Reply to referee 1

We would like to thank the reviewer for their constructive and positive feedback on our manuscript. Their recommendations have significantly improved the structure and content of the text. Below we provide a response to all their comments and suggestions, and indicate how we have altered the manuscript in response; our responses are in blue, altered text is in shaded in grey.

1. Line 35 Use of CCS as the overarching term for point-source CO2 mitigation is inappropriate because CCS has come to mean a very specific form of that mitigation https://en.wikipedia.org/wiki/Carbon_capture_and_storage

CCS is replaced by CO_2 emission mitigation throughout the manuscript.

2. Line 79-81 “The concept of AWL was first proposed by Rau and Caldeira more than two decades ago (Rau and Caldeira, 1999). It provides a geochemistry-based method for CCS in which the dissolution of carbonate minerals is artificially enhanced (Rau and Caldeira, 1999).”

   You mean -

   The concept of AWL was first proposed more than two decades ago by Rau and Caldeira (1999). It provides a geochemistry-based method for CO2 emissions mitigation in which the aqueous reaction of carbonate minerals with CO2 is enhanced due to the elevation of CO2 in typical waste combustion gases (Rau and Caldeira, 1999). ?

The sentences are adjusted according to the recommendations of the reviewer.

3. Line 90 Cite Caserini et al (2021) in initially introducing/describing BAWL.

The citation is added.

4. Table 1

   Row 1 - The initial values here are very uncharacteristic of low latitude, surface SW. Chou et al. et al 2015 are referenced as the source, and the values appear to be taken from their Table 1 (representing offshore and probably deep water samples) although I don’t see the specific At and DIC values used by the present authors. In any case, it is clear from Chou et al. et al Table 1 that the starting solutions were not air equilibrated, pCO2>700 uatms, thus DIC is elevated and pH and Omega are depressed. The more realistic starting conditions are listed in Chou et al. eta Table 2 where pH>8 and esp Omega(c) >4.5. The choice of starting conditions will have a very significant effect on the modeling outcomes of the present study, so I ask the authors to carefully justify their initial choice of values here.

   Row 2 The amount of DIC rise in equilibrium with 0.15atm CO2 will very much depend on the chemistry of the starting solution that I question above.

> Row 3 Ditto. Why does Omega(c) only rise to 0.203? In a perfect world under full CO2 and CaCO3 equilibrium OmegaC = 1. Granted, the kinetics for reaching this equilibrium are too slow to be reached in a practical application, but why is CaCO3 dissolution stopped at OmegaC=0.203 when the solution is still significantly carbonate undersaturated? The ratio of DeltaDICseq/DeltaDICcarb = 0.83/0.19 = 4.4. Shouldn't this be closer to 1? Or is there a huge amount of excess, unreacted CO2aq in solution?
>
> Rows 4 and 5 Values are highly dependent on the accuracy of the preceding conditions/modeling.

The reviewer is correct in his assertion that the outcomes of our thermodynamic modelling are dependent on the initial conditions. Therefore, we did not use hypothetical 'ideal' starting conditions – as these 'ideal' starting conditions are also location dependent, and would thus vary for each potential AWL reactor. Instead, we used data from published pilot studies. The aim of Table 1 was thus to give an example of the different states for a representative real life (bench-top) reactor setup. All the values calculated in Table 1 are based on the measured inlet and outlet A_T and DIC from the two-step bench-top reactor from Chou et al. (2015).

Note that the initial solution values from Table 2 from Chou et al. (2015) cannot be used for calculations as there are no measured values at the outlet for these starting conditions.

To avoid this confusion, we clarified the purpose of Table 1 upfront at Line 111-117:

"Table 1 shows the values for pCO_2, A_T, DIC, pH and Ω_{calc} in each of the four states for a representative case study, which is based on data reported from a two-step bench-top reactor consisting of a separate gas-liquid and liquid-solid reactor (Chou et al., 2015, further discussed below). The CO_2 concentration of the gas stream was 15%, while the pCO_2 of the atmosphere is fixed at 420 ppm. The A_T and DIC values at the inlet and outlet of the reactor are based on measured values (Table 1 in Chou et al., 2015). The remaining variables are calculated using the CRAN:AquaEnv package for the thermodynamic equilibria of acid-base systems in seawater (Hofmann et al., 2010)."

And expanded the caption of Table 1:

*"Theoretical values for alkalinity (A_T), dissolved inorganic carbon (DIC), pH and calcite saturation state (Ω_{calc}) in the four consecutive states of the example AWL reactor: (1) the process water that is used as intake (the process water was collected from an offshore station near the Hoping power plant and the inlet and outlet of the cooling water drainage of the Hoping power plant (Chou et al., 2015)) , (2) the process water with elevated DIC after CO_2 uptake, (3) the process water enriched in A_T and DIC after $CaCO_3$ dissolution, (4a) the unbuffered or (4b) buffered process water upon discharge. ΔDICseq is the DIC that is added to the process water due to dissolution from the gas stream and ΔDICcarb is the DIC added through the dissolution of $CaCO_3$. The pCO_2, A_T and DIC values (indicated by #) are based on values measured in a two-step AWL bench-top reactor (Chou et al., 2015). The values of A_T, DIC, pH, and Ωcalc (indicated with *) are calculated using CRAN:AquaEnv (Hofmann et al., 2010) for seawater at a temperature of 15 °C and salinity of 35."*

The reason Omega only rises to 0.203 at the reactor outlet, is because the dissolution reaction was too slow to completely buffer the saturation state drop. The omega is calculated for the values at the outlet given by Chou et al. and are before re-equilibration. We clarified this observation at Line 147 – 149:

> *"Note that the effluent at state 3 of the example two-step reactor was not in equilibrium with $CaCO_3$ dissolution ($\Omega_{calc} < 1$, Table 1), which indicates that the effectiveness of $CaCO_3$ dissolution in the reactor design of Chou et al. (2015) could still be improved."*

5. Equ 1 Only valid at low pH (<7). The stoichiometry changes as pH rises so as to accommodate the spontaneous formation of (alkalinity hog) CO3-- ; ACO2 + BH2O + CaCO3 ---> Ca++ CHCO3- + DCO3-- + ….. such that the total moles carbon added is A+1=C+D (<=2) and A<=1 (see eq 1 here https://bg.copernicus.org/articles/20/27/2023/)

This is correct, in a sense that the carbonate system re-equilibrates after the reaction, which will set the eventual stoichiometry of the overall reaction. However, we think this leads to a confusing way of writing the equations, as A, B, C, … are dependent on conditions and obscure the fact that the dissolution of calcium carbonate always creates two alkalinity. We have chosen to explain the re-equilibration step (see Line 133 of the original manuscript), and if one would combine Eq. (1) and Eq. (2) for a given pH, you would get the equation the reviewer refers to. We prefer to keep our approach, as we think this makes the overall process clearer for non-specialist readers.

6. Line 143-4 "However, one can easily show that equilibration followed by mixing, provides the same CO2 transfer as mixing followed by equilibration." This assumes that discharing a supersaturated CO2 solution into seawater will in fact equilibrate with air (on human-relevant timescales). That is unlikely to happen due the slow kinetics of air/sea gas exchange coupled with vertical SW mixing that will remove some of the supersaturated solution out of contact with air prior to equilibration. Gorey details here: https://www.nature.com/articles/s41558-024-02179-9

   Bottom line: Assuming air equilibration underestimates C storage because some excess CO2aq added in unbuffered AWL will not have a chance to degas to air.

Full equilibration with the atmospheric pCO_2 will indeed be prevented when surface residence times of the discharged process water is shorter than the air-sea equilibration timescale. So, when the process water is discharged below a strong stratification layer or in locations where the discharged water quickly reaches the deeper oceans, assuming full equilibration would underestimate the CO_2 storage potential (He & Tyka, 2023; Jones et al , 2014). However, as most AWL plants, like the AWL pilot plant in Wilhelmshaven (Germany; Kirchner et al., 2020), will be located near the coastal ocean with shallow mixed layers with relatively efficient air-sea CO_2 exchange, equilibration will take place on timescales of months up to a year (Jones et al, 2014; Geerts et al, 2025).

We added the caveat about air-sea CO_2 exchange variation and the possibility at non-equilibrium degassing at Line 117-125:

> *"We assume full re-equilibration with the atmosphere (unbuffered AWL) or full buffering with $Ca(OH)_2$ upon discharge into the sea (buffered AWL). In the well-mixed coastal zone, air-sea CO_2 exchange takes place on a time-scale of several weeks up to a year (Jones et al., 2014; He and Tyka, 2023; Geerts et al., 2025). However, when the surface residence time of the discharged process water is shorter than the air-sea CO_2 equilibration timescale, some of the*

dissolved CO_2 which is unbuffered by an A_T increase will move to deeper layers and full re-equilibration will not be reached (Jones et al., 2014; He and Tyka, 2023). When the process water is discharged below a strong stratification layer or directly in the deeper ocean full re-equilibration will also be prevented (Jones et al., 2014; He and Tyka, 2023). Therefore, assuming full re-equilibration represents a conservative lower bound of the CO_2 sequestration during AWL."

7. Fig 2 Should be modified depending on the (new) outcomes listed in Table 1.

See our response to comment 4

8. Line 178-80. "In a similar fashion, the final alkalinity value is the result of alkalinity addition during carbonate dissolution and possibly some extra addition during lime buffering"

   Unclear. If you are adding lime you are adding alkalinity, no "possibly" about it. Or are you saying that adding lime is a possibility? In this region of the text the discussion seems to move from AWL with an option to lime to one where liming is now assumed/required. Please be clear from the start about how you are treating AWL +/-liming.

This phrasing is indeed a bit confusing. We adjusted the sentence to make it clear that we mean that the final alkalinity is the result from carbonate dissolution, with extra alkalinity added by lime buffering in BAWL at Line 196-198

"In a similar fashion, the final alkalinity value is the result of alkalinity addition during carbonate dissolution and the alkalinity that is added during buffering with $Ca(OH)_2$ in the case of BAWL."

9. Line193-4 Full air equilibration after discharge is unlikely (https://www.nature.com/articles/s41558-024-02179-9)

See our response to comment 6.

10. Equ 8 Missing an operator between the 2nd the 3rd right hand terms?

A multiplication sign is added between the two terms for clarification.

11. Line 196-204. Assumes full air/sea CO2 equilibration, unlikely (https://www.nature.com/articles/s41558-024-02179-9)

See response to comment 6.

12. Line 219-225 Revise depending on outcomes in (revised) Table 1?

See our response to comment 4

13. Line 297-and after Flows and efficiencies are calculated from data in Table 2 with the implication that these values will be characteristic of AWL at scale, yet what is the evidence that the data in Table 2 represent optimized systems?

The idea of Table 2 is to calculate efficiency values for different existing/conceptual reactor designs. Since we are reviewing the existing literature, it is not our goal to represent optimized systems at scale. The operational stage of each specific example reactor is specified in row 1 of the operational conditions. To prevent misunderstanding, we clarified that these are values for prototype/conceptual reactors and that the efficiencies are calculated based on the inlet an outlet A_T and DIC, and the given water/gas flow rate at Line 321 – 325:

> *"The operational conditions and process efficiencies of these reactor designs are summarized in Table 2. The presented operational conditions are given for specific example reactor setups (bench-top (Chou et al., 2015) or pilot plant (Kirchner et al., 2020b)) or conceptual designs (Caserini et al., 2021) and the process efficiencies are calculated based on published data for a specific operational condition. Changes in reactor design or operational conditions will change these calculated efficiencies."*

14. Line 258 You mean 150,000 m^3, yet eq 20 is in units of tonnes/tonne and the assumes that 1L SW = 1kg?

Correct, the exponent should have been 3 (150 000 m^3) instead of 2 (150 000 m^2). This has been changed.

The units for eq. 20 at $m^3_{seawater}$/tonne of CO_2 , as is stated in the text: *'The volume of process water (m^3) that is used to capture one tonne of CO_2'*. We did notice a typo, 10^6 has to be 10^{-6}.

ΔDIC_{seq} is expressed in mol per unit of volume: $mM = \frac{10^{-3}\,mol}{L} = \frac{10^{-3}\,mol}{dm^3} = \frac{10^{-3}\,mol}{10^{-3}\,m^3} = \frac{mol}{m^3}$

The units for Eq. 20 are: $\frac{1}{mol_{CO_2} / m^3_{seawater}} \frac{10^{-6}}{g_{CO_2} / mol_{CO_2}} = \frac{10^{-6}}{g_{CO_2} / m^3_{seawater}} = 10^{-6}\frac{m^3_{seawater}}{g_{CO_2}} = \frac{m^3_{seawater}}{10^6\,g_{CO_2}} = \frac{m^3_{seawater}}{tonnes_{CO_2}}$

15. Line 293-6 What is the evidence that the efficiencies stated are representative of optimized systems?

See response to comments 4 and 13.

16. Line 301-2 You likely mean Rau (2011) rather than Caldeira and Rau (2000)? The former pub offers numerous results/data for a one step reactor. Compare/contrast with Chou et al. et al 2015 and you subsequent calcs?

The citation should indeed be Rau (2011). Results from Rau (2011) and Chou (2015) are compared in section 3.1 but comparing specific calculations is not possible as specific values for DIC, A_T, water/gas flow rate are not specified in Rau (2011).

17. Line 324-5 This does not jibe with Rau (2011) which states "Comparing resulting DIC and alkalinity to that of the original solutions and to ambient seawater demonstrates that 61-85% of the carbon originally added to the seawater remained in solution (Figure 2c), with

little change in alkalinity and with no visual evidence of carbonate precipitation after aeration."

The section in Rau (2011) that the reviewer refers to discusses the modified reactor in which seawater in equilibrium with the CO_2/air mixture was allowed to reside in the reactor for 1-2 weeks. This in essence becomes a two-step reactor with long residence time in the second reactor and is thus not applicable on the one-step reactor.

18. Line 327-8 "Consequently, the overall CO2 sequestration efficiency of a one-step reactor remains low due the lack of conversion from hydrated CO2 to HCO3-." Hydrated CO2 is HCO3- + H2CO3. What is apparently meant here is lack of conversion of hydrated CO2 balanced by Ca++ rather than by H+? Or do you mean lack of conversion of CO2 to carbonic acid? Anyway, how does this square with the 61-85% of the initially captured C shown to be air stable by Rau (2011)?

For the comparison with Rau (2011) see response to comment 17.

We agree with the reviewer that this formulation does not clearly represent the limiting step of $CaCO_3$ dissolution and the production of alkalinity. We have changed the sentence to better convey that we mean the buffering of the dissolved CO_2 by the increase in A_T at Line 348 – 350:

> *"Consequently, the overall CO_2 sequestration efficiency of a one-step reactor remains low due lack of $CaCO_3$ dissolution. A large fraction of the dissolved CO_2 remains unbuffered by the increase in A_T."*

19. Line 417-19 If the now alkalized and carbonated SW is discharged at the same pH as ambient SW the pCO2 must be higher than ambient? Don't you need to discharge at higher pH to avoid this? And wouldn't higher discharge pH beneficially help counter ongoing ocean acidification?

The reviewer raises a good point. Based on the alkalinity and DIC values at the end of the buffering reactor (BR) from Table 1 in Caserini et al. (2021), and given a seawater temperature of 10 °C, the pH and fCO_2 of the process water can be modelled using CRAN:AquEnv.

Under these conditions, the pH is 8 (as in Table 1 in Caserini et al. (2021)) and the fCO_2 is 0.00483 atm or 4830 µatm. Thus, under conditions presented by Caserini et al. (2021) the fCO_2 is indeed higher than ambient if the pH is at the same level as the surrounding seawater.

20. Line 435-332 Check out Langer et al for further discussion of limestone sources (in the US): https://www.researchgate.net/publication/283868780_Accelerated_weathering_of_limestone_for_CO2_mitigation_Opportunities_for_the_stone_and_cement_industries

We thank the reviewer for this resource, we have now included it in our reference list.

21. Line 443-6 Here and elsewhere "high water demand" is implied to be an AWL showstopper, yet the global supply of seawater seems rather limitless. What is apparently meant here is that the pumping costs of seawater can become prohibitive, yet so far no discussion of exactly what these costs are, especially relative to the (high) cost of the industry darling, CCS – capturing, concentrating and storing molecular CO2 underground.

We agree with the reviewer that the supply of seawater should not be seen as a limiting factor, we have adjusted the text accordingly at Lines 464 – 475:

> *"Significant volumes of water are needed to dissolve the CO_2 and dilute the resulting bicarbonate in the original reactor designs (10^4 - 10^5 tonnes of water per tonne of CO_2; Table 2) (Rau et al., 2007; Rau and Caldeira, 1999), although more recent designs have reduced the water demand by a few orders of magnitude (~ 10^3 tonnes of water per tonne of CO_2; Table 2). The high water demand and the accompanying pumping cost could limit the feasibility of the overall AWL process. Therefore, a low-cost water source such as cooling water from a power plant or other sources of recycled water should be used preferably (Rau and Caldeira, 1999). Due the required quantities of process water, the favored locations for (B)AWL reactors would be coastal regions as seawater is a virtually limitless source and the bicarbonate-containing effluent could be directly dumped and diluted in the ocean after degassing or buffering and removal of potential contaminants (Rau and Caldeira, 1999; Rau et al., 2001). Pumping costs could further be reduced by reusing the large volumes of seawater already pumped and used as power plant cooling water (Rau et al., 2007; Kirchner et al., 2021). However, the elevated temperature of the seawater during the cooling of the power plants would reduce the CO_2 dissolution into the seawater (Kirchner et al., 2021)."*

22. Line 447-8 Who has proposed the use of anything but seawater for AWL? The only places AWL will work are near the ocean, eps powerplants that use SW for cooling(?)

The different possible water resources were suggested in Rau and Caldeira (1999) on page 1807 in section 4: Water considerations.

AWL will indeed only be possibly economically feasible near the ocean and indeed especially when seawater used for cooling in power plants can be reused, limiting pumping costs. We have elaborated this paragraph to make it clear that seawater is the only viable option and that pumping costs could further be reduced by reuse of power plant cooling water, as outlined in our response to comment 21.

23. Line 458-9 "The BAWL reactor setup proposed by Caserini et al. consumes 0.4 tons of Ca(OH)2 to store 1 ton of CO2." Or 1/0.4 = 2.5 t CO2/t Ca(OH)2(?) Yet the delta DIC/deltaAlk in the surface ocean is about 0.85. Since 1 mole of Ca(OH)2=2 moles Alk, then the mole CO2 captured and stored per mol Ca(OH)2 should be 2x0.85/1 = 1.7 moles/mole. CO2= 44g/mol, Ca(OH)2= 74g/mol, Thus ,1 tonne of Ca(OH)2 is able to capture and store about 1.7x44/74 = 1 t CO2/tCa(OH)2 in seawater @pCO2= 420 uatms? Or does 2.5 t/t only apply to deep ocean, high pressures?

This sentence could lead to misunderstanding. We meant that 0.4 tons of $Ca(OH)_2$ was used on top of the 1.31 tonnes of $CaCO_3$ that was fully dissolved, as stated by Caserini et al. (2021). We decided to remove this sentence to avoid confusion.

24. Line 466-8 Seems pretty obvious from the previously published lit. Why even hint at the use of other water sources?

See response to comment 22.

25. Line 499-500 "..the increased alkalinity and pH could potentially limit ocean acidification.." You mean "…the increased alkalinity and pH would help counter ocean acidification and

its effect on marine biota, see for example Albright et al (2016)” https://www.nature.com/articles/nature17155

The sentence is adjusted according to the comment of the reviewer.

26. Line 514 How about inserting “All of the preceding argue for the use of relatively clean waste gas streams (such as from the combustion of natural gas) in (B)AWL applications.” ?

We have added the sentence.

27. Line 515-20 Bach (2024) specifically discusses the application of alkaline solids to marine sediments and the effect of alkalinity generation there. Discharge of dissolved alkalinity into surface waters some distance from sediments and with rapid dilution, as characteristic of (B)AWL, would seem to pose much less risk to benthic/sediment processes.

The discharge of dissolved alkalinity pose less risk than addition of alkaline solids to the sediment. We have highlighted this in this section and further discussed the potential negative feedback in the water column based on the recently published manuscript by Lehman & Bach (2025) at Line 541 - 549*:*

> *“The disposal of large volumes of process water in the surface water of the coastal zone can locally increase pH and mitigate the adverse effect of ocean acidification on calcifying phytoplankton. However, this implies a reduction of the efficiency of the CO_2 sequestration via AWL, as part of the produced A_T will be consumed and lead to CO_2 degassing (Lehmann and Bach, 2025). Additionally, mixing of this A_T enriched coastal water within the coastal sediment through porewater flushing or diffusion could potentially inhibit natural carbonate dissolution (Lunstrum and Berelson, 2022; Bach, 2024). If this would occur, the efficiency of the (B)AWL process would be reduced as the CO2 sequestration by AWL would be partially compensated by a loss of natural CO_2 sequestration. However, this is less likely to occur with (B)AWL than with mineral-based OAE where alkaline minerals are directly added to the coastal sediment and alkalinity can build-up in the porewater.”*

References

He & Tyka, 2023: https://doi.org/10.5194/bg-20-27-2023

Jones et al, 2014: https://doi.org/10.1002/2014GB004813

Kirchner et al., 2020: https://doi.org/10.1021/acs.est.9b07009

Geerts et al., 2025: https://doi.org/10.5194/bg-22-355-2025

Lehman & Bach, 2025: https://doi.org/10.1038/s41561-025-01644-0