

An evaluation of ex situ, industrial-scale, aqueous CO₂ mineralization

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ARTICLE INFO

Article history:

Received 17 May 2011

Received in revised form 7 September 2011

Accepted 26 September 2011

Available online 20 October 2011

Keywords:

Mineral carbonation

CO₂ mineralization

Permanent carbon sequestration

Beneficial use of CO₂

ABSTRACT

It is essential to objectively evaluate the many CO₂ mitigation strategies in order to prioritize investments of capital and research. Aqueous CO₂ mineralization is one potential strategy to permanently sequester CO₂, without the associated long-term monitoring and liability issues. Investigators are studying and optimizing aqueous CO₂ mineralization for the production of inorganic carbonates and are scaling up some of these processes. This paper adopts a life-cycle approach toward the evaluation of energy requirements and discusses other potential barriers for three CO₂ mineralization pathways: industrial caustics, naturally occurring minerals, and industrial wastes. This analysis is based on CO₂ capture from a 1 GW coal-fired power plant using one of the three mineral mineralization pathways. The investigators utilize consistent system boundaries and process-modeling assumptions, standard engineering calculations to estimate energy requirements, and publicly available data for upstream energy requirements and for the production of products/co-products. The results suggest that some industrial wastes show promise for CO₂ mineralization, but their availability is limited. The other pathways currently have large energy penalties and face other significant barriers, such as the production of large quantities of potentially hazardous waste and large-scale mining.

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1. Introduction

The United States (US) produced 5839 million tonnes CO₂ in 2008 (EIA, 2009), and carbon capture and storage (CCS) is one of several proposed strategies for reducing US and world greenhouse gas emissions (EPRI, 2009). It entails capturing a relatively pure CO₂ stream from an industrial source, such as a fossil-fuel power plant, transporting it to a storage location, and the long-term storage of the CO₂, in locations such as deep geological formations (IPCC, 2005). CCS offers the potential for continued use of fossil fuels with reduced CO₂ emissions, and a variety of CCS demonstration projects are currently underway (Herzog, 2011). However, the sequestration of CO₂ in geological formations faces a number of challenges including public perception, the potential for CO₂ escape, the requirement for long-term site monitoring and liability (Wilson et al., 2008; Herzog, 2011; IPCC, 2005). Consequently, aqueous mineral carbonation has been proposed as a strategy to permanently sequester CO₂ and even to potentially produce beneficial products, without the associated long-term monitoring and liability issues.

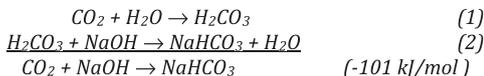
Several research groups are studying and optimizing aqueous-phase CO₂ mineralization for the production of inorganic mineral carbonates and are beginning to scale up the some of these proposed processes (Gerdemann et al., 2007; Reddy et al., 2010; EPRI, 2007). Some of these results have attracted industry and government investment. For example, the US DOE recently invested \$119 million to test innovative concepts for the beneficial use of CO₂ including inorganic mineral carbonates, building materials, and soil amendments (US DOE, 2010a,b). Zevenhoven et al. (2006) discuss the use of anthropogenic CO₂ emissions as resources for the production of mineral carbonates and other beneficial products, and summarize the world markets for a number of inorganic carbonates.

Given the variety of options for mitigating CO₂ emissions, the need for rapid action to address global climate change, and limited financial resources, it is essential to objectively evaluate these options and to prioritize investment strategies. One challenge in evaluating CO₂ mineralization is that few studies report mass and energy balances or discuss potentially significant environmental impacts, such as large-scale mining disposal of the resulting solid material (CSLF, 2010). This paper takes a step toward this evaluation and presents preliminary bounds for an energy balance for three CO₂ mineralization pathways: industrial caustics, naturally occurring minerals, and industrial wastes. It attempts to apply consistent system boundaries and to fairly evaluate process products and co-products for an industrial-scale CO₂ mineralization process.

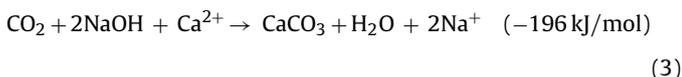
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1.1. Industrial caustics

Two CO₂ mineralization processes have recently been proposed that are based on the industrial caustic sodium hydroxide. One yields sodium bicarbonate (EPRI, 2007) and is given by reactions (1) and (2), where the $\Delta H_{\text{reaction}}$ at standard temperature and pressure is presented in parentheses.

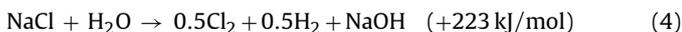


The other involves a brine solution containing calcium and/or magnesium ions and yields calcium or magnesium carbonates as shown in the following reaction (Constantz, 2009).



In order for reaction (3) to proceed to an appreciable extent, the pH must be greater than 9 in a brine solution (Druckemiller and Maroto-Valer, 2005).

Reactions (1)–(3) are exothermic and proceed rapidly to completion. However, they both rely on sodium hydroxide, which is produced by the energy-intensive chlor-alkali reaction process:



Because these mineralization processes are being commercialized, publicly available material and energy data are limited. However, this pathway can be evaluated using publicly available life-cycle inventory data and some estimates of theoretical minimum work requirements.

1.2. Naturally occurring minerals

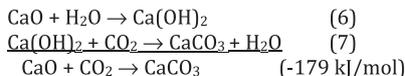
Naturally occurring mineral silicates are another pathway to CO₂ mineralization, as initially discussed by Seifritz (1990), Dunsmore (1992), and Lackner et al. (1995). Olivine, serpentine, and wollastonite are naturally occurring magnesium silicate compounds that react exothermically with CO₂ to form carbonates. These minerals are available in sufficient quantities to allow for CO₂ mineralization of current fossil-fuel reserves (Zevenhoven et al., 2006; IPCC, 2005), and these ores are inexpensive, approximately \$20/tonne (Gerdemann et al., 2007). One example of this reaction (for a pure form of olivine, fosterite) is given by:



Although the reaction of CO₂ with magnesium silicates is exothermic, it occurs slowly in nature, over a period of thousands of years. In order to identify more favorable kinetic conditions, Gerdemann et al. (2007) performed over 700 kinetic studies of mineral carbonation of olivine, serpentine, and wollastonite at varying temperatures, partial pressures of CO₂, solution chemistries, particle sizes, and pretreatment conditions. For the most promising conditions, they performed a feasibility study using ASPEN to estimate capital and operating costs. Huijgen et al. (2006) also performed process modeling for mineral carbonation of wollastonite (CaSiO₃) to estimate energy requirements and net CO₂ reduction. These studies concluded that mineral carbonation with naturally occurring minerals can be part of an integrated strategy for carbon sequestration.

1.3. Industrial wastes that contain reactive oxides

A number of industrial wastes contain significant fractions of reactive metal oxides, in particular CaO and MgO, that will react to form mineral carbonates as in the following example:



These reactions of CO₂ with metal oxides are exothermic. Consequently, some industrial wastes have been proposed for their potential in CO₂ mineralization including coal fly ash (Soong et al., 2006; Fernández Bertos et al., 2004; Montes-Hernandez et al., 2009; Reddy et al., 2010), steel/iron/blast furnace slag (Huijgen et al., 2006; Stolaroff et al., 2005; Eloneva et al., 2008), waste cement (Stolaroff et al., 2005; Iizuka et al., 2004), asbestos mine tailings, electrical arc furnace waste, cement kiln dust (Huntzinger et al., 2009; Gunning et al., 2010), lime kiln dust, paper ash, bauxite residue (Sahu et al., 2010; Bonenfant et al., 2008; US DOE, 2010c) and others. Gunning et al. (2010) studied 10 sources of industrial waste for suitability for CO₂ mineralization. The majority of these studies were performed at the laboratory scale, although Reddy et al. (2010) studied mineral carbonization of fly ash at the pilot scale. Fernández Bertos et al. (2004) and Gunning et al. (2010) found that the most reactive wastes tended to be those containing high concentrations of CaO, MgO, Na₂O, and K₂O. The theoretical maximum CO₂ uptake capacity of a waste can be estimated from the chemical composition of the waste using the Steinour formula (Steinour, 1959), in which the concentration of each species of interest is entered as a weight percent.

$$\begin{aligned} \text{CO}_2(\%) = & 0.785(\text{CaO}-0.7\text{SO}_3) + 1.091\text{MgO} \\ & + 2.09\text{Na}_2\text{O} + 0.93 \text{K}_2\text{O} \end{aligned} \quad (8)$$

2. Materials and methods

The following analysis is intended to provide bounds for energy use and is based on publicly available data. The basis for this evaluation is a theoretical 1 GW coal-fired power plant emitting 8×10^6 tonne CO₂/yr, which is captured by one of the three mineral carbonation pathways. The coal for this theoretical plant has a heating value of 30,000 kJ/kg, an ash content of 10% and a carbon content of 72.5%. The plant is 35% efficient, which is slightly higher than the 33% average efficiency of coal-fired power plants in the US (EIA, 2010). Several of the proposed pathways produce potentially valuable products/co-products, and this analysis includes an energy value for the products and co-products.

The evaluation includes major energy-consuming processes for each pathway, such as separation of CO₂ from the power plant flue gas, pumping of the liquids and slurries, compressors, mixers, and heaters. The blower energy requirement is not included because it is insignificant compared to other processes. For processes that are common across the three pathways, Table 1 summarizes assumptions associated with the low and high estimates. Assumptions that are only relevant to a single pathway are discussed in the each of the following sections. This analysis is a gate-to-gate estimation; it begins with flue gas entering the process and continues through the production of products or materials for disposal. It does not include the energy associated with the operation of the coal-fired power plant, mining of coal, the construction of the power or mineral carbonation plants, or the transportation of products.

Table 1

Assumptions used to obtain energy requirements for high and low cases that are common to more than one pathway.

Unit	Low	High
CO ₂ separation	16.7% energy penalty ^a	16.7% energy penalty ^a
Pump	80% efficiency	80% efficiency
Compressor	Isothermal, 80% efficiency	Adiabatic, 80% efficiency
Mixing	10 rpm, $N_p = 0.31$, 80% efficiency, impeller diameter 1/4 of reactor dimension, assuming a cube	30 rpm, $N_p = 1.27$, 80% efficiency, impeller diameter 1/4 of reactor dimension, assuming a cube
Heating	80% efficiency	80% efficiency

N_p : Power number of the impeller.

^a Katzer et al. (2007), assumes a sub-critical pulverized coal power plant using amine scrubbing for 90% CO₂ separation.

2.1. Industrial caustics and brine

Fig. 1 illustrates a simplified flow diagram of a theoretical industrial caustic pathway for the production of both calcium/magnesium carbonates and sodium bicarbonate. It shows the processes, inputs, products, and system boundaries that are included in the analysis. The analysis assumes complete conversion of the CO₂ to either calcium/magnesium carbonates or sodium bicarbonate. This pathway does not require the separation of CO₂ from flue gas.

One challenge for the evaluation of this pathway is the allocation of energy requirements between sodium hydroxide and the three potential co-products from the chlor-alkali process: hydrogen, chlorine, and hydrochloric acid. This can be done on a monetary value basis (Guinée, 2002). Because of the massive scale of CO₂ emissions, the adoption of this process for even one large coal-fired power plant could drastically reduce the monetary value of chlorine and hydrochloric acid. The production of 1 mol of sodium bicarbonate requires 1 mol of sodium hydroxide, and the production of 1 mol of calcium/magnesium carbonates requires 2 mol of sodium hydroxide. This results in the production ½–1 mol of chlorine gas (Cl₂) (or 1–2 mol of hydrochloric acid) for each mole of CO₂ mineralized. Consequently, the CO₂ emissions from a 1 GW coal-fired plant (8×10^6 tonne CO₂/yr) would result in chlorine production equaling 12–24% of world Cl₂ demand (World Chlorine Council, 2011). Widespread adoption of this pathway would generate vast quantities of chlorine or hydrochloric acid wastes.

The lower bound of energy required to produce sodium hydroxide is based on a Gibbs free energy minimum work calculation and the allocation of energy between sodium hydroxide, chlorine, hydrogen, and hydrochloric acid (see Supplementary data, Sections S.1 and S.2, for details). Briefly, the production of sodium hydroxide to mineralize all of the CO₂ from the theoretical 1 GW plant requires a minimum of 2.4 GW of energy. This energy can be allocated to the two products of value (sodium hydroxide and hydrogen). One kg of product from the chlor-alkali process contains approximately 0.523 kg sodium hydroxide, 0.464 kg chlorine gas, and 0.0131 kg hydrogen gas. Sodium hydroxide has a value of approximately \$440/tonne (ICIS, 2011), and hydrogen has a value of approximately \$18,500/tonne (National Hydrogen Association, 2010). Allocating the minimum work to sodium hydroxide yields 1.17 GW of energy required for the theoretical 1 GW power plant.

Alternatively, the hydrogen and chlorine gas can react to form hydrochloric acid and produce energy:



On the 1 GW basis, this reaction releases 1.5 GW and results in a net minimum energy requirement of 0.9 GW (details in Supplementary data, Section S.1). Hydrochloric acid is a waste and assumed to have

no value. In fact treatment and disposal of this waste would incur a cost.

For sodium hydroxide production, the upper bound of the life-cycle energy requirement is 6.9 MJ/kg chlor-alkali product (US DOE, 2011a), and this was apportioned on the same mass-adjusted monetary value basis as described for the minimum work calculation (see Supplementary data, Section S.2). This results in an upper-bound energy requirement of 3.4 MJ/kg sodium hydroxide (1.5 GW for the 1 GW power plant).

The same procedure is applied to estimate the energy requirements for the production of sodium bicarbonate to produce sodium hydroxide (Supplementary data, Section S.4).

The brine flowrate is another key factor in the evaluation of this pathway. It affects the energy requirements for mixing and pumping as well as the size of process equipment. The required brine flowrate is based on the concentration of alkali-earth ions (Ca²⁺ and Mg²⁺) in Dead Sea brine (4.59 and 1.76 wt%, respectively, low-energy estimate, Ma'or et al., 2006) and in seawater (0.04 and 0.13 wt%, respectively, high-energy estimate, Snoeyink and Jenkins, 1980). All of the calcium and magnesium ions are assumed to react to form products. The reactor volume is estimated using a range of liquid residence times from 5 to 30 min. The pumping requirement is based on head losses equivalent to 10 m (low) and 100 m (high).

Drying of the carbonate product is assumed to utilize low-grade heat from the power plant and to require no additional energy. The energy value for calcium/magnesium carbonates produced via this pathway is estimated at 0.073 MJ/kg based on the energy requirements for limestone mining, crushing and transportation (US DOE, 2011b).

Drying of the sodium bicarbonate product is also assumed to utilize low-grade heat from the power plant. In order to assess the value of the sodium bicarbonate product, one can consider its manufacturing process. Sodium bicarbonate is commonly produced in conjunction with soda ash. In the US, soda ash and sodium bicarbonate are typically produced from natural sources, and in Europe and Asia the Solvay process is typically employed. The lower-bound energy value for this product is estimated using a minimum work calculation for sodium bicarbonate production by the Solvay process (Supplementary data, Section S.5) to be 0.225 MJ/kg (58 MW on the 1 GW plant basis). The upper-bound energy value for the sodium bicarbonate product is estimated from the average energy required to mine and purify potash, soda ash and borate (0.33 MJ/kg, US DOE (2002) and 85 MW on a 1 GW plant basis). The world market for sodium bicarbonate is approximately 2.5 million tonnes/yr (Eurasian Chemical Market, 2011), and its current applications include cleaning productions, animal feed, cooking, pharmaceuticals, specialty chemicals, and fire suppression (SRI, 2009). The theoretical 1 GW power plant would produce of 6.4 million tonnes/yr of sodium bicarbonate, which would exceed current world demand. The adoption of this process for one or more power plants would likely reduce the world price for sodium bicarbonate, and this product is assumed to be a waste with no value. However, it is possible that additional or expanded beneficial uses for this product could be identified, and Section S.5 illustrates how the energy value for sodium bicarbonate is estimated.

2.2. Naturally occurring minerals

Fig. 2 shows a simplified process diagram for this pathway. In order to achieve reasonable reaction rates and conversions, this pathway requires the separation of CO₂ from a flue gas stream as input and a reaction at elevated temperature and pressure. Huijgen et al. (2006) and Gerdemann et al. (2007) estimate process energy requirements for mineral carbonization with wollastonite and olivine, two of the most promising mineral silicate candidates. They assume that the mining and product disposition occurs onsite.

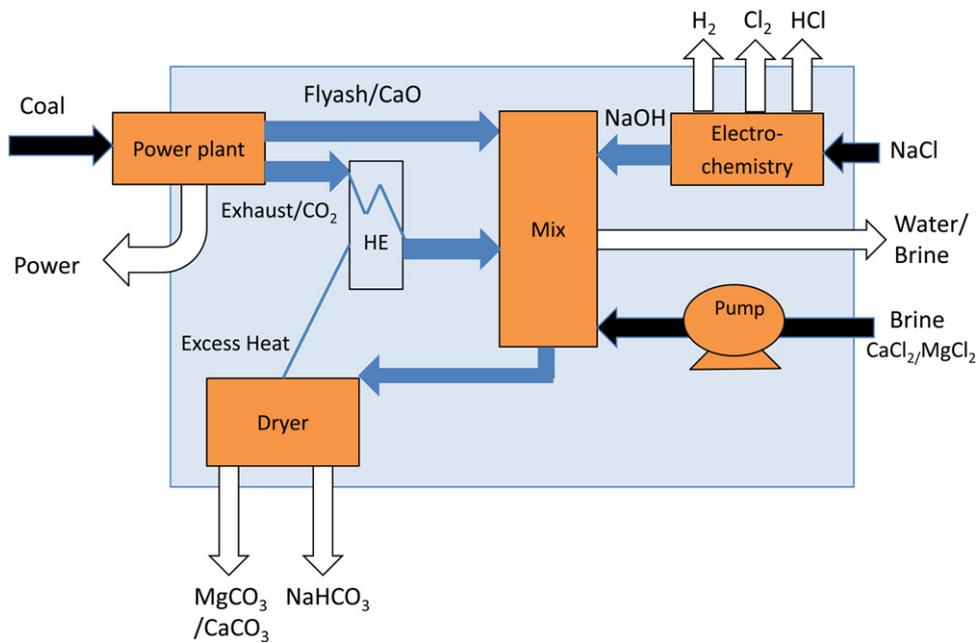


Fig. 1. Simplified process flow diagram for the production of Ca/MgCO₃ or NaHCO₃ from industrial caustics. It shows the processes evaluated (noted as orange boxes), material inputs (black arrows), products (white arrows) and system boundaries that are included in the analysis. HE: heat exchanger. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 2
Reaction conditions based on experimental studies.^{a,b}

	CaSiO ₃ (wt%)	Mg ₂ SiO ₄ (wt%)	Temperature (°C)	L/S	P (bar)	Residence time	Carb (%)	Tonne ore/tonne CO ₂ seq
Olivine		100	185	3.33	152	2 h	100	1.8
Wollastonite	84.4		200	2.5	35.5	2–30 min	75	4.5

L/S: liquid to solid ratio on a mass basis.

^a Huijgen et al. (2006).

^b Gerdemann et al. (2007).

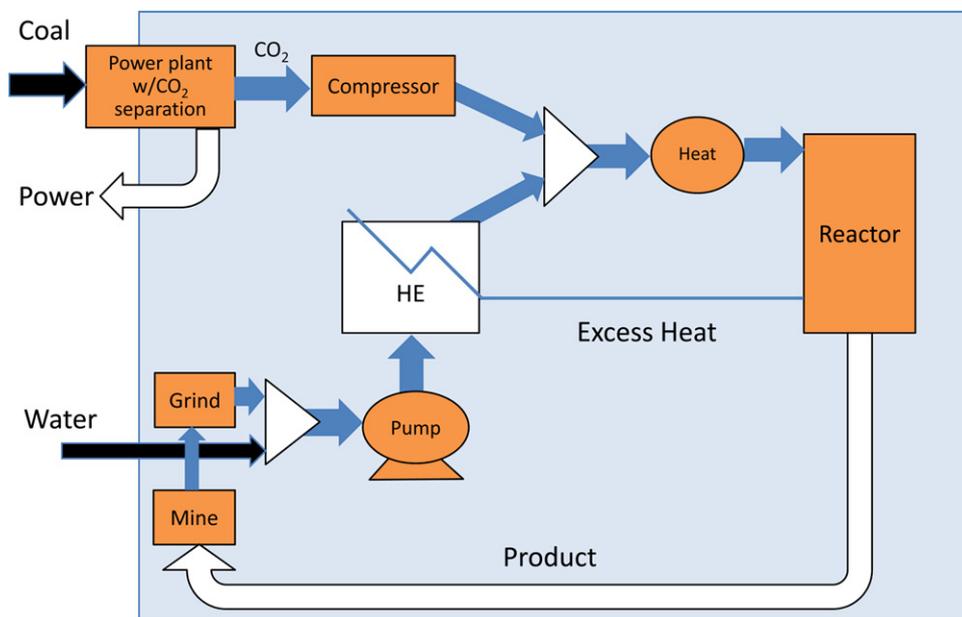


Fig. 2. Simplified process flow diagram showing mineral carbonation with naturally occurring minerals (based on Huijgen et al., 2006). It shows the processes evaluated (noted as orange boxes), material inputs (black arrows) products (white arrows) and system boundaries that are included in the analysis. HE: heat exchanger. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Their estimates include crushing/grinding, pumping, compression, heating, and other ancillary processes. Both studies identify grinding as an important process step and a major contributor to the overall energy requirement for this pathway. Their analysis did not include mining of the mineral, transportation, or CO₂ separation. Table 2 shows the key conditions of their theoretical mineral carbonation processes.

For the same process conditions, our estimates of energy requirements for compression, pumping and heating agree within 10% of Huijgen's results (Huijgen et al., 2006). The wollastonite energy requirements are then adjusted to achieve 100% carbonation, assuming that additional material will be pumped, heated, and reacted, and the compressed gas is recycled with minimal additional energy required. The olivine process energy requirements are estimated using the same assumptions. For both processes, we assume that excess energy from the power plant or the mineralization system is used to heat the slurry to 185 °C. Achieving higher temperatures, requires supplemental heat. For the wollastonite process, Huijgen's estimates include energy recovery from the carbonation step (Eq. (5)), but it is unclear whether this energy could be easily recovered (Huijgen et al., 2006).

To facilitate comparison of this pathway with other pathways, we included two potentially significant process steps, CO₂ separation and mining, within the system boundaries (Fig. 2). We assume a uniform energy penalty of 167 MW for separation of CO₂ from the flue gas (Katzner et al., 2007). For mining energy requirements, the lower estimate is based on limestone mining 12.3 kWh/tonne ore mined (79.7–199 MJ/tonne CO₂ sequestered), and the upper estimate is based on copper mining of 22.2 kWh/tonne ore mined (144–360 MJ/tonne CO₂ sequestered) (US DOE, 2002).

2.3. Industrial wastes

Although numerous industrial wastes have been proposed for CO₂ mineralization, most have been investigated only at the laboratory scale (i.e., Baciocchi et al., 2010; Fernández Bertos et al., 2004; Gunning et al., 2010; Huntzinger et al., 2009; Montes-Hernandez et al., 2009). Table 3 presents annual US production of several wastes that contain calcium and magnesium oxides and their concentration ranges. This list is not exhaustive but provides an indication of the scale of potentially useful wastes in the US. This analysis focuses on two wastes, fly ash and iron slag, for which process or pilot-scale data are available. For both wastes, we assumed that the carbonated mineral is disposed on site and does not require transportation. Table 4 provides the process conditions. The energy requirements are adjusted to 100% carbonation for comparison purposes.

2.3.1. Iron slag

The conditions are based on the work of Huijgen et al. (2006) who evaluated the mineral carbonation of steel slag experimentally and via ASPEN process modeling. The slag contains 56.8% CaSiO₃, 7.7% CaCO₃, and 35.5% FeO. Their process requires grinding of the slag to an average particle size <38 μm, mixing the slag with water (5:1 or 2:1, L/S, liquid to solid ratio on a mass basis), preheating the mixture, and pumping the mixture into a heated pressure vessel (35.5 bar and 200 °C). The difference between the low and high cases is a L/S ratio of 2:1 and 5:1, respectively. This process requires CO₂ separation.

2.3.2. Fly ash

The estimates are based upon the recent pilot study of CO₂ mineralization using a slipstream of the flue gas from the Jim Bridger power plant, which contains 12–13.6% CO₂ (Reddy et al., 2010). The flue gas passes through a 3.7 m high fluidized-bed reactor containing fly ash from the plant; the reactor operates at 60 °C and at a gas

flowrate of 0.142 m³/s. The fly ash contains 3.85% MgO and 7.5% CaO. The authors report that after 1.5–2 h of reaction, the mineralization capacity of the ash is not fully depleted. Our estimate did not include energy for solids handling.

3. Results

Table 5 summarizes the range of energy requirements for each pathway for CO₂ capture from a theoretical 1 GW power plant. It does not include energy recovery from the carbonation reaction.

3.1. Industrial caustics and brine

The net energy penalty for producing the sodium bicarbonate product via the industrial caustic pathway ranges from 45% to 78%. The main difference between the lower and upper bound energy requirement is the sodium hydroxide production estimate, with the lower estimate based on the minimum work calculation (Supplementary data, Section S.1) and the upper estimate based on life-cycle data for sodium hydroxide production (US DOE, 2011a).

The production of calcium/magnesium carbonates via the industrial caustic pathway has a large energy penalty, greater than 90% using a minimum-work calculation for sodium hydroxide production and a brine concentration corresponding to that in the Dead Sea. The upper-bound energy requirement bound is based on publicly available life-cycle energy requirements for sodium hydroxide production (US DOE, 2011a) and brine concentration corresponding to that in seawater.

3.2. Naturally occurring mineral pathway

Table 5 shows energy requirements for two of the more promising magnesium silicates for mineral carbonation, olivine (based on Gerdemann et al., 2007) and wollastonite (based on Huijgen et al., 2006). Both of these pathways require CO₂ separation, mining and grinding of the ore, reaction at elevated temperature and pressure, and relatively long reaction times. This results in an energy penalty of 55% (low estimate for olivine) to greater than 100% (wollastonite).

3.3. Industrial wastes

The two wastes included in this analysis use quite different process to achieve mineralization and illustrate the wide range of energy penalties. The Fe slag is ground and reacts with CO₂, which has been separated from flue gas, at elevated temperatures and pressures (Huijgen et al., 2006). The process is designed to achieve 67% carbonation in 2 h. However, when one includes the energy required to mine the ore and to separate CO₂ from the power plant's flue gas, this process would have more than a 100% energy penalty.

The CO₂ mineralization process with fly ash described by Reddy et al. (2010) employs a fluidized bed, flue gas, and operates at lower temperatures and near ambient pressure. This process achieves approximately 30% carbonation in a few seconds. Its energy penalty is the most favorable among those evaluated, ranging from 9 to 22%.

4. Discussion

4.1. Industrial caustics and brine

The energy balance for the production of sodium bicarbonate is more favorable (45–78% penalty) than that for the production of calcium or magnesium carbonates (90–100% penalty), primarily because sodium bicarbonate requires half the amount of sodium hydroxide (or other industrial caustics) compared to calcium or

Table 3
Annual production of selected US wastes that contain reactive oxides.

Waste	US production (tonne/yr)	Composition range (%)	Composition average (%)	Average (tonne/yr) ^a	Average plant (tonne/yr) ^b
Lime kiln dust	3.0 × 10 ^{6c}				
CaO			50 ^d	1.5 × 10 ^{6d}	4.0 × 10 ⁴
Fly ash	1.2 × 10 ^{8e}				
CaO		1–40 ^f	16 ^g	1.9 × 10 ⁷	2.4 × 10 ⁴
Cement kiln dust	1.4 × 10 ^{7h}				
CaO		11–45 ⁱ	28	3.8 × 10 ^{6j}	2.8 × 10 ⁴
MgO		0.4–2 ⁱ	1	1.6 × 10 ^{5j}	1.2 × 10 ³
Red mud ^k	7.8 × 10 ^{6k}				
CaO		2–8 ^{k,l}	5	3.9 × 10 ^{5k}	7.8 × 10 ⁴
Na ₂ O			6	4.7 × 10 ^{5k}	9.4 × 10 ⁴
Steel slag	8.1 × 10 ^{6m}				
CaO		38–42 ^{n,o}	40	3.2 × 10 ^{6o}	2.8 × 10 ⁴
MgO		8–9 ^{n,o}	9	6.9 × 10 ^{5o}	5.9 × 10 ³
Iron slag	9.1 × 10 ^{6p}				
CaO		32–52 ^{n,p}	42	3.8 × 10 ⁶	2.9 × 10 ⁴
MgO		5–15 ^{n,p}	10	7.1 × 10 ⁵	5.5 × 10 ³

^a Average composition multiplied by the US production.^b Average US tonne/yr of reactive component divided by the number of plants in the US.^c Schlag and Funada (2009).^d Miller and Callaghan (2004).^e American Coal Ash Association (2008).^f National Research Council (2006).^g Weighted average of concentration range of lignite, bituminous, and subbituminous coal production (EIA, 2011).^h US EPA (2008).ⁱ US EPA (1993).^j Portland Cement Association (2009).^k Red mud is also known as bauxite residue, USGS (2009a).^l Red Mud Project (2011).^m National Slag Association (2007).ⁿ Joshi and Arenicz (2011).^o USGS (2009b).^p Lewis (1992).**Table 4**
Reaction conditions based on experimental studies.^{a,b}

	Temperature (°C)	L/S	P (bar)	Residence time	Carb (%)	Tonne/tonne CO ₂ seq
Fe slag	200	2.5	35.5	2–30 min	67	6.8
Fly ash	60	–	1.1	2–10 s	30	4.8

L/S: Liquid to solid ratio on a mass basis.

^a Huijgen et al. (2006).^b Reddy et al. (2010).

magnesium carbonates. The production of sodium hydroxide is the main contributor to the energy penalty for this pathway. Eloneva et al. (2008) also identify the use of sodium hydroxide and the energy associated with its production as a key factor in an unacceptable energy penalty for a CO₂ mineralization process involving blast-furnace slag. Their process entails first leaching calcium from the slag using acetic acid and then adding sodium hydroxide to the

solution to achieve a high enough pH to precipitate the mineral carbonates. It requires 3.5 kg of sodium hydroxide for every kg of CO₂ sequestered (or 3.85 mol NaOH per mol of CO₂ sequestered). It is possible that a naturally occurring alkaline brine could be available that would reduce the need for sodium hydroxide and the energy required for this pathway. However, naturally occurring brines with a pH above 9 are rare, and a pH above 9 is necessary

Table 5
Energy requirements in MW for mineral carbonation of 100% of the CO₂ emitted from a 1 GW power plant via several pathways. Values denoted with a positive (+) sign indicate energy credits.

	NaOH (NaHCO ₃)	NaOH (Ca/MgCO ₃)	Olivine	Wollastonite	Fe slag	Fly ash
<i>Processes</i>						
Mining	–	–	18–32	45–81	–	–
CO ₂ separation	–	–	167	167	167	–
NaOH prod	450–775	900–1550	–	–	–	–
Compress	–	–	97–217	86–128	86–129	3–4
Fluid bed	–	–	–	–	–	89–216
Pumping	4	4–309	52 ^a	21–43	40–65	–
Mixing	0–5	0–10	–	–	–	–
Grinding	–	–	219	328	276	–
Heating	–	–	–	385–1040	529–1428	–
<i>Energy penalty</i>	454–780	904–1870	553–687	1032–1659	1098–2065	92–220
<i>Products</i>	0	+1	–	–	–	–

^a No range is shown because pumping energy primarily depends on pressure and L/S, and only one L/S is evaluated.

for reaction (3) to proceed to an appreciable extent. For example, a survey of over 2.5 million water samples available from the United States Geological Survey (USGS, 2011) reveals less than 1% have a pH of 9 or greater.

It is also possible that the production of calcium or magnesium carbonates could yield materials with cementitious properties (Fialka, 2010; Constantz et al., 2010), and materials with cementitious properties would have a greater energy value than those for Ca/MgCO₃. Because information on the cementitious properties of materials produced from this pathway is not publicly available, credits for it are not included in the analysis. Consequently, for the industrial caustic pathway to produce calcium or magnesium carbonates, the energy penalty is greater than 90%, even using a minimum-work calculation, and the energy value of this product is negligible compared to the energy required to produce it.

In addition, the brine source can play a significant role in the energy required for pumping and mixing. A brine with high concentrations of calcium and magnesium ions, such as the Dead Sea, would be more suitable than a brine with calcium and magnesium ion concentrations in the range of sea water.

As discussed in the approach section, the widespread adoption of this pathway would also result in the generation of large quantities of chlorine or hydrochloric acid wastes. For example, coal-fired power plants in the US generate 2125 million tonne/yr CO₂ (EIA, 2009); if all of the CO₂ from these plants were mineralized via this pathway it would produce over 30 times the world demand for chlorine (World Chlorine Council, 2011).

In summary, because the lower bound energy penalty is at least 45% and because of the chlorine/hydrochloric acid waste generation, the production of sodium bicarbonate via this pathway is only potentially viable on a small scale unless another source of alkalinity is available.

4.2. Naturally occurring mineral pathway

Table 5 shows that the energy penalty for this pathway is in the same range (55–100%) as reported by Gerdemann et al. (2007) and IPCC (2005). The requirements for CO₂ separation and mineral grinding are important factors in the large energy penalty. The results presented here are for olivine and wollastonite, which have a more favorable energy requirement than the more-common serpentine, which requires additional energy to remove chemically bound water (Gerdemann et al., 2007). Khoo et al. (2011) performed a life-cycle evaluation of CO₂ mineralization using serpentine, another mineral silicate, and flue gas from a natural gas combined cycle power plant, and they report energy penalty of approximately 90–125%. Their evaluation includes the same processes considered in this evaluation as well as transportation, but their process takes place at atmospheric pressure and has minimal grinding energy requirements compared to those used by Gerdemann et al. (2007) or Huijgen et al. (2006).

In addition to the energy requirements, the mining of the mineral silicates is another potential barrier to the adoption of this pathway on a wide scale. Each tonne of CO₂ requires 1.8–4.5 tonne of ore (Gerdemann et al., 2007; Huijgen et al., 2006), depending on the type of ore. If adopted for coal-fired power plants in the US, the scale of mining would exceed that of coal mining in the US and would have similar environmental impacts, such as land disturbance (Gerdemann et al., 2007).

Because this pathway has only received attention relatively recently and has only been studied at the laboratory scale, room for improvement exists. For example, recent studies, such as those by Krevor and Lackner (2011) and Baldyga et al. (2010), have identified weak acids that enhance the dissolution of natural silicate minerals and could potentially improve reaction rates. Brent et al.

(2011) propose the integration of mineral carbonation with power generation and other extraction/manufacturing processes involving magnesium silicates, such as the extraction of magnetite, nickel, and chromium from serpentine. This type of synergistic approach offers the potential to offset the energy penalty and costs associated with mineral carbonation using naturally occurring minerals. Another approach to offset the energy penalty with mineralization of naturally occurring minerals is presented by Werner et al. (2011) who propose direct mineralization of CO₂ in flue gas without the need for CO₂ capture, thereby avoiding the energy penalty associated with CO₂ capture.

This pathway requires process improvements to reduce the energy penalty before it could be considered feasible. In their cost evaluations of aqueous mineral carbonation, Huijgen et al. (2007) (wollastonite) and Khoo et al. (2011) (serpentine) also conclude that reducing energy demand for their proposed processes is important. Furthermore, the large-scale mining of magnesium silicates may limit the adoption of this pathway.

4.3. Industrial wastes

Table 5 shows that the energy penalty associated with CO₂ mineralization of iron slag is greater than 100%, making this process unlikely to be feasible. Heating, compression, CO₂ separation, and grinding are all significant contributors to this high energy penalty. Eloneva et al. (2008) also report on a related process, the mineralization of CO₂ with blast-furnace slag. As discussed in Section 4.1, their process is also unlikely to be feasible. It tends to produce more CO₂ than would be bound by the carbonation step, primarily due to the process's use of sodium hydroxide and its associated energy requirement (Eloneva et al., 2008).

The use of fly ash for CO₂ mineralization has low energy requirements, which makes this process attractive, but it may be difficult to achieve high levels of mineralization. However, Reddy et al. (2010) suggest that this type of process could be useful for reducing the need for CO₂ sequestration in underground saline aquifers. This process may also be useful in meeting greenhouse gas performance standards, like those adopted in California that require all new long-term commitments for baseload power generation have emissions no greater than a combined cycle gas turbine plant (1100 pounds of CO₂ per MWh) (California Public Utilities and Commission, 2007). Furthermore, the fly ash used in their study contains 7.5% CaO and 3.85% MgO, but some coals, such as lignites can produce ash containing up to 40% CaO (National Research Council, 2006), which could lead to greater extents of mineralization and potentially more rapid reactions. Finally, it may be possible to improve the reactivity of fly ash by grinding, thereby increasing the surface area and availability of reactive metal oxides. However, grinding fly ash would require additional energy, which would limit any potential benefits, as discussed for Fe slag and naturally occurring minerals.

The mineralization of CO₂ with fly ash could also help reduce the large quantity of fly ash that is currently disposed of, primarily in landfills. The US generates approximately 1.2×10^8 tonne/yr of fly ash, and 55% of this material is landfilled (American Coal Ash Association, 2008). Worldwide, approximately 70% of fly ash is landfilled (Montes-Hernandez et al., 2009). Reddy et al. (2010) estimate that 2 Gt of fly ash is available in US landfills.

Soong et al. (2006) also evaluated the mineral carbonation of fly ash with acidic waste brine from oil and gas recovery. Because this proposed process requires the addition of supplementary caustic (sodium hydroxide) to bring the mineral solution to a basic pH, the life-cycle energy requirements would not be as favorable as the fluidized-bed pilot process proposed by Reddy et al. (2010). In a related paper, Baciocchi et al. (2010) performed a laboratory evaluation of bottom ash from incineration of refuse-derived fuel at

moderate temperatures (30–50 °C) and pressures (1–10 bar). They were able to achieve 9% CO₂ uptake in approximately 10 h.

One challenge associated with using fly ash to mineralize CO₂ emissions from a power plant is that the power plant generates much more CO₂ than reactive fly ash constituents. For example, if the theoretical power plant is fired with a coal containing 10% ash with the same composition as reported by Reddy et al. (2010), it would generate over 100 times more CO₂ than could theoretically react with the reactive metal oxides in the fly ash. Supplementary data, Section S.6, contains the details of this estimate. It is possible that fly ash available in landfills or onsite could also be used in this mineralization process. Baciocchi et al. (2010) also reached a similar conclusion: mineralization using bottom ash from the incinerator they studied could only capture a maximum of 2% of the CO₂ emitted from that incinerator.

Other wastes show promise but need further study and optimization. Huntzinger et al. (2006) experimentally evaluated the mineral carbonation of cement kiln dust with the flue gas from a cement kiln and obtained 60% carbonation. Their process would have low energy requirements because it takes place at ambient temperatures and pressures, but their residence time (8 h) would need to be optimized to make the process industrially feasible.

In addition to the need for study and optimization, the greatest challenge to the adoption of this pathway is the availability of wastes containing reactive oxides (Table 3). The hypothetical 1 GW coal-fired plant would produce 8 million tonnes of CO₂ annually, which is a factor of 100 greater than the quantity of reactive oxides available from a typical plant, i.e., cement, lime, coal-fired power plant, etc. Likewise, US coal-fired power plants produce 2.1×10^9 tonnes CO₂ per year, and summing the available data in Table 3 shows annual production of approximately a factor of 100 less than CO₂ production. In addition, many industries that produce wastes with reactive metal oxides are looking to reduce these as a way to improve their profitability. For example, from 1990 to 2006, the US cement industry reduced the amount of landfilled cement kiln dust by 47% (Adaska and Taubert, 2008). In addition, new technology has allowed the use of previously landfilled cement kiln dust to be used as raw feedstock. However, Table 3 does not contain all wastes containing reactive oxides, and some waste materials are available in landfills.

The waste pathway may offer additional benefits including pH reduction, thereby converting some caustic hazardous waste to a non-hazardous classification, modification of material properties, and reduction of the potential for metals leaching from wastes (Fernández Bertos et al., 2004; Gunning et al., 2010). Thus, industrial wastes that contain reactive oxides and do not require energy-intensive grinding or reaction conditions show promise for CO₂ mineralization in some applications. Their use will vary with the individual waste properties and be limited by their availability. CO₂ mineralization via the waste pathway may first be applied in situations where carbonation offers additional benefits such as the ability for industry to meet emission targets or the ability to mitigate a waste stream, as also suggested by Gerdemann et al. (2007). Understanding and optimizing processes for CO₂ mineralization using industrial wastes may also lead to reduced energy requirements for the pathway of mineralization with naturally occurring minerals, which are much more widely available than wastes containing reactive metal oxides.

5. Conclusions

The challenge for the adoption of ex situ CO₂ mineralization on an industrial scale is to develop a process that is rapid, cost competitive, and energy efficient, and that does not generate other unacceptable environmental impacts. After considering the energy requirements associated with the most significant processes, the

results of this study suggest that some industrial wastes, such as fly ash, show promise for CO₂ mineralization. However, their availability is limited, approximately two orders of magnitude less than that required to treat CO₂ emissions from US coal-fired power plants. CO₂ mineralization may first be applied to remediate wastes and to meet emission targets, such as California's greenhouse gas performance standards. Because waste composition and physical properties vary by plant, further evaluation and pilot testing of individual wastes would be required in order to better assess the feasibility of CO₂ mineralization for specific wastes.

The naturally occurring mineral pathway would need to be optimized to become more energy efficient in order for this process to become feasible. The energy penalties for grinding and for CO₂ separation are barriers to this process. Another significant barrier to this process is the need for large-scale mining of the minerals. The industrial caustic pathway is unlikely to be feasible beyond a very small scale because of the energy required to produce sodium hydroxide and the generation of potentially hazardous wastes in the form of chlorine or hydrogen chloride.

Acknowledgments

This research was sponsored by the National Nuclear Security Administration under the "Accelerating Development of Retrofittable CO₂ Capture Technologies through Predictivity" through DOE Research Grant #DE-NA0000740.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijggc.2011.09.005.

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