

Zero Emission Coal Power, a New Concept

H.-J. Ziock, (ziock@lanl.gov; 505-667-7265), K. S. Lackner
Los Alamos National Laboratory
Mail stop D462
Los Alamos, NM 87545

D. P. Harrison, (harrison@che.lsu.edu; 225-388-3066)
Dept. of Chem. Engineering, Louisiana State University,
Baton Rouge, LA 70803-7303

Abstract

The Zero Emission Coal Alliance (ZECA) is developing an integrated zero emission process that will generate clean energy carriers (electricity or hydrogen) from coal. The process exothermically gasifies coal using hydrogen to produce a methane rich intermediate state. The methane is subsequently reformed using water and a CaO based sorbent. The sorbent supplies the energy needed to drive the reforming reaction and simultaneously removes the generated CO₂ by producing CaCO₃. The resulting hydrogen product stream is split, approximately 1/2 going to gasify the next unit of coal, and the other half being the product. This product stream could then be split a second time, part being cleaned up with a high temperature hydrogen separation membrane to produce pure hydrogen, and the remainder used to generate electricity via a solid oxide fuel cell (SOFC). The inevitable high temperature waste heat produced by the SOFC would in turn be used regenerate the CaO by calcining the CaCO₃ product of the reforming stage thereby generating a pure stream of CO₂. The CO₂ will be dealt with a mineral sequestration process discussed in other papers presented at this conference. The SOFC has the added advantage of doubling as an oxygen separation membrane, thereby keeping its exhaust stream, which is predominantly steam, free of any air. This exhaust stream is largely recycled back to the reforming stage to generate more hydrogen, with a slipstream being extracted and condensed. The slipstream carries with it the other initial contaminants present in the starting coal. Overall the process is effectively closed loop with zero gaseous emissions to the atmosphere. The process also achieves very high conversion efficiency from coal energy to electrical energy (~ 70 %) and naturally generates a pure stream of CO₂ ready for disposal via the mineral sequestration process.

Introduction

Fossil energy resources currently provide 85% of all energy consumed. They are readily available and could satisfy world energy demand for several centuries. The main fossil resource is coal. There is some uncertainty whether resource exhaustion could lead to a decline in the use of oil and gas over the next few decades. No such concerns exist with regard to coal. Based on studies by the United States Geological Survey coal resources exceed 10,000 Gigatons (Gt).

This number should be compared to an annual carbon consumption of 6.0 to 6.5 Gt of carbon in all fossil fuels combined. As technologies improve, interchangeability between the various fuels becomes easier. Thus, one can conclude that the use of fossil energy today is not limited by resource availability. As we will discuss below, it is the environmental concerns associated with its use that need to be resolved.

Initially these environmental concerns were limited to pollutants, like SO_x, NO_x, particulates, and heavy metals. Regulations concerning heavy metals, in particular mercury are being planned and will require tighter pollution control. The current debate on the health effects of fine particulates presage much more stringent controls. In the United States, PM 2.5 regulations are likely to be phased in to reduce fine particulate emissions for particle sizes down to 2.5 micrometer. Clearly, one sees a trend toward tighter pollution control, requiring more and more elaborate means of cleaning up any gases from coal processing and coal combustion.

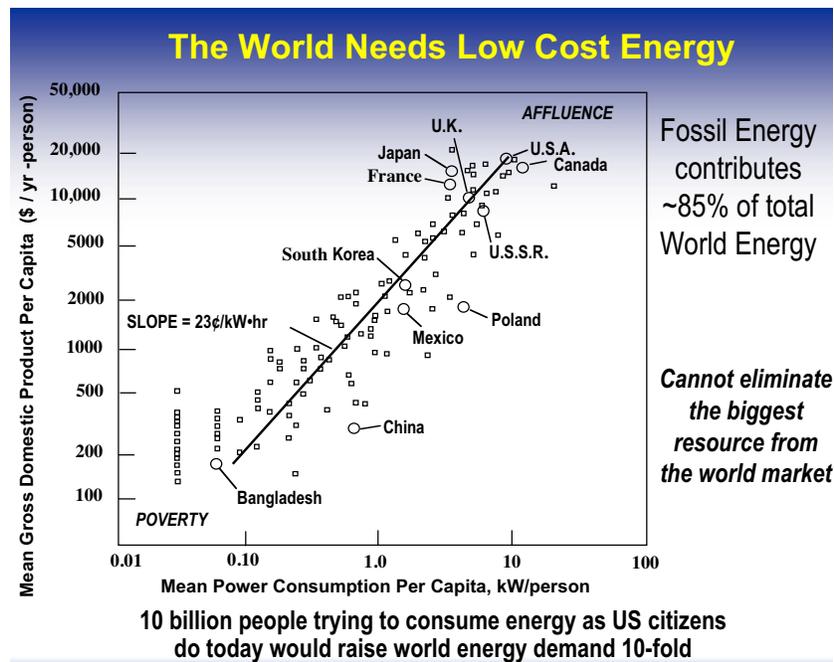
Over the last decade, carbon dioxide – the end product of fossil fuel combustion – has itself become a concern, mainly because of its role in climate change. Unlike the situation for pollutants like SO_x, it is not a single emission that causes harm, but rather it is the long term accumulation of carbon dioxide in the atmosphere due to myriad anthropogenic sources. Since coal is the most carbon intensive fuel, coal producers must address these issues early. Otherwise they will be the first to feel the pinch of carbon constraints. Carbon constraints to be effective need to aim for substantially zero emission. If one plans to collect all combustion products from a power plant, one needs to consider a design that collects all of its emission in solid form and completely eliminates emissions to the air.

Atmospheric carbon dioxide concentration could easily double by the year 2050. Current annual emission exceeds 1% of the preindustrial carbon content of the atmosphere. Carbon dioxide levels have risen from the preindustrial 280 part per million (ppm) to 370 ppm. At present, the rate of increase appears to be 1.7 ppm/year. Comparing total past anthropogenic emissions and the rise of atmospheric CO₂ levels implies that a little more than half of the carbon emissions from the combustion of fossil fuels actually stay in the air. The oceans and the terrestrial biosphere take up the remainder. Much research needs to be done to understand the details of these transfers, but the overall size is well established. Even at a low worldwide growth rate of 2% per annum, carbon dioxide levels in the atmosphere would exceed 500 ppm before 2050, or within the expected lifetime of a coal-based power plant built today.

In the long term, it is not the rate of emission that matters, but the level of carbon dioxide that is allowed to accumulate in the atmosphere. Unfortunately, halting the increase in level requires drastic emission reductions. At present, a large fraction of the carbon dioxide entering the atmosphere from fossil fuel consumption moves into other reservoirs, because these reservoirs still need to equilibrate with the increased levels in the atmosphere. Once the atmospheric levels of carbon dioxide are prevented from rising, the outflow from the atmosphere into the other reservoirs like the ocean and the terrestrial biosphere will drop rapidly. Model calculations suggest that in order to fix the total carbon dioxide level in the atmosphere, yearly emissions will have to fall by a factor of about 3 below those of 1990 in a matter of a decade or two. Energy efficiency and reduced economic growth may slow down, but cannot prevent the inexorable rise of carbon dioxide levels. Holding CO₂ concentrations constant at any acceptable level would require far more drastic emission reductions. Ten billion people sharing equally into 30% of present world CO₂ emissions would have a *per capita* allowance of 3% of today's *per capita* emission in the United States.

The arguments presented above are not particularly dependent on the level of carbon dioxide that is considered acceptable. A higher level will provide more time to stop carbon dioxide emissions, but whether one wants to stop at 400 ppm of carbon dioxide in the air or 600 ppm does not substantively change the reduction one needs to accomplish. To a good approximation the atmosphere acts like a finite reservoir, and levels will keep rising as long as emissions occur. The Kyoto treaty may set a target that is impossible to reach in the allotted time, but in the long run far more stringent reductions will be required, if the goal set by the United Nations Framework Convention on Climate Change in 1992 in Rio de Janeiro is going to be realized.

On the other hand, energy demand is going to rise rapidly over the course of the next century. In the twentieth century energy consumption grew from 30×10^{18} Joule/yr to 380×10^{18} Joule/yr. The vast majority of the world's population has not yet gone through the transition, which drove this growth in the developed world. In the coming century the world could repeat what Europe, Japan, and North America accomplished in the last century, but with a population base that is an order of magnitude larger.



The importance of energy to the world's economic development is hard to underestimate. Figure 1 shows the primary energy consumption per dollar of gross domestic product (GDP) in various countries. In spite of energy efficiency improvements, which already have been dramatic, the amount of energy required for a dollar of GDP is remarkably large. Without access to cheap and copious energy, the industrial development of the world is not possible. Preventing economic development would be a recipe for political unrest. Also, economic well-being is

Figure 1: Relationship between Energy and GDP

the best solution to the continuing population growth, as population growth has effectively stopped in all industrialized countries.

Thus, fossil energy will be needed as one of several contributors to satisfy the ever-growing energy demand. However, for fossil energy to play a major role in the next century, carbon dioxide emissions together with all other emissions to the air will have to be essentially eliminated. This does not only affect coal based power plants, but any use of fossil energy. However, it is important for the coal industry and the coal based power industry to recognize that theirs is the most carbon intensive fuel. Since power plants are such large and concentrated sources of carbon dioxide, they are also likely initial targets for mandated reductions. In the long run, emissions reductions must include natural-gas-based power as well as coal-based power. While it may be easier for natural gas to achieve zero emissions, the cost advantage of coal,

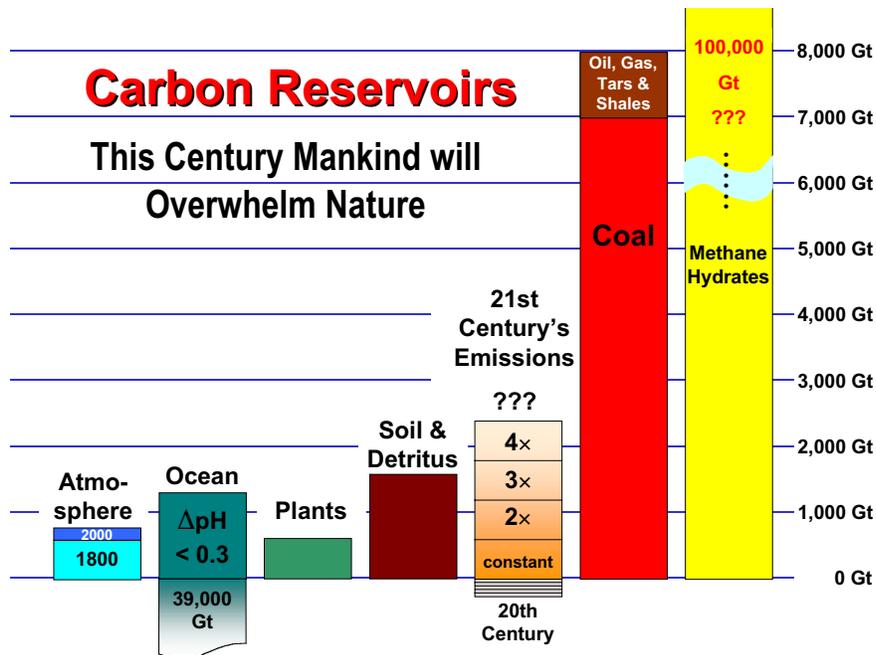


Figure 2: Size of natural carbon pools compared to fossil fuels reserves and to potential emissions in the new century. For emissions we show four blocks of 600 Gt each. 600 Gt would be the result of 100 years of constant emissions at the current rate. If the last century is any guide, the output could be five to six times larger. In the emission column below the zero line we show the far smaller total emissions of the 20th century, which in turn dwarfed the emissions of the 19th century. Individual blocks below the zero line represent 100 years of emission at the rate of 1900. The easily accessible carbon reservoirs with the exception of the ocean are comparable in size to the expected emissions of the next century. However, one would be hard pressed to actually double the existing biomass without substantively changing the environment. The ocean reservoir, at 39,000 Gt of carbon, is far larger, but its ability to take up carbon without environmental change is limited. Above the zero line, we are showing the amount of carbon that when dissolved in the ocean in the form of CO₂ would change its pH from top to bottom by 0.3. A reservoir we have not shown because it is not tightly coupled to the atmosphere is carbon stored in carbonate rocks, it is estimated to be $\geq 40,000,000$ Gt^[1]. The resource columns show that available fossil energy exceeds all likely demand for at least a century or two.

options are technological approaches that collect the carbon dioxide, preferably at its source and store it away permanently. The scale of the reservoirs needs to be virtually unlimited. We favor the formation of mineral carbonates from readily available magnesium or calcium silicates, because this natural process, which happens spontaneously on geological time scales, is virtually unlimited in its uptake capacity. Disposal in this form is exothermic and permanent and the end product is a material that is common in nature.

The Technology

Los Alamos National Laboratory together with the Zero Emission Coal Alliance (ZECA) is pursuing the development of the zero emission coal technology. ZECA is an alliance of industrial, government, and research institutions. ZECA's goal is to generate electricity or hydrogen from coal at high efficiency, without emissions to air.

which recently has become very large in the US, should easily overcome this advantage. Over the next few decades one will have to eliminate virtually all carbon dioxide emissions. The advantage of natural gas is a fleeting one, which should not obscure the enormous advantage that coal has when it comes to resource availability.

If fossil energy cannot be phased out, where could one put the fossil carbon after it has been turned into carbon dioxide? In the United States the *per capita* generation of carbon dioxide amounts to 22 tons per person per year. That is far more than could be reused in any form. Storage in various natural reservoirs may be feasible, but as indicated by figure 2, the capacities of all the naturally accessible sinks are far smaller than the amount they would be asked to accept. Thus, the only

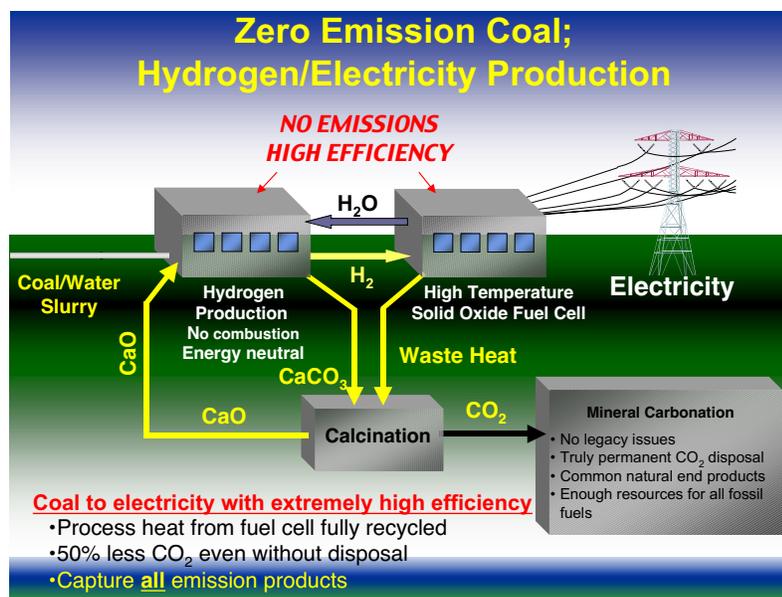


Figure 3: Outline of the ZECA process.

The ZECA process is illustrated in Fig. 3. It combines a coal-based electric power plant with a process for safely and permanently disposing of the carbon dioxide generated. The power plant is an ultra-efficient, coal-based power plant that updates the CO₂ acceptor process. Hydrogen is produced from steam and coal, and electricity from hydrogen in solid oxide fuel cells. Lime acts as the CO₂ acceptor. By removing CO₂ from the reaction products, the carbonation of lime drives the water-gas-shift and steam reforming reactions forward. Carbonation of the lime

also provides the heat necessary to run the hydrogen production to completion. To recycle the lime, we calcine the calcium carbonate with the waste heat from the solid oxide fuel cells while generating a concentrated stream of CO₂ ready for disposal. The coal gas is circulated through the plant without any gaseous emissions. Pollutants from the coal, like nitrogen, sulfur and heavy metal compounds or fine dust particles, leave the cycle either in liquid streams, or with solids.

The process includes CO₂ disposal by a chemical reaction with readily available mineral rock to form inert mineral carbonates. The reaction is exothermic and thermodynamically favored. The resulting materials are inert and environmentally benign. Since comparisons with conventional operations have shown the necessary mining of mineral rock to be economically feasible, the R&D focuses on the chemical transformation. Current process designs can generate magnesium carbonate from magnesium silicate rocks, but improvements in the processing steps are still required. The magnesium carbonate and silica end products are returned to the serpentine mine. The end products are stable thereby guaranteeing permanent sequestration of carbon dioxide.

Available mineral deposits far exceed mankind's capacity of generating carbon dioxide. The mining operations to obtain magnesium silicates would be large, but in terms of volumes mined and areas perturbed they are substantially smaller than the associated above-ground coal mines. Figure 4 shows a schematic of the coal-based power generation plant. The plant involves air and oxygen free hydrogen production and electricity production via a solid oxide fuel cell system. The hydrogen production process is an industrial, elevated temperature process that requires no air, involves no combustion, and requires no heat input. Aside from the coal, the process only uses water and CaO. Both are continuously recycled. A small fraction of the CaO is eventually lost in forming sulfides and sulfates whereas excess water needs to be removed from the cycle. The process is a variation of the proven CO₂ gas acceptor process.^[2] In addition to our work, several other groups are also employing variants of this process to produce hydrogen from a number of carbon-based fuels.^[3, 4]

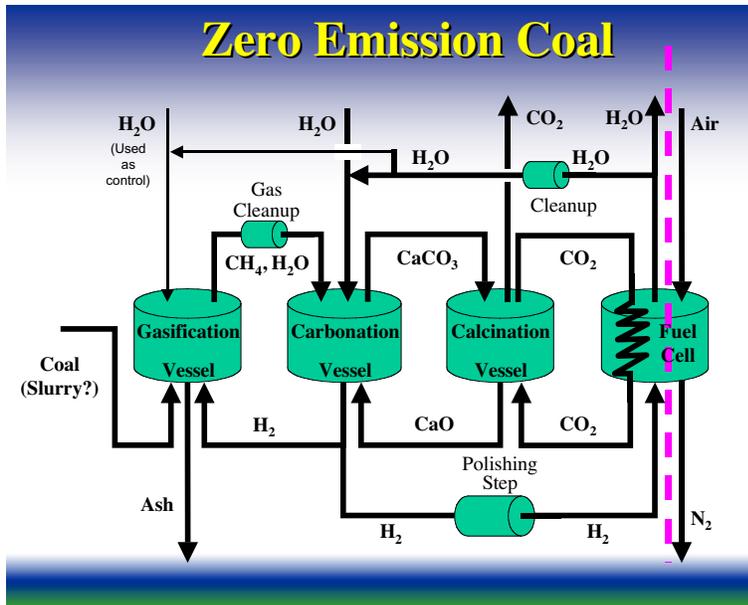
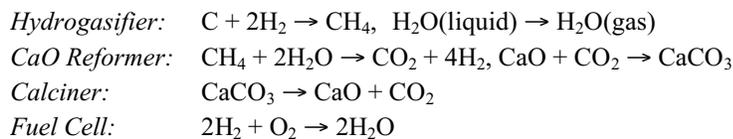
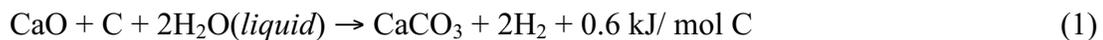


Figure 4: Schematic of the anaerobic hydrogen production and fuel cell system. Material flows are idealized to the predominant components. The major reactions are as follows:



carbon compounds, enters the carbonation vessel where it reacts with water to form CO_2 and hydrogen. The CO_2 is continuously removed from the reaction zone by binding it to CaO . The result is calcium carbonate and heat, which is necessary to drive the reaction to completion. The reactions within the mixture of liquid water, steam, and volatile hydrocarbons in this vessel neither consume nor generate heat. This is most easily seen by noting that the net reaction in the two vessels



is energetically neutral. Thus, if the first unit is thermally neutral so will be the second. If water enters the vessels as steam, the net reaction in the second vessel becomes exothermic. This provides an avenue to compensate for the inevitable heat losses that will occur in a realistic implementation of the process.

The gaseous product of the carbonation vessel contains four moles of hydrogen per mole of carbon that is introduced into the gasification vessel. Half of this hydrogen stems from the hydrogen in the methane that is generated in the gasification vessel and will be send back to maintain the gasification reaction. The other two moles of hydrogen are the product of equation (1) and derive from the water entering the steam-reforming vessel.

The two moles of hydrogen product not only took up the heat of combustion of carbon but also the heat of carbonation of calcium oxide. As a result, the hydrogen carries approximately 150% of the energy brought into the process by the carbon. By an accident of nature, the transfer of energy from carbon and calcium oxide to hydrogen can be achieved with nearly 100% efficiency. All the hydrogen is available for electricity generation from hydrogen, but some

Figure 4 is an idealized schematic listing only the dominant compounds produced in each step. Coal enters the gasification vessel either dry or as a slurry and is gasified with hydrogen. In contrast to the coal-based water-gas shift-reactions and steam reforming, hydro-gasification of carbon to methane is exothermic. By using predominantly hydrogen as a gasification agent, one avoids the need for external heat in the gasification process. Injecting some water or steam into the gasifier will eliminate the heat release and maintain a constant temperature in the gasifier vessel. By transforming the carbonaceous compounds of the fuel into gaseous forms, the gasifier separates out the ash, leaving it behind in the gasification vessel. The carbon, which is now in the form of volatile

fraction of the enthalpy of the reaction will be required to return the calcium oxide through calcination of the carbonate. As it turns out the theoretical efficiency of the fuel cell is limited to roughly 2/3 of the enthalpy of the hydrogen oxidation reaction, $\Delta G/\Delta H \sim 0.7$. The remaining enthalpy unavoidably shows up as heat and the temperature of the solid oxide fuel cell at about 1050°C is sufficiently high to apply this heat to the calcination process.

For a practical fuel cell the conversion process is only 50% efficient. Nevertheless, one still converts 75% of the energy brought into the process by the carbon into electricity. Energy is of course conserved. The fuel cell efficiency is measured against the heat of combustion of hydrogen, the overall conversion efficiency is measured against the heat of combustion of carbon. The hydrogen carries with it an “energy loan” from the CaO. Unless one has a free source of CaO, which typically is not available, the “energy loan” must be repaid. This is done in the calcination vessel by making use of the waste heat generated by the SOFC.

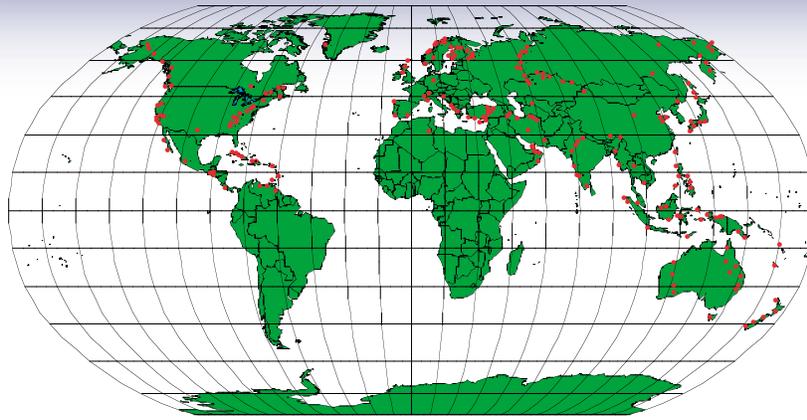
Since the process utilizes the waste heat of the fuel cell to ultimately generate additional hydrogen, it is highly efficient. In the theoretical limit of a pure carbon input, zero heat losses, and optimal performance of the fuel cell the efficiency of converting the heat of combustion of the carbon fuel into electricity would be 93%. Additional losses occur because heat will escape from the vessels and because a realistic conversion efficiency of a fuel cell is less than the thermodynamically allowed limit. Nevertheless, very high conversion efficiency, on the order of 70%, for the conversion of coal energy to electrical energy should be achievable. Compared to standard coal fired power plants this new process generates substantially less CO₂ for the same amount of electrical energy delivered. This in turn greatly reduces CO₂ disposal costs per unit of electricity.

If instead of the energy one tracks the free energy of the system, one sees immediately that not all the free energy of the carbon is utilized and turned into electricity. Even at the theoretical efficiency, some free energy has been lost, suggesting that the entropy of the system has increased as demanded by the second law of thermodynamics.

What makes the process economically attractive is the elimination of all emissions to the air without any additional effort. The process has no smokestack, as there is no combustion of coal. The ash from the coal is fully contained, making compliance with ever-tighter restrictions on particle emissions straightforward. A small amount of calcium oxide or calcium carbonate is used to capture the sulfur in the coal. The sulfur is pulled out of the reaction vessels in a solid form, thereby also eliminating hydrogen sulfide or SO_x emissions. Additionally, the reducing conditions inside the hydrogen production vessel do not lead to the formation of NO_x, and since there is no combustion involved, NO_x emissions are pushed to zero. Finally the CO₂ generated in the hydrogen production is initially extracted as a solid, before being converted to a concentrated gas stream. As this is an integral part of the hydrogen production process, no additional expenses are incurred in producing a concentrated stream of CO₂ exhaust.

Fig. 4. also shows that the process is essentially a closed loop. SOFCs transport oxygen ions through the electrolyte thereby acting as oxygen separation membranes. The hydrogen side of the fuel cell is never exposed to air and the product water is not diluted with nitrogen from air. Any unconverted hydrogen is simply recycled for a second pass. The closed nature of the process greatly simplifies the removal of any remaining contaminants introduced by the coal. Cleanup does not have to achieve air emission standards. It only has to be sufficient to protect all process units from detrimental effects. The rate of extraction of impurities must match the

Peridotite and Serpentinite Ore Bodies



Magnesium resources that far exceed world fossil fuel supplies

Figure 5: Magnesium resources.

mineral solids that will not leave a greenhouse gas legacy for future generations. Mineral carbonation occurs naturally on geological time scales and would eventually absorb all the additional carbon dioxide. The mineral carbonation concept is being developed by a collaboration that includes Los Alamos National Laboratory, the Albany Research Center, Arizona State University and the National Energy Technology Laboratory. Carbon dioxide reacts with magnesium rich silicates, serpentine or olivine, forming magnesium carbonate, silica and possibly water. The end products are all naturally occurring. The reaction is exothermic and it may be possible to harness the heat. The magnesium carbonate product is thermodynamically favored and hence the disposal is truly permanent.

The necessary magnesium silicates exist in vast, rich deposits worldwide, as is shown in Fig. 5. A single deposit in Oman contains over 30,000 cubic kilometers of magnesium silicates, which alone could handle all of the world's coal. The necessary scale of operation is large but not unreasonably large. The mining operation suitable for a large electric power plant is smaller than that for a large open pit copper mine.

The end products from the carbonation process would be used to refill the mine. Based on copper ore mining and milling costs, and the likely required plant size for the chemical processing, a disposal cost of \$15-20 per ton of CO₂ would not be unreasonable. Even a recent IEA study^[5] agrees that the mining, crushing, milling and reclamation costs are low, around \$7 to \$10 per ton of CO₂. The study noted that the difficulty lies in the design of an efficient chemical process. Simple processes that bring together the CO₂ and the serpentine rock in a direct reaction are potentially very low in cost. If the size of the plant is determined by a residence time of the solids that is on the order of an hour, the containment vessels, even if they are pressure vessels, will add little to the cost of the plant. In a recent study, the group at Albany has demonstrated a process that promises a very simple implementation.^[6] In effect; CO₂ in contact with olivine or serpentine, water, sodium bicarbonate, and sodium chloride transforms the bulk of the rock into magnesium carbonates and silica. The NaHCO₃ and NaCl play the role of catalysts and are not consumed in the process. The Albany process sidesteps the concerns raised

rate of injection with the coal, but some impurities may cycle many times through the system before they are removed. Letting internal concentrations build up simplifies the extraction process. This is in contrast to present day systems, which vent directly into the atmosphere and therefore require extremely high removal efficiencies.

Carbon dioxide will be permanently disposed of by reacting it with abundant naturally occurring minerals to form harmless stable

by the IEA in their report^[5] and suggests an implementation for the mineral carbonation process that including mining would be on the order of \$15 to \$20 per ton of CO₂. With a power plant operating at 70% efficiency, this would be about 1¢ US/kWh of electricity.

In conclusion, coal has an important and even dominant position in the energy future for the world. It is important that the value of this resource be recognized and utilized. We are confident that the technological solutions exist that will allow the realization of “green” coal, which can be used to ensure a clean world and a long term, prosperous, healthy, and secure global economy.

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