

CARBON DIOXIDE DISPOSAL IN CARBONATE MINERALS[†]KLAUS S. LACKNER^{†,§} & CHRISTOPHER H. WENDT[¶]
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Abstract – We introduce a safe and permanent method of CO₂ disposal based on combining CO₂ chemically with abundant raw materials to form stable carbonate minerals. Substantial heat is liberated in the overall chemical reaction so that cost will be determined by the simplicity and speed of the reaction rather than the cost of energy. Preliminary investigations have been conducted on two types of processes, involving either direct carbonation of minerals at high temperature or processing in aqueous solution. Promising raw materials are identified in both cases. For aqueous processing, a chemical cycle employing well-known reactions is proposed for digesting and carbonating the raw material. Cost estimates, based on comparison with standard industrial and mining practice, are encouraging. Necessary raw materials are surveyed and vast quantities are found to be easily accessible. Amounts are sufficient to allow utilization of the large known fossil-fuel reserves while avoiding build-up of atmospheric CO₂.

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1. Introduction

The available reserves of fossil fuels are sufficient to provide energy for centuries to come.¹⁻³ However, there is a serious concern that long term use of increasing amounts of fossil fuels will cause significant climate changes.⁴⁻⁸ This concern arises from the inevitable production of CO₂, which traditionally has been disposed of by dilution in air. In response, a variety of schemes for collection and disposal of CO₂ have been investigated recently.⁹⁻¹³ It appears that the disposal issue is the more difficult one. All of the proposed schemes involve the long term storage of CO₂ in solid, liquid or gaseous form. Given the very large volumes of CO₂ produced and the fact that storage would have to be permanent, a major concern about these schemes is the possibility of an accidental release, a possibility with serious consequences, as demonstrated in past natural disasters.¹⁴ The essential difficulty is that CO₂ is a gas at atmospheric pressure and ambient temperature, and therefore it can only be prevented from mixing with the atmosphere by creating and maintaining a physical barrier between the two.

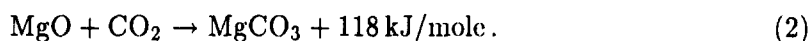
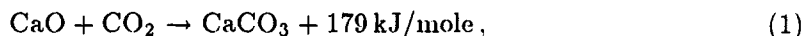
Here, we introduce an alternative, safe and permanent method of CO₂ disposal that is based on the chemical fixation of CO₂ in the form of carbonate minerals. There is no possibility of CO₂ release from the disposal site, because it will be chemically incorporated into a mineral substance which remains naturally in the solid state. In fact a substantial amount of energy would be required to regenerate CO₂ from the mineral substance, which is chemically equivalent to calcite, magnesite or dolomite. These minerals already exist in very large quantities at the earth's surface, and they are known to be stable on time scales of millions of years. Furthermore, from the same facts that imply energy would be required to regenerate CO₂, it is clear that heat energy is given off in the process of forming the carbonate mineral. This makes the prospect of a cost-effective implementation plausible. The situation is in marked contrast to schemes that recycle CO₂ back into carbon plus oxygen,¹⁵ which require at least as much energy input as was obtained from the original combustion process that produced the CO₂.

The minerals formed in disposing of CO₂ will be calcium and magnesium carbonates. We discuss fundamental chemical processes that could be used to form these minerals artificially. We argue that the necessary raw materials are available in vast quantities, far exceeding the known fossil fuel reserves. As already stated, the exothermic nature of the carbonation reaction implies that all the processes we outline are net energy producers. Therefore the main constraint for a cost-effective implementation is the speed of the reaction. We compare two basic approaches to achieving the necessary reaction rate: solid-gas reactions of raw materials at high temperature and reactions in aqueous solution. For the latter case we propose a cycle based on well-known chemical reactions, in which the only net inputs are CO₂ and readily available minerals. By comparing to industrial mining and refining processes it appears that costs could be held to a reasonable level.

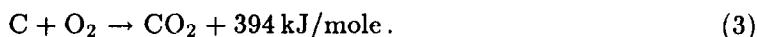
While the availability of such a technology may be considered an insurance policy in the short run, in the long run greatly increased use of fossil fuels could render it absolutely necessary.

2. Chemical Fixation of Carbon Dioxide

In the presence of CO₂, minerals containing substantial amounts of magnesium oxide or calcium oxide can undergo a carbonation reaction. The basic reactions are exemplified by the oxides of Ca and Mg,



The energy released in these reactions is substantial; it may be compared with the main power-producing reaction in the burning of fossil fuels, *viz.*,



Pure calcium and magnesium oxides are rarely found in nature, but many common minerals may be regarded as a chemical combination of these oxides with others to form a silicate matrix. The chemical binding into the matrix reduces the energy released in the carbonation reaction but does not change its exothermic character.

Calcium and magnesium are the only common elements that form stable carbonate minerals. The alkali carbonates are excluded on the grounds that they are readily soluble in water. The remaining alkali earths form stable carbonates but are too rare for practical consideration. Of the other common elements only iron forms a carbonate which is at least marginally stable.

The carbonation of calcium and magnesium bearing minerals is common in nature, although it occurs on geologic time scales. Similarly, artificial materials like cement gradually carbonate over periods of years.¹⁶ The challenge is to speed up these natural reactions to the point where CO₂ can be fixated at the same rate that it is generated in the burning of fossil fuels.

3. Raw Materials

In order to bind large quantities of CO₂ economically, it is necessary to start with common rocks that are rich in magnesium or calcium. Of course we rule out limestone, dolomite and magnesite because they are already carbonated. In contrast, igneous rocks are essentially free of carbonates.

Table 1. Amounts of Mg- or Ca-bearing rock required to bind chemically the CO₂ released in the combustion of carbon. R_C is the mass ratio of rock to carbon burned. R_{CO_2} is the corresponding mass ratio of rock to CO₂. The MgO and CaO fractions are taken from Ref. 17 except for serpentinite which is from Ref. 18.

Rock		MgO, wt%	CaO, wt%	R_C	R_{CO_2}
Peridotites	Dunite	49.5	0.3	6.8	1.8
	Harzburgite	45.4	0.7	7.3	2.0
	Lherzolite	28.1	7.3	10.1	2.7
Serpentinite		~40	~0	~8.4	~2.3
Gabbro		~10	~13	~17	~4.7
Basalt	Continental tholeiite	6.2	9.4	26	7.1

Ultramafic igneous rocks contain large amounts of magnesium oxide bound into a silicate structure.¹⁷ The richest is dunite with about 50% magnesium oxide by weight. Peridotites in general are similar but slightly less rich on average, as are the serpentinites commonly associated with them. Basalt and gabbro incorporate on the order of 10% each of calcium and magnesium oxides. Many other igneous rocks contain calcium and magnesium oxides but only at a level of 5% or less.

The amount of calcium oxide required to bind the CO₂ produced in burning one ton of carbon is 4.7 t. In the case of magnesium oxide, 3.4 t are required per ton of carbon. For rocks which are composed only in part of these oxides the corresponding scale factors are shown in Table 1.

Peridotite, serpentinite, gabbro and basalt are all found in large amounts as components of ophiolite complexes.¹⁹⁻²¹ Many of these complexes are believed to represent slices of ancient oceanic crust and upper mantle which have been incorporated into the continental crust. In North America the main examples are in the mountains of the Pacific Northwest and of the Northeast, although smaller occurrences can be found elsewhere. The Klamath mountains of northern California alone contain exposed peridotite slabs covering a total area of about 1000 km² with thickness of order 1 km,^{22,23} corresponding to a mass of 3000 Gt. Similar, or even much larger, deposits occur elsewhere in the world. The total accessible amounts of peridotite and serpentinite are therefore expected to significantly exceed the worldwide coal reserves which are estimated to be 10,000 Gt.^{2,3}

Another large source of CaO and MgO is provided by continental flood basalts. A typical example is the Columbia River flood basalt of North America, which forms a sheet,

200,000 km² in area, with an average thickness of 1 km.²⁴ Even considering that this rock contains calcium and magnesium oxides at only the 15% level, this single deposit would allow the binding of CO₂ from 23,000 Gt of coal. The annual world-wide fossil carbon consumption is presently about 6 Gt.^{2,8}

Volcanic glasses and zeolites might be of interest because the Ca and Mg are chemically more accessible than in most minerals, as we shall discuss in the next section. Although mineable deposits of these materials are known, they are not large compared to coal deposits. Most of them have the further disadvantage of a low concentration of calcium and magnesium oxides.

While Ca- and Mg-bearing minerals are available in abundant quantities, it is likely that only certain minerals can be processed economically. Thus, a detailed comparison of mineral availabilities will be most useful once a detailed design is in place for processing. For now our conclusion is that a number of calcium and magnesium bearing minerals exist in abundances far exceeding that of fossil fuels, and some of these are quite rich in magnesium.

4. Processing Methods

There are two approaches to the carbonation of calcium and magnesium oxides: (a) direct carbonation, which binds CO₂ from its gaseous form with minerals in the solid state, and (b) aqueous processes which extract magnesium and calcium ions from minerals into solution, followed by precipitation of either the carbonate or an intermediate product which is carbonated in a separate step. The advantage of the direct carbonation approach is its inherent simplicity. However, if the reaction kinetics in direct carbonation processes are unfavorable, then the aqueous approach may be preferred.

4.1. Direct Carbonation at High Temperature

The carbonation reaction with gaseous CO₂ proceeds very slowly at room temperature. The reaction accelerates with increased temperature. However, if the temperature is raised too much the chemical equilibrium shifts so that free CO₂ is favored over the bound form. By comparing the free energies of the reactants and reaction products, we can estimate the highest allowable temperature that still allows spontaneous binding of CO₂. This temperature is a function of the partial pressure of the CO₂ in the reactor.

Figure 1 shows the free energy of formation of calcium and magnesium carbonates from the oxides as a function of temperature, for two different pressures. At each temperature, the free energy change $\Delta G(T, P)$ is defined in terms of the standard free energy change,

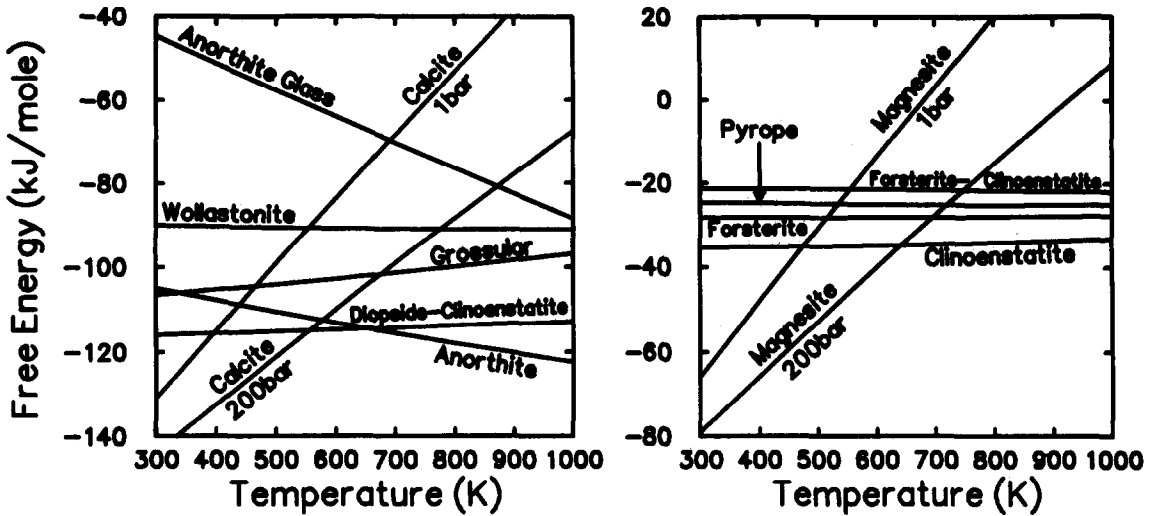
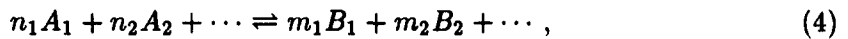


Fig. 1. The free energies of formation of carbonates and of common Ca- and Mg-bearing minerals, plotted as function of temperature. Free energies are given relative to the oxides, CaO, Al₂O₃, SiO₂, and CO₂, rather than relative to the elements. The first panel shows Ca-bearing minerals, the second Mg-bearing minerals. To facilitate the comparison, all free energies are normalized with respect to one mole of reacting CaO or MgO. The free energy change in the carbonation reaction of a mineral is given by the difference in free energy of the mineral and that of the carbonate (calcite or magnesite). The free energy of the carbonate depends on the partial pressure of CO₂ and is plotted for pressures of 1 bar and 200 bar. If the free energy difference is negative, which requires low temperatures, the reaction will proceed spontaneously towards the carbonate, whereas at higher temperatures the free energy difference changes sign and the reaction proceeds towards the oxides.

$\Delta G_0(T)$, at 1 bar and the activities of the reactants and products. For a reaction of the form



it is given by

$$\Delta G = \Delta G_0 + RT \log \left(\frac{[B_1]^{m_1} [B_2]^{m_2} \dots}{[A_1]^{n_1} [A_2]^{n_2} \dots} \right). \tag{5}$$

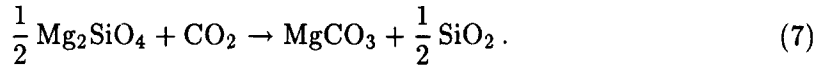
If ΔG is negative, the reaction proceeds spontaneously to the right. In our case, the only activity that differs substantially from unity is that of CO₂, *i.e.*

$$[CO_2] = P_{CO_2} / 1 \text{ bar}. \tag{6}$$

In the case of calcium oxide at 1 bar of CO₂ pressure, the free energy change in the carbonation reaction is negative for temperatures less than 1160 K and therefore favors

the binding of CO₂. At higher pressures the allowable temperature is substantially larger, *e.g.* at 200 bar it is 1670 K. The corresponding equilibrium temperatures are lower for magnesium oxide (680 K at 1 bar and 930 K at 200 bar).

The equilibrium temperatures can be calculated in a similar fashion for direct carbonation of common minerals containing magnesium or calcium oxide. For example, in Figure 1 the free energy of formation from the oxides is shown for magnesite (MgCO₃) and forsterite (Mg₂SiO₄) which is the major constituent of peridotite rock. For the latter the free energy represents the binding of the magnesium oxide into the forsterite structure. It must be accounted for in the overall carbonation reaction



The difference between the free energies for magnesium carbonate and forsterite gives the change in free energy for the overall reaction. (By definition the free energies of CO₂ and SiO₂ are zero.) The equilibrium temperature is therefore given by the intersection point of the two lines, which occurs at 515 K for $P_{\text{CO}_2} = 1$ bar. For temperatures lower than this the carbonation reaction proceeds spontaneously.

In some carbonation reactions the product oxides may also be bound into a silicate structure. In such a case the free energy of the bound state, relative to the simple oxides, should be taken into account. This is a very small effect for the common case where silicon and aluminum oxides are produced together and it is therefore neglected in most reactions. However, the effect is larger in cases with uncarbonated calcium or magnesium among the products (partial carbonation). For example, in some temperature ranges a partial carbonation of forsterite is thermodynamically favored, producing enstatite plus magnesite as follows:



For this case, the difference in free energies, relative to oxides, is shown in figure 1 for forsterite minus enstatite, and the equilibrium temperature may again be read off from the intersection with the magnesite curve.

Thermodynamic data are available for a number of abundant calcium and magnesium bearing minerals, and have been used to estimate the maximum carbonation temperatures shown in Table 2. Also included are the simple oxides and hydroxides of calcium and magnesium. It is apparent that although the equilibrium temperatures T_{max} for pure calcium and magnesium oxides differ by 600 K, the corresponding difference between calcium and magnesium bearing minerals is much smaller. This may be attributed to a stronger binding of calcium oxide into the silicate structure. Another important consequence of

Table 2. Thermodynamic properties of carbonation reactions, based on data from Ref. 25. T_{\max} is the maximum carbonation temperature for $P_{\text{CO}_2} = 1$ bar. Where applicable, T_{deh} refers to the dehydroxylation temperature, estimated from the equilibrium point with $P_{\text{H}_2\text{O}} = 1$ bar. The enthalpy of reaction, $\Delta H(T_{\max})$, is normalized to one mole of CO_2 and is corrected for heat of dehydroxylation when appropriate. The heat ΔQ is the energy required to heat the original mineral and CO_2 to the higher of T_{\max} and T_{deh} , normalized to one mole of CO_2 . The initial temperature is assumed to be 298K. In cases where dehydroxylation occurs at a lower temperature than the carbonation, the mineral is replaced with its dehydrated form after the dehydroxylation temperature is reached. It is assumed that the released water escapes and that it is not heated to T_{\max} .

Mineral and Carbonation Reaction		T_{deh} K	T_{\max} K	ΔH kJ/mole	ΔQ kJ/mole
Calcium Oxide	$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$	—	1161	-167	87
Magnesium Oxide	$\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$	—	680	-115	34
Calcium Hydroxide	$\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	791	1161	-68	114
Magnesium Hydroxide	$\text{Mg}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O}$	538	680	-37	46
Wollastonite	$\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2$	—	554	-87	37
Clinoenstatite (Pyroxene)	$\text{MgSiO}_3 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{SiO}_2$	—	474	-81	23
Forsterite (Olivine)	$\frac{1}{2}\text{Mg}_2\text{SiO}_4 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{1}{2}\text{SiO}_2$	—	515	-88	24
Diopside (Pyroxene)	$\frac{1}{2}\text{CaMg}(\text{SiO}_3)_2 + \text{CO}_2 \rightarrow \frac{1}{2}\text{CaCO}_3 + \frac{1}{2}\text{MgCO}_3 + \text{SiO}_2$	—	437	-71	19
Grossular (Garnet)	$\frac{1}{3}\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \frac{1}{3}\text{Al}_2\text{O}_3 + \text{SiO}_2$	—	465	-67	28
Anorthite (Feldspar)	$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$	—	438	-81	39
Anorthite Glass	$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$	—	691	-148	121
Pyrope (Garnet)	$\frac{1}{3}\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{1}{3}\text{Al}_2\text{O}_3 + \text{SiO}_2$	—	533	-92	40
Talc	$\frac{1}{3}\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{4}{3}\text{SiO}_2 + \frac{1}{3}\text{H}_2\text{O}$	712	474	-44	64
Tremolite (Amphibole)	$\frac{1}{7}\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + \text{CO}_2 \rightarrow$ $\frac{2}{7}\text{CaCO}_3 + \frac{5}{7}\text{MgCO}_3 + \frac{8}{7}\text{SiO}_2 + \frac{1}{7}\text{H}_2\text{O}$	839	437	-37	72
Chrysotile (Serpentine)	$\frac{1}{3}\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{2}{3}\text{SiO}_2 + \frac{2}{3}\text{H}_2\text{O}$	808	680	-35	78

this binding is the difference between anorthite (CaAl₂Si₂O₈) and the amorphous solid of the same chemical composition, labeled "anorthite glass." Anorthite is very stable and carbonates spontaneously only at temperatures below 440 K for $P_{\text{CO}_2} = 1$ bar, whereas the corresponding temperature for its glass analog is 690 K. Such a large difference in allowable operating temperature will likely have a strong effect on the achievable reaction rate.

Some examples in Table 2 are complicated by the fact that upon heating to the temperature range of interest, the mineral loses chemically bound water and changes its crystal structure, prior to carbonation. The temperature at which this dehydroxylation occurs is shown as T_{deh} , and can be either above or below the maximum carbonation temperature. For the calculation of T_{deh} it is necessary to specify the intermediate product formed by dehydroxylation, but this can depend on poorly understood kinetic factors. In the cases of amphibole and talc, we have assumed that dehydroxylation results in the intermediate formation of simple minerals (diopside, clinoenstatite and quartz) that satisfy the stoichiometric constraints and that result in a low T_{deh} . In the case of serpentine we used the free energies corresponding to the intermediate formation of silica and magnesium oxide. In the former case the large binding energy of oxides into the minerals precludes the formation of separate oxides while in the latter case experimental evidence suggests that an amorphous mixture of the two oxides is actually produced.¹⁸

Table 2 shows that the two minerals common in peridotite rock, forsterite and pyroxene, do allow use of increased temperature to promote carbonation reactions. We also considered partial carbonation reaction for these minerals (see Fig. 1), but they are not listed in the table. Although kinetics may favor one of the partial carbonations, thermodynamically they result in carbonation temperatures and energy releases that are similar to those listed.

Serpentine has an advantage over forsterite and pyroxene because it contains chemically bound water which is rapidly driven off at temperatures above 870 K, leaving behind a metastable non-crystalline amorphous material with greatly increased chemical reactivity.¹⁸ After cooling to a lower temperature, this increased reactivity should allow the subsequent carbonation to proceed quickly. Similar to the case of the amorphous analog of anorthite, discussed earlier, it is expected that the maximum carbonation temperature of this amorphous material is well above that of forsterite. We therefore estimate it from the carbonation temperature of magnesium oxide. If dehydroxylation indeed leads to the equivalent of simple oxides MgO and SiO₂, dehydroxylation and carbonation could be performed in a single process at one temperature. Based on the available thermodynamic data, this would require operation at a CO₂ pressure of approximately 20 bar.

The increased chemical reactivity observed in dehydrated serpentine may also be expected in other minerals containing chemically bound water. A prime example is zeolite,

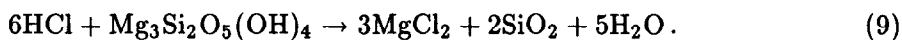
which takes up CO₂ readily after water has been removed by heating.²⁶⁻²⁸ The advantage of zeolites is that the hydration and carbonation proceeds quickly, even at low temperatures and low pressures. However sufficiently large amounts of calcium and magnesium rich zeolites appear to be unavailable.

In all cases, the energy released in the carbonation process could be used to heat the reactants up to the process temperature. Table 2 shows the amount of heat released for each mineral, corrected for heat of dehydroxylation where appropriate. Also listed is the heat required to raise the temperature of the reactants from room temperature to the maximum process temperature. In some cases, for example that of serpentine, the energy required for heating exceeds the heat released in the reaction. Nevertheless, the process could be made energy self-sufficient if the heat extracted from the reaction products is used to heat additional reactants. In the case of serpentine at least 55% of the heat invested must be recovered in the cooling step.

The maximum reaction rates achievable for direct carbonation of the various minerals are not yet known. The thermodynamic constraints of Table 2 indicate however that at least for some cases, high temperatures can be used to speed the reactions. CaO is known to be carbonated on a time scale of 1 min at temperatures above 550°C.²⁹ Experiments are underway to measure the carbonation rates as a function of temperature for the pure oxides, hydroxides and minerals containing calcium or magnesium. Our preliminary results for CaO, Ca(OH)₂ and Mg(OH)₂ have demonstrated carbonation at temperatures consistent with predictions from the thermodynamic estimates.^{30,31}

4.2. Aqueous Chemistry

As an alternative to the direct carbonation of minerals discussed so far, the magnesium and calcium content could first be extracted in aqueous solution. This option may provide more favorable reaction rates. The extraction could proceed by way of various agents, such as hydrochloric acid, caustic soda, sulfuric acid or steam. For example, serpentine dissolves quickly in hydrochloric acid, forming magnesium chloride in solution and leaving behind silica gel,^{18,32} *i.e.*

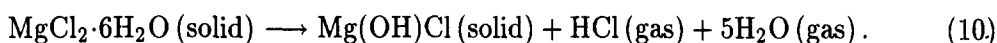


Similarly, ground olivine decomposes in hydrochloric acid while releasing enough heat to maintain boiling temperature, a process used in a pilot plant for magnesium manufacture from olivine.³³ Subsequently, the carbonation could proceed by precipitating calcite and magnesite from the solution by addition of CO₂ or the precipitation of calcium and magnesium hydroxides followed by dry carbonation in a separate step. The latter possibility is attractive because it would allow one to perform the carbonation step at a relatively high

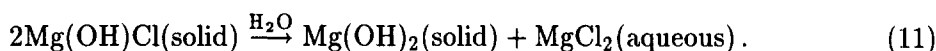
temperature. As a result, the heat released in the exothermic carbonation reaction is not lost but can be used in the other steps of the processing chain.

Whatever agent is used to extract the magnesium and calcium from the mineral, it must be easily recoverable at the end of the process. Furthermore, because of inevitable losses, it must not be expensive. These considerations lead us to focus on hydrochloric acid.

In the case of HCl, it is straightforward to regenerate the acid after dissolving the magnesium or calcium component of the rock. In the case of a magnesium bearing rock, acid is consumed in treatment of the rock to produce magnesium chloride in solution. This solution also contains excess acid. After boiling off the water and excess acid, heating to 150°C results in decomposition of magnesium chloride, regenerating the hydrochloric acid, *i.e.*



After solution in water, Mg(OH)Cl repartitions as follows:



The magnesium chloride is again cycled through the acid recovery step whereas the magnesium hydroxide precipitate is ready for carbonation. This part of the process is used industrially in the production of Mg(OH)₂ plus HCl from MgCl₂ which in turn has been extracted from seawater.³⁴ In the present case, HCl is cycled back to the mineral decomposition step. Since Mg(OH)₂ is the only substance removed from our overall process cycle, it is clear that no net HCl is consumed.

The carbonation of Mg(OH)₂ in a separate step releases substantial heat which could drive the other steps. Carbonation would proceed in analogy with direct carbonation of serpentine, already discussed: dry Mg(OH)₂ is heated in an atmosphere of CO₂ to a temperature of approximately 680 K. Thermodynamically, the carbonate is favored over the hydroxide and the resulting reaction to form MgCO₃ plus water vapor evolves a substantial amount of heat, as seen in Table 2. Our preliminary experimental evidence indicates that the kinetics of this process is quite favorable.

If CaCl₂ is extracted from the original mineral, either in place of or in addition to MgCl₂, an additional step is necessary. The solution, which contains CaCl₂ and excess acid, is first neutralized by addition of Mg(OH)Cl. This leads to the precipitation of Ca(OH)₂ which is carbonated in a separate step. Remaining behind is magnesium chloride which is processed in the fashion described above.

An obvious complication occurs when the raw mineral contains appreciable amounts of sodium or potassium. In this case, acid is consumed in the formation of sodium or

potassium chlorides. In contrast to the case of magnesium or calcium chloride it is difficult to regenerate the acid consumed in this way. A preprocessing step intended to leach out alkali elements could be used to solve this problem. In any case, two of the most promising materials, peridotites and serpentinites, are virtually free of alkali contaminants. This is in contrast to other rocks containing magnesium or calcium, *e.g.* basalt and gabbro, which always contain significant amounts of sodium and potassium. Contamination with small amounts of iron does not result in net losses of acid.³³

The aqueous chemistry approach is clearly more complex than direct carbonation. However, a cycle like the one we have described shows promise because the individual steps are simple and apparently fast, and in fact most are already used by industry.

5. Implementation and Economics

Given the large amounts of rock which must be mined and processed for CO₂ fixation (Table 1), it is certainly a challenge to hold costs down to an acceptable level. Whether this challenge can be met cannot be answered before a large-scale implementation is designed and a detailed cost estimate is produced. This in turn should be deferred until laboratory work identifies the most promising processes. At that point, the costs must be considered in the context of other power generation costs and the possible long-term benefits of eliminating CO₂ emissions into the atmosphere. Particularly the latter is subject to changing knowledge and attitudes. For the present, however, it is worthwhile to compare CO₂ fixation to other large-scale mining and chemical operations in order to make a crude guess at costs.

Because other techniques are available for marginal reductions in CO₂ emissions, some at very low cost,³⁵ we regard CO₂ fixation primarily as an option to be used in case it is later decided that more drastic CO₂ reductions are necessary. In principle past emissions of CO₂ could even be compensated by direct removal from the atmosphere. If the increased energy needs in the coming centuries are to be met by burning the large reserves of fossil fuels, CO₂ disposal technology will certainly be needed. Society may be willing to pay a fairly high price for it, such as a factor of two or three increase in the base price of electricity. For example, if a severe global warming trend in the future is attributed to CO₂ buildup then one may justify cost increases in part by comparison to potentially large economic losses caused by the warming.

We are addressing only the CO₂ fixation process. There are additional costs associated with extracting, concentrating, and shipping of CO₂ produced by the fossil fuel combustion. In the case of coal-fired electric power plants, careful estimates of these costs have been as low as 3¢/kWh.¹³ For illustration we have set a similar target cost for the fixation process.

The conversion from 3¢/kWh to a budget per ton of rock carbonated depends on the amount of CO₂ liberated per kWh and on the amount of rock needed per ton of CO₂. Coal mined in the US releases between 87 g and 97 g of CO₂ per MJ of heat generated.^{36,37} The average for electric utilities is 89 g/MJ. For a coal-fired power plant with energy conversion efficiency of 33%, the budget of 3¢ per kWh translates to \$31 per ton of CO₂ or \$115/t C. In order to convert this to a budget per ton of rock that has to be mined and carbonated, we need to specify its calcium or magnesium content. In the example of a peridotite, Table 1 shows that 2 t of rock are required per ton of CO₂. This implies an allowable cost for mining and processing of \$15 per ton of peridotite. For a less rich Ca- or Mg-bearing rock, the allowable budget per ton of rock is proportionately smaller.

We do not know of a large-scale mining and chemical processing industry which is directly comparable to the proposed CO₂ disposal method. However, many elements are in common with well known operations and therefore it is interesting to consider the overall costs per ton of material for a few of these.

Although digging costs can be less than \$1/t,³⁸ typical costs per ton of material for products such as sand, crushed stone and common clays are about \$4/t.³⁸ For other products, additional processing steps raise the cost. For example, typical copper ores must be ground in mills to allow separation of concentrate by flotation or other means, which adds an operational cost of about \$4 per ton of ore.³⁹ We note that the total cost of copper mining and refining can be judged from the lower end of copper prices over the last several years (78¢/lb⁴⁰) and the average ratio of ore to final product (a factor of 200 by weight⁴¹). The resulting estimate of \$9 per ton of ore includes mining, grinding, separation and processing of concentrate as well as backfill of gangue materials. A number of metals reclaimed from dilute ores exhibit similar costs per ton of ore,⁴² which may be explained by the fact that these operations have many elements in common. The budget of \$15/t for CO₂ fixation would allow for this minimum set of operations plus about \$5 to \$7 for further chemical processes.

Products such as lime, cement and caustic-calcined magnesia are priced in the range of \$50/t to \$100/t,^{34,43,44} substantially higher than allowed for CO₂ fixation. To see where the additional costs arise, we consider the example of cement which sells for \$60/t.⁴⁴ Major considerations are the heating of raw materials to 1500°C, grinding both before and after heating, and the fact that the raw materials are 1.8 times the finished product by weight. We observe that CO₂ fixation could have a lower cost because it provides its own heat energy, it would employ lower temperature reactors, it requires only a single grinding operation, and it could achieve larger economies of scale. In cement manufacture, energy costs are about 30% of the total,⁴⁵ so the non-energy cost amounts to \$23 per ton of raw material.

The comparison with copper mining is encouraging, but suggests that the CO₂-fixation budget is likely to be marginal, which puts a number of obvious constraints on any operation. Since the processes we have discussed are energy self-sufficient, it is the equipment used in the processing which will drive the cost. It must therefore be as simple as possible. Below we consider four basic schemes of mineral carbonation for CO₂ disposal.

Direct carbonation can be achieved in a rotary kiln type operation or a fluidized bed process. In order to keep the process energy self-sufficient there has to be some provision for heat exchange between the hot reaction products and the cold reactants. This can be achieved in part by counterstreaming CO₂ which is already a participant in the reaction. Direct carbonation is likely to be the most favorable if any of the abundant raw materials, after grinding, are found to react quickly with CO₂ at elevated temperature. Costs will be seriously affected if high pressures are required in the operation.

A variant of the direct carbonation would be to pump the CO₂ directly into an underground deposit of porous, magnesium or calcium bearing, rock. In contrast to permanent underground storage of CO₂ gas, this process results in a chemically stable product and therefore poses substantially less long-term risk. Although the reaction is hindered by low temperatures it is aided by naturally high pressures. The carbonation could proceed more slowly than in an industrial reactor while still going to completion on the time scale of a few years. It could be economical even for materials relatively poor in calcium and magnesium oxide. The major difficulty lies in finding deposits that are sealed to the outside yet allow transport of the CO₂ throughout the deposit without cementing in and sealing off the injection well.

The third and fourth basic approaches rely on aqueous chemistry. The process where calcium or magnesium bearing rock is decomposed by acid is more complex than direct carbonation because it involves a number of separate steps. In principle the reaction agents, water and acid, are not consumed, and small losses can be made up. The process is exothermic and can provide for its own energy needs. The complexity of the operation is a consequence of maintaining these benefits. The necessity of the acid regeneration step is an obvious example. Furthermore, a large amount of energy is involved with regeneration of the acid, because the water changes state from liquid to gas and back. To remain energy self-sufficient, heat exchangers would be required to recover the heat liberated in the condensation for use in the vaporization step (in combination with heat provided by the carbonation step). Another consideration of economic interest is the chemical aggressiveness of the solution which may require expensive containment vessels, particularly if pressure is applied for operation at elevated temperatures.

It is interesting to compare the aqueous process with the industrial production of magnesium hydroxide from magnesium chloride brine, which then is calcined to magnesia.

Current prices of low grade magnesia are below \$100/t.³⁴ The element in common with our proposed carbonation scheme is the production of Mg(OH)₂ plus HCl from MgCl₂. The differences are that large volumes of seawater are used here to provide the MgCl₂, rather than rock treated with HCl, and that the Mg(OH)₂ is calcined to make MgO instead of being carbonated. Our allowable budget corresponds to a requirement that the overall carbonation process be less expensive by a factor of three than the overall magnesia production process. We note that calcination requires energy input, whereas carbonation actually releases energy. Furthermore, the carbonation process would operate on a much larger scale than magnesia production, and there are no purity requirements on the product. Given these considerations, our budget goal may already be attainable with this process.

The last case we consider is a modification of the aqueous chemistry approach where the immediate product is sodium carbonate rather than magnesium or calcium carbonate. This would be advantageous in a situation where only sodium bearing rock is available or economical to process. As before, a fairly complex process is probably required for the extraction and carbonation of sodium. Once the sodium carbonate is produced, it could be mixed with seawater whereupon calcium carbonate would be precipitated and sodium chloride would replace calcium chloride in the water. While in principle possible, the low concentration of calcium in seawater requires the processing of extremely large amounts of water. Furthermore, the chemistry of the seawater is changed to the extent that calcium ions are replaced by sodium ions. For these reasons we consider this alternative unpromising.

It is clear that the constraint of simplicity is best served by the direct carbonation schemes. However, this advantage over the aqueous approach could easily be lost if reaction kinetics required use of high temperatures and therefore high pressures. This possibility suggests that the requirements for each of the processes should be more extensively investigated in the laboratory. The most important trade-off is likely to be between the speed and the complexity of the final process.

The final economic consideration concerns the scale and location of the operation. The large scale of operations is clear from table 1, which shows that the material mined is about ten times the corresponding coal by weight. This may be compared to the overburden removed in coal strip mining, which averages ten times the thickness of the coal seam⁴⁶ or about twenty times the weight of the coal. Since the amounts of carbonate to be produced are so vast, they would have little potential value to the economy. The low allowable cost per ton and the large volumes involved make it clear that the operation must be concentrated at the location of the minerals to be carbonated and that the carbonates must be redeposited at the same location. Rail transportation expenses are prohibitive, at about \$35/t for a distance of 1000 km.⁴⁷ This makes it necessary to transport the CO₂ to the

carbonation site. If the CO₂ is produced in power plants it can be concentrated and shipped via pipeline at low cost.^{9,10} However, a large fraction of the CO₂ is produced from burning fossil fuels in small amounts in many locations. The CO₂ released in these distributed emissions cannot be collected economically at the point of origin but an equivalent amount could be collected directly from the air at the site where minerals for CO₂ fixation are available.

6. Conclusions

CO₂ can be bound in stable form without any input of energy. The necessary raw materials are more than sufficient to allow utilization of the known coal reserves without accumulation of carbon dioxide in the atmosphere. Although challenging, it is plausible that a simple process, similar to one of those we have outlined, can be operated at acceptably low cost.

In order to bring this possibility to reality, an experimental program needs to be conducted. The experiments should address the issue of reaction kinetics, and subsequently the operation of test reactors which implement complete processes. There are two main areas of investigation corresponding to the two routes considered for achieving favorable reaction rates: utilization of elevated temperatures and/or pre-digestion of raw material in aqueous solution. We have indicated promising starting points for both types of process.

Based on the results of such experiments, it will be possible to compare technologies in detail, select the optimal one, and provide more precise cost estimates. The practical demonstration of forming carbonate minerals artificially for CO₂ disposal will provide a key ingredient in considering the option of fossil fuel use in the centuries to come.

7. References

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