

Reply to referee 2

The paper is a useful summary of the chemistry and the applicability of accelerated weathering of limestone or buffered accelerated weathering of limestone, and it deserves publication. Minor comments below.

We would like to thank the reviewer for the positive feedback and the constructive comments. 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. Lines 39-59. Please revise this section because it could lead to confusion among “enhanced weathering”, “enhanced rock weathering”, “mineralization”, and “carbonation” (in the case the mineral obtained is a carbonate mineral). The studies by Rau and Caldeira, 1999, Renforth and Kruger, 2013, Caserini et al., 2021, cited as “enhanced rock weathering” processes, could be better identified as accelerated weathering of limestone, to avoid confusion with enhanced weathering (that is a CDR approach that removes atmospheric carbon).

The start of this paragraph is rewritten to prevent confusion with enhanced weathering as CDR technology, Line 38 – 59:

“Industrial point-source CO₂ emissions from waste gas streams can be partially mitigated by geochemical-based processes in which CO₂ is reacted with solid carbonate or silicate rocks in the presence of water, which aims to enhance the natural weathering process of carbonate and silicate rocks (Rau and Caldeira, 1999; Renforth and Kruger, 2013; Caserini et al., 2021). This targeted weathering process can take place in situ, in which CO₂ is first captured from the flue gas and then injected into suitable silicate rock formations (basalts and ultramafic rocks). The CO₂ is then trapped by a carbonation reaction with the ambient silicate rock, thus ensuring a permanent, geological storage (Matter and Kelemen, 2009; Romanov et al., 2015; Gadikota, 2021; Cao et al., 2024). However, there are certain geomechanical risks associated with geological storage of CO₂, such as CO₂ leakage, induced seismicity, the loss of well integrity and surface uplift (Song et al., 2023). Moreover, suitable rock formations for storage are not always in close proximity to the CO₂-emitting installations, thus requiring compression and transport of CO₂.

Alternatively, the chemical weathering can also be executed under controlled conditions in a land-based reactor, close to the industrial point source. Mitigation of CO₂ emissions via such reactor-based methods can follow two main approaches, depending on whether silicates are used as feedstock material (usually referred to a “ex-situ mineral carbonation” technologies; Romanov et al., 2015; Gadikota, 2021, or “mineralization”; Campbell et al., 2022) or whether carbonates are used as weathering substrates (referred to a as “accelerated weathering of limestone”; Rau and Caldeira, 1999). In ex-situ mineral carbonation (ESMC), a finely-ground silicate mineral (e.g. olivine Mg₂SiO₄) is fed into a reactor, where it reacts at elevated temperature and pressure with CO₂ from a flue gas to eventually form stable carbonates (e.g. magnesite Mg₂SiO₄) - see recent reviews (Snæbjörnsdóttir et al., 2020; Veetil and Hitch, 2020; Thonemann et al., 2022). Alternatively, during the accelerated weathering of limestone (AWL), CO₂ is stripped from the flue gas using a mixture of seawater and limestone (CaCO₃) (Rau and Caldeira, 1999; Renforth and Henderson, 2017), and the resulting effluent is discharged into the sea. “

2. Line 52-55 Please specify that what is called “ex situ mineral carbonation” (methods where alkaline minerals react with CO₂, producing solid carbonate minerals) is also called “mineralization”, as in Campbell et al (2022) <https://doi.org/10.3389/fclim.2022.879133>.

Mineralization is added as an alternative name for ex-situ mineral carbonation at Line 50 -53:

“Mitigation of CO₂ emissions via such reactor-based methods can follow two main approaches, depending on whether silicates are used as feedstock material (usually referred to a “ex-situ mineral carbonation” technologies; Romanov et al., 2015; Gadikota, 2021, or “mineralization”; Campbell et al., 2022), ...”

3. line 62: please specify that the CO₂ removed by ocean alkalinization is atmospheric CO₂

Adapted.

4. line 63. I don’t see the need to add “chemical” between natural and weathering, since all the weathering processes are chemical processes.

‘chemical’ is removed.

5. Lines 91, 93, 99, and others: It is not clear what “upon discharge” means: just before the discharge of the process water or after the discharge? Sometimes, it seems just before (i.e.: ... buffering with Ca(OH)₂ upon discharge into the sea), in other cases, just after the discharge in seawater (upon re-exposure to atmospheric conditions, aqueous CO₂ which is not stabilized by the increased AT will degas back to the atmosphere)

Clarified.

“After discharge into the surface ocean, there is no longer any CO₂ transfer to the atmosphere”

“The process water is discharged into the sea without any further treatment after which it re-equilibrates with the atmosphere at the lower pCO₂ (pCO₂ ≈ 0.00042 atm), and the excess CO₂ (i.e., the part of DIC not stabilized by the increased alkalinity) will degas back to the atmosphere.”

“... (4a) the unbuffered or (4b) buffered process water after discharge into the surface ocean.”

6. Line 99 “(4a-b) the unbuffered or buffered”. Please clarify that 4a is unbuffered and 4b is buffered.

Adjusted according to the suggestion of the reviewer.

7. Lines 119-125 (table 1). It should be stated in the title what (1) (2) (3) (4a) and (4b) in the first column means. Since just before figure 1 there is (i) (ii) (iii) and (iv), there could be some misunderstanding.

The different states with number and explanation are now explicitly stated in 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 Hopping power plant and the inlet and outlet of the cooling water drainage of the Hopping 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. $\Delta\text{DIC}_{\text{seq}}$ is the DIC that is added to the process water due to dissolution from the gas stream and $\Delta\text{DIC}_{\text{carb}}$ is the DIC added through the dissolution of CaCO_3 . The $p\text{CO}_2$, 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 Ω_{calc} (indicated with *) are calculated using CRAN:AquaEnv (Hofmann et al., 2010) for seawater at a temperature of 15 °C and salinity of 35.”

8. Line 124: the pH for 4a, unbuffered process water upon discharge, is 8.16, quite high, very close to the 8.27 for the buffered case. The pH is quite higher than in Caldeira and Rau 2000 <https://doi.org/10.1029/1999GL002364>. Please add some comments on this point.

The pH in Table 1 (4a) is calculated in R using the CRAN:AquaEnv package. The pH in state 4a is calculated based on the alkalinity content at the outlet of the reactor and the DIC content after full re-equilibration with atmospheric $p\text{CO}_2$.

In Caldeira and Rau (2000), the pH for the “degassed to seawater Ω_{calc} ” is based on the alkalinity at the outlet of the reactor and the Ω_{calc} of 4.14. In this case, the seawater is not fully equilibrated with the atmospheric $p\text{CO}_2$ (0.000402 atm) and the $f\text{CO}_2$ of the seawater is still at 0.014808 atm. If we calculate the pH for Caldeira and Rau (2000) using an outlet alkalinity of 14808 $\mu\text{mol kg}^{-1}$ and full equilibration with the atmospheric $p\text{CO}_2$, we get a pH of 8.5 due to the higher alkalinity compared to our example.

9. Lines 145-149. Add more recent experimental studies:

Hartmann, J., Suitner, N., Lim, C., Schneider, J., Marín-Samper, L., Arístegui, J., Renforth, P., Taucher, J., & Riebesell, U. (2023). Stability of alkalinity in ocean alkalinity enhancement (OAE) approaches – consequences for durability of CO_2 storage. *Biogeosciences*, 20(4), 781–802. <https://doi.org/10.5194/bg-20-781-2023>

Moras, C. A., Bach, L. T., Cyronak, T., Joannes-Boyau, R., & Schulz, K. G. (2022). Ocean alkalinity enhancement – avoiding runaway CaCO_3 precipitation during quick and hydrated lime dissolution. *Biogeosciences*, 19(15), 3537–3557. <https://doi.org/10.5194/bg-19-3537-2022>

References included.

10. Lines 221-224. I would further clarify the reason behind the additional CO_2 removal through liming. This represents a novelty of this study that was not addressed in Caserini et al. (2021), because buffered AWL is a carbon dioxide storage process. In contrast, ocean liming is a carbon dioxide removal process.

In this context, liming is meant as the addition of $\text{Ca}(\text{OH})_2$ in the buffering reactor before discharge of the process water to the sea. The use of “liming” could indeed cause misunderstanding. It is changed to “buffering with $\text{Ca}(\text{OH})_2$ ”.

11. Line 258. I think the exponent of the unit of measurement is 3, not 2.

The exponent is changed to 3.

12. Line 427-428. I would provide more details about this calcination-free process as a method for $\text{Ca}(\text{OH})_2$ recovery, since $\text{Ca}(\text{OH})_2$ recovered from steel slag is obtained through calcination, then used in the steel industry, and ultimately ends up in the steel slag. Furthermore, I would elaborate on whether this process has other potential environmental side effects and provide more insights into its availability, as it depends on the residuals of an industrial process.

We do not think expanding on the process of forming $\text{Ca}(\text{OH})_2$ fits within the scope of our paper, and would distract from the overall message.

13. Lines 461-462. Please provide a reference for the value of 1 ton of CO_2 produced per ton of $\text{Ca}(\text{OH})_2$.

The value is changed to 1 – 1.8 tonnes of CO_2 per tonne of $\text{Ca}(\text{OH})_2$, and we included two new references:

Oates, 2008: ISBN: 978-3-527-61201-7

Simoni et al., 2022: <https://doi.org/10.1016/j.rser.2022.112765>

14. Lines 504-514. It's worth adding that the problems of trace metals or other pollutants are much lower if AWL or BAWL are used just for the storage of the CO_2 produced by calcination, i.e. in the case of electric calcination

Included at Line 539 -541:

“To potential negative effects from trace elements and other pollutants can be mitigated by using of relatively clean waste gas streams (such as from the combustion of natural gas or calcination of CaCO_3) in (B)AWL applications.”

15. Lines 515-521. Regarding potential impacts on marine biota, I would also cite the recent study by Sánchez et al. (2024).

Sánchez, N., Goldenberg, S. U., Brüggemann, D., Jaspers, C., Taucher, J., & Riebesell, U. (2024). Plankton food web structure and productivity under ocean alkalinity enhancement. *Science Advances*, 10(49), eado0264. <https://doi.org/10.1126/sciadv.ado0264>

Included.