



PROGRESS ON BINDING CO₂ IN MINERAL SUBSTRATES

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ABSTRACT

Based on current estimates of reserves, coal could satisfy even a very much increased world energy demand for centuries, if only the emission of CO₂ into the atmosphere could be curtailed. Here we present a method of CO₂ disposal that is based on combining CO₂ chemically with abundant raw materials to form stable carbonate minerals. A major advantage of this method is that the resulting waste product is thermodynamically stable and environmentally neutral. It is therefore possible to store large quantities permanently with minimal environmental impact and without the danger of an accidental release of CO₂ which has proven fatal in quantities far smaller than contemplated here. The raw materials to bind CO₂ exist in nature in large quantities in ultramafic rocks. They are readily accessible and far exceed what would be required to bind all CO₂ that could possibly be generated by burning the entire fossil fuel reserves. In this paper we outline a specific process that we are currently investigating. Our initial rough cost estimate of about 3¢/kWh is encouraging. The availability of a CO₂ fixation technology would serve as insurance in case global warming, or the perception of global warming, would cause severe restrictions on CO₂ emissions. If the increased energy demand of a growing world population is to be satisfied from coal, the implementation of such a technology would be unavoidable. Published by Elsevier Science Ltd

KEYWORDS

Carbon Dioxide Disposal; Carbonate Mineral; Peridotite; Serpentinite; Magnesium Oxide; Calcium Oxide; Greenhouse Effect; Power Plant Emission; Emission Control.

INTRODUCTION

An economic method of CO₂-disposal in solid form would eliminate the potential danger of climate changes due to greenhouse gas emissions from burning fossil fuels. The availability of such technology would allow the large coal reserves (estimated at 10,000 Gt (United Nations, 1993)) to satisfy the growing demand for world-wide energy without an impact on atmosphere and climate. More immediately, such a technology could protect a large investment in energy infrastructure in case that strict limits on future CO₂ emissions are deemed necessary.

In this paper we report on the current state of our effort to develop a method of binding CO₂ as chemically inert mineral carbonate. We outline a process that we consider viable and we discuss a preliminary cost estimate. Our discussion will leave out the extraction of CO₂ from flue gases and their transportation to the disposal site which has been studied by others and is much better understood than the disposal (Audus *et al.*, 1995). Also, these steps would be in common with many other disposal methods (Booras & Smelser, 1991; Hendriks *et al.*, 1991; Herzog *et al.*, 1993; Steinberg & Cheng, 1985).

There are two major reasons for considering disposal of CO₂ as a carbonate mineral. First, the oxides of calcium and magnesium are available in nature in quantities vastly exceeding those of fossil fuels, even if one limits oneself to those that are not already carbonated. Secondly the carbonation reaction, that binds CO₂ to calcium oxide or magnesium oxide, is thermodynamically favored and exothermic even if one starts from natural minerals in which these oxides are chemically bound into a silicate structure. Thus, at least in principle, there is no need to consume energy which suggests that the cost could be held low. The widespread presence of natural carbonates, which is explained by their thermodynamic stability, demonstrates that the waste product we generate is environmentally benign and stable.

A major advantage of mineral carbonate disposal is that it avoids long term storage of CO₂ as a free phase. Storing gigatons of a substance that is gaseous at ambient surface conditions is fraught with risk. Just as in nuclear waste disposal, any storage system would have to be guaranteed as safe for centuries against the possibility of an accidental release. A natural disaster in 1986 at Lake Nyos, Cameroon, has demonstrated these hazards (Kling *et al.*, 1987). The waters deep in the crater lake had been saturated with CO₂ from underwater volcanic vents. Due to an instability in the layering, the lake turned over causing a sudden release of a CO₂ bubble on the order of 0.1 km³ (Freeth, 1994) or about the weekly output of a single gigawatt power plant. The gas overflowed the crater rim and, because it is heavier than air, flowed down a valley killing 1700 people. The danger of a sudden gas release from the storage site is completely eliminated in our approach, because the mineral carbonate once formed is stable and the reaction cannot be readily reversed.

RESOURCES

The only common oxides that readily form stable mineral carbonates are calcium and magnesium oxides. The prototypical reactions are those of the pure oxides which at 179 kJ mol⁻¹ and 118 kJ mol⁻¹ respectively are very exothermic. The heat release may be compared with the enthalpy of reaction in burning carbon to CO₂ which is 394 kJ mol⁻¹.

Pure CaO and MgO are rare in nature, but many common minerals may be regarded as a combinations of these oxides with others forming a silicate matrix. The large scale of fossil fuel consumption, which amounts to 6 Gt of carbon per year world-wide, requires that mineral deposits used in the disposal must be very large. Fortunately there are very large deposits rich in magnesium or calcium, or both. Of course, we exclude deposits that are already carbonated, like limestone. Instead, we consider igneous deposits that are essentially free of carbonates.

Ultramafic igneous rocks are rich in magnesium oxide. The richest is dunite. It belongs to the peridotite group and contains ~50% magnesium oxide by weight as forsterite. In its pure form forsterite contains 60% magnesium oxide. Peridotites in general have high magnesium content, as do serpentinites that are frequently associated with them. In North America the largest deposits are in the West. Large areas of California are covered by serpentine or serpentinitized peridotites. An exposed peridotite slab in the Klamath mountains of Northern California with a size of about 1000 km² by 1 km or about 3,000 Gt (Irwin, 1977; Lindsley-Griffin, 1977) demonstrates the scale of the deposits. Other large deposits are found in the Northeast. There are many more smaller deposits, for example in Ontario, Maine, Virginia and Texas. Peridotite can be found all over the world (Coleman, 1977; Nicolas, 1989). In the context of CO₂ disposal, one should mention Scandinavia and Japan. The total amount of magnesium oxides found in such readily accessible deposits far exceeds the worldwide coal reserves which are estimated to about 10,000 Gt.

The deposits of calcium oxides in basalts are even larger and more widespread. The Columbia River flood basalt is an example of a large deposit. It forms a sheet about 1 km thick with a volume of 200,000 km³ (Hooper, 1982). This sheet alone could absorb all the CO₂ generated from the estimated world coal reserves 2.5 times over. There are even larger flood basalt sheets, *e.g.*, the Dekka flats in India. However, large deposits containing calcium oxide are rarely as rich as magnesium bearing deposits. In most cases one must settle for calcium oxide concentrations between 9 and 13%. From the standpoint of material processing, this gives a clear advantage to magnesium bearing minerals.

Table 1. Abundant rock types rich in magnesium and calcium oxide. The table is taken from Lackner *et al.* (1995). R_C is the mass ratio of rock needed for CO₂ fixation to carbon burned. R_{CO_2} is the corresponding mass ratio of rock to CO₂.

Rock Type		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

Binding the CO₂ derived from burning one ton of carbon requires 4.7 t of CaO or 3.3 t of MgO. In the table we give the equivalent amounts for the different types of rocks. Magnesium rich deposits have a big advantage in the amount of material that needs to be processed, which turns out to be about 7 to 10 times the amount of carbon burned. The excavation of magnesium bearing minerals would actually be smaller in scope than most coal mining, because one avoids the overburden typical for coal mining. In terms of mass ratios, these overburdens typically amount to a factor of 20.

ECONOMICS

In the absence of a detailed design we compare an outline of the carbonation disposal process to the cost of existing industrial processes. From this comparison we conclude that a cost of \$15 per ton of raw mineral is not an unreasonable goal. For peridotite, this corresponds to \$30/t of CO₂ which compares favorably to the Scandinavian CO₂ tax of \$50/t (Kaarstad, 1995). At a conversion efficiency of 33%, complete disposal would add 3¢ to the kWh. The cost of CO₂ collection and pipelining may add another 3¢. At a base price of electricity of 3¢/kWh, coal would still be competitive with nuclear energy.

Here we give a simple outline of our estimate. For additional detail see Lackner *et al.* (1995) and references therein. We consider a process in which raw material is dug up, crushed and ground. Thereafter a small number of processes, e.g. leaching, distilling and reverse calcination are performed to bind CO₂. The final step is the disposal of the resulting materials. For purposes of this discussion, we assume that none of the resulting products have any economic value.

Digging, crushing and grinding of rock costs about \$4/t. In copper mining this even includes a flotation process to separate out the copper sulfide. The entire cost of copper refining can be estimated conservatively from a recent low in copper prices to be below \$9/t of ore. This cost includes not only the refinement process but also the disposal of waste tailings. Copper mining also operates on a very large scale (measured in ore throughput) and thus is likely to take advantage of economies of scale. The operations performed directly on the ore are simpler than what we are proposing. If we neglect the costs that arise in the processing of the much smaller amounts of copper sulfide and raw copper, this comparison sets a lower limit. Other comparisons can be made to the production of lime, magnesia and alumina. Expressed in terms of the cost per ton of raw material input, all these processes range between \$20 to \$50 per ton, *i.e.*, 1.5 to 3 times more expensive than the goal we have set ourselves. On the other hand these processes are at least as complex as those we are considering. They consume energy, and it can be shown that they have not fully made use of the available economies of scale. Indeed the lime and cement making which has the largest throughput comes closest to our goal, whereas the manufacture of magnesia, which is performed at a scale at least three orders of magnitude too small, is the most expensive. Therefore, we consider these numbers as loose upper limits that quite likely can be significantly reduced.

CHEMISTRY

We have found (Lackner *et al.*, 1995) that for all common calcium and magnesium bearing minerals the carbonate reaction is exothermic and under ambient conditions it is favored thermodynamically. Because of the high entropy of gaseous CO₂, the equilibrium shifts towards free CO₂ as the temperature increases. This results in an upper limit to the process temperature which is quite high for the carbonation of calcium oxide ($P_{\text{CO}_2} = 1$ bar at 890°C), but which is relatively low for the carbonation of magnesium oxide (410°C). For the most common minerals, which we have investigated, this temperature limit ranges from to 170°C to 410°C.

Since the carbonate is the thermodynamically favored state, the goal is to identify a reaction path that with minimal losses in energy can achieve this ground state at reasonable reaction rates. The simplest approach would be direct carbonation of a mineral powder in a gas solid reaction. This would have the advantage that the heat of the reaction would be released at high temperatures and with minimum dilution. The problem of this approach is that the reaction kinetics for calcium and magnesium silicates tends to be too slow and that raising the temperature in order to speed up the reaction kinetics is prohibited by thermodynamic constraints.

We exposed a number of minerals ground to a grain size of 50 to 100 μm to a CO₂ atmosphere (0.78 bar) at various temperatures (140 to 300°C) below the calcination point. Carbonation in most cases was insignificant even when the exposure lasted for days. The direct carbonation of minerals is therefore likely to require higher pressure or pretreatment. At high pressures (340 bar) we succeeded in carbonating a serpentinite to about 30% of the stoichiometric limit by flowing carbon dioxide through a packed bed of serpentinitized powder. We are currently exploring pretreatment options for serpentinite that have been suggested in the literature and which could improve the efficacy of this process (Drăgulescu *et al.*, 1972).

An alternative approach is carbonation of pure hydroxides or oxides, which would have to be extracted from the minerals in a prior processing step. We found from the literature (Bhatia & Perlmutter, 1983) as well as from our own experiments that the carbonation of CaO and Ca(OH)₂ progresses rapidly. One can achieve near completion in minutes. However, the high reactivity of calcium oxides and hydroxides is counterbalanced by their low concentrations in naturally occurring minerals. The measured rate of carbonation of MgO under atmospheric pressure turned out to be far too slow to be of practical interest. The reaction rate of Mg(OH)₂ on the other hand appears to be very promising and we are developing a processing scheme based on this reaction (Lackner *et al.*, 1996).

In our first experiments with Mg(OH)₂, we obtained significant carbonation by slowly flowing CO₂ ($P_{\text{CO}_2} \sim 0.5$ bar) over a bed of Mg(OH)₂ powder in runs that extended over 12 hours (Butt *et al.*, 1996). The average grain size was 20 μm and about 8% of the stoichiometric maximum carbonation was achieved. In more recent experiments with similar powders we obtained 8% of the stoichiometric maximum in about 10 minutes ($P_{\text{CO}_2} = 0.78$ bar). We are still investigating the details of the kinetics which is governed by a complicated interaction between the water being driven off the magnesium hydroxide and the CO₂ that enters the powder. Published data concerning the water release vary and it appears that complications like crack formation in the grain can greatly affect the outcome of the reaction.

Further experiments on Mg(OH)₂ are investigating the effects of varying grain size, gas flow, temperature and pressure on the overall kinetics. Below the thermodynamic maximum temperature, an increase in temperature drastically increases the rate of the initial uptake of CO₂. It also raises the level of carbonation that is achieved before rates level off. We have observed that slight pressure increases of 0.2 bar raise the rate of uptake and the maximum uptake for a given temperature. However, we expect that the major advantage of increased pressure will come from raising the operating temperature. Based on thermodynamic arguments, doubling the pressure would allow one to raise the temperature by more than 30°C which based on current data should drastically increase the level of carbonation. Currently we are working on experiments in an intermediate pressure range (10 to 100 bar). This pressure regime is of great interest because it can be contained in an industrial setting. Furthermore, pipeline delivery of CO₂ to the disposal site would already have precompressed the gas to these pressures so there would be no additional energy penalty. At even higher pressures (340 bar and 500°C), we have already shown that the reaction goes to completion in less than 2 hours. These results will be reported in more detail at a later date.

The cost of the process is critically affected by the reaction time, and simple estimates suggest that the reaction needs to go to completion in less than one hour. It is likely that the dehydroxylation and concurrent carbonation of magnesium hydroxide can be performed well within this constraint. However, the final experiments demonstrating this point are still outstanding.

To extract magnesium hydroxide from mineral rock we are studying a well known aqueous process for magnesium extraction in order to adapt it to our situation. In summary, forsterite and serpentinite rocks are decomposed in hydrochloric acid, yielding magnesium chloride in solution. The hydrochloric acid can then be recovered in a series of steps leading to hydrochloric acid, water and magnesium hydroxide. The magnesium hydroxide is then carbonated in a gas-solid reaction at elevated pressure and temperature (see Fig. 1). The advantage of the gas-solid reaction is that the reaction heat can be captured for use in the earlier steps of the process. If the efficiency of the process is not sufficient to actually make use of this heat energy, we have already shown that the carbonation of magnesium hydroxide can also be performed in an aqueous environment where reaction rates can be fast even at low pressures, but where heat recovery is simply not feasible. This reaction was completed in less than 30 minutes when using 20 μm magnesium hydroxide powder.

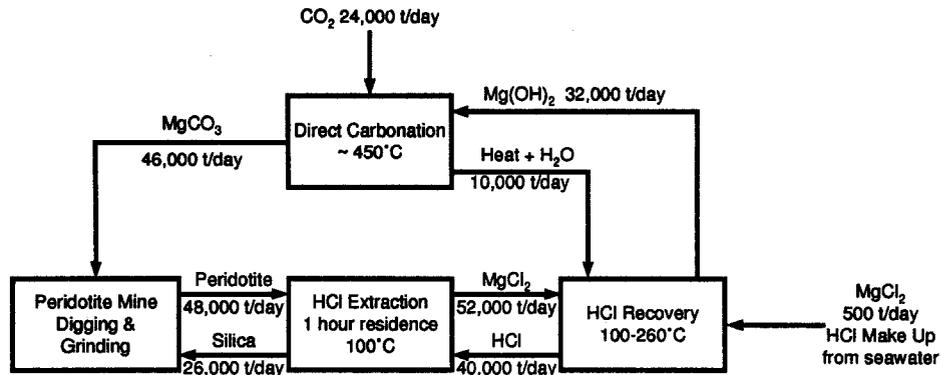


Fig. 1. A diagram of the material flows in CO₂ disposal. The absolute rates of processing are geared to match the CO₂ output of a power plant with 33% conversion efficiency that produces 1 GW of electric power.

We have reproduced results obtained in the forties (Houston, 1945) and fifties (Barnes *et al.*, 1950) on the extraction of magnesium from forsterite and serpentinite. The process can be performed rapidly at about 100°C. It is slightly exothermic and can maintain its own operating temperature. The end-product is magnesium chloride in aqueous solution. The silica can be precipitated as silica gel, by gradually raising the pH of the solution, for example by adding MgCl(OH) which is produced in a later step of the process.

For a successful recovery of the hydrochloric acid, it is important that the formation of soluble chlorides is minimized. Fortunately, all peridotite rocks are remarkably free of alkali ions, which contribute less than 1% to the mineral mass. Therefore the irreversible formation of alkali chlorides is not a serious problem. A frequent and unavoidable contamination in all peridotites is iron oxide which is also extracted in the acid leaching as iron chloride. Fortunately, neutralizing the solution with MgCl(OH) will cause the complete precipitation of iron oxides and hydroxides while forming additional magnesium chloride. It has been shown by Houston that a straightforward unoptimized design will readily recover 95% of the hydrochloric acid (Houston, 1945).

The acid recovery begins with concentration of the magnesium chloride solution to form hydrated magnesium chloride crystals of composition MgCl₂ · nH₂O with $n = 6$. With gradual heating, the water is driven off in steps moving from $n = 6$, to approximately $n = 1$. Further heating of the $n = 1$ powder leads mostly to the formation of HCl and MgCl(OH) rather than additional water release (Smith & Veazey, 1932). MgCl(OH) is readily disassociated into MgCl₂ and Mg(OH)₂ by reintroducing it into aqueous solution. Thus we have a complete cycle for the recovery of the hydrochloric acid which is akin to the process used in the manufacture of magnesium hydroxide from seawater (Copp, 1994).

We have performed the individual steps in the laboratory and have found that without optimization for high reaction rates the process can be performed with residence times of about 30 minutes which puts it well within our goal. Future work will aim to improve the speed of the reaction and most importantly we will try to develop, at least in a simulation, a process that minimizes heat losses. Given the large amount of water that is repeatedly recycled through these steps a careful design that avoids heat loss is absolutely critical making this process economically viable.

CONCLUSIONS

We have identified the outline of a viable process for disposal of CO₂ in the form of carbonate minerals. Based on our first cost estimates we are encouraged to pursue this line of research further.

At this point we are favoring a specific implementation using Mg(OH)₂ extracted from peridotite or serpentinite rock. However, the direct solid gas reactions with minerals at higher pressure are still under study and may reveal practical alternatives using these same minerals or others such as basalt. Another possibility, which is related in principle, is the direct carbonation of underground calcium bearing minerals by injection of CO₂ at high pressure into suitable reservoirs (Bachu *et al.*, 1994).

The major advantage of disposal in carbonate minerals is that the environmental impact is minimal. Carbonate minerals are already common in nature and therefore the disposal is safe. The most obvious impact arises from mining which is comparable in scope to the mining of coal in the first place. Our approach completely avoids the danger of a sudden accidental release of the CO₂ into the atmosphere, and it does not require safeguards for preventing a slow re-introduction of the CO₂ which could cause a climate problem in a few generations hence. The stability of the waste product is guaranteed by the thermodynamic stability of carbonate minerals and it is demonstrated by much larger natural deposits.

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