Risk Assessment and Mitigation Tools

A. Hurtado, S. Eguilior, J. Rodrigo-Naharro, L. Ma, and F. Recreo

Abstract Developing engineering projects involving geological systems, such as the Carbon Capture and Storage technologies (CCS), is a complex task with significant challenges. Often the subsoil is poorly investigated and projects often face difficult management of risk components related to uncertainties in the geological environment. Understanding and assessing the environmental risks in these projects should provide satisfactory answers to questions regarding whether CO_2 can leak and what would happen, specifically regarding the consequences for safety, health and the environment. It is worth noting the importance of giving an adequate answer to these questions, among other reasons, due to its influence on the public acceptance of this technology. There is a clear relationship between the early estimation of environmental risks and the social acceptance of technologies. This allows overcome both mistrust and erroneous concepts that citizens could have in relations to them. As indicated in Guide 1 for the application of the European CCS Directive, the environmentally safe management of CO_2 geological storage must be a fundamental objective in any project associated with CCS processes. All this has to be integrated with monitoring strategies for verifying the behavior of the site.

Keywords Risk assessment · Monitoring CO_2 · Bayesian Networks · SRF methodology · Mitigation

1 Introduction

Developing engineering projects involving geological systems, such as the Carbon Capture and Storage (CCS) technologies, is a complex task with significant challenges. Often the subsoil is poorly investigated and projects often face difficult

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management of risk components related to uncertainties in the geological environment. Understanding and assessing the environmental risks in these projects should provide satisfactory answers to questions regarding whether CO_2 can leak and what would happen, specifically regarding the consequences for safety, health and the environment [1]. It is worth noting the importance of giving an adequate answer to these questions, among other reasons, due to its influence on the public acceptance of this technology. There is a clear relationship between the early estimation of environmental risks and the social acceptance of technologies, since a reasonable guarantee that the society could benefit of the use of these technologies avoiding secondary negative effects is pursued. This allows overcome both mistrust and erroneous concepts that citizens could have in relations to them.

Both safety and long-term risk management of CO_2 Geological Storage (CGS) should be considered as a part of a continuous and iterative process throughout the life cycle of the project, which, based on appropriate methodologies, has to establish a robust and reliable framework that should identify, evaluate and manage both risks and uncertainties in each of the associated phases of the project, including: (i) the identification and early selection of geological formations; (ii) its characterization; (iii) the development of the project; (iv) the operating period; (v) the post-closure operations in the pre-transfer phase of control of the facility; and (vi) the transfer of responsibilities. During all of them, risk management will aim at continuous improvement in the knowledge of the system and its associated risks in order to help attaining project objectives. As indicated in Guide 1 for the application of the European CCS Directive [2] the environmentally safe management of CGS must be a fundamental objective in any project associated with CCS processes, which must be present in all phases of the project.

Within the different focuses and methodologies it will be necessary to reflect, know and take into account the positive aspects of each one of them, as well as its limitations in order to get the best out of each one in the different phases of its development. Thus, for example, already from the first phase, consisting of the site selection, the need to incorporate risk management (RM) arises and it will be an activity that will require specific research [3] for the development of methodologies that allow applying a systemic point of view and tools that enable the integration of available knowledge and the treatment of the high uncertainties associated with these initial phases. All this has to be integrated with monitoring strategies for verifying the behavior of the site.

The main objectives of the monitoring applied to a CGS, are those related to: (i) the control of the storage operation (e.g. capacity, injectivity, containment); (ii) the control of the risks associated with possible CO_2 leakages (e.g. contamination of shallower aquifers, escapes to the surface); and (iii) the calibration of the numerical models simulating the behavior of CO_2 for the long term to estimate the evolution of both risks and operation as accurate as possible. To achieve these objectives, monitoring systems should cover three aspects: (i) monitoring the operation of injection; (ii) monitoring for verification (location, distribution and migration of CO_2, integrity of wells and seal formation); and (iii) monitoring the environment [4].

Finally, monitoring is intimately related to risk analysis and mitigation or remediation measures. In this sense, risk assessments should provide the basis for those measures, which are aimed to prevent any risk to the environment or human health in case of CO_2 leakages from a geological storage of CO_2.

2 General Elements of Risk Analysis and Assessment Methodologies

At the international level, and among the different directives and guides [5], there is a broad consensus on the definition of «risk». A typical definition in the field of engineering project management is one that qualifies Risk as any uncertain event o condition such that, if it occurs, it has an effect—either positive or negative—on a project objective [6]. The exact wording of the different definitions may vary, but they all coincide in the definition from two components. The first one is referred to "uncertainty", since risk is something not materialized which may or may not occur. The second one refers to what would happen if said risk were to materialize, that is, its impact or consequences, since risks are always defined in terms of their effect on the objectives of the project.

Risk Management (RM) tools allow to face the knowledge and control of the same in a wide variety of human activities, industrial or not. Thus, the RM allows structuring the effort of an organization to identify, measure, classify and assume, eliminate, mitigate, transfer, or control the different levels of risks associated with a project. Figure 1 shows a possible structure of a RM process. The different phases are general for all management systems, although their framing may vary among methodologies, and should be considered as part of a continuous and iterative process throughout the life cycle of the project. A fundamental aspect is the need to ensure the identification of all significant risks, from which the corresponding measures can be taken (risk analysis). An unidentified risk allows neither its evaluation nor its monitoring, reduction or cancellation. After the analysis phase, the risk evaluation phase can be considered through which the severity of consequences of risk materialization—it previously identified in the risk analysis phase—and the probabilities associated with said materialization could be estimated and, based on adequate methodologies, to establish a robust and reliable framework that allows to evaluate both consequences and uncertainties in each of the phases of the project.

2.1 Analysis and Evaluation of Environmental Risks in Geological Storage of CO_2

The risk analysis and subsequent risk assessment process should be tailored to the relevant stage of development of the project, reflecting the decisions to be made and

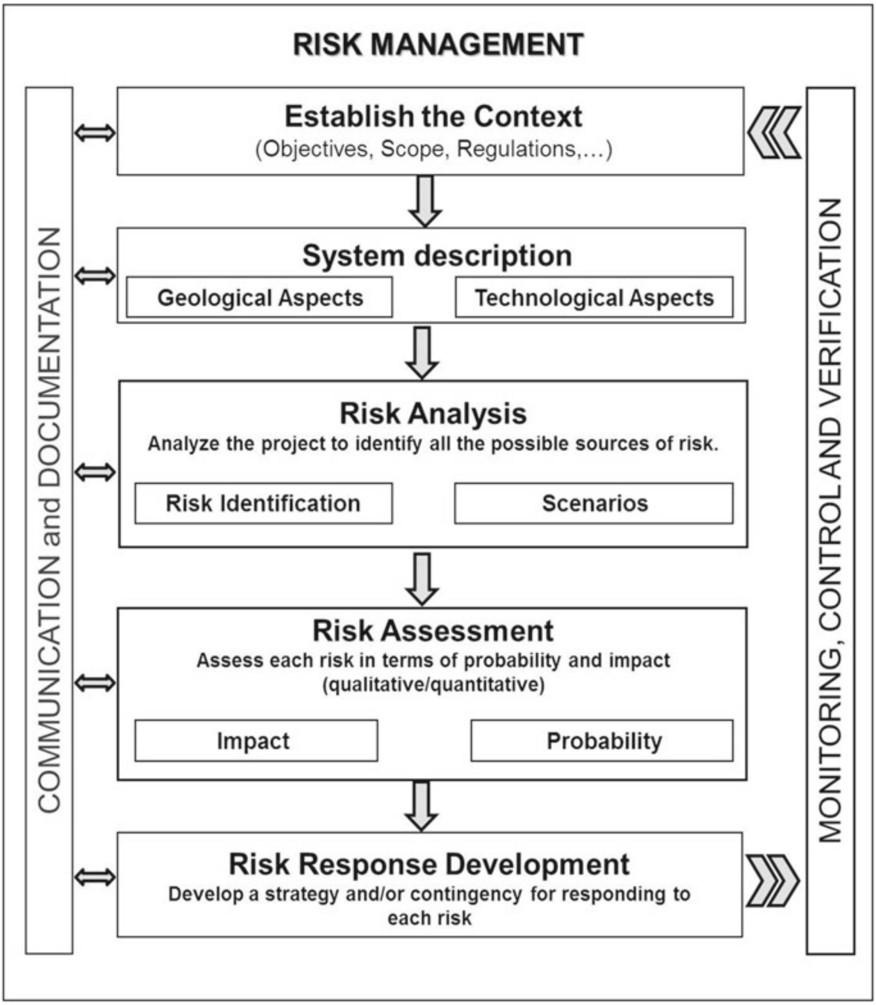


Fig. 1 Risk management steps

the level of available detailed information. In addition, it must be noted that no one project is the same as another [7] due to variations imposed by the geology of each site and its behavior in connection with the process of CO_2 injection. Thus, the level of risk will vary from one site to another, i.e., it is not advisable to take decisions based on an a priori general risk prioritization.

2.1.1 Risk Analysis

The objective of this phase is the identification of all the risks that may directly or indirectly give rise to undesired consequences in the project. In this context, consideration will have to be given to:

- The features of the different elements that make up the system.
- Events and processes both internal and external to the system.

The risks identified will depend on the context of the evaluation: objectives, premises, scope, regulations, spatial and/or temporal limits, and so on.

At this stage, the elements (characteristics with their properties, chemical and physical processes, events than can alter its normal evolution) which affect behavior and evolution of the system are identified and classified.

The main issue at this phase is whether it is possible to ensure that the set of risks is complete. It is impossible to demonstrate strictly but a review process open to broad groups in the scientific community is probably the best way to reasonably ensure that the risk analysis is complete. So, it is important:

- To follow an approach that allows us to guarantee and defend that the list obtained is sufficient for the evaluation that is being carried out.
- To document all judgments and their reasoning.
- To be iterative and flexible.
- To allow a systematic and orderly visualization of the system.

In the risk analysis phase different sources are usually used (e.g. literature review, expert elicitation, historical records or experience gained in analogous disciplines). In addition, different systematic approaches [8] are available, such as the FEP (Features, Events and Processes) methodology that identifies the characteristics, events, and project specific processes that are used to explore the sources of project risks and to generate a comprehensive range of evolution scenarios thereof; failure trees, used to identify risk scenarios; or the Failure Mode and Effect Analysis (FMEA) methodology for failure mode analysis and its effects [9, 10].

An important aspect in assessing long-term risks of a project is the identification of the possible scenarios of evolution of the system. The need to conduct a scenario development in performance and risk assessments arises from the fact that it is virtually impossible to accurately predict the evolution of the system over time.

The scenarios development phase aims to achieve a set of illustrative scenarios of system behavior through time to provide a reasonably complete picture of the evolutionary paths of the system. These scenarios shall define the context, in broad terms, in which to perform the steps of modelling and consequence analysis since, in order to quantify the potential impacts and risks associated with the project, one needs to assess its possible long-term behavior in the geological medium as well as to define possible migration pathways and mechanisms, that will depend on the scenario under consideration.

Among systematic methodologies used to develop scenarios, one can mention the systems analysis approach, which includes FEPs analysis methodology, successfully applied in the field of radioactive waste disposal to assess the problem of long-term radioactive waste behavior in geological media [11] and which is also the approach adopted, for example, within the CGS performance and security evaluation in the Weyburn project [12].

2.1.2 Risk Assessment

Once the risks have been identified, it will be necessary to assign values to each of the identified failure scenarios (probability) and to the impacts on each initially defined objective (impact function). The total risk of the system will be the sum of the probability of each scenario by its impact function (Eq. 1).

$$Risk = \sum_{i=1}^{N} (Probability)_i \cdot (Impact)_i; \quad N\, is\, the\, number\, of\, scenarios \tag{1}$$

For risk assessments to be consistent and meaningful, the application of appropriate methodologies in the evaluation of probability and impact is essential. Assessment methodologies can be divided into two broad categories: qualitative and quantitative. Technological maturity or gaps in knowledge in the evolution of disturbed natural systems, as well as the project phase, determine the nature of the assessment to be used.

In the qualitative ones, the assignation of probabilities and impacts is made through significance levels. When there is a lack of specific information and/or knowledge, a qualitative risk assessment can be sufficiently effective. Qualitative approaches classify risks through scores that allow them to be compared. They often use qualitative methods to assign estimates of probability and/or consequences, and then use quantitative tools to classify and evaluate them in more detail. They can serve as a platform towards a quantitative system, particularly when detailed data is lacking, and can be used as a means to capture subjective opinions, open discussions, and become in a framework for identifying where an additional analytical effort is required.

The most common qualitative methods are: the two-dimensional Probability—Impact matrix, the Bow-Tie diagrams [13], the Vulnerability Evaluation Framework (VEF), the Structured "What-If" Techniques (SWIFT), the Multi-Criteria Assessment (MCA) [8, 14], and the Selection and Classification Framework or Screening and Ranking Framework (SRF) [15]. This latter one has been satisfactorily used in early environmental risks assessments focused on its effects on Health, Safety and the Environment (HSE) [16], for the selection of possible CO_2 geological storage sites [17]—a clear example of a geo-project with an important limitation both in initial data and in knowledge about the evolution and consequences of disturbed natural systems. Among qualitative methodologies, Expert Judgment (EJ) constitutes an essential tool used to request informed judgments based on the training and experience of experts.

The quantitative risk assessment develops numerical estimates of the probability of occurrence and of the magnitude of the impact in the different scenarios. The quantitative approaches have used approaches for uncertainty treatment based on EJ combined with risk matrices (e.g. Schlumberger's Carbon Workflow), evidence supported logic (e.g. CO2TESLA) and Bayesian Networks (BN) [18]. In quantitative approaches, these methodologies are combined with specific software codes for calculating impacts, and they are applied through performance assessment models which, based on a global view of the system, provide the ability to simulate the dynamic evolution of the entire system (e.g. CO2-PENS, Certification Framework, QPAC-CO2 [15], ABACO2G (Aplicación de Bayes al Almacenamiento de CO_2 Geológico) [19] or NRAP-IAM [20]) or parts of it, such as wells, or impacts on aquifers in case of a leakage [9].

Quantitative methods are used in well-known systems, where the level of uncertainty is relatively low, and use approaches that directly address uncertainties. They measure the credibility of a hypothesis based on the evidence that supports it. They can be represented by a probability density function, if the frequentist concept of probability is used, or make use of the uncertain or approximated reasoning, related with fuzzy logic or similar models. The approaches used by the latter may be grouped as follows: Empirical (MYCIN, Prospector); Approximated Methods; Diffuse Logic; Dempster-Shafer Theory and BN.

3 Risk Assessment of a CO_2 Geological System

This section presents the risk analysis and evaluation process in the initial selection and characterization stages of a site, from the perspective of formal risk analysis. It is designed with the aim of developing the methodologies and technologies that facilitate the CGS in low permeability and fractured carbonate formations (limestones, dolomites, and carnioles of the Lower Jurassic), the primary objective for the development of CCS technologies in Spain, as these lithologies possibly have the greatest potential for geological storage in Spain.

Once the criteria and performance indicators had been defined [21], the first step was to carry out a risk analysis and evaluation of the possible locations where a CO_2 storage system could be located. This allowed to classify the zones from the point of view of their environmental risks and to help in the selection of a site [17]. Once the site was selected as an initial step for the risk evaluation, the main leakage scenarios [22–24] were identified, namely:

- Leakage through wells.
- Leakage due to fracturing of the seal rock due to overpressurization.
- Leakage through the seal rock pore system, either due to overpressures or the presence of an undetected area of high permeability.
- Leakage through an existing fault.
- Migration of the brine from the formation.

Later on, a methodology was developed and applied to evaluate the risks associated with them [18]. It is a probabilistic approach that allows us to explicitly deal with the uncertainties associated with the ranges of variability of the parameters, the scenarios and the conceptual models of the processes involved in each scenario. To do this, an integrated tool was developed and implemented that has allowed addressing the fate and effects of the injected CO_2, also including uncertainties in the predictions.

3.1 Application of the Environmental Evaluation of HSE Risks in the Site Selection Phase

Selecting a safe site, capable of sequestering CO_2 for long periods of time and with minimal risk is the first step in a Geological CO_2 Storage project, and it requires specific research [3]. In this case the methodology developed by Oldenburg [25] has been applied to three candidate areas for the location of a pilot CO_2 injection plant in the western part of the Basque-Cantabrian Basin: Huérmeces, Huidobro and Leva, in the Burgos province of Spain (Fig. 2).

The methodology makes use of the available information of qualitative type (studies, reports, publications, EJ) as an approximation for the evaluation of possible combinations of probabilities and consequences. Many of the properties and values considered in these early phases involve estimates that can be measured and modeled in later phases. Given the usual absence of direct data in the early stages of the project, maintaining uncertainty as an input and output value in the methodology is a key condition.

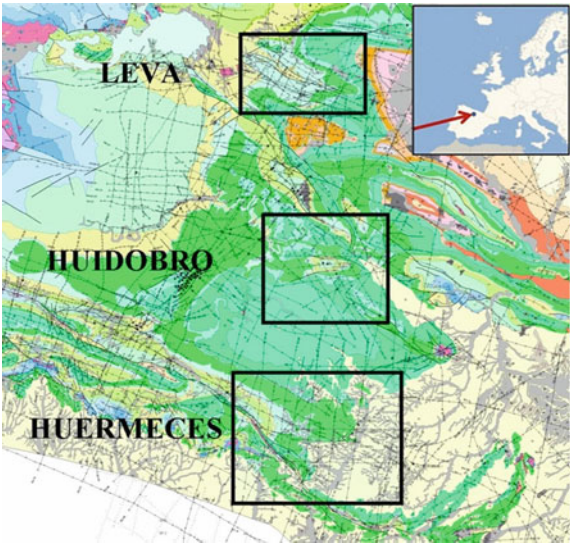


Fig. 2 Study areas

The methodology supports the evaluation of different sites and different scenarios (e.g. related to well technology options, water management, etc.) in one or more specific locations. This process allows us to compare different options, which in turn facilitates the decision-making process. Furthermore, this approach constitutes a powerful communication tool to inform stakeholders through knowledge sharing and, in particular, about the assessed risks.

The methodology is flexible and can be adapted to the different types of projects where globally it will allow evaluating the main aspects related to their safety, including those focused on: (1) the natural properties of the site and (2) the technological properties of the project. The main aspects related to risk are described according to their characteristics (c_i), that is, the fundamental parts into which the project can be divided from the point of view of its HSE risks. These, in turn, are broken down into attributes (a_i), which determine how characteristic ci is competent in fulfilling its HSE risk-oriented function. Finally, these attributes are divided into properties (p_i), based on whose values the performance of the attributes with respect to HSE risks will be determined.

Table 1 shows the characteristics and attributes associated with an assessment of the risks of a CO_2 Storage and Table 2 shows an example of the characteristic/attribute/property set.

Properties values entered by the evaluator represent "proxies" or reasonable substitutes for site or technology-related characterization data or modeling results, which may not be known at the time of evaluation. Thus, for example, the "lithology" property of the "Primary Seal" attribute (see Table 2) is used as an indicator of permeability and porosity. The subjacent idea is that permeability and porosity distributions may not be available in the early stages of the project, but lithology gives an initial adequate representation of these properties. Associates uncertainties are entered through confidence values associated with each property. Therefore, each property has two values assigned: one will measure its performance with respect to risk; the other, the evaluator's confidence in the assigned value. These allocations,

Table 1 Characteristics and attributes for a geological CO_2 storage system. The HSE risk of the system will be evaluated based on the values and uncertainties associated with each of them

Geological storage of CO_2	
Characteristics	Attributes
Potential for primary containment	Primary seal
	Depth
	Reservoir
Potential for secondary containment	Secondary seal
	Shallower seals
Attenuation potential	Surface characteristics
	Groundwater hydrology
	Existing wells
	Faults

Table 2 Example of a group of characteristics/attributes/properties, as well as the risk element to which it is associated in a CO_2 geological storage [25]

Characteristics	Attributes	Properties	Proxy for
Potential for primary containment	Primary seal	Thickness	Likely sealing effectiveness
		Lithology	Permeability, porosity
		Demonstrated sealing	Leakage potential
		Lateral continuity	Integrity and spill point
	Depth	Distance below surface	Density of CO_2 in reservoir
	Reservoir	Lithology	Likely storage effectiveness
		Permeability and porosity	Injectivity, capacity
		Thickness	Areal extent of injected plume
		Fracture or primary porosity	Migration potential
		Pore fluid	Injectivity, displacement
		Pressure	Capacity, tendency to fracture
		Tectonics	Induced fracturing, seismicity
		Hydrology	Transport by groundwater
		Deep wells	Likelihood of well pathways
		Fault permeability	Likelihood of fault pathways

together with the available information and the adopted decisions, should be included in the evaluation to allow transparency and traceability of the process [25].

The methodology makes use of the "multiple barrier system" concept, widely developed in research on ensuring the safety of systems involving geological media, such as the geological storage of radioactive wastes [26]. Thus, in anticipation of a failure in the primary containment system, it is necessary to evaluate the attenuation capacity of HSE impacts by the secondary levels of the geological system, and the possibilities of attenuation of impacts must also be examined and evaluated, for instance, the fast dispersion in the atmosphere of possible contaminants or their mixture with geological/natural/environmental waters up to safe levels, as well as the reaction times to reach dangerous concentrations [27]. All this will depend on the characteristics of both the contaminants and site location and land surface.

The main benefit of the methodology is that it formally expresses both the knowledge and the associated uncertainties, so that in future iterations it could be revisited and modified should new data were available.

The system supports a wide degree of versatility, allowing the evaluator to assign different weights based on the relative importance for risk of the different characteristics/attributes/properties. The transparency of the system and its simplicity allows any reviewer to modify the assigned weights and perform further analyses to compare the effects of those changes on the system response. The results of the methodology allow, on the one hand, to compare the risks associated with different locations (or different scenarios for the same site), as it can be seen in Fig. 3. In addition, it is also possible to examine the relationships between the evaluations of the attributes and their certainties, establishing comfort zones and zones where the attributes should improve their characterization (see Fig. 3). Finally, it should be noted that the safety areas of system operation will be defined, in much more advanced phases, by the values of the system's fundamental behavior indicators (or Key Performance Indicators—KPI [28]), associated with monitoring activities, which is not feasible in the earliest stages.

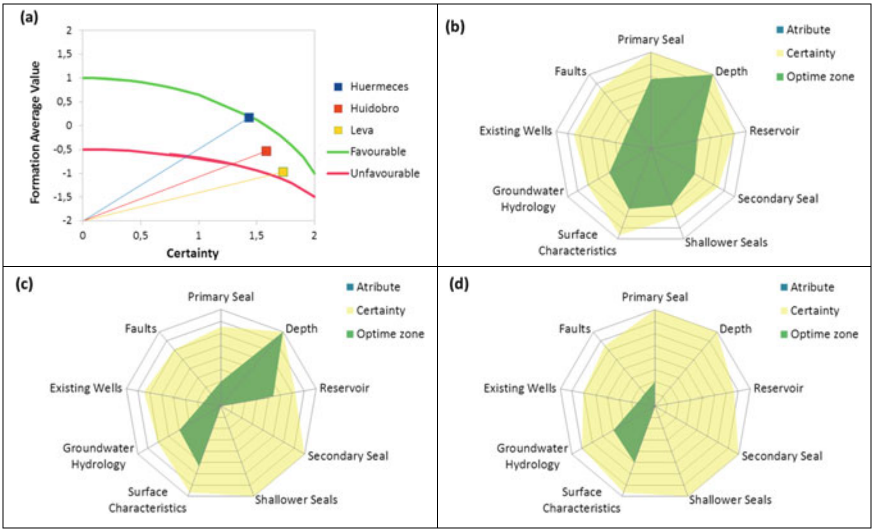


Fig. 3 Risks associated with different alternative sites for a CO_2 geological storage project (**a**). Valuations of different attributes and their uncertainties for the Huermeces (**b**), Huidodro (**c**) and Leva (**d**) sites

3.2 Environmental Risks Assessment Using Bayesian Networks

This section documents the activities which have been carried out in order to move forward to a quantitative estimation risk model. The advanced model is based on the determination of the probabilistic risk component of a geological storage of CO_2 using the formalism of BN. To this end, the first step was to define a BN for the evaluation of system's risks. The behavior of the network was validated with qualitative calculations through comparisons with the results of the SRF methodology. Subsequently, quantitative models were included: the time evolution of the CO_2 plume during the injection period, the time evolution of the drying front, the evolution of the pressure front, decoupled from the CO_2 plume progress front; and the implementation of escape submodels, and leakage probability functions, through major leakage risk elements (fractures/faults and wells/deep boreholes) which together define the space of events to estimate the risks associated with the CGS system. Then a quantitative probability risk functions of the total system CO_2 storage and of each one of their subsystems (storage subsystem and the primary seal; secondary containment subsystem and dispersion subsystem or tertiary one) were obtained.

Bayesian Networks [29] are acyclic directed graphs in which the nodes represent random variables and the arcs represent direct probabilistic dependences between them. They allow the structure of a geological storage system to be represented as a graph of the qualitative interactions that exist in the set of variables to be modeled to estimate the risk of leakage in the storage complex and in each of its subsystems, structures and components. The ad hoc directed graph structure that reflects the causal structure of the storage complex model offers a modular view of the relationships and the interactions that exist between its different variables, which enables to make predictions about the effects due to causes external to the system. Injection scenarios, among others, are the most immediate external causes to a storage system. The BN can be seen in Fig. 4.

3.2.1 Application of the Proposed Methodology to the Zone of Huérmeces

The initial BN model is oriented towards the estimation of the probability of risk of leakage in a CGS from EJ, and therefore from qualitative-type data. This model evaluates the combination of the probability of leakage from the primary containment and from the secondary one, as well as the edaphic capacity of attenuation of those potential escapes. The model takes into account and establishes relationships among the variables that define the storage system.

The application of the proposed methodology was implemented in the Huérmeces zone of the BN model built for estimating the risk of leakage (see in Fig. 5 the BN probability of leakage model at the CGS). The calculated probability range is defined

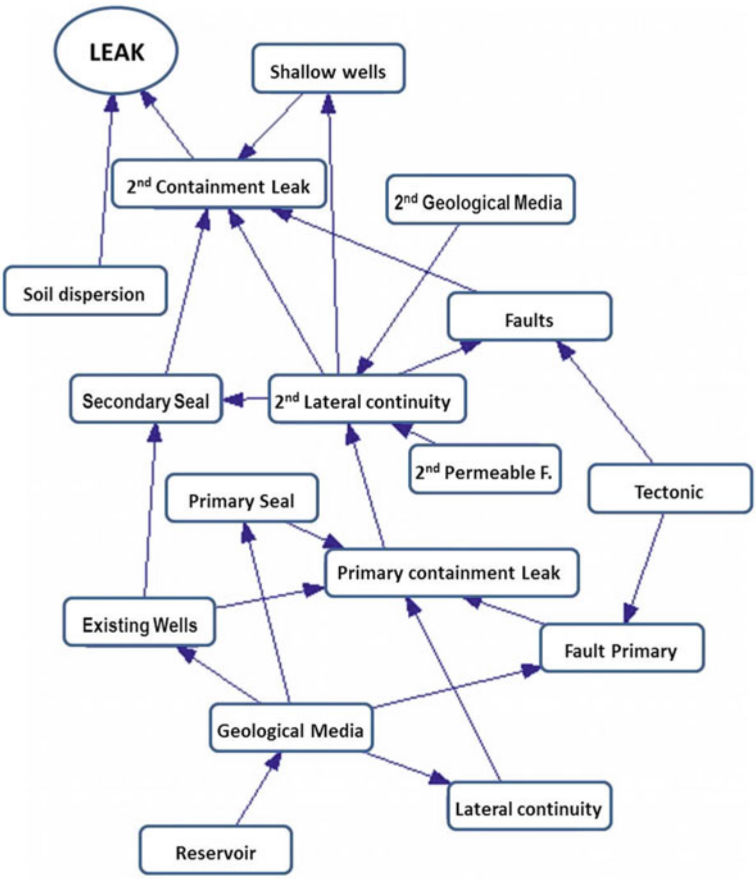


Fig. 4 Bayesian network. Main nodes

by the BN represented in Fig. 5 for the greater (and lower) values of the variability range.

Red and green variables contribute with information to the model. In the BN which determines the upper range (see Fig. 5a), a value of ≈79% is reached, of which, ≈66% indicate a probability trend in favor of leakage. On its turn (see Fig. 5b) obviously the percentage of nodes with information is maintained, but only ≈34% of them indicate probability trends in favor of leakage.

The risk of leakage probability range estimated for the study area is $p \in [0.656, 0.329]$ with a d value of $d = 0.654$. By eliminating from the model those variables related to the edaphic capacity of attenuation of the potential escapes (variables which, at the current stage of development of the project do not give information), the associated probability range is $p \in [0.562, 0.408]$, with a d value of $d = 0.308$ (eliminating variables without information, the uncertainty associated with the calculus diminishes). The results obtained are shown in Fig. 6. The comparison of these

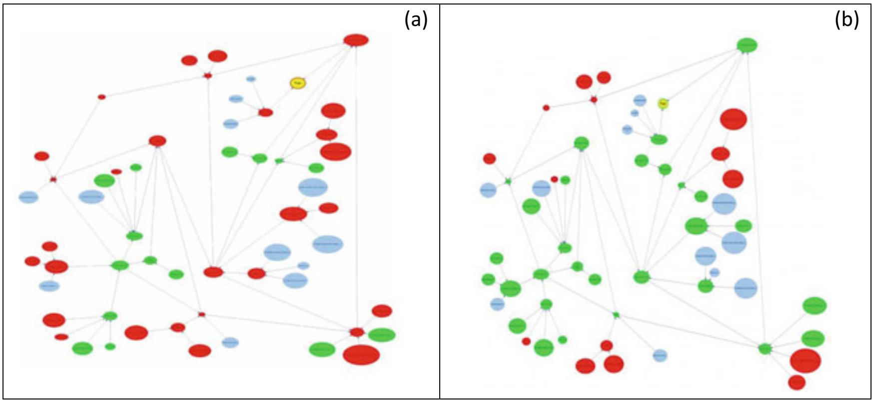


Fig. 5 Bayesian Network of the risk of leakage probability model in a CGS applied to the study area of Huérmeces; **a** corresponds to the network with the higher values of the variability ranges of the variables, and **b** to the application with the lower values. The color code applied refers to the risk probability value estimated for each variable as follows: Red: Probability value greater than 0.5 (its behavior relative to risk is negative), Green: Probability value lower than 0.5 (its behavior relative to risk is positive, a value in favor of safety), and Blue: Probability value equal to 0.5 (its behavior relative to risk is neutral)

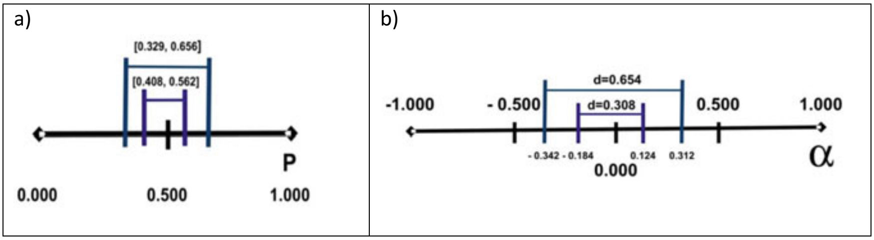


Fig. 6 Graphical representation of results from the application of BN models, the full one and that one without the edaphic capacity, to estimate the probability of the risk of leakage in a CGS applied to the study area of Huérmeces: **a** Probability ranges; **b** "α" and "d" values

results with those obtained in the former evaluation of this same zone with the SCF methodology, seems coherent as both methodologies conclude with a classification of the study zone at an intermediate level of goodness for the CGS, with similar final results in relation to the uncertainties estimation. The BN also allows us to carry out a sensitivity analysis, the results of which can be seen in Fig. 7.

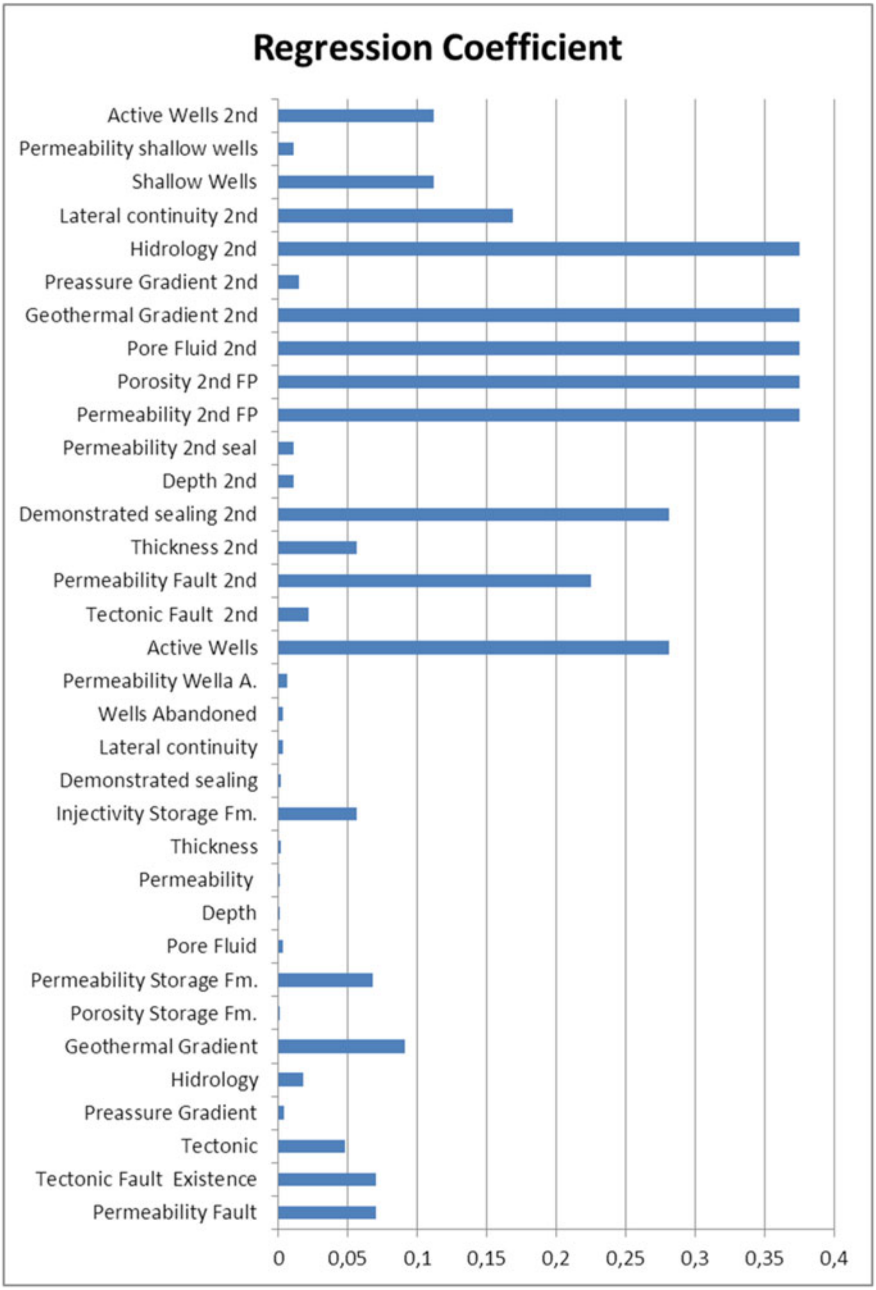


Fig. 7 Results of the sensitivity analysis of the Bayesian Network

3.2.2 Evolution of the BN Model. Probabilistic Model for the Integrated Evaluation of a CGS Performance

In a BN, the estimation of the a priori probabilities by EJ would be only the initial starting point. The Bayesian methodology enables to move gradually from qualitative-type models to quantitative-type models and the combination of both types for probability estimates. Using this flexibility, progress has been made towards the development of a quantitative risk assessment model for the CO_2 injection phase which has enabled to obtain the quantitative probability functions for the total CO_2 storage system, and those of each subsystems (storage—primary seal subsystem; secondary containment subsystem, and tertiary- or dispersive-subsystem). The models used are based on recent studies on the injection of CO_2 into a deep permeable aquifer saturated with brackish fluid from a single injection well, the pressure field generated and the possible leaks through risk elements such as wells or faults [19]. These models are analytical and/or semi-analytical and can be used as a first approximation for calculating leakage probabilities through the above mentioned scenarios. The main characteristics of the models for the scenarios under study will be the following:

- CO_2 plume evolution model: The general scheme of study of a CGS safety corresponds to that of a secular equilibrium system altered by the introduction of CO_2. The injected CO_2 will remain, in its practical entirety and for hundreds of years, as a separate phase enriched with CO_2, the migration of which will be governed by the biphasic flow [CO_2-connate brackish fluid] controlled by injection and hydraulic pressures, and buoyancy associated with density differences. This is due to the fact that the geochemical reactions that may occur between the CO_2 injected, the storage formation rock, the seal formation and the cations in solution in the formation water will take place on time scales of thousands of years [30] since the dissolution of the CO_2 it will be limited by the diffusion and although there may be momentary increases due to local density instabilities, the time scale is on the order of hundreds to thousands of years [31]. From both observations, it appears that during the injection, the displacement is due to a drainage process in which the non-wetting fluid (CO_2) displaces the connate brackish fluid. This shift leaves the connate brackish fluid to residual saturation in the biphasic zone. Hence, the maximum risk of leakage will correspond to the time when CO_2 remains as a separate mobile phase and when the pressures exerted on the medium are high, that is, during the injection period. This is the critical period for risk assessment. For this reason, the first stage of implementing quantitative models for risk assessment is aimed at this phase. The modeling of the evolution of the plume will allow estimating the maximum expected range of the plume for the conditions imposed during the modeling, which is essential in estimating the risk, since it determines the space of events within which are the elements of risk.
- Pressure field model. The injection of CO_2 requires the application of a pressure higher than the storage formation fluid. During the injection operation, the pressures in the aquifer will be distributed radially, from a maximum value located

at the injection well that will decrease almost proportionally to the distance. The necessary overpressure and its area of influence will depend on the receiving aquifer characteristics, its fluids, the amount of CO_2 injected, and the time required for the injection. Applying excessive pressures can lead to hydraulic fracturing of the permeable formation, therefore, for a safe injection operation the maximum admissible injection pressure has to be known. The permanent control of this variable is essential and it will be necessary to anticipate the pressure to which hydraulic fracturing will develop (or movements in fractures) from an estimate of the state of stress to which the formation is subjected at the injection point depth. In sedimentary series the maximum pressure in the vertical direction increases with depth due to the increasing load caused by the increasing thicknesses of rock and fluid. The average value of this increase (lithostatic gradient) is 1 psi/ft (1 lb per square in./foot = 22,620.59 kg m^{-2} s^{-2} $\approx$ 22 MPa km^{-1}), and varies between 22 and 26 MPa km^{-1}. The average hydraulic gradient is 10 MPa km^{-1} or 0.43 psi/ft [32].

- Model of leakage through risk structures. Wells and Boreholes: One of the potential scenarios of risk in a geological storage of CO_2 is the deep wells and boreholes existing in the area of influence of the site, since they can directly put into contact the storage formation with the atmosphere or with shallower aquifers. In this context, it is necessary to differentiate between the CO_2 injection wells, on which a specific regulation that is being developed in various countries would be applied, and other wells already present in the area affected by the CO_2 storage, with characteristics that will depend on its function, year of construction, type of abandonment, etc. Assessing the risk associated with wells will require reliable estimates of both the amount of CO_2 that can migrate through the wells and their probability. In addition, the associated risk will depend on the consequences of said migration, since "risk" implies that the leaked CO_2 may affect a target to be protected and cause harm either to people (in their health, or economic damage), to the environment or to the infrastructure or other assets. In our case, the risk associated with the wells will be determined and integrated into the methodological approach to solve the risk evaluation problems derived from CGS activities, based on the use of BN and Monte Carlo probability. Within this methodology, the "well" model will incorporate the calculation of both the escape rates, which depend fundamentally on the leakage mechanisms, and their probabilities, taking into account all the uncertainties associated with both aspects through Monte Carlo modeling.
- Model of leakage through risk structures. Faults and Fractures: The safe CGS requires that the seal formations can guarantee its long term integrity, this is, the time in which the CO_2 will remain in a supercritical state before entering the dissolved phase as CO_{2aq}. Certain geological structures, especially the faults and fractures that intersect the seal formation and the areas affected by them can suppose preferential paths for the leakage of CO_2. For the purposes of consideration in risk assessment, faults can be considered as two-dimensional conduits whose permeability varies spatially along the fault plane. The permeability in the

direction of the fault is likely to be low in the sections with fill or seal material and the sections in which the fault is clogged will control the flow of CO_2 along it; hence, the importance of taking into account variations in permeability in evaluating the risk associated with faults in a geological storage of CO_2 [33]. In its migration to lower pressure areas, the injected CO_2 may find other fractures connected with the main one, or other permeable formations in which to disperse. In both cases, there will be an attenuation of the ascending flux of CO_2 that must be quantified to estimate the risk. This attenuation will reduce the flow in the fracture, but will also extend the presence of CO_2 in a larger area. Therefore, for a fracture to be considered a risk structure because it constitutes a preferred way of leak it is not necessary for it to reach the surface, it is enough that it may constitute a leakage way to permeable formations of interest such as drinking water aquifers, now or in the future.

Figure 8 shows an example of obtained results from the application of said calculation module where it is possible to visualize stochastic solutions of the dynamic evolutions of the leakage rate by deep well/borehole and by fault/fracture. These results can substitute the probabilities obtained by EJ in the BN and to advance towards quantitative results. In addition, a BN allows us to realize sensitivity analyses and obtaining which parameters introduce more uncertainty in the final results (see Fig. 7). This aspect is essential so that the advance in the characterization of the system is maximizing the benefits in the final reduction of uncertainty.

4 Estimators of the Behavior of a CO_2 Storage Complex

This section is focused on which indicators of the performance of the storage complex and what environmental criteria and security should satisfy the assessment of the long-term risks of a geological storage of CO_2.

The IPCC 2005 [34] classifies the impacts on safety and the environment related to the escape of CO_2 from a geological storage, in two large sections or categories: environmental impacts and on safety of local character, and global effects that could result from the escape of the stored CO_2 into the atmosphere. A CO_2 storage complex should meet the following criteria of acceptability related to CO_2 Containment (global effects) [35] and HSE risk (local effects):

Containment

1. As a design objective for the containment, it is proposed that the mass of CO_2 retained in the storage complex after 1000 years after the injection period is at least 99% of the total CO_2 injected, that is to say that the maximum allowable leakage of mass of CO_2 in 1000 years is less than 1% of the total CO_2 injected.
2. The annual leakage rate corresponding to this containment level is 0.001%/year, which means a retention period of 100,000 years.

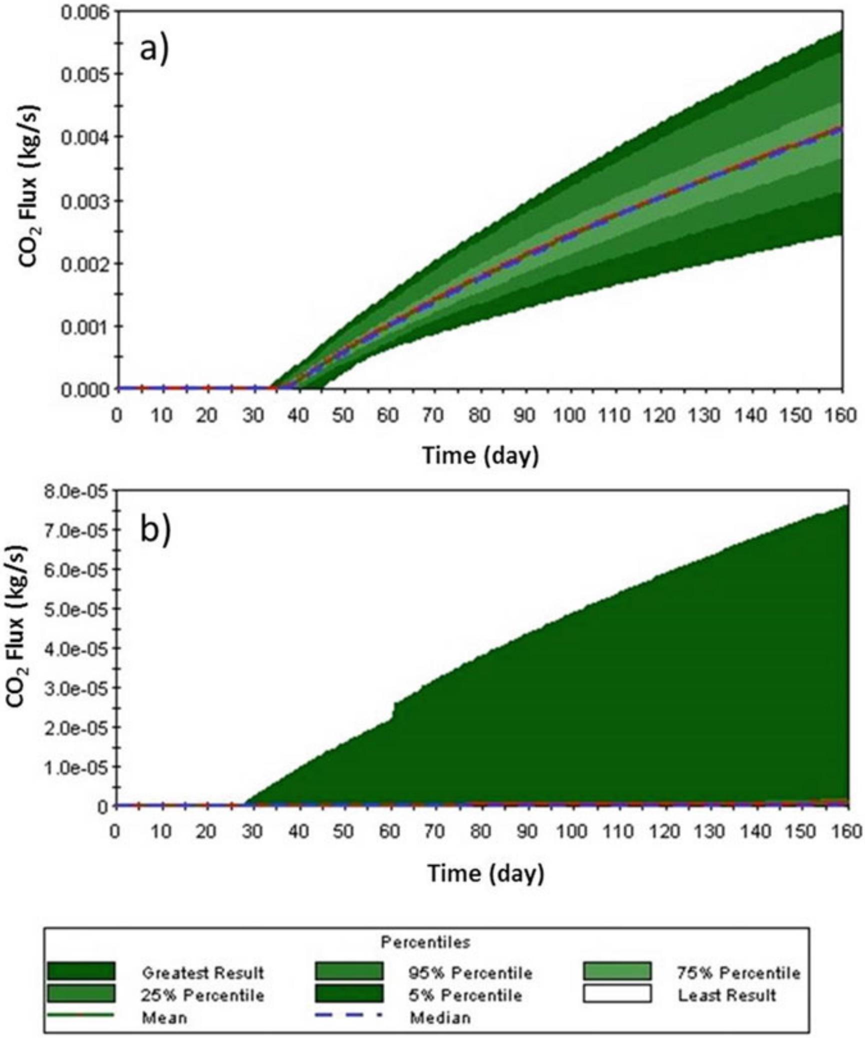


Fig. 8 Probability density functions of CO_2 leakage rates through risk elements: **a** faults; **b** open well

3. The containment is considered to be acceptable if there is a probability greater than or equal to 80% that 99% of the injected mass remains confined in the storage complex during the first 1000 years. That is, a threshold value of leakage risk of 20% of losing the maximum acceptable mass of CO_2.

HSE risk

1. It would be considered unacceptable for the social risk quotient to exceed $1{\cdot}10^{-3}$ deaths/year, by extrapolation of the acceptability criterion for large dams admitted by ANCOLD [36].
2. It would be considered marginally acceptable if that risk quotient was between that value and $1{\cdot}10^{-4}$ deaths/year.
3. Gas-phase CO_2 concentrations in air above the storage complex may not exceed 0.5% or 5000 ppm (Continuous Public Permissible Exposure Limit for 8 h, US Occupational Safety and Health Administration, 1986) or 9150 mg/m^3 according to the Spanish INSHT [37] as a result of the simultaneous action of leakage from storage and the natural emanation of the site determined as a baseline prior to injection.
4. In the shallow soil or subsoil, the concentration of CO_2 must not exceed 5% in air volume and in no case, 20% as a result of CO_2 leakage from the storage complex.
5. The concentration of CO_2 in the dissolved phase in groundwater due to the geological storage of CO_2 should not have an impact on acidification that promotes the mobilization of heavy metals in the aquifers of the underground basin of the site.

Performance criteria are proposed to quantify such functionalities or capabilities, essential for the containment and isolation of CO_2, and to establish the degree of compliance with which the storage complex (storage formation—seal formation) and its subsystems and components must respond to meet the operational requirements. In practice and for regulatory purposes, the performance of a specific geological storage of CO_2 is qualified by **indicators** that assess its degree of acceptability.

4.1 Indicators of Seal Formation Performance

The physical properties of the seal formation that contribute to the isolation of injected fluids under the operating conditions required for storage and on which performance indicators for the storage system can be established are:

Extension and lateral continuity of the seal formation

- It is a necessary condition that the seal geological formation has sufficient extension and lateral continuity to fully cover the area affected by the injection of CO_2 at the moment of the dissipation of the pressure gradients. This area includes both the area occupied by the CO_2 injection and that of the potentially larger area affected by the pressure changes associated with the injection.
- The quantitative criterion of performance to be satisfied is that said area is at least equal to the surface of the maximum extension achievable by the injected CO_2 plume until the dissipation of thermo-hydro-mechanical-chemical (THMQ) gradients.

- In the case of discontinuities, lateral changes of facies, wedges or others, the performance criterion could be satisfied if the discontinuities in a lithological level were in turn sealed by overlapping levels of the confining system of equivalent petrophysical characteristics (porosity and permeability).

Inlet capillary pressure

- The quantitative criterion of performance to be satisfied is that the pressure of the CO_2 column plus the injection pressure is lower than the capillary pressure of the confining system.
- The injection pressure may not exceed a value that may lead to the propagation of fractures in the confining seal formation [38].

Permeability

- The quantitative criterion of performance to be satisfied is that the permeability is less than or equal to that corresponding to lithologies of pelitic fraction (clays, shales or siltstone) measured in mD (milli Darcy), that is, lower than 0.1 mD ($\approx 10^{-12}$ cm^2 of intrinsic permeability, k).

4.2 Indicators of the Storage Formation Performance

The physical properties of the storage formation that contribute to the isolation of the injected fluids under the operating conditions required for storage and on which performance indicators for the storage system can be established are:

Thickness and surface area of the injection area

- Although a minimum thickness cannot be established, given that the injection ratio is directly proportional to the average permeability and thickness, a utility value can be given with respect to the thickness that is defined by $permeability \times thickness \geq 10^{-13}$ m^3 [39].

Porosity

- It is the fundamental factor for the storage capacity of the reservoir. The porosity values are usually in a range between 10 and 30% [40]. An optimal storage rock is one with a total porosity value of more than 20%, but total porosities of 12% are perfectly adequate to contain high amounts of CO_2.

Permeability

- Injectivity is directly proportional to the permeability and inversely to the viscosity of the fluid phase injected. One of the interesting characteristics of CO_2 is its low viscosity with respect to that of water (around an order of magnitude). Due to this, the permeability of the formation does not represent a limiting criterion with respect to the injection of CO_2, since the volumetric injection ratios can be important both in formations with high or low permeability values [41].
- A storage formation with a permeability of "good aquifer" (more than 1 m/day), is not necessarily a good storage rock of CO_2 since it makes the control of injected CO_2 difficult. A good storage rock should have effective permeabilities greater than 10 mD and are optimal permeability values of 300 mD.

Injection pressure

- The injection pressures must be greater than 83 bar [42] and will be limited by the tensional state of the seal formation and the reopening of fractures that affect the storage formation. The reservoirs of hydrocarbons with effective traps have a pore pressure gradient value of less than 17.4 kPa/m, which could be considered initially as a safety criterion for the site.
- The sustained pressure will be lower than the fracture pressure, i.e. the pressure at which fractures can be initiated or propagated in the injection zone [38].
- During the injection the pressure in the injection zone cannot exceed 90% of the fracture pressure of the injection zone [38].

5 Monitoring, Verification and Mitigation Tools

Projects for the geological storage of CO_2 should include technical guides for monitoring, verification and accounting of CO_2 stored in geological formations in order to help ensure safe, effective and permanent CGS in the appropriate reservoirs [43]. Monitoring techniques can be applied in atmosphere, near-surface and subsurface to ensure that injected CO_2 remains in the storage formation and that both CO_2 injection process and pre-existing wells do not jeopardized the CO_2 storage complex.

The most usual atmospheric monitoring techniques are optical CO_2 sensors, atmospheric tracers, and eddy covariance flux measurements. On the other hand, near-surface monitoring methods are used to detect potential CO_2 leakages from a CO_2 storage complex, including geochemical monitoring both in the soil and vadose zone and in the near-surface groundwater, surface displacement monitoring, and ecosystem stress monitoring. Furthermore, subsurface monitoring of a CGS project covers a wide range of techniques for monitoring the spread of the CO_2 plume, assessing the area of high pressures caused by the CO_2 injection, and determining that the CO_2 plume is migrating into zones that do not damage resources or jeopardize the integrity of the reservoir [43]. Besides this, the plume of CO_2 should be monitored continuously within the reservoir to ensure that freshwater aquifers and ecosystems are well protected.

Monitoring, verification and accounting plans are necessarily related to risk analysis and subsequent mitigation measures. The expected range values of the different parameters associated with the performance of a CGS can be predicted by monitoring, which supposes an important step forward to an appropriate safety and risk analysis. At the same time, risk analysis allows the identification of the most important elements affecting the behavior of the CO_2 storage system. The visualization of these elements is of great interest in order to avoid mitigation or corrective measures. Consequently, it has to be analyzed the possible leakage pathways that threat the safety of the CO_2 storage facility, also considering the existing and novel mitigation tools and/or remediation measures in case of CO_2 escapes from a CGS. These techniques can be applied whenever the performance of the CO_2 storage system is not as the originally expected. Mitigation methodologies and mitigations tools are dealt with in Sect. 5.2.

5.1 Methodology for the Measurement of CO_2 Leakages and Dissolved and Free Associated Gases

One of the most important aspects concerning the performance assessment of a CGS is to increase the knowledge of the interaction between CO_2 and the storage and sealing formations, as well as the physico-mechanical resistance of the cap rock. Measurements to be carried out in a CGS constitute important tools to evaluate the capacity of the sealing formation or cap rock to retain CO_2, as well as dissolved and free associated gases. Consequently, CO_2 leakages and associated gases either dissolved or free, could indicate that the integrity of the CGS is jeopardized. For this reason, monitoring of these gases through their measurement should be carried out periodically in order to assess: (i) the performance of the CO_2 storage system; (ii) the capacity of the sealing formation to retain these gases; and (iii) the possible impacts of these gases released on the environment and people.

These measurements mainly include CO_2, either dissolved or free, diffuse soil CO_2 flux and CO_2 contents in soils (~1 m depth). Nevertheless, among the dissolved and free gases the concentration of N_2, O_2, Ar, CH_4, Ne, He, H_2 and ^{222}Rn could be also determined. If possible, it is also advisable to determine the concentration of ^{222}Rn in soils (~1 m depth) since this radioactive gas has frequently been used for the detection of fracture/fault systems that constitute potential pathways for gas leakages [44, 45]. Recently, ^{222}Rn determinations have been also used for monitoring the migration of CO_2 from a CGS, since CO_2 acts as a carrier gas for ^{222}Rn in a regime of advective transport and, consequently, CO_2 escapes from deep-seated sources may carry significant amounts of ^{222}Rn [46–49]. Therefore the determination of ^{222}Rn can also be indicative, in an indirect way, of the CO_2 escapes from a CO_2 storage system.

5.1.1 Methods of Sampling and Analysis of Dissolved Gases

The methods for determining the composition of dissolved gases (CO_2, N_2, O_2, Ar, CH_4, Ne, He, H_2) are generally conducted following two different criteria: (i) the total extraction; and (ii) the partial extraction. The method based on the first criterion [50] uses mechanical pumps and it is rarely used since it is complex and long sampling times are required. Furthermore, the total extraction of gases is not verified.

The partial extraction process generally involves the use of an inert gas (Ar, He, N_2) as carrier [51–53]. The carrier gas is introduced into the sample holder containing the liquid (Fig. 9a) therefore causing the partial extraction of the dissolved gases. This method, although it is characterized by its speed of execution and the availability of the materials, has the following disadvantages: (i) the concentration of the carrier gas cannot be determined; (ii) the injection of the carrier gas is complex and involves a high risk of contamination of the water sample; and (iii) the quantity of the gas extracted is generally low due to the dominant presence of the carrier gas. Consequently, these drawbacks limit the applicability of this method, often restricted to the determination of few species [54].

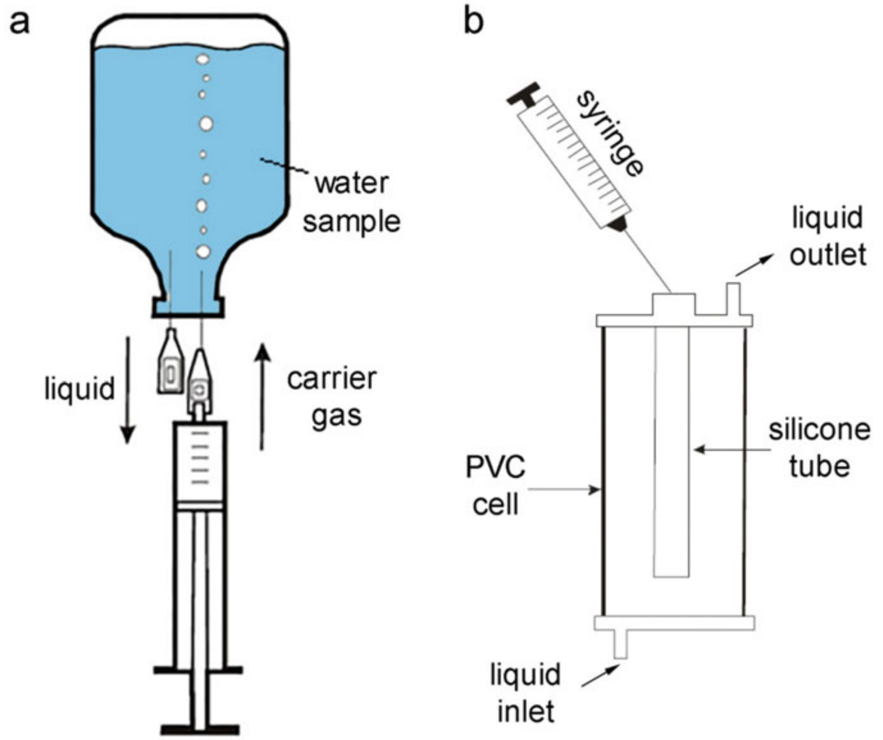


Fig. 9 Systems used for the extraction of dissolved gases: **a** by introducing a carrier gas, **b** through a permeable membrane ([54] modified)

Another method for the extraction of dissolved gases is by means of a silicone tube located inside a PVC cell, in which a constant flow of the liquid is maintained in order to extract the volatile compounds (Fig. 9b) [55, 56]. Nevertheless, this technique is difficult to use directly in the sampling site since it requires large amounts of sample. Furthermore, the permeation process through the silicone tube can cause fractionation of the gases, consequently modifying their original composition [54].

In addition to the abovementioned methods, dissolved gases can also be sampled by means of: (i) Niskin bottles, which are appropriate to collect water samples within the water column at different depths; (ii) the glass syringe method; and (iii) the direct immersion of vials of ~200–300 mL in which the vacuum (10^{-1}–10^{-2} Pa) is previously formed [54].

Sampling and analysis for ^{222}Rn dissolved is different with respect to the previous methods since samples are collected in low diffusion vials and filled up to the half with the so-called "scintillation cocktail". Spectra of ^{222}Rn and its descendants allow calculating the concentration of ^{222}Rn, expressed in Bq/L, as well as its uncertainty. Finally, the concentration of ^{222}Rn at the time of sampling was obtained considering its half-life (3.8 days). The wide popularity of liquid scintillation counting (LSC) is a consequence of numerous advantages, which are high efficiencies of detection, improvements in sample preparation techniques, automation including computer data processing, and the spectrometer capability of liquid scintillation analyzers permitting the simultaneous assay of different radionuclides. However, the main drawback of LSC is one of sensitivity.

5.1.2 Methods of Sampling and Analysis of Free Gases

The method used for sampling free gases is different depending if water sample shows or not bubbling. For the first case, the method basically consists of covering the wellhead with a latex bag (e.g. swimming cap) and then waiting for a "gas bag" (Fig. 10a). The gas is subsequently extracted (Fig. 10b) and, finally, it is injected into a vial previously filled with distilled water and punctured with a double-wall entry needles (Fig. 10c). The gas injection displaces the water through the aforementioned needle, accumulating this gas inside the vial. This method is quick, economic and easy to apply, although it is conditioned to the presence of bubbling waters.

For the second case, when no bubbling waters appear, it has to be firstly checked the presence of CO_2 by means of a portable CO_2 IR detector either at the wellhead or at depth. Once CO_2 is detected, the method consists of pumping this gas through a membrane pump through a tube, which has to be located at the depth in which the gas is detected. The output of the pump is connected to another tube, which in turn is attached to a hypodermic needle (Fig. 11). The gas transfer to the vial is performed following the same abovementioned method. This method is slower and more expensive compared to the previous one. Although can be tedious in operation, it has the main advantage that it can be applied in most of the wells.

Chemical determination of free gases can be carried out by means of a gas chromatograph coupled to a DSQ quadrupole mass spectrometer.

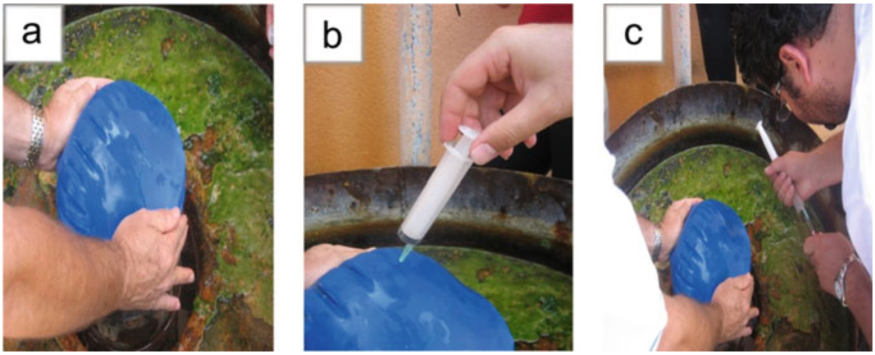
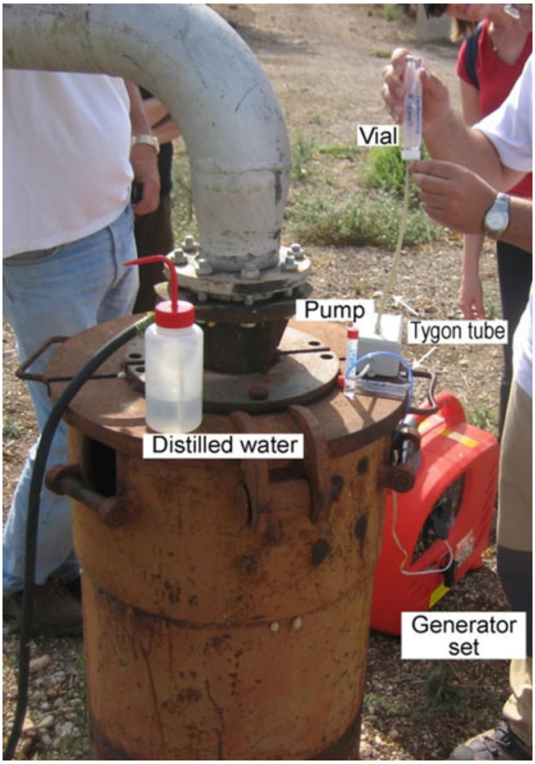


Fig. 10 **a** Latex bag used to retain gases in the wellhead for bubbling waters. **b** Plastic syringe with a hypodermic needle attached to extract the gas. **c** Injection of the gas into the vial filled with distilled water

Fig. 11 Example of a free gas sampling in a non-artesian well, once CO_2 was previously detected



5.1.3 Methods of Sampling and Analysis of Surficial CO_2 Flux

In relation to surficial CO_2 flux, measurements should be performed under favorable weather conditions, particularly during dry and meteorologically stable periods, in order to avoid the possible influence of rainfalls and the subsequent soil humidity. Since CO_2 is relatively soluble in water, environmental conditions are very important since they considerably affect their corresponding values.

Diffuse CO_2 flux was measured through the accumulation chamber method [57–63], which was originally used for agriculture purposes [59–62]. However, this method has extended its applications in the last two decades, including the measurements of CO_2 degassing in volcanic and geothermal environments [64–70] and for monitoring emissions from landfills [71, 72] being the main advantages its sensitivity, low cost, simple operability and high-speed data acquisition. On the contrary, the main drawbacks of this method is that diffuse CO_2 flux measurements can be affected by different factors, such as the variability of the surficial parameters (porosity, permeability), biological respiration, meteorological parameters (temperature, atmospheric pressure, wind speed), etc.

The material used for the diffuse CO_2 flux measurements includes: (i) an inverted chamber, with known dimensions, composed by a device that mixes the air in the chamber headspace; (ii) an Infra-Red (IR) spectrophotometer; (iii) an Analogical–Digital (AD) converter; and (iv) a Palmtop Computer (PC) (Fig. 12). To perform these measurements, the accumulation chamber is placed above the soil surface, allowing the CO_2 accumulation. Then, the gas is pumped towards the CO_2 IR detector with a flow rate of ~20 mL s^{-1}. Later, the gas is returned to the camera, therefore minimizing the disturbances of the gas naturally released from soil. Finally, the signal emitted by the IR is transmitted by the AD to the PC. In order to convert the volumetric

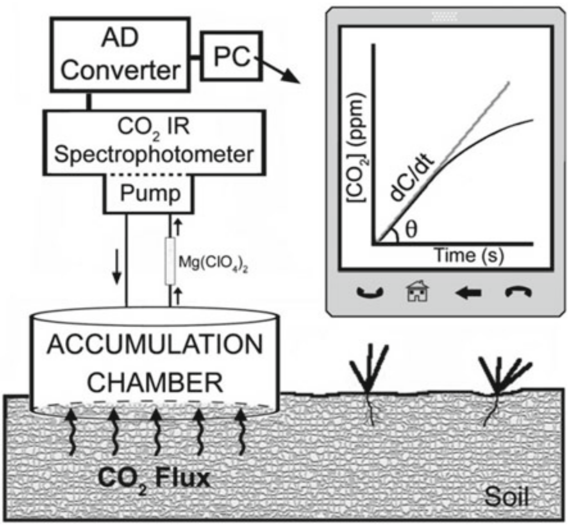


Fig. 12 Schematic representation of the accumulation chamber method used for the diffuse soil CO_2 flux measurements [48]

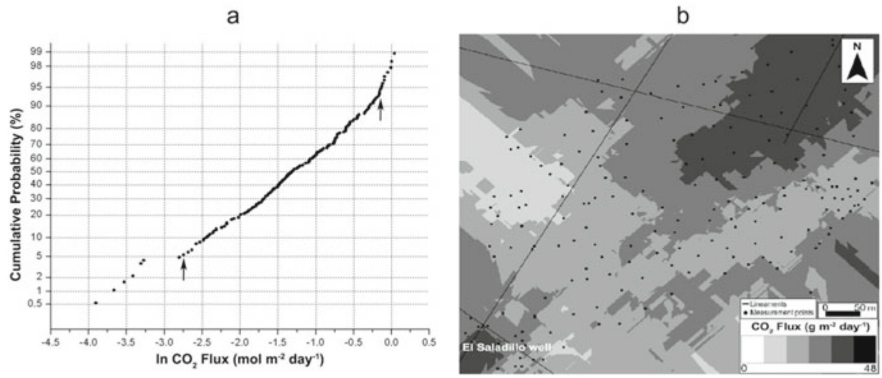


Fig. 13 **a** Cumulative probability plot corresponding to ln CO_2 flux showing the existence of three populations by means of the two inflection points, identified by arrows. **b** Mapping of the surficial distribution of the diffuse soil CO_2 flux by means of kriging estimation. Both examples are from the El Saladillo site (Murcia, SE Spain) [48]

concentration obtained (ppm s^{-1}) into mass concentration units (g m^{-2} day^{-1} or mol m^{-2} day^{-1}), it has to be considered the temperature, pressure and the volume of the chamber [73].

Computation of the total CO_2 flux is performed according to Sinclair [74] method, which is a graphical procedure usually used for geochemical data consisting of grouping the CO_2 values in different log-normal populations by considering the inflection points. Consequently, this method uses probability graphs, being a single log-normal population represented by a straight line, whilst a curve with $n - 1$ inflection points shows the theoretical distribution of n overlapped log-normal populations (Fig. 13a). Therefore, different populations from a data set can be recognized by using this method. The parameters needed to determine the total CO_2 flux of each population are calculated by using the Sichel [75] method, including the estimated percentage of each observed population, the flux mean value and the corresponding standard deviation. The total CO_2 output for each population is calculated by multiplying the site area, the ratio of each population and the mean CO_2 flux value. The 95% confidence interval was also calculated by using the Sichel's t-estimator [75]. By adding the sum of each individual population, it can be obtained the total CO_2 released to the surface. Besides this, these data can also be processed by means of kriging estimation and sequential Gaussian simulation methods [76], in order to map the spatial distribution of the CO_2 flux (Fig. 13b).

5.1.4 Methods of Sampling and Analysis of CO_2 and ^{222}Rn in Soils

Similarly to surficial CO_2 flux, CO_2 and ^{222}Rn concentration (~1 m depth) should be measured during dry and meteorologically stable periods, since these gases are relatively soluble in water and consequently their concentrations could be modified.

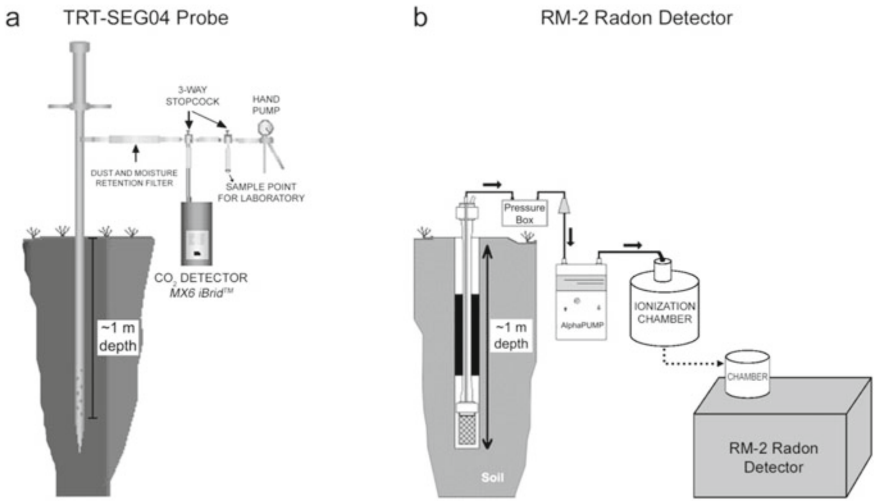


Fig. 14 **a** TRT-SEG04 probe for CO_2 concentration measurements. **b** RM-2 radon detector for determining ^{222}Rn concentration [49]

For CO_2 measurements, a probe for extracting soil gases is used, pumping the soil gases to a CO_2 detector. If necessary, a hand pump can be additionally coupled to extract the gases (Fig. 14a). For ^{222}Rn concentration, a Radon detector is used, being composed of an air suction pump coupled to ionization chambers equipped with a counter-photomultiplier device (Fig. 14b). The main advantages of both methods are their simplicity and that they are designed for in situ rapid analysis of CO_2 and ^{222}Rn, while the most important drawback is that measurements can be affected by the physical characteristics of the soil, especially porosity and moisture content, because they affect the gas transport in the soil.

In addition, it is essential to compile a base map of the emissions of free gases before the CO_2 injection, which can be used as a reference to compare it to others that will be carry out after the CO_2 injection at the site selected for CO_2 storage. An increase in the concentration of both gases in soils could be indicative of failures in the cap rock of the CGS. Therefore, the main objective is the detection, sampling, measurement and characterization of dissolved and free gases of the site selected, in order to determine variations in the concentrations once the anthropogenic CO_2 has been injected. The isotopic signature of the CO_2 detected in surface, either as dissolved inorganic carbon (DIC) or as a free gas, can serve as a tracer of the CO_2 stored.

5.1.5 Isotopes

The isotopic characterization of the dissolved and free gases is useful to determine their origin. Particularly, the isotopic values of C are used to determine the source

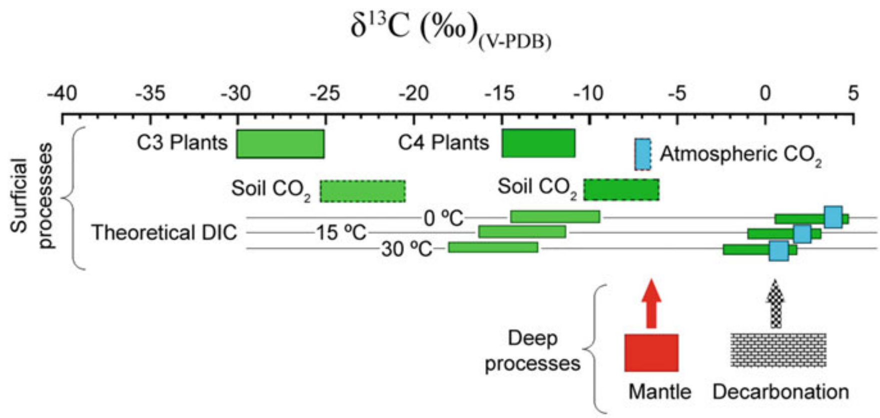


Fig. 15 Representation of the theoretical $\delta^{13}C$ values from the possible carbon sources, which include: (i) surficial processes: C3 plants [79], C4 plants [80], and atmospheric CO_2 [81]; and (ii) deep processes (inorganic C): mantle [82] and decarbonation [83]. CO_2 in the soil is about 4.5‰ heavier than the plant biomass [84, 85]. The isotopic difference between CO_2 and DIC depends on both pH and temperature. This value is close to 0‰ at about pH 5, but is relatively independent of pH between 7.5 and 8 [86]. For the theoretical DIC calculation, the calcite-CO_2 equation described by Romanek et al. [86] for temperatures of 0, 15 and 30 °C has been considered (figure modified after [87])

of CO_2 and therefore can represent an excellent tracer for CO_2 [77] considering the very negative $\delta^{13}C$-CO_2 values (~−30‰) related to the fossil fuel combustion [78]. In order to establish the possible carbon sources, the theoretical $\delta^{13}C$ values for the main carbon reservoirs can be plotted (Fig. 15), by including: (i) surficial processes: C3 plants [79], C4 plants [80], and atmospheric CO_2 [81]; and (ii) deep processes (inorganic C): mantle [82] and decarbonation [83].

In addition to $\delta^{13}C$, there are several isotopes than can be used to support the origin of gases. Among them, it can be highlighted the isotopes of noble gases, particularly He and Ne, which are typical trace gases of natural CO_2 reservoirs that can be used to differentiate inorganic sources.

Helium is highly diffusive with a diffusion coefficient about ten times that of CO_2 [88] also being physically stable, chemically inert and non-biogenic. Moreover, the $^3He/^4He$ ratio can be used to trace the presence of mantle magmas and deep gases, so it is frequently applied to distinguish between mantle and cortical sources, since mantelic CO_2 tends to be ^3He-enriched [89]. The ratio R/Ra (where R is the measured $^3He/^4He$ ratio and Ra is that of the air, i.e. 1.39E−06) can be as low as 0.0001 in the crust due to the radioactivity of U and Th and the formation of α particles (^4He), although this ratio is usually around 0.02 from crustal fluids [90–92]. Nevertheless, R/Ra ratio can take different range values in other geodynamic environments, such as: ~8 ± 1 in the Mid-Ocean Ridge Basalt (MORB) coming from the upper mantle [93–96]; ~10–30 in the Ocean Island Basalt (OIB) indicating a helium degassing source from the lower mantle [97, 98]; and ~5–8, related to subduction zones [90]. On the other hand, Neon is a light and very inert atmospheric gas with a $^4He/^{20}Ne$ ratio of 0.318 in air and 0.274 in waters [99]. Nevertheless, this ratio is $1{\cdot}10^7$ for cortical fluids and 1000 for mantle fluids [90]. Consequently, relatively low values of the $^4He/^{20}Ne$ ratio indicate that the sample has an important atmospheric contribution.

Finally, $\delta^{15}N$ values are widely applied to trace volatile sources in hydrothermal or volcanic systems. For this reason, they are usually used to investigate mantle geochemistry and global volatile cycles. According to the origin of the sample, this nitrogen isotope can take different values: (i) 0‰, related to the atmosphere; (ii) -5 ± 2‰, which is assigned to the upper mantle; and (iii) 0–10‰, derived from subduction zones sediments [100, 101].

All these stable isotope ratio analysis can be determined by using a mass spectrometer, being very convenient to follow the referencing strategies and techniques described by Werner and Brand [102].

5.2 Mitigation Tools

It is well known the existence of a wide variety of methods for mitigating and/or correcting the possible effects of CO_2 leakages from a CGS. It has also been demonstrated that the mitigation or correction techniques are more effective close to the source of the CO_2 escape rather than near the surface, where the detection of CO_2 is more difficult since it tends to be dispersed.

Undesired CO_2 leakages could occur within or out of the reservoir via faults/fractures or along the wellbore, being three the main causes of the loos of the safe behavior of the CO_2 storage complex [103]: (i) the loss of the reservoir's integrity; (ii) the existence of fractures and/or faults that could constitute possible pathways for CO_2 leakages; and (iii) the loss of the well integrity. These causes, as well as their possible mitigation/correction measures, are discussed in detail in the following sections. Firstly, it should be remembered that the application of these measures is the last option to consider since an adequate previous planning, including monitoring and risk assessment, could avoid carrying out these unexpected measures.

5.2.1 Loss of the Reservoir's Integrity

The loss of the reservoir's integrity can be mainly due to the following different reasons: (i) a discontinuity or compartmentalization of the geological storage formation, therefore leading to a significant increase of the pressure in the injection well; (ii) an unexpected fluid flow within the reservoir, e.g. the spread of the CO_2 plume beyond the desired region, such as a fault/fracture zone or discharge point, or the migration of the CO_2 plume through the cap rock; and (iii) the creation or reactivation of faults and/or fractures in the reservoir, or in the cap rock, caused by stress changes during CO_2 injection [104–107], since the stress path has a deep effect on stress dynamics and fracturing/faulting when injecting into a depleted reservoir [105].

Corrective measures, basically based on pressure, can be applied within the CO_2 reservoir [103, 108]. These measures include: (i) the permeability reduction by injecting gels/foams or by immobilizing the CO_2 through solid reaction products [109]; (ii) the change of injection strategy, which can potentially prevent or retard CO_2 from arriving at undesired migration pathways (faults, fracture zones or discharge points) and could also represent an efficient measure compared to active remediation from an economic point of view; and (iii) the localized injection of brine, hence creating a competitive fluid movement.

The methods aimed to reduce the permeability of CO_2 storage reservoirs by using the polymer-gel injection are conditioned by different parameters such as polymer type, molecular weight, polymer concentration, crosslinker concentration, ratio of polymer-to-crosslinker and temperature [108].

Fluid movement within a CO_2 reservoir is based not only on reservoir properties (structural dip or spatial heterogeneity in permeability and/or porosity) but also it can be managed by distributing the reservoir pressure. In this sense, CO_2 migration can also be managed by either brine extraction or CO_2 backproduction [110]. In any case, these both measures create pressure gradients towards the extraction point, consequently enforcing a specific flow direction [103].

5.2.2 Existence of Fractures and/or Faults

The possibility of reducing or disrupting CO_2 leakages through faults and/or fractures has been considered by assessing the efficacy of reducing pressure to lower the leakage rate or by using sealants (e.g. gels or foams) to interrupt the escape. In addition, other possibilities have been tested, like transferring CO_2 through a fault in a compartment originally unconnected to the main reservoir, improving the sealing capacity of the cap rock by injecting N_2 before or during CO_2 injection [111]; or by generating a flow barrier above the cap rock by creating a reverse pressure gradient.

Remediation of CO_2 leakages by CO_2 flow diversion

The principle of remediation of CO_2 leakages by CO_2 flow diversion towards close compartments from the CO_2 storage reservoir through hydraulic fractures or deviated wells (Figs. 16 and 17) requires the creation of a pathway for fluid migration between the CO_2 storage reservoir and the leaky and neighboring compartments, since the CO_2 reservoir and neighboring compartments are originally not connected (see Fig. 17). In this sense, compartmentalized saline aquifers or gas reservoirs represent geological settings potentially suitable for remediation by flow diversion.

In the case of relevant CO_2 leakages from a CGS, pressure relief can be achieved by diverting CO_2 from the CO_2 storage complex to non-connected parts of the reservoir, or to adjacent aquifers and/or reservoirs. This fluid migration can be performed by hydraulic fracturing (fracking) across a sealing fault that separates adjacent compartments, or also by drilling a well. The effects of flow diversion as a remediation option were evaluated from a real field case in the North Sea, concluding that this flow is a possible remediation option for specific depleted gas fields or saline aquifers, being

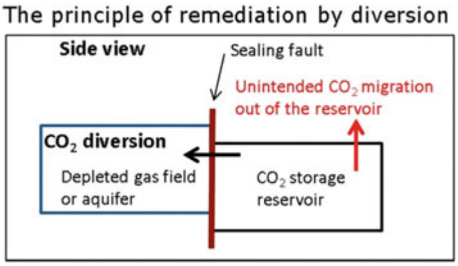


Fig. 16 The principle of remediation of CO_2 leakages by flow deviation from the CO_2 storage reservoir to the adjacent unconnected reservoir. Hydraulic connection between the two reservoirs separated by a sealing fault could be achieved by drilling a deviated well or by creating hydraulic fractures through the fault seal ([112] modified)

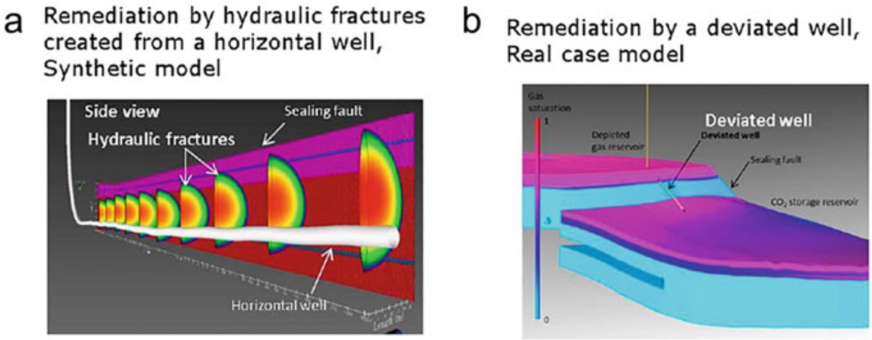


Fig. 17 **a** Breaching of fault seal by hydraulic fracturing, **b** or by drilling a deviated well. These two methods enables lateral migration of fluids between the two adjacent reservoirs separated by a sealing fault [112]

two the key factors controlling the efficiency of flow diversion: (i) the conductivity and the pressure difference between the two reservoirs; and (ii) the permeability of the receiving reservoir. This type of remediation in a saline aquifer is relatively slow compared to an adjacent depleted gas field, due to the small pressure difference between the two compartments [113].

Fault sealants

The oil and gas (O&G) industry generally uses different techniques to reduce the flow rate of a given fluid or to maximize oil or gas recovery by injecting fluids with specific properties. Some of these methods should be appropriately selected or adapted for reducing or interrupting CO_2 escapes through fractures and/or faults, such as the injection of polymer-gel in order to seal the fault, consequently diverting the flow within the reservoir [114].

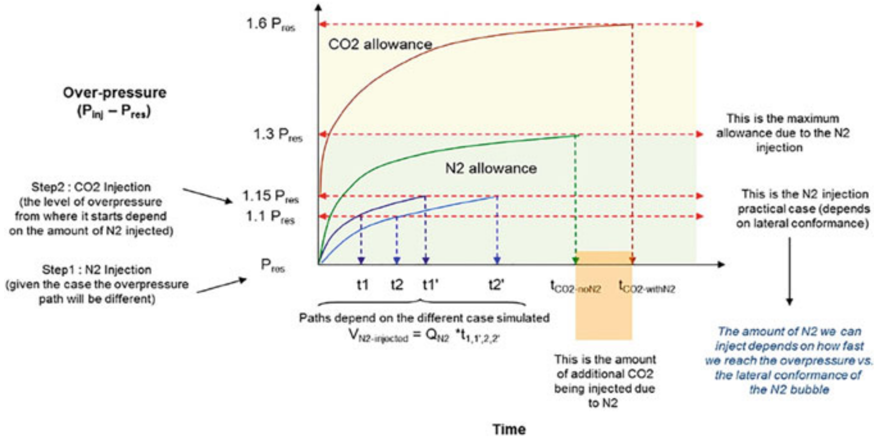


Fig. 18 Conceptual design of a N_2 injection previously to the injection of CO_2 [111]

Barriers

The use of barriers is mainly focused on: (i) checking a mitigation way to prevent CO_2 leakages by injecting N_2 in the cap rock; and (ii) testing a hydraulic barrier after CO_2 leakage by injecting water in a permeable layer above the cap rock.

Regarding the first use, current CGS projects in deep saline aquifers are naturally limited, among other parameters, by entry pressures encountered in cap rocks, consequently limiting over-pressures allowed during the storage process. The injection of N_2 just below the sealing formation, previously to the injection of CO_2, could be a protective measure to increase the storage safety by lowering the leakage risk and by increasing the maximum allowable reservoir pressure [111]. The concept governing the injection of N_2 is summarized in Fig. 18.

The concept of the beneficial impact of the injection of N_2 on the cap rock, consequently increasing the pressure, is based on the higher N_2–brine interfacial tension (IFT) compared to the CO_2–brine IFT. As a maximum possible effect (i.e. pure N_2-brine systems) IFT could increase by two times, yielding correspondingly to the same increase of allowable pressure. Nevertheless, the main disadvantage is that N_2 injection decreases the CO_2 storage capacity and the trade-off must be analyzed carefully, since the IFT spread decreases rapidly with the mixing ratio of CO_2 in the N_2 [111].

As regards the second use, this corrective measure aims at countering the main driving force of the CO_2 upwards migration which is the pressure build-up under the leak by injecting brine into the shallower aquifer, thus creating a hydraulic barrier [115]. This remediation technique, which can be applied at low cost but is only temporary, will decrease the CO_2 leakage rate occurring across the cap rock.

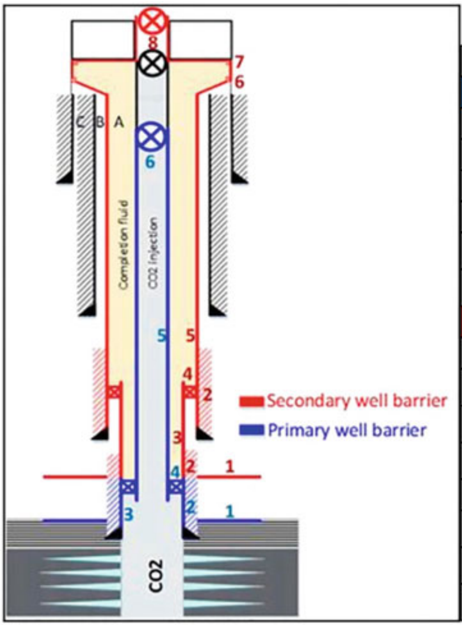
5.2.3 Loss of Well Integrity

Measures aimed to mitigate or correct the loss of well integrity in case of CO_2 escapes are well documented and, consequently, can be consulted at the best-practice recommendations from the O&G industry, which has a great experience in this field. Therefore, this best-practice portfolio of remediation technologies can also be applicable to CO_2 injection wells. Furthermore, new developments and emerging technologies should also be considered, including gels, smart cement and polymer resins.

Oil and Gas best practices

Experience from O&G industry has revealed that wells constitute the highest risk of CO_2 leakages from a CGS [116] being mainly caused by the failure of the barrier elements. Carbon dioxide leakages mainly occur due to the poorly cemented casing, casing failure and/or improper abandonment [117].

From the best-practice recommendations of the O&G industry, a generic and systematic approach has been used to discuss the most critical well barrier elements, only considering one type of well and a typical CO_2 injection well equipped with primary and secondary well barrier elements (Fig. 19). The best analogue for a CO_2 injection well in an O&G setting has been employed for this analysis, which could be considered as an operating gas well with high CO_2 contents and high gas/oil ratio. The basic well design for both O&G and CO_2 wells is almost identical except for the materials used, which are more critical for CO_2 [112].



No.	Well barrier component
PRIMARY WELL BARRIER	
1	In-situ formation (impermeable and moveable)
2	Liner cement (below production packer)
3	Liner tubular (below production packer)
4	Production packer
5	Completion string (tubing, components)
6	Downhole safety valve (including control line)
SECONDARY WELL BARRIER	
1	In-situ formation (impermeable and moveable)
2	Casing cement (above production packer)
3	Production liner (above production packer)
4	Production liner packer
5	Production casing
6	Casing hanger seal
7	Tubing hanger seal (neck seal)
8	Wellhead / surface tree

Fig. 19 Well barrier elements for a typical CO_2 injection well [112]

The occurrence of CO_2 leakages means that both primary and secondary barrier components of the CO_2 injection well fail simultaneously. Early escape events are mainly often related to: (i) an inaccurate well design; (ii) an incorrect material selection; and (iii) a wrong installation of the well barrier elements. However, late leakages are frequently associated with: (i) corrosion and/or erosion of materials; and (ii) degradation and/or fatigue of materials. Finally, failures or defects in the well barrier elements are linked to common mitigation and remediation techniques generally used in the O&G industry. Since these practices can be complex and expensive, it is advisable to perform some preventive actions in order to reduce the risk of failures [112].

Novel materials and emerging technologies

New developments and breakthrough technologies for mitigation and remediation of CO_2 leakages from wells are being tested nowadays. The objective is to inject a solution in the surroundings of a well in a selected depth interval (usually a few meters) in order to seal the near well bore formation, therefore reducing porosity and permeability ideally down to zero and not allowing CO_2 to flow at that depth. Consequently, the porosity should be filled with a solid, being this solid the result of the precipitation of some components of the injected solution [118]. Although there is a wide variety of methods that can be used to treat the surroundings of a well [119] there are new emerging processes that are promising, such as the use of: (i) CO_2 reactive suspensions; (ii) polymer-based gels; (iii) smart cements with a latex-based component [120]; and (iv) polymer resin for squeezing.

CO_2 reactive suspensions have been studied for reducing the permeability in the near-well region, highlighting those suspensions that use silicate based solutions since they have high performance, long term chemical stability, good injectivity (low viscosity and no particles) and no or little environmental impact [118].

The use of smart cements with a latex-based component is focused on the self-sealing under high pressure and temperature conditions when they are exposed to CO_2. These cements have demonstrated to be effective in reducing their permeability either through the casing-cement or cement-rock interfaces, or through the fractures within the cement itself [120].

The sealing ability of a commercially available temperature-activated polymer resin with respect to cement failure at laboratory scale was proved to be fairly successful in plugging the designed leak paths for the two selected leakage scenarios: cement-casing debonding and fractures in annular cement. The results showed that the permeability and the average fracture thickness were significantly reduced after the treatment with this resin [121].

Finally, once the mitigation and corrective measures have been exposed, it is essential to always keep in mind that the application of these measures represents the last possibility to avoid CO_2 leakages. For this reason, an appropriate previous planning, including monitoring and risk analysis, is very important and useful in order to not carry out these undesirable measures that reveal the failure of a CGS.

6 Concluding Remarks

The proposed methodology assumes an approach to the problems of risk analysis derived from CGS activities. The development of models based on BN for the description of these systems is not an easy task. However, although very sophisticated methods are actually applied, it is an attractive tool because it allows the possibility of making decisions under conditions of uncertainty together with the fact of being a natural way of making connections between the different elements and the simplicity of its maintenance. Furthermore, the proposed methodology, given its conceptual development, allows realizing mathematical analyzes (zones of maximum and minimum variation, zones of stability, etc.), sensitivity analysis to determine both the variables that contribute the most uncertainties to the system as well as the different conceptual models, which are fundamental for the treatment of system uncertainties, etc., all of which are basic activities in the analysis of risks of any CGS project.

From the development of the proposed methodology and its application to a study area, it can be concluded that it allows evaluating the probability of risk of leakage probability from an area with potential capabilities as a CGS site, solely from qualitative-type of data. From the comparison of the proposed methodology with the methodology of recognized prestige called Selection and Classification of Formations it can be concluded that they coincide in the qualification of the area. Both evaluations have a qualitative character. However, although the route of the Selection and Classification of Formations methodology ends at this point, for the proposed methodology it means the starting point, since, starting from the relationships already established between the different variables, it will gradually progress to quantitative modeling.

The BN formalism allows generating a Risk Analysis process in which progressively and without a solution of continuity, it would pass from being based on modeling of a pure qualitative type, to Risk Analysis based on qualitative-quantitative mix of modelling to, finally, attain a RA based on pure quantitative modeling. This would allow to embrace the CGS project as a whole, through a continuous RA process, from the initial stages, characterized by a shortage of available information, thanks to the adoption of a subjective perspective of the probability concept, and to the application of EJ. Undoubtedly, these initial analyses will not be without biases and heuristics. However, this initial problem would be progressively overcome based on the advance in the available information and the generation of modeling based on physical/chemical-mathematical models that would be gradually replace the qualitative estimates based on EJ [122–124].

Furthermore, this RA should help identify not only potential locations for CGS sites, but also approximations for enhanced measurement, monitoring and verification activities. Monitoring is an essential part of the entire risk management for CGS, as well as the remediation measures to be applied in case of unexpected events that can compromise the safety of a geological storage of CO_2.

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Glossary

BN Bayesian Networks
CCS Carbon Capture and Storage
CGS CO_2 geological storage
DIC Dissolved inorganic carbon
EJ Expert Judgment
FEP Features, Events and Processes
FMEA Failure Mode and Effect Analysis
HSE Health, Safety and the Environment
IFT Interfacial tension
IR Infra-Red
KPI Key Performance Indicators
LSC Liquid scintillation counting
MCA Multi-Criteria Assessment
MORB Mid-Ocean Ridge Basalt
OIB Ocean Island Basalt
RM Risk management
SRF Screening and Ranking Framework
SWIFT Structured "What-If" Techniques
THMQ Thermo-hydro-mechanical-chemical
VEF Vulnerability Evaluation Framework

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