Referee #2

Overview:

The manuscript from Flipkens et al. explores the suitability of two by-products of the cement industry, cement and lime kiln dusts (CKD and LKD, respectively). Using laboratory experiments, they report first estimates on the dissolution kinetics of such feedstocks in natural seawater, both using short- and long-term experiments, while expanding on the risks for $CaCO_3$ precipitation and potential trace metals release. Finally, CDR estimates are given, assuming the use of all available CKD and LKD, and considering inorganic thresholds and water quality and safety guidelines.

Overall, I found the manuscript very enjoyable to read. While some people may express reluctance to consider such by products for OAE, their significant alkalinity release makes them suitable candidates, and the presented data support this. The introduction is rather comprehensive, and most required information is already provided. The material and method section is also mostly complete with some smaller comments pointed out below. The results section is rather dense, yet all required information is well presented. Finally, the discussion is convincing and reports well on the implication of kiln dust based OAE. Some further points could be added to the discussion, especially when it comes to the alkalinity generation. While LKD was following estimates, the nearly doubling alkalinity generation from CKD is yet to be fully addressed. I believe a more detailed discussion could benefit the paper. It would be beneficial to try and characterise the amorphous phases that clearly seem to be the responsible factor. I do not request further analyses but rather consider whether using the elemental composition of CKD (Table A1), an estimate of the amorphous phases' composition could be derived. Another point that could benefit from further interpretation is the fate of KD and especially the potential secondary minerals precipitated. It is clear that non soluble phases such as $CaCO_3$ would eventually sink and as described, potentially dissolve on the seabed. It would also be the case for secondary $CaCO_3$ formed from the high alkalinity generated. One could consider discussing the dissolution on the seabed of both the $CaCO_3$ from KD and the freshly precipitated $CaCO_3$ in the water column. The overall potential would probably increase, and if it is significant, it would be worth mentioning. Finally, a smaller point regarding the turbidity discussion. Discussing such environmental guideline is a great idea and of high importance. Unless I am mistaken, the turbidity is reported for 24h. In line 343, it is mentioned that the KD particles would remain in the surface ocean mixed layer for about one hour. Therefore, one could safely assume that after 1h the turbidity is back to low enough levels that new KD could be added. Under such assumption, the overall KD release could be increased, ultimately increasing the CDR potential. If it is correct, it could be quicky discussed.

Considering the minor comments mentioned above, and once they have been addressed, I am fully supporting the publication of the manuscript.

We thank the reviewer for their insightful feedback and thorough review of the manuscript. In response to your first suggestion, we have expanded the discussion regarding the alkalinity generation from CKD, which was higher than expected based on the mineralogical composition. By comparing the major elemental composition determined via ICP-OES with that derived from crystalline phases identified by XRD, we now attribute the excess to the potential presence of amorphous calcium aluminosilicates, alkali sulfates, and poorly crystalline lime phases. These phases could possibly explain a significant portion of the previously unexplained alkalinity release. Additionally, as suggested by Reviewer 1, we now discuss the potential contribution of calcium silicates to alkalinity generation in CKD (changes in the manuscript text (blue) are highlighted in yellow below).

In LKD, alkalinity release was fully attributed to the dissolution of portlandite ($Ca(OH)_2$) and lime (CaO), whereas in CKD these phases explained only about half (54 ± 3 %) of the observed alkalinity release. Calcium silicates (e.g. larnite Ca_2SiO_4) are also alkalinity-generating phases that occur in minor amounts in CKD. They originate form the raw materials used in cement production (e.g. iron ore, clay, or shale) and exhibit a relatively high reactivity in water (Brand et al., 2019; Adekunle, 2024). Dissolution of the larnite present in our CKD sample (~ 2.1 %) could account for 17 ± 1% of the observed A_T release, which hence provides a substantial additional contribution. The remaining ~29% of the alkalinity released from CKD likely originated from dissolution of amorphous phases, including (partially dehydrated) clay minerals, reactive amorphous silica, and kiln-derived materials such as fly ash or slag (Khanna, 2010; Pavía and Regan, 2010). ICP-OES analysis revealed 8.0 % Ca, 2.7 % K, 0.7 % Na, 0.9 % S, 1.6% Fe and 3 % Al that were not accounted for by the crystalline phases detected via XRD (Table 2 and Table A1). This suggests the possible presence of amorphous calcium aluminosilicates, alkali sulfates, and poorly crystalline CaO or $Ca(OH)_2$, which may have contributed to the remaining alkalinity upon dissolution in seawater (Hu et al., 2024; Nikolov et al., 2025).

Furthermore, we adjusted the wording in line 197 from "congruent" to "generally in line" to soften the phrasing and clarify that the element compositions measured via ICP-OES and those derived from XRD were not an exact match.

The observed elemental composition was generally in line with the XRD results, showing high calcium contents in both CKD (27.8 wt%) and LKD (44.9 wt%), which fall within the range previously reported for CKD (14–46 %) and LKD (20–49 wt%) (Collins and Emery, 1983; Pavía and Regan, 2010; Latif et al., 2015; Drapanauskaite et al., 2021; Dvorkin and Zhitkovsky, 2023).

We thank the reviewer for the valuable suggestion to discuss the potential dissolution of secondary $CaCO_3$ precipitates after they settle and become buried in the sediment. We have now addressed the possible contribution of both $CaCO_3$ included in kiln dust as well as freshly precipitated secondary $CaCO_3$ for alkalinity generation through subsequent dissolution on the seabed. This has been incorporated into the manuscript as follows:

Prolonged exceedance of critical saturation thresholds can trigger "runaway $CaCO_3$ precipitation", leading to a net A_T loss, as seen at the highest LKD concentration after 15 days (Fig. 2A) (Moras et al., 2022). Under natural conditions, freshly precipitated aragonite may redissolve after dilution in the ship's wake, especially when not yet fully crystallized, recovering some of the lost alkalinity due to secondary precipitation (Hartmann et al., 2023). Aragonite precipitates that settle onto the sediment at the deployment site may undergo further metabolic dissolution provided that geochemical conditions are favourable, offsetting the earlier alkalinity loss (see Section 4.4). However, these fine-grained precipitates could also disperse far from the deployment site, thus complicating monitoring, reporting, and verification (MRV) of CDR via kiln-dust-based OAE. So, despite that some secondary aragonite may redissolve, its formation is best minimized to maximize the alkalinization potential. Based on our temporal dissolution data (Fig. 1A-B), it is recommended to adjust the OAE dispensing and deployment procedure in such a way, that dilution to $\Omega_{Arg} < 5$ occurs within minutes as to minimize secondary mineral precipitation.

Furthermore, we added a statement in the section on the longer term fate of unreacted phases to note that secondary $CaCO_3$ precipitates could undergo the same fate as the residual calcite in the kiln dust.

In coastal and shelf environments, this residual material would rapidly settle to the seafloor. The residual fraction consists primarily of $CaCO_3$ phases (52 % in CKD and 72 % in LKD). When residual $CaCO_3$ or freshly precipitated secondary $CaCO_3$ become mixed into the seabed through local

hydrodynamics and bioturbation, porewater acidification resulting from microbial degradation of organic matter can trigger metabolic $CaCO_3$ dissolution (Rao et al., 2012; Kessler et al., 2020).

The turbidity guidelines indeed specify values that should not be exceeded for more than 24 hours. The wording in line 343 was incorrect: 85% of the LKD particles and all CKD particles would remain suspended in a 200 m water column for at least one hour, not "about" one hour. This has now been changed in the text.

Using our measured particle size distribution and assuming particle sinking follows Stokes' law, all CKD particles and the majority of LKD particles (85 ± 2 % V/V) will remain in the surface ocean mixed layer (assumed to be 200 m) for at least one hour, thus allowing sufficient time for most reactive phases to dissolve and generate alkalinity (Appendix A Sect. A2).

We do agree that particle settling time is a key factor in determining how frequently kiln dust can be applied without exceeding turbidity guidelines. This consideration has now been added to the sentence noting that application rates should be adjusted according to ship discharge rates and local hydrodynamics.

In real applications, kiln dust will be rapidly mixed into much larger volumes of surface water, meaning that the allowable concentration in the input stream will depend on the discharge rate, the intensity of local turbulence, and the kiln dust settling time (which is primarily determined by particle size).

Comments:

Line 6: I am not sure whether "ocean liming" is a suitable keyword here, considering it investigates kiln dust potential for OAE rather than lime. But this can be up to the authors.

We understand the potential confusion. We included "ocean liming" as a keyword because the primary alkalinity-generating phases in the kiln dust are quicklime (CaO) and hydrated lime ($Ca(OH)_2$). That said, other phases are present as well, so it is indeed debatable whether kiln dust perfectly aligns with the conventionally used definition of ocean liming, such as the one by Renforth et al. (2013), who describe Ocean Liming as "the addition of alkalinity in the form of calcium or magnesium oxide/hydroxide (CaO or MgO) to increase ocean pH and CO_2 uptake." Nevertheless, we believe this research is highly relevant to the ocean liming community. Lime kiln dust is a by-product of lime production, and its potential use for OAE should be recognized, especially since it could possibly increase the overall CDR potential per tonne of calcined limestone when considered alongside the produced lime. For these reasons, we prefer to retain "ocean liming" as a keyword for the paper.

Line 34: I believe brackets are missing and should read "brucite ($Mg(OH)_2$)".

Indeed, brackets have been added.

Line 42: one could argue the use of "rapid" here, as it can take month to years before the alkalised water equilibrates with atmospheric CO_2. Please edit accordingly.

We agree that the word rapid was misplaced. Although the release of alkalinity is rapid, the subsequent atmospheric CO_2 drawdown indeed occurs more slowly. Therefore, we replaced CO_2 sequestration with seawater alkalinization, so the sentence now reads as follows:

Ocean liming has the benefit of rapid seawater alkalinization upon deployment, and offers the potential to remove gigatons of atmospheric CO_2 annually, with ample global reserves to support deployment (Caserini et al., 2022; Foteinis et al., 2022).

Line 57: consider moving "hence" at the start of the sentence.

"hence" was moved to the start of the sentence.

Line 69: has this method been tested and proven to be reliable and efficient at dissolving such product? If so, a reference (or in-house quality control) could be inserted.

The HF–HClO$_4$–HNO$_3$ digestion is a strong total digestion method and is widely used to dissolve refractory and silicate-rich matrices. The fact that measured major element concentrations slightly exceed those inferred from XRD for the crystalline phases indicates that the digestion effectively dissolved the crystalline material, as well as the amorphous and poorly crystalline fractions, which are expected to dissolve even more readily.

In-house quality control (blanks, duplicates, and certified reference materials (CRM)) was performed. Although the CRM used (river clay ISE 921) differs in matrix from our sample, recoveries were within 98–109%, supporting the efficiency and consistency of the digestion. Additional information on the CRM and elemental recovery ranges have now been added to the text.

Quality control measures included a blank, two certified river clay standards (ISE 921), and a duplicate sample. Recorded elemental concentration were between 98 % and 109 % of certified values.

Lines 87-88: how long was the seawater aerated for? Was there any check to confirm equilibration? (pH measurements, pCO$_2$, etc.).

The seawater was aerated for 24 hours, as described in the text. For Experiment I, both pH$_T$ and alkalinity of the initial seawater were measured, while for Experiment II, alkalinity and DIC were analyzed, allowing calculation of pCO$_2$. Values ranged from 458 to 557 µatm, indicating that seawater pCO$_2$ remained a little above the atmospheric level (~420 µatm). This has now been clarified in the text as follows:

Filtered (<0.2 µm) seawater from the Eastern Scheldt (saline water body in The Netherlands adjacent to the North Sea; salinity 32.3 ± 0.5) was obtained from Stichting Zeeschelp (Kamperland, The Netherlands). The filtered seawater (FSW) was aerated for 24 hours before use, yielding an initial seawater pCO$_2$ of 458–557 µatm.

Line 111: how were DIC samples taken? Given the gas sensitivity of these samples, it would be interesting to report whether a peristaltic pump was used or any other apparel.

DIC samples were collected by simply opening the vials and withdrawing water with a syringe. To minimize atmospheric exposure, DIC samples were always taken first, before any other analytes. This has now been clarified in the text as follows:

Duplicate samples for dissolved inorganic carbon (DIC), dissolved metals, turbidity, and A$_T$ analysis were collected on both sampling days by drawing water with a syringe right after opening the vials (analytical procedures are described in Sect. 2.3). DIC samples were collected first to minimize the exposure time to the atmosphere.

Given that samples were taken over a timescale of only a few minutes from stagnant water, the uptake of atmospheric CO$_2$ during sampling is expected to be very small. A more important source of CO$_2$ exchange likely stemmed from the small headspace that unavoidably forms when closing any vial after normal filling. This headspace allows CO$_2$ to equilibrate with the sample over the full duration of the incubations (1 or 15 days), causing DIC increases that partially mask DIC losses through secondary mineral precipitation at higher kiln dust application levels.

This CO$_2$ uptake influenced the results in both experiments. In Experiment I, it caused a decrease in seawater pH and an underestimation of the fraction of dissolved reactive phases, as discussed in Lines 350–354. In Experiment II, the focus was on alkalinity generation and potential secondary mineral precipitation. While A$_T$ is not directly affected by atmospheric CO$_2$ exchange, DIC is affected. As a result, the reported aragonite saturation state is likely lower than the true peak values during the incubations, which may influence the inferred critical aragonite saturation threshold. Moreover, we cannot quantitatively estimate the amount of CaCO$_3$ that precipitated accurately because the observed DIC loss reflects both secondary mineral precipitation and CO$_2$ uptake from the small vial headspace. Despite these uncertainties, the derived critical aragonite saturation state ($\Omega_{Arg} \approx 5$) aligns well with your previous findings using lime, suggesting that any resulting error is likely small.

Moreover, under natural conditions, atmospheric CO$_2$ drawdown would occur alongside alkalinization, though more slowly, progressively altering aragonite saturation levels. To highlight this ongoing process, and to clarify that our experimental setup was not designed to study completely unequilibrated solutions, we added the following text to the manuscript:

Duplicate samples for dissolved inorganic carbon (DIC), dissolved metals, turbidity, and A$_T$ analysis were collected on both sampling days by drawing water with a syringe after opening the vials (analytical procedures are described in Sect. 2.3). DIC samples were collected first to minimize exposure time to the atmosphere. Nevertheless, some CO$_2$ exchange inevitably occurred during the incubations because the vials contained a small headspace, meaning the solutions could partially re-equilibrate with the air. However, this also reflects natural deployment conditions, where atmospheric CO$_2$ exchange occurs alongside alkalinization, although at a slower rate.

Line 125-126: since the pH has been measured and later reported on the total scale, it would be beneficial to report it as pH$_T$ throughout the text

We agree and have changed pH to pH$_T$ throughout the text.

Line 150: salinity has no unit, please remove the "ppt". alternatively, you could report the ionic strength instead, but it is not required

ppt has been removed from the text.

Line 164: I believe PHREEQC provides saturation indexes, not saturation states. The term Ω is usually used only for CaCO$_3$ if I am correct

You are correct that PHREEQC outputs saturation indices (SI), not saturation states (Ω). To obtain saturation states, we converted the PHREEQC-derived SI values using $\Omega = 10^{SI}$. We have clarified this in the manuscript as follows:

Saturation index (SI) values for kiln dust mineral phases were calculated using PHREEQC Interactive (version 3.7.3-15968) with the LLNL thermodynamic database (Parkhurst and Appelo, 2013). Saturation indices were converted to saturation states (Ω) according to $\Omega = 10^{SI}$.

Regarding the terminology, although Ω is most commonly associated with the saturation state of CaCO$_3$, the symbol can be used more broadly for other minerals as well. In this study, Ω is used to denote the saturation state of each mineral evaluated, not exclusively CaCO$_3$.

Lines 164-169: I am not sure I understand correctly. First it is said that saturation states were calculated with PHREEQC (line 164). Then, it is said that ΩA and ΩC were not computed in PHREEQC. Why that?

Thank you for pointing this out. To clarify, aragonite and calcite saturation states were not computed in PHREEQC, but calculated using the AquaEnv R package. This approach was chosen because most studies reporting CaCO₃ saturation states use Seacarb or CO2SYS, rather than PHREEQC for computation. The LLNL PHREEQC database employed in our study uses thermodynamic data from Plummer and Busenberg (1982) to calculate CaCO₃ saturation states, whereas Seacarb, AquaEnv, and CO2SYS generally use solubility product constants from Mucci (1983) and carbonic acid dissociation constants from Lueker et al. (2000).

Saturation states for other mineral phases present in the kiln dust could not be calculated in AquaEnv and were therefore derived using PHREEQC. The rationale for using AquaEnv to calculate CaCO₃ saturation, ensuring consistency with commonly used thermodynamic data and facilitating comparison with other studies, has now been added to the text.

Aragonite and calcite saturation states were not computed in PHREEQC but were instead calculated using the AquaEnv package in R, as described previously (Hofmann et al., 2010). AquaEnv uses carbonic acid dissociation constants from Lueker et al. (2000) and solubility product constants for CaCO₃ from Mucci (1983), which differ from the thermodynamic data used in the LLNL PHREEQC database to describe the carbonate system. We used the AquaEnv approach to remain consistent with the methodology commonly applied in most OAE studies.

Line 246: I believe that "for CKD is missing after the 1.3 mmol g -1 .

This was indeed missing and "for CKD" has now been added to the text. Furthermore, the number 1.3 has been changed by 1.7 to take into account potential additional alkalinity generation through calcium silicate dissolution as requested by reviewer 1.

The maximum specific alkalinity release for LKD (8.02 ± 0.53 mmol g^{-1}) was more than three times higher than that of CKD (2.38 ± 0.16 mmol g^{-1}). Moreover, the LKD value was in good agreement with the theoretical prediction (8.8 mmol g^{-1}; see section 3.1), while the CKD value deviated more substantially from the theoretical estimate (1.7 mmol g^{-1}).

Line 264: it would be great to have the 0 on the y axis of tile B.

We agree and have added 0 on the y-axis of the figure 2B.

Lines 293-294: how can turbidity be slightly greater yet significantly greater? Do you mean statistically significantly greater?

Yes, this indeed needs to be statistically significantly greater. The term "statistically" has now been added to the text.

Line 310: it would be great to have the 0 on the y axis of tile B.

We agree and have added 0 on the y-axis of the figure 4B.

Line 330: I believe "be" should be deleted.

Indeed, we removed "be" from the text.

References:

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(3)   Hu, M., Dong, T., Cui, Z., Li, Z., 2024. Mechanical behavior and microstructure evaluation of quicklime-activated cement kiln dust-slag binder pastes. *Materials. 17* (6), 1253. doi:https://doi.org/10.3390/ma17061253

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(5)   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. *Biogeosci. Disc. 20* (4), 781-802. doi:https://doi.org/10.5194/bg-20-781-2023

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(8)   Lueker, T. J., Dickson, A. G., Keeling, C. D., 2000. Ocean pCO2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO2 in gas and seawater at equilibrium. *Mar. Chem. 70* (1-3), 105-119. doi:https://doi.org/10.1016/S0304-4203(00)00022-0

(9)   Mucci, A., 1983. The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *Am. J. Sci. 283* (7), 780-799. doi:https://doi.org/10.2475/ajs.283.7.780