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Abstract

We have successfully developed the foundation for sequestration of carbon dioxide in mineral form. The purpose of this technology it is to maintain coal energy competitive, even when in the future environmental and political pressures will require a drastic reduction in carbon dioxide emissions. In contrast to most other sequestration methods, ours is not aiming at a partial solution of the problem, or at buying time for phasing out fossil energy. Instead, our goal is to obtain a complete and economic solution of the problem, and thus maintain access to the vast fossil energy reservoir. Such a technology will guarantee energy availability for many centuries even if world economic growth exceeds the most optimistic estimates. Our approach differs from all others in that we are developing an industrial process which chemically binds the carbon dioxide in an exothermic reaction into a mineral carbonate that is thermodynamically stable and environmentally benign.

Background and Research Objectives

Unless environmental constraints prohibit their use, fossil fuels, in particular coal, could easily satisfy the rising world energy demand for many centuries [1, 2]. Thus, the fate of fossil fuels in the energy mix of the next century will largely be determined by technological advances that allow for the safe and permanent disposal of carbon dioxide. To this end various schemes for the disposal of carbon dioxide are being developed. Our approach is based on forming stable and environmentally benign mineral carbonates (see list of publications). The process appears to be economically viable, it is environmentally safe, and it is based on readily available resources. In contrast to nearly all competing carbon dioxide removal schemes [3], ours does not just aim at reducing the pain of phasing out fossil fuel, but rather its purpose is to maintain fossil fuels economically viable and competitive in a growing world energy market.

Over the last two centuries, the carbon dioxide content of the atmosphere has increased by about 30% due to human activities [4, 5]. More than half of this increase occurred within the last 30 years. There is a growing scientific [6–10] and political consensus that the excess carbon dioxide in the air should not be tolerated, because it could negatively impact climate and environment.

The need to curtail CO_2 emissions could have severe economic repercussions for the US and the world. In the short term, the successful development of a carbon dioxide disposal technology would provide insurance against the possibility that political pressures or actual climate changes would force a drastic reduction in carbon dioxide emissions. At risk in the US are investments on the order of a trillion dollars in power plants and mining infrastructure.

In the long term, the issue is the increasing energy demand fueled by economic and population growth throughout the developing countries. Rapid economic growth of the developing countries is highly desirable politically. Indeed economic growth is probably the only way of slowing down and stopping the explosive population growth and its concurrent political instability. The empirical correlation between economic development and a reduction in population growth is well established. Economic growth in turn is tightly linked to increased energy generation. This suggests that ample, low cost energy is critical for the political future of the world. A world population of ten billion, with a per capita energy consumption that matches that of the US today, would consume ten times more energy than is currently generated. An average growth of 4.7% per year in world energy consumption, which is not far from recent growth [11], would accomplish such increase in 50 years.

As the world energy demand grows, it will become almost certainly necessary to eliminate carbon dioxide emissions from fossil fuels. Elimination of carbon dioxide emissions, by way of a disposal technology, will position fossil fuel power well to compete for a large share of this growing future market. In contrast to public belief, fossil energy is not about to run out and it has clear advantages over all its competitors. Nuclear energy is politically tainted and, more importantly, its general use presents a serious proliferation risk. Renewable energy resources may become serious competitors in the distant future, but today they are still far too costly and have not proven themselves on the scale at which fossil energy is routinely used. Coal energy could easily satisfy the increasing demand, but the industry must position itself well with regard to environmental issues. Without such a technology, a large part of the this market will have to be ceded to more expensive energy forms.

The project we are reporting on here, started from the simple observation that the formation of carbonates from calcium oxide and magnesium oxide is thermodynamically favored and indeed occurs in nature. Our goal has been to develop the concept, to show that it is viable and outline its possible implementation. We have successfully reached our goal and have developed a process which clearly merits further development. We also have been able to attract additional funding that will allow for the continuation of this research. Additional research will allow us to move from a proof of principle to a pilot plant implementation.

Importance to LANL's Science and Technology Base and National R&D Needs

National security, to a large extent, rests on energy security and environmental security. These are areas of interest to the Laboratory and the Nation. Recently, the National Laboratories were challenged by the President of the United States and the Secretary of the Department of Energy to contribute to the solution of the Greenhouse problem. This project significantly contributes to the ability of the Laboratory to address these issues.

Scientific Approach and Accomplishments

We started this project from the observation that the formation of carbonates at least in some cases is exothermic. This made it clear to us that carbon dioxide is not the unavoidable end product of the combustion of coal or other fossil fuels, but that instead it should be possible to move to an energetically even lower state of carbon, namely a mineral carbonate. The carbonate is stable. To free the carbon dioxide would require a significant supply of energy. We also knew that such carbonation processes already occur in nature, albeit on geological time scales. Thus we proposed to find a way of accelerating the process to the point that it would become of commercial interest. Our research of the last three years has proven this basic concept to be valid.

The first phase of our project amounted to verifying that thermodynamics indeed favors the formation of carbonates for readily available minerals. Our first publications on the subject dealt with this issue. We demonstrated that thermodynamically the formation of solid mineral carbonates is favored for a large number of common calcium and magnesium bearing minerals and that these minerals exist in vast quantities in nature. We found that igneous rocks containing calcium or magnesium in uncarbonated form are plentiful and far exceed even the most optimistic estimates of abundance of coal, oil and natural gas. Thus we established that availability and thermodynamics allowed for the disposal of carbon dioxide as solid carbonate mineral. Thermodynamic stability of the end product also indicates that the disposal is safe and permanent, as is evidenced by the stability of natural carbonates. The exothermicity of the reaction gives hope for a cost-effective implementation of the process that avoids the cost of bringing in additional energy.

In a second phase we demonstrated a possible implementation of the carbonation scheme.

The high concentrations of magnesium in readily available peridotite and serpentinized peridotite rocks lead us to focus our effort on magnesium bearing minerals, Table 1. Therefore, we developed a method for carbonating magnesium hydroxide and in addition an acid extraction process to leach magnesium from serpentinite and peridotite rock. The kinetics of the carbonation reaction of magnesium hydroxide is quite complex. We found in our experiments that it depends strongly on the details of the processing scheme, e.g., on temperature, partial pressures of water and carbon dioxide as well as on the form of the magnesium hydroxide. We have begun an intensive experimental study of the process because the gas-solid carbonation is a potentially rate limiting step in any process implementation. We have been successful in demonstrating the reaction on a laboratory scale. At a pressure of 50 bar the reaction goes virtually to completion in less than 30 minutes. This would be sufficient for consideration in an industrial application. However, we expect that because of the largely unexplored parameter space further significant improvements will be possible prior to actual implementation.

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	~0.0	~8.4	~2.3
Gabbro		~10.0	~13.0	~17.0	~4.7
Basalt	Continental tholeiite	6.2	9.4	26	7.1

Table 1: Magnesium and calcium oxide content of common rock types that could be used for binding carbon dioxide. The ratios R_C and R_{CO_2} give the mass ratio of the mass of rock required to the mass of carbon or carbon dioxide respectively that can be bound.

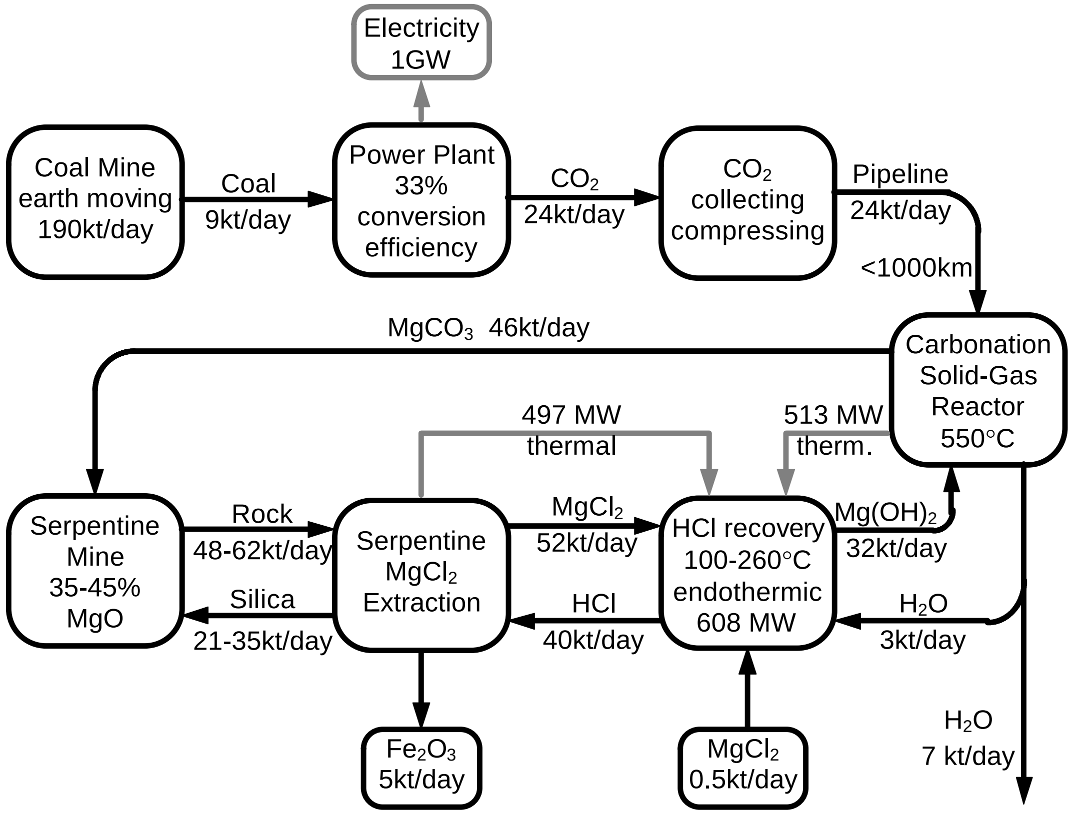

Figure 1: Flow diagram for mass flows in the combined, coal mining, power plant and carbon dioxide removal operation. The numbers are chosen to reflect the overall mass flow for a gigawatt power plant with a conversion efficiency of 33%. This number is quite conservative, even for existing power plants.

Magnesium hydroxide can be obtained from mineral rock through an acid extraction step. The most promising approach is based on a hydrochloric acid extraction that yields the magnesium in form of $MgCl_2$. In a second step, the HCl is quantitatively recovered and the $MgCl_2$ is transformed into $Mg(OH)_2$ which can then be carbonated. The overall process is exothermic. An outline of the process is shown in Figure 1. Future work will revolve around process designs that take advantage of the overall energy release in the process.

Our current results can be summarized as follows:

- The mineral resources for this project exist in the form of serpentinite and peridotite rock. The mineable ores are of a form that can be readily processed. In the US the material is conveniently located in the vicinity of major population centers.

- The mining crushing and milling of the ore is possible at a cost which we estimate at about \$8 per ton of CO_2 disposed. The estimate is based on comparison with very similar processing steps in existing industries. To set the scale \$10/ton of CO_2 amounts to \$0.01/kWh electric at 33% conversion efficiency. At higher efficiencies the cost is correspondingly lower.
- We have outlined a specific process that allows us to extract magnesium hydroxide from peridotite or serpentinite rock. This process would deliver the iron oxide contained in the rock in a useful form generating a credit of \$10/t of CO_2 at current prices for iron ore.
- We have demonstrated the feasibility of carbonating magnesium hydroxide in an exothermic reaction at pressures far below those at which CO_2 would be delivered from a pipeline. We believe that the cost of this process can be held quite low, i.e. measured in a few dollars per ton of CO_2.
- With successful heat management we expect to cover all energy demands from internally generated heat. If this assumption is satisfied, the cost of the disposal plant could be quite low leading to a total cost of the disposal process of perhaps \$15/t of CO_2. This estimate does not include any credits. Costs would escalate rapidly if substantial amounts of additional energy would have to be supplied either in the form of heat or in the form of work performed in the compression of gases.

Additional research to further develop the basic concepts is already underway. Separately funded a more detailed analysis of the available ores has been prepared [12]. We also have started a collaboration with Chichibu Onoda Corporation in Tokyo to further refine the carbonation step. In addition work in Los Alamos is progressing on the HCl recovery step and alternative implementations of the extraction process.

Over the last few years a number of other approaches have been suggested elsewhere to sequester carbon dioxide [5]. Most prominent among them are ocean disposal and deep aquifer disposal. In comparison with these and other methods of carbon dioxide disposal or sequestration ours has a number of advantages. Nearly all of these advantages are based on the fact that the end product of the process is a thermodynamically favored, stable solid. This makes it easy to argue that the end product is benign and that it cannot revert over time back into carbon dioxide. Re-release of carbon dioxide could be hazardous under certain circumstance but in any case it would lead to a postponement rather than elimination of the Greenhouse effect.

The advantages of the carbonation disposal are the following:

- The disposal is safe. The waste products are stable and are already common in nature. They are known to be environmentally benign and non-hazardous. Most importantly there is no possibility for an accidental release of CO_2 which has proven lethal in natural disasters of comparatively small scale.
- By confining waste disposal to a mining site, we minimize the environmental impact. In contrast, dilution in the ocean, just like in the atmosphere, sets the stage for future environmental problems caused by upsetting the carbon balance and the pH of large oceanic regions. In our case, the impact is limited to a change in surface profiles in an area that is an order of magnitude smaller than in surface coal mining.
- Because of the thermodynamic stability and safety of the end product, disposal does not pose legacy problems for future generations. Other methods e.g. aquifer disposal, may require indefinite monitoring of disposal sites or could lead to a severe greenhouse problem in the future when total CO_2 seepage from storage sites starts to exceed today's emissions.
- Our solution is permanent and complete. Resources and disposal sites far exceed the available fossil fuel reserves. The availability of this technology guarantees fossil fuels as a viable energy source. As a consequence, there will be no energy shortage for centuries to come.
- Most importantly, our method is economical. While an above ground process at first appears more costly, in practice every disposal scheme involves a number of such steps. If, as is likely, we succeed in a design that avoids the use of additional energy, the cost of the process compares favorably with that of competing approaches. We base our optimism on the fact that the process is exothermic and thermodynamically favored. We consider $15/t of CO_2 a realistic goal.

In summary, we have accomplished what we set out to do. We have taken a simple idea and shown that there are no fundamental obstacles to its implementation. We have shown that the necessary resources exist and are readily accessible, we have demonstrated the basic chemistry of the process and have made significant progress towards an actual plant design that could reasonably achieve a disposal cost on the order of $15/t of CO_2. At this price, our disposal scheme would be competitive with other less desirable disposal options as well as with all presently available alternative energy resources. Additional work will be required to progress from a viable approach to an actual implementation.

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