely measured by a thermostated capacitance manometer (MKS Baratron®). A 1.2 cm³ aliquot is then taken out of that volume at a pressure adjusted between 0.1 and 100 mbar (depending on the expected Ar composition).

Purification of this aliquot is performed under the action of two titanium foam traps during 30 mn, the first one being heated to a temperature of 750°C and the second one being maintained at ambient temperature (21°C). The purification process is monitored thanks to a Pirani jauge. The hot titanium oven is cooled down to ambient temperature and then a precise fraction of the purified gas is admitted into a portion of the line equipped with two activated coal traps and a getter (SAES Getters) GP50 ST707 operating at 3V. One of the cold traps is maintained at liquid nitrogen temperature (–198°C) in order to trap the heavy gases, Ar and Kr while He and Ne are analysed by the mass spectrometer before they are evacuated. Then the temperature of the trap is raised to ambient temperature for Ar and Kr to be desorbed and enter the spectrometer for analysis.

The mass spectrometer is a Prisma quadripole QMA/QME200 (Pfeiffer Vacuum) with an open ion source. The analyser allows measurements of compounds with a *m/z* ratio (mass over charge) from 1 to 100 a.m.u (atomic mass unit). The mass spectrometer is equipped with two detectors, a Faraday cup and an electron multiplier (SEM) that can be used alternately. The SEM provides with a gain of 10 000 compared to the Faraday cup and therefore allows to detect very little quantities of gas.

For each sample, the response of the spectrometer is calibrated by performing systematic analyses of a purified air dose (Calibrated Dose) for which the quantities of He, Ne, Ar and Kr as well as the $^{40}Ar/^{36}Ar$ ratio are controlled weekly by an air standard analysis. The $^{40}Ar/^{36}Ar$ isotopic ratio is calibrated against the Ar pressure in the mass spectrometer whenever the source is tuned (approximately once a month). All of the analyses are performed with the SEM, comprising 15 successive measurements of the signals associated to *m/z* ratios 3, 4, 18, 20, 21, 22, 28, 36, 38, 40, 44, 82, 84 and 86. The drift of the signal is corrected to the time of introduction of the gas and the residual background noise measured prior to introduction of the sample is subtracted. The isobaric interferences of $^{40}Ar^{++}$ and $^{20}Ne^{++}$ are corrected by a calibration made on the background noise and controlled by the measurements of the $^{20}Ne/^{22}Ne$ et $^{20}Ne/^{21}Ne$ ratios. Interference of CO_2 on mass 44 with ^{22}Ne is always negligible.

A blank for the entire line is measured every week and does not exceed 1 ± 2% of the signal of a Calibrated Dose (DC). The mean blank is subtracted to the signal of the sample and its standard deviation is integrated to the uncertainty of the sample analysis.

Control over the introduction pressure of the sample allows a very low detection limit implying no limitation when analyzing natural samples. Global relative uncertainty (at 1σ) for quantification of noble gases with this method is of: He: ± 10%; Ne: ± 20%; Ar: ± 5%; Kr: ± 8%, and for quantification of the ratio $^{40}Ar/^{36}Ar$ ± 1%.

2 RESULTS

2.1 Soil Samples

A total of 15 soil samples have been analysed 3 times during 3 surveys different.

2.1.1 Gas Characterization

Soil samples have been analysed three times over a one year period, March 2009, September 2009 and March 2010. The reported data is from low depth measurements made at –1 meter. The two campaigns performed in March were characterised by a high degree of humidity and cold temperatures (Gal *et al.*, 2011). This was not the case in September with more favourable fall weather. Considering the average percentage of each gas (O_2, N_2 and CO_2) in each soil sample, three families can be distinguished:

– family 1: soil samples with an amount of CO_2 above 2.92 ± 1.31%, corresponding at an amount of O_2 below 16.95 ± 4.25% (soil-samples = soil-Rousse 1, 24a, 24b and 25);

– family 2, soil samples with an amount of CO_2 comprised between 1.35 ± 0.60% and 2.92 ± 1.31%, corresponding at an amount of O_2 comprised between 19.43 ± 1.04% and 16.95 ± 4.25% (soil-samples = soil-Rousse 34, 16, 11, 20, 14, 5, 7 and 28);

– family 3, soil samples with an amount of CO_2 below 1.35 ± 0.60%, corresponding at an amount of O_2 above 19.43 ± 1.04% (soil-samples = soil-Rousse 17, 33 and 22).

Using all these soil sample analyses, a correlation between O_2 and CO_2 can be determined with a linear relationship equal to $CO_2(\%) = 10.884 - 0.47717 \times O_2(\%)$ with a correlation coefficient equal to $R^2 = 0.898$.

2.1.2 CO₂-Carbon Isotopes

CO_2-carbon isotopes have been measured for each soil sample and a correlation between $\delta^{13}C_{CO_2}$ (‰) and $1/(\%CO_2)$ in log scale is represented in Figure 3. A mixing process is calculated between two pure end-members represented by first, atmospheric air ($CO_2 \approx 0.04\%$ and $\delta^{13}C_{CO_2} \approx -7.5‰$) and second, pure biological soil with an hypothetical CO_2 content equal to 100%.
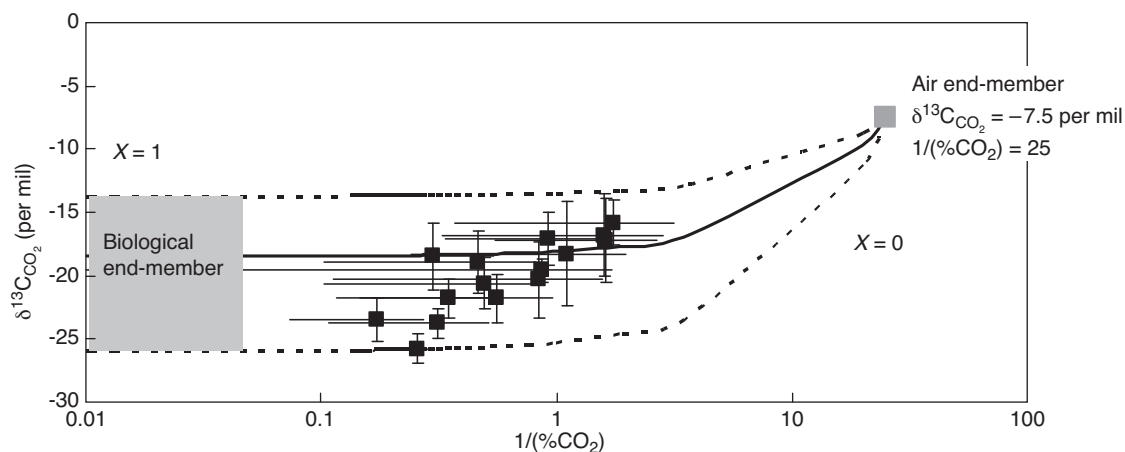
Figure 3

$\delta^{13}C_{CO_2}$ (per mil) in function of $1/(\%CO_2)$ in a log scale, for soil samples at Rousse.

This mixing process is defined in the equation below:

$$\delta^{13}C_{CO_2}\ mixingprocess =$$

$$\frac{\delta^{13}C_{CO_2\ soil} \times [CO_2]_{soil} \times X + \delta^{13}C_{CO_2\ air} \times [CO_2]_{air} \times (1-X)}{[CO_2]_{soil} \times X + [CO_2]_{air} \times (1-X)}$$

with *X* corresponding to a decimal proportion comprised between 0 and 1.

2.1.3 Noble Gases Compositions

Noble gases compositions for 4 soil samples (soil-Rousse 34, 17, 1 and 25) have been measured. Considering the error bars of the measurements, the compositions of these 4 soil samples, for the noble gases, are in the same range as that of air (atmosphere) *(Fig. 4)*. Indeed, when normalized to the composition of the air, the ratio for each element of noble gases is ≈ 1 (comprised between 0.93 ± 0.12 and 1.09 ± 0.12 for soil-Rousse 34; comprised between 0.66 ± 0.23 and 1.81 ± 0.82 for soil-Rousse 17, which is the sample with the highest dispersion; comprised between 0.99 ± 0.04 and 1.09 ± 0.01 for soil-Rousse 1 and comprised between 0.82 ± 0.09 and 1.16 ± 0.01 for soil-Rousse 25) *(Fig. 4)*.

Knowing the chemical composition of these soil samples and the CO_2-carbon isotopes and noble gases composition, a mixing curve can be establish in order to assess the eventual leakage between the reservoir in which the CO_2 will be injected and the surface. This approach is discussed after.

2.2 Gas Fields, Fuel Gas and Injected CO₂

2.2.1 Rousse Initial Gas Composition

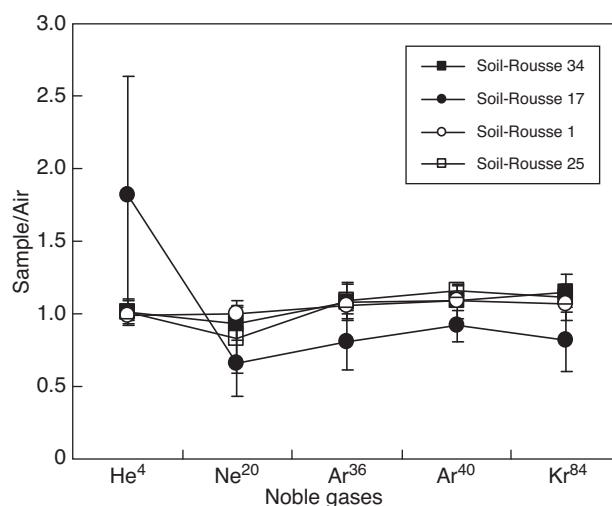The Rousse #1 gas composition has been determined once in 2009.

Figure 4

Noble gas composition in Rousse soil samples, normalized to the composition of the atmosphere.

This gas field or gas reservoir (Rousse #1) is mainly composed of CH_4 with a molar percentage of 81.4%. Then, heavier gases, C_2H_6, C_3H_8, nC_4H_{10}, iC_4H_{10}, and C_5 are present with decreasing percentages: 5.3% for C_2H_6, 2.7% for C_3H_8, 1.6% for nC_4H_{10}, 0.9% for iC_4H_{10} and 0.7% for C_5. This gas also contains 5.0% of CO_2. Finally, little amounts of N_2 and H_2S (0.9% and 0.8% respectively) and traces of H_2, He and O_2 (<0.1%) have been measured.

An analogous composition for Rousse #3 has been obtained, showing the similarity of the reservoirs.

The fuel gas has been analysed twice and shows a good reproducibility of the measurement. The obtained composition is slightly different from the Rousse gases as it comes from many other gas reservoirs. The major gas is again CH_4 but

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with a percentage equal to 92.75 ± 0.25% (average of 2 measurements). The respective amounts of heavier gases, *i.e.* C_2H_6, C_3H_8, nC_4H_{10}, iC_4H_{10}, and C_5, are relatively low compared to gases of Rousse#1 and Rousse#3 fields (between 4.23 ± 0.02% for C_2H_6 to 0.05 ± 0.05% for C_5).

2.2.2 Injected CO$_2$

The injected CO_2, resulting from the oxy-combustion of this fuel gas, has also been sampled during Spring 2010 (in March 2010 and the injection was stopped two months before) by flushing the stainless steel tube with the gas of the pipeline at a pressure of 3-4 bar. This CO_2 stream has the following composition: 88.5% of CO_2, 9.6% of O_2 and 1.9% of N_2. These results prove that the oxy-fuel combustion unit was not at an optimal configuration at this period and is discussed later.

2.2.3 CO$_2$ C-Isotopes Compositions

C-isotopes composition analyses of these gases (gas fields, fuel gas PV4410 and injected CO_2) allow us to discriminate these pure end-members with a better precision. Moreover, these C-isotopes compositions describe the baseline of these systems and can be introduced in mixing processes to evaluate the composition evolution and the displacement of injected CO_2. Rousse #1 and Rousse #3 have almost the same $\delta^{13}C_{CH_4}$ with a measured value of −40.8‰ for Rousse #1 and −40.4‰ for Rousse #3.

For $\delta^{13}C_{C_2H_6}$, the C-isotopes composition are relatively different between these two gases but of the same order of magnitude (−24.6 ± 0.1‰ for Rousse #1 and −23.5‰ for Rousse #3).

The main difference concerns the $\delta^{13}C_{CO_2}$ which is equal to −2.4‰ for Rousse #1 and ±0.4 ‰ for Rousse #3. For heavier hydrocarbons, C-isotopes compositions were not perormed because of the presence of H_2S in these samples.

The fuel gas has been studied twice, once in 2009 and once in 2010. The obtained $\delta^{13}C_{CH_4}$ is reproducible and equal on average to −43.0 ± 0.2‰. For C_2H_6, the same observation can be made and $\delta^{13}C_{C_2H_6}$ is equal to − 24.9 ± 0.5‰. The major difference concerns the $\delta^{13}C_{CO_2}$ which is very different between 2009 and 2010. Indeed, $\delta^{13}C_{CO_2}$ was equal to − 25.6‰ in 2009 and to −19.2‰ in 2010. The C-isotope of $\delta^{13}C_{CO_2}$ in 2009 was attributed to an oxidation of C_2H_6 and as discussed in the Discussion part. We thus retain the 2010 value (−19.2‰) for the $\delta^{13}C_{CO_2}$ of the fuel gas. Finally, $\delta^{13}C_{C_3H_8}$ was measured in 2010 and is equal to −19.0‰.

For the injected CO_2, $\delta^{13}C_{CO_2}$ is equal to −39.8‰, very different from the fuel gas signature.

2.2.4 Noble Gases Compositions

Noble gases of Rousse #1 and Rousse #3 fields have been analysed from the samplings performed in 2009. Their respective compositions are reproduced. Indeed, a high amount of ^{4}He is detected ($\approx 65 \pm 0.5$ ppm) which is 13 times higher than the ^{4}He concentration of the Air. On the contrary, the concentrations of other noble gases in the reservoirs are very low. For both Rousse #1 and Rousse #3, ^{20}Ne concentration is equal to $\approx 0.03 \pm 0.01$ ppm, ^{36}Ar concentration is equal to $\approx 0.06 \pm 0.02$ ppm, ^{40}Ar to $\approx 21 \pm 1$ ppm and ^{84}Kr to $\approx 0.002 \pm 0.0001$ ppm. All these concentrations are very low compared to the air concentrations. This difference is significant in order to distinguish the gas fields Rousse #1 and Rousse #3 from the others pure end-members and soil noble gases *(Fig. 5)*.

Some differences in the noble gas content appears between the two samples for the Fuel (PV440) sampled in 2009 and 2010. Indeed, the first gas aliquot can be compared to Rousse #1 and Rousse #3 gases with a high amount of ^{4}He and low amounts of other noble gases. However, the second sample collected a year later contained higher concentrations of Ne, Ar and Kr.

The injected CO_2 stream has been sampled only in 2010. The composition of this injected CO_2 is different from the air composition with a higher amount of ^{4}He (44.74 ± 8.64 ppm) and a lower amount of ^{20}Ne (5.21 ± 1.60 ppm). Concerning argon, the amounts of ^{36}Ar and ^{40}Ar are equivalent to standard values in the air with a concentration of 28.10 ± 3.56 ppm (31 ppm for the air) and 9 173 ± 824 ppm (9 340 ppm for the air) respectively. The concentration of ^{84}Kr for the injected CO_2 is different from the air: it is equal to 6.89 ± 0.82 ppm compared to 0.62 ppm for the air.
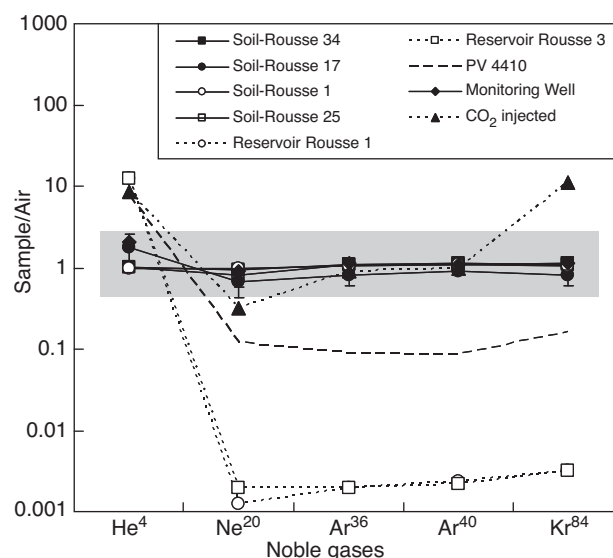

Figure 5

Noble gas composition in Rousse soil samples, Rousse gas fields, PV4410 (fuel gas), and Monitoring Well, normalized to the composition of the atmosphere.

These results show that the composition of the injected CO_2 is different from the air except for the argon element *(Fig. 5)*.

Finally, the noble gases composition of a fluid sampled from the monitoring well at a depth of 45 m nearby Rousse #1 has been analyzed twice in 2009 and 2010 and is equal to the air composition *(Fig. 5)*.

3 DISCUSSION

The results of the composition of the main gases (O_2, N_2 and CO_2), as well as the CO_2-carbon isotopes and noble gases composition for the soil samples, allow us to determine a baseline. This baseline is essential to understand what will happen after the CO_2 injection. Furthermore, if geochemistry analyses of pure end-members like:

– initial gas of the storage site;
– fuel gas;
– injected CO_2 and;
– combustive gas are performed;

it may be possible to predict the mixing processes that occur in the gas field after CO_2 injection and to identify the geochemistry signature of the CO_2 that will stored underground. The approach using mixing curves may well respond to the need to trace the CO_2 from injection to storage and to ascertain the surface baseline.

To better understand the natural CO_2 present in soil, several studies have proposed correlations between CO_2 concentration in soil and C-isotopes composition. CO_2 present in soil and resulting from a biological activity, the C-isotope composition is different between CO_2 in soil and CO_2 in atmosphere. A correlation between CO_2 concentration and C-isotope composition has been put in evidence by Wei Liu (Liu *et al.*, 2006). These authors found that the equation:

$$\delta^{13}C_{CO_2} = 4.70 \times 10^3 \times \left(\frac{1}{CO_2}\right) - 21.4$$

explains the relation between $\delta^{13}C$ (in ‰) and CO_2 (in ppm). This equation can be compared to our proposed equation that is equal in the same units to:

$$\delta^{13}C_{CO_2} = 5.92 \times 10^3 \times \left(\frac{1}{CO_2}\right) - 23.26$$

A good agreement between these two equations is found.

A significant uncertainty exists on the C-isotopes composition of CO_2 present in soil as related from the data set. To define a domain in which the soils studied in the south of France could be represented, we may determine two pure end-members defined by:

– the air (with an hypothesis made on the CO_2 concentration taken equal to 0.04% (400 ppm) and an hypothesis on the $\delta^{13}C_{CO_2}$ taken equal to $-7.5‰$) and;

– the biological CO_2 in soil with an arbitrary percentage equal to 100%.

When we describe $\delta^{13}C_{CO_2}$ as a function of $1/(\% CO_2)$ and represent all soil samples from Rousse site analysed in this study, a domain of $\delta^{13}C_{CO_2}$ for CO_2 in soil is defined between -13.7 and $-26‰$ with an average of $-18.5‰$ which is in good agreement with the average of all measurements realized in soil for $\delta^{13}C_{CO_2}$ with value equal to $\pm -20‰$ (Liu *et al.*, 2006).

Concerning the others pure end-members, the composition of gas fields Rousse #1 and Rousse #3 are representative of all the most well known gas fields.

The compositions of the fuel gas and the injected CO_2 are more surprising and should be discussed. Indeed, the composition of the injected CO_2 is linked to the composition of the fuel gas because of the combustion of the latter. The combustion is performed using an oxy-combustion process. The principle of oxy-combustion is to replace the air by oxygen with a purity at least equal to 95% in order to limit the amount of nitrogen in the combustion products. But the combustion using pure oxygen increases the temperature of combustion. Indeed, for natural gas, the adiabatic temperature of combustion increases from 1 900°C with air to 2 800°C with oxygen at 95% (Lecomte *et al.*, 2010).

Concerning the oxy-combustion process used at the Lacq CCS storage pilot site, oxygen production is performed by a cryogenic distillation represented schematically in Figure 6.

Normally, this process produces pure O_2 which allows a perfect combustion of fuel gas but the process was not optimized during the first survey as substantial O_2 (9.6%) remained in the injected CO_2. Moreover, the presence of nitrogen (N_2) at a percentage equal to 1.9% highlights a problem with the purification step. This observation can be made too with noble gases specially for argon (^{40}Ar) which has, for the CO_2 injected, a concentration equal to the concentration of air (9 173 ± 824 ppm), whereas the fuel gas (precursor of CO_2 injected) has a little amount of ^{40}Ar (812 ± 807 ppm).

With the analyses of the geochemistry of the different involved pure end-members, in our case:

– initial gas in the storage site;
– fuel gas;
– injected CO_2;
– O_2 used in the oxy-combustion process (not yet analysed in our case);
– soil gases (previously defined from mixing processes between the atmosphere and the biological soil, *Fig. 3*) and finally;
– air;

we can predict the best mixing process to discriminate the injected CO_2 from natural CO_2 present in soil and air. With this approach, an eventual leakage of the storage can be distinguished easily. This mixing process is represented in Figure 7 where $(^4He \times {}^{84}Kr)/^{20}Ne$ is represented as a function

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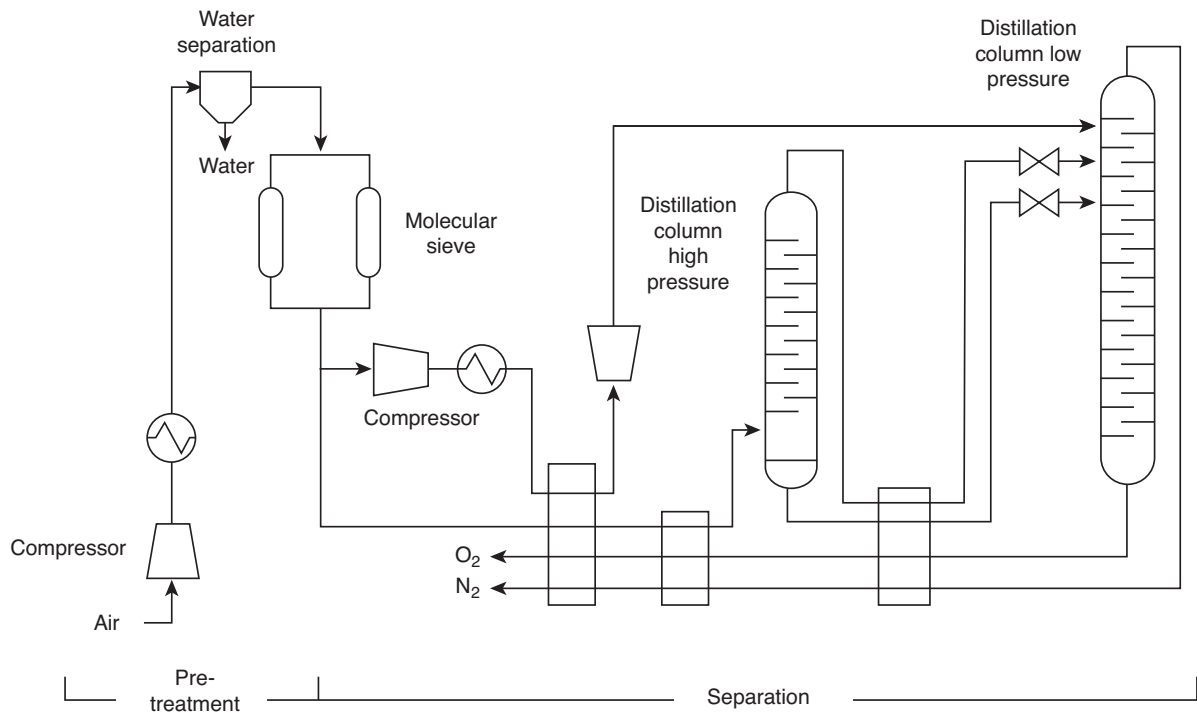
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Figure 6

Representation schematic of the distillation process of O$_2$ used in oxy-combustion (modified from Lecomte *et al.*, 2010).
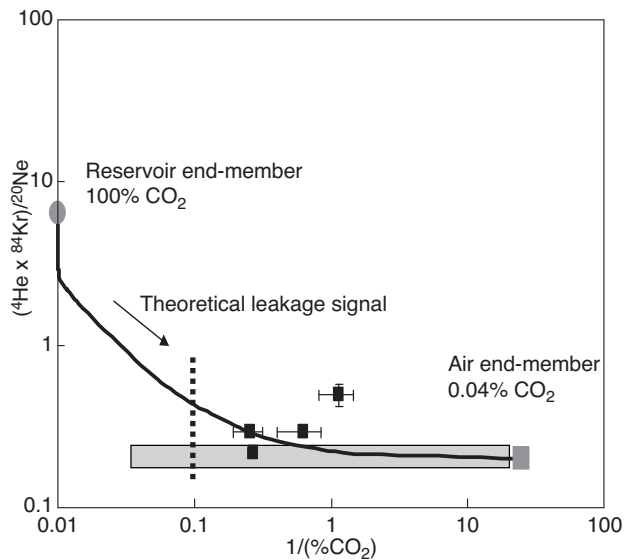

Figure 7

Theoretical Leakage signal from an hypothesis considering the reservoir Rousse 1 with CO$_2$ at a percentage equal to 100% and considering a mixing process between this reservoir and the air, in a case of a leakage. The proportion of the mixing vary from 100% of CO$_2$ coming from reservoir to 0.04% of CO$_2$ coming from air. This leakage signal is represented by measurements of CO$_2$ and noble gases of soil samples.

of 1/(%CO$_2$). We have not observed any leakage in the pilot site. This figure is an hypothesis of a leakage considering the reservoir Rousse 1 with CO$_2$ at a percentage equal to 100% and considering a mixing process between this reservoir and the air, in a case of a leakage. The proportion of the mixing vary from 100% of CO$_2$ coming from reservoir to 0.04% of CO$_2$ coming from air. The soil points are represented in this figure and we can observe, considering exceptional value and data errors, that we could distinguish the CO$_2$ coming from reservoir of the CO$_2$ coming from air, if the concentration of CO$_2$ in the soil is superior to 10% (1/%CO$_2$ = 0.1). In conclusion, this representation allows to determine without ambiguity the origin of the CO$_2$ for a given sample provided it contains more than 10% of CO$_2$. It is possible to determine if this CO$_2$ comes from biological CO$_2$, from air or from the storage.

The proposed approach could also be extended to the monitoring of intermediate aquifers if wells were available.

CONCLUSIONS

In this paper, we present a methodology to distinguish without ambiguity the origin of CO$_2$ between CO$_2$ injected in a process of geological storage from a natural CO$_2$ present in sub-surface. This methodology is based on a high resolution

geochemical analysis of fluids from gas fields, fuel gas used in the process, CO_2 resulting from fuel gas combustion, O_2 used for oxy-combustion (not analysed yet in our case), CO_2-soil defined with gas analyses in soil, atmospheric air content and possible mixing processes.

Results show that a geochemical signature of each end-member is distinct and may help us predict the evolution of CO_2 in a case of an eventual leakage from a gas field to the surface.

Moreover, even if it's not discussed in this paper, this methodology allows us to predict the amount of dissolved CO_2 and the amount of precipitated CO_2. Indeed, in a case of a diffuse leakage (which will be the most current case in a CO_2 storage), we can predict the evolution of CO_2 concentration and noble gases concentrations, in function of time, depth and their own properties (their own diffuse coefficient). From these modelling results and from *in situ* analyses, in the reservoir or in an aquifer, of CO_2 concentration and at less one noble gas concentration which diffuse more rapidly than CO_2 (*in situ* analyses will be performed during time: before, during and after CO_2 injection), effective diffuse coefficient of this noble gas will be modified from the *in situ* analyses in order to determine the ratio between this effective modelling diffuse coefficient and the experimental diffuse coefficient. From this ratio, we can determine the dissolved CO_2 amount even if the concentration is too low to be determined. The modelling can be adjusted from these results.

ACKNOWLEDGMENTS

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