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Energy Procedia 4 (2011) 2494–2501

Energy Procedia

www.elsevier.com/locate/procedia

GHGT-10

Carbon capture and utilization: preliminary life cycle CO_2, energy, and cost results of potential mineral carbonation

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Abstract

Mineral carbonation has been identified as a potentially suitable means of CO_2 sequestration in Singapore due to the nation's lack of land for geological or deep ocean storage of CO_2. In this article, the total energy, CO_2 emissions and costs of mineral carbonation are investigated using a life cycle assessment (LCA) approach. The life cycle investigation took into account energy and greenhouse gas emissions from mineral mining activities and shipment, the recovery of CO_2 based on amine scrubbing technology and simulated scenarios of the net energy requirements for the carbonation process based on 'ideal' and worst case energy requirements. The CO_2 avoided results from a total of 4 scenarios were in the range of 106.9 kg to 175.9 kg per 1 MWh. The percentage sequestration effectiveness results are from 32.9% to 49.7%. The life cycle costing results are 105.6 USD/tonne CO_2 avoided and 127.2 USD/tonne CO_2 avoided for two of the most favorable scenarios. However, it is highlighted that various engineering challenges have to be overcome before the 'ideal' carbonation reaction conditions represented in the simulation model can be achieved. The results will most likely fluctuate somewhere between the ideal and worst case conditions. The main energy penalties and associated CO_2 emissions come mostly from CO_2 recovery, pre-treatment and mineralization process itself.

Keywords: Life cycle assessment; CO_2 mineralization; simulation; energy use; CO_2 avoided

1. Introduction

International concerns over global warming have identified the urgent need for large-scale sequestration, reduction, or utilization of CO_2. Any aims to effectively capture and store large volumes of CO_2 should take into account the life cycle of energy use, and overall carbon footprint of the sequestration system itself [1-2]. In Singapore, mineral carbonation has been identified as the most suitable means of CO_2 sequestration due to lack of land for geological storage and ocean territories [3-4]. Moreover, carbon sequestration via mineralization is also suggested as the safest and most stable way of locking away large amounts of CO_2 [5]. Huge deposits of alkaline-

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doi:10.1016/j.egypro.2011.02.145

earth (Mg-based) silicate minerals of the peridotite and serpentinite families exist in countries around Singapore. Two of these sources were indentified to be scattered around Kalgoorlie mining areas in Western Australia (WA) and Tasmania, Australia.

2. Mineral carbonation

A simulation study of the energy requirements for carbonation using serpentine is presented here. Thermodynamic calculations were carried out using HSC Chemistry 6.0 [6] and corrected data for $MgCO_3$ [7] to explore the possible sets of operating conditions, including the range of temperature and pressure for which the carbonation process can be feasible. The following reaction pathway was applied [8]:

$$1/3[3MgO\cdot 2SiO_2\cdot 2H_2O] \rightarrow MgO + 2/3\ SiO_2 + 2/3\ H_2O(g) \quad (1)$$
$$MgO + H_2O(g) \rightarrow Mg(OH)_2 \quad (2)$$
$$Mg(OH)_2 + CO_2(g) \rightarrow MgCO_3 + H_2O(g) \quad (3)$$

The net resultant reaction is:

$$1/3\ [3MgO\cdot 2SiO_2\cdot 2H_2O] + CO_2(g) \rightarrow MgCO_3 + 2/3SiO_2 + 2/3H_2O \quad (4)$$

The process flow diagram for the carbonation steps are shown in Figure 1. The overall process is exothermic and hence energy is released in the form of heat which is conveniently used to separate the solid products MgO and SiO_2. This assumption can be made if negligible energy input is required for separation of serpentine into MgO, SiO_2 and H_2O. The stream data for the process is documented in Table 1. The results, displayed as Figure 2, are generated by the application of pinch analysis [9]. From the grand composite curve (Figure 2), the hot and cold utilities required are 1843 MW and 3320 MW respectively. The highest amount of energy required for the carbonation process is formulated according to the hot utility shown in the graph.

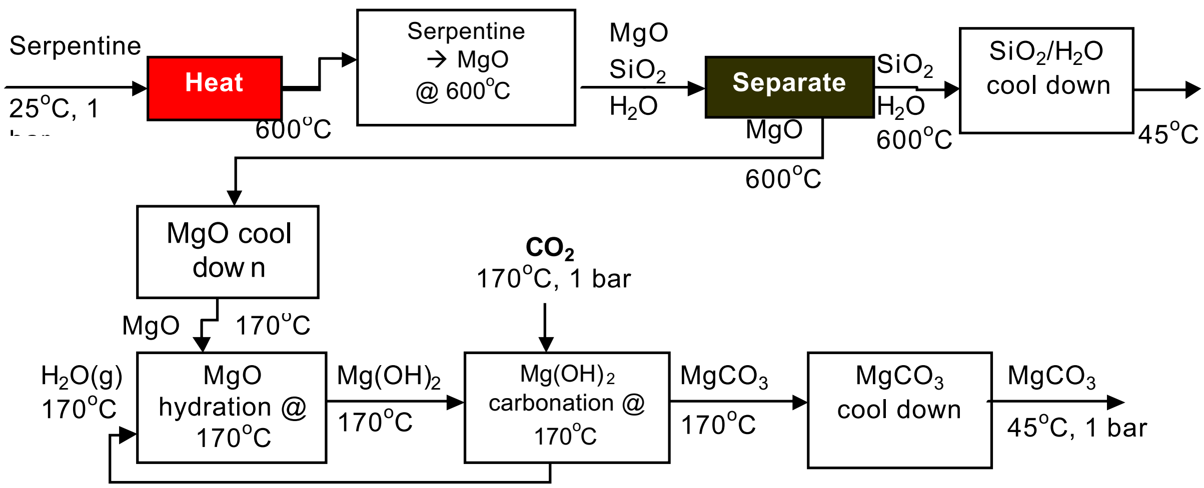

Figure 1 Block flow diagram for carbonation

Table 1 Stream data for temperature interval analysis (based on 1 tonne CO_2/s and $\Delta T = 10^oC$)

Stream		$T_{in}(^oC)$	$T_{out}(^oC)$	MCp (MW/K)	Heat Load (MW)
C1	Preheat	25	600	2.8	1596
C2	Mg-Si → MgO	600	600.5	3630	1815
H1	MgO → $Mg(OH)_2$	170	169.5	3609	-1805
H2	$Mg(OH)_2$ → $MgCO_3$	170	169.5	1727	-864
H3	$MgCO_3$ cool down	170	45	2.0	-250
H4	MgO cool down	600	170	1.1	-467
H5	SiO_2/H_2O cool down	600	45	2.7	-1503

Figure 2 Grand composite curve

The energy required for the pretreatment of serpentine was estimate with the help of the thermodynamic data reported by King et al. [10] along with the effective heat capacities and temperature provided by Penner et al. [11]. According to the authors, the energy required for pretreatment was calculated by:

$$Q = C_P \Delta T \qquad (5)$$

Where Q = heat (cal/mol); C_P = cal/Kmol @ temperature T1 (K); and ΔT = T1 – T0 (298K).

From (5), the heat treatment of serpentine at 630°C (CP = 89.26 cal/K mol) requires 206 kWh/tonnne to heat the mineral, while dehydroxylation of the mineral requires another 87 kWh/tonne. The total for energy consumption for the heat treatment process is thus 293 kWh/tonne [11].

The uptake of CO_2 by the minerals may be enhanced by taking advantage of the heat released by the exothermic carbonation reaction. Realistically, the conversion rates can be between 80-90% [4-5]. Based on the simulation results (Figures 1 and 2), the net energy requirement for mineral carbonation are as follows:

- ***Ideal case***, where it is assumed that the carbonation reaction generates enough heat energy to feed itself (energy input = energy output). The conversion of minerals to carbonate for an ideal case is taken to be 90%.
- ***Worst case scenario***, where virtually none of the heat energy can be recovered for use. Therefore the maximum net energy required is simulated to be 1850 MJ/tonne CO_2 carbonated. The extent of reaction for this case is taken as 80%.

3. Life cycle assessment

The case study of the LCA covers mineral mining, crushing and packaging of mineral rocks, before shipment to Singapore. Next the CO_2 recovery from a natural gas combined cycle (NGCC) power plant is taken into account, and finally, CO_2 carbonation. The functional unit selected is 1 MWh generated from the NGCC power plant in Singapore. The goal of the LCA is to compare the life cycle CO_2 (or carbon footprint), energy requirements and costs of mineral carbonization in Singapore for four scenarios, which are tabulated in Table 2. The life cycle system boundary, along with the input-output flow of energy and CO_2, is illustrated in Figure 3. Within the LCA system, the following activities are considered to model the energy requirements and CO_2 emissions:

- Mining, crushing and packaging of minerals from Kalgoorlie mining area in Western Australia (WA) and Tasmania, Australia.
- Shipment of mineral rocks to Singapore. The nearest ports from WA and Tasmania to Singapore are Fremantle and Melbourne. The shipment distances are 6991 and 3986 kilometers respectively.
- The recovery of CO_2 from the flue gas of an NGCC power plant based on amine scrubbing technology. The CO_2 recovery rate is 90% with an energy penalty of 16%.
- The simulated energy and extent of reaction for CO_2 mineralization are based on the 'ideal' and 'worst' cases. In both cases, the ratio of serpentine to CO_2 is considered to be 2:1.

The LCA scenarios are as follows:

1. Minerals purchased from WA and processed with 'ideal case' mineralization reaction
2. Minerals purchased from WA and processed with 'worst case' mineralization reaction
3. Minerals purchased from Tasmania and processed with 'ideal case' mineralization reaction
4. Minerals purchased from Tasmania and processed with 'worst case' mineralization reaction

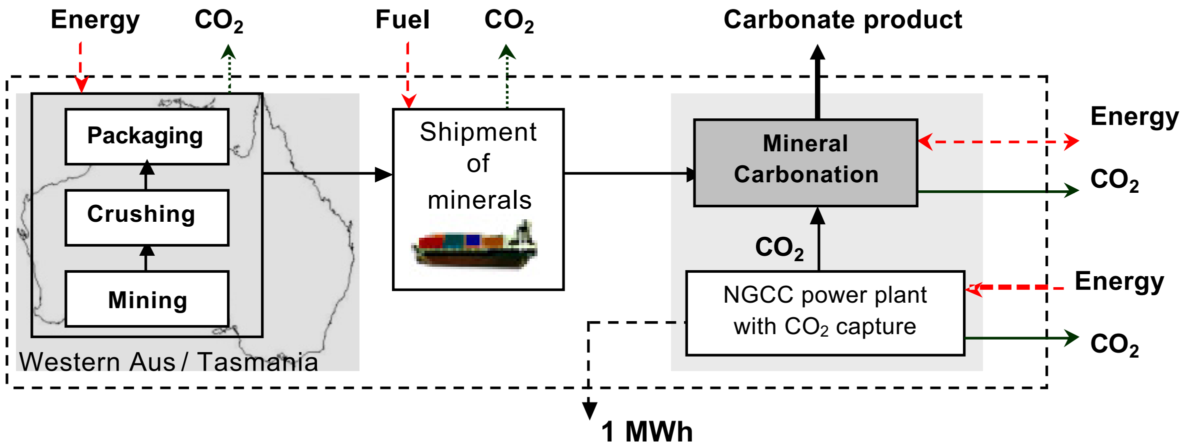

Figure 3 Life cycle stages

The energy requirements for mineral mining, crushing and packaging are extracted from EcoInvent [12] and Hangx and Spiers [13]. These total energy requirements are assumed to be similar to limestone rock mining. The associated CO_2 emissions due to energy usage differ from place to place. The CO_2 inventory is extracted from Hydro Tasmania [14] and CARMA [15]. The energy requirements of CO_2 recovery from a power plant in Singapore is calculated based on amine scrubbing utilizing monoethanolamine or MEA. The energy penalty for an NGCC power plant is 16% with CO_2 recovery rates of 90% [16]. Energy demands (electricity and heat) for amine scrubbing of CO_2 from the power plant flue gas can be as high as 3570 MJ/tonne CO_2 [17]. Carbon dioxide emissions from shipment are also taken from EcoInvent [18].

4. Results and discussions

4.1. Source of mineral

The total CO_2 from mineral sourcing and transportation is shown in Figure 4. It is observed that shipment takes up the main portions of each graph, especially for cases 3 and 4. This is due to the large transport distance travelled for the delivery of minerals to Singapore. Comparatively, emissions from mining activities are less significant. However, it should be highlighted that only CO_2 emissions were considered. A large amount of air pollution from mining activities is dust, which has a detrimental affect on human health [19]. This environmental and health concerns should be taken into consideration for further LCA studies.

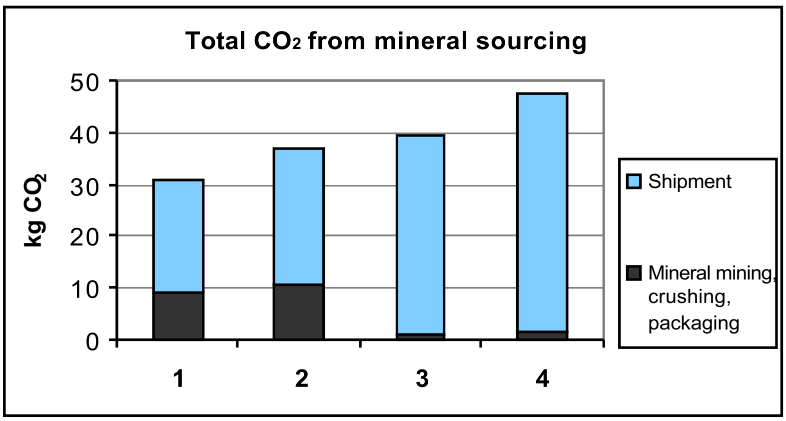

Figure 4 CO_2 from mineral mining and shipping

4.2. Life cycle CO_2 and energy use

The LCA results for CO_2 and energy use are displayed in Figure 5 and 6 respectively.

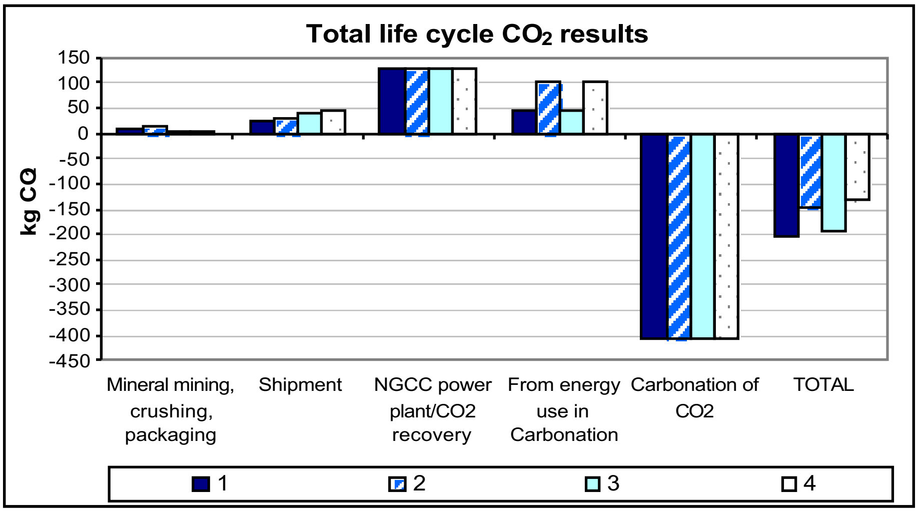

Figure 5 Life cycle CO_2 results

From Figure 5, the inverted peaks represent the amount of CO_2 carbonated and prevented from entering the atmosphere. It is observed that the most preferred case is scenario 1, where the minerals are obtained from WA and the energy requirements for carbonation is ideally supplied by the heat generated from its own exothermic reaction. It is also highlighted that the main concerns of greenhouse gas emissions are actually from, principally, the CO_2 recovery system and, next, the energy used for pre-treatment and carbonation. Compared to these two stages the emissions from mining and transportation are very much less significant. Scenario 4 turned out to be the least favorable option. The benefits are mostly reduced by the large amount of emissions arising mainly from CO_2 recovery, pre-treatment and carbonation.

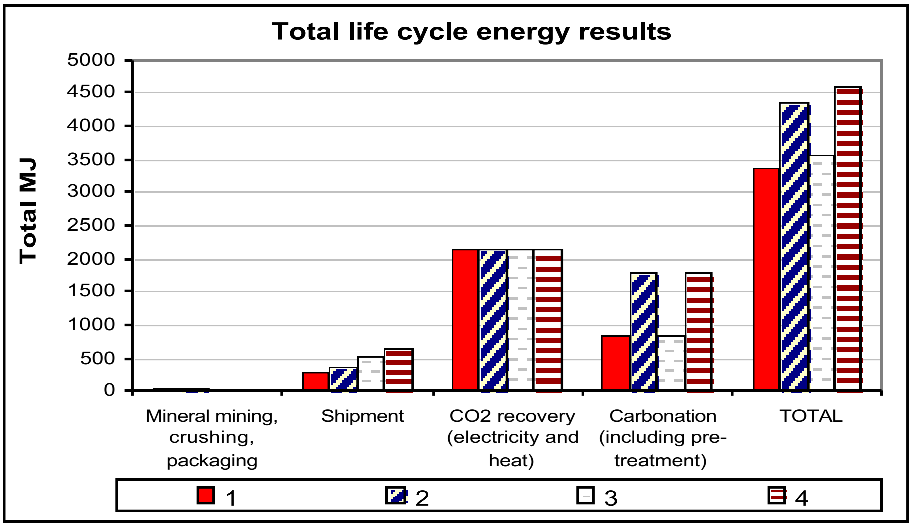

Figure 6 Life cycle energy results.

While the CO_2 emissions of Figure 5 are mostly influenced by the potential amount of CO_2 carbonated, energy use (Figure 6) is dominated by the energy requirements of the CO_2 recovery system. Before CO_2 can be carbonated, there is an intermediate step of separating and recovering it from the power plant's flue gases. Highly intensive energy demands are required for amine scrubbing of CO_2, especially for the heat regeneration process. In this article, heat energy demands of 3570 MJ/tonne CO_2 is used, but even higher energy demands of up to 4500 to 5700 MJ/tonne was reported by Harkin et al. [20] for the same CO_2 removal technology.

Energy requirements for carbonation are process-dependent and it is influenced by a wide range of parameters including the energy required to separate MgO from serpentine, heat, pressure and other reaction kinetics [7-8, 10-11]. The energy requirements for both pre-treatment and carbonation deserve further explorations and experiments to make the entire process feasible.

4.3. CO_2 voidance and percentage sequestration effectiveness

The amount of CO_2 avoided can be defined as:

$$CO_2\ avoided = NGCC_{CO2} - \Sigma\ CCS_{CO2} \quad (6)$$

Where $NGCC_{CO2}$ = amount of CO_2 emissions from NGCC power plant without any capture system in place. This value is reported to be 380 kg/MWh.

$\Sigma\ CCS_{CO2}$ = the accumulated CO_2 emissions totalled from mineral mining, transportation, CO_2 recovery and carbonation.

From here, the percentage sequestration effectiveness is calculated as:

$$\frac{Amount\ of\ CO_2\ Carbonated\ -\ [\Sigma\ CCS_{CO2}]}{Amount\ of\ CO_2\ Carbonated}\ x\ 100\% \quad (7)$$

The graphical illustration of the total CO_2 avoided is displayed in Figure 7. The results are shown in table 2.

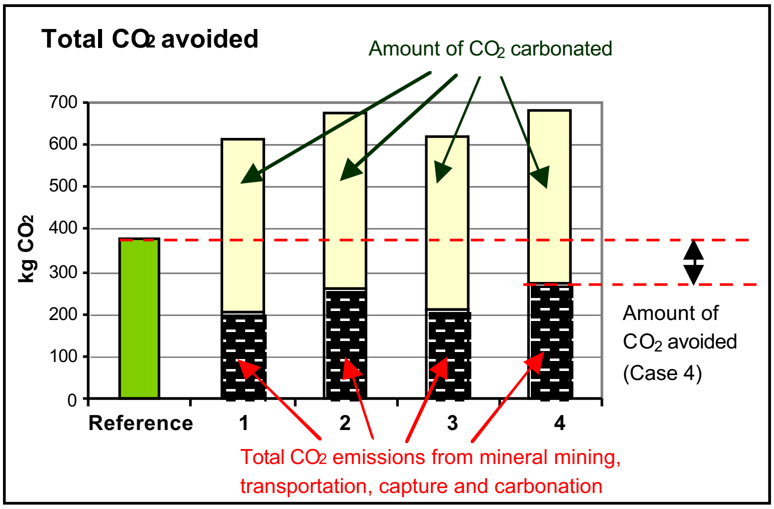

Figure 7 Amount of CO_2 avoided

Table 2 Total CO_2 avoided and percentage sequestration

Scenarios	1	2	3	4
CO_2 Avoided (kg)	175.2	117.6	166.3	106.9
Percentage sequestration effectiveness	49.7%	35.5%	47.5%	32.9%

Based on the results, scenario 4 is omitted and the costs of scenarios 1, 2 and 3 are investigated.

4.4. Simplified life cycle costs

Life cycle costing is a method that can be used to take into account the cost components of materials and energy flows within an LCA system. A simplified life cycle costing (LCC) is carried out according to the following equation:

$$\text{Life cycle cost} = C_{Capital} + C_M + R_{CO2} + C_T + C_{NG} \quad (8)$$

Where $C_{capital}$ = *capital cost of equipment, including maintenance*
C_M = *cost of minerals in USD/tonne*
R_{CO2} = *cost of CO_2 recovery from flue gas (USD/tonne CO_2)*
C_T = *cost of transportation/shipment (USD/tonne-km)*
C_{NG} = *cost of energy from natural gas for mineralization process (USD/MJ)*

Data for transportation were estimated from shipping rates, distance between ports (and subsequently the duration of time at sea), and shipping rates from Lloyd's Shipping Economist [21]. As a conservative estimate, the cost of CO_2 recovery and price of natural gas are taken from IPCC [15] and Johnson and Keith [22]. The costs of minerals were taken from U.S. geological survey [23]. The compiled costing data are shown in table 3.

Table 3 Life cycle cost data

Cost parameters			
C_M (USD/tonne)	R_{CO2} (USD/tonne CO_2)	C_T (USD/tonne-km)	C_{NG} (USD/MJ)
7	33.0	0.00018	0.003

Without considering $C_{capital}$, the results for scenarios 1, 2 and 3 are USD 88, 150 and 106 per tonne CO_2 avoided respectively. IPCC reported that $C_{capital}$ may be estimated as 20% of the total (LCC) [24]. By incorporating this cost component, the LCC results are adjusted to be 105.6 USD/tonne CO_2 avoided for scenario 1, 180 USD/tonne for 2, and 127.2 USD/tonne CO_2 avoided for scenario 3. In comparison, a report from IEA [25] on energy technologies in year 2050 suggests carbon capture and storage projects are projected to cost less than 150 USD per tonne CO_2 avoided. Hence, the cost results for all three scenarios fall within a reasonable range.

5. Conclusions and recommendations

Based on the 4 scenarios, the CO_2 recovery of 90% from the NGCC flue gas resulted in a total of 175.2, 117.6, 166.3 and 106.9 kg CO_2 avoided per 1 MWh delivered to consumers. The range of sequestration effectiveness is from 32.9% to 49.7%. Further analysis estimated the life cycle costing (LCC) results to be 105.6 USD/tonne CO_2 avoided for scenario 1 and 127.2 USD/tonne CO_2 avoided for scenario 3. From the overall results, scenarios 1 and 3 turn out to be the most favourable. However, in reality the 'ideal' conditions represented by scenarios 1 and 3 are not easily achievable. The results will most likely fluctuate somewhere between scenarios 1 and 2; or 2 and 3. Apart from simulation work focusing on thermodynamics, experimental studies should target at obtaining the optimal net energy generation in the range between these two scenarios.

The results indicate that main focus for the entire carbon capture and utilization system should primarily be on reducing the energy demands for CO_2 removal technologies [17], as well as, optimizing the use of heat energy generated by the exothermic carbonation reaction. Currently, experimental studies focusing on dry carbonation of Si and Mg silicates have been rather slow and are hindered with various engineering limitations [7-9]. One of the main goals is to optimally utilize the amount of heat produced by the carbonation reaction, which in principal, can be recovered as a high enthalpy system [26]. Another technical challenge lies in the extraction of magnesium from the minerals without the use of chemicals or high energy demands [3-5].

Apart from CO_2, LCA investigations of carbon capture and storage should also expand to include other kinds of pollution, including dusts, acidic gases, and solid wastes. Such studies are exemplified by Khoo and Tan [1-2] and Singh et al. [27]. The authors compared a wide range of environmental aspects from a myriad of options for CO_2 recovery technologies, transportation, and storages. Apart from global warming impacts alone, the environmental concerns of acidification, eutrophication, human toxicity to air and water, and solid waste were taken into account.

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