

Factors Influencing CO₂ and Energy Penalties of CO₂ Mineralization Processes

Pavan Kumar Narahariseti, Tze Yuen Yeo, and Jie Bu^{*[a]}

Carbon mineralization is one of the carbon capture utilization, and storage (CCUS) technologies that can be used to capture large quantities of CO₂ and convert it into stable carbonate products that can be stored easily. Several CO₂ mineralization processes have been proposed; however, there are no commercial-scale projects because there are still significant issues that need to be improved before commercialization can take place. In this work, we evaluate the CO₂ and energy penalties related to the most well-known types of mineralization processes developed to date, in which the mineralization reaction takes place directly under aqueous conditions, high pressures

and temperatures, and compared these with newer T-P swing processes and ball-mill reactor processes, which are under development. The data used in the evaluation are taken from published literature. By comparing the three processes, we identify important variables that contribute to high CO₂ and energy penalties so that future research can focus on optimization of these variables. It is observed that slurry concentration (heating) and particle size (grinding) are critical factors, with mineral calcination and operating pressure constituting other important factors.

1. Introduction

An estimated 32.2 Gt of CO₂ was emitted in 2013, according to the International Energy Agency (IEA).^[1] To reduce this amount, the IEA announced a goal of sequestering 9 Gt/yr of CO₂ by 2050 to maintain a two degree scenario in which the average global temperature rise can be limited to 2 °C. This amounts to a total capture of about 120 Gt of CO₂ between 2015 and 2050. A comparison of the difference between the intended nationally determined contributions (INDC) from the most recent Conference of Parties (COP21) in Paris, and the projected 450 scenario (which is a scenario in which there is a 50% chance of keeping the temperature rise within 2 °C) showed that the INDC pledges were still insufficient to limit global warming to acceptable levels.^[2]

In mineralization, CO₂ is converted into a carbonate form by reaction with a metal ore.^[3] When analysing the carbon capture and storage/utilisation/mineralisation processes, three basic factors must be considered. These include stability of the final product and/or the possible re-emissions of CO₂ into the atmosphere, the scale of the CO₂ capture that is possible, and the cost of the process, and income if any. The change in Gibbs free energy of the process is negative and hence the products are inherently stable (based on reported data^[3,4]). In addition, it is reported that CO₂ mineralisation can be used to potentially capture more than 10,000 Gt of carbon, given the availability of suitable raw materials.^[5,6] This amount is far

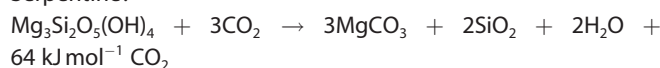
greater than the 120 Gt (9 Gt/yr) of carbon that must be captured, as recommended by IEA.^[2] The main means of disposal of CO₂ mineralization products is predicted to be through low-value uses such as construction material (roads and buildings), mine filling and/or land reclamation and, hence, CO₂ mineralization overall is expected have low revenue streams.^[6] In view of this, some CO₂ mineralisation technologies are focusing on the high value of the products that are produced^[7-9] and this can potentially offset some of the costs of mineralization.

Although the terms “CO₂ mineralization” and “mineral carbonation” are popular nowadays, the process was earlier called artificial rock weathering whereby scientists tried to improve the kinetics of a process that occurs in nature. The overall reactions of rock weathering of some of the suitable mineral ores include:^[10-14]

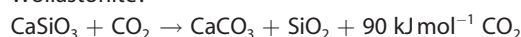
Olivine:



Serpentine:



Wollastonite:



Olivine and serpentine reactions are related in that olivine is a precursor to serpentine. The literature in the area of CO₂ mineralization is wide. A review of various publications between 1990 and 2004 is available^[13] and also between 1990 and 2010.^[14] According to these literature reviews, it was 1990 when CO₂ carbonation using silicates was mentioned for the first time.^[15] However, elements of the knowledge to perform CO₂ mineralization were available much earlier in the form of

[a] P. K. Narahariseti, T. Y. Yeo, Dr. J. Bu
Institute of Chemical and Engineering Sciences
A*STAR (Agency for Science, Technology and Research)
1 Pesek Road, Jurong Island
Singapore 627833 (Singapore)
E-mail: bu_jie@ices.a-star.edu.sg

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extraction of magnesium from serpentine and forsterite^[16,17] and recovery of acid through MgCl₂ hydrolysis^[18] for which MgO is the by-product. Furthermore, knowledge of carbonation of calcium/magnesium oxides was also available much earlier than 1990 and it was understood that CaO reacts rapidly with CO₂; however, the reaction of CO₂ with MgO is slow. In some reviews,^[13,14] the established classification into direct and indirect carbonation is presented in addition to various sub-classifications. In addition to these, there are several other publications in the area of CO₂ mineralization and these can be broadly grouped based on the respective research group. Briefly, these research groups are the National Energy Technology Laboratory (NETL),^[10–12] Comans et al.,^[13,19,20] Zevenhoven et al.,^[21–25] Jie Bu et al.,^[7–9] Shell Global Solutions, The Netherlands & collaborators,^[26,27] Maroto-Valer et al.,^[5,6,28,29] and others.^[30–37] Although most of this research focussed on inorganic acids, there are others who used organic acids. A complete literature review is beyond the scope of this work and readers who are interested in the same may read other articles in the literature.^[38–45]

Considering that direct aqueous carbonation (DAC) is one of the pioneering processes, estimation of CO₂ and energy penalties of the same serves as a good baseline and other processes that are in development can be compared with the same once evaluation of DAC is performed. Hence, we seek to understand further the DAC processes that are described in literature by NETL.^[11] More recently, the T-P swing double step carbonation process,^[36] which avoids high temperature and pressure and utilises pH swing is being developed to avoid the large CO₂ and energy penalties associated with high-pressure carbonation. In view of this, we present an evaluation of the T-P swing process in addition to the DAC process so that we can compare a pioneering CO₂ mineralization process with an upcoming process to better understand the variables that impact CO₂ and energy penalties of the CO₂ mineralization process.

2. CO₂ Capture Efficiency and Electricity Penalty

We have identified that two critical factors are important in addition to the three basic factors of capacity, stability of final product and cost of the process. These are the CO₂ penalty and the electrical energy penalty. The definition of CO₂ penalty is a straightforward indicator of the effectiveness of a CO₂ sequestration process. A smaller CO₂ penalty is clearly more desirable than a large value, and processes with CO₂ penalties above 100% are actually emitting more CO₂ into the atmosphere than they are sequestering. CO₂ penalty and capture efficiency are defined by Equations (1a) and (1b):

$$CO_{2,i}^H = H_i \times h \quad (1a)$$

$$CO_{2,i}^E = E_i \times e \quad (1b)$$

where, H_i is the amount of heat energy (GJ) used in process i , and h is the CO₂ emissions factor when unit heat is used. E_i is the amount of electrical energy used (kWh) and e is the CO₂

emissions factor (of a power plant when no CO₂ is captured) when unit electricity is used. $CO_{2,i}^H$ and $CO_{2,i}^E$ are the CO₂ emissions due to the use of heat and electricity in process step i in the CO₂ capture process, respectively. Then, Equations (1c), (1d) and (1e) are used:

$$P_i^{CO_2}(\%) = \frac{CO_{2,i}^H + CO_{2,i}^E}{CO_{2, \text{mineralized}}} \quad (1c)$$

$$P_t^{CO_2} = \sum_{i=1}^I P_i^{CO_2} \quad (1d)$$

$$\eta_t^{CO_2} = 1 - P_t^{CO_2} \quad (1e)$$

where, $P_i^{CO_2}$ is the CO₂ penalty for a given process step, $P_t^{CO_2}$ is the total CO₂ penalty and $\eta_t^{CO_2}$ is the net CO₂ capture efficiency.

For the purpose of this work, we calculated the CO₂ emissions from natural gas and coal when they are used for the generation of heat and electricity. This is done using data available at the U. S. Energy Information Administration,^[46] however, the calculations are not shown here. When natural gas is used as fuel, e is 0.43 kg/kWh (electricity) and h is 50.643 kg/GJ (heat). When coal is used as fuel, e is 0.996 kg/kWh (electricity) and h is 89.92 kg/GJ (heat). Given that electricity generation involves mechanical components and high Carnot losses, the emissions per unit of usable electrical energy are higher than the emissions per unit usable heat. Furthermore, we can see that the emissions per unit of energy are higher for coal when compared with natural gas.

To calculate the electricity penalty on a power plant, we only consider the use of electrical energy. This is deliberate because the use of heat energy is not usually taken from the power plant but is used in other internal equipment. Use of electricity affects the net energy that existing power stations can sell to the open market. In other words, CO₂ mineralization process will add to the parasitic losses at power plants and hence overall electrical energy available for sale to open market reduces. Hence, a high electricity penalty requires the construction of additional power plants and this adds to the investment burden and overall CO₂ emissions. In view of this, it is important that the electricity penalty of the process is low. The electricity penalty per tonne of CO₂ captured and avoided at a power plant is defined by Equations (2a) and (2b):

$$E_{\text{captured}}(\%) = \frac{K_{CO_2}}{K^P} \times 100 \quad (2a)$$

$$E_{\text{avoided}}(\%) = \frac{E_{\text{captured}}(\%)}{\eta_t^{CO_2}} \quad (2b)$$

where, K_{CO_2} is the electricity consumed in the capture of CO₂ produced by a given power plant, K^P is the total electrical energy generated by the power plant, is the electricity penalty per tonne of CO₂ captured and is the electricity penalty per tonne of CO₂ emissions avoided. is important to understand the electricity losses on the power plant due to the CCSU process.

3. Process Evaluation: DAC Process

3.1. Process Conditions and Basis of Design

Data for the DAC process is taken from the pioneering research work that has been published earlier.^[10,11] Here, we perform a process evaluation of their process for five different scenarios in which three different minerals were used and the operating conditions were optimised by the researchers. This helps us understand the energy and cost drivers for CO₂ mineralisation. Figure 1 shows a schematic of the CO₂ mineralisation process. Briefly, the mineral undergoes grinding and the final particle size is dependent on the type of mineral ore and the scenario being studied. Furthermore, olivine and wollastonite are directly used in the carbonation step upon grinding; however, serpentine undergoes calcination to eliminate the hydrated water. Although the slurry concentration is high (30% w/v slurry^[11]), it is assumed that heat recovery is achieved through the inclusion of a heat exchanger, although it is difficult to perform heat integration with slurries. Furthermore, it is assumed that water used for slurry preparation is not recovered. In addition, differences in the energy required for pumping slurries composed of different particle size mineral is not considered. Pure CO₂ is produced through an amine absorption process or the pressure/vacuum swing adsorption processes, and it was reported^[47] that the energy required for the amine process is large; hence, adsorption based processes are being developed to reduce the energy demand. The CO₂ pressure from a vacuum swing process is less than 1 bar,^[47] whereas that from the pressure swing processes may be about 3.5 bar, based on breakthrough and Langmuir models given in literature.^[47] In comparison, natural gas is transported over short

distances at about 200 psi (13.8 bar) and higher.^[48] In view of these different values that are available, it is assumed that pure CO₂ at a pressure of 1 atm is available from a vacuum swing adsorption process and that it is physically close to the DAC process. We have assumed that pure CO₂ is used in the DAC process instead of flue gas because a large amount of flue gas would need to be compressed to high pressure and this necessitates an additional energy penalty. However, we do not perform an optimization and do not compare the energy penalty of using flue gas and compression thereof with the energy penalty of producing pure CO₂.

It must be mentioned here that pre-treatment of olivine and wollastonite involves grinding, whereas serpentine must also be heat treated to remove the bonded water. However, olivine and wollastonite are more finely ground and hence the total energy required for different types of ores must be thoroughly analysed. Two cases each are analysed for olivine and serpentine and one case for wollastonite is analysed. The different processes that are studied in this work are labelled as DAC 1–5 and presented in Table 1. The operating conditions, conversions, residence time in the reactor and particle size are given in Table 1. From data presented in literature^[11] and reproduced in Table 1, we can see that conversion is directly related to the particle size. In view of this, it is important to understand the effect of enhancing the conversion by using more energy for grinding. Although the conversions presented in Table 1 are between 61% and 92% in 6 h, other researchers have observed that it is possible to achieve 70% conversion of olivine in 4 h and 90% conversion in less than 24 h at a temperature of 180 °C and 20 bar pressure.^[49] It must be noted here that the slurry concentration is 9%, which is less than the 30% concentration that was used in the literature.^[11] However, these

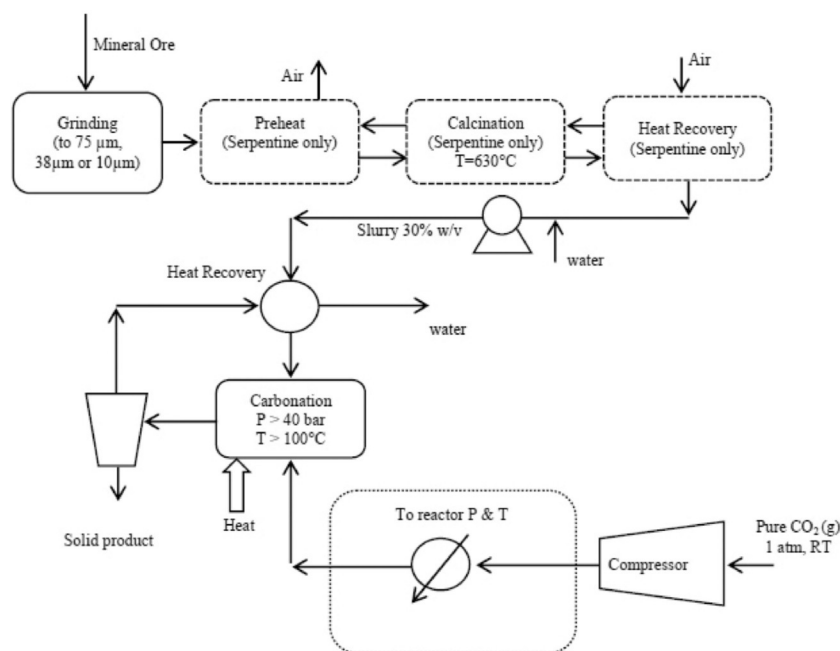


Figure 1. Schematic of the DAC process that is analysed in this work. Modified PFD based on the process described in Refs. [10] and [56]: CO₂ is assumed to be available at atmospheric pressure from a vacuum swing adsorption process. Intercooling to 38 °C is achieved using water from the cooling tower.^[58]

Table 1. Summary of minerals, operating conditions, and mineralization capacity based on data in Ref. [10] for a 1 M tonnes per year mineral processing plant. Mineral flow: 42.35 m³ h⁻¹; water for slurry: 247.06 m³ h⁻¹ (30% w/v); operating hours per year: 8500 h; sp. gravity of mineral: 2.5. Serpentine losses: 10% weight as moisture in calcination.

	DAC 1 Olivine (Mg ₂ SiO ₄)	DAC 2 Serpentine (Mg ₃ Si ₂ O ₅ (OH) ₄)	DAC 3 Wollastonite (CaSiO ₃)	DAC 4 Olivine (Mg ₂ SiO ₄)	DAC 5 Serpentine (Mg ₃ Si ₂ O ₅ (OH) ₄)
M ²⁺ (%)	27.90	24.60	31.60	27.90	24.60
M ²⁺ (tonnes/yr)	279,000	221,400	316,000	279,000	221,400
Temperature (°C)	185	155	100	185	155
Pressure (atm)	150	115	40	150	115
Mineral conversion (%)	81	92	82	61	62
Particle size after grinding (μm)	10	38	10	38	75
CO ₂ capacity (tonnes/yr)	505,185	400,889	347,600	505,185	400,889
CO ₂ converted (tonnes/yr)	409,200	368,818	285,032	308,163	248,551

data^[49] are not used here because low slurry concentration leads to large heat requirements.

Table 1 shows the metal content of the different mineral ores. The "Basis of Design" of this process is 1 M tonnes/yr of mineral ore. From the metal content, the maximum amount of CO₂ that can be mineralized and the amount of CO₂ that is mineralised under the experimental conditions (given in Table 1) can be calculated and these are also shown in Table 1. We note here that there is a 10% weight loss of serpentine mineral due to calcination.

3.2. Production of Supercritical CO₂

According to published work^[50] supercritical CO₂ can be produced by several routes. A detailed optimization to obtain the best route is beyond the scope of this work. However, it is important to understand two important routes. The first is the direct compression of CO₂ gas to produce supercritical CO₂ and the second is the production of liquid CO₂ followed by pumping and heating to produce the same. Before we analyse further, it is important to understand the mechanism of compression. Several compression pressure ratios are mentioned in literature. Most are in the range of 2 to 4, whereas some suggest a ratio that is less than 2. Briefly, some studies^[51–53] have used pressure ratios that are above 2. In contrast, researchers^[50] have presented the development of a Ramgen compressor by the U.S DoE^[54] because there are difficulties associated with CO₂ compression ratios that are above 2. In view of this, we assume an upper limit of 2 on the pressure ratio in the compression calculations we perform in this work. As suggested by others,^[50] we assume that compressor intercooling is achieved by water from a cooling tower and that the temperature of CO₂ after cooling is equal to 38 °C. The amount of water required to achieve the required cooling is calculated by assuming 10 °F approach temperature for a cooling tower water (ARI conditions; American Refrigerant Institute) from which the energy required for pumping water is calculated by assuming a discharge pressure of 1 bar. Table 1 shows the reactor pressure for the five DAC processes and Table 3 shows the energy required for compressing CO₂ from 1 atm to reactor pressure for the different cases.

3.3. Energy Calculations

The electricity used in CO₂ feed preparation and carbonation is significant, and when combined with the grinding energy, can impose a very high electricity penalty on a power plant that supplies part of its electricity to a CCU process. Analysis of the five scenarios based on available data indicates that DAC5 is the most energy-efficient DAC process, in terms of electricity used per tonne of CO₂ captured. The low-intensity grinding in DAC5 means that it consumes the least total electricity of the five processes analysed here. The following subsections provide a more in-depth analysis of the various aspects regarding energy use in the five DAC processes under consideration.

3.3.1. Energy for Pretreatment (Grinding and Activation)

Before the mineral ore is fed into the reactor for the process of CO₂ mineralisation, it is pretreated, which involves grinding and heat treatment. Grinding is performed to achieve the required particle size so that mass transfer increases. Energy required for grinding of the different mineral ores is taken from literature.^[11] Other researchers^[55,56] presented the energy required for grinding of serpentine and these values closely match those that were presented in literature.^[11] In view of this, the energy required for grinding (kWh/tonne of mineral) of the different mineral ores that are used in this work is taken from literature^[11] and the same is presented in Table 2a. The amount of energy required for grinding is directly related to the final particle size; the latter are presented in Table 1. Ground olivine and wollastonite ores are used directly in the CO₂ mineralization reactor, whereas serpentine is heat-treated at 630 °C.^[11] Briefly, the process involves heating the serpentine in a furnace and the products of the furnace are cooled while simultaneously preheating the air. This hot air is used to pre-heat the serpentine before it enters the furnace. According to published works^[55,56] the latent heat of dehydration of serpentine is 0.36 GJ/tonne and the solid must be brought to 630 °C from room temperature for calcination. The specific heat of serpentine is 1.09 MJ/tonne K.^[57] To raise the temperature of serpentine from 25 °C to 630 °C, 0.66 GJ/tonne of energy is required. However, by recovering heat from the hot solids that exit the furnace (50% heat recovery efficiency), we estimate

Table 2. Summary of: a) electrical energy required for various steps. b) Heat energy required for various steps. If the "heat of carbonation process" is negative, it is considered as "0" because the exothermic energy cannot be recovered through heat integration.

a	DAC 1	DAC 2	DAC 3	DAC 4	DAC 5
Electricity for Carbonation (CO₂ and Water) (kWh/tonne Mineral)	67.0	55.1	35.1	53.4	39.8
Water pumping (kWh/tonne Mineral)	12.0	8.2	4.7	12.0	8.2
CO ₂ compression (kWh/tonne Mineral)	54.4	46.4	30.1	41.0	31.2
CO ₂ cooler (kWh/tonne Mineral)	0.7	0.5	0.3	0.5	0.4
Grinding (kWh/tonne Mineral)	233	83	167	83	13
TOTAL Electricity (kWh/tonne Mineral)	300.0	138.1	202.1	136.4	52.8
b	DAC 1	DAC 2	DAC 3	DAC 4	DAC 5
Total Heat required for pre-treatment (GJ/tonne mineral)	0	0.41	0	0	0.41
Heat for pre-treatment of Mineral (GJ/tonne mineral)	0	0.65	0	0	0.65
Possible heat recovery during pre-treatment (GJ/tonne mineral)	0	-0.24	0	0	-0.24
Heat to Carbonation Process (GJ/tonne mineral)	0	0.118	0	0.291	0.197
Mineral-Heating (to reach reactor temperature from RT) GJ/tonne mineral	0.18	0.14	0.08	0.18	0.14
Water Heating incl. heat recovery (GJ/tonne mineral) (to reach reactor temperature from RT)	0.23	0.21	0.24	0.23	0.21
Exothermic Energy (inside the reactor) GJ/tonne mineral	-0.69	-0.39	-0.49	-0.26	-0.26
CO ₂ Heating GJ/tonne mineral	0.07	0.04	0.00	0.05	0.02
TOTAL Heat (GJ/tonne mineral)	0.00	0.00	0.00	0.21	0.12

that only an additional 0.29 GJ/tonne of serpentine is necessary to heat serpentine instead of the 0.66 GJ/tonne. Hence, the total energy required for serpentine activation is 0.65 GJ/tonne (0.36 + 0.29). It must be added here that the hot air exiting the furnace carries steam (from dehydration) and it is possible to extract additional usable *low grade heat energy* equivalent to 0.24 GJ/tonne of serpentine (after accounting for 40% loss on heat recovery). That is, a total of 0.65 GJ/tonne is required for dehydration and 0.24 GJ/tonne of heat can be recovered for other uses. Hence, the net energy for serpentine activation is 0.41 GJ/tonne and the same is listed in Table 2b. It must be emphasised here that the low-grade heat can only be used in other applications and the net energy input required for this process may be 0.65 GJ/tonne in reality; however, for the purpose of this work, we assume that other processes sit parallel to the CO₂ mineralization process and hence the 0.24 GJ/tonne of energy can be easily recovered; i.e. it is not wasted.

3.3.2. Energy Required for the Production of Pure CO₂

It was reported that pressure/vacuum swing adsorption processes typically use electrical energy at between 250–675 kWh per tonne of CO₂. The lower electrical energy demand is related to vacuum swing adsorption processes in which the CO₂ outlet pressure is less than 1 bar and the higher electrical energy is from pressure swing processes in which the CO₂ outlet pressure is below 3.5 bar.^[47] In our work, we have assumed that CO₂ is available in pure form from the vacuum swing adsorption process at 1 atm. Since the literature on CO₂ purification is wide spread, both in terms of technologies and publications available, we do not consider a detailed analysis of CO₂ penalty from CO₂ purification. Furthermore, the focus of our work is the comparison of the direct aqueous carbonation process with upcoming CO₂ mineralization technologies, and

readers who are interested in CO₂ penalty from CO₂ purification processes may refer to the literature.^[47]

3.3.3. Energy for CO₂ Compression

A detailed study on the energy required for compression of CO₂ has been presented.^[50] Two major routes can be considered. They are direct compression to supercritical state, while the CO₂ is only in the gas phase during compression and compression-cooling to produce liquid CO₂ followed by pumping to supercritical pressure. The authors concluded that compressing the CO₂ to around 15–20 bar and then cooling it to produce liquid CO₂ followed by pumping of liquid CO₂ to reactor pressure may be energy efficient compared with direct compression to reactor pressure; however, they^[50] did not perform the calculations. We have calculated that production of liquid CO₂ followed by pumping to supercritical state requires energy of the same order of magnitude (results not presented) as that required for compressing CO₂ to supercritical state while remaining in the gas phase. This is due to the fact that energy is required to remove the latent heat of condensation of CO₂. In view of this, we consider that CO₂ is compressed to the reactor pressure in a multi-stage compressor with inter-cooling. The schematic of the process is shown in Figure 1. As described earlier, the pressure ratio of CO₂ is less than 2 according to published work.^[50] Hence, if CO₂ at atmospheric pressure needs to be compressed to reactor pressure, then multiple compressors with intermittent cooling are required. The energy required for cooling the CO₂ can be estimated by using the following equations.^[58] Temperature of product gas is calculated by Equation (7a), the specific heat of CO₂ as a function of temperature can be calculated by Equation (7b) and the work done by the compressor is given by Equation (7c):

$$T_2 - T_1 = \frac{T_1}{\eta_c} \left[\left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (7a)$$

$$\bar{c}_p = -3.7355 + 3.0529T^{0.5} - 0.041034T + 2.4198 \times 10^{-6}T^2 \quad (7b)$$

(J/mol/K)

$$W_c = \frac{C_p^2 T_2 - C_p^1 T_1}{\eta_s^c} \quad (7c)$$

where T is temperature, p is pressure, and \bar{c}_p is specific heat at constant pressure with the subscripts "1" and "2" referring to the initial and final states; η_c is the isentropic efficiency of the compressor, γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume, W_c is the energy required to drive the compressor, and η_s^c is the shaft efficiency of compressor.

When liquid CO₂ is used, the enthalpy change due to condensation can be calculated from the Mollier Chart (Pressure-Enthalpy chart) for CO₂. In the case of liquid CO₂, the energy required for pumping it to the reactor temperature and pressure needs to be calculated from the above equations and the compressor charts.

To avoid the complexity of calculations using the above equation and the Mollier Chart, we use Aspen 8.0^[59] to simulate the process of CO₂ compression-cooling and pumping of slurry to reactor temperature and pressure. Aspen is a reliable simulation tool that is widely used in the petroleum and petrochemical industry. In view of this, the energy required to compress CO₂ is calculated using Aspen 8.0. The input pressure for the first stage, the compression ratio for the later stages and the amount of CO₂ that is compressed are used as the input variables in Aspen 8.0. Isentropic efficiency of 85% and mechanical efficiency of 95% are assumed for CO₂ compression.^[50] It is assumed that concentrated CO₂ is available from a vacuum swing adsorption process at a pressure of 1 atm. The energy required to compress the CO₂ from a pressure of 1 atm to the operating pressure that is listed in Table 1 is given in Table 2a. The amount of CO₂ that is compressed in each scenario is given in Table 1. Change of pressure due to intercooling may be estimated by using van der Waals equation of state for non-ideal gases, and doing so suggests that 11, 10, 8, 11, 10 stages are required at a compression ratio of 1.9 for each of the five processes that are being studied. In our detailed calculations, we consider the loss in pressure due to cooling. Based on this Scheme, a detailed Aspen simulation model is set up for the same and the energy results are presented in Table 2a and 2b.

3.3.3. Energy for Water Compression

In addition to CO₂, the slurry must also be pumped in to the reactor at a pressure that is equal to the operating pressure of the reactor. It is assumed that the solids in the slurry are incompressible and the energy required for pumping the water is simulated in Aspen 8.0. The driver efficiency and the pump efficiency are assumed to be 90%. In addition to increasing

the pressure, the slurry (ground mineral ore + water) must be heated from room temperature to the reactor operating temperature.

3.3.4. Energy for Carbonation Reactor

The energy required for carbonation is calculated as a combination of energies that are required for different individual processes that happen within the carbonation reactor or just before material enters the reactor. CO₂ and water are to be heated to the reactor temperature. This is calculated in Aspen 8.0 after accounting for heat recovery from products of the reactor; only water is considered in heat recovery and solid products are not considered because heat recovery from solids is difficult. Energy required to heat the solids is calculated by using the values of specific heat of mineral (1.09 kJ kg⁻¹ K⁻¹ for all types of mineral). The details are presented in Table 2b. Given that all these energy exchanges happen within or close to the reactor, we assume a high heat recovery efficiency of 100% for exothermic energy and heat balance between hot CO₂, solids and water. Heat of the reaction (exothermic energy) of the mineralization process is calculated using HSC 6.1.

3.4. CO₂ Penalty Calculations

From our analysis of the CO₂ penalties of the five DAC process scenarios, we can make some interesting observations regarding good process design for CCU processes. Firstly, it is advisable to reduce the use of electricity (in particular coal-fired electricity) in CCU processes, because these often have very high emissions per unit energy supplied. This also suggests that whenever possible, thermal energy is preferred as the input to the process. Secondly, since grinding is a major consumer of electricity, it is advisable to reduce the intensity of grinding, and use larger mineral particles for mineralization. However, this may be a problem in the DAC processes because the extent of reaction is strongly correlated with particle size. This can be remedied in the case of serpentine, for which (relatively) coarse particles are heat-treated before supplying into the mineralization reactor (for example in DAC5). This allows a higher degree of conversion to be achieved, and also significantly reduces the CO₂ penalty of the process.

3.4.1. CO₂ Penalty (Natural Gas as Fuel)

Table 3a shows the total CO₂ penalty for each of the scenarios when natural gas is used for heating and for generation of electricity. It can be seen that the largest CO₂ penalty is for olivine, wollastonite and serpentine when finer grinding is performed. This is not entirely unexpected, because fine grinding requires more energy and hence the CO₂ penalty would be large; however, what is important to note is that the CO₂ penalty is large after accounting for the higher conversion and this is a noteworthy observation.

Clearly, the choice of the mineral ore influences the CO₂ penalty more and this can be directly attributed to the particle size. It is important to note here that the CO₂ penalty for ser-

Table 3. a) Summary of the CO₂ penalty [using Eqs. (1a)–(1d)] for the different processes when natural gas is the fuel. CO₂ emissions (natural gas): 0.43 kg/kWh; 50.643 kg/GJ. b) Summary of the CO₂ penalty [using Eq. (1a)–(1d)] for the different processes when coal is the fuel. CO₂ emissions (coal): 0.996 kg/kWh; 89.92 kg/GJ.

a	DAC 1 [%]	DAC 2 [%]	DAC 3 [%]	DAC 4 [%]	DAC 5 [%]	Remarks
Pre-treatment	24.5	15.3	25.2	11.6	10.6	
Grinding	24.5	9.7	25.2	11.6	2.2	Electricity
Activation	0.0	5.6	0.0	0.0	8.4	Heat
Carbonation reactor	0.0	0.0	0.0	3.4	2.4	Heat
Mineral heating	2.2	2.0	1.4	2.9	2.9	
Water heating	2.9	2.9	4.2	3.9	4.3	
Heat of reaction	−8.5	−5.4	−8.7	−4.2	−5.4	
CO ₂ heating	0.9	0.5	0.0	0.9	0.5	
Feed preparation	7.0	6.4	5.3	7.5	6.9	Electricity
CO ₂ compression	5.7	5.4	4.5	5.7	5.4	
Pumping water for CO ₂ intercooler (cooling tower)	0.1	0.1	0.0	0.1	0.1	
Pumping slurry water	1.3	1.0	0.7	1.7	1.4	
Total CO₂ penalty	31.5	21.7	30.5	22.5	19.9	
Electricity penalty on power plant	31.5	16.1	30.5	19.0	9.1	

b	DAC 1 [%]	DAC 2 [%]	DAC 3 [%]	DAC 4 [%]	DAC 5 [%]	Remarks
Pre-treatment	56.7	32.4	58.4	26.8	20.0	
Grinding	56.7	22.4	58.4	26.8	5.2	Electricity
Activation	0.0	10.0	0.0	0.0	14.8	Heat
Carbonation reactor	0.0	0.0	0.0	6.1	4.2	Heat
Mineral heating	3.9	3.5	2.4	5.2	5.2	
Water heating	5.2	5.2	7.4	6.8	7.7	
Heat of reaction	−15.1	−9.6	−15.5	−7.5	−9.5	
CO ₂ heating	1.6	0.9	0.1	1.6	0.9	
Feed preparation	16.3	14.9	12.2	17.3	16.0	Electricity
CO ₂ compression	13.2	12.5	10.5	13.2	12.5	
Pumping water for CO ₂ intercooler (cooling tower)	0.2	0.1	0.1	0.2	0.1	
Pumping slurry water	1.6	0.9	0.1	1.6	0.9	
Total CO₂ penalty	73.0	47.3	70.6	50.2	40.2	
Electricity penalty on power plant	73.0	37.3	70.6	44.1	21.2	

pentine pretreatment is lower compared with the CO₂ penalty for fine grinding for olivine and wollastonite. Table 3a shows the CO₂ penalty for the energy used to take CO₂ at 1 atm and room temperature to reactor conditions. It should be mentioned here that the CO₂ penalty is largely associated with the energy required for the number of stages of compression and not the absolute final pressure.

3.4.2. CO₂ Penalty (Coal as Fuel)

Table 3b shows the total CO₂ penalty for each of the scenarios when coal is used for heating and for generation of electricity. Table 3b shows the CO₂ penalty associated with the production of CO₂ at reactor conditions. The overall trend of CO₂ penalty is similar to that when natural gas is used as fuel. However, the actual values are about twice that when natural gas is used as fuel. This is expected since coal is a poor form of energy when CO₂ emissions per unit energy are considered.

We can see from Table 3a and 3b that the CO₂ penalty is large when the mineral is more finely ground. Any benefit due to increased conversion by using fine particles is lost due to the large energy required for grinding. In view of this, we can conclude that it is probably better to use large particles of the mineral ore instead of spending extra energy on grinding.

In summary, we can conclude that DAC5 has the lowest CO₂ penalty at 19.9% when natural gas is used as fuel and 40.2% when coal is used as fuel. Of the total CO₂ penalty, we can see from Table 3a and 3b that the majority of the CO₂ penalty is due to the calcination step for DAC5 and grinding is the major cause for other cases. Given that calcination is performed using heat energy and heat energy has low CO₂ emissions per unit of useful energy compared with electrical energy, DAC5 has low CO₂ emissions.

3.5. Electrical Energy Penalty

From both an economic and energy efficiency point of view, the electricity penalty is an important parameter that has to be seriously considered when evaluating a DAC process. In general, the electricity penalty refers to the parasitic energy loss imposed on the power plant that supplies electricity to the DAC process. This reduction in output to the market represents a loss in revenue for the power plant. This has two significant consequences, in that the power plant now has to raise prices for consumers to compensate for the loss in revenue, and also to increase production to meet market demand, which in turn leads to more CO₂ emissions.

Thus, it is desirable to have a DAC process that consumes as little electricity as possible, and imposes a small electricity penalty on its accompanying power plant. Again from our analysis, we find that DAC5 has the smallest electricity penalty due to its savings in grinding. Although its thermal energy requirements are among the highest of the five DAC processes considered here, it matters less in terms of energy penalties because the use of thermal energy in a separate installation does not in any way affect the electricity output of a power plant; i.e. the power plant still produces and sells according to the nameplate capacity. The amount of natural gas/coal used for heating purposes does not in any way affect the power plant nameplate capacity because the fuel is purchased from the open market.

The CO₂ emissions of power plants that use natural gas is 0.43 kg/kWh; i.e. generation of 2326 kWh produces 1 tonne of CO₂. From Table 2a, we can see that 52.8 kWh of electricity is required for processing 1 tonne of serpentine (DAC5) and the rest of the energy required for the process is given as heat. It can be seen from Table 3 that the electricity penalty varies between 9.1% and 31.5% when natural gas is used as fuel, and it varies from 21.2% to 73.0% when coal is used as fuel in the CO₂ mineralisation process. In view of this, the heat intensive processes such as serpentine activation and heating of the carbonation reactor are best performed using natural gas as fuel. Furthermore, electricity should preferably be produced by natural gas based power plants. However, most of today's power plants are based on coal and hence it is unlikely that electricity penalty can be as low as 9.1% and it is more likely to be 21.2% for DAC5.

One tonne of serpentine at 75 μm captures about 0.25 tonnes of CO₂ (0.248 tonnes, Table 1); hence capture of 1 tonne of CO₂ requires 212.9 kWh of electricity (DAC5). Given that CO₂ capture efficiency is 81.1% (penalty of 19.1%), 1 tonne of CO₂ avoided requires 262.5 kWh of energy. Similarly, the electricity penalty is 9.1% (ca. 212.9/2326) based on CO₂ captured (and not CO₂ avoided) when serpentine ground to 75 μm is used as mineral and natural gas is the fuel of choice. Hence, we can conclude that a minimum increase in power plant capacity should be 9.1% over existing capacity. Alternatively, if this energy can be generated by increases in power plant efficiency and reduced CO₂ emission per kWh of electricity, the electricity penalty on power plants can be met.

We can see that the particle size follows the order DAC5 > DAC2 = DAC4 > DAC1 = DAC3 whereas the electricity penalty follows DAC5 < DAC2 < DAC4 < DAC1 < DAC3. When particle size is the same, the nature of the material becomes important. In summary, we can conclude that the electricity penalty is inversely proportional to the particle size because more electrical energy is required in grinding. We can see that serpentine ground to only 75 μm shows the lowest electricity penalty amongst all the processes; this is clear because it consumes the lowest amount of electricity. In contrast, it used heat for calcination and hence the overall CO₂ penalty is about the same as that for other mineral ores. In view of this, the adaptation of serpentine depends on optimization of the conversion of the process so that CO₂ and electricity penalty is low.

Hence, it is important that research is focussed on improving the conversion of large particle size mineral ores and this can possibly be achieved by choosing an appropriate buffer and/or by chemical treatment.

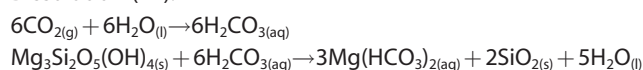
4. Process Evaluation: T-P Swing Process and Ball-Mill Reactor

4.1. Process Conditions and Basis of Design

Lizardite, a member of the serpentine group, is used in the double step T-P swing process and also in the single-step ball-mill reactor. In view of this, the same general formula can be used for lizardite as that of serpentine used in DAC process, and this provides us an opportunity to compare the three processes. Here, we perform an analysis of four sets of experiments that were performed (S1, S2, S3 and S4), where S1 and S4 are the single-step carbonation in the ball mill reactor (SBR process), and S2 and S3 are the double-step carbonation processes using the T-P swing process (TPS process). For the purpose of this work, we have chosen the best possible conversion at 50 °C and 20 wt% slurry concentrations in the single-step ball-mill reactor as S1. The researchers^[36] have also reported that a higher conversion of up to 88.8% is possible at 90 °C and 1 wt% slurry conversion and we perform the analysis of the same as S4. It must be mentioned here that single-step reaction without ball milling was also presented^[36] at the same conditions as that of S1; however, it was observed that the conversion was lower, at only about 15% compared with 30% for S1. In view of this, we expect that the CO₂ and energy penalty would be larger than S1 and hence we do not present further analysis of the same.

The double-step carbonation process uses two reactors, the first is a low-temperature, high-pressure reactor in which dissolution of magnesium from the mineral ore occurs and the second is a high-temperature, low-pressure reactor in which the magnesium carbonate precipitates due to the change in pH associated with temperature and pressure change.^[36] Preliminary experiments were conducted to demonstrate the concept and further optimisation of the process conditions to improve the conversion are necessary.^[36] Briefly, the process consists of a dissolution reactor (R1) at 30 °C (sometimes higher or a reactor under changing temperature conditions) with a CO₂ pressure of 5 bar and the precipitation reactor (R2) at 90 °C and 1 bar. The chemical reactions that occur in the process are described below and a schematic of the process is shown in Figure 2.

Dissolution (R1):



Precipitation (R2):



The CO₂ and serpentine dissolve in R1. Pumping of CO₂-laden gas to R2 is optional and not performed in the scenarios we considered; hence, the energy required for compressing CO₂

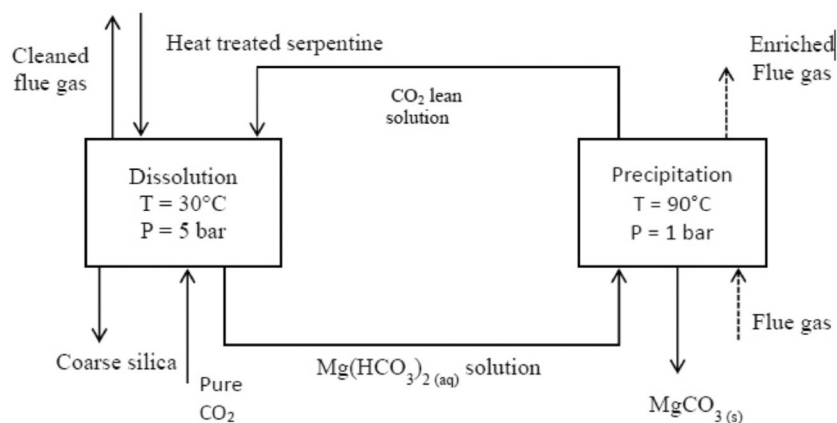


Figure 2. Simplified schematic of the double-step carbonation process. Flue gas supply to the precipitation reactor is optional. Enriched flue gas from precipitation reactor may be supplied to dissolution reactor in place of pure CO₂.

to the pressure of R2 is neglected. Furthermore, it is assumed that the T-P swing is performed only once. Repeated T-P swings would of course lead to larger energy demand and heat losses thereof. A three-stage compressor with cooling-water-based intercooling is considered for compression of CO₂ to reactor pressure. The researchers^[36] have used simulated flue gas in their experiments. For the purpose of our analysis, it is assumed that CO₂ is available in pure form at 1 atm, just as we have considered for the DAC process. We do not consider the optimization of using pure CO₂ and energy and CO₂ penalty thereof vs. energy required for compressing flue gas (10–15% CO₂) to reactor pressure.

It was reported that 20 μm or 125 μm particles were used in the double-step carbonation process,^[36] with 20 μm showing better conversion. In the case of single-step carbonation, 127 μm particles were used and conversion was observed to be 30% in a ball-mill reactor at 50°C. Different experiments were conducted for the double-step carbonation process and we consider the best results among them at 35.6% conversion when 20 μm particles are used and 22.4% conversion when 125 μm particles are used; both experiments are conducted at a slurry concentration of 1 wt%. The dissolution reactor was supplied with pure CO₂ and was at 30°C when 125 μm particles were used and a linear temperature gradient of 30°C to 90°C was used when 20 μm particles were used. In spite of this, the energy required for this temperature gradient is not considered in our analysis. In both the double step carbonation experiments, the precipitation reactor was at 90°C with no CO₂ supply.

Data presented in literature^[11] can be used to show that a logarithmic relationship exists between the final particle size and the amount of energy required for grinding (plot not shown) and it was also reported^[11] that this is independent of the mineral used. By using this relationship, we can estimate that 168 kWh/tonne mineral of energy is required for producing 20 μm particles and this is double the 83 kWh/tonne mineral required to produce 38 μm particles (DAC2). In contrast, only 12.5 kWh/tonne mineral of energy is required to produce particles that are 125 μm.

4.2. Energy Calculations and CO₂ Penalty

The energy required for the various process steps is summarised in Table 4. We make two critical assumptions while doing these calculations. We assume that the exothermic energy of the mineralization process is utilised fully and that this happens after the slurry leaves R1 and reaches R2. Irrespective of the slurry concentration and difficulties associated with heat integration with slurries, we assume that energy can be extracted from the hot stream leaving R2 to pre-heat the cold stream entering R2 with an approach temperature of 20°C and no further heat transfer losses are considered. The additional heat that is necessary to raise the temperature of the cold stream from 70°C to 90°C is assumed to be supplied externally. We can see from Table 4 that the majority of the electrical energy is due to the demand for grinding the mineral ore. Furthermore, the slurry concentration of a mere 1 wt% necessitates a lot of energy to reach the operating temperature of 90°C. The majority of the heat energy is used in raising the slurry temperature to the reactor temperature (R2), although the exothermic energy offsets some of the demand for heat energy. For the purpose of this work we also consider that the heat gain due to final stage compression of CO₂ can be recovered, and we can see from Table 4 that this energy is small compared with the exothermic energy. Given that these occur within the process lines and the reactors, we assume that there are no losses in this energy integration. It can be seen from Table 4 that the energy required is largely influenced by the slurry concentration, particle size and conversion. The amount of water and the mineral required would be high when the slurry concentration and conversion are low, thus necessitating the use of large amounts of energy for grinding of the mineral and heating the water.

4.3. Comparison of the Three Processes: DAC, SBR and TPS

S1 is clearly a better example of the CO₂ mineralization processes because although the conversion is comparable to S2, it uses a reasonably high slurry concentration of 20 wt%. It must

Table 4. a) Summary of the experimental conditions of the T-P swing process in comparison with the DAC5 process. SBR: Single-step ball-mill reactor. SSR: Single-step reactor without ball milling. DS: Double-step process. HPR: High-pressure reactor. DAC5 uses antigorite with 24.6% Mg²⁺ and 10% moisture content. S1 to S4 uses Lizardite, assumed to be bone dry. b) Summary of the electrical and heat energy requirements of the T-P swing process in comparison to the DAC5 process.

a	S1	S2	S3	S4	S5	DAC5	
Method	SBR	TPS	TPS	SBR	SSR	HPR	
Conversion	30.0%	35.6%	22.4%	88.8% ^[a]	15.0%	62%	
Mineral required (tonnes/tonne CO ₂ captured)	6.992	5.892	9.365	2.362	13.99	4.023	
Slurry concentration (w/w %)	20	1	1	1	20	30	
Water for slurry (tonnes/tonne CO ₂ captured)	35.0	589.2	936.5	236.23	1398.5	8.45	
Particle size (μm)	125	20	125	125	125	75	
b	S1 ^[b]	S2	S3	S4 ^[b]	S5 ^[c]	DAC5	
Grinding energy (kWh/tonne CO ₂ captured)		87.41	989.94	117.06	29.53	174.81	52.3
Energy for CO ₂ compression (kWh/tonne CO ₂)		40.81	40.81	40.81	40.81	40.81	125.71
Energy for cooling compressed CO ₂ (kWh/tonne CO ₂)		0.22	0.22	0.22	0.22	0.22	1.29
Pumping water (kWh/tonne CO ₂)		4.81	81.01	128.74	32.48	9.61	33.12
Total electrical energy (kWh/tonne CO₂ captured)		133.24	1111.97	286.83	103.03	225.45	212.42
Activation (GJ/tonne CO ₂ captured)		2.87	2.42	3.84	0.97	5.73	1.65
Water heating (GJ/tonne CO ₂ captured)		3.65	61.58	97.86	24.69	7.67	0.86
Mineral heating (GJ/tonne CO ₂ captured)		0.19	0.16	0.26	0.06	0.38	0.57
Exothermic energy		-0.90	-0.90	-0.90	-0.90	-0.09	-1.06
Energy gain from heat due to final compression step		-0.05	-0.05	-0.05	-0.05	-0.05	0.1
Total Heat required (GJ/tonne CO₂ captured)		5.77	63.21	101.02	24.78	12.48	2.12
[a] Refers to magnesium leached and not MgCO ₃ formed. [b] Energy required for ball-mill reactor is not included. [c] Ball milling not used.							

be mentioned here that the grinding energy involved in a ball-mill reactor is not considered in S1 because it can only be measured experimentally. Similarly, the energy required for using a ball mill in S4 is also not considered in this work. This is especially so because the process is a combination of reaction, deposition of products of the reaction on the surface of the particles, and grinding to eliminate the depositions. In view of this, any comparison of DAC5 with S1 must take this into consideration. Here, we can compare the TPS and SBR processes with DAC5, because all these use serpentine, and present the same in Tables 4 and 5. We can see from Table 4 that the energy required for compression of CO₂ is large in DAC5 and the same is relatively small in the TPS and SBR processes. This is clearly due to the lower operating pressure of the latter processes. In contrast, the amount of heat energy required by the TPS and SBR processes is large, especially since the conversion is low and the slurry concentration is low and the combined effect requires a much larger energy than the DAC5 process. When we compare S1 with S4, it is clear that the electricity penalty can be reduced to a considerably lower value of 3% when natural gas is used as fuel; this is due to

high conversion and ignoring the energy required for the ball mill reactor, which must be estimated from experiments. Although the electricity penalty of S4 is low, the amount of heat energy required to maintain 90 °C in S4 (1 wt% slurry concentration) is much higher than in S1 (20 wt% slurry concentration) but not as high as that in S2 and S3, which are at same 1 wt% and this is due to the higher conversion and the requirement thereof to heat less slurry to achieve the required CO₂ capture.

Table 5 shows the CO₂ penalty and electricity penalty of the TPS and SBR processes against the DAC5 process. We can see that the electricity penalty on S1 is considerably lower than for the DAC5 process because the operating pressure is lower. Furthermore, the particle size considered in S1 is 125 μm, whereas that in DAC5 is 75 μm. Here, we have not considered the energy required for the ball mill and this must be accounted for if the process is scaled up. Although grinding is an energy intensive process, the use of a ball mill to overcome the mass transfer resistance by clearing the product deposition on the serpentine particles may be less energy intensive and it may be worthwhile extending this research further to improve the

Table 5. a) Summary of the CO₂ and electricity penalty when natural gas (NG) is used as fuel. CO₂ emissions (natural gas): 0.43 kg/kWh; 50.643 kg/GJ. b) Summary of the CO₂ and electricity penalty when coal is used as fuel. CO₂ emissions (coal): 0.996 kg/kWh; 89.92 kg/GJ.

a	S1 [%] ^[a]	S2 [%]	S3 [%]	S4 [%] ^[a]	S5 [%] ^[b]	DAC5 [%]	Remarks
Pretreatment	18.3	54.8	24.5	6.2	36.6	10.6	
Grinding	3.8	42.6	5.0	1.3	7.5	2.2	Electricity
Activation	14.5	12.2	19.4	4.9	29.0	8.4	Heat
Carbonation reactor	14.7	307.9	492.1	120.6	34.2	2.4	Heat
Mineral heating	1.0	0.8	1.3	0.3	1.9	2.9	
Water heating	18.5	311.8	495.6	125.0	37.0	4.3	
Heat of reaction	-4.5	-4.5	-4.5	-4.5	-4.5	-5.4	
CO ₂ heating	-0.2	-0.2	-0.2	-0.2	-0.2	0.5	
Feed preparation	2.0	5.2	7.3	3.2	2.2	6.9	Electricity
CO ₂ compression	1.8	1.8	1.8	1.8	1.8	5.4	
Pumping water for CO ₂ intercooler (cooling tower)	0.01	0.01	0.01	0.01	0.01	0.1	
Pumping slurry water	0.2	3.5	5.5	1.4	0.4	1.4	
Total CO₂ penalty	35.0	367.9	523.9	129.9	72.9	19.9	
Electricity penalty on power plant	5.7	47.8	12.3	4.4	9.7	9.1	
b	S1 ^[a]	S2	S3	S4 ^[a]	S5 ^[b]	DAC5	Remarks
Pretreatment	34.5	120.3	46.2	11.7	69.0	20.0	
Grinding	8.7	98.6	11.7	2.9	17.4	5.2	Electricity
Activation	25.8	21.7	34.5	8.7	51.6	14.8	Heat
Carbonation reactor	26.1	546.7	873.8	214.1	60.7	4.2	Heat
Mineral heating	1.7	1.4	2.3	0.6	3.4	5.2	
Water heating	32.9	553.7	880.0	222.0	65.7	7.7	
Heat of reaction	-8.1	-8.1	-8.1	-8.1	-8.1	-9.5	
CO ₂ heating	-0.4	-0.4	-0.4	-0.4	-0.4	0.9	
Feed preparation	4.6	12.2	16.9	7.3	5.0	16.0	Electricity
CO ₂ compression	4.1	4.1	4.1	4.1	4.1	12.5	
Pumping water for CO ₂ intercooler (cooling tower)	0.02	0.02	0.02	0.02	0.02	0.1	
Pumping slurry water	0.5	8.1	12.8	3.2	1.0	0.9	
Total CO₂ penalty	65.2	679.2	936.9	233.1	134.7	40.2	
Electricity penalty on power plant	13.3	110.8	28.6	10.3	22.5	21.2	

[a] Energy required for ball-mill reactor is not included. [b] Ball milling not used.

conversion from the current 30% to about 60% or more at 30% slurry concentration, as for the DAC5 process.

Overall, the DAC5 process has considerably lower CO₂ penalty compared with the current state of the art SBR process (S1), and the electricity penalty of the S1 process is potentially lower than that of the DAC5 process and this is subject to quantifying the electrical energy required to run the ball-mill reactor. Furthermore, the SBR processes have better CO₂ penalty compared with the TPS processes due to better conversion. In view of this, we can fairly state that the DAC5 process performs better in terms of the overall CO₂ penalty at the current state of the art and the SBR processes, which use a ball-mill reactor at lower operating pressure, shows promise for further research to increase the conversion at a higher slurry concentration.

4.4. Factors Influencing CO₂ and Energy Penalties

From this study we can see that there are six key factors that influence the CO₂ and energy penalty. They are the conversion, slurry concentration, mineral activation, grinding (particle size), operating pressure and temperature. The four factors other than the conversion and heating energy are defined in the ex-

perimental protocol, whereas conversion is an observed parameter, and energy for heating can be calculated from the amount of water/slurry concentration. In view of this, it would suffice to focus our analysis on four parameters; namely, slurry concentration, mineral activation, particle size and operating pressure. Slurry concentration and particle size play the biggest role in contribution towards the CO₂ and energy penalties and it is preferred to have a high slurry concentration of 30% and a large particle size of 125 μm. However, a high slurry concentration and large particle size are associated with poor conversion and this leads to the requirement for large amounts of mineral ore, which must be ground and activated. When the slurry concentration falls from 30% to 1%, we can see that the CO₂ penalty for heating water increases from 8% (DAC5) to 880% (S3) when coal is used as fuel. Furthermore, when the particle size is reduced from 125 μm to 20 μm, the CO₂ penalty increases from 3% (S4) to 99% (S2), pointing to the fact that slurry concentration and particle size are critical factors. In contrast, mineral activation leads to a CO₂ penalty of between 9% and 35% and CO₂ compression leads to a CO₂ penalty of between 4% and 13% in each of the five processes presented in Table 5 b, indicating that they are important factors, but not as critical as the slurry concentration and particle size.

Although the CO₂ penalty of the DAC process is low in general, these processes use a chemical additive or a buffer. In contrast, the SBR and TPS processes do not use chemical additives or buffers. Whereas this is an advantage, the slurry concentration is usually lower than in the DAC5 process, leading to an overall higher CO₂ penalty caused by the energy required to heat large amounts of water in the slurry. The SBR and TPS processes exploit a critical feature of the process of CO₂ mineralization, whereby the amount of magnesium leached is the highest at low slurry concentrations and precipitation of magnesium carbonate is higher at a high slurry concentration. Given that the first step, leaching, cannot be avoided, a low slurry concentration appears to be inevitable. Since it is difficult to concentrate the slurry, the TPS process relies on heating the low concentration slurry to 90 °C and eliminates some of the CO₂ and precipitate MgCO₃ in the process. However, we have seen earlier that heating slurry with low concentration leads to a large CO₂ penalty. It must be mentioned here that we assume that the energy required for heating water is only required for an approach temperature of 20 °C with potential heat integration. In case heat integration is poor, the energy and thus the CO₂ penalty thereof would be much larger than that calculated here.

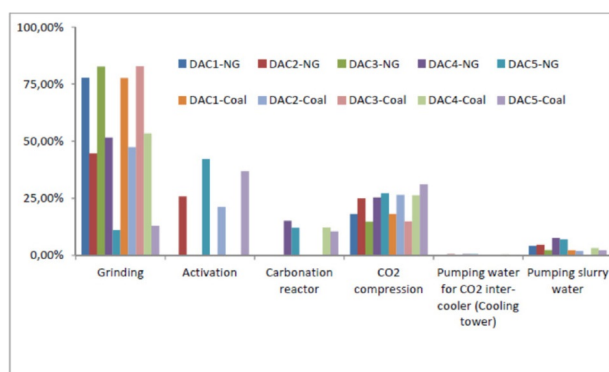


Figure 3. Distribution of CO₂ penalty for the different DAC processes when natural gas (NG) or coal is used as fuel. It can be seen that grinding followed by CO₂ compression are the largest contributors to CO₂ penalty.

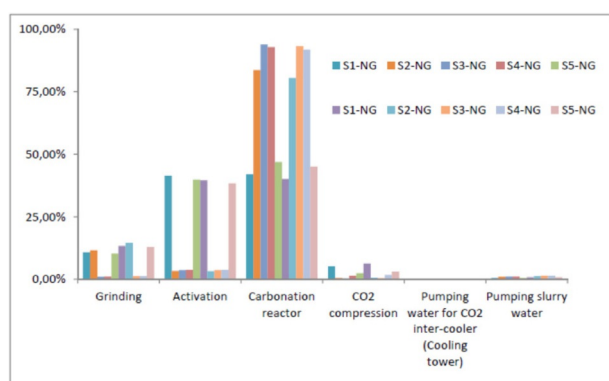


Figure 4. Distribution of CO₂ penalty for the different SBR/TPS processes when natural gas (NG) or coal is used as fuel. It can be seen that carbonation reactor is the largest contributors to CO₂ penalty and this is due to the low (high) slurry concentration (water content).

Figure 3 and Figure 4 summarises the relative CO₂ penalty of the different subprocesses within the DAC, SBR and TPS processes. It can be seen that grinding followed by CO₂ compression contribute the maximum to CO₂ penalty in the DAC process. This is due to the small particle size that is used in the process and also to the high pressure of the carbonation reactor. In contrast, the energy required for the carbonation reactor in the SBR/TPS processes is the largest, which is not unexpected because the slurry concentration in these processes is rather low and hence large amounts of water must be heated to the reactor temperature. Furthermore, where applicable, the energy required for activation of the mineral (serpentine) also contributes to a large CO₂ penalty.

5. Conclusions

In this paper, we evaluate five scenarios for a direct aqueous pressure carbonation (DAC) process as described in published literature. The scenarios are based on work done by NETL, in which process parameters such as the reaction conditions, feed pretreatment and conversion etc. are specified. Next, we have performed a scenario analysis on the TPS and SBR processes that are under development.

By analysing and comparing the five scenarios of the DAC process, we have identified the mineral pretreatment steps (especially intensive grinding) and CO₂ compression as the largest energy consumers in all cases. Whereas smaller mineral particles allow for a higher conversion of CO₂ into carbonates, the intensive grinding needed to obtain fine particles often imposes a very high electricity penalty on power plants. Similarly (but to a lesser degree), the compression of CO₂ to reaction conditions also consumes a fair amount of electricity, further increasing the electricity penalty of the DAC process. In comparison, the SBR and TPS processes have larger CO₂ penalties due to its low conversion and slurry concentration, which requires a large amount of mineral to be ground and a larger amount of water to be heated to reactor conditions. However, S1 has the potential to reduce the grinding energy by optimising the use of a ball-mill reactor, which is subject to further experiments. Considering that it is possible to increase the conversion at a lower slurry concentration such as that in S4, it is of interest to optimise the SBR process further to achieve higher conversion at lower temperatures so that the energy required for heating the reactor becomes negligible.

By analysing the scenarios, we have identified DAC5 as the most suitable of the five that we have studied. This scenario stands out among the five despite (or maybe even because of) some counterintuitive ideas in its implementation. By avoiding intensive grinding and substituting part of the mineral pretreatment energy requirements with heat instead of electricity, DAC5 has the most effective pretreatment methods compared with the other scenarios. Despite not using very fine particles and its slightly lower reaction conversion, it is the most energy efficient process and has the lowest CO₂ penalty per tonne of CO₂ captured compared with the other scenarios.

This suggests that extremely fine particles and a high conversion are not necessarily crucial or desirable attributes when

considering the best operating conditions for a DAC process. This idea is supported by the fact that it often takes increasingly more energy to grind already small particles to even finer meshes, and this effort spent on grinding is often not worth the returns in slightly higher conversions in the carbonation reaction.

To reiterate, it is important to focus our research on selection of mineral ore, minimising the electricity required by reducing the operating pressure, improving the conversion, and on minimising the heat required by the process. Amongst these, improving the conversion of large particles is of utmost importance. The ball-mill reactor shows promise in reducing the grinding energy and further investigation is necessary to quantify the electrical energy required by the process. In conclusion, the success of CO₂ mineralisation is strongly dependent on furthering research with a focus on minimisation of the CO₂ and electricity penalties.

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Conflict of interest

The authors declare no conflict of interest.

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