Electronic Supplementary Information (ESI) for

Emerging concepts in intermediate carbon dioxide emplacement to support carbon dioxide removal

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1. Details on materials excluded from analysis

Currently, our understanding of $SiCO_4$ is very limited and it appears that $SiCO_4$ is not thermodynamically stable under ambient conditions. High pressures of 18 GPa and temperatures of around 470 °C are needed to form $SiCO_4$ from SiO_2.[1] Aluminium carbonate has some uses in medicine, where $Al_2(CO_3)_3$ is used as an anti-acid for acid reflux, stomach inflammation, and ulcers; however, chemists argue that it only exists in solution and decomposes into $Al(OH)_3$ and CO_2 when trying to isolate it. Iron(II) carbonate commonly forms on steel and iron surfaces leaving an iron carbonate scale. Its CO_2 mass fraction is 38.0 CO_2 wt.-% and its CO_2-density is 1482 kg/m^3. $FeCO_3$ can be regenerated upon heating the salt to 500–733 °C which results in the formation of Fe_3O_4 and a mixture of CO and CO_2.[2] Closing the carrier loop with iron is more challenging compared to alkaline earth metals as Fe_3O_4 does not readily react with CO_2. The Fe_3O_4 would need to be converted to $FeCl_2$ or elemental iron in order to close the carbonate loop. The existence of pure titanium carbonate is not sufficiently documented and might only exist in a meta stable form. Manganese carbonate is a common fertilizer and food additive with a CO_2 mass fraction of 38.3 CO_2 wt.-% and a CO_2-density of 1195 kg/m^3. Upon heating to 100–300 °C in an oxygen free atmosphere, $MnCO_3$ decomposes into MnO and CO_2. However, in the presence of O_2, MnO oxidizes to the more stable MnO_2. Converting MnO back to carbonate without air exposure will be challenging. No information on bicarbonates were found for Si, Al, Fe, Ti and Mn compounds. Ammonium carbonate has a relatively high CO_2 mass fraction with 45.8 CO_2 wt.-% and a CO_2-density of 687 kg/m^3 despite its low overall density of 1500 kg/m^3. Problematic for the storage of $(NH_4)_2CO_3$ is that it slowly decomposes at standard temperature and pressure to form bicarbonate (when exposed to air) or directly NH_3, CO_2 and H_2O. Ammonium bicarbonate has a slightly higher CO_2 mass fraction with 55.7 CO_2 wt.-% and a CO_2-density of 883 kg/m^3; however, $(NH_4)HCO_3$ decomposes at temperatures around 36 °C,[3] which makes both, $(NH_4)_2CO_3$ and $(NH_4)HCO_3$, not very suitable for CO_2 storage.

Strontium and barium carbonate are very dense compounds with high molecular masses. Their CO_2 mass fractions, and CO_2-densities are 29.8 CO_2 wt.-% and 22.3 CO_2 wt.-%, and 1043 kg/m^3 and 956 kg/m^3 respectively. The reaction enthalpies of the regeneration of these two carbonates are high (234.5 kJ/mol and 243.5 kJ/mol) which is detrimental from an energy efficiency perspective but hints at faster reaction kinetics of the CO_2 fixation process. Also, the CO_2 regeneration temperatures are high.[4,5]

Methane can also be generated from CO_2 and H_2, but as a gas it also comes with its own transportation issues, and is excluded from this analysis. Ethanol is also not included, as it is expected to be derived from biomass and not directly from CO_2. Carbon dioxide can also react directly with elemental magnesium to form a carbon soot and magnesium oxide, but conversion back to CO_2 from elemental carbon would not be logical given the stability of carbon and the oxygen required.

Finally, ammonia is another H_2 carrier, which can react with CO_2 to form urea giving 73.3 CO_2 wt.-% (with the understanding CO is transported) under harsh conditions in a well-established production process (Equation 1).[6] Urea has a very low density (0.73 kg/m^3) and would be transported as a liquid. Urea's upstream ammonia production via the Haber-Bosch process requires high temperatures and pressures, which in combination require over 2% of the world's energy consumption.[7] Therefore, developing novel pathways to produce urea under milder conditions (i.e., atmospheric) or from wastes and flue gas with less energy input, has been the focus in recent years.[8–10] Urea has wide use in the industrial and agricultural sectors, as resin and fertilizer. Similar to methanol, the urea market is approximately 200 Mt globally.

$2NH_3 + CO_2 \rightleftharpoons NH_2OCONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$ Equation 1

Hydrogen production from urea is theoretically feasible via processes such as urea electrolysis.[11] Research has focused on ways to recover H_2 from the precursor ammonia, but so far the cracking of ammonia remains a challenge. However, if this challenge is solved, it is unclear what value would come from delivering CO_2 by way of urea. Lastly, due to the energy intensity of generating ammonia, and as the use of urea and nitrogen fertilizers can produce the greenhouse gas emission N_2O, rigorous life-cycle evaluation of the urea-based CO_2 storage pathways need to be evaluated.[12]

2. Storage Tank Specifications

Table S1. Storage tank or silo parameters used to estimate land footprint and number required. LCO_2: cryogenic liquid CO_2. FA: formic acid.

	Weight Capacity kg	Volume Capacity m³	Height m	Diameter m	Safety Spacing m	Reference
Bulk solids	50,000	28	1.5	3	3	approximated
Bulk solids	~15,000,000	8,483	27	20	15	[1]
LCO_2	30,000	27	8.3	2.4	2.4	[2]
LCO_2	100,000	110	11.9	4	4	approximated
Methanol/FA	30	28	1.5	3	15	approximated
Methanol/FA	10,932,600	15,618	21	32	50	Cal Jet gasoline T-4 tank

3. Additional Results of Transportation Analysis

This study conducts a first order analysis of the storage and transportation of carbon dioxide by means of pipeline, cryogenic liquid trucks, solid and liquid chemical carrier materials-based trucks, and adsorption-based trucks transporting CO_2 using MOF-packed trailers. A scenario was modelled where a region has 1 million tonnes of CO_2 capture per year that requires truck or pipeline transportation (Table S2). For pipeline, CO_2 is assumed to be transported at 150 atm and 40 °C. Liquid CO_2 is transported at 22 atm and -18 °C, giving 1022 kg/m^3. Metal-organic framework-packed trailers store CO_2 at 55 atm and 25 °C. The number of trucks, and diesel consumed in the transport of this mass of CO_2 was estimated for candidate materials. The emissions associated with transportation were estimated to understand the

[1] Example bulk storage tank for mineral powder and gravel. 15,000 tons coal storage silo in Xinyang, China. www.silobuilder.com/project/six-silos-built-in-xinyang.html

[2] Example polyurethane insulated CO_2 storage tank. www.ascoco2.com/us/co2-and-dry-ice-equipment/co2-storage/polyurethane-insulation-co2-storage-tank

distance that could be travelled by truck before the stored CO_2 in the truck was exceeded by the direct emissions from diesel consumption. We refer to this as the breakeven distance.

Table S2 Key results of the CO_2 transportation analysis for a 1 $MtCO_2$/year regional hub for candidate materials, liquid CO_2 trucks (LCO_2), and pipeline. Modes of transport are sorted by break-even distance, which is how far a truck could travel before emitting more CO_2 that it carries and how far a pipeline could carry CO_2 at a rate of 1 $MtCO_2$/year before the emissions associated with recompression would exceed the amount transported.

Parameter	Gross weight (outbound)	Gross weight (inbound)	CO_2 transported	Number of trucks needed	Energy intensity	Break-even distance
	tonne/truck	tonne/truck	tonne/truck	trucks/day	MJ/tCO_2-km	km
Pipeline	-	-	-	-	0.15	63,358
Methanol	70	18	71.5	39	0.46	30,640
Formic acid	70	18	49.7	56	0.67	21,315
Oxalic Acid	70	19	49.5	56	0.68	21,076
LCO_2 trucking	70	21	49.0	56	0.69	20,662
Future MOF	66	28	38.6	71	0.89	16,037
MOF	52	28	24.2	114	1.32	10,822
$NaHCO_3/NaOH$	70	43	26.5	104	1.42	9,996
$MgCO_3/MgO$	70	44	26.4	104	1.43	9,954
$MgCO_3/Mg(OH)_2$	70	54	26.4	104	1.50	9,466
$CaCO_3/CaO$	70	48	22.3	123	1.73	8,227
$CaCO_3/Ca(OH)_2$	70	57	22.3	123	1.80	7,891
$NaHCO_3/Na_2CO_3$	70	51	13.3	207	2.95	4,818

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