

Abstract: Realistic alkalinization scenarios, considering technical and regulatory constraints, as well as spatial restrictions, are proposed and examined. Results provide a set of stylistic projections of alkalinity addition for different spatial settings and different temporal timeframes spanning from as early as 2030 and up to 2100. The technologies considered include ocean liming, coastal enhanced weathering, and electrochemical pathways using desalination brines. Among others, these estimates can be used to constrain model simulations that will be carried out in Work Package 4.

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1. Introduction

1.1 Context

OceanNETs is a European Union project funded by the Commission's Horizon 2020 program under the topic of Negative emissions and land-use based mitigation assessment (LC-CLA-02-2019), coordinated by GEOMAR | Helmholtz Center for Ocean Research Kiel (GEOMAR), Germany. OceanNETs responds to the societal need to rapidly provide a scientifically rigorous and comprehensive assessment of negative emission technologies (NETs). The project focuses on analyzing and quantifying the environmental, social, and political feasibility and impacts of ocean-based NETs. OceanNETs will close fundamental knowledge gaps on specific ocean-based NETs and provide more in-depth investigations of NETs that have already been suggested to have a high CDR potential, levels of sustainability, or potential co-benefits. It will identify to what extent, and how, oceanbased NETs can play a role in keeping climate change within the limits set by the Paris Agreement.

1.2 Purpose and scope of the deliverable

Removing carbon dioxide (CO_2) from the atmosphere by increasing ocean alkalinity (ocean alkalinity enhancement, 'OAE') could form part of national or international strategies for net-zero carbon emission targets. However, previous modelling experimentation has been largely driven by attempts to elicit a specific response in the Earth/ocean-system models. There has been no work constrained by what might be 'realistic' for current and future supply chains. The aim of this deliverable is to set out a series of OAE deployment scenarios that are:

- i) Constrained by technical limits of supply chains or transformation technologies,
- ii) Contextualised by forecasts for future energy systems, and
- iii) Integrate recent and ongoing information from life-cycle assessments (LCAs).

The intention is that these scenarios will be adapted for use by ocean/carbon cycle modellers within the OceanNETs consortium. The work builds upon previous deliverables from WP6 that conceptually describes the case studies. This could be used within deliberative work with stakeholders, or to help constrain or contextualise economic or governance work. It is anticipated that this will be further developed across the whole consortium into case-studies, which may further refine the deployment scenarios with economic, regulatory, social, or environmental constraints.

Geographic scope: In an attempt to be OAE technology agnostic, we have postulated a global scenario that is constrained only by mineral extraction. Regionally, our scenarios focus on the deployment of ocean liming (OL) and electrochemical approaches in Europe. The European electrochemical scenarios are augmented with additional scenarios that consider desalination in the Middle East (that may otherwise create an incorrect assumption about the global potential of electrochemical approaches if the European context was thought universally applicable).

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1.3 Relation to other deliverables

This deliverable relates to WP2 and WP4.

2. Summary of scenarios

3. Background Drivers

3.1 Overview of OAE approaches

A range of approaches have been proposed to artificially increase ocean alkalinity to remove carbon dioxide from the atmosphere (Renforth and Henderson, 2017). These include spreading minerals directly onto the land surface (Hartmann et al., 2013), coastal environments (Meysman and Montserrat, 2017), or the open ocean (Harvey, 2008; Köhler et al., 2013). Some have suggested adding minerals to reactors to accelerated mineral dissolution through elevated pressure or electrochemistry (House et al., 2007; Rau, 2011), or the transformation of minerals into more soluble forms (Kheshgi, 1995). This deliverable considers deployment scenarios associated with two approaches: ocean liming and electrochemistry.

Electrochemical Approaches (EA): These approaches use electrochemistry within reactors to promote acidic and basic conditions around the anode and cathode respectively. The basic solution created at the cathode may be used to increase ocean alkalinity. The acidic solution formed at the anode is neutralised by reaction with silicate minerals. The movement of large volumes of seawater is not untypical in desalination or power station cooling, and the application of electrochemistry to seawater for the creation of alkaline products (NaOH) is mature (albeit at a relatively small scale). However, the combined reaction system, appropriate electrode configurations and materials, and waste acid management remain at an early stage of development. Furthermore, to produce one mol of NaOH 212 kJ are consumed (House et al., 2007).

3.2 Wider context

For OL the main component technologies are mature (technology readiness level, "TRL", 9) and limestone is abundant and readily available. Therefore, when governance, policy, and public acceptability for OL also mature, the existing component technologies could support its direct scaling up. For this reason, here future expansion and growth rates for OL are based on historical data for the capacity utilization of its main component technologies and particularly the cement and lime industries (Figure 1).

Figure 1: Historical global (left) and European (right) production for cement and lime. Forecasts based on the method presented in (Renforth, 2019) for SSP3 and 5 are shown in red and blue respectively.

Regarding the electrochemical alkalinity production, future projections about the annual growth rate of the produced desalination brines, and by extension of available alkalinity, were based on estimates about population growth in the examined spatial extents, considering a low and a high growth scenario. For context, in Figure 2 the projected population growths for Europe and Middle East (including North Africa) are given (low and high scenarios).

Figure 2: Population growth (min and max) estimates for Europe (left) and Middle East (right) (taken from IIASA).

Furthermore, in Figure 3 the total desalination capacity from different water sources, and its spatial extent, is given. As can be seen, the desalination industry is based, by and large, in seawater while nearly half of its brine output is found in the Middle East and North Africa.

Figure 3: Global state of desalination in 2019 (Figure taken from (Jones et al., 2019)).

Finally, apart from capturing atmospheric CO2, both OL and EA are responsible for some carbon emissions during their life cycle. However, since both technologies are energy intensive, their carbon footprint is projected to decrease and fully decarbonise along with electricity. For OL the carbon penalty was taken from initial LCA estimates, whereas for EA the electricity requirement to produce 1 mol of NaOH (House et al., 2007) was considered. To estimate the future carbon penalty of both OL and EA existing estimates for electricity decarbonisation were considered (Figure 4).

Figure 4: Carbon dioxide emission intensity of global energy generation for low emission SSP scenarios (taken from IIASA).

3.3 Technical constraints on OAE approaches

The existing natural resources of rocks containing carbonate and silicate minerals have the potential of sequestering thousands of Gt of $CO₂$ (Bach et al., 2019) or, in theory, even more since hundreds of trillions of tons of such materials are near the Earth's surface (Sverdrup et al., 2017). Therefore, the existing carbonate rock resources are potentially not limiting for OL. However, the infrastructure and equipment for their mining and comminution as well as their further processing (e.g., calcination) and spreading in the oceans, may be limiting. To constrain the growth rate of OL historical data about the utilization capacities of the mining, the cement, and the lime industries were collected and modelled. By doing so the spare capacities of these industries were identified and these were used to drive the future growth rate of OL.

For EA, since brines are currently a waste product their availability is not a limiting factor, and in theory these can be fully explored for OAE. Here, a limited deployment scenario was considered where desalination brines of up to 1 km from the coastline are used by EA and a widespread deployment scenario where desalination brines of up to 10 km from the coastline are used for EA. The growth rate for each scenario was driven by population

growth (low growth for the limited deployment scenario and high growth for the widespread deployment scenario).

Rock extraction and processing: The construction aggregates industry includes the blasting, mining, and crushing of rocks together with gravel and sand extraction (Langer, 2001), which is estimated to produce 47-59 billion tons, with the mean value being 50 billion tons, potentially increasing to 60 billion tonnes by 2030 (JXSC, 2021). Of the 53 billion tonnes of primary and secondary resources that were mined in 2012 globally, 66% were silicate-based materials and the remaining was limestone (Sverdrup et al., 2017). Data on the global production of crushed stone/aggregate are not widely available. However, various per capita consumption rates are considered in Figure 5, and annual rates of change are presented in Figure 6 (for total mineral extraction at a continental scale).

Figure 5: Various national annual aggregate consumption per capita for 2017.

Figure 6: Regional mineral extraction data, showing total production (top left), and annual rates of change (taken from (Reichl and Schatz, 2022).

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Figure 7: Historic production of cement and lime, and the annual rate of change.

Alkalinity generation through electrochemical approaches: An analogue to electrochemical approaches for alkalinity generation is the large-scale production of sodium hydroxide by the chlor-alkali industry. In 1990, 43 Mt of sodium hydroxide were produced globally, which had risen to 72 Mt by 2013. The 5-year rolling average rate of expansion was typically between 2 and 4% (Figure 8).

Figure 8: Historic production of sodium hydroxide from the chlor-alkali industry (left), and the annual rate of change (right).

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3.4 Opportunities for integration

Fine material from the aggregate industry: Part of the mass of material handled at a rock extraction facility is often referred to as 'fines' (material that is too small for use as aggregate usually <4 mm). The size, and subsequent 'quality', of the aggregate is carefully controlled by crusher operational parameters and screens that separate out the required size fraction. Effort is made to reduce the production of the waste fines, which are stockpiled and sometimes used in redevelopment of the site (Woods et al., 2004). Such material is not widely documented, but could be as much as 20% of the mass of production (Manning and Vetterlein, 2004).

Spare capacity in the cement and lime industries: Establishing new infrastructure for the processing of the extracted minerals, such as crushing facilities or new kilns for limestone calcination, could be relatively expensive and curtail the upscaling rate (see Section 5 below). Given that calcination is already undertaken at Gt scale globally in the cement industry and 100's Mt in the lime industry, here we explore the possibility of using spare capacity within these existing industries to create hydrated lime for OL (see Appendix).

Table 2: Estimates for the spare capacity of cement and lime plants for OL in Europe, USA, and Asia.

To estimate the potential spare capacity of the lime and cement industry, data for lime and cement production were gleaned from the literature. For Europe's total cement clinker production historical data published by the Cement Sustainability Initiative (CSI) and Eurostat were used, while for lime production historical data published from the European lime association (EuLA) were employed (European Commission, 2017). For USA and China data published from (U.S. Geological Survey, 2020) were used, the latter considering only cement's spare capacity. The estimates for cement and lime spare capacity are summarized in Table 2.

Coupling with desalination: The desalination industry removes large volumes of seawater and produces waste brine which is typically returned to the ocean. Concentrated brine may have energetic advantages for electrochemical engineering, as well as removing the need for dedicated water movement. As such, coupling EA with desalination has been proposed (Davies et al., 2018). We have included this within our scenario.

More than 95 million m^3 of desalinated water is produced daily (51 billion m^3 annually), generating more than 141 million m^3 day⁻¹ of brine that is typically discharged into the oceans negatively affecting receiving ecosystems (Jones et al., 2019). Recent estimates suggest that by 2030 the global desalination capacity could be expand by as much as 40% (Ihsanullah et al., 2021). However, as mentioned above the 5-year rolling average rate expansion for NaOH production was typically between 2 and 4% (Figure 8) and therefore EA expansion when using desalination brines is based on estimates on population growth which extent up to 2100. Assuming that salt (sodium chloride, NaCl) concentration can be 8% in brines, this translates to 4.1 Gt of NaCl which can produce around 3.3 Gt of HCl and 3.7 Gt NaOH. Furthermore, to neutralise the produced HCl, one mol of alkaline mineral (e.g., MgSiO3) is required per mol of neutralised HCl (NASEM, 2022). Finally, to provide a spatial restriction in the calculations, desalination brine production data from (Jones et al., 2019) were used, assuming that only brines that are up to 1 km (low deployment) or up to 10 km (widespread deployment) from the coastline will be used for OAE. Table 3 summarizes the annual brine production that was considered here.

Table 3: Estimates for desalination potential capacity for OAE in Africa, America, Asia, Europe, and Oceania (reference year 2019, data taken from (Jones et al., 2019)).

***values refer to the 10 km brine capacity, the values for the 1 km are around 48% lower.**

4. Deployment Scenarios

4.1 Global Rock Extraction Scenarios

Figure 9 presents potential expansion scenarios for crushed limestone production. Annual expansion rates were simulated to mimic previous maxima (Figure 9), such that in the highest production scenario it would not be unreasonable to sustain a 4-5% increase for several decades. Predicted future rock aggregate demand was subtracted from the total material, and quarry fines were added to prove quantities to additional available rock for OAE.

Figure 9: Forecasted rock extraction scenarios determined from the annual % change (left panel). The total carbonate aggregate produced and available material for OAE (right panel). High and low rates of growth were derived from Figure 6.

Assuming that 25 kWh are required for every tonne of material (e.g., for blasting extraction, and comminution to approximately 100 um (Renforth et al., 2013) emission intensities are calculated and shown in Figure 10.

Figure 10: Emissions associated with the high and low rock extraction scenarios in Figure 9.

4.2 Hydrated Lime Production

Assuming a maximum expansion rate of ~7% (high) and ~5% (low) profiled according to Figure 11 (constrained by previous maximum expansion rates, Figure 9), and exploitation of spare capacity scaling to 2050 (see Section 5.0), then total hydrated lime production in Europe that may be useable for OL could scale to between 100-150 Mt/yr by 2100. We assume new capacity will be regulated such that production will result in net-zero emissions, and that exploitation of spare capacity will be limited by the deployment of carbon capture and storage (see Section 5.0). Given this, the emissions associated with hydrated lime production is relatively small, and relatively short-lived as economies and industries decarbonates in the latter half of this century.

Figure 11: High and low production scenarios for hydrated lime for ocean liming, and the associated emissions from production.

4.3 Electrochemical alkalinity production

First the estimates for the total alkalinity (NaOH) production for the two examined regions, i.e., Middle East (which also includes North Africa) and Europe (which also includes a minor part of central Asia), are shown (Figure 12). Specifically, the Shared Socioeconomic Pathway (SSP) database was used to simulate different futures for population growth (low and high growth rate) for the reference period 2030 to 2100. The different patterns for population growth for each region were assumed to represent the possible futures for the total desalination output. As such, the growth rate of for the limited and the widespread scenario were driven by population changes in each region (low growth was assumed for the limited deployment scenario and high growth for the widespread scenario). Results are shown in Figure 12, where it can be seen that the largest potential for electrochemical alkalinity production through desalination brines is in the Middle East. Europe may contribute a smaller extent (an order of magnitude lower) to NaOH potential capacity (Figure12).

Figure 12: Total alkalinity (NaOH) capacity from desalination brines for the reference period 2030 to 2100.

However, the underlying challenge with electrochemical alkalinity production using desalination brines is the carbon emissions associated with the energy demand. As a result, contemporary use may be limited by the emissions intensity of electricity production, but as electricity decarbonizes the carbon penalty of this technology is reduced (Figure 13).

Figure 13: Total life cycle CO2 emissions of EA for the limited and widespread deployment scenario considering a low and a high scenario for the carbon emissions of the global electricity mix. Reference period 2030 to 2050.

5. Conclusions

A series of realistic alkalinization scenarios, restricted by technical constraints in different spatial extents was presented for ocean liming and electrochemical alkalinity production using desalination brines. Even though these stylistic projections provide future pathways for OAE they are also associated with limitations and dependencies, which are summarised below.

Deployment of Carbon Capture and Storage: For OL the main challenge pertains to the high thermal energy input of existing calciners, which is required for $CaCO₃$ decomposition to CaO, and particularly to the need to capture and store the process $CO₂$ emissions (through carbon capture and storage) from limestone decomposition. This suggest that for OL, decarbonised and energy efficient kilns should be used. (IEA, 2018) suggests that CCS deployment may reach 88% by 2050, increasing from ~20% in 2030. Specifically, it has been suggested that CCS and relevant technologies will nearing maturity for commercial deployment in the 2020–2035 timeframe (after 2030 efficiency will be nearing optimisation), while in the 2035–2050 they will be deployed rapidly (Rissman et al., 2020). Therefore, any spare capacity that may exist currently will not be considered 'usable' until 2030, after which is exploitation factor scales between 0 and 1 between 2030 and 2050.

Expansion of mineral extraction and processing: Our method for upscaling uses past expansion rates to constrain future potential. As such, we simplify the complexities in developing new or existing mineral extraction sites. Theoretically, a new mine can commence operation in 5 years or even sooner. Regarding the required infrastructure, the estimates for a new cement plant suggest that this can take between 8 to 10 years and its construction roughly

2 years (Bliss et al., 2012). However, if policy was to support large scale OAE it might be feasible to have the permit in 5 years or less, as in the case with new mines where a new mining permission requires around 3 years (Mineral Products Association, 2021). In parallel, the required equipment (e.g., crushers, calciners, and CCS) could be ordered so, in theory, a new plant could be built in parallel with the new mine and both could be ready within 5 years or less.

Use of desalination brines for electrochemical alkalinity production: Most likely, it will be a number of years for electrochemical pathways to reach maturity, however, in the context of this work a very optimistic scenario for the starting date of the deployment of this technology at scale was 2030.

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Appendix

S1 Regional descriptions of rock extraction

Europe: In EU 28 and the European Free Trade Association (EFTA) countries the construction aggregates industry is by far the largest non-energy extractive industry, with 15,334 companies currently employing more than 200,000 people at 26,054 sites (UEPG, 2020). Population growth, along with the need to maintain existing and/or construct new infrastructure, has rendered the construction aggregates industry resilient, even during the past financial crisis and the ongoing COVID-19 pandemic. For example, during the past two decades (reference period 1997-2018) the production output of construction aggregates in Europe (EU member countries, associates, and candidates) has ranged from around 2.2 to 3.1 billion tons (**Fig. S1**) (BGS, 2019; UEPG, 2020). Currently, more than 3 billion tons of construction aggregates are produced in Europe (EU 28 and EFTA), with the crushed rocks production being 1.43 billion tons (provisional estimates for 2018) (UEPG, 2020).

Figure S1*: Construction aggregates production by EU, associates, and candidate countries for the reference period 2004-2018. (production data taken from (Minerals4EU, 2021))*

Therefore, compared to the global construction aggregates output (50 billion tons (JXSC, 2021)) EU's output amount to 5%, while for the case of Europe as a continent in 2020 its total minerals production was nearly 7% of the total global output. (**Fig. S2**). Here, a more conservative assumption was considered, assuming that 50% of the maximum spare capacity will be available.

Figure S2*: Total minerals production by continents (not including bauxite) for the reference period 1984-2020. Data taken from (Reichl and Schatz, 2022).*

USA: The construction aggregates output in Europe is on par with the one in USA, where crushed stones production in 2019 amounted to 1.53 Gt (up from 1.42 in 2018), while sand and gravel production was at 0.97 Gt in 2019 (up from 0.94 in 2018) (USGS, 2020). Fluctuations have been observed in USA's construction aggregates output. which before the 2008 financial crisis was more than 3 Gt, then sharply dropped by 35% (less than 2 Gt) in 2010 (JXSC, 2021), while currently is around 17% lower (USGS, 2020) than the 3 Gt yr.-1 mark. As such, USA is responsible for around 5% of the global construction aggregates output (50 billion tons (JXSC, 2021)). For the case of America as a continent (Latin and North America) its total minerals production in 2020 was much higher and amounted to 21% of the total global output. However, the spare capacity of the total minerals production in America is most likely lower than Europe's since it appears to be relatively stable during the past 25 years (**Fig. S2**). Nonetheless, spare capacity is available (e.g., mines typically do not operate 24/365).

Asia: In Asia it appears that a strong and expanding mining industry is in place and particularly after 2002 where a steep growth rate was observed (**Fig. S2**). Most likely, the local economic growth will not be able to underpin such steep growth rates in the longterm suggesting that large opportunities for spare capacity exists in Asia, particularly when considering that the total minerals production expanded by 98% in the reference period 2002 to 2019. Furthermore, some fluctuations have also been observed, with the minerals production for 2019 being 7% lower than the minerals production for 2020.

A2 Regional descriptions of cement and lime production

Europe: In the EU28 existing estimates for cement clinker production vary, since for example in 2015 the Cement Sustainability Initiative (CSI) put this number at 125 Mt whereas Eurostat at 105 Mt (European Commission, 2017). However, both data suggest a similar trend for the years that their estimates correspond, while CSI estimates indicate a sharp drop (13%) in EU28 clinker production, from 144 Mt in 2007 to 125 Mt in 2015 (**Fig. S3**). Regarding the total cement production in EU28 this was 163 Mt in 2016 (European Commission, 2017) and the same spare capacity for the cement clinker production was assumed, i.e., 13%.

On the other hand, from 2003 to 2007 lime production increase from around 28 Mt to 35 Mt, whereas a steep drop in lime production followed with the output being 24 Mt in 2009. Thereafter small fluctuations were observed, with lime production in 2016 being again 24 Mt (European Commission, 2017). Therefore, it appears that lime has a significantly higher spare capacity than cement, i.e., around 31%, albeit its production output is also significantly lower. The aforementioned values for EU28 are assumed to represent the current situation in Europe.

Similarly to CEW, a 50% allocation to both cement and lime spare capacity was assumed to be available for OL. Therefore, cement's spare capacity amounts to 6.5% (total production 163 Mt) whereas lime's amounts to 15.5% (total production 24 Mt).

Figure S3*: Total cement clinker production in Europe according to CSI (Cement Sustainability Initiative) and Eurostat (European Commission, 2017).*

USA: during the last 30 years (reference period 1992 to 2020), the annual lime production has fluctuated from around 16 Mt 20 Mt, with lime production in 2020 being 16 Mt (**Fig. S4**). This suggest that a spare capacity of at least 20% is available. The same spare capacity was also observed in cement production, since in 2019 cement production was 89 Mt, while the clinker capacity was 103 Mt (USGS, 2020), i.e., 20% spare capacity. It should be noted that here and elsewhere the percentage of spare capacity that is considered corresponds to the most recent production value, which is typically lower than previous historical outputs. This acts as an additional safety factor in our calculations.

Again, a 50% allocation to both cement and lime spare capacity was assumed to be available for OL. Therefore, cement's spare capacity amounts to 10% (total production 103 Mt) whereas lime's amounts again to 10% (total production 16 Mt). On the other hand, in South America Brazil cement production in 2019 was 55 Mt and the clinker production was 60 Mt, which suggest that a much lower spare capacity exists. As such, here we focus only on USA's cement and lime output as a representative of the American continent, particularly when considering the very existence of pure carbonate rock outcrops in South America (Caserini et al., 2022).

Figure S4*: Lime production fluctuations in USA for the reference period 1991-2019. (production data taken from (USGS, 2020).)*

Asia: As was the case for the spare capacity of the total minerals production, the spare capacity of the lime and cement industry in Asia is probably miniscule due to the strong demand for these products. For example, according to (USGS, 2020), worldwide China is the main cement producer with a 2.2 Gt output in 2019, followed by India with 320 Mt production in the same year. However, in both countries, the clinker capacity is lower than the cement production, suggesting that low opportunities for spare capacity exists. However, this is not the case for other countries in Asia, since, for example, in 2019 in Iran, Russia, and Turkey cement production is at 60, 57, and 51 Mt, respectively, with the corresponding clinker capacities being 81, 80, and 92 Mt. Therefore, spare capacity also exists in Asia. However, China is the main player in this industry, and also pure carbonate

rocks outcrops are available (Caserini et al., 2022) and therefore China's total cement production (2.2 Gt) was considered for Asia's spare capacity, while the spare capacity that was considered in the mining sector (7%) was also used here. Again, a 50% allocation was considered making the cement and lime spare capacity at 2.5% of the total (2.2 Gt).

A3 Additional Opportunities not modeled here

Conversion of solid fossil fuel extraction equipment: To further underpin the potential of the spare capacity of the mining industry, the existing mining activities for solid fossil fuel extraction can be considered. Specifically, as we move towards a decarbonise economy fossil fuel mining will minimize or even cease to exist and therefore existing infrastructure (equipment) and manpower could be re-employed for alkaline minerals extraction (Caserini et al., 2022). In Fig. S4 the year-round mining output for coal (steam and coking) and lignite is shown and surprisingly apart from lignite coal mining is on the rise. Specifically, the production of "steam" coal (a grade between bituminous and hard coal (anthracite) that was used to steam locomotives) appears to have steeply increase after 2002, reaching an output of 5.7 Gt in 2020 while the total output (coal plus lignite) in the same year was 7.4 Gt. In has been suggested that as the solid fossil fuel extraction industry contracts the equipment and manpower could be relocate to limestone mines, i.e., to OL (Caserini et al., 2022). The overall growth rate pattern for solid fossil fuel extraction (Fig. S4) corresponds, to a good degree, to growth rate pattern minerals production (Fig. S1), suggesting that as the economy decarbonises further opportunities for spare capacity will be available globally.

Figure S4*: Total production of solid mineral fuel for the reference period 1984-2020. Data taken from (Reichl and Schatz, 2022).*