



Article Monitoring Offshore CO₂ Sequestration Using Marine CSEM Methods; Constraints Inferred from Field- and Laboratory-Based Gas Hydrate Studies

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Abstract: Offshore geological sequestration of CO₂ offers a viable approach for reducing greenhouse gas emissions into the atmosphere. Strategies include injection of CO2 into the deep-ocean or oceanfloor sediments, whereby depending on pressure-temperature conditions, CO₂ can be trapped physically, gravitationally, or converted to CO₂ hydrate. Energy-driven research continues to also advance CO₂-for-CH₄ replacement strategies in the gas hydrate stability zone (GHSZ), producing methane for natural gas needs while sequestering CO_2 . In all cases, safe storage of CO_2 requires reliable monitoring of the targeted CO₂ injection sites and the integrity of the repository over time, including possible leakage. Electromagnetic technologies used for oil and gas exploration, sensitive to electrical conductivity, have long been considered an optimal monitoring method, as CO2, similar to hydrocarbons, typically exhibits lower conductivity than the surrounding medium. We apply 3D controlled-source electromagnetic (CSEM) forward modeling code to simulate an evolving CO₂ reservoir in deep-ocean sediments, demonstrating sufficient sensitivity and resolution of CSEM data to detect reservoir changes even before sophisticated inversion of data. Laboratory measurements place further constraints on evaluating certain systems within the GHSZ; notably, CO₂ hydrate is measurably weaker than methane hydrate, and >1 order of magnitude more conductive, properties that may affect site selection, stability, and modeling considerations.

Keywords: carbon sequestration; CO₂ offshore storage; marine CSEM; gas hydrates

1. Introduction

Geological sequestration of CO_2 , including storage in the marine environment, can facilitate a variety of strategies for reducing greenhouse gas emission and meeting net-zero carbon targets [1–5]. Numerous theoretical, laboratory, and, in some cases, field investigations have been conducted on the containment of CO_2 as a liquid, gas, dissolved-phase, or as a solid gas hydrate phase, under relatively cool conditions, such as in deep-ocean settings [6–10] or in moderate- to deep-ocean-floor sediments [11–18], yielding insight into the physical, geochemical, kinetic, and thermodynamic factors involved in these complicated multiphase systems. Offshore sequestration offers an alternative approach to more conventional strategies involving CO_2 storage in warmer terrestrial settings, for example, as supercritical CO_2 injected into deep porous rocks, sedimentary saline environments, depleted oil and gas reservoirs, or in mineral carbonation scenarios (e.g., [4,19] and references therein).

Deep-ocean sediments at relatively high-pressure and low-temperature conditions offer volumetrically near-unlimited and long-term containment of CO_2 , provided sufficient permeability to inject CO_2 . Due to the high solubility of CO_2 in seawater and the high compressibility of liquid CO_2 relative to seawater, liquid CO_2 becomes neutrally buoyant at roughly 2500–3000 m depth, conditions that do not exist in terrestrial settings but are common in oceanic settings [11]. Injecting CO_2 into ocean-floor sediments below roughly



Citation: Constable, S.; Stern, L.A. Monitoring Offshore CO₂ Sequestration Using Marine CSEM Methods; Constraints Inferred from Field- and Laboratory-Based Gas Hydrate Studies. *Energies* **2022**, *15*, 7411. https://doi.org/10.3390/ en15197411

Academic Editors: Ingo Pecher, Zachary M. Aman, Ray Boswell and Ross Anderson

Received: 30 August 2022 Accepted: 7 October 2022 Published: 9 October 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 3000 m water depth and a few hundred meters of sediment is predicted to enable stable and potentially long-term (on a geologic timescale) sequestration of CO_2 , even in the event of geomechanical disturbance [11,14,16,18]. At these conditions, CO_2 resides in its liquid phase, denser than the overlying seawater or pore fluid, causing the injected CO_2 to remain gravitationally "trapped". In the event of possible leakage, or conversion to gas phase or upward migration, CO_2 will form gas hydrate (described below) with the sediment pore water when pressure–temperature conditions reach the CO_2 hydrate stability zone. In this context, CO_2 hydrate formation can serve as a self-healing process that greatly slows the CO_2 diffusion rate and creates a low-permeability secondary cap on the system [11,14,16,18]. Teng and Zhang [17] reviewed and modeled the short- and long-term fate of injected CO_2 stored in deep-sea sediments over different geologic and operational conditions, including multicomponent flow considerations and the impact of hydrate formation on storage efficiency.

Gas hydrates, also called clathrate hydrates, are crystalline solids consisting of hydrogenbonded water molecules forming polyhedral cage-like structures stabilized by "guest" molecules of appropriate size, including CO₂ and methane (CH₄), and form naturally where temperature, pressure, and gas supply combine to make them stable [20]. In the marine environment, natural gas hydrates—most commonly methane hydrate—form in continental shelves below roughly 500 m water depth depending on local conditions, marking the upper limit of the so-called gas hydrate stability zone (GHSZ) [21]. Downslope, the GHSZ thickens as pressure increases, with thickness limited at its base by the geothermal gradient. Significant interest remains in advancing methane hydrate research for climate mitigation efforts and to better understand the role of methane hydrate in the carbon cycle, as well as in its potential as a bridging fuel—as a transitional energy source with lower net carbon emissions than oil and coal—while existing challenges in the conversion from fossil fuels to renewable energy sources are addressed [22,23].

In related CO_2 storage research, numerous efforts have examined mixed CO_2/CH_4 gas hydrates and related physical chemistry processes involved during CO₂-for-CH₄ replacement, including processes and issues surrounding possible sequestration of CO_2 by injection into deep methane hydrate-forming deposits with concurrent production of methane [24-37]. In CO₂-for-CH₄ replacement, chemical disequilibrium is presumed to induce transformation of the original CH_4 hydrate into a CO_2 -rich hydrate [36]; CO_2 is thermodynamically favored in the hydrate phase compared to CH_4 at relevant conditions, and both form a structure I hydrate [20], as do mixtures of these gases [33]. Laboratory experiments reveal that this exchange process does not necessarily involve macroscale dissociation of the hydrate phase [27,29,37], thus ideally allowing capture and storage of CO_2 with little to no loss of hydrate-bearing sediment strength or related environmental disturbance. Additional advantages are that the exothermic nature of CO₂ hydrate formation promotes CH_4 hydrate dissociation, and CO_2 hydrate, unlike methane hydrate, is denser than seawater and hence can be gravitationally trapped in marine environments. At the field scale, however, additional factors and dynamics of the natural environment complicate the replacement strategy and this is a direction of active research, including possible blockage of methane production due to rapid CO₂ hydrate formation [35]. Zheng et al. [38] provide a comprehensive review of the various approaches to CO_2 sequestration that involve gas hydrates—including storage in seawater, sediments under the sea floor, permafrost regions, and in methane hydrate reservoirs via CO₂–CH₄ exchange—and also address technical feasibility and potential storage capacity considerations.

A critical component for safe and reliable CO_2 sequestration strategies involves monitoring the injection of CO_2 into the targeted region and verifying long-term stability and integrity of the storage reservoir, including possible leakage. Since the early 2000s, a variety of geophysical methods have been applied towards monitoring geological and marine storage of CO_2 (reviewed in [39,40]), including both seismic and nonseismic technologies, with increasing application of electromagnetic (EM) or electrical technologies that complement seismic or gravity measurement methods [41–51]. EM methods are considered particularly useful for monitoring CO_2 sequestration where displacement of pore fluid by CO_2 increases electrical resistivity.

We limit our focus to marine controlled-source electromagnetic (CSEM) technology, now long established for offshore hydrocarbon reservoir exploration and appraisal [52,53] and long considered for production-induced reservoir changes [54], as the technique can be exceptionally sensitive to electrically resistive structures—such as oil, gas, and gas hydrate [55]. Although the resolution of CSEM surveying is inherently lower than that of seismic methods, time-lapse approaches allow measurement of even small variations in resistivity and provide superior intrinsic resolution to potential-field methods such as gravity and magnetic surveying [53]. Marine CSEM is now used successfully to image resistive structures within the gas hydrate stability field [56–62], hence its obvious application for offshore CO_2 storage efforts (e.g., [44,47,49,50]). For example, using the CSEM "Vulcan" system [63], specially developed to image resistive subseafloor features in the shallower section, Kannberg and Constable [61] were able to characterize methane hydrate in marine sediments offshore Southern California at basin scales, and resolved seafloor resistivity down to a fraction of an Ω .m for low-resistivity sediments. When jointly interpreted with geologic structural information from seismic reflection surveys, CSEM methods provide a broad understanding of gas migration pathways in hydrate-bearing sediments and hence may be particularly applicable to monitoring CO₂ reservoir stability, geometry, and possible leakage.

In this study we illustrate the value of using CSEM data to monitor CO₂ sequestration in the deep seafloor by running simulations with the 3D forward modeling code of Weiss and Constable [64] (FDM3D CSEM). This code uses a Cartesian staggered grid for the model mesh and a finite-volume approach to solving the electromagnetic curl-curl equations, with demonstrated success for modeling thin, resistive structures in the seafloor [64]. Although similar to the finite-difference approach, the finite-volume method allows a more accurate representation of the strongly varying fields near the transmitter through the use of quadrature integration. This code has limitations in the interpretation of real data; for example, it assumes infinite water depth, and the Cartesian mesh cannot represent bathymetry very well, so we implemented the 2D finite-element code of Key [65] for routine inversion of real data. However, FDM3D has several advantages for carrying out the simulations we present here. It employs a quasi-minimal residual (QMR) algorithm to solve the linear system of equations using less computer memory, it is fast and easy to use, running easily on a modern laptop computer, and it is freely available through an open-source GNU license (see Data Availability Statement).

Lastly, we review additional physical properties measurements that may influence the measurement or stability of hydrate-bearing marine sediments where CO_2 hydrate can either form as a cap on stored CO_2 below, or replace methane hydrate in the GHSZ. Laboratory measurements on well-characterized materials are useful for calibration of geophysical measurement techniques and can help augment mixing models, and by extension can help guide long-term stability assessment. Moreover, we might expect that as modeling efforts continue to advance, so will the need for increasingly well-constrained input parameters. While different compositions and/or structures of gas hydrates may in some cases exhibit similarities in physical properties, in other respects they in fact exhibit strikingly different behavior from one another: dissociation behavior, ductile strength, and electrical properties are three prime examples discussed below.

2. Methods

Electrical resistivity can be used to discriminate between various types of materials (including rock types), and provides important information on the porosity and pore geometry of geologic formations as well as the nature of pore fluids. Borehole resistivity logs are hence commonly utilized for hydrocarbon exploration and gas hydrate characterization. CSEM technology, on the other hand, facilitates remote and noninvasive mapping of the resistivity distribution of the subsurface without the need for boreholes. Most commonly,

marine CSEM sounding employs an electric dipole source towed just above the seafloor to transmit a time-varying electromagnetic field (usually a few discrete frequencies), which in turn is modified by the presence of subsurface resistive structure. The amplitude and phase of the propagating fields are detected and logged by an array of electric and magnetic dipole field receivers placed on the seabed or towed behind the transmitter.

The physics of these modifications can be divided into three basic phenomena. The first is electromagnetic induction, characterized by the skin depth, or diffusive scale length, which is inversely proportional to conductivity and frequency. In a uniform medium, the field strength falls off exponentially with distance, with the skin depth determining the exponential scale length. The second is the galvanic effect associated with conductivity boundaries. Conservation of charge (and thus current) requires that the electric field must be different on the two sides of such a boundary, and this difference is proportional to the conductivity contrast. The third is geometric spreading: for a dipole transmitter, the fields fall off as the cube of distance. The modeling codes we use to simulate and invert field data incorporate all the physics by numerically solving the appropriate partial differential equations with suitable boundary conditions.

The most significant difference between the land and marine environments is that the skin depths of the seafloor rocks are larger than the skin depth in seawater, so the signals measured close to the seafloor are dominated by energy that has propagated in the target of interest, that is the seafloor geology. On land, energy can propagate through the atmosphere and it contributes significantly to the signals that are measured in the frequency domain. The theory and historical development of the marine CSEM method, with specific application to sub-seafloor hydrocarbon reservoirs or similarly resistive layers, is reviewed in [53,55].

Here, an FDM3D model domain was built from a uniform grid of $100 \times 100 \times 100$ cells (101 nodes in each direction), with each cell being 200×200 m in the horizontal directions and 100 m in the vertical direction, for a total model size of $20 \times 20 \times 10$ km. Horizontal electric field transmitters in both the x/east and y/north directions were located near the seafloor in the central 5 km of the model; 26 in total at 13 locations. Receivers were scattered across the seafloor spaced 500 m apart in a 5×5 km grid; 441 in total (Figure 1). It is computationally efficient to use a small number of transmitters and a large number of receivers in the simulations. In practice, given the ability to tow a CSEM transmitter continuously through seawater, real data would be collected using a relatively small number of receivers and a large number of transmitters. However, electromagnetic field behavior is reciprocal, in that transmitters and receivers can be exchanged and the same fields measured, meaning that the data simulated here could be realistically acquired in the real world. In recognition of that, the transmitters were placed 1 m above the seafloor and the receivers 50 m above the seafloor, opposite to how data are collected in practice. Transmission frequency was set to 0.25 Hz.

In a classic sensitivity study, forward model data would be generated, realistic levels of noise added, and then inverted to see if the structures in the original model could be recovered. This is a sensible procedure for determining if, for example, a particular EM survey could determine total volume of gas in a given reservoir structure. However, not only is the huge computational cost of 3D inversion not necessary to demonstrate the utility of CSEM monitoring of sequestration activity (and we further note that 3D CSEM inversion codes are only recently becoming publicly available), but we also suggest that it is not even appropriate for the question at hand. Inversions seek to solve for the electrical conductivity structure of the entire model domain, because this is usually unknown prior to the collection of data. For timelapse monitoring, however, detailed knowledge of the host rock's conductivity structure is not needed, as we are primarily interested in changes at the reservoir level. Furthermore, the smooth regularization that is ubiquitous in modern inversion codes acts to smear out the effects of sharp conductivity boundaries, and will equally smear out the effects of conductivity changes, giving a pessimistic view of data sensitivity. It is also important to recognize that inversion models depend as much on the

regularization penalties as the actual data, and a sharp temporal change in conductivity will be distributed as a gradual spatial change in the host rock conductivity in ways that might not be intuitively apparent or even helpful, a topic we return to below.



Figure 1. Model conductivity and transmitter/receiver layout exemplified by a 1500 m radius target structure. (a) Plan view at target depth showing locations of transmitters (o) and receivers (+) projected from the seafloor. (b) Section view showing target structure at a depth of 1000 m below seafloor. The entire model computation domain is shown.

It is also relevant to recognize that the engineers know how much CO_2 has been pumped into the sediment, and at what depth. What is necessary to know is where it is moving to from there. We demonstrate that the actual data are very sensitive to where changes occur, and examination of the data themselves may tell the engineers what they need to know. This is the approach we take here. That said, comparing the responses of informed forward model simulations of the various possible migration scenarios with the data would also provide valuable information, and 3D inversion will be used to fully exploit the data collected. However, comparison of independently inverted beforeand-after inversion models is not likely to address this, for reasons already articulated. Rather, new inversion algorithms that invert the actual changes directly, constrained by the known geometry of the sequestration horizons and the amount of CO_2 injected, should be developed. While this is well beyond the scope of the present work, we hope the results presented here will motivate others to perform this.

3. Results

We can illustrate the sensitivity of CSEM data to a CO₂ sequestration scenario using a relatively simple model. Background seafloor conductivity is taken to be 1 S/m, typical of marine sediments, and seawater conductivity 3.2 S/m, typical of deep water. A reservoir

target is placed 1000 m below seafloor, a little deep for CO_2 sequestration but not unrealistically so. The thickness of 100 m is one commonly used in simulations and is conveniently one cell tall in our model. We assign the reservoir a conductivity of 0.01 S/m, a value used by [46] but on the low side of other studies. While a simple model, this is consistent with those used in other studies [40,44,46] and has the advantage of being identical to the canonical oilfield model [64], allowing comparisons to be made with many existing studies designed to examine the use of CSEM for oilfield exploration (e.g., [53,54]). The 3000 m diameter reservoir thus constructed and shown in Figure 1 would take 14 years to accumulate in 35% porosity sediments filled to 60% saturation CO_2 at an injection rate of 10 million tons of CO_2 per year, considered to be a realistic injection rate [66] and less than the current U.S. Department of Energy targets [67].

The FDM3D code computes the three orthogonal components of the complex electric and magnetic fields at every receiver location, so each simulation generates over 100,000 real data points which have fairly complex behavior depending on the particular geometry of the transmitter and receiver pairs. One of the simpler components to interrogate is the phase of the vertical electric field in the radial direction (taken to be within 45° of the inline direction of a transmitter). Phase varies less with transmitter/receiver geometry than amplitude and varies linearly, while amplitude varies exponentially, with range and conductivity. The radial field mode is known to be sensitive to thin resistive targets [53,64]. Finally, navigation errors have a smaller impact on phase than amplitude [68], making this a more robust measurement for repeat CSEM studies.

In Figure 2 we take the difference in vertical field phase between the background structure (i.e., the CSEM response of the host rock without the CO2 reservoir) and reservoirs 750, 1000, and 1500 m in radius. The data are projected onto points that lie midway between the transmitter positions and the receiver positions, and averaged where multiple midpoints lie on the same physical position. Data with a transmitter–receiver range of less than 1000 m are excluded, as are any points with electric field amplitudes less than 5×10^{-15} V/Am², a realistic noise floor for real data. The plots are scaled by the largest difference in phases, which for the phase convention in FDM3D is positive as resistive structure is introduced, and are between 5 and 20 degrees. It is routine to fit modern CSEM data to within 1 degree during inversion, so these values are well within the resolution of the method. It is clear from these plots that the phase jumps sharply within 100 to 200 m of the edge of the reservoir; thus, reservoir size can be tracked quite effectively using these data.



Figure 2. Radial mode 0.25 Hz vertical electric field phase change between background and reservoir, projected onto transmitter–receiver midpoints (white dots) and averaged over all data. (**a–c**) Target reservoirs with radii of 750, 1000, and 1500 m, respectively, outlined in red. Transmitter locations shown as black circles. Note the change in phase scale between plots.

As we already stated, the engineers in control of injection know the total mass (and approximate volume) of CO_2 sequestered. Knowing the diameter of the resulting reservoir is useful information and will depend on the thickness and saturation that is achieved. However, of greater interest is the development of significant heterogeneity in the reservoir structure. In Figure 3, we show the effect of a "breakout" on the edge of an otherwise

orderly reservoir. Such behavior could be problematic if the CO_2 is migrating along an unknown fault structure or variation in permeability. The difference between the breakout model and the background is dominated by the main reservoir response, but taking the difference between the breakout response and the 1500 m radius reservoir clearly shows where the breakout is developing. This highlights the value in taking stepwise differences of the data, rather than differencing only against the baseline measurements, and argues for collecting datasets more closely spaced in time than might otherwise be apparent.



Figure 3. Similar data as shown in Figure 2, except we take the difference between the 1500 m radius model and a model, as shown, where there is a breakout to the southeast. The CSEM data clearly show where the changes have occurred in the reservoir.

While the model simulations we presented clearly show that the marine CSEM method is sensitive to changes in reservoir structure, it is worth testing the assertion that complications in the background conductivity structure are not important. We therefore varied the background conductivity in 800 m \times 800 m patches one vertical cell tall (100 m), randomly drawing the background conductivity from a lognormal distribution of conductivity. We computed the response of this background model and then inserted the 1500 m radius reservoir as before. The difference, shown in Figure 4 alongside the difference for the uniform background, is almost identical to the previous results.



Figure 4. Simulation of the 1500 m radius reservoir in a heterogenous background geology. (**a**) Model conductivity structure. (**b**) The 1500 m response in a uniform background as shown in Figure 2. (**c**) The response in the heterogeneous background.

4. Discussion

4.1. CO₂ Stored in Deep Marine Environments; Monitoring Considerations

The simple simulations we presented are designed to show that the CSEM method is sensitive to the types of structures that CO_2 sequestration creates, and that changes observed during CO_2 injection are detectible and track the location of the change in a way that is visible even in raw data. The resolution of the CSEM method depends on the depth of the target, so by choosing to illustrate the utility of the method using models with a relatively deep target we are presenting the pessimistic case. Shallower reservoirs, including those in the GHSZ, would result in a stronger electromagnetic signature more easily visible and with sharper lateral resolution.

We are not suggesting that data analysis stop at visualization, but rather that if changes can be seen in the data themselves, then more rigorous modeling will prove even more useful. Indeed, lateral changes are easy to visualize, but changes in vertical structure, such as leakage from the reservoir and formation of shallower hydrate, will require more sophisticated methods than we present here. For example, for simplicity we used only one frequency, chosen to be sensitive to the target depth, but it was shown that inclusion of several frequencies dramatically improves resolution of CSEM during inversion [69] and is useful to resolve vertical structure, since the skin depth, or characteristic decay length, of electromagnetic signals decreases with increasing frequency. In addition, it is likely that small-scale variations in permeability, particularly those parallel to bedding, will result in injection geometries that are not homogeneous, as was modeled here, but stacked thin layers, as was observed at Sleipner [70]. Such thin layers are difficult to fully resolve with seismic methods, and certainly would be below the resolution of CSEM methods. However, they would result in significant electrical anisotropy, which can be resolved using a combination of radial (in-line) and azimuthal (broadside) CSEM data or a combination of CSEM and magnetotelluric data, a passive EM imaging method [53,69].

Although 3D inversion will certainly be required to achieve the full potential of the data, we suspect that repeat regularized inversion of individual snapshots of the reservoir will prove disappointing, as the regularization projects sharp changes seen in the data across smooth conductivity models. More work in this regard is needed, and hopefully our simple study will help motivate this. A first step was developed [71] in which instead of comparing independent inversions of two time-lapse CSEM datasets, the data response predicted by the baseline inversion model is perturbed by the data differences (the data type we discuss here) and then inverted. The difference between the two models thus generated is less dependent on the characteristics of the baseline model than independent inversions would be.

There are many practical aspects to sequestration or production monitoring, some of which have been discussed before [54] and which tend to concentrate on the ability to replicate the navigation of repeat surveys. Likely, navigation will be tightly constrained around the infrastructure required for CO_2 sequestration, and permanent installation of instruments will be possible. While calibrating instruments and maintaining that calibration to better than 1% is challenging, demonstration that the phase of the CSEM signal carries the required information sidesteps this issue to some extent; GPS timing signals can be sent to all instruments, as has already been performed in CSEM surveying [63], allowing phase to be measured precisely even when amplitude is uncertain.

4.2. CO₂ Storage as Hydrate in the GHSZ; Insights from the Laboratory

In addition to the considerations of CO_2 storage monitoring discussed above are the related geotechnical issues involved with site selection itself, and here we turn our attention to environments in, or proximal to, the GHSZ. Laboratory measurements can help guide long-term stability assessment, and an important role for lab studies on marinehydrate-bearing sediments is careful measurement of controlled systems with known grain characteristics, formation history, and gas hydrate concentration, to calibrate logs and geophysical measurement techniques and to augment mixing models [72]. Numerous investigations have focused on the distribution and articulation of the hydrate phase within sediments as well as the characteristics of the sediment components (e.g., grain size, shape, mineralogy), sediment index properties (e.g., porosity, permeability, compressibility, permittivity), complex effects of particle mobility, and pore fluid chemistry. Waite et al. [73] provide a comprehensive pre-2009 review of research investigating solubility and formation considerations, thermal properties, fluid migration, EM properties, and seismic wave

provide a comprehensive pre-2009 review of research investigating solubility and formation considerations, thermal properties, fluid migration, EM properties, and seismic wave speeds of hydrate-bearing sediments. A selection of more recent investigations on mechanical properties and water saturation effects includes [74–78], a mere fraction of the work on this broad topic. In many cases, THF hydrate is used in experiments as it is stable under easily accessible temperature and pressure conditions and can be formed over short laboratory timescales. However, THF forms a structure II hydrate, unlike methane and CO_2 that both form sI hydrate, at conditions relevant to Earth. Considerably less attention has been directed to the possible influence of the specific composition of the gas hydrate phase itself, and its possible effects on the stability or monitoring of formations within the GHSZ that might be suitable for carbon storage efforts.

To this end, we review a selection of in-house (or associated) lab experiments demonstrating the measurable, and in some cases quite significant, departure in physical properties that distinguish pure CO_2 hydrate from pure methane hydrate. H₂O ice is compared as well, illustrating why in some cases it is an exceptionally poor analogue for gas hydrate. Our basis of comparison is that all hydrate samples discussed below—over the course of 25 years—were prepared by virtually identical methods and apparatus, in the same laboratory, from the same distilled-deionized water source and scientific-grade gas sources, and in most cases monitored throughout synthesis by the same instrumentation [79,80]. For mixed hydrate/sediment aggregates, silica sand or silt standards were consistently used. During development of synthesis methods, X-ray and neutron diffraction verified sample purity and the expected lattice parameters (e.g., Figure 3 in [80]), and stoichiometry was measured using a custom flow meter and gas collection apparatus (Figure 5 in [79]; also [80] and references therein). While useful insights and trends can be gleaned from experimentation on analogue materials such as THF hydrate [74], dissociation behavior, ductile strength, and electrical properties are three notable examples where specific composition and/or structure of the gas hydrate critically influence material behavior.

Dissociation. CO_2 hydrate is far less prone to dissociation than methane hydrate when each is slowly warmed outside of its stability field [80] and does not exhibit complex temperature-dependent dissociation behavior, as is observed in pressure-release experiments on CH_4 hydrate (i.e., anomalous preservation, first described in [79]). Instead, CO_2 hydrate dissociation appears to be governed by one dominant characteristic: regardless of the pressure-temperature pathway CO_2 hydrate follows to conditions outside its stability field, for instance, by increasing temperature or by decreasing pressure, the bulk of the material resists dissociation (at least on a laboratory timescale) until temperatures reach within a few degrees of the ice point, whereupon all remaining CO_2 gas is released [80]. We may expect that the extremely sluggish dissociation rates play in favor for deterring CO_2 leakage. Interestingly, while CO_2 hydrate and CH_4 hydrate exhibit contrasting dissociation behavior, *dissolution* of these two end-member hydrates exhibits fully predictable behavior, fitting a diffusive boundary-layer model that incorporates relative gas solubilities appropriate for the setting [81].

Strength. Rheological testing of a selection of gas hydrates was conducted in a triaxial gas apparatus using standard rock mechanics methods, including encapsulated samples, elevated confining pressures to suppress macroscopic fracture, and a pore pressure line communicating gas to the sample to maintain it within its equilibrium stability field throughout testing (Figure 12 in [79]; see also [82,83]). Figure 5, modified from [83], illustrates the exceptional plastic flow strength contrast between various gas hydrates and water ice. For example, at 263 K (-10 °C) and strain rate 3.5×10^{-6} s⁻¹, the steady-state stress supported by polycrystalline water ice is roughly 1.5 MPa, compared with ~10 MPa

for CO₂ hydrate, ~39 MPa for methane hydrate, and close to 100 MPa (extrapolated) for sII methane–ethane hydrate [83].



Figure 5. Rheological strength contrasts of gas hydrates and ice. (**a**) Ductile flow, plotted as log σ vs. reciprocal temperature (Arrhenius plot) of sI methane hydrate, sI CO₂ hydrate, sII methane–ethane hydrate, and H₂O ice. Modified from Figure 4 in Durham et al. [83]. Here, σ denotes stress. Strain rate is 3.5×10^{-6} s⁻¹. Not only are gas hydrates substantially stronger than water ice, but they can also exhibit strength contrasts amongst different structures (sI vs. sII) as well as different compositions of the same structure (sI CH₄ vs. CO₂ hydrate). Adding a uniform mix of 50 vol.% quartz sand to either CH₄ or CO₂ hydrate (gray lines) increases strength by ~2× with respect to the pure end-members. (**b**) Indium-jacketed composite sample of methane hydrate ("MH", bottom) and ice (top) between two end caps, illustrating the manifest strength contrast whereby sample strain is accommodated by the significantly weaker ice phase (modified from Figure 1 in [82]). The sample was a near-perfect cylinder prior to testing.

Importantly, the results reveal that significantly different rheologies are exhibited by at least some sI vs. sII hydrocarbon hydrates, as well as between compositions of the same structure hydrate (sI methane hydrate vs. sI CO_2 hydrate), including at temperatures above the ice point that are directly relevant to marine sedimentary environments. The high strength of gas hydrates may even be of consequence for marine-hydrate-bearing formations where hydrate concentrations are low. If conditions permit high effective normal stresses (high confining pressure relative to pore pressure), frictional resistance and cohesion between sediment grains may be high enough that time-dependent plastic deformation within the weakest grains of the aggregate governs macroscopic strength [83]. In the case of methane-hydrate-bearing or CO_2 -hydrate-bearing sediment formations, the hydrate is the weakest phase, and its response may have a markedly different effect than previously predicted.

Can the distinct rheologies illustrated in Figure 5 be explained? The contrast in ductile strength between ice I_h and sI methane hydrate is at first glance surprising as they share similarity in oxygen–hydrogen bond angles and lengths, as well as density [20]. However, as postulated in [82], two key factors lend insight into their contrasting behavior: (1) the rate of molecular water diffusion may be as much as two orders of magnitude slower in gas hydrate than in ice, rendering it more creep-resistant, and (2) unit cell considerations likely render glide-and-climb motions of dislocations, as well as self-diffusion, more difficult and thus increase the resistance of sI hydrate to intracrystalline plastic deformation (as per [20], the cubic hydrate sI unit cell parameter of 1.20 nm, with 46 water molecules per unit cell, is roughly twice the linear dimension of ordinary hexagonal ice I_h , with cell

parameters a = 0.45 and c = 0.74 nm and four water molecules per unit cell). The rheological contrast between sI methane hydrate and sI CO₂ hydrate, on the other hand, remained an enigma, despite the demonstrated veracity of the behavior itself [83]. We now suspect that point-defect and lattice-imperfection factors implicated in the more recently discovered electrical property contrasts between CO₂ hydrate and CH₄ hydrate (discussed below) may likely also be rooted in other diverging responses, including rheology. Of note, in addition to the measurable strength contrast exhibited by these two sI hydrates, the slope of the data (proportional to activation energy E_a as plotted in Figure 5) is also different, with CO₂ hydrate instead sharing commonality with warm-temperature ice in a manner similar to Figure 6.

Conductivity. Electrical conductivity (σ) was obtained from frequency-dependent impedance measurements made on pure, polycrystalline sI CO_2 hydrate [84], on samples synthesized by identical methods as used above for dissociation, dissolution, and rheological testing [79-83] and compared with pure sI CH₄ hydrate conductivity formed and measured in the same apparatus [85]. We previously demonstrated how EM studies in the field can benefit from salinity-conductivity insights gained from laboratory measurement of σ made on CH₄ hydrate with variable amounts of ionic impurities, sediments, or brines [86–88], and now find that composition of the guest molecule itself can significantly influence σ as well (Figure 6). In the case of pure CO₂ hydrate vs. pure CH₄ hydrate, there is over an order of magnitude difference, with pure CO_2 hydrate being more conductive. The state of excess CO_2 in the pore space at CO_2 hydrate grain junctions (either as gaseous or liquid CO_2 in the pore space) caused no apparent changes to impedance—nor was it expected to. We speculated that the rather extreme fit of CO_2 molecules into small cages of the sI clathrate structure leads to cage distortion and formation of additional charge carriers, in general agreement with interpretations noted by previous researchers (see [84] and references therein).

Also of note is that activation energy E_a (represented by the slope of the data fits shown in Figure 6) of CO_2 hydrate is nearly identical to that of the H_2O ice used to synthesize our samples, 46.5 and 45.3 kJ/mol, respectively, suggesting commonality in charge carrier; presumably Bjerrum defects, and different from methane hydrate [84,85]. E_a of pure methane hydrate is 34.8 kJ/mol, about 33% lower than CO₂ hydrate, and, interestingly, remains nearly unchanged upon addition of ionic impurities-including, but not limited to, those derived from sediments—further highlighting differences from CO_2 hydrate. From this observation and results from [86], we concluded that the electrical conductivity of "pure" methane hydrate is actually determined by trace (0.005% NaCl) impurities in the seed ice or introduced during handling [88]. We proceeded to estimate that the order of magnitude increase in conductivity of the MH + 0.25 wt% NaCl sample (Figure 6, purple squares) was a result of a maximum 0.05% NaCl being incorporated into the methane hydrate lattice, the balance of the NaCl presumably remaining in a nonconnected (and thus virtually undetectable) NaCl-H₂O phase. Adding more NaCl into the closed system of the conductivity cell resulted in formation of interconnected brine channels that dominated sample conductivity, and methane hydrate prepared from seawater ice (shown and described in [87,88]) exhibits, as expected, significantly higher conductivity than all fluid-free hydrate samples we tested, including CO₂ hydrate. In an open system such as seafloor sediments, fluid exclusion is possible, and we can infer that the conductivity of the MH + 0.25% NaCl sample is representative of methane hydrate formed in a seawater environment that has become virtually fluid-free. In that case, the sizable difference in σ between CO₂ hydrate and CH₄ hydrate shows promise for the application of EM methods towards monitoring CO₂ hydrate formations in the GHSZ in settings where high-conductivity seawater or brines do not dominate the system, or in monitoring leakage from potential CO2 sequestration sites.



Figure 6. Electrical conductivity (σ) versus reciprocal temperature for pure CO₂ hydrate compared with pure H₂O ice, pure methane (CH₄) hydrate, CH₄ hydrate doped with 0.25 wt% NaCl (the near-maximum impurity content in CH₄ hydrate without formation of a discrete saline fluid phase), and CH₄ hydrate containing 10, 45, and 50 vol.% of quartz sand or silt. Modified from data reported in [84–88]. CO₂ hydrate exhibits measurably higher conductivity than all methane-hydrate-bearing samples tested here, including those with varying ionic impurity contents. Unlike pure CH₄ hydrate, CO₂ hydrate is also more conductive than ice.

5. Conclusions

The use of electromagnetic methods to monitor CO_2 sequestration in the marine environment has been proposed and discussed for some time, although not yet employed in practice. Here, we demonstrated that using data visualization of CSEM data differences is effective in observing important sequestration processes in the deep marine environment and likely shallower zones relevant to the GHSZ. This supports the idea that the CSEM method could be a powerful geophysical tool to monitor CO_2 sequestration in the marine environment, either as a gravitationally stable fluid phase or as a stable gas hydrate phase (or both). The figures presented in this paper show a useful response in a very small fraction of the entire dataset, suggesting that rather than carrying out repeated inversions of entire datasets and looking for changes in the resulting models, we should develop methods to invert the data differences directly.

Electromagnetic methods are also used in the terrestrial environment, and our results support the idea that CSEM methods are sensitive to conductivity changes associated with sequestration in general. However, there are differences between the terrestrial and marine environments. On land, the CSEM response is diluted by energy propagation in air and it is difficult to measure the vertical electric field component, but there is the advantage of being able to precisely control the repeat geometry of the transmitters and receiver placement.

Lastly, we draw upon quantitative laboratory measurements of methane and CO_2 hydrate properties to guide discussion of how gas hydrate may play a role in marine CO_2 sequestration efforts. In particular, critical differences in dissociation behavior, strength, and electrical conductivity may in some cases influence the monitoring strategy and even the stability of sequestered CO_2 in regions within or proximal to the GHSZ. Our final comment is that we hope to see carbon capture and storage (CCS) technologies—including,

but not limited to, those discussed here—safely implemented in practice, as the planet is past the point where reducing CO_2 emissions will prevent catastrophic global warming, leaving CCS as our primary recourse.

Author Contributions: Both authors contributed equally to this work and authorship is alphabetical. Conceptualization, S.C. and L.A.S.; methodology, S.C.; software, S.C.; formal analysis, S.C.; investigation, S.C. (CSEM and modeling) and L.A.S. (literature and laboratory experimental review); resources, S.C.; writing—original draft preparation, L.A.S. and S.C.; writing—review and editing, L.A.S. and S.C.; visualization, S.C. and L.A.S.; funding acquisition, S.C. and L.A.S. All authors have read and agreed to the published version of the manuscript.

Funding: The electrical conductivity data presented here were collected under support from U.S. Department of Energy contract DEFE0028972 and Interagency Agreement DE-FE0026382 between the U.S. Geological Survey Gas Hydrate Project and the U.S. DOE/NETL. S.C. acknowledges support from the Scripps Seafloor Electromagnetic Methods Consortium.

Data Availability Statement: The FDM3D code used in this study can be downloaded from http: //anodyne.unm.edu/Public/FDM3D/. Data reported in this paper are available on the Open Source Framework repository at: https://osf.io/5F7C4/ and https://doi.org/10.17605/OSF.IO/SCJNG.

Acknowledgments: The authors thank Chester Weiss for making the FDM3D code available. We gratefully acknowledge Jeffery Roberts (LLNL, UCSD), Tom Lorenson (USGS), and three anonymous reviewers for expert evaluation of the manuscript. Any use of trade, firm, or product names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Conflicts of Interest: The authors declare no conflict of interest.

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