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GHGT-12

Laboratory experiments for the assessment of the physical and chemical impact of potential CO₂ seepage on seawater and freshwater environments.

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Abstract

This study focuses on a laboratory experimental injection of CO₂ through calcareous and siliceous sediments both in freshwater and seawater aimed to identify the physical and chemical effects of CO₂ seepage and to assess the ability of the system to return towards the original conditions once the CO₂ injection is stopped. A rapid acidification of the water column during the CO₂ injection and reduction in the dissolved oxygen concentration was measured as well as enhanced weathering of the sediments. A partial recovery towards the initial values of pH has been recorded following the stop of the CO₂ injection.

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1. Introduction

During the last decades atmospheric greenhouse gases concentration and in particular carbon dioxide is increasing at an extremely fast rate contributing to the majority of the observed global warming and associated climate change; if remediation strategies will not be widely applied in short term further extreme and likely irreversible changes are forecasted [1, 2]. Currently the atmospheric concentration of CO₂ is 25 % higher than the one in the first middle of the 20th century reaching values of 398.06 ppm in February 2014 with an increase of about

0.62% respect to the value in February 2013 [3] Carbon Capture and Storage (CCS) is considered a reliable strategy for reducing the increasing of the atmospheric concentration of CO₂ and the induced global warming. CCS aims to the capture and concentration of CO₂ emitted from large anthropogenic sources (i.e. fossil-fuels fired power plants, and industrial production facilities), its transport and final injection in suitable geological structures for its permanent storage [4].

Considering the anthropogenic global CO₂ emissions, calculated to be around 30Gt in 2010 [5] and the values of the targets for the planned reduction of greenhouse gases emissions for the current and future periods (as example the UK is to reduce of 80% its CO₂ emissions by 2050 and considering that in 2012 the total UK net emissions of CO₂ were estimated in 479.1 Mt the total volume of CO₂ which is to be stored in the next years just for the UK is of several Mt) the global CO₂ that is to be stored is of the order of magnitude of several billions of tons [6,7]. In 2012 seventeen large-scale CCS facilities aimed to the geological storage of anthropogenic CO₂ were identified worldwide with the potential to store 37 MtCO₂ annually as part of EOR projects, in saline-aquifers or in depleted hydrocarbons-fields. Further 55 CCS projects are in development with a storage potential of 104 MtCO₂ [8,9].

CO₂ storage areas can be located onshore or offshore; the latter is also defined as sub-seabed storage being the main geological formations considered as target for the storage below the seafloor. The main storage area for UK will be the sub-seabed of the North Sea using as hosting formations depleted hydrocarbon fields and, mostly, brine aquifers; the storage potential is considered elevate with estimated values of about 17Gt CO₂ in the Southern North Sea [10-14]. Currently the only commercial-scale sub-seabed CO₂ storage project is in the North Sea from the Sleipner offshore gas platform controlled by Statoil which developed this project aiming to inject 20 MtCO₂ in a brine hosted in the Utsira sandstone about 800 m below the seafloor offshore Norway. Since its beginning the Sleipner CCS has stored almost 12 million tonnes of CO₂ separated by the extracted natural gas. The overall cost of CCS for this project is of about 100 million USD, but its largely offset by the fact that storing the CO₂ exempts Statoil from the payment of the carbon tax introduced by the Norwegian Government and that in 2013 was about USD 70 per tonne of emitted CO₂ [15-18]. The integrity of the reservoir and the absence of leakage are fundamental issues for any CO₂ storage project; potential leakage can happen from failure in the sealing caprock (e.g. fracture or faults) corrosion in abandoned wells and malfunction of the injection or transport rig [19-21]. In these situations CO₂ may migrate outside the boundaries of the planned storage site affecting the surrounding environment. In particular CO₂ can affect the quality of groundwater, due to acidification, mobilization of potential pollutants such as heavy-metals [22] or contamination from fluids displaced by the advancing CO₂ front [23]. The stored CO₂ will generally move upwards, due to its buoyancy in respect to the pore-fluids and for capillary effects, towards the top-layers of the storage area up to the sealing caprock [24,25]. If the sealing is compromised the CO₂ and associated fluids may therefore leak. In this case soil and sedimentary cover will be affected by the chemical effects due to the increased concentration of CO₂ [26, 27].

Developing reliable detection and monitoring techniques for CO₂ leakages and assess their impact on the environment is also a legal requirement as indicated in the article 28 of the EC Directive on the geological storage of carbon dioxide: *“Monitoring is essential to assess whether injected CO₂ is behaving as expected, whether any migration or leakage occurs, and whether any identified leakage is damaging the environment or human health”* [28].

In submerged storage areas, such as in sub-seabed storage sites or in onshore reservoirs partially covered by bodies of water (e.g. lakes, rivers, and coastal areas) the seepage will affect not only the sedimentary cover but also the water column. The main effect of CO₂ leakage is a drop in the pH due to dissolution of CO₂ in the water with consequences on the local biota [29,30]. Another effect is the reduction in dissolved oxygen which is displaced by the CO₂ creating hypoxic conditions potentially harmful [31,32].

Seepage of acidic fluids may enhance the weathering of sediments and rock and, in case of large fluxes in poorly consolidated material, can have also a mechanical destabilizing effect [33-36]. For the purpose of geological storage CO₂ is generally injected as fluid in supercritical phase [37] but, mostly in relatively shallow-water as in the North Sea, if a failure of the injection well arises the following drop in pressure may trigger a phase-change generating large volumes of gaseous CO₂ [38]. Gas blow-outs under offshore rigs are known to cause a loss of buoyancy due to the reduced density of the gas-water mixture leading to possible sinking of the floating sections; in case of CO₂ blow-out the consequences are likely to be lesser than the ones caused by natural gas because CO₂ will not ignite as natural gas does [39].

The physical and chemical consequences of potential CO₂ seepage from sub-seabed storage areas have been studied mostly from a theoretical point of view or by the development of mathematical models [40-42]. Natural methane

seepages were investigated using sonar techniques to quantify the rate of the emissions [43-45]; imaging techniques were also tested both in laboratory and in the field as measuring device for gas bubbles in water [46,47]. Laboratory experiments assessed the characteristics of bubbles rising from submerged granular beds as proxy for the behaviour of methane seeps in aquatic environments [48].

The chemical effect of CO₂ release on sediments and water was studied through batch-experiments as it may affect the quality of water bodies overlying CO₂ storage mostly in terms of acidification and increasing in the concentration of ions following the weathering of the sediments and rocks exposed to high concentration of CO₂ [49,50]. The impact of CO₂ seepage on sediments and water has also been investigated by flow –reactor experiments [51]. Recently a field-scale controlled release of CO₂ from the seafloor in shallow-water allowed for the testing of monitoring procedures and instruments [52].

This paper presents the results of laboratory-scale experiments with a controlled release of CO₂ through porous sedimentary layers and water. The aim is to assess the main changes in the chemistry of water and sediments during the injection and in the following post-injection and to identify relations between the bubble behaviour and the granulometry and setting of the sedimentary layers.

2. Experimental methodologies

The experimental work is focused on the use of a specifically-designed laboratory apparatus where it is possible to generate controlled seepage of CO₂ trough sedimentary layers overlaid by water (Fig. 1). The system can be considered as a simplified experimental model for CO₂ leakage from storage sites in aquatic environments, such as sub-seabed or onshore areas underlying water bodies as lakes, rivers or coastal zones.

The equipment is composed by a vertical transparent plastic column (2 m length, 0.4 m diameter) divided in a base section (0.6 m length), and a top section (1.4 m length). The base section is filled with the sediments and a series of ports along its perimeter host Rhizon samplers which are used to collect pore-water. CO₂ is fed through an injector placed in the middle of the bottom layer of the sediments and its flux is controlled by a regulator and a mechanical flowmeter (floating sphere) in the range of 0- 3 bar and 0 – 0.6 liters/minute. The column is filled with water up to a maximum volume of 180 liters; the top of the column can be sealed with a lead connected by a hose to an extraction system to vent the CO₂ outside the laboratory during the injection phase. The pressure of the CO₂ is controlled by the regulator and maintained at values sufficient to overcome the hydrostatic pressure inside the column thus allowing the gas to stream; the system operates at atmospheric pressure. A detailed description of the apparatus is in [53].

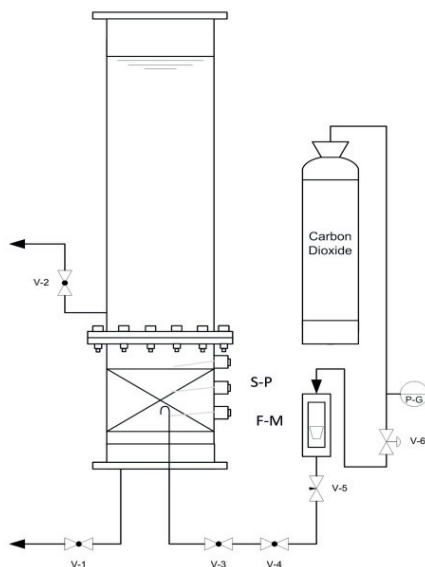


Fig. 1. Schematic diagram of the laboratory equipment. S-P, sampling ports; F-M, flowmeter; P-G, pressure gauge and gas regulator.

Three experiments were performed (A, B, C). In A and B calcareous sediments were used in freshwater and seawater respectively; in C siliceous sand and seawater were used. The aim was to identify the differences in the chemical response of calcareous and non calcareous sediments and of freshwater and seawater once exposed to CO₂. The calcareous sediments used in A and B experiments were composed by a basal layer of crushed limestone commercially available as TRUCAL (high-purity calcite) overlaid by Maerl which is a natural calcareous sand made by fragments of seashells and loose coralline algae composed up to 15% by aragonite [54]. Maerl is common along the shores of UK and its sensibility to ocean acidification makes it a good sample for the tests [55,56]. In experiment C marine sand composed mainly by quartz and sanidine was used as a single sedimentary layer. Details of the chemical composition and granulometry of the sediments are given in Table 1.

Table 1. Chemical composition, density and mean size of TRUCAL and Maerl

Sediment type	Ca	Mg	Density	Dimension
	%	%	Kg/m ³	mm
TRUCAL	55.6	0.3	2690	0.55
Maerl	33.8	2.33	n/d	>3

During the experiments CO₂ was vented for 120 minutes at a flow-rate of 0.3 l/min and was followed by a post-injection phase of “recovery” to quantify the capacity of the system to buffering the acidification and return to the original pre-injection values of pH, alkalinity and dissolved oxygen. This is relevant to assess the self-recovery potential of a natural system which has been exposed to CO₂ seepage once remediation procedures stopped the leak. Before the injection a baseline for pH, redox, alkalinity and dissolved oxygen was measured; details are in Table 2.

Table 2. Baseline of the main chemical parameters before the CO₂ injection

Experiment	pH	Redox	Alkalinity	D. O.
		Mv	ppm	mg/l
A water column	7.60	138.0	130	6.03
A maerl	7.99	N.D.	135	N.D.
A TRUCAL	7.84	N.D.	135	N.D.
B water column	8.12	200.0	146	6.01
B maerl	8.15	N.D.	148	N.D.
B TRUCAL	8.13	N.D.	150	N.D.
C water column	8.11	203.5	161	6.02
C sand	8.09	N.D.	163	N.D.

Inside the water column during the injection phase the following parameters were recorded: redox, temperature, total dissolved solids, dissolved oxygen and pH. Samples of pore water were collected inside the sediments for measuring pH and alkalinity which was also measured in samples collected from the column.

During the recovery period pH, redox, dissolved oxygen, and alkalinity were recorded.

The data in the column were acquired using a water-quality meter (Hanna Instruments HI-9110); this meter has a probe connected to a hand-held data-logger and it is able to record pH, temperature, redox, dissolved oxygen,

electric conductivity and total dissolved solids. The probe was lowered inside the column from the accessible top-lid down to the interface between sediments and water where the values were recorded.

The pH of the pore water was measured in the samples collected by the Rhizon with a portable meter (Hanna Instruments HI-98140).

The alkalinity was calculated as total CaCO_3 by titration on the collected samples. In the experiments with seawater the titration method was cross-validated with the use of a portable photometer for saltwater (Hanna Instruments HI-755) for alkalinity values up to 300 mg/l CaCO_3 as this is the maximum value which can be measured with the instrument. Higher values were determined by titration only. The accuracy of the readings is: pH ± 0.02 , ORP ± 1.0 mV, E.C. $\pm 1\%$, D. O. $\pm 3\%$, T ± 0.15 °C, Alkalinity $\pm 5\%$.

Through the transparent walls of the column it was possible to observe the behavior of the emitted bubbles during the injection phase in terms of distribution of the emission points and frequency of gas release. The induced modification to the structure of the sediments due to the accumulation of the gas creating pockets and channels was visible along the walls. The limited dimensions of the column and the related boundary effects should be addressed when analyzing the data.

3. Discussion

The results are analyzed dividing the experiments in an injection phase and recovery phase.

3.1. Injection phase

During the injection phase the main chemical parameters were recorded using the multi-parametric probe inside the water column and collecting samples of pore water.

3.1.1. pH trend in the water column and in the pore water

Figure 2 shows the pH trend in the water column during the CO_2 injection in experiments A and B. A drop in the values was observed during the experiments; this drop was slightly steeper in seawater than in freshwater with a difference in pH of 0.3 and 0.2 units after 20 minutes of injection in seawater and freshwater respectively. For the following 100 minutes and until the end of the injection (120 minutes total time) the pH continued to decrease steadily but with a progressively reduced drop. The trend can be defined by a reverse-power curve. The same trend was observed during experiment C highlighting that the influence of the chemical composition of the sediments at the scale of these experiments is negligible in terms of pH changes within the water column.

This trend is likely due to the dissolution rate of CO_2 in water with a first fast dissolution followed by a slower intake once the water is progressively saturated.

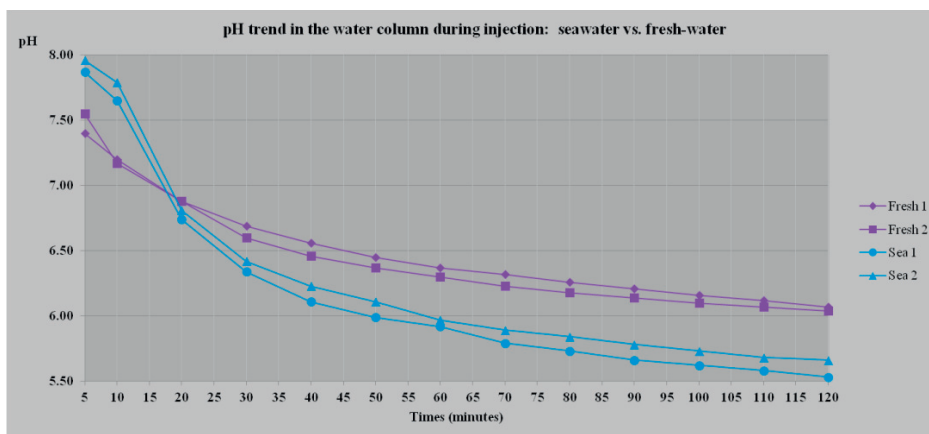


Fig. 2. pH trend in the water column during the CO_2 injection.

During experiments A and B in the pore water in the first minutes of injection the pH dropped sharply; during the rest of the injection the values were more stable and well above the values reached in the water column (Fig. 3).

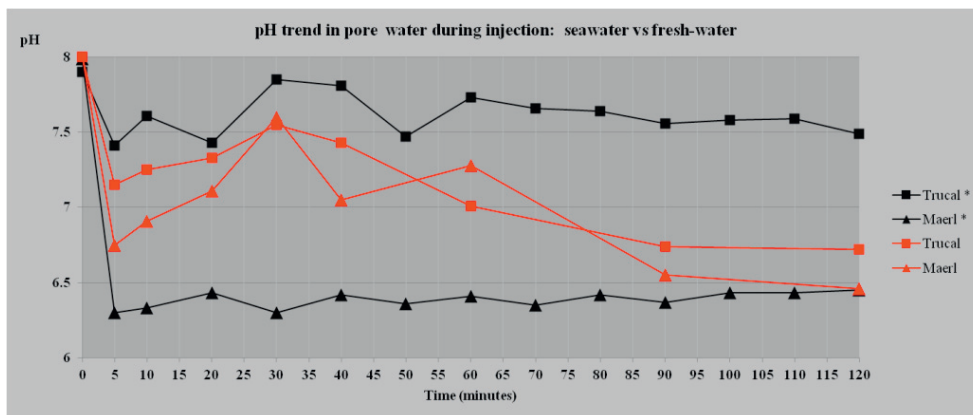


Fig. 3. pH trend in the pore-water during the CO₂ injection; * values are in freshwater

The observed fluctuations in pH can be explained considering that the pore water becomes acidic due to the dissolution of the CO₂ causing weathering of the calcareous components of the sediments, and this in return triggers a buffering effect leading to a stabilization of the pH. The changes are more evident in the Maerl pore water likely because of the coarser dimension of the sediments allowing for larger channels inside the layer with faster CO₂/water circulation facilitating the CO₂ dissolution. A similar trend in the pH of pore water was observed also in experiment C but with a general sharper reduction in the pH; this can be explained by the presence of calcareous components within the siliceous sand, likely fragment of marine shells, which act as buffer for the pH but at lesser extent than the calcareous sediments used in A and B experiments.

3.1.2. Dissolved oxygen and redox potential

The dissolved oxygen concentration trend in the water column shows an irregular behaviour with a general decrease during the injection phase with values reduced from around 4-5 mg/l at the beginning to about 3.5 mg/l at the end of the injection both in freshwater and seawater.

The trend can be explained considering that the dissolution of CO₂ in water displaces the other dissolved gases (i.e. oxygen) with complex exchanges between dissolved and free-gas phase within the rising bubbles and the surrounding water. The factors controlling the exchange rates include the partial pressure of the gasses, the value of their dissolution constant, the magnitude of the flux and the interaction time between bubbles and water [57].

The redox potentials reflect the changes in dissolved oxygen remaining always positive thus indicating that the system remains in oxidizing conditions during the injection phase.

3.1.3. Alkalinity

Changes in alkalinity during the injection phase in experiments A and B are due to the dissolution of calcareous sediments following the exposure to the acidic environment caused by the dissolution of CO₂ in pore water. This is highlighted in the measured values for Maerl with alkalinity increasing from about 150 mg/l to 900 mg/l and 400 mg/l in experiment A and B respectively. The higher alkalinity in freshwater (experiment A) is likely favoured by the under saturation in carbonates of freshwater allowing for a higher dissolution rate of the calcareous sediments when exposed to acidification. An increase in alkalinity was also observed in experiment C with values up to 480 mg/l at the end of the injection. This increase in dissolved CaCO₃ in the pore water of sand which is mostly composed of quartz can be explained by the presence of calcareous fragments (e.g. shells) of organic origin. The water column also shows an increase in alkalinity during the injection phase but with values well below the ones of the pore water.

3.1.4. Bubbles behaviour

The emerging of the bubbles from the sediments shows a delay in respect to the starting of the injection and the streaming of the bubbles is not constant being characterized by a pseudo-cyclical behaviour with emissions points scattered over the surface of the sediments. The initial delay is explained by the sediments trapping a certain volume of CO₂ within the pore space before allowing it to escape. The scattered emission of bubbles, both as spatial distribution and rate, is caused by the accumulation of gas and formation of preferential paths within the sediments due to the displacement of the granules by the flowing gas. Under the experimental conditions of these tests the average interval between the bubbles emissions was of about 30 seconds in experiment A and B and up to two minutes in experiment C. Similar behaviours were observed in experiments using gas flowing through granular beds and water columns [48]. The observation through the transparent walls highlighted that the CO₂ flowing through the sediments creates preferential paths displacing part of the finest deposits; where larger voids are present the gas can accumulate originating pockets within the sedimentary layer. The observed pseudo-cyclic emission is explained by the bubbles being emitted intermittently once the pressure of the gas trapped inside the pockets overcomes the local hydrostatic head which in this setting was about 0.15 atm.

3.2. Recovery phase

At the end of the CO₂ injection the system underwent to a period of recovery during which pH, dissolved oxygen and alkalinity values were recorded.

3.2.1. pH trend in the water column and in the pore water

The observed pH values in the water column during the recovery phase show a liner trend towards the initial pre-injection values (Fig.4).

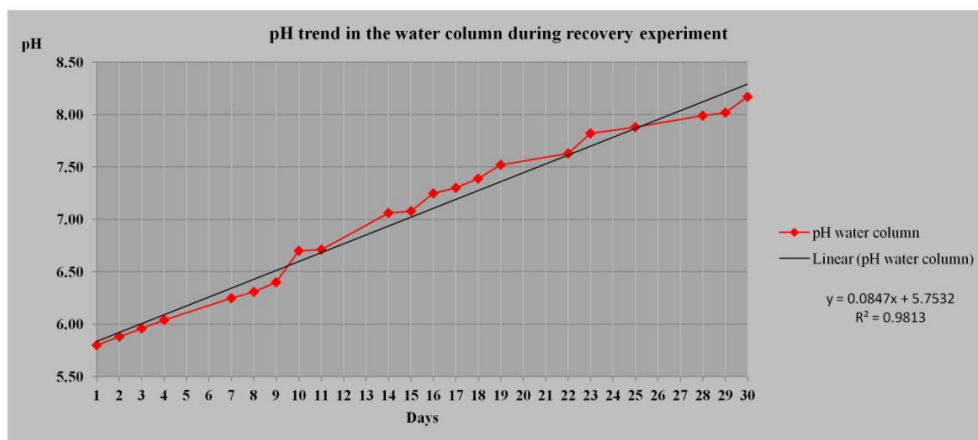


Fig.4. Linear trend of the pH in the water column during the recovery phase

An explanation of this linear trend is that the CO₂ is steadily degassing from the water until its partial pressure is back in balance with the one expected for water in equilibrium with the atmosphere. The pH of the pore water is stable during the recovery phase due to the dissolution of CaCO₃, similarly to that observed during the injection phase, causing a buffering effect which opposes to acidification leading to the almost constant observed values.

3.2.2. Dissolved oxygen and redox potential

During the post-injection period the dissolved oxygen concentration in the water column progressively increases from values around 3.5 mg/l at the end of the injection phase up to about 5.0 mg/l at the end of the recovery. The origin of this increase is linked to the degassing of the excess CO₂ and intake of atmospheric gases. The final values remain below the pre-injection concentration highlighting a long-lasting effect of CO₂ seepage in water leading to hypoxic conditions. A different trend was observed in experiment B when the dissolved oxygen values increased steadily following the development of algae within the column reaching values up to 7.5 mg/l from the 6.5 mg/l recorded at the beginning of the injection phase. This is likely due to the fact that the photosynthesis of the algae is producing oxygen and consuming CO₂.

3.2.3. Alkalinity

In experiment B during the recovery phase the alkalinity of the water column is almost stable with values around 360 mg/l for the first 11 days; it is followed by an increasing up to 420 mg/l at day 14 and then drops to 240 mg/l at day 18 showing further reduction in the following days down to about 200 mg/l. The alkalinity of maerl increases sharply after the first day from 414 mg/l to 630 mg/l and then the trend is more irregular with a final value of 590 mg/l at the end of the recovery phase. A similar trend is recorded for the alkalinity of Trucal with a generic increase from 132 mg/l at the beginning of the recovery to 800 mg/l at the end. In the experiment A the alkalinity of the pore water in the maerl reached higher values likely due to an easier dissolution of calcareous sediments in freshwater which is under-saturated in CaCO₃ respect to seawater. A more irregular trend was observed in experiment C with a final increase of alkalinity from 435 mg/l to 600 mg/l at the end of the 30 days of recovery.

3.3. Temperature and TDS

The measured water temperature reflected the one of the ambient surrounding the reactor ranging between 18 and 22 °C; no variation was observed along the water column during any phase of the experiment. A small increase of the Total Dissolved Solids concentration (0.5 – 0.7 g/l) was observed during the recovery period in respect to the pre-injection values and it is likely linked to some degree of evaporation which increased the salinity of the water. This is supported by a loss of volume of about 10 litres during the 30 days of recovery.

4. Conclusions

The observed chemical effects of the CO₂ injection are a general acidification of the water, with reduction in the dissolved oxygen concentration displaced by the CO₂. In case of large leakage this could generate plumes of hypoxic water which may affect the local biota. It should be noted that in these experiments the volume of water is confined inside the limited space of the column; in open sea, currents, convective movements and waves will disperse the plume of acidified water, leading from one end to the diffusion of the plume and on the other to its progressive dilution. Depending on the magnitude of the leakage the dispersion of the acidified water can mitigate the consequences (i.e. a small plume will easily be mixed with the surrounding water therefore reducing its acidity) or may induce larger effects (i.e. a big plume of contaminated water may be dispersed over an area much wider than the footprint of the actual leakage). An accurate estimate of the CO₂ flux is therefore extremely important for assessing the environmental consequences of potential leakages. The sharp drop in pH in pore water at the beginning of the injection can be used to detect the first stages of seepage even in absence of emission of bubbles. This could be the case when a front of acidified fluids moves from the storage area through the overlying layers following seepage when the CO₂ is totally dissolved in the water.

The exposition to acidified fluids has a long-lasting effect in terms of calcareous dissolution even after the seepage is terminated as highlighted by the increased values of alkalinity in the pore water. This is to be addressed when considering the overall environmental impact of CO₂ emissions. The effects on Maerl can be considered as indicative of what may happen to the skeleton and shells of calcareous marine life-forms in case of CO₂ seepage and, more in general, as consequence of ocean acidification.

A feedback between mechanical effects of the gas flowing inside the sediments and induced changes, with formation of preferential paths and gas-pockets was also observed. The accumulated gas was released once its

pressure reached values above the hydrostatic head of the overlying water column with intermittent streaming. In a real scenario of leakage the hydrostatic head will be much bigger (up to a few atm considering as example the average depth of the seafloor in the North Sea) and this may lead to larger gas accumulation and sudden burst able to displace great volumes of sediments from the seafloor with potential consequences on the stability of moored rigs [34,35]. Moreover such intermittent emission may be difficult to be localized requiring continuous monitoring over large areas in an attempt to locate both the gas plumes in the water or evidence of gas-charged sediments in the sub-seafloor [58,59]. Correlating the sedimentary setting of the seafloor with the behavior of the emitted bubbles can help in defining a reliable monitoring strategy and methodology.

During the post-injection period a partial recovery of the system was observed with increase in pH towards the original values. This highlights a general recovery potential of the seawater once the seepage is remediated. In a real scenario, such recovery should also be facilitated by the mixing with surrounding water less affected by the CO₂ seepage.

Building on these results further experiments in more complex settings can be developed; it would also be possible to compare the laboratory outcomes with the study of submarine areas where a natural release of CO₂ is present [60].

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