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Interdisciplinary results of an Italian research project on methane recovery and carbon dioxide storage in natural gas hydrate reservoirs

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ABSTRACT

Natural gas hydrates (NGH) are found in marine sediments on continental and island slopes, in deep-water sediments of lakes and seas inland, and in polar sediment on continents and continental shelves. NGH constitute the biggest hydrocarbon resources on earth, representing a reservoir of sustainable fuel, thanks to the possibility of the so-called CO_2-CH_4 replacement process. If CO_2 is injected into NGH sediments, it causes CH_4 release and CO_2 hydrate formation. The extraction of gas from NGH, combined with carbon capture, presents significant potential advantages in energy infrastructure and in various economic and political contexts, aligning with future green policies. This paper contributes to the advancement of knowledge by reviewing the findings of a three-year Italian research project focused on methane recovery and carbon dioxide disposal in NGH. The consortium comprises seven multidisciplinary italian partners. The paper introduces a novel process wherein the CO_2-CH_4 replacement process is integrated with methane purification and CO_2 recirculation, which has been experimentally tested and represents a new advancement in gas hydrate science. Experimental tests at microscopic and macroscopic levels, show that the efficiency of the process strongly depends on the mutual influence among the properties of water, sediment and the involved gaseous species. Energy evaluations show that the ratio between the energy spent to complete an entire cycle of replacement and recirculation over the stored energy in the recovered methane is 17%, resulting in a beneficial energy balance, while economic analysis show that the transition could generate, even in the short term, large high-impact cash-out.

KEYWORDS

Natural gas hydrates; CO_2-CH_4 replacement; membrane; carbon storage; clathrate hydrates

1. INTRODUCTION

Natural gas hydrate (NGH) occurs in both marine and terrestrial environments. In marine sediment, NGH is stable almost along all continental margins in several hundred meters below the seafloor; onshore NGH is present below the permafrost and, in a metastable condition, in the permafrost. In fresh water, such as inland lakes, NGH is stable in deep-water sediment. In polar sediments, NGH is stable below the subsea permafrost area; in polar marine sediments, where water depths exceed about 300 m and bottom water temperatures approach 0° C, NGH is stable for hundred meters below the sea level. [1]. Thus, NGH produce remarkable bottom-simulating reflector (BSR). The best approach is based on the estimation of seismic -both compressional and shear wave- velocities provided by conventional 2D reflection data or Ocean bottom Seismometer data. Then, the seismic velocities are analysed by using theoretical approaches that describe the behaviour of the velocities versus NGH and free gas concentrations [2-3]. The NGH reservoir present in Peninsula Antarctica can be considered as a natural laboratory and, for this reason, samples acquired in the past in this region can be considered. The NGH reservoir present offshore Antarctic Peninsula was studied by using multidisciplinary approach in the last decades [1].

Expeditions off the Antarctic Peninsula, including three Italian Antarctic cruises, showed the presence of the diffused and discontinuous BSR indicating NGH presence [1,4]. Two gravity cores were analyzed, revealing various hydrocarbon gases and suggesting a thermogenic origin, possibly indicating deeper hydrocarbon reserves, supported by seismic data analysis [5].

Worldwide estimates of NGH deposits range from $2.5x10^{15}$ m^3 to $3.0x10^{18}$ m^3. These estimates indicate that the organic carbon contained in NGH reservoirs is approximately twice the amount found in all currently recoverable worldwide conventional hydrocarbon resources [6-8].

Therefore, NGH represent a resource of fuel, that could be assimilated to renewable sources thanks to the so-called CO_2-CH_4 replacement process. In fact, injecting CO_2 into NGH sediments leads to the release of methane (CH4) and the formation of CO_2 hydrate. Literature indicates that the CH_4-CO_2 hydrate conversion spontaneously occurs, even if the extent of CO_2-CH_4 exchange is limited by different molecular diameters [9]. This process constitutes a distinct opportunity to extract an energy resource, CH_4, while simultaneously sequestering a greenhouse gas, CO2. NGH reservoirs can thus serve as both sources of CH_4 and storage sites for CO_2, bolstering the concept of a carbon-neutral fuel source.

Concerning CO_2 replacement process, literature has proven the effectiveness of the process in water phase and in porous media systems, determining also the CH_4 production rate [10]. In-situ combustion was also proposed improving CO_2 injectivity and avoiding premature CO_2 hydrate formation [11]. In accordance with the review in [12], there are some research aspects which should be addressed: the authors of the paper highlighted key issues like the influence of water properties during formation and replacement reaction, the role of sediments' physical chemical properties, the possible change in the mechanical stability of the reservoir after the replacement and the development of reservoir models.

The present paper contributes to the state of the art, answering to the above-mentioned key issues with the results obtained by a three-year Italian research project on the topic of the methane recovery and carbon dioxide disposal in NGH reservoirs. The consortium is multidisciplinary and interdisciplinary and formed by seven partners: University of Perugia UNIPG (with Applied Physics and Structural geology groups), Politecnico di Torino POLITO (with the Applied Physics group), University of Camerino UNICAM (with the Analytic chemistry group), Istituto di Oceanografia e Geofisica Sperimentale OGS, University "G. D'Annunzio" Chieti-Pescara UNICH, University Sapienza Rome and University of Ferrara UNIFE (with the Energy Economics group). Several are the key aspects addressed in the project.

One important aspect that is considered in the project during the CO_2 injection in the NGH sediments is the efficiency of the replacement. In a real process, considering also the occupancy of the small and large cages, not all the recovered methane is replaced by the injected CO_2: it means that the output gaseous flux is not just pure methane, but a binary CO_2-CH_4 mixture, which needs an additional separation section to obtain pure methane for energy purposes [13].

In their study [14], the authors deliver an in-depth evaluation of the CO_2 capture methodologies, particularly focused on the efficiency of membrane-based gas separation, which seems to be suitable for separating methane from the CO2 which did not take part in the replacement. In particular, the Matrimid 5218 membrane presents a notable structure for gas separation applications [15]. The main properties of Matrimid are its inherent free volume, exceptional selectivity and permeability for both organic and inorganic gases [16-18]. Its efficacy, especially in CO_2/CH_4 separation, is validated against known performance metrics [19].

The mechanical properties of gas hydrates are another important aspect to investigate. There are several literature data on pure methane hydrates [20-21], while mixed CO_2/CH_4 hydrates properties, after and pre-replacement process are less investigated. Moreover, properties and property changes of the lithology that characterize the hosting sediments are far to be clearly understood. For CO_2-bearing samples, higher strength, with respect to methane hydrates, has been reported in literature [22] whilst others report more complicated behaviour for both short-term [23-24] and long-term [25-26] deformation. In particular, Luo et al. [27] highlight a decrease of the Young's modulus of about 20 % on CO_2 saturated-samples compared to CH_4 specimens as dissociation of hydrates has been proved to provoke weakening up to collapse of the sediments [28], as well as production of methane was observed to cause instability and local failures in permafrost regions [29], Thus, whilst it is clear that hydrates generally replace water from the pores, resulting in stiffer frame clearly improving the mechanical properties of the hosting sediments, the effect of CH_4 or CO_2 is still very poorly known [23].

The comprehension of the mechanical, morphological and chemical characteristics of gas hydrates is the basis for the development of simulation models for marine NGH reservoirs. In fact, velocity and resistivity are also influenced by sediment characteristics such as type, porosity, permeability, and pore fluid salinity. Therefore, further laboratory data are necessary to validate the full spectrum of electrical model behaviour.

On the other hand, the integration of co-located seismic and resistivity data, although independent, can enhance gas hydrate estimates. This is because inversion results provide seismic velocity and electrical resistivity, both sensitive parameters to gas hydrate content. Carcione and Tinivella [30] developed an approach based on Biot theory to partially frozen porous media saturated with a mixture of two immiscible, viscous, compressible fluids. This model can be approximated in the low frequency (seismic) range. Resistivity is widely used to estimate the GH and the free gas concentrations from core analysis [31]. To calculate the GH concentration of a deposit, modified Archie's law extracting the amount of pore space filled with GH from the over-all porosity [32]. The above mentioned selected theoretical models should be modified and integrated in order to fit the experimental data.

Finally, literature lacks economic studies on gas hydrates (NGH), particularly concerning the impact of GH exploitation on the methane market. By employing Life Cycle Assessment (LCA) and Levelized Cost of Energy (LCOE) methodologies, such studies could attract private investment, inform strategic decisions for industry and regulators, and assess the economic ramifications on emission trading systems and the natural gas market. LEC benchmarking is crucial for comparing different energy sources, especially regarding CO_2 costs. NGH exploitation, coupling natural gas production with carbon capture techniques, opens enormous potentially advantages for infra-gas competition and shaping future green policies and economic scenarios.

In the paper, the obtained body of knowledge significantly beyond the state of the art on the chemical, physical and geotechnical properties of marine NGH, on the CO_2-CH_4 replacement mechanism and on the development of a theoretical geophysical model of the marine NGH reservoir is discussed.

On the basis of the presented literature and in particular on the review in [12], which sets the main key issue to address in the future, the novelty of the results concerns: i) comprehension of the effect of sediment (grain size and composition), salinity and water properties on gas hydrate morphology, on NGH formation and CO_2 replacement; ii) mechanical behaviour of CH_4–CO_2 mixed clathrates; iii) development of theoretical model of gas hydrates in nature.

In addition, the CO_2-CH_4 replacement process is coupled with a methane purification and CO_2 recirculation section, which was tested experimentally. To the best of our knowledge, the process is new in the gas hydrate science and constitutes a technological improvement towards the effective management of NGH as a fuel source and CO_2 storage option

Finally, the review of the experimental results is enriched with the energy evaluation of the proposed integrated process is discussed, as well as a discussion on the effect of the NGH exploitation with carbon capture on the natural gas market and policy scenarios.

2. The project and the Italian Gas Hydrate Consortium

The research proposes an innovative technological solution for methane production from marine NGH and the simultaneous sequestration of carbon dioxide in a single process, in which the CO_2-CH_4 replacement process is coupled with a separation section (Fig. 1). In this section, methane and CO_2 are separated via membrane to obtain pure methane for energy purposes and pure CO_2 to be recirculated in the sediment.

This is necessary because the CO_2-CH_4 replacement process has a theoretical limit of 75%, so the output of the replacement process is a gaseous mixture that needs further treatment to be applied at full scale in the energy sector.

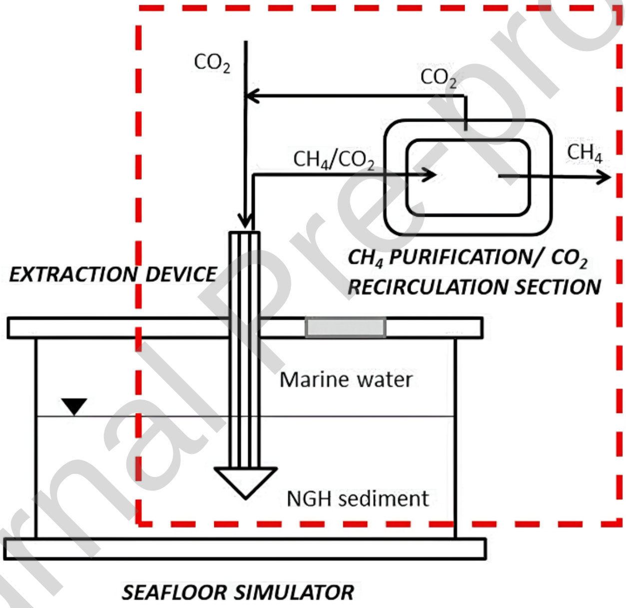


Fig. 1. Schematic of the proposed process.

To determine the performance of the proposed process, the project developed several experimental and theoretical activities.

UNIPG was in charge of the artificial reproduction of the NGH sediments, the macroscopic investigation on the effects of sediments properties and also the preparation of the samples for further analysis. The UNIPG and Sapienza geological group performed the geological and mechanical characterization of the samples before and after the CO_2-CH_4 replacement process. Also UNICH prepared NGH samples for further analysis. UNICAM used the NGH samples from UNIPG and UNICH for microscopic investigations, via Raman analysis and SEM microscopy. Experimental data were used by OGS to modify the theoretical model and by POLITO to perform research on the membrane-based separation section. UNIFE carried out an economic analysis. The flowchart is shown in Fig. 2.

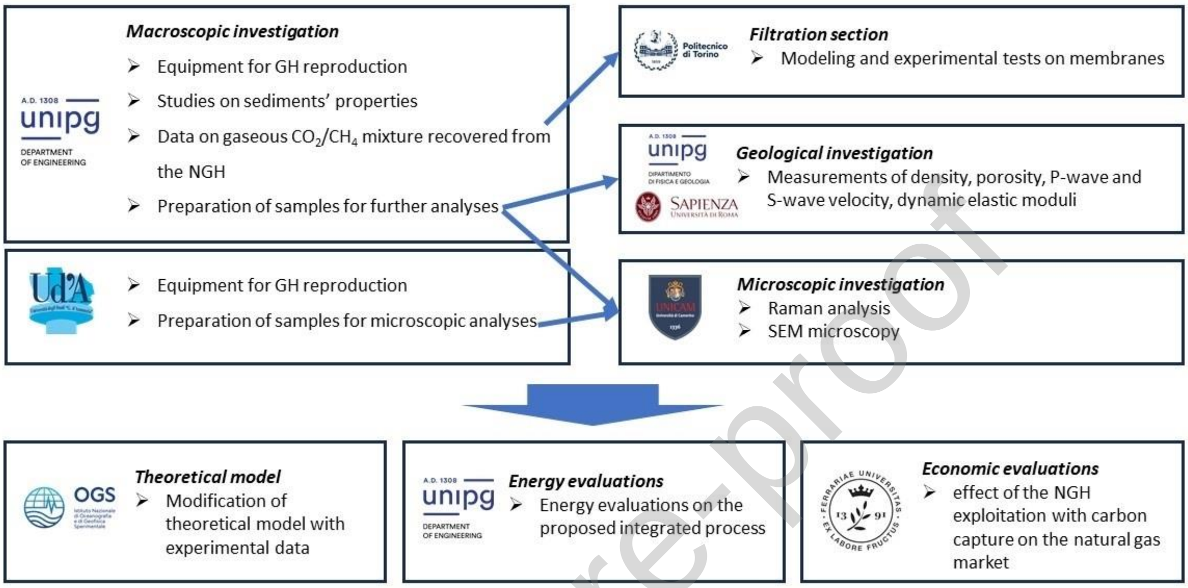


Fig. 2. Flowchart of the research activities.

The Consortium of partners assembles the Italian gas hydrate research community together with competencies, not strictly related to the gas hydrate science, in the field of the engineering (POLITO) and economics (UNIFE).

The Italian gas hydrate community is a multidisciplinary group engaged in gas hydrate research for over 30 years. OGS has been a key player over the past decades, focusing on theoretical elastic models to describe the dependences between velocity and gas hydrate and between velocity and pore pressure; seismic modelling to describe the seismic effect of hydrate, geophysical explorations; investigation on the mutual effect of hydrate stability and climate change [32,33].

Since 2003, the Gas Hydrate Facility at the University "G. d'Annunzio" of Chieti-Pescara has been active in clathrate hydrate research, covering areas from fundamental studies (kinetics and thermodynamics of hydrate promoters/inhibitors) to field applications in energy and space technologies [34-37].

The University of Perugia is one of Europe's leading research groups in gas hydrate science, with fifteen years of expertise in hydrate-based processes for energy applications like methane and hydrogen storage, natural gas hydrate exploitation, and CO_2 storage [38-40].

The University of Camerino, through the Environmental Chemistry Research Laboratory, specializes in characterizing the chemical and morphological aspects of hydrates and their environments [41,42].

3. MATERIALS AND METHODS

This section describes the experimental equipment used for macroscopic and microscopic investigations on NGH samples, the methodology used for the development of the theoretical model, the experimental tests on the separation section and the methodology for the energy and environmental evaluations.

3.1 Reactors and experimental tests for hydrate formation and CO_2 replacement

The experimental tests of NGH formation and CO_2 replacement are carried out on four different reactors: three reactors at UNIPG labs and one at UNICH labs.

The UNIPG research group has three reactors, one in a thermostatic bath and two placed in a cooling room. The first one has an internal cylindrical volume of 949 $cm^3$and it is positioned inside a thermostatic bath refrigerated by a chiller. A detailed description of the reactor is available in [13,43].

Similarly, the other two reactors, positioned inside a cooling room, have a cylindrical shape and a volume of 1 L. A detailed description of the reactors is given in [38].

The three reactors (Fig. 3) are equipped with several temperature sensors and pressure gauge to build the experimental p-T curves.

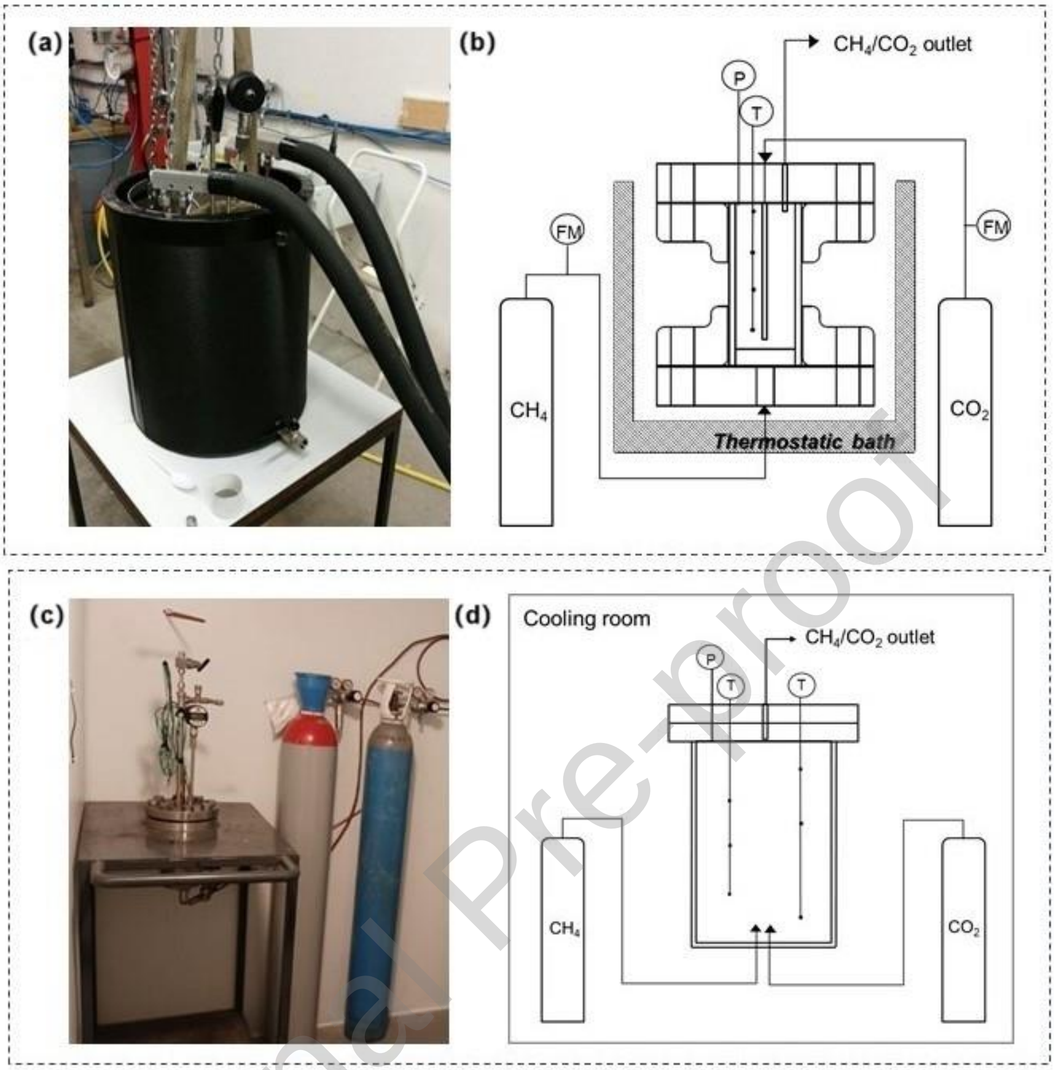


Fig. 3. UNIPG reactors: a) picture of the reactor in the thermostatic bath; b) schematic of the reactor in the thermostatic bath; c) picture of the reactor in the cooling room; d) schematic of the reactor in the cooling room.

NGH formation starts with methane injection in the sediments saturated with water, which pressurizes the reactor to the initial pressure P$_i$. During hydrate formation, temperature starts increasing due to exothermicity and the internal pressure decreases. The formation is completed when T and P are constant. Equation (1) and Equation (2) calculate respectively the number of hydrate moles formed in the system and the pore saturation.

$$n_{hyd} = \frac{V_{pore}\left(P_i Z_f - P_f Z_i\right)}{Z_f\left(RT - \frac{P_f}{\rho_{hyd}}\right)} \tag{1}$$

$$s_H = \frac{n_{hyd}\frac{1}{\rho_{hyd}}}{V_{pore}} \tag{2}$$

Where: P_i and P_f are the initial and final system pressure respectively; Z_i and Z_f are the compressibility factors, ρ_{hyd} is the ideal molar density of hydrate, n_{hyd} is the number of formed hydrate moles and V_{pore} is the total volume of sand pores. A detailed description of the methodology is given in [13].

At the end of the hydrate formation tests, the dissociation occurs and the pressure increase is used to quantify the total moles of CH4 involved in the hydrates.

For CO_2 replacement tests instead, at the end of the formation, CO_2 is injected with two different methodologies: depressurization or thermal stimulation.

In the first method, pressure reduction destabilized methane hydrates, and pure carbon dioxide was injected. Thermal stimulation involves CO2 injection while increasing internal temperature while maintaining pressure relatively constant. Two gas analyses were conducted: the initial analysis measured the composition of the gaseous phase before the replacement, while the second analysis assessed the composition of hydrates at the conclusion of the process.

Some values can be calculated: moles of CH_4 hydrates involved in the replacement process and new CO_2 hydrates were formed. A detailed description of the two processes is given in [44].

During the project, UNIPG performed several experimental tests via the described experimental equipment on the effect of sediments' properties, such as salinity, grain size or typology of sands. A complete illustration of the UNICH reactor (fabricated and assembled by RDPower s.r.l. in Terni, Italy), employed to produce gas hydrates is presented in Fig. 4. The reactor, , is composed of AISI 316L stainless steel with an internal volume of 350 mL and an operating pressure up to 20 MPa. The details of the equipment is given in [35-37].

Fig. 4. Picture of the multiple-reactor apparatus (left panel); picture of the PLC control system (right panel). Modified with permission from Ref [37] Copyright (2017) ACS.

The aim of hydrates synthesis in the UNICH reactor was the preparation of CH_4 and CO_2 hydrates and hydrate after the CO_2 replacement in presence of different media (Table 1) to characterize them by Raman spectroscopy and microscopic characterization (SEM images). Hydrate samples were synthesized in a custom copper sample holder placed inside the reactor and then transferred to a Linkam THMS600 cell for low-temperature Raman characterization. Gas hydrates were formed at 1 °C and a constant pressure of 3.5 MPa for CO2 and 7.0 MPa for methane. This pressure was chosen to prevent CO_2 liquefaction at higher pressures. The samples were maintained under these conditions for 24 hours. After formation, the hydrates were stabilized by subcooling, and the pressure was gradually released to allow for the removal of the formed hydrates.

Table 1. Media used for the formation of gas hydrates and respective concentrations and volume.

	CH_4 Hydrate	CO_2 Hydrate	CO_2/CH_4 Hydrate
UP water	1mL	1mL	1mL
Seawater	1mL	1mL	1mL
SDS	0.2 mg/mL	-	0.2 mg/mL
Natural sediment	1.396 g/mL	1.336 g/mL	1.363 g/mL
Synthetic sediment	1.335 g/mL	1.321 g/mL	1.364 g/mL

For CO_2 replacement, following the stabilization of CH_4 hydrates for 5 days, the pressure was reduced from 7 MPa to approximately 3.5 MPa, and cooled CO_2 was introduced into the reactor at a constant pressure. Throughout the gas phase exchange, the hydrate was stabilized by lowering the temperature to prevent CH_4 hydrate dissociation. The gas mixture composition was monitored at the end of the exchange using an IR detector (Premier series of IR gas sensors by Dynament (UK) for CO_2 and CH_4).

3.2 Microscopic characterization

The morphological characterizations of gas hydrates synthetized in different experimental condition were performed by using Field Emission scanning electron, coupled with an energy dispersive X-ray spectrometer and with a temperature-controlled equipment that allows to acquire SEM images up to the temperature of −30 °C. The samples were stored in liquid nitrogen and transferred to the cooling stage in the SEM instrument at a temperature of -25 °C.

In this case, the representative portions of the hydrate samples were transferred to the homemade SEM sample holder and transferred to the cool stage (all operations on the samples, from selection to portion cutting, were carried out in liquid nitrogen) [41,45].

Raman spectra of gas hydrates were obtained according to method reported in [41,45]; in this application, customized copper sample holders were used and the samples were transferred to the Linkam unit of Micro-Raman; to avoid the formation of the condensed water at the low operating temperature, a flow of nitrogen was used.

3.3 Mechanical characterization

The mechanical characterization has been performed by measuring porosity, density, P-wave and S-wave velocities of 51 specimens, with the boundary conditions of ambient pressure and temperature = -40 C. We realized 25 mm diameter by 25 mm height cylindrical specimens. Specific cases were realized via 3D printing (Fig. 5(a)) being filled by synthetic well-sorted spherical spheres with diameter of 150-250 µm made of Pure Quartz (PQ) as shown in Fig. 5(b-d). Another set of cases was filled with a Natural Sand (NS) showing typical tholeiitic basalts composition [46]. The Natural sands is characterized by a poorly sorted and angular grains ranging from ~2 mm to ~0.5 mm in size (Fig. 5(b-f)). Each sample was weighted immediately after removal from the chiller and precisely measured with a digital calliper. Then Bulk density (ρ_b) has been calculated by meaning of weight/volume ratio.

Grain density (ρ_g) of PQ and NS was measured by using a helium pycnometer. We used a Anton Paar Ultra-pyc 5000 that is characterized by an accuracy of 0.02% and repeatability of 0.01%.

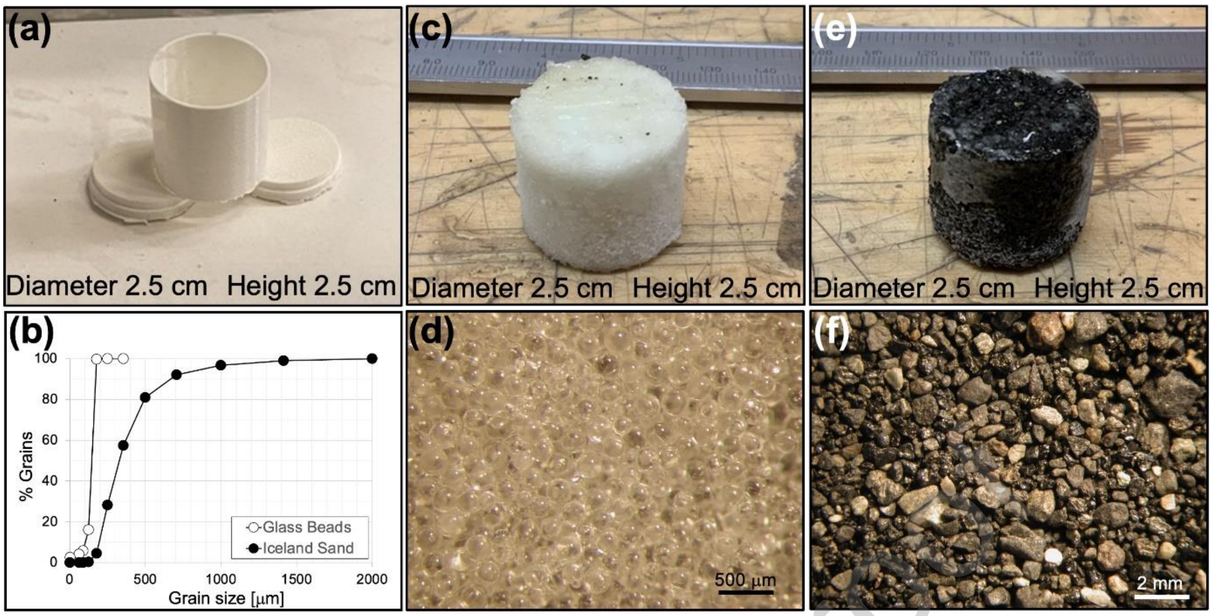


Fig. 5. a) Sample cases b) Grain size curve of both Pure Quartz (PQ) and Natural Sand c) NS hydrate sample and d) Optical microscope image of NS e) NS hydrate sample and f) Optical microscope image of NS. Reprinted with permission from Ref [44] Copyright (2023) Elsevier.

Knowing bulk density of each sample and the grain density of the two sands (from pycnometer measurements), total porosity (φ_t) has been calculated with the equation $\varphi_t = (\rho_g-\rho_b)/(\rho_g- \rho_h)$ by assuming $\rho_h=0.93$ to be the density of the hydrates [47]. It is worth noting that the effective (connected) porosity (φ_e) can be assumed as equal as the total porosity (φ_t) since all samples were made of unconsolidated sediments.

A multiplexed Mistras Eurosonic system ultrasonic device USB 8 M 8-channels generator has been used for Elastic wave velocity measurements. This ultrasonic device generator works with piezoelectric transducers with a frequency of 1 MHz. Two identical P-wave (or S-wave) transducers were attached to the two circular bases of the sample to allow signal propagation through the sediments using the pulse transmission technique [48]. The filtering, amplification and quantification of the waveform was controlled by the USB 8 M device. Waveforms were then recorded by using the software "Mistras Ultrasonic EuroscanV" and then exported as text files. A custum-made Python coden has been then used to pick the first arrival of both P- and S-waves. To be noted that the errors associated to such methodology is on the order of 10^{-4} to 10^{-2} [17]. All measurements of elastic wave were conducted in the axial direction of the samples at ambient pressure and temperature conditions. After laboratory measurements, we calculated dynamic elastic moduli (Ed and νd) as reported in [43]. All measurements have been conducted at the Engineering Department Laboratory of the University of Perugia and at the Rock Mechanics and Earthquake Physic Laboratory at Sapienza Earth Science Department.

3.4 Theoretical model

In literature, several theoretical models are available to describe the elastic properties of the NGH bearing sediments [49]. Here, we have adopted the method proposed by Carcione and Tinivella [50]; here Biot theory was modified in order to consider partially frozen porous media and a fluid part composed by a mixture of two immiscible, viscous, compressible fluids. All details are reported in [49]; we reported only the main concepts. The above theory includes, moreover, the effects due to (i) the interaction between grain and NGH (described by the tortuosity terms) and (ii) the grain cementation, and the consequent increase of the matrix rigidity, due to the high NGH concentration [50]. The cementation is included in the theory thanks to the percolation theory [3] that models the transition from a discontinuous state (low NGH concentration without cementation) to a continuous state (high NGH concentration with the presence of cementation between the grains). The model was calibrated by using Ocean Drilling Program data as reported in [51], in order to estimate all the empirical parameters involved in the velocity evaluation. This model is approximated in the range of seismic frequency by using the approach of the Biot-Gerstma-Smith equations. The theory allows models of both compressional and shear wave velocities versus NGH concentrations. Then, the theoretical velocity is used to estimate the concentration by fitting the velocity estimated from seismic or laboratory data [2, 3]. The theoretical model and this approach was successfully validated in the previous works by using both well, laboratory and seismic data [52, 53]. Note that if NGH/free gas is present, the experimental velocity is higher/lower than the theoretical velocity evaluated for water bearing sediments.

3.6 Gas separation section

In the PoliTo lab, a constant volume/pressure decay membrane-based gas separation test rig was employed to assess the isothermal permeability and selectivity of membranes, with particular reference to CO_2 and CH_4 (Valves V1 and V2 in Fig. 6). Valve V3 is a diverting valve that allows gas to enter a 1L supply tank. Valve V4 facilitates gas flow through a series of two pressure reducers, stabilizing output pressure despite supply pressure variations during testing. Valve V5, a three-way valve, directs the gas to either the feed side or the permeate side of the membrane. The climate chamber, made of FDM, houses the membrane and can regulate temperature from -20°C to 80°C. Valve V6 isolates the permeate side from the feed side. TI and PI are temperature sensors and pressure transducers, respectively. Valve V7 connects the permeate side to the exhaust and a volumetric flow meter, directing flow either directly to exhaust or through the flow indicator depending on the position of V9 (a three-way valve). A vacuum pump system is available to evacuate any gases in the circuit.

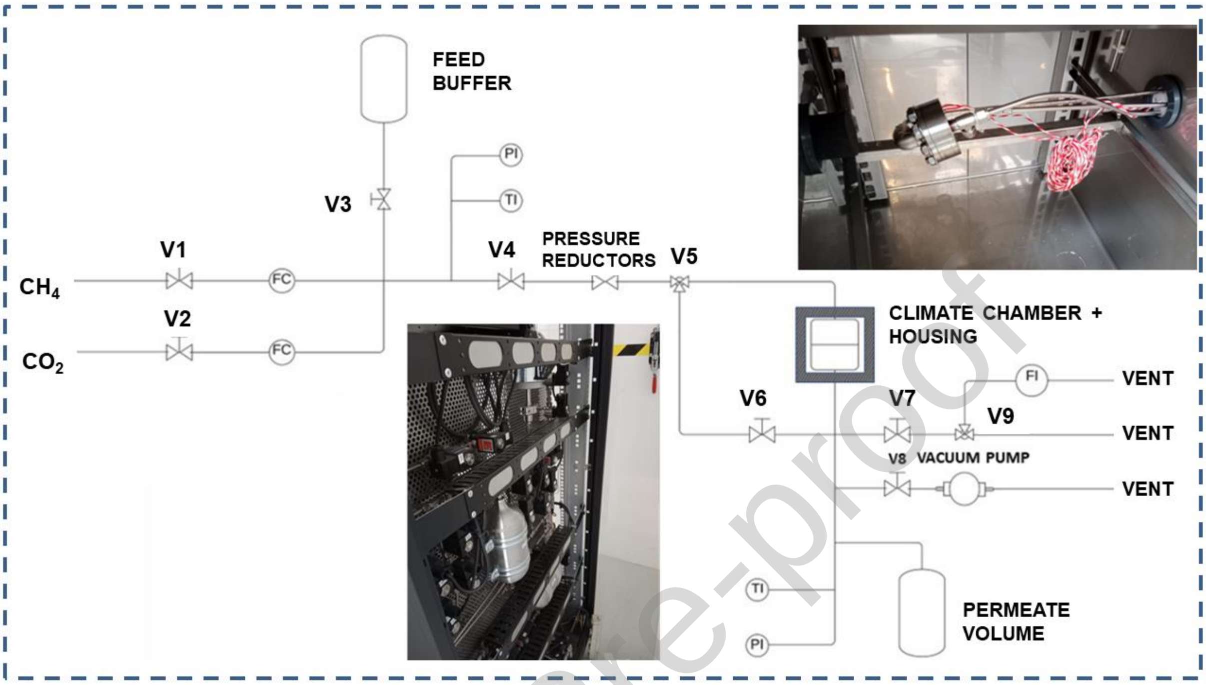


Fig. 6. Plant diagram for gas separation with membranes. Experimental bench of the Polytechnic of Turin located at the "CO_2 Circle Lab" laboratory in the "Environmental Park" innovation hub.

The tested membrane was Matrimid 5218 membrane, synthesized by the Università di Bologna through the polycondensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diaminophenylindane with a blend of two cycloaliphatic monomers. Matrimid chemical structure and membrane tested in the test rig are shown in the Supplementary Material.

Isothermal tests were conducted at 20°C with supply pressures ranging from 2-8 bar to assess the membrane permeability to CH_4 and CO_2. Permeability and selectivity were evaluated when the permeate pressure curve slope is linear (**Error! Reference source not found.**).

$$P_i(p_f) = \frac{V_d \cdot l}{\Delta p \cdot A \cdot R \cdot T}\left(\frac{dp}{dt} - \frac{dp_{leak}}{dt}\right) \tag{3}$$

$$\alpha_{i/j} = P_i/P_j \tag{4}$$

Where P_i is the permeability of gas i in Barrer, V_d is the permeate volume equal to 20.76 cm^3, l is the membrane thickness in cm, Δp is the pressure difference between feed side (p_f) and permeate side of the membrane in $cmHg$, A is the surface of the membrane equal to 5.91 cm^2, R is the gas constant equal to 0.2782 $\frac{cm^3\ cmHg}{K\ cm^3_{STP}}$, T is the working temperature in Kelvin (all the experiments were performed at 293.15 K), $\frac{dp}{dt}$ is the derivative of permeate pressure in time in $\frac{cmHg}{s}$, and $\frac{dp_{leak}}{dt}$ is the derivative of leakage pressure in time.

The description of the experimental setup is given in [54]. The theoretical framework for analyzing methane upgrading from NGH reserves via a countercurrent membrane module is inspired by [55], emphasizing designs with multiple separation stages for efficiency. Particularly, a two-stage series configuration with recirculation is highlighted for its effectiveness in methane sweetening, accommodating four distinct case studies based on pressure differential methods. The authors in [14] proposed an optimization model focusing on optimal configurations, system design, and operational conditions to achieve desired methane purity, considering constraints like pressure limits and membrane area. This model employs multi-objective optimization, balancing specific membrane area and energy consumption against process requirements and constraints, utilizing project-specific input data for feed concentration, temperature, and pressure.

3.7 Energy evaluations

The proposed technological solution, which includesCO_2 injection and methane release from hydrate geological sites was modeled and evaluated in terms of mass and energy balances.

As shown in Fig. 1, the system boundaries include: i) CO_2 injection in the NGH sediment; ii) CO_2-CH_4 output mixture filtration by membranes; iii) CO_2 recirculation. The reference functional unit is the unitary physical amount of injected CO_2 (expressed either in kg or in Nm^3). The evaluation uses experimental data from lab tests and on theoretical calculations and it is aimed to compare the energy consumption for methane recovery and for CO_2 sequestration to the energy amount contained in the recovered methane to.

The CO_2-CH_4 replacement process presents some energy costs: the first one is that related to the CO_2 compression for its injection in the sediment. The compression workwas calculated as a multi-stage adiabatic process with inter-cooling with a compression efficiency of 85%. The experimental data shown in [56] were used to complete the calculation: i) injection pressure of about 30 bar; ii) the percentage of CO_2 injected in the reactor which forms hydrates is equal to 25 %; iii) the percentage of the effective replacement is equal to 55%. In addition, the gaseous CO_2/CH_4 mixture for the separation section is considered equal to 70% CO_2-30% CH_4 in volume as discussed in [44]. The energy consumption of the separation section is equal to 4.9 MJ/kg$_{CH4}$ and the purity of the obtained methane is equal to 98.5%, as described in Section 4.5 of the present paper. The methodology used for the calculations is given in [13].

3.8 Economic evaluations

Considering the most promising technologies, the strands of institutional support and incentives and the first international experiences, the analysis of the innovative NGH based process, is based on the fact that a strategic repositioning of the industrial operators and a multi-year financial investment strategies is fundamental.

In this study, a regulation system was applied to give room for new efficient incentives to grasp private investments. For Investors the optimal Medium/Long Term allocation for financial resources generated by Medium/Long Term accumulation can only be on sectors and/or industries that make their Medium/Long Term connotation their main characteristic, both for their intrinsic solidity patrimonial, and because their offer has to face a widespread demand that wants security and builds its rigidity around it. It is quite clear that rigidity of Energy demand is a topic item for our Deal under investigation and it gives room for IRR no longer contingent, so attracting institutional investors searching for opportunities to invest in fully collateralized regulated essential asset. So, “public interest” is the best way di fulfill the hedging profile of investments in a fully privatized world.

We applied “implementation tests” for a regulatory model that could give room for effective and efficient private investment’s incentive. It is crucial for such a capital intensive sector. In particular, the so-called “RAB Regulation Model” (Fig. 7) is applied in a lot of European utility regulation experiences [57].

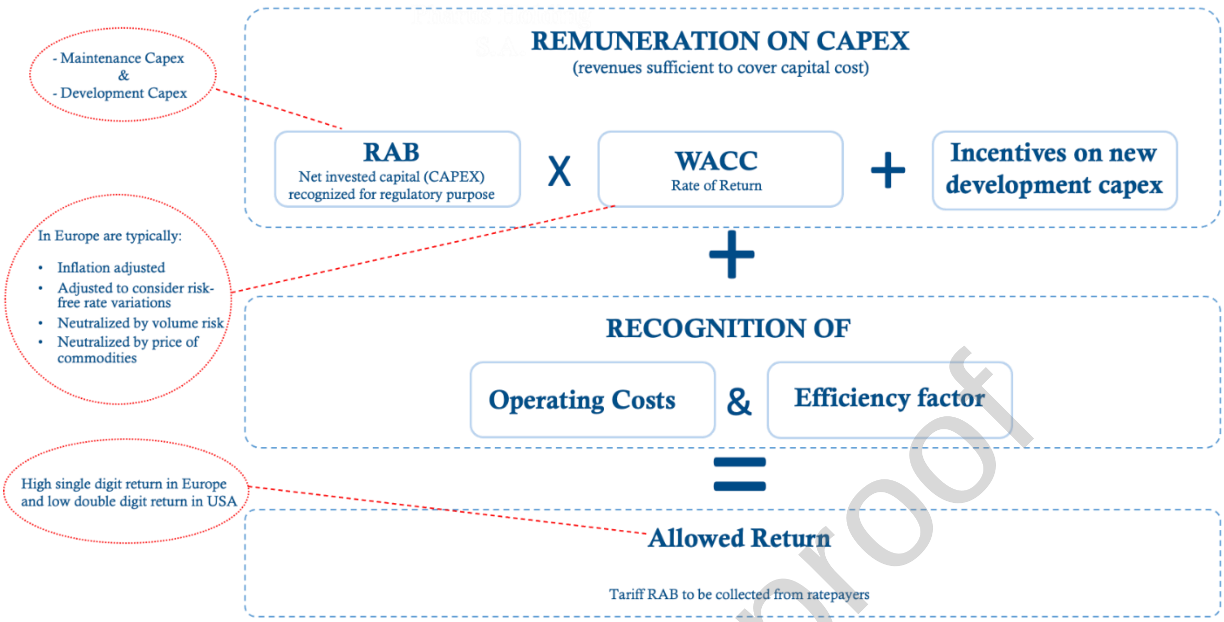


Fig. 7. RAB Regulation Model scheme.

By a comparison of international regulatory experiences in Capital Incentives Regulatory Schemes, consistent affordability could be found for the scheme of “RAB Regulation Model” applied today as “optimal” European scheme to implement an effective incentive regulation public strategy to improve infrastructural energy investments.

4 RESULTS AND DISCUSSION

4.1 Hydrate formation and CO_2 replacement

UNIPG completed experimental tests on how the sediments’ properties affect both the methane hydrate formation and CO_2 replacement.

The effect of water salinity was investigated in a pure quartz sediment saturated with hydrates at 10% [56], showing the inhibiting effect of salt (37 g l^{-1} NaCl) on the methane hydrate formation. As a matter of fact, the amount of methane moles entrapped in the hydrate phase with respect to the total moles injected inside the reactor passes from 12% in pure water to 7% in salt water. As far as the CO_2-CH_4 replacement is concerned, the trend is opposite. With salt, the percentage of methane moles effectively replaced by CO_2 is equal to 55 % in presence of salt instead of 32 % in pure water. In parallel, during CO_2 injection not only replacement takes place, but also new CO_2 hydrate formation. Also new CO_2 hydrates decrease in presence of salt, passing from 50% to 47% of the total moles in the hydrate phase. In presence of salt, the decrease in the formed hydrate moles is lower for CO_2 than for CH_4. In the Supplementary material, the comparison between mass balances in presence of pure water and salt water are shown in graphs.

This promoting effect of salt on the replacement process was investigated also in [58], finding that the inhibiting effect of salt is stronger for methane hydrates rather than for CO_2 hydrates. This brings to a larger distance between the p-T profiles of the two types of hydrates and, therefore, from a thermodynamic point of view, sodium chloride can be considered a promoter of the CO_2-CH_4 replacement process, as shown in Fig. 8. The new contribution to this point lies on the differential thermodynamic inhibition by NaCl resulting in higher distancing between the two equilibrium curves due to salinity.

The results on the inhibiting effect of NaCl on pure hydrate formation are consistent with literature, as reported in [59]. As far as the CO_2/CH_4 replacement process is concerned, it is well-known that, from the point of view of phase equilibrium, the equilibrium curve of CO_2 hydrate is lower than that of CH_4 hydrate [60]. As specified in [61], longer induction time and lower hydrate formation due to initial salinity, can be caused by the lower energy state of the system.

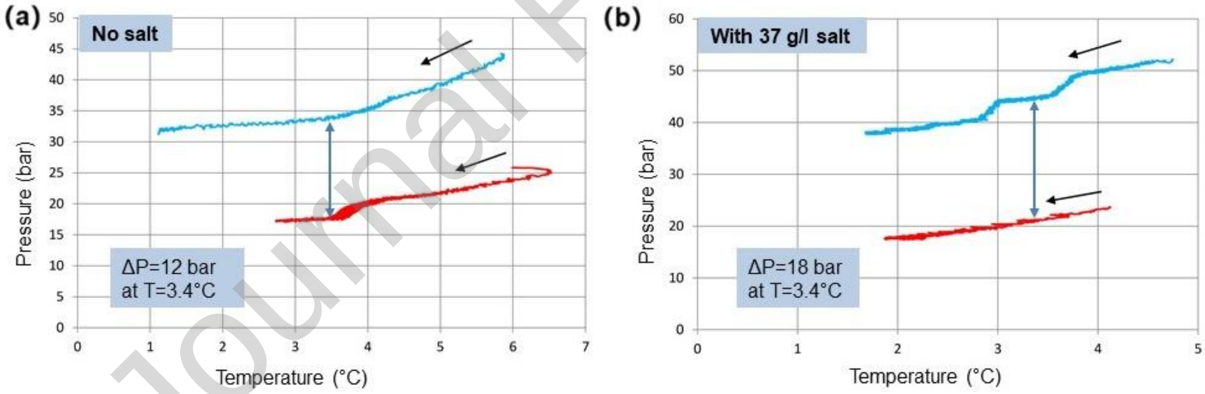


Fig. 8. p-T curves of methane hydrates and CO_2 hydrates with and without salt. Modified with permission from Ref [58] Copyright (2020) MDPI.

Also the nature of the sediment affects the methane hydrate formation. In [62], a sediment formed by pure quartz was compared to a natural sand with similar porosity but with heterogeneity in terms of grain size and chemical composition. The pure quartz sand was an homogeneous sediment, with grain diameters equal to 200 μm and spherical shape. The natural sand instead had a diverse grainsize distribution (mainly in the range 100-600 μm) and several compounds in addition to SiO_2. Results show that the heterogeneous grainsize and porosity, the chemical composition of the sediment affect the formation process. In particular, methane hydrate formation requires higher pressures and longer time in presence of natural sand rather than pure quartz. While pure quartz sand may influence the formation process just as porous media, the natural sand acts like both a thermodynamic and a kinetic inhibitor, due also to the significant reduction of the hydrate formation rate with the decrease of pressure. This can be explained also in terms of permeability, a parameter that affects the hydrate formation rate. In [63], the authors affirmed that sands with a regular pore size, as in the tested pure quartz sand (with constant shape and size of the grains) have higher permeability values and therefore higher hydrate formation rates.

The effect of grainsize on both methane hydrate formation and CO_2 replacement was also experimentally tested in [64]. Two sediments with different grainsize were compared: 150-250 μm and 400-500 μm. The methane hydrate formation was faster and more massive in presence of the 150-250 μm size sediment, while the CO_2 replacement and also the amount of CO_2 capture was higher in presence of 400-500 μm size sediment. So, a sediment which is favorable with methane hydrate formation and inclined to preserve the hydrate structure in it, could bring to a reduced exchange between the guest species and therefore a lower extent of the CO_2-CH_4 replacement. Making a comparison with literature, the trend is confirmed by [65]: silty sand with a diameter of 30-50 μm improves the water conversion in hydrates, favoring the formation. UNIPG produced also several types of hydrate samples, with and without sand, to study at a microscopic level the replacement process. In particular, the CO_2-CH_4 replacement process was performed via thermal stimulation and depressurization. In both cases, the final concentration of CO_2 in the hydrate phase was about 71% in volume [44].

4.2 Microscopic characterization

Temperature-controlled SEM observation provided morphological and physical properties related to composition and to gas hydrate preparation conditions. In particular, the morphologies of different gas hydrates produced from UNIPG are reported in the Fig. 9 [42]; as it is possible to observe the surface of gas hydrates, prepared in ultrapure water (CO_2GHs), shows spherules with sizes of few tens of micrometres while the gas hydrates prepared in presence of sediments($CO_{2(sand)}$GHs), show a more compact morphology as in NGH with the presence of very dense crystals separated by empty spaces. In addition, the SEM images of mixed hydrates, (CH_4/CO_2)GHs, show a morphology similar to those present on CO_2GHs; in this case, the increase in the specific surface area of the gas hydrates can probably favour the adsorption of gas molecules in the formation of hydrates.

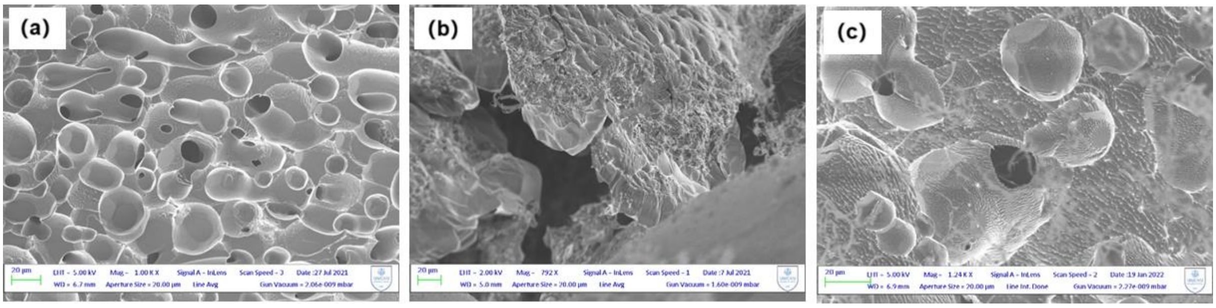


Fig. 9. SEM images showing the surface morphology of different types of gas hydrates from UNIPG: (a) CO_2GHs, (b) CO_2(sand)GHs, and (c) (CH_4/CO_2)GHs. Modified with permission from Ref [42] Copyright (2022) Elsevier.

The morphologies of the gas hydrates produced from UNICH in different experimental conditions are reported in Fig. 10.

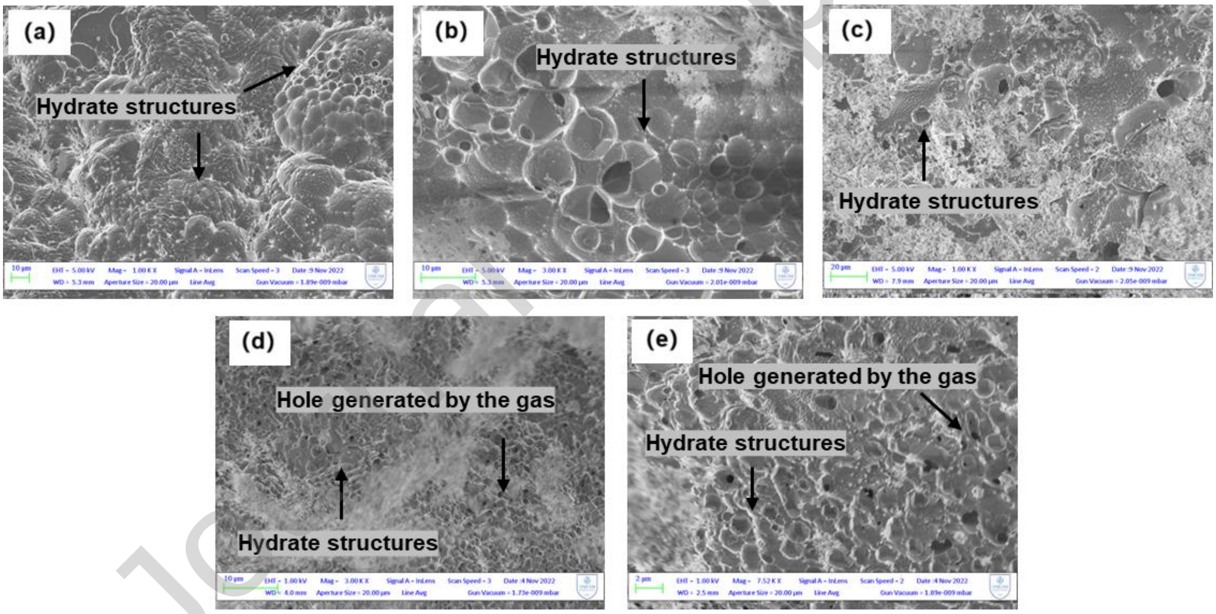


Fig. 10. SEM images of CO_2/CH_4-hydrates in (a) SDS, (b) natural sand, (c) synthetic sand, (d) UP water, and (e) seawater from UNICH. Modified with permission from Ref [44] Copyright (2022) Elsevier.

The obtained results demonstrated how different experimental conditions can influence the morphology of gas hydrates; also in this case, the nucleation modalities of the water crystals that formed the respective gas hydrates strictly depended on the composition of the gas and on the presence or absence of sediments.

Raman measurements of the of CO_2GHs and CO_2(sand)GHs, produced from UNIPG, confirmed the gas uptake in the hydrate structures by identification of the fingerprint of CH_4 and CO_2 in the hydrates. The Raman spectra of CO_2GHs and CO_2(sand)GHs related to OH stretching bands of water at different temperatures are reported in Fig. 11(a,b); the study of these bands can in fact describe the changes in the main properties of water molecules in the hydrate structure due to the effect of temperature [66,67].

In particular, the CO_2 hydrates in the presence of sand were characterized by a less ordered structure showing a stability that was maintained with the variation of temperature; the shifts of the CO_2 Fermi diad permitted to describe the expansion of the cages. The calculated SD indices related to OHs of water, showed high correlation with the increase of temperature (Fig. 11(c)); in this case CO_2(sand)GHs showed the least ordered water structure, while (CH_4/CO_2)GHs the most ordered one, with the most quantity of CO_2. These results confirmed therefore a favourable replacement of methane and that, through this process, a stronger lattice was obtained when compared to that containing only one species [42]. In addition, with the increase of temperature on CO2GHs_sand, a linear blue shift of the CO_2 Fermi-diad peaks (Fig. 11(d)) has been obtained, demonstrating an enlarge of the cage respect due to the presence of sand.

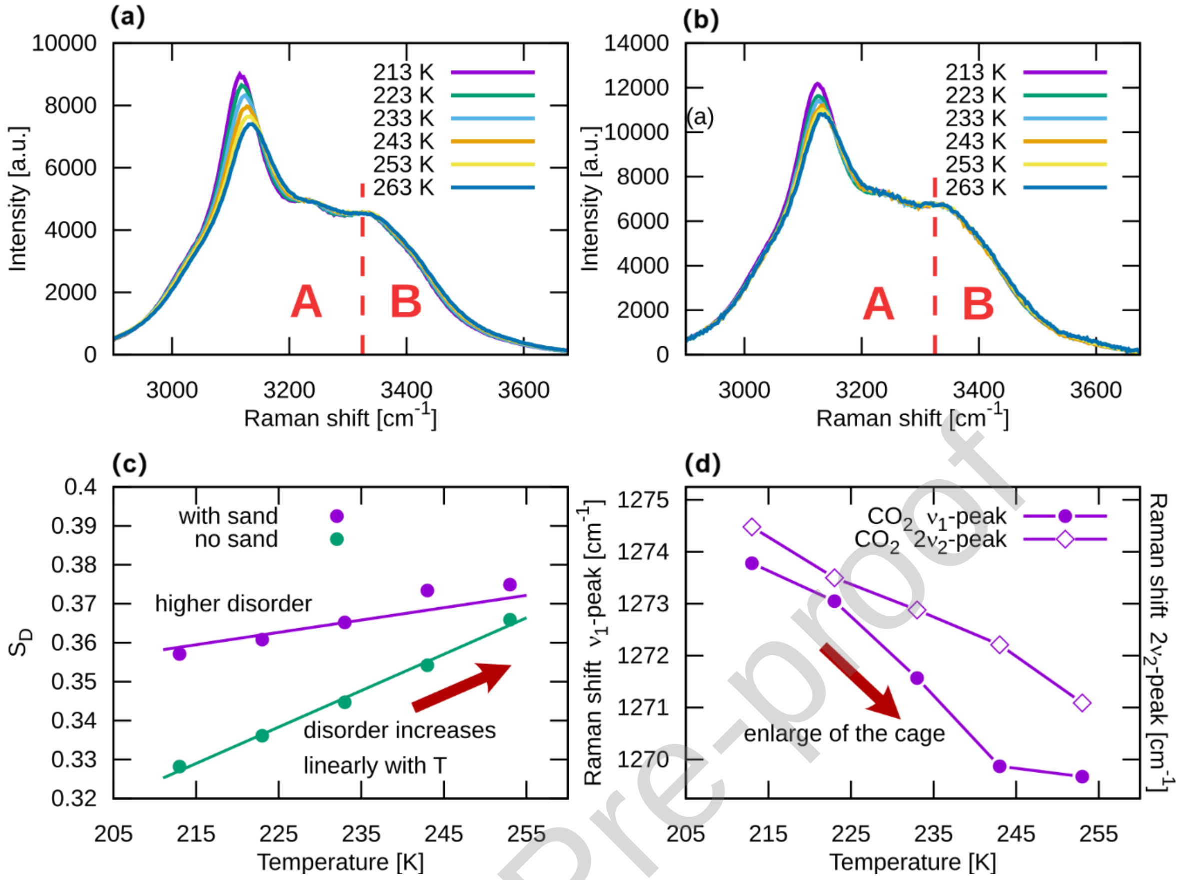


Fig. 11. Raman spectra of OHs vibration bands at different temperatures of CO2GHs (a) and CO2(sand)GHs (b); correlation of SD concentration index as function of change in temperatures (c) Raman shift of CO2 Fermi diad at different temperatures of CO2GHs_sand (d). Modified with permission from Ref [42] Copyright (2022) Elsevier.

Gas hydrates produced from UNICH (CH_4-GHs CO_2-GHs, and CO_2/CH_4-GHs) were analysed by Raman spectroscopy to investigate the structural changes in the water cages, the gas uptake in the hydrate structure, the CH_4 cage occupancies, the hydration number, and the yield of CO_2 replacement at constant pressure [45]. These measurements showed a high occupation of large cages in all samples (> 96 %) and a high variability in the occupation of small cages for CH4-hydrates. Raman spectra of CO_2/CH_4-hydrate obtained by replacement process in different experimental conditions and reported in in Supplementary Material. highlighted the presence of both CO_2 and CH_4 in the hydrate structure, confirming the success of the exchange experiments.

The cage occupancy calculation of CO_2/CH_4-GHs showed that the higher yield of replacement can be obtained in UP water as opposed to natural sand and seawater. When natural sand and seawater were used to prepare the gas hydrates a noticeable amount of CH_4 was displaced by CO_2.

In these measurements, the calculation and comparison of SD indexes allowed to estimate the structural rigidity of the investigated samples. In fact, when hydrates are prepared in both seawater and synthetic sand, the SD index reveals that CH4-hydrate exhibits the highest rigidity (the lowest SD), while CH4/CO2-hydrate shows the least rigidity (the highest SD) [45]. These aspects are shown in the Supplementary material.

4.3 Mechanical characterization

The main aim of the mechanical characterization in this work was to give representative input data for the modelling exercise. We then tested two end-members sediments to clarify the role of lithology variations combined with the mechanical changes induced by the replacement process. Axial P- and S- wave velocity, together with bulk density and porosity measured on both PQ and NS pre and after replacement from [44] are reported in Table 2. A detailed description of these data is reported in [44], while from a general point of view in can be firstly observed that Natural Sand (NS) is characterized by higher porosity and faster seismic velocities, with larger V_p/V_s ratios in comparison to synthetic PQ sands. This is a counterintuitive data since usually smaller grains lead to higher porosity that should correspond to lower velocity [68]. However, the angularity of the NS sediments and the matrix velocity (much higher for NS) is crucial in increasing porosity and velocity respectively, justifying the observed data [44].

As previously noticed, the two families of sample (PQ and NS) were investigated both pre and post CO_2 replacement highlighting clear differences. Results reported in table 2 shows that for pre replacement PQ, the mean V_p is 2.73 km/s and V_s is 1.51 km/s. For post-replacement samples V_p increases of about 12% for being mirrored by V_s that show an increase of about 16% for . NS samples are characterized by a similar behaviour; here the replacement process results in an increase of P-wave Velocity from 3.31 km/s up to 3.37 km/s ad S-wave Velocity from 1.74 km/s up to 1.81 km/s.

From a general point of view, after CO_2 replacement process we observe an increase of the mean seismic velocity for both sediments while the V_p/V_s ratio on both NS and PQ samples sightly decrease. Calculated E_d shows a mean value of 9.67 GPa that reaches 13.06 GPa (+35%) on PQ samples pre and post replacement respectively. Similarly, E_d goes from 12.95 GPa to 15.1 GPa (+16%) on NS samples after replacement while Dynamic Poisson’s ratio (ν_d) show almost constant values pre and post replacement for both PQ (0.26) and NS (0.30). To be noted that E_d values for PQ are larger with respect to static Young’s modulus (E_s) values measured on similar hydrate-bearing sediments made of quartz sand by Li et al. [69]. This is due to the well-known differences between dynamic (derived from seismic wave measurements) and static (derived from deformation test) elastic moduli as extensively reported in literature [70-72] that usually results in larger values for dynamic moduli with respect to static. Summarizing, CO_2 presence clearly increases V_p and E_d when hosted in natural sediments whilst this increase is much lower for synthetic sands. The most important differences between the two sediments, are grain shape, grain size, and level of sorting being those very important features for the mechanical behaviour of sediments [73,74]. Thus, replacement process surely influences the mechanical properties of hydrates however, the amount of these changes are likely to be strongly related the characteristics of the reservoir matrix in terms of lithology.

Table 2: Results of the samples mechanical characterization

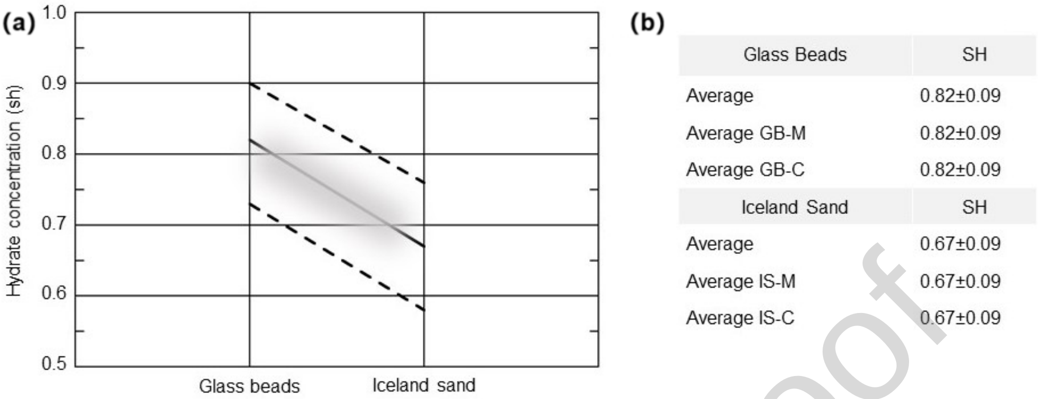
Glass Beads	**Bulk density [gr/cm^3]**	**Porosity [%]**	**Vp [km/s]**	**Vs [km/s]**	**Vp / Vs**	**Ed [GPa]**	**nd**	**Lithology**
Average	1.67 ± 0.0209	52.64 ± 1.3308	2.90 ± 0.0029	1.63 ± 0.0162	1.81 ± 0.0009	11.37 ± 0.81	0.26 ± 0.026	Well sorted, well rounded 100% SiO_2 sands. Grain size: 150-250 um
Average GB-M	1.67 ± 0.0211	53.01 ± 1.3413	2.73 ± 0.0027	1.51 ± 0.0151	1.85 ± 0.0009	9.67 ± 0.46	0.26 ± 0.022	
Average GB-C	1.68 ± 0.0207	52.27 ± 1.3024	3.07 ± 0.0030	1.74 ± 0.0174	1.77 ± 0.0009	13.06 ± 0.15	0.26 ± 0.013	
Differences %	0.69 ± 2.07	-1.39 ± 2.49	12.33 ± 0.811	15.68 ± 0.638	-3.88 ± 1.257	34.99 ± 4.76	-0.06 ± 8.56	

Iceland Sand	Bulk density [gr/cm^3]	Porosity [%]	Vp [km/s]	Vs [km/s]	Vp / Vs	Ed [GPa]	nd	Lithology
Average	1.66 ± 0.0210	62.34 ± 1.3352	3.34 ± 0.00334	1.77 ± 0.0177	1.90 ± 0.0380	13.98 ± 0.30	0.30 ± 0.04	Poorly sorted, poorly rounded tholeiitic basalt sands. Grain size: ~0.5 - ~2 mm
Average IS-M	1.64 ± 0.0215	63.31 ± 1.3713	3.31 ± 0.00331	1.74 ± 0.0174	1.93 ± 0.0385	12.95 ± 0.27	0.30 ± 0.04	
Average IS-C	1.68 ± 0.0204	61.28 ± 1.2991	3.37 ± 0.00337	1.81 ± 0.0181	1.87 ± 0.0374	15.10 ± 0.39	0.30 ± 0.04	
Differences %	2.40 ± 2.15	-3.21 ± 2.053	1.67 ± 5.975	4.22 ± 2.36	-2.88 ± 1.618	16.54 ± 2.08	-2.01 ± 13.25	

4.4 Theoretical model

The mechanical characterization of the gas hydrate samples has been used to estimate the hydrate concentrations by using the model proposed by [3, 75] as described in the section 3.4. The elastic properties of the components (natural sand or pure quarts, gas hydrate and water) and the Poisson ratio of the system (Table 2) are used as input parameters. We used the Poisson ratio because it is directly related to the mechanical properties of the samples. For the samples created with the natural sediments, we adopted the values reported in Waite et al. [76], while the mechanical properties of samples created with the pure quartz are provided by the manufacturer.

The hydrate concentration (sh) of the samples is estimated, increasing the sh in the theoretical formula until the theoretical Poisson ratio fits the measured one. We obtain the same results for all values indicated in Table 2 as Average, Average GB-M and Average GB-C. For the glass beads, the sh is equal to 0.82 with an error equal to 11%, while for the natural sediments, the sh is equal to 0.67 with an error equal to 13%. Therefore, the two types of sediments have the same hydrate concentration considering the estimated error (Fig. 12). Finally, we draw the conclusion that the samples are partially hydrate saturated.



Glass Beads	SH
Average	0.82±0.09
Average GB-M	0.82±0.09
Average GB-C	0.82±0.09
Iceland Sand	SH
Average	0.67±0.09
Average IS-M	0.67±0.09
Average IS-C	0.67±0.09

Fig.12. Hydrate concentrations with the estimated error for the two types of sediments.

4.5 Gas separation section

Pure-gas permeability isotherms were measured for CH_4 and CO_2 at 20°C and the results are shown in the Supplementary material. The permeability of the Matrimid membrane to CO_2 is not very high but remained approximately constant at 8 barrers at different test pressures. On the contrary, the membrane has an excellent ability to select the gas to pass. The selectivity varies during the different tests with an average value of around 60 and a methane permeability of around 0.13 barrer.

In addition to the membrane permeability and selectivity, other input data for the separation system were used for the model. In particular, the gaseous flow rate is equal to 2.2 m3std/s and the gaseous mixture is 28.59% CH_4 and 71.41% CO_2 at a pressure of 31.16 bar. These are the xperimental data presented in [44].

As results of the optimisation model, the configuration composed of two stages in series with recirculation and two compressors (see Fig. 13) was chosen for the methane upgrade. The optimised system is able to recover 97.1% of the methane contained in the methane obtained from CO_2 replacement with a purity of 98.5%, able to be injected into the grid [14]. Therefore, only 0.61 MW of chemical energy was not recovered and recirculated into the methane extraction system. The specific electricity consumption is 3.5 MJ/kg_{CH4} produced, while the total specific energy consumption (i.e., electrical energy and not recovered chemical energy) is 4.9 MJ/kg_{CH4}, achieving a separation efficiency of 90.5%.

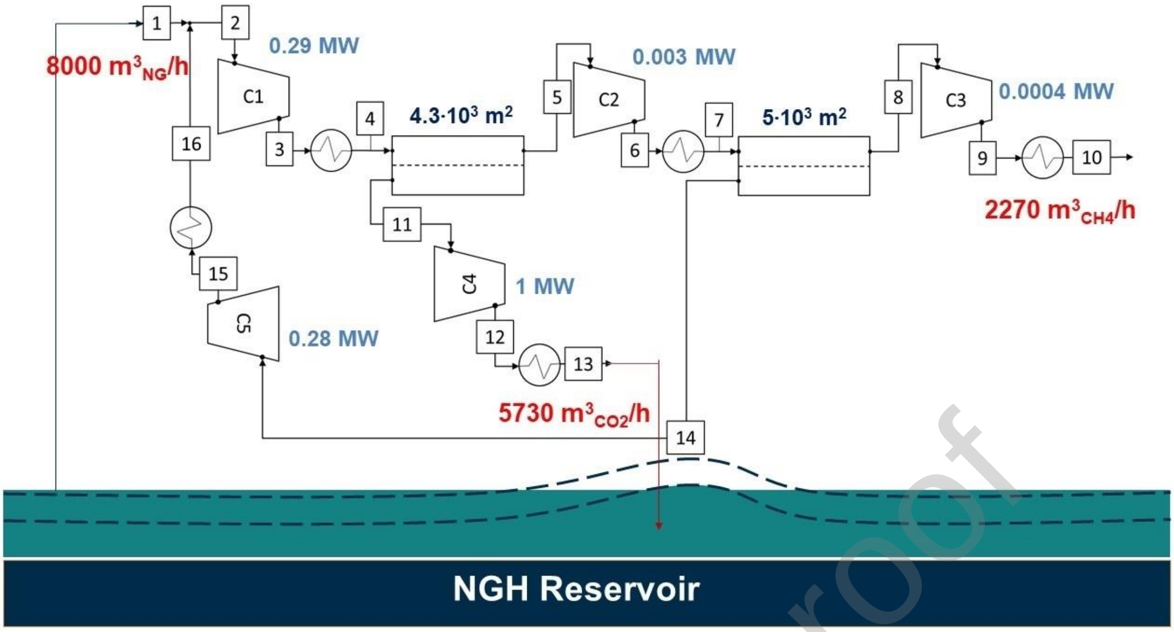


Fig. 13. Mass and energy balance of the system optimisation model.

Table 3. Operating parameters calculated for the proposed configuration in accordance with the steps in Fig. 13.

Stream/Property	Q [m^3(STP)/s]	CO_2 [%]	CH_4 [%]	P [bar]	T [°C]
[1]	2.24	71.4%	28.6%	31	20.0
[2]	2.69	74.4%	25.6%	31	20.0
[3]	2.69	74.4%	25.6%	68.01	67.6
[4]	2.69	74.4%	25.6%	68.01	20.0
[5]	1.08	38.0%	62.0%	68.01	20.0
[6]	1.08	38.0%	62.0%	69.63	21.3
[7]	1.08	38.0%	62.0%	69.63	20.0
[8]	0.63	1.5%	98.5%	69.63	20.0
[9]	0.63	2.0%	99.0%	70	20.3
[10]	0.63	2.0%	99.0%	70	20.0
[11]	1.61	99.0%	1.0%	1	20.0
[12]	1.61	99.0%	1.0%	31	292.8
[13]	1.61	99.0%	1.0%	31	4.0
[14]	0.45	89.0%	11%	1	20.0
[15]	0.45	89.0%	11%	31	292.6
[16]	0.45	89.0%	11%	31	20.0

4.6 Energy evaluations

The energy balance of the proposed process is here discussed while the Figure containing the comparison between the recovered and spent energy is shown in the Supplementary material. The results of both the recovered and spent energy is related to the experimental data described in the previous sections. With a heat of combustion of 45000 kJ kg^{-1}, the recovered energy is 5025 kJ per each kg of injected CO_2 (corresponding to 0.111 kg_{CH4} recovered for each kg of injected CO_2).

The energy cost for CO_2 compression at 30 bar is equal to 322 kJ/kg_{CO2}, while the specific energy cost for the membrane-based separation is equal to 520 kJ/kg_{CO2}. These are the two main costs. In addition, there is also the energy consumption due to the recirculation of the CO_2 separated in the separation section, which is quite low and equal to 8 kJ/kg_{CO2}. The ratio between the spent energy and the stored energy in the recovered CH_4 is 17 %, showing a favourable energy balance.

4.7 Economic evaluations

The economic analysis considers the significant structural impact of transforming the traditional CH_4 production chain into a sustainable “new primary source”. This transformation is made possible by extracting CH_4 from NGH reservoirs in an environmentally neutral manner. This neutrality is achieved by simultaneously injecting CO_2, which enables a new mode of carbon capture and storage. This innovative approach has the potential to create a significant shift in the evolution of international energy mixes [57].

The theme of the security of energy supplies and, therefore, of the availability of essential inputs in the energy generation chains has recently regained its obscured centrality in national and international energy policies and strategies. Not only were the pricing implications the first consequence, but the prospects for national energy (gas) security are of major concern. The European Community has tried to launch a common strategy to recover security of energy supplies. This certainty can only be based on various synergistic lines of action for the purpose:

i. increase in systemic energy efficiency and demand-side management actions, overall with the aim of minimizing the extent and rigidity of Energy Demand in Europe;
ii. the inevitable growth in the demand for energy correlated to economic growth argues in favor of researching and magnifying a new European Taxonomy pragmatically oriented towards not excluding nuclear energy generation and the natural gas supply

chain; all the more reason it can only welcome the development of the NGH associated with the hydrate-based carbon capture extraction processes;

iii. a renewed regulation and management of the storage system is central and functional to maximizing energy security, obviously focused on the security of available supplies.

The global NGH reserves are substantial enough to replace the traditional oil and gas resources. Consequently, NGH has emerged as a strategic and commercially viable resource of global interest in the 21st century. Its industrialization holds significant potential for optimizing the world's energy mix, promoting green development, and achieving peak carbon dioxide emissions and carbon neutrality. The feasibility of CO_2 replacement in hydrate sediments represents a breakthrough in Carbon Capture and Storage (CCS) research and could significantly impact CO2 accounting. Two future integration and application of low-emission gases stemming from innovation acting on NGH could be:

i. Liquefied environmental neutral NGH are as likely to play a key role in the decarbonisation of a lot of sectors in the medium to long term;
ii. NGH could be input for an environmental neutral production of Hydrogen, possibly associated with CCS technologies.

When the technology transition goes from a pilot scale to full industrial scale, it could result in large cash-out (especially CapEx) with significant short-term impacts.

Consequently, clear evidence of a positive return might not be evident in the medium to long term. Therefore, it is crucial to study the alignment between the economic and financial profiles of gas price reductions and the sustainability of the necessary investments. The results of "implementation tests" confirm that a "RAB Regulation Model" could be effective to the reduction of the risk perceived by investors and the opportunity to realize interesting and attractive IRRs in the medium-long term, giving room for effective incentives for private investments in such a sector [77].

5 CONCLUSIONS

The present paper intends giving an overview of the main experimental results obtained by an interdisciplinary Italian research project on the NGH exploitation, with respect to the state of the art, and, on the basis of the experimental results, presenting the overall energy, geophysical and economic evaluations.

The main focus of the project was to develop an integrated process, coupling the CO_2-CH_4 replacement process in NGH sediment with a separation section in which the output CO_2-CH_4 mixture is treated to obtain pure methane for energy purposes and pure CO2 to be reinjected in the NGH sediment. This is an innovative technological solution for the transition to the industrial application of NGH.

Generally, the efficiency of the CO_2-CH_4 replacement process strongly depends on the mutual influence among the properties of water, sediment and the involved gaseous species. At a microscopic level, different organizations of water molecules forming the hydrate crystals depend not only on the gas species and on the presence of sediments, but also on the different experimental conditions.

The main findings are hereunder summarized:

- The presence of salt water positively affects the CO_2 replacement: the percentage of methane moles effectively replaced by CO2 is 55% instead of 32% with pure water.
- NaCl salt brings a differential thermodynamic inhibition on CO_2 and CH_4 hydrates resulting in higher distancing between the two equilibrium curves, resulting in an increase of the methane moles replaced in presence of salt water.
- Both with thermal stimulation and depressurization, the final concentration of CO_2 in the hydrate phase was about 71% in volume.
- The nature of sediment, such as the grainsize, has a great influence on the CO2-CH4 replacement: sediments, which are favourable for methane hydrate formation and help preserve the hydrate structure, as small grainsize sediments, might hinder the CO_2-CH_4 exchange process.
- CO_2 presence in the hydrate phase clearly increases V_p and E_d when hosted in natural sediments much more than in synthetic sands. This was confirmed by Raman analysis: through the replacement process, a stronger lattice is obtained when compared to that containing only one species.
- The mechanical characterization of the produced gas hydrate samples was used to estimate the hydrate concentrations and confirm that they were partially saturated
- A Matrimid membrane with a high selectivity, measured by tests, was used in an optimization model. The optimised process recovers 97.1% of the methane contained in the output mixture obtained from CO_2 replacement with a purity of 98.5%, proper to be injected into the grid.
- The energy evaluations show that the ratio between the energy spent to complete an entire cycle (CO_2 replacement in NGH and purification of the obtained CH_4) over the stored energy in the recovered CH_4 is 17%, resulting in a beneficial energy balance. The technology transition from a pilot scale to full industrial scale could give large cash-out

(especially CapEx) with significant short-term impacts; even though the evidence of a positive return might not be evident in the medium-long term.

- A “RAB Regulation Model” could be effective to the reduction of the risk perceived by investors and the opportunity to realize interesting and attractive IRRs in the medium-long term, giving room for effective incentives for private investments in such a sector.

DECLARATION OF COMPETING INTEREST

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Beatrice Castellani is an advisory board member for Green Carbon and was not involved in the editorial review or the decision to publish this article. The other authors declare that they have no competing financial interests or personal relationships that may have influenced the work reported in this study.

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Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Beatrice Castellani is an advisory board member for Green Carbon and was not involved in the editorial review or the decision to publish this article.

Graphical abstract