Silicate Production and Availability for Mineral Carbonation

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Ⓢ *Supporting Information*

ABSTRACT: Atmospheric carbon dioxide sequestered as carbonates through the accelerated weathering of silicate minerals is proposed as a climate change mitigation technology with the potential to capture billions of tonnes of carbon per year. Although these materials can be mined expressly for carbonation, they are also produced by human activities (cement, iron and steel making, coal combustion, etc.). Despite their potential, there is poor global accounting of silicates produced in this way. This paper presents production estimates (by proxy) of various silicate materials including aggregate and mine waste, cement kiln dust, construction and demolition waste, iron and steel slag, and fuel ash. Approximately 7−17 billion tonnes are produced globally each year with an approximate annual sequestration potential of 190−332 million tonnes C. These estimates provide justification for additional research to accurately quantify the contemporary production of silicate minerals and to determine the location and carbon capture potential of historic material accumulations.

1. INTRODUCTION

Recently, there has been increasing research into the carbonation of silicate minerals as a strategy to remove carbon from the atmosphere. The concept, first published by Seifritz,[1] develops those proposed by Berner and colleagues.[2,3] Through mineral carbonation, the weathering of silicate minerals on land and the precipitation of carbonates in oceans is a natural negative feedback mechanism that stabilizes the Earth's climate over geological time scales. Various strategies have been explored to intentionally accelerate the weathering of silicate minerals containing divalent cations (predominantly Ca and Mg) to precipitate carbonate through eq 1[4]

$$M^{2+} + CO_3^{2-} \leftrightarrow MCO_3 \downarrow \qquad (1)$$

Early work[5,6] investigated the carbonation of olivine and serpentine at high pressure and temperature. This 'reactor' method has been applied to artificial materials including slag,[7,8] cements,[9] and ashes.[10,11] Exploiting natural weathering processes within soils, others have investigated the formation of pedogenic carbonates as a mineral carbonation technology.[12,13] Deeper subsurface carbonation is possible through CO_2 gas injection into reactive silicate rock formations, complementing storage by injection into unreactive saline aquifers.[14−16]

Irrespective of the mineral carbonation method used, the efficacy is primarily limited by material availability (and cost). Calcium and magnesium-bearing silicate minerals are present in various artificial material (and waste) streams. This paper explores the quantities, sources, production histories, fate within the environment, and the maximum carbonation potential of such materials, focusing on 'waste' silicates. It is timely in light of current discussions regarding geoengineering, where silicate carbonation is prominent.[17] However, the maximum potential

of this technology is limited because of inadequate accounting of available materials. Material streams containing silicate minerals (i.e. cement waste, construction and demolition waste, slag) should no longer be considered as wastes, because they have an intrinsic carbon capture value. Our estimated carbon capture potential provides justification for industry and regulators to develop monitoring procedures and strategies to exploit this carbon capture function.

2. CARBONATION OF SILICATES

Commonly produced calcium and magnesium silicate minerals vary in chemical composition, crystal structure, and carbonation potential. They often occur in association with glasses and gels, and with the calcium hydroxide mineral portlandite, which also undergo carbonation. Table 1 gives examples of free energies (ΔG_r) of carbonation reactions that produce calcite or magnesite at 25 °C, expanding on previous tabulated data[6] to include artificial minerals. For negative values of ΔG_r a reaction is predicted to take place and to give off energy. Positive values of ΔG_r indicate a reaction that will only take place with energy inputs.

To facilitate comparison, Table 1 normalizes the calculated values for ΔG_r to the number of moles of carbonate produced. The preponderance of negative values for ΔG_r shows that the majority of widely occurring calcium silicate minerals (and portlandite) are predicted to undergo carbonation reactions under ambient conditions.

Table 1. Carbonation Reactions and Their Associated Free Energy Changes (ΔG_r) at 25 °C, 1 atm, Overall and Normalized to the Number of Moles of Carbonate Mineral Product[a]

mineral/ material	formula	occurrence	ΔG_f, kJ/mol	carbonation reaction	ΔG_r, kJ/mol	ΔG_r, kJ/mol carbonate
Portlandite	$Ca(OH)_2$	Portland cement	−898.0	$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O$	−81.50	−81.50
Larnite	Ca_2SiO_4	cement clinker	−2191.2	$Ca_2SiO_4 + 2H_2CO_3 = 2CaCO_3 + H_4SiO_4$	−127.20	−63.60
Anorthite	$CaAl_2Si_2O_8$	basic rocks	−4007.9	$CaAl_2Si_2O_8 + H_2CO_3 + H_2O =$ $CaCO_3 + Al_2Si_2O_5(OH)_4$	−57.80	−57.80
Jennite	$Ca_9Si_6O_{16}(OH)_2.6H_2O$	hydrated cement	−2480.8	$Ca_{1.67}SiO_{1.57}(OH)_{4.2} + 1.67H_2CO_3 =$ $1.67CaCO_3 + H_4SiO_4 + 1.77H_2O$	−90.51	−54.20
Rankinite	$Ca_3Si_2O_7$	cement clinker/slag	−3748.1	$Ca_3Si_2O_7 + 3H_2CO_3 + H_2O =$ $3CaCO_3 + 2H_4SiO_4$	−146.30	−48.77
Akermanite	$Ca_2MgSi_2O_7$	slag	−3667.5	$Ca_2MgSi_2O_7 + 3H_2CO_3 + H_2O =$ $2CaCO_3 + MgCO_3 + 2H_4SiO_4$	−127.90	−42.63
Forsterite	Mg_2SiO_4	basic rocks; slag	−2053.6	$Mg_2SiO_4 + 2H_2CO_3 = 2MgCO_3 + H_4SiO_4$	−66.80	−33.40
Wollastonite	$CaSiO_3$	metamorphic rocks	−1549.0	$CaSiO_3 + H_2CO_3 + H_2O = CaCO_3 + H_4SiO_4$	−27.00	−27.00
Tobermorite	$Ca_5Si_6O_{16}(OH)_2.4H_2O$	hydrated cement	−1744.4	$Ca_{0.83}SiO_{1.53}(OH)_{2.6} + 0.83H_2CO_3 =$ $0.83CaCO_3 + H_4SiO_4 + 0.13H_2O$	−13.66	−16.46
Diopside	$CaMgSi_2O_6$	basic rocks	−3026.8	$CaMgSi_2O_6 + 2H_2CO_3 + 2H_2O =$ $CaCO_3 + MgCO_3 + 2H_4SiO_4$	−26.20	−13.10
Chrysotile	$Mg_3Si_2O_5(OH)_4$	metamorphic rocks	−4032.4	$Mg_3Si_2O_5(OH)_4 + 3H_2CO_3 =$ $3MgCO_3 + 2H_4SiO_4 + H_2O$	−39.20	−13.07
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	metamorphic rocks	−11574.6	$Ca_2Mg_5Si_8O_{22}(OH)_2 + 7H_2CO_3 + 8H_2O =$ $2CaCO_3 + 5MgCO_3 + 8H_4SiO_4$	−33.10	−4.73
Enstatite	$MgSiO_3$	basic rocks	−1458.3	$MgSiO_3 + H_2CO_3 + H_2O =$ $MgCO_3 + H_4SiO_4$	0.14	0.14
Laumontite	$CaAl_2Si_4O_{12}.4H_2O$	metamorphic rocks	−6772.0	$CaAl_2Si_4O_{12}.4H_2O + H_2CO_3 + H_2O =$ $CaCO_3 + Al_2Si_2O_5(OH)_4 + 2H_4SiO_4$	90.70	90.70
Water	H_2O		−237.1			
Kaolinite	$Al_2Si_2O_5(OH)_4$		−3797.5			
Calcite	$CaCO_3$		−1128.5			
Magnesite	$MgCO_3$		−1029.5			
(Carbonate)$_{aq}$	H_2CO_3		−623.2			
(Silica)$_{aq}$	H_4SiO_4		−1307.8			

[a] NB: reactions for jennite and tobermorite use mineral formulae corresponding to those cited in ref 19, the source of the data for ΔG_f. Formulae and values for ΔG_f for other reactants, including dissolved carbonic acid, and products, including dissolved silica, are also given. For internal consistency, all thermodynamic data, except ΔG_f for jennite and tobermorite, are from ref 20.

Despite favorable free energy changes, the mechanisms of carbonation depend on kinetic factors, such as dissolution rate and reactive surface area. Dissolution rate can vary by several orders of magnitude.[18] In addition, bulk materials consist of mixtures of minerals listed in Table 1 with others that may not be of interest, reducing carbonation potential.

3. NATURAL CALCIUM SILICATES

Naturally occurring basic and ultrabasic igneous rocks are rich in calcium and magnesium, in some cases exceeding 50% CaO + MgO. Globally, the largest expanses of exposed basic silicate rocks are flood basalts[21] (e.g., Deccan Traps in Western India, Siberian Traps in Northern Russia); other examples occur in the USA (Columbia Plateau, Washington/Oregon) and the UK (the Great Whin Sill and related rocks, Northumberland/Southern Scotland; Antrim Basalts, Northern Ireland). The IPCC considers costs and benefits associated with extracting silicates specifically for carbonation.[22] Energy requirements are between 180 and 2300 kWh (primarily associated with processing the raw material) and costs are between $55−430 per tonne (t^{-1}) of CO_2 captured using a wet carbonation reactor. However, the carbon capture potential is large ($10^2 - 10^4$ $GtCO_2$) and is an order of magnitude larger than the anthropogenic greenhouse gas contribution to the atmosphere over the next 100 years.[6] Additional to mining explicitly for carbonation, a complementary strategy is to use silicates produced in waste streams whose embodied energy is shared with a primary product and the value of the material is dictated primarily by its carbon capture potential.

Igneous rocks containing silicate minerals are mined for use in construction as building stone and aggregate, generally close to the extraction site. Currently there is little interest in documenting global production of these materials. On a national basis, the UK extracts approximately 60 million tonnes (Mt) of igneous rock annually (a^{-1}; 70% crushed and used as aggregate), approximately 28% of total UK aggregate production.[23] The United States produces 1.72 billion tonnes (Gt) of crushed stone a^{-1}, igneous rocks comprising 24% (16% granitic, 8% basic).[24] Inefficiencies in the crushing process overall produce around 20% of fine-grained material too small to be used as aggregate.[25]

Primary aggregate crushing produces 3%-5% of fine material, depending on the method used.[26] Postprimary crushing may produce fines of up to 40 wt % of the raw material.[25] We estimate the production of igneous quarry fines in the UK to be around 20 Mt a^{-1}, extrapolating global fines from igneous aggregate production[27] to be 3.3 Gt a^{-1}. Although speculative, this estimate is similar to the IPCC's estimated potential for carbonation of natural silicates.[22] Presently, fine material that cannot be sold tends to be stockpiled and can be used for site redevelopment after extraction.[28]

Extraction of other minerals and ores produces byproduct including 'overburden' and 'tailings'. For example, two chrysotile mines in Northern Canada produced 50 Mt of tailings in 50 years of operation with carbonation potential.[29] Total mine waste production between 1910 and 1980 in the US is approximately 40 Gt (from mining Cu, Fe, U, Mo, Zn, Au, Pb, and Ag).[30] Using global production statistics for Cu, Pb, Ni, and Zn (around 40 Mt a^{-1} collectively[31,32]) and typical grades of ore between 0.5 and 25%, the global production of waste from metal mining activity is between 2 and 7 Gt a^{-1}. Tailings mineralogy is highly dependent upon the host geology but may be suitable for carbon capture. Extraction processes and subsequent storage on site may have resulted in partial carbonation of these materials. Additional work is required to assess the global carbonation potential of mine waste, the location of stockpiles, and the degree to which carbonation has already occurred.

4. CEMENT, CONSTRUCTION, AND DEMOLITION WASTE

Approximately 2.8 Gt of Portland cement are manufactured annually worldwide for use in the construction industry, by heating calcium carbonate (from mined limestone), with aluminosilicate materials (from clay or fly ash), to between 1300 and 1500 °C. The mineralogy of the resulting cement clinker depends on the Ca/Si ratio of the raw materials and is dominated by a mixture of di- and tricalcium silicates.

Until the start of the twentieth century, the global cement industry was dominated by the US and the UK.[33] Toward the mid twentieth century emerging economies such as Japan substantially increased cement production, partly because of increasing demand due to urbanization. Importantly, there has been recent rapid growth of cement production in Brazil, Russia, India, and China, which account for the majority of the cement manufactured today.[31] Approximately 2.8 Gt of cement are produced annually, and nearly 60 Gt of cement have been manufactured since the mid 1920s (Figure 1), contributing around 14 Gt carbon into the atmosphere.[34]

The manufacture of 1 t of cement uses approximately 1.7 t of raw material and produces 150−200 kg of waste as 'kiln dust'.[35] Therefore, 9−12 Gt of kiln dust may have been produced globally, with a carbon capture potential of 1.2−1.7 Gt C (based on a CaO content of 65%). Although the fate within the environment of this material is unknown, it is likely to have partially or fully carbonated.

Most of the 60 Gt of cement produced globally has been used for construction. The flux of material out of this pool is a heterogeneous waste stream composed of unused/recycled material produced during construction and demolition (C&D waste). A proportion of the waste is composed of calcium bearing minerals derived from hydration of cement paste. The exact quantity of C&D waste produced in the UK has not been comprehensively
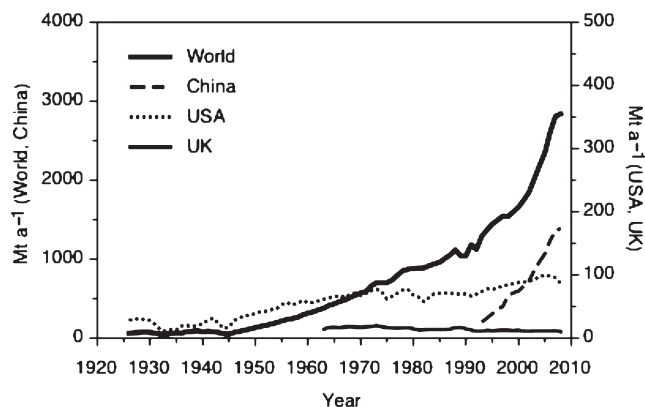

Figure 1. Historic production of cement.

established, and available data are becoming increasingly dated.[36,37] A recent report[38] suggests that 40−45 Mt a^{-1} of C&D waste is either spread on registered sites or disposed in landfill; this is approximately 51% of the total UK production of C&D waste. In this study, the total quantity of C&D waste was obtained from a survey[38] of demolition crusher operators, in which the output of active crushers was calibrated against population density, as a proxy, to estimate the total recycled aggregate. C&D waste disposed into landfill is recorded by operators using weighing stations and was estimated nationally by extrapolation.[38] The accuracy of such estimates is limited, yet this study provides the baseline for current UK government policy which calls for a 50% reduction in C&D waste to landfill by 2012.[39]

There is no widespread quantification of C&D waste, which makes estimation of global production difficult to establish. The data that are available are generally for developed countries.[38,40−42] Using population as a proxy (http://www.un.org/popin/-accessed ninth September 2010), a crude estimation of global C&D waste production is 1.4−5.9 Gt a^{-1} (21% from construction and 79% demolition[37]).

Production of C&D waste is likely to depend on numerous factors including waste policy, economic prosperity, historic construction activity, availability of mineral resources, and construction practice. An economically developing country which now has a strong construction sector, but little historic urban construction activity, is likely to produce more construction waste than demolition waste.[43] The opposite may be true for a country with a longer history of development.[37,44] A comprehensive investigation of the differences in C&D waste quantities and characterization has yet to be undertaken and is unlikely to be possible until construction practice includes the routine measurement and reporting of material flow.

Reuse of C&D waste as a 'secondary aggregate'[45,46] and as raw material for brick manufacturing[47] has been suggested as an alternative to landfill. However, use as a structural material is limited by the possible presence of low strength or high expansion materials (bitumen, gypsum, organic matter, etc.), and there may be detrimental aesthetic consequences for brick manufacture. The composition of C&D waste is dependent on the material content of the building under construction/demolition, rarely estimated in detail.[37] The CaO content of construction waste varies from 10 to 20%.[37,44,48,49] Cement based products form the largest component of the waste stream at 35.5%[37,43,46] but could reach 67%,[44] highlighting the heterogeneous nature of
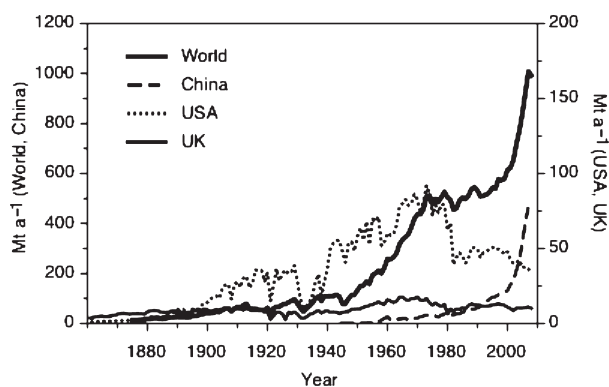
Figure 2. Historic production of pig iron.

Figure 3. Historic production of coal.

the material, and giving a range of CaO contents. Combining the production statistics (by proxy) with the typical chemical compositional information, it is estimated that construction and demolition waste has a carbon capture potential of 9−37 and 24−100 MtC a^{-1}, respectively.

5. IRON AND STEEL MAKING SLAG

Three Mt of blast furnace slag and 1 Mt of steel slag are produced annually in the UK.[50,51] Iron and silicate minerals within iron ore react with $CaCO_3$ and $CaMg(CO_3)_2$ (from limestone and dolomite) in a blast furnace at 1300−1600 °C to form pig iron and slag. The quantity of slag depends on ore purity and is usually between 250-1200 kg per tonne of produced iron for ore purities between 20 and 65% Fe.[52] Blast furnace slag presently is not classified as a waste and is widely reused as secondary aggregate in concrete, as fill in road construction,[53] or for soil stabilization.[51]

Steel is manufactured by refining pig iron or scrap steel using oxygen and $CaCO_3/CaMg(CO_3)_2$ fluxes in a basic oxygen furnace.[52] The resulting slag contains free lime (CaO) and is 'weathered' prior to use. However, in the UK only 10% of steel slag is reused;[51] 90% is stockpiled or disposed of in landfill.

The chemical composition of both slags varies considerably, typically containing 38−46% CaO and 6−12% MgO.[51,54] Consequently, the carbon capture potential for slag is between 99 and 135 kg C t^{-1}.

In the UK, slag production increased with the development of the iron and steel industry in the early nineteenth century. Pig iron output rose from about 1.5 Mt a^{-1} (1840s) to almost 18 Mt a^{-1} in the 1960s.[55] Steel gained increasing importance in the 1860s; previously it had not been produced on a large scale. In the latter half of the century steel manufacture quickly became the single largest use of UK iron.[56] In the latter half of the 19th century the USA became the largest producer of iron and steel (15 Mt a^{-1}) rising to around 100 Mt a^{-1} presently.[57] In 1992 China became the largest manufacturer of iron (and steel in 1996) producing around 970 Mt a^{-1} today (500 Mt steel and 470 Mt iron in 2008;[58] Figure 2).

Using these production statistics and the iron/steel to slag ratios discussed above, it is estimated that global slag production is 250−300 Mt a^{-1} from iron manufacture and between 130 and 200 Mt a^{-1} from steel production. Overall, between 12,200 and 15,900 Mt of slag have been created since the 1870s, much, particularly from pig iron, being sold or reused. In the US, recorded sales of slag since 2001 vary between 75 and 100% of production,[59] and slag from old stockpiles is often extracted and
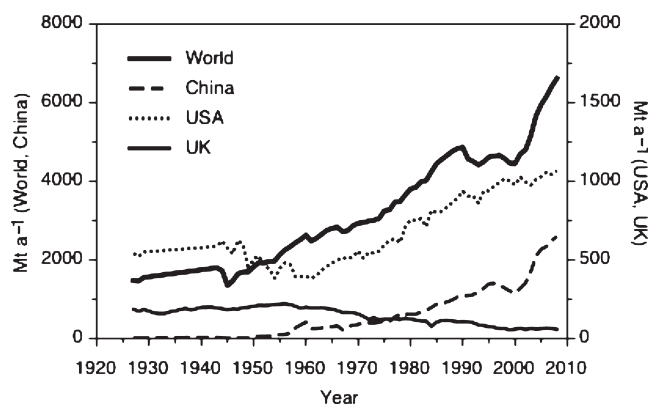
sold.[27] Assuming the majority of steel slag and around 20% of iron slag remains stockpiled, it is estimated that 5.8−8.3 Gt of slag have been stockpiled, spread on land, or disposed of in landfill globally since the mid 19th century, with a total carbon capture potential of 0.5−1.1 GtC (based on a CaO and MgO content of 38−46% and 6−12% respectively). Furthermore, current production of slag has a maximum carbon capture potential of 44 −59 Mt C a^{-1}.

Iron and steel slag readily weathers under ambient environmental conditions, initially involving dissolution of loosely bound free lime (or portlandite). Further weathering results in the breakdown of complex silicate minerals (including rankinite, larnite, and akermanite — see Table 1) and glasses.[60] Investigation of historic slag deposits demonstrates the presence of carbonate minerals in the soil,[13] both diffuse and as distinct concretions. Carbon isotope analysis has demonstrated that these carbonate minerals contain, and so sequester, C from an atmospheric source. Published descriptions of the weathering of slag[61] report high (>11) pH drainage waters containing substantial quantities of Mg, Ca, Fe, Sr, and dissolved Si.

6. FUEL ASH AND COMBUSTION PRODUCTS

Residual combustion products (fuel ash, bottom ash, boiler slag, etc.) are produced in coal fired power stations; UK annual production is approximately 6 Mt.[62] Other ashes potentially suitable for carbonation include biomass ash, municipal solid waste incineration ash, paper sludge incineration ash,[63] together amounting to about 10^2 Kt a^{-1}. Carbonation of ashes may form part of a waste stabilization process undertaken to limit environmental impacts.[63]

A third of the UK's electricity is produced from the annual combustion of approximately 60 Mt of coal.[64] In the US, about half of the country's electricity is generated using coal (around 1 Gt a^{-1}).[65] Rapid growth in the power industry in the 1920s and 1930s came at a time when many countries, such as Japan and the USSR, were industrializing rapidly. This industrialization required advanced electricity distribution networks, and so many countries developed their electricity generating capacity during this period. At this time coal was the only raw material from which electricity could be generated economically, and world consumption of coal rose dramatically.[65]

The second half of the twentieth century has seen increased demand for electricity in response to economic development, especially in India and China.[65] Compared with alternative fuels such as oil and nuclear, coal is attractive because of its abundance and low cost. Some of the world's largest electricity consumers such as the US, China, and India have substantial reserves of coal,

Table 2. Carbon Capture Potential of Silicate Minerals

material	approximate divalent cation content	global production (Mt a^{-1})	carbon capture potential (MtC a^{-1})	historically produced (Mt)
fines from aggregate production	3% CaO 3% MgO nominal	3300	51	unknown
mine waste	unknown	2000−6500	unknown	unknown
cement kiln dust	65% CaO	420−568	59−79	9000−12,000 (since 1926)
construction waste	14% CaO	294−1239	9−37	maximum limited by cement production around 60 Gt
demolition waste	10% CaO	1106−4661	24−100	
blast furnace slag	38% CaO and 12% MgO	250−300	29−35	7900−9500 (since 1875 - 80% potentially reused)
steel making slag	45% CaO and 7% MgO	130−200	15−23	4200−6400 (since 1875)
lignite ash	20% CaO 1% MgO	32−61	2−3	7600−14,600 (since 1927)
anthracite ash	3% CaO 1% MgO	20−46	<1	
bituminous ash	3% CaO 1% MgO	146−276	1−3	
total			190−332	

and thus the global increase in coal consumption for electricity generation is likely to continue. A total of approximately 6.5 Gt of coal are produced annually, and 257 Gt have been produced since 1927[58] (Figure 3).

Typically, the CaO content of coal and lignite fuel ashes and combustion products ranges between 1 and 10%, but it can reach 20−30%.[66−70] Assuming an ash to fuel ratio of 70 kg t^{-1}, (based on coal to ash production in the US[71]) but recognizing variability in ash content,[72] the global production of ash may be around 200−400 Mt a^{-1}, derived from bituminous coal (73.5%), lignite (16.2%), and anthracite (10.3%).[31]

Assuming a CaO content of 10%, fuel ash has a carbon capture potential of 3−6 Mt C a^{-1}. It is estimated that between 4.2 and 8.3 Gt of ash have been produced since 1980.

7. CARBONATION POTENTIAL AND STRATEGIES

Globally, the total carbonation potential of waste silicate minerals is 190−332 Mt C a^{-1} excluding carbonation of historically produced material from stockpiles (Table 2). This is comparable in potential to other carbon capture and storage technologies and is equivalent to 20−30% of a 'stabilization wedge' needed by 2050 to prevent atmospheric CO_2 exceeding 500 ppm.[73] The maximum carbon capture potential of materials historically produced and stockpiled is unknown but could be of the order of 10^3 Mt C. Some of this material may have carbonated naturally, but a substantial quantity may remain unreacted.

In Table 2, the maximum carbonation potential is calculated by assuming that all of the available calcium and/or magnesium in the material is converted to carbonate ($CaCO_3$, $MgCO_3$; 1 mol of cations captures 1 mol of carbon), which is unlikely in practice. Depending on the material, carbonation method and temperature, and pretreatment processes, reported carbonation efficiencies vary from 10 to 60% for untreated natural silicates to 40−90% with heating or mechanical pretreatment.[22] Carbonation efficiency of artificial silicates is generally reported >70%

[e.g., refs 7 and 9] without pretreatment. A full review of this technology is beyond the scope of this paper.

The production of slag and cement in a blast furnace and rotary kiln provides a point source of CO_2 which could be captured and stored using conventional CCS technology. The material produced would contain a negative carbon footprint if it was subsequently carbonated (similar, in part, to ocean alkalinity modification[74]). Otherwise, the carbonation of waste silicate minerals is only partially closing the loop on the CO_2 emitted during manufacture, at best compensating for decarbonation reactions and not emissions associated with the combustion of fossil fuels.

This paper provides justification for additional work to more accurately assess the carbonation potential and efficiency of annually produced or stockpiled artificial silicate minerals. Priorities for additional research include the following

- Collation of data from silicate producers (cement kilns, iron and steel works, coal fired power stations, igneous rock quarries, mines, etc.) to assess the annual production of silicates as a byproduct of human activity. Representative chemical and mineralogical analysis is required to determine maximum carbonation potential.
- Additional comparative research is required on all mineral carbonation techniques (including injection into underground rock formations and carbonation in the soil) in order to develop appropriate strategies for individual silicate sources.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. The production statistics used in this paper are available as .xls files. This material is available free of charge via the Internet at http://pubs.acs.org.

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