



Review

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, deep-water sediments of inland lakes and seas, and polar sediments on continents and continental shelves. NGH constitutes the largest hydrocarbon resource on Earth, representing a reservoir of sustainable fuel owing to the possibility of a so-called CO₂–CH₄ replacement process. If CO₂ is injected into NGH sediments, CH₄ is released and CO₂ hydrate formed. The extraction of gas from NGH, combined with carbon capture, presents significant potential advantages in the energy infrastructure and various economic and political contexts, aligning with future green policies. This study 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. This study introduces a novel process wherein the CO₂–CH₄ replacement process is integrated with methane purification and CO₂ recirculation, which has been experimentally tested and represents a new advancement in gas hydrate science. Experimental tests at the microscopic and macroscopic levels showed that the efficiency of the process strongly depends on the mutual influence of 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 shows that the transition could generate—even in the short term—large high-impact cash-out.

1. Introduction

Natural gas hydrates (NGH) are found in both marine and terrestrial environments. In marine sediment, NGH is stable almost along all continental margins hundred meters below the seafloor, whereas

onshore NGH exists below the permafrost and in 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 the water temperature approaches 0 °C at the

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bottom, NGH is stable for a hundred meters below sea level [1]. Thus, NGH produces a remarkable bottom-simulating reflector (BSR). The best approach is based on the estimation of seismic velocities (both compressional and shear wave) provided by conventional two-dimensional reflection data or ocean bottom seismometer data. The seismic velocities were then analyzed using theoretical approaches that describe the behavior of the velocities versus the NGH and free gas concentrations [2,3]. The NGH reservoir present in Peninsula Antarctica can be considered a natural laboratory, and for this reason, samples acquired in the past from this region can be considered. In recent decades, NGH reservoirs in the offshore Antarctic Peninsula have been studied using a multidisciplinary approach [1].

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

Worldwide estimates of NGH deposits range from $2.5 \times 10^{15} \text{ m}^3$ to $3.0 \times 10^{18} \text{ m}^3$. These estimates indicate that the organic carbon contained in NGH reservoirs is approximately twice the amount found in all currently recoverable conventional hydrocarbon resources [6–8].

Therefore, NGH is a fuel resource, that can be assimilated into renewable sources owing to the so-called CO_2 – CH_4 replacement process. Injecting CO_2 into NGH sediments leads to the release of CH_4 and the formation of CO_2 hydrates. Previous studies indicate that CH_4 – CO_2 hydrate conversion occurs spontaneously, 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 the greenhouse gas CO_2 . Thus, NGH reservoirs serve not only as sources of CH_4 but also as storage sites for CO_2 , bolstering the concept of a carbon-neutral fuel source.

Concerning the CO_2 replacement process, previous research has proven its effectiveness in water phase and porous media systems, as well as in the CH_4 production rate [10]. In situ combustion has also been proposed to improve CO_2 injectivity and avoid premature CO_2 hydrate formation [11]. In accordance with previous studies [12], some research aspects should be addressed: the authors of the paper highlighted key issues such as the influence of water properties during the formation and replacement reaction, the role of the sediments' physicochemical properties, the possible change in the mechanical stability of the reservoir after replacement, and the development of reservoir models.

The present study contributes to the state of the by answering the above-mentioned key issues with the results obtained from a three-year Italian research project on the topic of methane recovery and carbon dioxide disposal in NGH reservoirs. The consortium is multidisciplinary and interdisciplinary and formed by seven partners: University of Perugia UNIPG (Applied Physics and Structural Geology groups); Politecnico di Torino POLITO (Applied Physics group); University of Camerino UNICAM (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 (Energy Economics group). Several key aspects of this project are addressed.

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

In another study [14], the authors investigated CO_2 capture methodologies in depth, particularly focusing on the efficiency of membrane-based gas separation, which seemed to be suitable for separating methane from CO_2 that did not participate in the replacement. In particular, the Matrimid 5218 membrane has a notable structure for gas-

separation applications [15]. The main properties of matrimides are their inherent free volume, exceptional selectivity, and permeability for both organic and inorganic gases [16–18]. Its efficacy, particularly for CO_2 /CH₄ separation, has been validated against known performance metrics [19].

The mechanical properties of gas hydrates (GHs) are another important aspect that must be investigated. Several studies have been conducted on pure methane hydrates [20,21], whereas the mixed CO_2 /CH₄ hydrate properties after and before replacement processes have been less investigated. Moreover, the properties and property changes of the lithology that characterize host sediments are far from being clearly understood. For CO_2 -bearing samples, higher strength with respect to methane hydrates has been reported in Ref. [22], while others have reported more complicated behavior for both short-term [23,24] and long-term [25,26] deformation. In particular, Luo et al. [27] highlighted an ~20% decrease in the Young's modulus of CO_2 saturated-samples compared to CH_4 specimens, as hydrate dissociation has been proven to weaken sediments up to the point of collapse [28], and evolved CH_4 has been observed to cause instability and local failures in permafrost regions [29]. Therefore, while it is clear that hydrates generally replace water from the pores, resulting in stiffer frames and clearly improving the mechanical properties of the hosting sediments, the effect of CH_4 or CO_2 is still very poorly understood [23].

Understanding the mechanical, morphological, and chemical characteristics of GHs is the basis for developing simulation models for marine NGH reservoirs. 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 behavior of the electrical model.

However, the integration of co-located seismic and resistivity data, although independent, can enhance gas hydrate (GH) estimates. This is because the inversion results provide the seismic velocity and electrical resistivity, both of which are sensitive to GH content. Carcione and Tinivella [30] developed an approach based on Biot's theory for partially frozen porous media saturated with a mixture of two immiscible, viscous, and compressible fluids. This model can be approximated within a low-frequency (seismic) range. Resistivity is widely used to estimate GH and free gas concentrations from core analyses [31]. To calculate the GH concentration of a deposit, the modified Archie's law extracts the amount of pore space filled with GH from the overall porosity [32]. These theoretical models were modified and integrated to fit the experimental data.

Finally, economic studies on NGH are lacking, particularly those concerning the impact of GH exploitation on the methane market. By employing life cycle assessment (LCA) and leveled cost of energy (LCOE) methodologies, such studies can attract private investment, inform strategic decisions for industries and regulators, and assess the economic ramifications of emissions trading systems and the natural gas market. LCOE benchmarking is crucial for comparing different energy sources, particularly CO_2 costs. NGH exploitation, coupled with natural gas production and carbon capture techniques, has enormous potential advantages for infrastructure gas competition and shaping future green policies and economic scenarios.

In this paper, the effects of 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 are discussed.

Based on the literature, in particular a review article [12], that outlines a key issue to address in the future, the current article covers: (i) the effect of sediment (grain size and composition), salinity, and water properties on GH morphology, NGH formation, and CO_2 replacement; (ii) the mechanical behavior of CH_4 – CO_2 mixed clathrates; and (iii) the development of theoretical models of GHs in nature.

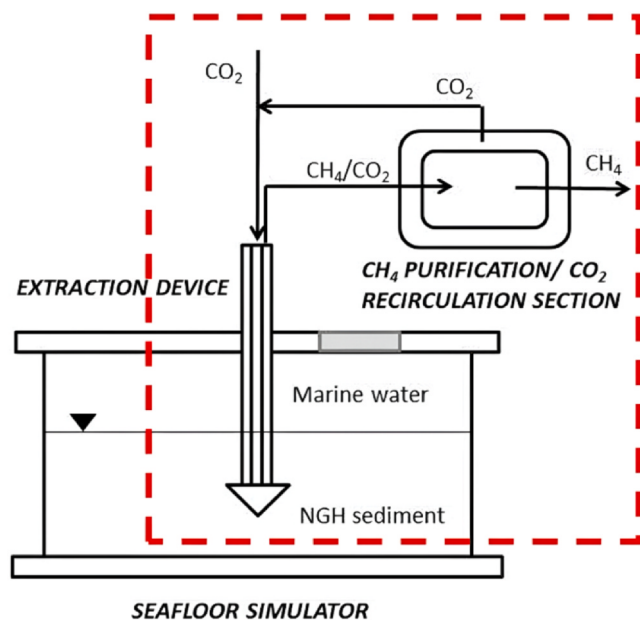


Fig. 1. Schematic of the proposed process.

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

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

2. The project and the Italian Gas Hydrate Consortium

This study 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, CH_4 and CO_2 are separated via a membrane to obtain pure methane for energy purposes, and pure CO_2 is recirculated into the sediment.

This is necessary because the CO_2 – CH_4 replacement process has a theoretical limit of 75%, so its output is a gaseous mixture that requires further treatment for full-scale application in the energy sector.

In this project, we developed several experimental and theoretical models to determine the performance of the proposed process.

UNIPG was responsible for the artificial reproduction of NGH sediments, the macroscopic investigation of the effects of sediment properties, and the preparation of samples for further analysis. The UNIPG and Sapienza geological groups geologically and mechanically characterized the samples before and after the CO_2 – CH_4 replacement process. In addition, the UNICH group prepared NGH samples for further analysis. UNICAM analyzes NGH samples from UNIPG and UNICH using Raman spectroscopy and scanning electron microscopy (SEM). The experimental data were used by the OGS to modify the theoretical model and by POLITO to research membrane-based separation. UNIFE conducted an economic analysis. A flowchart of this process is shown in Fig. 2.

The Consortium of Partners unites the Italian GH research community with competencies not strictly related to GH science in the fields of engineering (POLITO) and economics (UNIFE).

The Italian GH community is a multidisciplinary group that has been engaged in GH research for over 30 years. The OGS has been a key player in the past decades, focusing on theoretical elastic models to describe the dependences between velocity and GH and between velocity and pore pressure; seismic modelling to describe the seismic effect of hydrates; geophysical explorations; and investigation of 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 actively researching clathrate hydrates, covering aspects ranging from fundamental properties (kinetics and thermodynamics of hydrate promoters/inhibitors) to field applications in energy and space technologies [34–37].

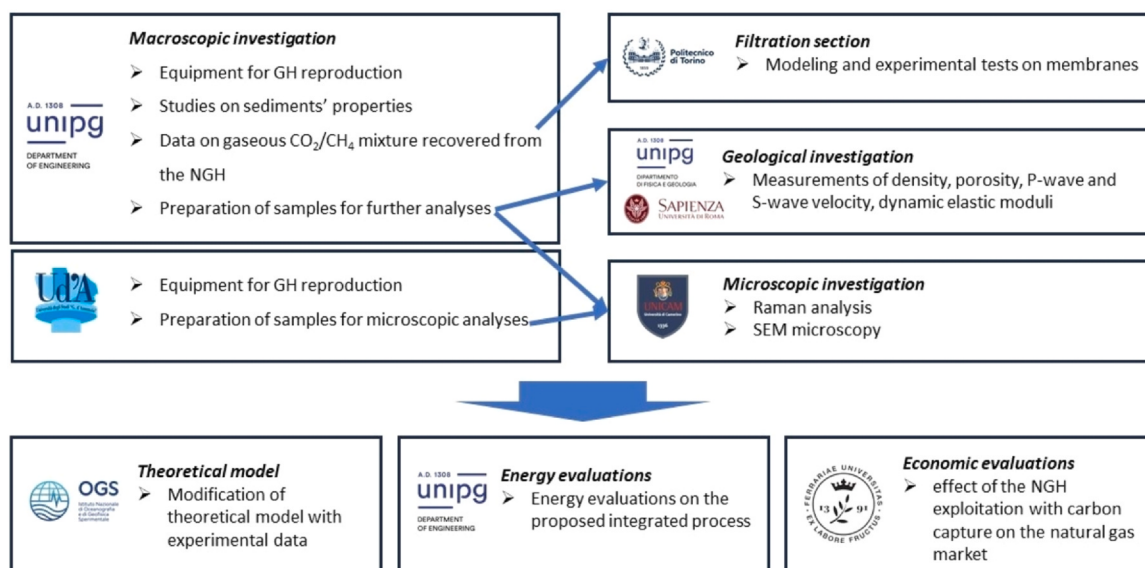


Fig. 2. Flowchart of the research activities.

The University of Perugia is one of Europe's leading research institutions in GH science, with 15 years of expertise in hydrate-based processes for energy applications, such as methane and hydrogen storage, natural GH exploitation, and CO₂ storage [38–40].

Through their Environmental Chemistry Research Laboratory, the University of Camerino 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 the macroscopic and microscopic investigations of NGH samples, the methodology used to develop the theoretical model, the experimental tests performed in the separation section, and the methodology for the energy and environmental evaluations.

3.1. Reactors and experimental tests for hydrate formation and CO₂ replacement

Experimental tests of NGH formation and CO₂ replacement were conducted in four different reactors: three at UNIPG labs and one at UNICH labs.

The UNIPG research group has three reactors: one in a thermostatic bath and two in a cooling room. The former has an internal cylindrical volume of 949 cm³ and was placed inside a thermostatic bath refrigerated using a chiller. A detailed description of the reactor is provided elsewhere [13,43].

Similarly, the other two reactors positioned inside the cooling room have cylindrical shapes and volumes of 1 L. A detailed description of these reactors is provided in a previous publication [38].

The three reactors (Fig. 3) were equipped with several temperature sensors and a pressure gauge to obtain the experimental P-T curves.

NGH formation begins with methane injection into sediments saturated with water, which pressurizes the reactor to the initial pressure, P_i . During hydrate formation, the temperature starts to increase owing to exothermicity, and the internal pressure decreases. Formation was complete when T and P were constant. Eqs. (1) and (2) were used to calculate the number of hydrate moles formed in the system and pore saturation, respectively.

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

$$S_H = \frac{n_{\text{hyd}} \frac{1}{\rho_{\text{hyd}}}}{V_{\text{pore}}} \quad (2)$$

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 this methodology is provided elsewhere [13].

Dissociation occurred at the end of the hydrate formation tests, and the pressure increase was used to quantify the total number of moles of CH₄ involved in the hydrates.

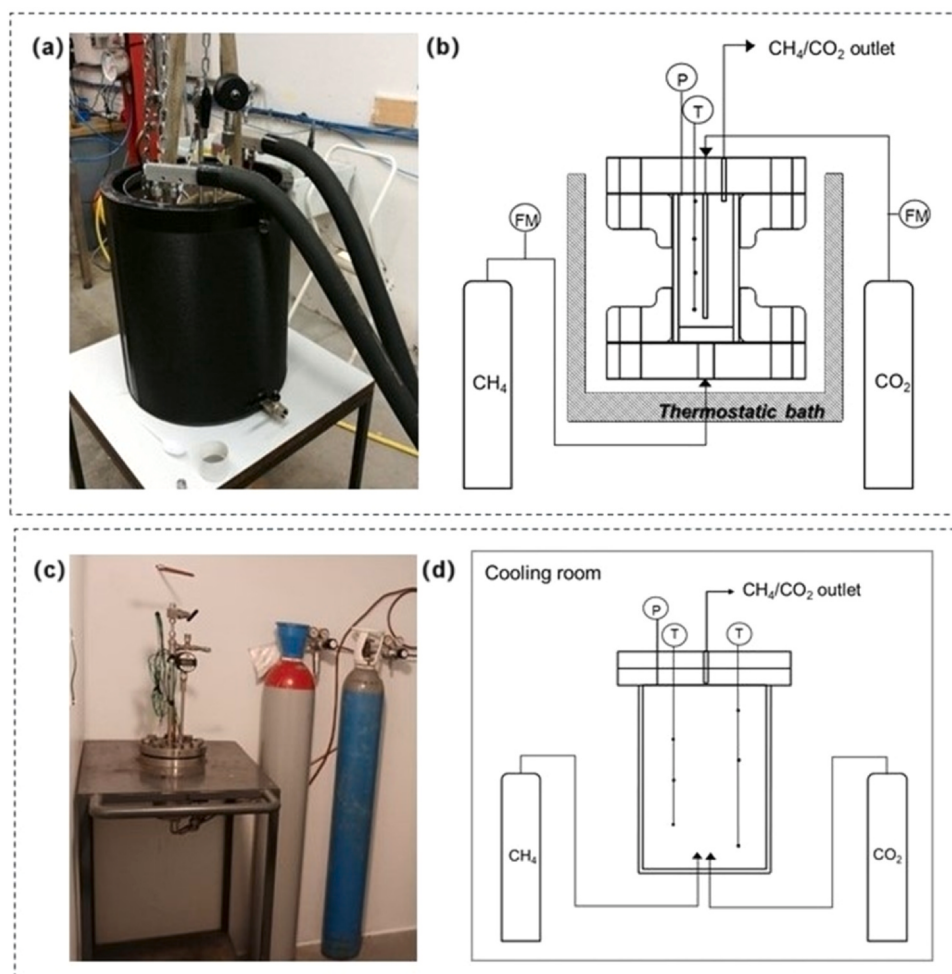


Fig. 3. UNIPG reactors: (a) photo of the reactor in the thermostatic bath; (b) schematic of the reactor in the thermostatic bath; (c) photo of the reactor in the cooling room; (d) schematic of the reactor in the cooling room.

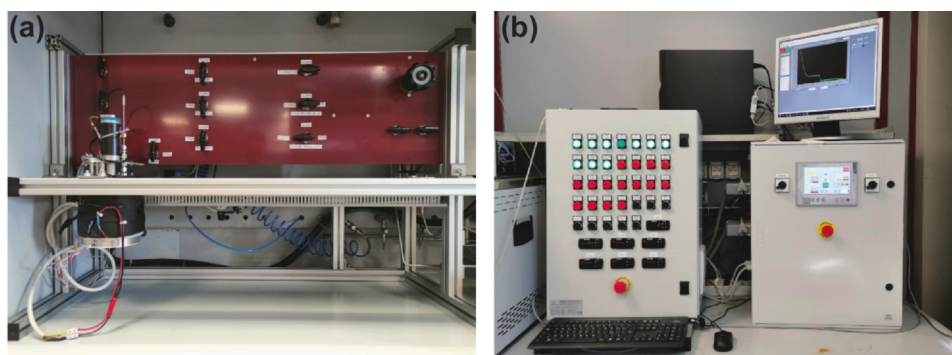


Fig. 4. (a) Photo of the multiple-reactor apparatus. (b) Photo of the PLC control system. Modified with permission from Ref. [37]. Copyright 2017, ACS.

For the CO₂ replacement tests, at the end of the formation, CO₂ was injected using two different methodologies: depressurization or thermal stimulation.

In the first method, pressure reduction destabilizes the methane hydrates, and pure CO₂ is injected. Thermal stimulation involves injecting CO₂ while increasing the internal temperature and maintaining a relatively constant pressure. Two gas analyses were conducted: the initial analysis measured the composition of the gaseous phase before replacement, while the second one assessed the composition of the hydrates at the end of the process.

The number of moles of CH₄ hydrates involved in the replacement process and newly formed CO₂ hydrates can be calculated. A detailed description of these two processes is provided in Ref. [44].

During the project, UNIPG performed several experiments using the equipment described above to study the effect of sediment properties such as salinity, grain size, and sands type. A complete illustration of the UNICH reactor (fabricated and assembled by RDPower s.r.l. Terni, Italy) employed to produce the GHs is presented in Fig. 4. The reactor was composed of AISI 316 L stainless steel and had an internal volume of 350 mL and operating pressure of up to 20 MPa. Details of the equipment are provided in Refs. [35–37].

The aim was to use the UNICH reactor to prepare CH₄ and CO₂ hydrates in different media (Table 1) and characterize them using Raman spectroscopy and SEM. The hydrate samples were synthesized in a custom copper sample holder placed inside the reactor and transferred to a Linkam THMS600 cell for low-temperature Raman characterization. GHs were formed at 1 °C and a constant pressure of 3.5 MPa for CO₂ and 7.0 MPa for CH₄. This pressure was selected to prevent CO₂ liquefaction at higher pressures. The samples were maintained under these conditions for 24 h. After formation, the hydrates were stabilized by subcooling, and the pressure was gradually released to allow the removal of the formed hydrates.

To replace CH₄ with CO₂, after stabilizing the CH₄ hydrates for 5 d, the pressure was reduced from 7 MPa to ~3.5 MPa, and cooled CO₂ was introduced into the reactor at a constant pressure. Throughout the gas phase exchange, the hydrate was stabilized by lowering the temperature to prevent CH₄ hydrate dissociation. The composition of the gas mixture was monitored at the end of the

exchange using an IR detector (Premier series of IR gas sensors by Dynament (UK) for CO₂ and CH₄).

3.2. Microscopic characterization

GHs synthesized under different experimental conditions were morphologically characterized using a field emission scanning electron microscope, coupled with an energy-dispersive X-ray spectrometer and a temperature control device that allows the acquisition of SEM images at temperatures as cold as –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, representative portions of the hydrate samples were transferred to a homemade SEM sample holder and then to the cooling stage (all operations on the samples, from selection to portion cutting, were performed in liquid nitrogen) [41,45].

Raman spectra of GHs were obtained according to a previously reported method [41,45]; in this application, customized copper sample holders were used, and the samples were transferred to the Linkam unit of the micro-Ramanspectrometer. To avoid water condensation at low operating temperatures, a flow of nitrogen was applied.

3.3. Mechanical characterization

The porosities, densities, and P- and S-wave velocities of 51 specimens were determined using the boundary conditions of ambient pressure and a temperature of –40 °C. We fabricated cylindrical specimens 25 mm in diameter and 25 mm in height. 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,e). Another set of cases were filled with natural sand (NS) having a typical tholeiitic basalt composition [46]. The NS contained poorly sorted, angular grains ranging in size from ~2 mm to ~0.5 mm (Fig. 5(c,d,f)). Each sample was weighted immediately after removal from the chiller and measured precisely using a digital caliper. Then bulk density (ρ_b) was calculated by measuring the weight/volume ratio.

The grain density (ρ_g) of PQ and NS was measured using a helium pycnometer (Anton Paar Ultra-pyc 5000) with an accuracy of 0.02% and repeatability of 0.01%.

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

A multiplexed Mistras Eurosonic system ultrasonic device (USB 8 M 8-channels generator) was used for the elastic wave velocity measurements. This ultrasonic device generator was operated with piezoelectric transducers at a frequency of 1 MHz. Two identical P-wave (or S-wave)

Table 1

Media used for the formation of GHs and respective concentrations and volumes.

	CH ₄ Hydrate	CO ₂ Hydrate	CO ₂ /CH ₄ Hydrate
UP water	1 mL	1 mL	1 mL
Seawater	1 mL	1 mL	1 mL
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

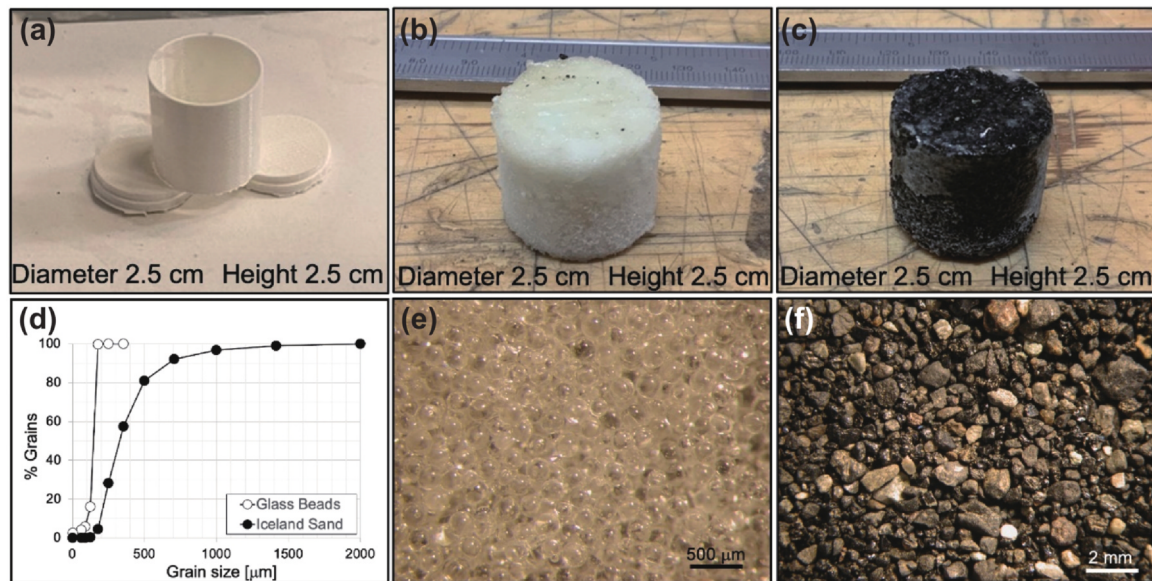


Fig. 5. (a) Sample cases. (b) PQ hydrate sample. (c) NS hydrate sample. (d) Grain size curves of PQ and NS. (e) Optical microscope image of PQ. (f) Optical microscope image of NS. Reprinted with permission from Ref. [44]. Copyright 2023, Elsevier.

transducers were attached to the two circular bases of the sample to allow signal propagation through the sediment using a pulse-transmission technique [48]. The filtering, amplification and quantification of the waveform were controlled by the USB 8 M device. Waveforms were then recorded by using the software “Mistras Ultrasonic EuroscanV” and exported as text files. A custom-made Python code was used to select the first arrival of both the P- and S-waves. Note that the errors associated with such a methodology are on the order of 10^{-4} to 10^{-2} [17]. All elastic wave measurements were conducted in the axial direction of the samples under ambient pressure and temperature. After laboratory measurements, we calculated the dynamic elastic moduli (E_d and ν_d) according to a previous study [43]. All measurements were conducted at the Engineering Department Laboratory of the University of Perugia and Rock Mechanics and Earthquake Physics Laboratory in the Sapienza Earth Science Department.

3.4. Theoretical model

Several theoretical models are available to describe the elastic properties of NGH-bearing sediments [49]. Here, we adopted the method proposed by Carcione and Tinivella [50], in which the Biot theory was modified to consider partially frozen porous media and a fluid composed of a mixture of two immiscible, viscous, and compressible fluids. Complete details are reported in Ref. [49]; we report only the main concepts. Moreover, the above theory includes the effects of (i) the interaction between the grain and NGH (described by the tortuosity terms) and (ii) grain cementation, and the consequent increase in the matrix rigidity owing to the high NGH concentration [50]. Cementation is included in the theory owing to the percolation theory [3], which models the transition from a discontinuous state (low NGH concentration without cementation) to a continuous state (high NGH concentration with cementation between the grains). The model was calibrated using Ocean Drilling Program data as reported in Ref. [51], to estimate all the empirical parameters involved in the velocity evaluation. This model was approximated in the range of seismic frequencies using the Biot-Gerstma-Smith equations. This theory allows for models of both compressive and shear wave velocities vs. NGH concentrations. The

theoretical velocity was then used to estimate the concentration by fitting the velocity estimated from seismic or laboratory data [2,3]. The theoretical model and approach were successfully validated in previous studies using well, laboratory, and seismic data [52,53]. If NGH/free gas was present, the experimental velocity was higher or lower than the theoretical velocity evaluated for water-bearing sediments.

3.5. 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 the 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 1 L supply tank. Valve V4 facilitates gas flow through a series of two pressure reducers, stabilizing the output pressure despite supply pressure variations during testing. Valve V5, a three-way valve, directs the gas to either the feed or permeate sides of the membrane. The climate chamber, composed of FDM, houses the membrane and can regulate temperature from -20°C to 80°C . Valve V6 isolated the permeate side from the feed side, where TI and PI are the temperature and pressure sensors, respectively. Valve V7 connects the permeate side to the exhaust and a volumetric flow meter, directing the flow either directly to the exhaust or through the flow indicator depending on the position of V9 (a three-way valve). A vacuum pump was used to evacuate any gas in the circuit.

The tested membrane was a Matrimid 5218 membrane synthesized by Università di Bologna through the polycondensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diaminophenylindane with a blend of two cycloaliphatic monomers. The chemical structures of the matrix 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 to 8 bar to assess the membrane permeability to CH_4 and CO_2 . The permeability and selectivity were evaluated when the slope of the permeate pressure curve was linear (Eq. (3)).

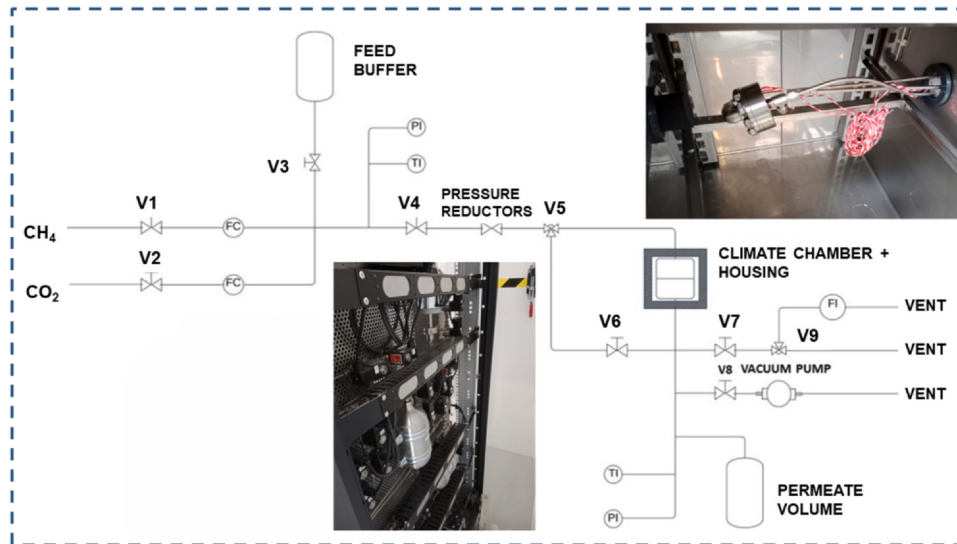


Fig. 6. Plant diagram for gas separation with membranes. Experimental bench of the Polytechnic of Turin located at the "CO₂ Circle Lab" laboratory in the "Environmental Park" innovation hub.

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

$$\alpha_{i/j} = P_i/P_j \quad (4)$$

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 $0.2782 \frac{\text{cm}^3 \text{cmHg}}{\text{K cm}^3 \text{STP}}$; 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 $\frac{\text{cmHg}}{\text{s}}$, and $\frac{dp_{leak}}{dt}$ is the derivative of leakage pressure in time.

The experimental setup is given in Ref. [54]. The theoretical framework for analyzing methane upgrading from NGH reserves via a countercurrent membrane module is inspired by Ref. [55], emphasizing designs with multiple separation stages for high efficiency. Particularly, a two-stage series configuration with recirculation was highlighted for its effectiveness in methane sweetening, accommodating four distinct case studies based on pressure differential methods. The authors in Ref. [14] proposed an optimization model focusing on optimal configurations, system design, and operational conditions to achieve desired CH₄ purity, considering constraints such as 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.

3.6. Energy evaluations

The proposed technological solution, which includes CO₂ injection and CH₄ release from hydrate geological sites was modelled and evaluated in terms of mass and energy balances.

As shown in Fig. 1, the system boundaries included: (i) CO₂ injection in the NGH sediment; (ii) CO₂-CH₄ output mixture filtration by membranes; (iii) CO₂ recirculation. The reference functional unit is the unitary physical amount of injected CO₂ (expressed either in kg or in Nm^3).

The evaluation used experimental data from laboratory tests and theoretical calculations to compare the energy consumption for methane recovery and for CO₂ sequestration with the amount of energy contained in the recovered CH₄.

The CO₂-CH₄ replacement process presents some energy costs, the first one is that related to the CO₂ compression for its injection in the sediment. The compression work was calculated as a multi-stage adiabatic process with inter-cooling with a compression efficiency of 85%. The experimental data shown in Ref. [56] were used to complete the calculation: (i) injection pressure of about 30 bar; (ii) the percentage of CO₂ 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 CO₂/CH₄ mixture for the separation section is considered equal to 70% CO₂-30% CH₄ in volume as discussed in Ref. [44]. The energy consumption of the separation section is equal to $4.9 \text{ MJ/kg}_{\text{CH}_4}$ 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 Ref. [13].

3.7. Economic evaluations

Considering the most promising technologies, strands of institutional support and incentives and the first international experience, the analysis of the innovative NGH based process, is based on the fact that a strategic repositioning of 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 focus, both for their intrinsic patrimonial solidity, and because their offer must face a widespread demand that wants security and builds its rigidity around it. Clearly, the rigidity of energy demand is a topic item for our deal under investigation and it gives room for IRR to no longer be contingent, thus attracting institutional investors searching for opportunities to invest in fully collateralized regulated essential assets. So, "public interest" is the best way to fulfill the hedging profile of investments in a fully privatized world.

We performed implementation tests for a regulatory model that could allow 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) has been applied to many European utility regulations [57].

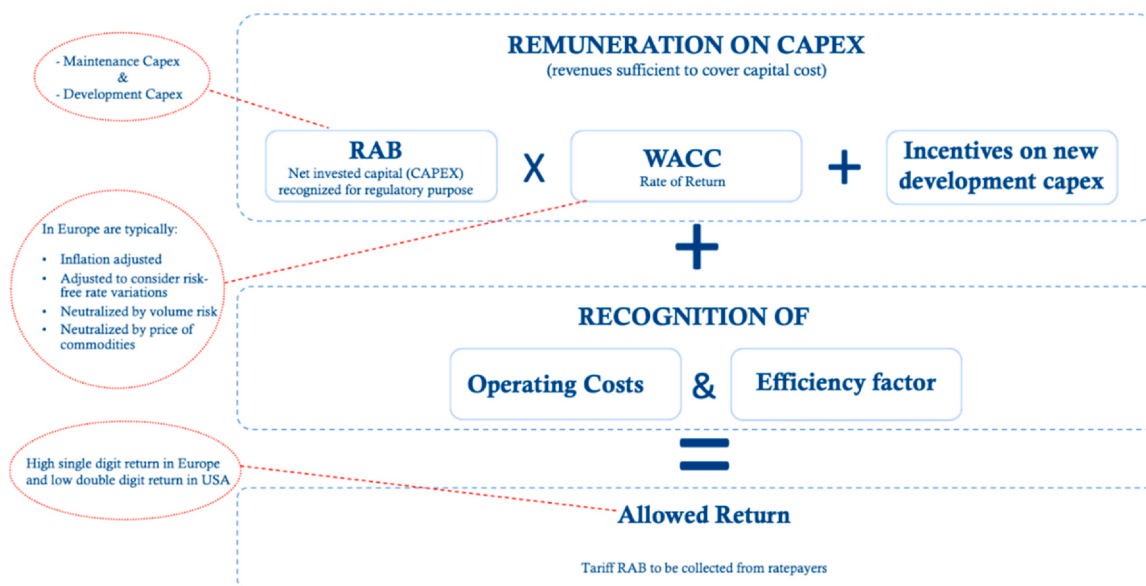


Fig. 7. RAB regulation model scheme.

By a comparison of international regulatory experiences in capital incentives regulatory schemes, consistent affordability was found for the scheme of “RAB Regulation Model” applied today as optimal European scheme for implementing an effective incentive regulation public strategy to improve infrastructural energy investments.

4. Results and discussion

4.1. Hydrate formation and CO₂ replacement

UNIPG conducted experiments on how the properties of sediments affected both methane hydrate formation and CO₂ 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 CH₄ hydrate formation. As a matter of fact, the number of CH₄ moles entrapped in the hydrate phase with respect to the total moles injected inside the reactor increased from 12% in pure water to 7% in salt water. The opposite trend was observed CO₂–CH₄ replacement. In the presence of salt, the percentage of methane moles effectively replaced by CO₂ is 55%, compared with 32% in pure water. In parallel, during CO₂ injection, replacement occurs along with new CO₂ hydrate formation. Furthermore, in the presence of salt, the formation of CO₂ hydrates decreased from 50% to 47% of the total moles in the hydrate phase; the decrease in the number of hydrate moles formed was lower for CO₂ than that for CH₄. 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 Ref. [58], finding that the inhibiting effect of salt is stronger for CH₄ hydrates rather than for CO₂ 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, NaCl can be considered a promoter of the CO₂–CH₄ 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 Ref. [59]. As far as the CO₂/CH₄ replacement process is concerned, it is well-known that, from the perspective of phase equilibrium, the equilibrium curve of CO₂ hydrate is lower than that of CH₄ hydrate [60]. As specified in Ref. [61], longer induction time and lower hydrate formation due to initial salinity, can be caused by the lower energy state of the system.

In addition, the nature of the sediment affected CH₄ hydrate formation. In Ref. [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

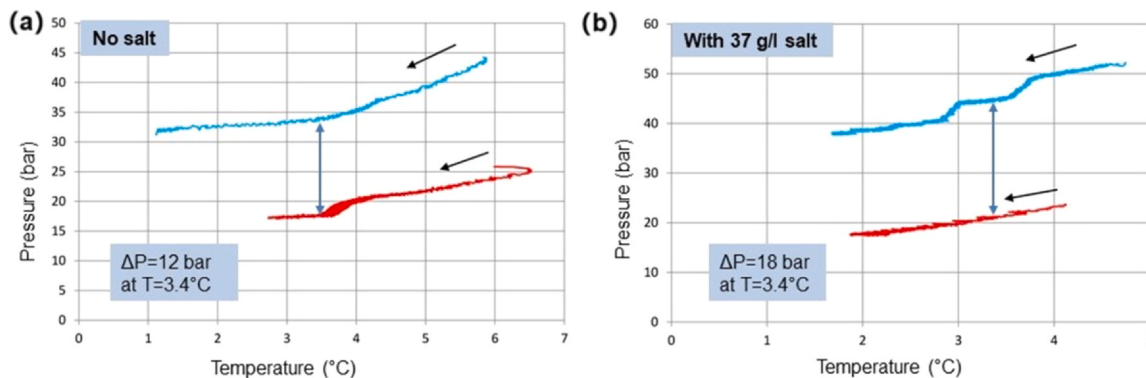


Fig. 8. (a) P–T curves of methane hydrates and CO₂ hydrates with salt. (b) P–T curves of methane hydrates and CO₂ hydrates without salt. Modified with permission from Ref. [58]. Copyright 2020, MDPI.

addition to SiO₂. Results show that the heterogeneous grainsize and porosity, the chemical composition of the sediment affect the formation process. In particular, CH₄ hydrate formation required higher pressures and longer durations in the presence of natural sand than in the presence of 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 Ref. [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 effects of grain size on CH₄ hydrate formation and CO₂ replacement was also experimentally tested in Ref. [64]. Two sediments with different grainsize were compared: 150–250 µm and 400–500 µm. The CH₄ hydrate formation was faster and more massive in presence of the 150–250 µm size sediment, while the CO₂ replacement and also the amount of CO₂ capture was higher in presence of 400–500 µm size sediment. So, a sediment which is favourable with CH₄ 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 CO₂–CH₄ replacement. Making a comparison with literature, the trend is confirmed by Ref. [65]: silty sand with a diameter of 30–50 µm improves the water conversion in hydrates, favoring the formation.

UNIPG also produced several types of hydrate samples with and without sand to study the replacement process at the microscopic level via thermal stimulation and depressurization. In both cases, the final concentration of CO₂ 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 GH preparation conditions. In particular, the morphologies of different GHs produced from UNIPG are reported in the Fig. 9 [42]; as it is possible to observe the surface of GHs, prepared in ultrapure water (CO₂GHs), shows spherules with sizes of few tens of micrometres while the GHs prepared in presence of sediments (CO₂(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, (CH₄/CO₂)GHs, show a morphology similar to those present on CO₂GHs; 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.

The morphologies of the GHs produced from UNICH under different experimental conditions are shown in Fig. 10.

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

Raman measurements of the CO₂GHs and CO₂(sand)GHs, produced from UNIPG, confirmed the gas uptake in the hydrate structures by identification of the fingerprint of CH₄ and CO₂ in the hydrates. The Raman spectra of CO₂GHs and CO₂(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 CO₂ hydrates formed in the presence of sand processed a less ordered structure showing a stability that was maintained with the variation of temperature; the shifts of the CO₂ 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 CO₂(sand)GHs showed the least ordered water structure, while (CH₄/CO₂)GHs the most ordered one, with the most quantity of CO₂. Therefore, these results confirmed the favorable replacement of methane and the formation of a stronger lattice than that obtained in the presence of only one species [42]. In addition, with the increase of temperature on CO₂GHs_{sand}, a linear blue shift of the CO₂ Fermi-diad peaks (Fig. 11(d)) has been obtained, demonstrating an enlarge of the cage respect due to the presence of sand.

The GHs produced by UNICH (CH₄-GHs CO₂-GHs, and CO₂/CH₄-GHs) were analysed by Raman spectroscopy to investigate the structural changes in the water cages, the gas uptake in the hydrate structure, the CH₄ cage occupancies, the hydration number, and the yield of CO₂ 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 CO₂/CH₄-hydrate obtained by replacement process in different experimental conditions and reported in Supplementary Material highlighted the presence of both CO₂ and CH₄ in the hydrate structure, confirming the success of the exchange experiments.

The cage occupancy calculation of CO₂/CH₄-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 GHs a noticeable amount of CH₄ was displaced by CO₂.

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 (lowest SD), while CH₄/CO₂-hydrate shows the least rigidity (highest SD) [45]. These aspects are shown in the Supplementary material.

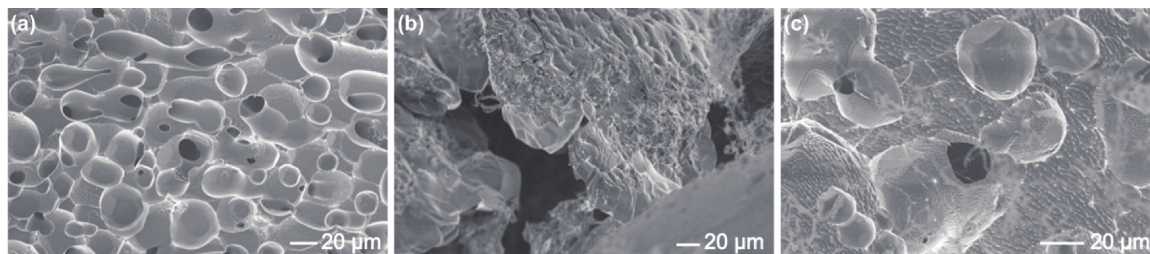


Fig. 9. SEM images showing the surface morphology of different types of GHs from UNIPG: (a) CO₂GHs, (b) CO₂(sand)GHs, and (c) (CH₄/CO₂)GHs. Modified with permission from Ref. [42]. Copyright 2022, Elsevier.

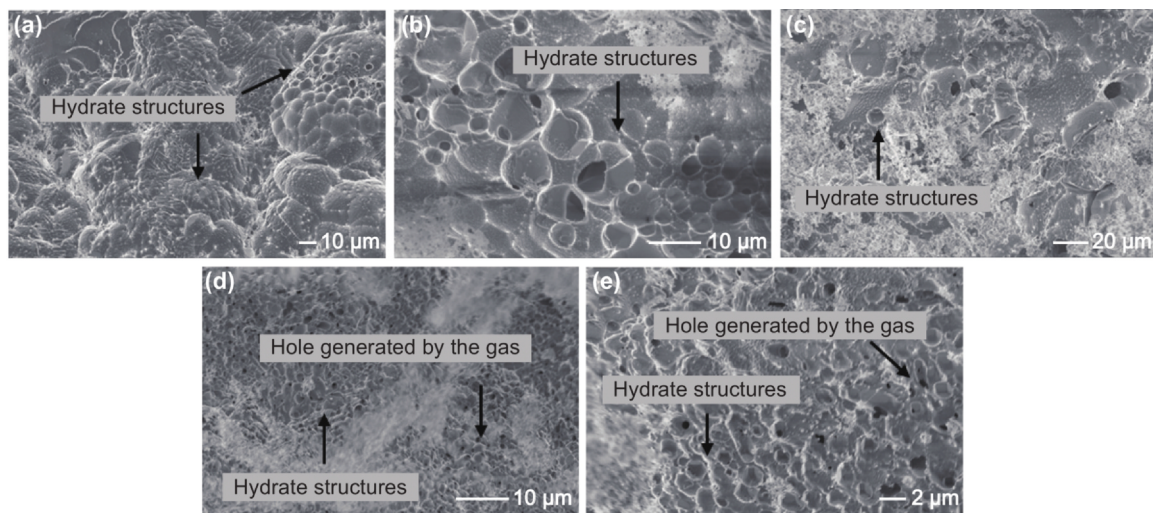


Fig. 10. SEM images of CO_2/CH_4 -hydrates in (a) SDS, (b) natural sand, (c) synthetic sand, (d) UP water, and (e) seawater from UNICH. Modified with permission from Ref. [44]. Copyright 2022, Elsevier.

4.3. Mechanical characterization

The main aim of 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 Ref. [44] are reported in Table 2. A detailed description of these data is reported in Ref. [44]. Generally, NS is characterized by high porosities and fast seismic velocities, with larger V_p/V_s ratios than

synthetic PQ sands. This is counterintuitive because smaller grains usually lead to higher porosity, which should correspond to a 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%. NS samples are characterized by a similar

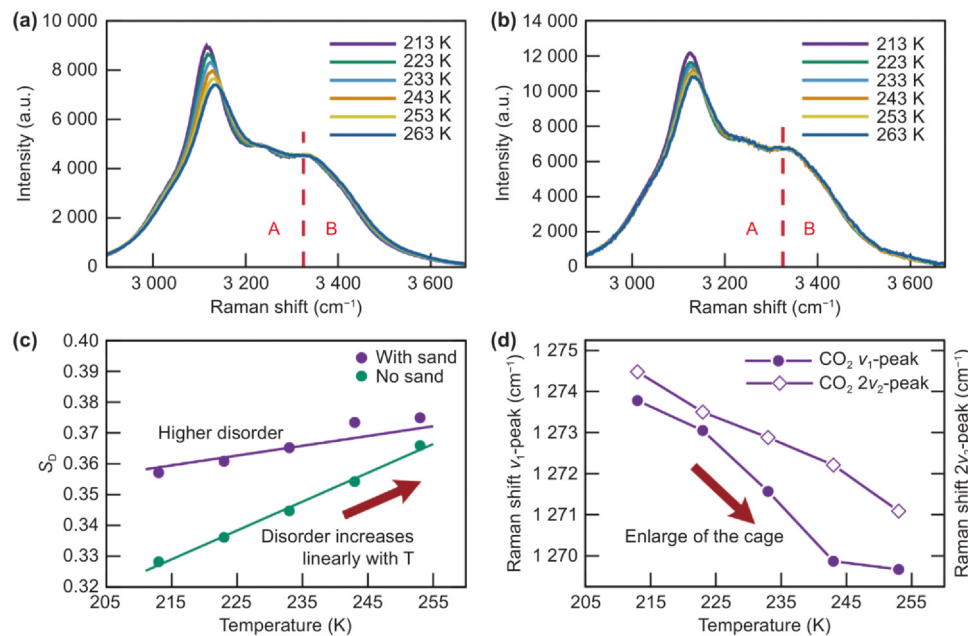


Fig. 11. Raman spectra of OHs vibration bands at different temperatures of (a) CO_2GHs and (b) $\text{CO}_2(\text{sand})\text{GHs}$. (c) Correlation of SD concentration index as function of change in temperatures. (d) Raman shift of CO_2 Fermi diad at different temperatures of $\text{CO}_2\text{GHs}_{\text{sand}}$. Modified with permission from Ref. [42]. Copyright 2022, Elsevier.

Table 2

Results of mechanical characterization of the samples.

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
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	rounded 100%
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	SiO ₂ sands. Grain
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	size: 150–250 μm
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
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	rounded tholeiitic
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	basalt sands. Grain
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	size: ~0.5 – ~2 mm

behaviour; here the replacement process results in an increase of P-wave Velocity from 3.31 km/s up to 3.37 km/s and S-wave Velocity from 1.74 km/s up to 1.81 km/s.

Generally, after CO₂ 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 slightly 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 ranged from 12.95 GPa to 15.1 GPa (+16%) on NS samples after replacement while the dynamic Poisson's ratio (ν_d) was almost constant values pre and post replacement for both PQ (0.26) and NS (0.30). Notably, the E_d values for PQ were 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. In summary, the presence of CO₂ 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.

4.4. Theoretical model

The mechanical characterization of the GH samples has been used to estimate the hydrate concentrations by using the model proposed by Refs. [3,75] as described in the Section 3.4. The elastic properties of the components (natural sand or pure quartz, GH 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 Ref. [76], while the mechanical properties of samples created with the pure quartz were 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, considering the estimated error, the two types of sediments had the same hydrate concentration (Fig. 12). Thus, it was concluded that the samples were partially hydrate-saturated.

4.5. Gas separation section

Pure-gas permeability isotherms were measured for CH₄ and CO₂ at 20 °C and the results are shown in the Supplementary material. The permeability of the Matrimid membrane to CO₂ 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 CH₄ 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 m³ std/s and the gaseous mixture is 28.59% CH₄ and 71.41% CO₂ at a pressure of 31.16 bar. These are the experimental data presented in Ref. [44].

As results of the optimization model, the configuration composed of two stages in series with recirculation and two compressors (see Fig. 13) was chosen for the methane upgrade. For each step of Fig. 13, Table 3 shows the calculated operating parameters. The optimized system is able to recover 97.1% of the methane after CO₂ 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 CH₄ 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%.

4.6. Energy evaluations

The energy balance of the proposed process is discussed here, 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 45,000 kJ kg^{−1}, the recovered energy is 5025 kJ per each kg of injected CO₂ (corresponding to 0.111 kg_{CH₄} recovered for each kg of injected CO₂).

The energy cost for CO₂ 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 incurred in this process. In addition, energy is consumed owing to the recirculation of the CO₂ 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 CH₄ is 17%, indicating a favourable energy balance.

4.7. Economic evaluations

The economic analysis considers the significant structural impact of transforming the traditional CH₄ production chain into a sustainable

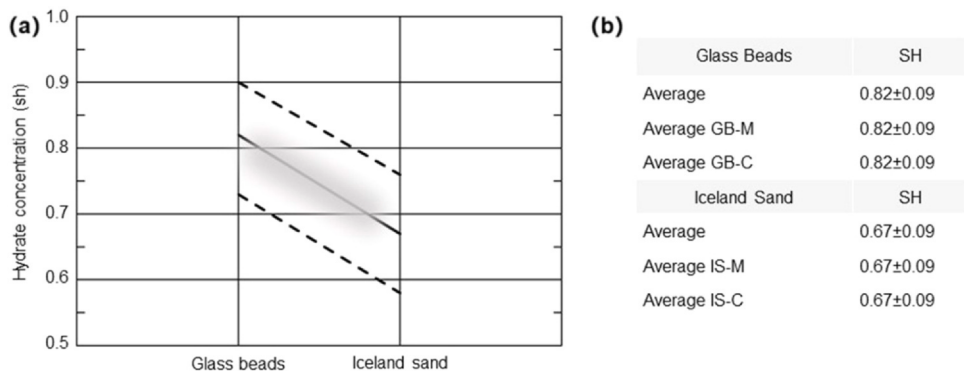


Fig. 12. Hydrate concentrations with the estimated error for the two types of sediments. (a) Profile of the hydrate concentration (sh). (b) Numerical values of sh and related errors.

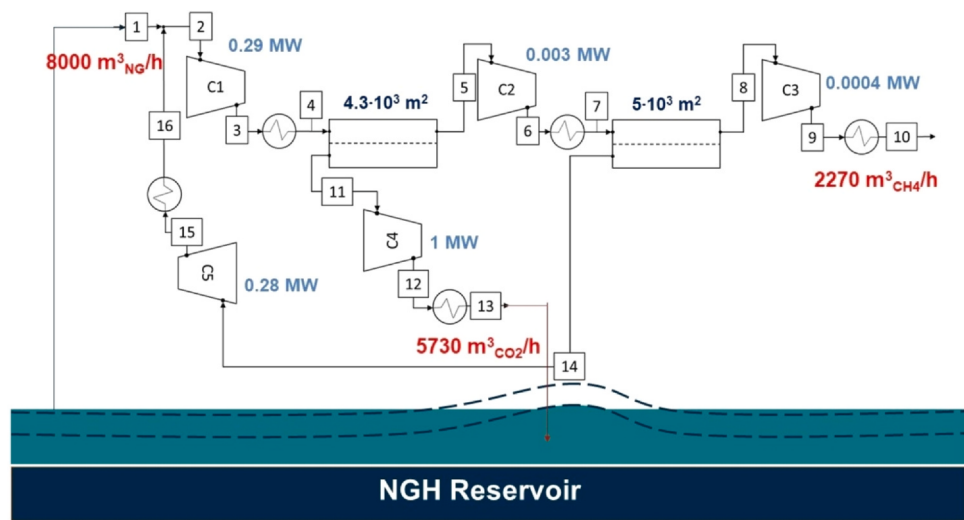


Fig. 13. Mass and energy balance of the system optimization model.

“new primary source”. This transformation is made possible by extracting CH₄ from NGH reservoirs in an environmentally neutral manner. This neutrality is achieved by simultaneously injecting CO₂, 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 attempted to launch a common strategy for recovering energy supply security, which can only be achieved through synergistic lines of action.

- 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 favour of researching and magnifying a new European Taxonomy pragmatically oriented towards not excluding nuclear energy generation and the natural gas supply chain; this is all the more reason to develop NGH-based carbon capture extraction processes.
- iii. 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 CO₂ emissions and carbon neutrality. The feasibility of CO₂ replacement in hydrate sediments represents a breakthrough in carbon capture and storage (CCS) research and could significantly impact CO₂ accounting. Two future integrations and applications of low-emission gases stemming from NGH-derived innovation are as follows:

- 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.

A technology transition from pilot scale to full industrial scale could result in a large cash out (particularly 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

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

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 provides an overview of the main experimental results obtained by an interdisciplinary Italian research project on NGH exploitation with respect to the current state-of-the-art technologies. The results of the overall energy, geophysical, and economic evaluations are presented.

The main focus of the project was to couple the CO₂–CH₄ replacement process in NGH sediment with a separation section in which the output CO₂–CH₄ 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 CO₂–CH₄ 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 facilitated CO₂ replacement; the percentage of methane moles effectively replaced by CO₂ was 55%, compared with 32% for pure water.
- NaCl salt brings a differential thermodynamic inhibition on CO₂ and CH₄ hydrates resulting in a larger distance between the two equilibrium curves and more moles of CH₄ replaced in the presence of salt water.
- With thermal stimulation and depressurization, the final concentration of CO₂ in the hydrate phase was about 71% in volume.
- The nature of sediment, such as the grain size, 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 grain size sediments, might hinder the CO₂–CH₄ exchange process.
- CO₂ presence in the hydrate phase clearly increases V_p and E_d when hosted in natural sediments much more than in synthetic sands. Through the replacement process, the lattice was stronger than the lattice obtained when only one species was incorporated, as confirmed by Raman analysis.
- The produced GH samples were mechanically characterized to estimate the hydrate concentrations and confirm that they were partially saturated.
- A Matrimid membrane with high selectivity, as measured by tests, was used in the optimization model. The optimized process

recovered 97.1% of the methane contained in the output mixture after CO₂ replacement (98.5% purity), to be directly injected into the grid.

- The energy evaluations show that the ratio between the energy spent to complete an entire cycle (CO₂ replacement in NGH and purification of the obtained CH₄) over the stored energy in the recovered CH₄ 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.

CRediT authorship contribution statement

Federico Rossi: Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Michela Giustiniani:** Writing – original draft, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Roberto Fazioli:** Writing – original draft, Validation, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Andrea Rossi:** Visualization, Validation, Methodology, Investigation, Formal analysis. **Salvatore F. Cannone:** Writing – original draft, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Marco Zannotti:** Visualization, Resources, Methodology, Investigation, Formal analysis. **Umberta Tinivella:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Massimiliano Barchi:** Validation, Supervision, Project administration, Funding acquisition. **Rita Giovannetti:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Giorgio Minelli:** Validation, Supervision, Project administration, Investigation, Data curation, Conceptualization. **Beatrice Castellani:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andrea Nicolini:** Validation, Resources, Project administration. **Alberto Maria Gambelli:** Methodology, Investigation, Data curation. **Pietro Di Profio:** Writing – original draft, Validation, Supervision, Project administration, Funding acquisition, Data curation,

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Declaration of competing interest

Beatrice Castellani is an editorial board member for Green Carbon and was not involved in the editorial review or the decision to publish this article. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.greenca.2024.09.001](https://doi.org/10.1016/j.greenca.2024.09.001).

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