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How underground systems can contribute to meet the challenges of energy transition

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The paper provides an overview of the several scientific and technical issues and challenges to be addressed for underground storage of carbon dioxide, hydrogen and mixtures of hydrogen and natural gas. The experience gained on underground energy systems and materials is complemented by new competences to adequately respond to the new needs raised by transition from fossil fuels to renewables. The experimental characterization and modeling of geological formations (including geochemical and microbiological issues), fluids and fluid-flow behavior and mutual interactions of all the systems components at the thermodynamic conditions typical of underground systems as well as the assessment and monitoring of safety conditions of surface facilities and infrastructures require a deeply integrated teamwork and fit-for-purpose laboratories to support theoretical research. The group dealing with large-scale underground energy storage systems of Politecnico di Torino has joined forces with the researchers of the Center for Sustainable Future Technologies of the Italian Institute of Technology, also based in Torino, to meet these new challenges of the energy transition era, and evidence of the ongoing investigations is provided in this paper.

Keywords: *hydrogen, underground storage, energy transition, well testing, reservoir modeling, microfluidics, offshore facilities, monitoring, biochemistry.*

Il contributo dei sistemi sotterranei alle sfide della transizione energetica. *L'articolo fornisce una panoramica dei numerosi aspetti tecnici e scientifici e delle sfide che devono essere affrontate per effettuare lo stoccaggio sotterraneo di anidride carbonica, idrogeno e miscele di idrogeno e gas naturale. L'esperienza acquisita sui sistemi energetici sotterranei e sui materiali viene integrata con nuove competenze per rispondere adeguatamente alle necessità connesse alla transizione dai combustibili fossili alle fonti rinnovabili. La caratterizzazione sperimentale e la modellizzazione delle formazioni geologiche (inclusi gli aspetti geochimici e microbiologici), il comportamento dei fluidi e del flusso e le reciproche interazioni tra tutti i componenti del sistema alle condizioni termodinamiche tipiche degli stoccaggi sotterranei nonché la valutazione e il monitoraggio delle condizioni di sicurezza degli impianti e delle infrastrutture di superficie richiedono una squadra di lavoro profondamente integrata e laboratori dedicati per supportare la ricerca teorica. Il gruppo del Politecnico di Torino che si occupa di sistemi di stoccaggio di energia a larga scala ha messo a sistema le sue competenze con quelle dei ricercatori del Center for Sustainable Future Technologies dell'Istituto Italiano di Tecnologia, sempre con sede a Torino, per rispondere a queste nuove sfide della transizione energetica. Nell'articolo viene fornita evidenza delle attività di ricerca attualmente in corso.*

Parole chiave: *Idrogeno, stoccaggio sotterraneo, transizione energetica, prove di pozzo, modellistica di giacimento, microfluidica, piattaforme offshore, monitoraggio, biochimica.*

1. Introduction

According to the 2030 climate & energy framework defined in the Paris Agreement (https://ec.europa.eu/clima/policies/strategies/2030_en), the key targets for 2030 are to cut **greenhouse gas emissions** by at least 40% compared to the 1990 levels and to achieve at least a 32% share of renewable energy and at least a 32.5% improvement in energy efficiency.

Renewable sources are considered key to decarbonize energy systems and reduce dependency on fossil fuels, as stated by the Mission Innovation Program (http://mission-innovation.net/). However, despite the availability of solar energy and wind power, technologies relying on these sources are not fully viable yet due to their unstable and intermittent nature (Rodrigues *et al.*, 2014; Benetatos *et al.*, 2019). Therefore, solutions to match the high-frequency variation of renewable energy production with the electricity demand are fundamental for energy transition. In this view, large-scale energy storage can provide means for balancing supply and demand, increasing energy security, promoting a better management of the grid and allowing convergence towards a low carbon economy. To this end, both electrical storage technologies – such as rechargeable batteries and supercapacitors (Scalia *et al.*, 2021; Lamberti *et al.*, 2015) – and chemical storage are currently under investigation.

Chemical storage implies transforming electrical power into chemical energy in the form of H_2, which can then be used as such or combined with captured CO_2 to produce green CH_4 (referred to as the gas-to-power technology), thus it is very versatile. One way to ensure large-scale storage of chemical energy is to use the storage capacity of underground reservoirs, since geological formations have the potential to store large volumes of fluids with minimal impact to the environment and society (Matos *et al.*, 2019).

Furthermore, strategies for CO_2 capture and permanent storage have been developed to compensate for CO_2 emissions from burning fossil fuels and to meet the challenge of drastically reducing CO_2 emissions in the next future. While long-term CO_2 underground storage is often regarded as an essential mitigation option to reduce greenhouse gases into the atmosphere and contrast climate change, temporary underground storage could be a strategy to match the quantity of captured CO_2 and the quantity of CO_2 that can be transformed into value-added fuels and chemicals.

Based on the above, it is evident that underground storage systems can play a fundamental role in the transition to a decarbonized and more sustainable energy future. To this end, the Underground Energy Systems group of Politecnico di Torino has teamed up with the researchers of the Center for Sustainable Future Technologies of the Italian Institute of Technology (IIT), also based in Torino, to work together and tackle these new challenges. By joining forces, we can complement expertise on rocks and fluids characterization, CO_2 capture and reduction, hydrogen, materials, conversion and safety of offshore facilities, numerical modeling and underground gas storage to address the issues posed by energy transition. New laboratory facilities within the Competence Center SEASTAR – Sustainable Energy Applied Sciences, Technology & Advanced Research have also been established to carry out experimental investigations in support of the ongoing research. Research on H_2 and CO_2 underground storage is under development.

2. Well testing: more than 20 years' experience in geo-energy

Pressure transient analysis to characterize underground formations from a production/shut-in sequence applied to a well began in the early 1930's both within and peripheral to petroleum engineering. Over the years, the technological improvement of pressure gauges and the mathematical development of interpretation models made these tests an oil industry standard methodology for well performance and reservoir characterization for various physical reservoir concepts and flow conditions (Gringarten *et al.*, 1979; Bourdet *et al.*, 1983; Agarwal, 1980; Coelho *et al.*, 2005).

Conventional well testing consists of analyzing the pressure transient recorded down-hole during production of the reservoir fluids at either a constant or variable rate, and subsequent shut-in phase. Typically, during exploration activities there are no infrastructures to collect the hydrocarbons produced during well tests, thus it is common practice to flare them; this involves emissions of unburned hydrocarbons, carbon monoxide and nitrogen oxides. Over the last twenty years, significant evolution in HSE's policies, driven by technological advancements and a societal push toward sustainability, allowed alternative well testing methods to gain increased consideration. Alternative technologies fit into the sustainable path in different ways (Verga *et al.*, 2016): injection tests, suited for reservoir characterization without surface production and thus eliminating greenhouse gases emissions (they can be complemented with Wireline Formation Testing for reservoir fluid sampling) (Levitan, 2003; Beretta *et al.*, 2007); harmonic pulse testing, suited for well monitoring in production and storage fields without interruption of ongoing operations (which could compromise conventional well test interpretation) and for well and thermal front monitoring in geothermal systems.

2.1. Injection Testing

An injection test consists in injecting a fluid (commonly brine, diesel or nitrogen) in a reservoir zone and monitoring the pressure response during the injection period and the subsequent fall-off period, in which the well is shut-in and the pressure tends to return to the initial equilibrium value. If the hydrocarbons originally in place and the injected fluid are not miscible, the physics of injection tests is characterized by the presence and movement of two phases in the reservoir. Along with analytical solutions (Levitan, 2003; Ramakrishnan & Kuchuck, 1993; Boughrara *et al.*, 2007; Habte & Onur, 2014) and numerical simulation (Verga *et al.*, 2008; Azarkish *et al.*, 2006; Verga *et al.*, 2011), an interpretation approach leveraging consolidated interpretive tools is presented in the technical literature (Beretta *et al.*, 2007; Verga *et al.*, 2012).

Examples of successful injection tests were published in the scientific literature: test of a naturally-fractured light-oil carbonate reservoir using brine as the injection fluid (Beretta *et al.*, 2007); test of a light oil reservoir in Algeria where diesel was injected (Tripaldi *et al.*, 2009); and, test of a depleted dry gas (i.e., methane) field, which could potentially be converted into an underground gas storage, where the injection fluid was nitrogen (Azzarone *et al.*, 2011).

2.2. Harmonic Pulse Testing (HPT)

HPT is a well testing technique in which the injection or production rate is varied periodically. The pressure response to the imposed rates, both in the pulser wells and in the observer well(s), can be analyzed in the frequency domain to evaluate the reservoir properties. Although harmonic testing entails a much longer rate sequence than conventional testing to obtain the same information (Hollaender *et al.*, 2002), the main advantage of this approach is that it does not require the interruption of production nor the knowledge of the previous rate history. In storage scenarios, well monitoring is essential to guarantee market delivery targets (gas volume and rate) but interrupting the production before and during a test is often unfeasible for the very same reasons.

The concept of harmonic testing was first proposed by Kuo (1972) and later developed by several authors (Rosa & Horne, 1997; Hollaender *et al.*, 2002; Ahn & Horne, 2010; Fokker & Verga, 2011; Fokker *et al.*, 2012; Fokker *et al.*, 2013; Sun *et al.*, 2015, Salina Borello *et al.*, 2016, Fokker *et al.*, 2017, Viberti *et al.*, 2018). In Fokker *et al.* (2018) analytical models are presented for HPT interpretation on a graph analogous to the log-log diagnostic plot for the most common scenarios (I.A.R.F., single boundary, partial penetration, horizontal well, closed reservoir).

Real applications of HPT are documented in the literature for hydrocarbon reservoirs, aquifers, storage fields, and geothermal systems. Rochon *et al.* (2008) characterized single and multilayer reservoirs. Fokker *et al.* (2013) characterized heterogeneities of a sandstone aquifer (Renner & Messar, 2006). Salina Borello *et al.* (2016) assessed the deliverability of a gas well in a storage field and identified turbulence effects. Well deliverability estimation is provided by Shoaib *et al.* (2018). Recently, the application of harmonic pulse testing was successfully extended to geothermal systems (Salina Borello *et al.*, 2019; Fokker *et al.*, 2020).

3. Integrated multiscale static and dynamic modeling of underground porous media

The ability to predict the future performance of an underground system for different development, production or storage strategies mainly depends on the possibility to reliably describe the system – be it a reservoir, aquifer or storage – by integrating all the available geological, geophysical, petrophysical, testing and production information and simulating the fluid dynamics taking place within it (Benetatos & Viberti, 2010). To this end, it is common practice to rely on a 3D numerical reservoir model. The model is first generated to accurately reproduce the structural and petrophysical properties of the underground system (static modeling) and then implemented to describe the evolution of pressure and fluid saturations in space and time (dynamic modeling). Due to a generally enhanced awareness of environmental and safety issues the same model is often further extended to account for the rock mechanical properties and to simulate potential consequences of the induced variations of the stress conditions. Furthermore, dealing with CO_2 or H_2 storage also demand for including relevant geochemical phenomena such as rock dissolution or salt precipitation, which can alter the rock petrophysical properties.

3.1. Static reservoir modeling

The static model of a reservoir can be considered as the final product of the structural, stratigraphic, lithological and petrophysical modeling activities. A deep integration among them is necessary in order to generate a representative static model (Benetatos & Giglio, 2019).

The construction of a 3D static model begins with the dataset creation and the quality check of all the available well log, geophysical and geological data including sedimentological information. The available 2D seismic sections or 3D high resolution seismic datasets are used for the identification of the main horizons, geological trends and faults if present as well as for the extraction of seismically derived lithological and petrophysical properties. The structural model and the subsequent stratigraphic model are of primary importance for the definition of the internal reservoir architecture and for the continuity and connectivity of the sedimentary bodies.

The volume of interest (i.e., the reservoir) is divided into elements called blocks (or cells). Each block is assigned values of the local petrophysical properties: fluid saturations and porosity dictate the amount of hydrocarbons stored in the reservoir, whereas permeability defines the ease with which fluids can flow through porous media and thus well productivity or injectivity. The values of the petrophysical parameters usually derive from well and core data (Viberti, 2010; Viberti *et al.*, 2012) but their distribution in the model is controlled by deterministic or statistical methods. In the last decades, geostatistics has become a valuable tool in geological modeling, offering techniques for the integration of multiscale data, mapping their uncertainties and distributing properties into 3D reservoir models.

3.2. *Dynamic reservoir modeling*

The objective of reservoir dynamic modeling is to build a 3D numerical model able to simulate the dynamic behavior of a given underground system. The main input data for dynamic reservoir modeling comes from different sources and includes: the static model, fluids thermodynamic behavior (Pressure-Volume-Temperature or PVT data), rock-fluid interaction properties, initial pressure and temperature conditions, well data, production history if any, and forecast targets and constraints. Pressure profiles versus depth are obtained through well measurements. Laboratory routine analyses on cores provide information about horizontal and vertical permeabilities; special core analyses are performed to obtain capillary pressures and relative permeability curves. Fluid samples are collected and analyzed in laboratories to obtain PVT fluid properties. Well testing is a common and powerful tool to get reliable estimates of well productivity, permeability of the formation, and evidence of possible heterogeneities within the test drainage area. The grid cells obtained from the static model are connected through flow equations describing the fluid flow under pressure variations.

The basic workflow consists of five steps: data acquisition, model design, initialization, history matching and forecast. The design of a simulation model is influenced by the type of process to be modeled, the complexity of the fluid-mechanics problem, the objectives of the study, the quality of the data, and the time and budget constraints. Common simulators consider only three fluids (black oil models), namely oil, water and gas, and isothermal conditions, with the temperature depending on the local geothermal gradient; more complex processes require to account for all the fluid components (compositional models) and for the thermal variations of the system. The initialization phase consists in assigning the initial saturation and pressure distributions, verifying the thermodynamic and hydrostatic equilibrium, and double-checking the hydrocarbons volumetric evaluations performed with the static model. In the history matching phase, the model is calibrated based on the available measured pressure and production data, by modifying the input parameters through a manual or assisted back analysis approach. Once the model is properly calibrated, productivity and recovery forecasts are performed for different field development scenarios.

The static and dynamic modeling approach for underground gas storage analysis follows the same workflow as a conventional reservoir study; however, there are issues, which are specifically relevant to gas storage. These include varying gas composition, reservoir temperature (slight) reduction due to repeated injection of “cold” gas, enhanced effects of petrophysical heterogeneities on the pressure response due to the cyclical withdrawal and injection of gas at high rates resulting in rapid and significant pressure variations and hysteresis of gas-water relative permeabilities (Verga, 2018).

The chemical composition of the stored gas can go from natural gas (typically methane with small percentages of heavier hydrocarbon components) to CO_2, to H_2 or any mixture of the above. CO_2 is very distinctive because it exhibits super-critical behavior at reservoir conditions. Obviously, composition variations affect the gas PVT behavior and thus the dynamics of the system, because pore pressure is intrinsically connected to gas compressibility which, in turn, is a function of gas composition. Compositional models are therefore needed to accurately simulate the effects induced by gas composition variations due to injection.

3.3. *Microscale analysis*

In recent years, the availability of new technologies to characterize pore spaces with a high level of detail supported the growing interest in pore-scale modeling. For example, X-ray micro-CT imaging allow reconstruction and visualization of a 3D porous medium with a resolution sufficient to identify grains and pores (Wildenschild & Sheppard, 2013). Thanks to this technique, a realistic representation of the reservoir rock can be obtained and used as an input for further geometrical and hydrodynamic analyses. In addition, algorithms able to reproduce 3D synthetic porous media with given grain size distribution, porosity and anisotropy have become increasingly abundant. The output is a 3D binary image.

At macroscale, fluid flow is modeled by averaging the microscopic continuity and momentum equations over a representative elementary volume (REV) and the porous medium is parameterized mainly by porosity and permeability. The fundamental equation of fluid motion in porous media is Darcy's equation. However, at microscale, porous media are complex materials characterized by a chaotic structure and tortuous fluid flow, with pore and grain dimensions varying over a wide range. To address the crooked fluid paths through the porous structure, the concept of tortuosity (geometrical, which is based on distances, or hydraulic, which is based on the actual flow paths) was introduced. Moreover, to account for pore space interconnections, the concept of effective porosity was introduced. These microscale properties can be estimated through a geometrical investigation of the pore space using specific algorithms, such as medial axis or path-finding algorithms, and by performing hydrodynamic simulations at the pore-scale (Viberti *et al.*, 2020). When fluids saturate the rock pores, the interactions between the different components depend on the physical and chemical properties of fluids and solid boundaries. All displacement phenomena are governed by local capillary pressure and by its instabilities. Fluid displacement on a pore-by-pore basis is composed of a sequence of equilibrium steps, where fluids reach an equilibrium position (energy balance) following Young-Laplace equation. In water-wet permeable media, non-equilibrium capillary pressure conditions can cause water layers to swell and spontaneously fill the pore throats, thus disconnecting and trapping the non-wetting phase (Roman *et al.*, 2017): this is called snap-off, and is very relevant in many processes including CO_2 sequestration.

3.3.1. Microfluidics for pore-scale investigation

Microfluidics has expanded from chemical and biological applications to energy and environmental fields. Unlike traditional core flooding experiments, in which transport properties are indirectly calculated by measuring the pressure drop across a rock sample, microfluidic chips enable direct visualization of the fluid dynamics in synthetic porous media.

A microfluidic chip is a microdevice whose outer dimensions range from hundreds of microns to centimeters. The device is usually constituted of two layers: the lower layer hosts the microfluidic patterns and the optically transparent upper one seals the circuit and allows for the visualization of the fluid flow. For microfluidic devices simulating rocks, the microfluidic patterned core mimics the porous network, and the inlet and outlet channels connect the pore network to the inlet and outlet ports. The internal features range from nanometers to hundreds of microns. The devices can be fabricated with a variety of additive and subtractive manufacturing techniques and all the materials of technological relevance can be selected: glass, silicon, polymers, composites and geomaterials (Jahanbakhsh *et al.*, 2020).

Glass is one of the most commonly employed materials, and historically one of the first to be used, together with silicon. Its optical transparency, hardness, chemical and thermal stability are indeed extremely well suited for applications in the geological and petroleum engineering field. Among the very many types of Si/glass microfluidics fabrication methods (Park *et al.*, 2004; Ciprian *et al.*, 2007; Marasso *et al.*, 2008; Marasso *et al.*, 2011; Henley *et al.*, 2012Ku *et al.*, 2018; Kumar Mishra *et al.*, 2019), micro powder blasting, relying on physical erosion by an abrasive powder jet accelerated towards the substrate, or laser micromachining are technological options enabling cheap, fast and complex three-dimensional micro-structuring. Pore network structures can also be generated on the surface of silicon wafers, using essentially the same methods as for the generation of pore network patterns on glass. Since silicon is opaque in the visible spectrum, direct optical visualization of fluid flow processes inside pore network structures is only possible at the surface of a silicon wafer bonded to a transparent substrate. To this purpose, a glass-silicon-glass architecture is typically used with anodic bonding as the dominant technology enabling complex multi-level microfluidic systems. The main advantage of using silicon over glass substrates is its ability to generate pore network structures with very high (sub-nanometer) resolution and accuracy.

Transparent polymers are also considered valid options for the fabrication of microfluidic devices, being significantly cheaper than silicon or glass (Marasso *et al.*, 2014; Tsao, 2016). Photolithography, 3D printing and/or molding processes are the most common manufacturing techniques (Vitale *et al.*, 2013; Vitale *et al.*, 2015; Bertana *et al.*, 2018). 3D printing is undoubtedly the most recent approach for microfluidics. It allows moving directly from digital design data to manufacturing. Though still limited for large volume needs, it is perfectly suited for microfluidic systems with moderate resolution but high level of complexity, outrunning in this sense more conventional manufacturing techniques. Polymers are generally more versatile than silicon or glass, available in a wide range of compositions and thus of physicochemical properties, cheaper, allow for surface modification, and can easily be bonded. However, this also implies that the surface tends to undergo undesired modifications during processing, which requires additional stabilization. Moreover, polymers can be blended with nanostructured materials to provide composites with improved characteristics and performance (Quaglio *et al.*, 2011). The main drawbacks of polymers are their reduced chemical and mechanical resistances, that limit their application with solvents and make them unsuitable to withstand high temperatures and high differential pressures.

Main applications of microfluidics in the oil and gas field are related to the investigation of water/oil separation (Quaglio *et al.*, 2019), drainage and imbibition processes (Gunda *et al.*, 2011), enhanced oil recovery (Gaol *et al.*, 2020), CO_2 underground storage (Amarasinghe *et al.*, 2021), carbonate reservoirs and dissolution processes (Soulaine *et al.*, 2021) and PVT measurements (Molla and Mostowfi, 2021).

4. Underground storage

4.1. Storage as a discipline

The concept of storing natural gas underground in geologic formations arose from the need to balance the divergence between a constant gas supply and the seasonal and daily variability of gas consumption. The first successful underground storage of natural gas in a depleted gas reservoir occurred in 1915 in Ontario, Canada. Since then, hundreds of facilities have been developed. Underground gas storage (UGS) may be defined as the long-term safe isolation of natural gas within geological formations. Thus, two of the most important characteristics of an underground storage are its ability to hold natural gas for future use and the rate at which that gas can be withdrawn. Depleted gas and oil reservoirs, deep saline formations, salt caverns and un-minable coal beds are the favorable candidates for safe geological storage of natural gas, but several reconditioned mines are also in use as gas storage facilities.

Historically, depleted gas or partially depleted gas reservoirs have been the most sizeable and commonly used formations for natural gas storage. A depleted field typically represents the most suitable option because of its proven ability to contain and trap gas on a geological timescale. Pressure is used to force the gas into and out of the porous and permeable reservoir while a sealing caprock prevents vertical fluid migration. However, if the original formation pressure is exceeded during storage operations to increase the working gas volume (i.e. delta-pressure conditions are applied), there is a risk that the caprock may fail to confine the gas. Thus, both the hydraulic sealing capacity and the mechanical resistance of the caprock must be carefully investigated. Geomechanical analyses are also needed for evaluation of potential subsidence and induced (micro)seismicity. A significant advantage of depleted fields is the level of knowledge already gained and readily available: information about the geological, structural, petrophysical characteristics and fluid-flow properties are inherited from the exploration and production phases. From a commercial standpoint, depleted reservoirs typically provide very good storage efficiency, both in terms of movable gas volume and injection/withdrawal gas rates. Deep saline aquifers represent a common alternative for UGS. The development and management of saline aquifers require that the original formation pressure is exceeded to displace the water initially saturating the pores of the rock to accommodate the gas. Therefore, the sealing capacity of the caprock, the presence of spill points (depths below which the gas may “escape” from the geological structure) as well as the rock mechanical integrity must be assessed in order to prevent gas leakage. Salt caverns and excavated rock caverns (such as coal and granite) are generally developed in regions where reservoirs are not available. They are typically much smaller in volume than either depleted reservoirs or aquifers but can provide high delivery rates (Benetatos *et al.*, 2013).

The successful development of a UGS must include an appropriate site selection based on subsurface information and subsequent performance analysis, preferably based on an integrated geological, geochemical, fluid-dynamic and geomechanical approach. To this end, the same basic sets of information as a typical reservoir study are used: geophysics, geology, well logging and core analysis, well testing and production history, rock compressibility. Furthermore, an adequate monitoring program to satisfy technical and safety regulations together with social and environmental concerns must also be conceived to ensure the long-term feasibility of the project, especially if delta-pressure conditions are applied. However, even though the UGS industry has borrowed much of its knowledge from other industries (primarily oil and gas reservoir engineering and production), it has also needed to develop a technology of its own to meet specific challenges and concerns (Verga, 2018).

4.2. Carbon capture, utilization and storage and hydrogen storage

Underground storage of carbon dioxide and hydrogen is quite similar to the underground storage of natural gas. In fact, most of the past and ongoing underground CO_2 and H_2 storage projects use the experiences of the underground natural gas storage in each and every aspect, such as site specifications, storage techniques, monitoring and even cost life cycle or economic viability. The major difference is represented by the physiochemical properties of CO_2 and hydrogen that require more attention than natural gas especially in terms of leakage, monitoring, chemical affinity and potential chemical, biological or microbial reactions.

Long-term CO_2 underground storage is regarded as an essential mitigation option to reduce greenhouse gases in the atmosphere and contrast climate change. CCUS (Carbon Capture, Utilization and Storage) encompasses all the methods and technologies to remove CO_2 from the industrial flue gas and from the atmosphere, followed by CO_2 recycling or by safe and permanent storage options (IEA, 2020). In this perspective, a dualism exists between CO_2 utilization and storage – as if one technology was alternative rather than complementary to the other. The authors believe that, as opposed to permanent geological sequestration, temporary underground storage should be part of the CCUS process as a strategy to efficiently couple CO_2 capture with CO_2 valorization options, i.e. the storage acts like a "buffer". In this approach, CO_2 storage is fully integrated with valorization technologies leading to a virtuous CO_2 cycle, or the three C's: Capture, Cache and Convert (Bocchini *et al.,* 2017). Each industrial segment could operate independently and optimize its own value chain with an expected significant efficiency enhancement, largely offsetting the cost due to storage. There are several technologies for CO_2 sequestration and re-use; some of them are already available in the market whereas others, at present, still need a further step of development to become industrially appealing, an example being the RECODE EU project (recodeh2020.eu). Furthermore, deploying all of them at the same site still requires significant efforts. The capture process can be attained either from the atmosphere or at the emission source, such as power plants, cement plants or biomass plants where a conversion process – *i.e.* combustion – produces carbon dioxide-rich flue gases. Among the possible separation techniques, the amine scrubbing technology is very mature and has been industrially employed for over 50 years in post-combustion separation. However, amines have major drawbacks: they are toxic/corrosive and require a large amount of energy to be regenerated. Other technologies such as the use of ionic liquids can solve some critical issues (Latini *et al*,. 2019) as they feature negligible vapor pressure, non-corrosiveness and low energy demand (Davarpanah *et al*,. 2020). Following CO2 capture, the valorization process to obtain chemicals and fuels can be exploited both as a direct conversion process, or as the final step of a value chain. Several (bio)chemical approaches can be designed to obtain the desired molecules, and each of them can be valueable in specific application conditions. The biocatalytic route exploits ad-hoc developed microorganism strain to obtain the desired products (Vasile *et. al.*, 2021), electrochemical valorization (Zeng *et al.*, 2018 and 2021; Bejtka *et al.*, 2019, Zeng *et al.*, 2021) exploits renewable energy sources to power the system (Sacco *et al.*, 2020), while thermocatalytic processes, can take advantage of hydrogen from renewables in the power to gas approach. In the chemical catalytic approaches, the challenge is to select and optimize processes and materials highly selective, efficient, inexpensive and environmentally friendly, able to be competitive in the energetic transition (Kamkeng *et al.*, 2020). At present, CO and formic acid are considered to be the most economically viable molecules in electro catalytical processes (Jouny *et al.*, 2020), while thermocatalysis is more efficiently exploited to obtain methane, methanol and more complex C2 molecules (e.g. ethylene).

Currently, hydrogen is generally stored as a gas in very high-pressure vessels, or in liquid form at very low temperatures in heavily insulated vessels. Such vessels are expensive, heavy and inconvenient. Geological storage is a possible option to store large quantities of hydrogen and therefore large amounts of energy over long timescales. This is the reason why underground H_2 storages has been given serious consideration. Hydrogen can be stored using either salt caverns or porous formations like saline aquifers or depleted gas and oil fields. While hydrogen has already been stored successfully in salt caverns for industrial use, experiences with subsurface porous media hydrogen storage are relatively scarce. Although large-scale underground storage of hydrogen is possible thanks to the technology of underground storage of natural gas and carbon dioxide, additional investigations are needed to assess technical feasibility and safety with respect to caprock tightness, diffusivity, interactions with the reservoir rocks with potential subsequent changes of the storage properties, reactions with microbial communities and compatibility with materials. All these aspects are currently being investigated by the PoliTO-IIT research team with equipment suitable to run experiments even at the challenging pressure and temperature conditions typical of deep underground geological formations.

4.2.1. EoS and phase behavior

Hydrogen and methane are in gaseous phase at both reservoir and standard conditions due to their critical constants and phase diagram. When storing H_2 in a depleted reservoir, the description of the interaction between fluids (H_2, hydrocarbons and water) and the volumetric behavior of the resulting gas mixture requires the adoption of a compositional fluid model. The fluid behavior is defined by an Equation of State (EoS) which must be properly selected for the range of pressure and temperature conditions of the physical system under investigation. The two most used EoS implemented in compositional reservoir simulators are the cubic equations called Soave-Redlich-Kwong, originally conceived by Redlich and Kwong in 1949 and subsequently improved by Soave in 1972, and Peng-Robinson, in which a further modification to the Soave-Redlich-Kwong equation was introduced in 1976. The GERG-2008 EoS can also approximate well the thermodynamic properties of natural gases and other mixtures for a wide range of mixture compositions, pressure and temperature.

4.2.2. Diffusion

One of the issues to be addressed for gas storage is the sealing capacity of reservoir caprocks to prevent upward gas migration. In gas reservoirs evidence proves that methane diffusion through caprocks is negligible even over geological times. Conversely, H_2 and CO_2 diffusion through reservoir caprocks has to be properly evaluated as well as diffusion of any gas mixture in the case of storage in aquifers.

Hydrogen diffusivity mainly takes place in the water saturating the caprock (Hemme & Van Berk, 2018; Vinsot *et al.*, 2014); the gas first dissolves in the water and then diffuses through it. Solubility and diffusivity of CH_4, H_2 and CO_2 in pure water are shown in Tab. 1.

Diffusivity coefficient measured at ambient pressure should represent an overestimation of diffusivity at reservoir pressure because theoretical values of free molecular diffusivity coefficient for most gases show a direct proportionality with temperature and an inverse proportionality with pressure (Roberts, 1972). Inverse correlations between diffusion coefficients and pressure were experimentally observed for diffusion of He in rocks (Pandey et al., 1974.), CH_4 in rocks (Schlomer et al., 2004), CH_4 in coal (Wang et al., 2016) and H_2 in clay (Boulin et al., 2008). Diffusion is higher for dry samples because hydrogen diffuses directly in the empty pore spaces: measurements on dried argillites samples were close to 10-7 m^2/s while tests on the same argillite at different water saturation values showed diffusion was two orders of magnitude lower than for dry samples. In water saturated clay rocks, measured H_2 diffusion was found in the range 10-12-10-10 m2/s (Krooss, 2008; Aertsens, 2009; Jacops et al., 2012; Vinsot et al., 2014; Jacops et al., 2015). Water salinity could also have an impact on diffusivity. According to Panfilov (2016) caprocks saturated with water represent an impermeable barrier to hydrogen, and numerical simulations with a hydrogeochemical modeling approach confirmed that the loss of hydrogen by diffusion through the caprock at reservoir conditions is negligible (Carden and Paterson 1979; Krooss, 2008; Hemme et al., 2018). The diffusion values of H2-CH4 mixtures measured by the PoliTO-IIT research team at standard pressure and reservoir temperature are also in the range 10-10-10-11 m^2/s and seem to confirm the sealing capacity of clayey caprocks.

Tab. 1 – Solubility and diffusivity of CH_4, H_2 and CO_2 in pure water (Engineering toolbox, 2008;Wise & Houghton, 1966;Tamimi *et al.*, 1994).

Gas	Solubility in water (g/kg)		Diffusivity in water (m2/s)	
	@ 20°C, 0,1 MPa	@ 60°C, 0,1 MPa	@ 20°C, 0,1 MPa	@ 60°C, 0,1 MPa
CH_4	0.023	0.007	$2.4\ 10^{-9}$	$6.7\ 10^{-9}$
H_2	0.0016	0.0012	$5.0\ 10^{-9}$	$13.1\ 10^{-9}$
CO_2	0.16	0.6	$1.67\ 10^{-9}$	$4.2\ 10^{-9}$

4.2.3. Biochemistry

Biogeochemical analyses need to be carried out with the main aim of assessing the potential changes in the stored gas mixture and in petrophysical properties due to microbial activities within the reservoirs selected for underground storage of CO_2 or H_2. Several studies have estimated that generally between 10^3 and 10^6 microbial cells per milliliter of water can be found in deep underground formations (Ivanova, 2007; Gniese, 2014; Itävaara, 2016) and it is well known that microbial communities can deeply affect the activity of UGS with respect to: (i) loss of stored gas and, as a result, loss of energy value; (ii) damage to plant and technical equipment due to biocorrosion and clogging caused by biofilm formation and biomass accumulation; (iii) safety risks to operators mainly due to the production of hydrogen sulfide, which is highly toxic (West, 2011; Gniese, 2014).

The recent development of powerful molecular biology tools, such as high-throughput Next-Generation Sequencing (NGS) technologies, has allowed for a targeted and detailed study of the deep microbiota, characterized by non-culturable microorganisms that cannot be analyzed by standard laboratory techniques. Samples of formation fluids and sediments can be collected prior to injection for a baseline on microbial composition to be compared with changes induced by the presence of insufflated CO_2 or H_2. In both cases, microbiological analysis is useful to identify and monitor the biogeochemical processes, which can affect the consumption and diffusion of the gas within the reservoir during storage. Numerous studies of microbial communities in the deep biosphere have revealed that – based on their metabolic pathways – four main classes of microorganisms can be distinguished: methanogens, sulphate reducers, homoacetogenic bacteria and iron reducers, with the first two posing the greatest risks to the storage site (Leung, 2014; Heinemann, 2021).

In the case of CO_2 storage, it is extremely unlikely that microorganisms can survive direct exposure to supercritical CO_2. However, it has been proven that, after the injection phase, different microbial classes can be exposed to the gaseous or dissolved phase of CO_2 and metabolize it to proliferate. The direct effect of CO_2 is its potential role as oxidant compound that can be used as an energy source (e.g. for methane production), while the indirect effect is the reduction of the pH level, altering the composition of the microbiota and leading to a reduction in the microbial diversity (Gulliver, 2016).). It has been shown by experimental evidence that resilient microbial populations can have both favourable and unfavourable effects on the capacity, integrity and safety of a storage site (Gniese, 2014). For example, biofilm formation can potentially help to “lock in” the injected CO_2 and prevent its migration as plume. Conversely, the activation of some microbial metabolisms, e.g. methanogenesis, can lead to methane production and potential leakage (Mu & Moreau, 2015). Although the effects related to microbial activity may be small and almost undetectable at the beginning of the storage period, they can become very difficult to control and costly to remediate if autocatalytic reactions are triggered (West, 2011).

The studies needed to ensure safety and efficiency of a H_2 storage are even more complex than those required for CO_2 since the experience and practical applications of underground H_2 storage are to date very limited (Heinemann, 2021). From a biochemical point of view, the insufflation of hydrogen can trigger the proliferation of all the hydrogenotrophic microorganisms, which belong to the four aforementioned metabolic classes. It has been proven that the risks of H_2 loss is higher when more terminal electron acceptors for microbial metabolic activities, like CO_2 and sulfate, are available. Therefore, a detailed mineralogical-petrographic analysis of the reservoir and caprock is needed to assess the content of sulfate- and carbonate-based minerals (e.g. calcite, dolomite and siderite) (Flesch, 2018; Hemme & Van Berk, 2018).

The PoliTO-IIT research team is applying its expertise in microbiology and reactor engineering in order to: (i) carry out the characterization of microbial profile of the microbiota in depleted reservoirs of interest for potential conversion into storages, and (ii) study the microbial metabolic activities by means of a multiphase reactor system (installed in the SEASTAR facilities) that has been specifically designed to reproduce reservoir conditions (max pressure = 200 bar and max temperature = 150°C), with solid rock samples, microfluidic chips, bacteria and flow of gas/liquid mixtures . The microbiological analysis is carried out by means of taxonomic and relative abundances determination of deep microbiota through NGS sequencing of the 16S ribosomal subunit, with specific targets for both bacteria and archaea populations. The study is complemented by the use of functional genes for the characterization of the metabolic activities of methanogenic archaea (*mcrA*) and sulphate-reducing bacteria (*dsrB*) (Ranchou-Peyruse, 2019).

4.2.4. Geochemistry

Geochemistry plays an important role in CO_2 storage. The reactivity of carbonate and silicate minerals is at the heart of porosity and pore geometry changes in rocks injected with CO_2, which ultimately control the evolution of flow and transport properties of fluids in porous (Noiriel & Daval, 2017). Supercritical CO_2 at the pressure and temperature conditions typical of subsurface storage is soluble to a limited degree in water and saline brine but enough to transform the brine into a carbonic acid solution. The acidified brine can dissolve silicate minerals in the rocks, a form of silicate rock “weathering”, the extent of which depends on the availability of divalent cations contained in silicate minerals and the kinetics of mineral dissolution. The second part of the weathering cycle, which can also occur in underground reservoirs, is the recombination of released divalent cations like Ca, Mg and Fe with dissolved CO_2 to form solid carbonate minerals. Intuitively, an increase in permeability is likely to occur due to dissolution while carbonation should lead to a permeability reduction by globally decreasing the reservoir porosity. However, the evolution of permeability also depends on how the pore space is affected by reactions, e.g.: non-uniform precipitation patterns emphasize the permeability decrease by increasing the pore roughness; crystallization pressure resulting from precipitation of carbonates or salts could induce fracturing and the creation of new flow paths. Thus the prediction of permeability evolution in reservoirs is somewhat challenging due to the number of factors that can affect the dynamics of flow path enlargement or clogging. In addition, sample-size limitations restrict the ability to predict reliable porosity-permeability relationships at larger scales.

4.3. Geomechanical issues

Pressure changes caused in geological formations by fluid production and/or storage affect the rock stress state. If the variations of the rock stress state are significant, they could jeopardize the formation integrity and induce microfracturing, faults (re)activation and ground movements. Therefore, current regulations and public concerns call for geomechanical analyses to assess safety conditions in terms of stored gas containment, earthquake hazard and subsidence magnitude and extension. Geomechanical models, based on mechanical properties derived from lab and in-situ measurements, are strongly connected to the static and dynamic models. The geomechanical model simulates the stress state variations, verifies rock integrity and potential fault slippage, and calculates the rock deformation, which can propagate to the surface and induce ground movements. If ground movement surveys are available, a back-analysis procedure is carried out: the rock mechanical parameters are calibrated until a satisfactory match is achieved between simulated and measured deformations. The Interferometric Synthetic Aperture Radar (InSAr) acquisition technique is widely adopted for ground movements surveys due to its high accuracy (millimeters) on large areas (Berardino *et al.*, 2003; Ferretti *et al.*, 2001).

In the case of natural gas storage, seasonal ground movements can be correlated with withdrawal/injection operations. Gas pressure changes in the geological formations cause variations of effective stresses; if these variations are significant, they could affect the formation integrity and induce microfracturing, faults (re)activation and ground movements. Therefore, avoidance of these issues calls for geomechanical analyses to assess safety conditions.

The analysis of ground movement surveys induced by the storage systems located in the Po Plain, Italy (depth is in the range 1-1.5 km), shows a consistent relation between pressure variations and corresponding subsidence/rebound at the surface level (Codegone *et al.*, 2016; Coti *et al.*, 2018; Benetatos *et al.*, 2020). This UGS-related pressure variations due to the withdrawal/injection phases affect the formation cyclically and over relatively short periods (typically 5-7 months). The correlation between gas injection/extraction and upward/downward ground movements indicates that the formations behave elastically (Teatini *et al.*, 2011; Ferronato *et al.*, 2013). When a depleted reservoir is converted into a storage, it is initially refilled with gas; this phase generates a pressure increase and thus a decrease of the effective stresses (unloading). The subsequent cycles of gas withdrawal (loading) occur in the elastic field, with a stiffer behaviour than in primary production, where the quasi-monotonic pressure decrease occurring over decades can induce a consistent time-dependent behaviour of the sandy reservoir materials (Musso *et al.*, 2021). The simulation of the deformations induced by gas withdrawal/injection cycles requires an appropriate choice of the relevant parameters by selecting the reference range of strains of the process from lab tests (Marzano *et al.*, 2019, Rocca *et al.*, 2019). Furthermore, the transverse isotropy of the clastic formations can affect their mechanical response during storage cycles, as in the case of wellbores (Deangeli & Omwanghe, 2018; Parkash & Deangeli, 2019; Deangeli *et al.*, 2021).

4.3.1. Microseismicity monitoring

Microseismic monitoring is the passive observation of very small-scale earthquakes (i.e. magnitude less than zero) which occur in the underground because of geothermal operations or gas storage which cause a stress state change. During stress redistribution, sudden slips can occur along pre-existing zones of weakness such as faults or fracture networks, releasing energy in the form of seismic waves which are known as microseismic events. These micro-earthquakes are typically too small to be felt on the surface but can be detected by borehole seismic sensors with an adequate resolution in order to register even very low magnitude events at the depths of the geological formations involved in the injection or withdrawal operations. The spatial and temporal variations in microseismicity can be used to monitor changes in the stress field and hence potentially be used to monitor perturbations in fluid pathways as well as top-seal and well-bore integrity.

The design of a microseismic network for monitoring purposes must be based on a detailed analysis of the local and regional faults systems, especially in areas where infrastructures and/or urban settlements are present. Prior to installation of the instruments, a careful mapping of all the possible sources of noise is necessary as well as a quantitative analysis of the noise levels at the selected locations.

4.4. Conversion of offshore facilities

In the case of an offshore (partially) depleted reservoir to be converted into CH_4-H_2 mixtures or CO_2 storage facility, this also implies the conversion of the platform originally designed for hydrocarbon production. This option is particularly attractive because it allows minimizing the environmental impact that is typical of complete platform decommissioning, in particular for the subsea ecosystem that has grown around the jacket, and because it offers a cost-saving solution for the implementation of the equipment needed for underground gas storage.

The accidental release of dangerous (flammable and/or toxic) high pressure gases are one of the key safety issues for offshore platforms. Thus, an efficient CFD model has been developed (Carpignano *et al.*, 2017; Moscatello *et al.*, 2021) to simulate accidents with the aim of using the simulation results as a driver for effective design choices. The model, called SBAM model, is being validated by experimental activities, where model predictions are compared with the dispersion of a low concentration methane release into a scaled mock-up of an oil&gas platform (scaled 1:10) in the SEASTAR facilities of the PoliTO-IIT research team (Gerboni *et al.*, 2020; Moscatello *et al.*, 2020). The program of the research aims at extending the application of the model for the simulation of potential accidents involving CH_4-H_2 mixtures and CO_2.

Along with CH_4-H_2 or CO_2 storage, other complementary conversion options have been taken into account for the production of photovoltaic (PV) energy and use of this renewable energy for the separation and delivery of desalinated seawater for civil use, and recovery of raw materials such as lithium from the resulting brine.

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