

AMERICAN CERAMIC SOCIETY

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emerging ceramics & glass technology

AUGUST 2010

Preeminent Professionals ACerS Awards 2010



- Paradigm shift: Greenhouse gas *utilization*
- MS&T pre-meeting planner
- PACRIM9 call for papers

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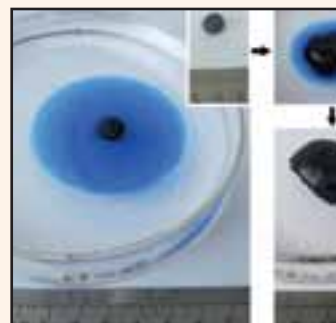
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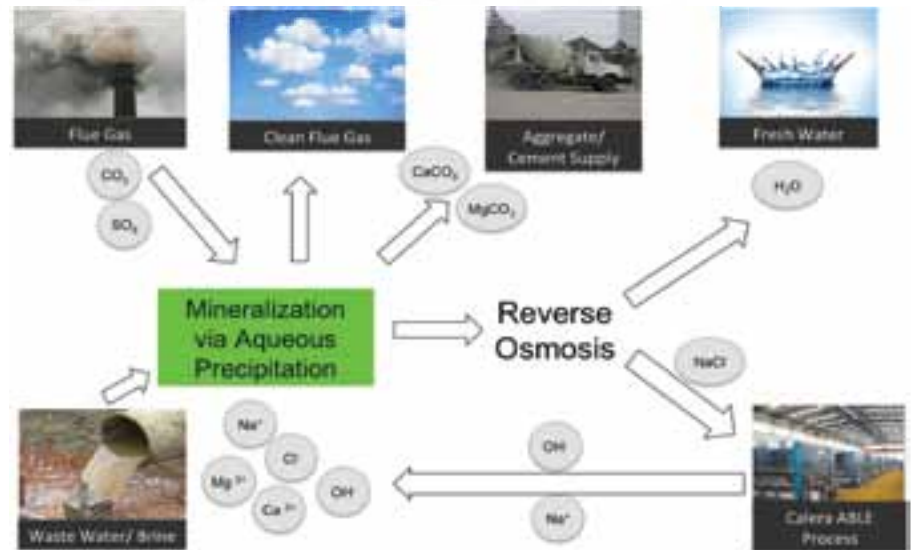
ACSB7, Vol. 89, No. 6, pp 1–56. All feature articles are covered in *Current Contents*.

CO₂ – Going beyond sequestration

Researchers know that for most of the last 425,000 years, carbon dioxide levels in the atmosphere had remained within a narrow band of 200–300 parts per million by volume. Today, however, CO₂ levels are growing and were already about 380 ppmv in 2007.

Some experts estimate that even with huge increases in noncarbon renewable and nuclear energies, CO₂ levels will still climb and could reach 550 ppmv by 2050. Climatologists say that at 550 ppmv, environmental conditions will be dire (full collapse of all coral reefs) and at 750 ppmv, the effects would be catastrophic.

In a speech at the 2007 California Clean Innovation Conference, Caltech chemistry professor Nathan Lewis reported that for the world to stabilize CO₂ levels at 550 ppmv, there would have to be



Finding a use: One example is Calera Corporation's roadmap for putting CO₂ to work.

a successful global campaign to increase energy efficiency, *plus* world leaders would have to make available as much new carbon-free energy as is being produced today by all of the oil, natural gas, coal and nuclear industries combined.

One added problem is that nature doesn't have a quick breakdown mechanism for CO₂ in the atmosphere. Even if CO₂ levels are stabilized at 550 ppmv, researchers estimate that it would take 500–5000 years for CO₂ to decay to where atmospheric concentrations return to the 300-ppmv level.

To mitigate this dilemma, one well-known proposal is CO₂ sequestration, i.e., purifying, compressing and hiding it someplace "safe." Current proposals include compressing and pumping CO₂ into deep ocean sites, deep oil and gas wells, and deep underground aquifers.

Each of these proposals has unique and major drawbacks. The effects from concentrations of CO₂ in deep oceans is unknown but is certain to cause significant pH changes. Deep oil and gas wells? There simply aren't enough of them.

There may be enough deep underground sites, but underground storage is difficult for geological and technical reasons. Thousands of leak-proof sites (leaking less than 0.1 percent) would be needed and significant geological changes would likely occur because of rock fractures and upheavals.

More problematic is that all of the sequestration proposals require significant

energy inputs to work, because the CO₂ would have to be captured, isolated, compressed and then piped long distances.

Just in time, alternative routes to CO₂ "storage" have begun to draw serious interest: Put the CO₂ to beneficial use directly or in a converted form as a replacement for current feedstock somewhere in industry.

The shift in thinking is this: If sequestration has significant risks and limitations and brings its own set of energy demands, doesn't it make more sense also to find new uses for CO₂ that may require less energy?

The Department of Energy has been moving quickly to accelerate research into CO₂ utilization. Recently, the agency's National Energy Technology Lab issued \$5.5 million in grants for feasibility-level research into several proposed technologies. On a larger scale, the DOE either has provided or will provide over \$110 million to test performance and scalability of six industrial CO₂ utilization pilot projects.

Along similar lines, we present on the following pages new work being conducted by a group at the University of Toledo, led by ACerS member Abdul-Majeed Azad, who is exploring the use of converting CO₂ into fuel for fuel cells or raw materials for synthetic fuel and chemical production.

– Peter Wray

Putting CO₂ to Use

CO₂ utilization examples

Alcoa Inc., Skyonic Corp. and Calera Corp. Each company is working to demonstrate the conversion of flue gas CO₂ into carbonates that can be used for construction material, soil additives and cement production feedstock.

Phycal LLC and Touchstone Research Lab Each company is building a CO₂-to-algae-to-biofuels facility, where the CO₂ will be used to cultivate microalgae.

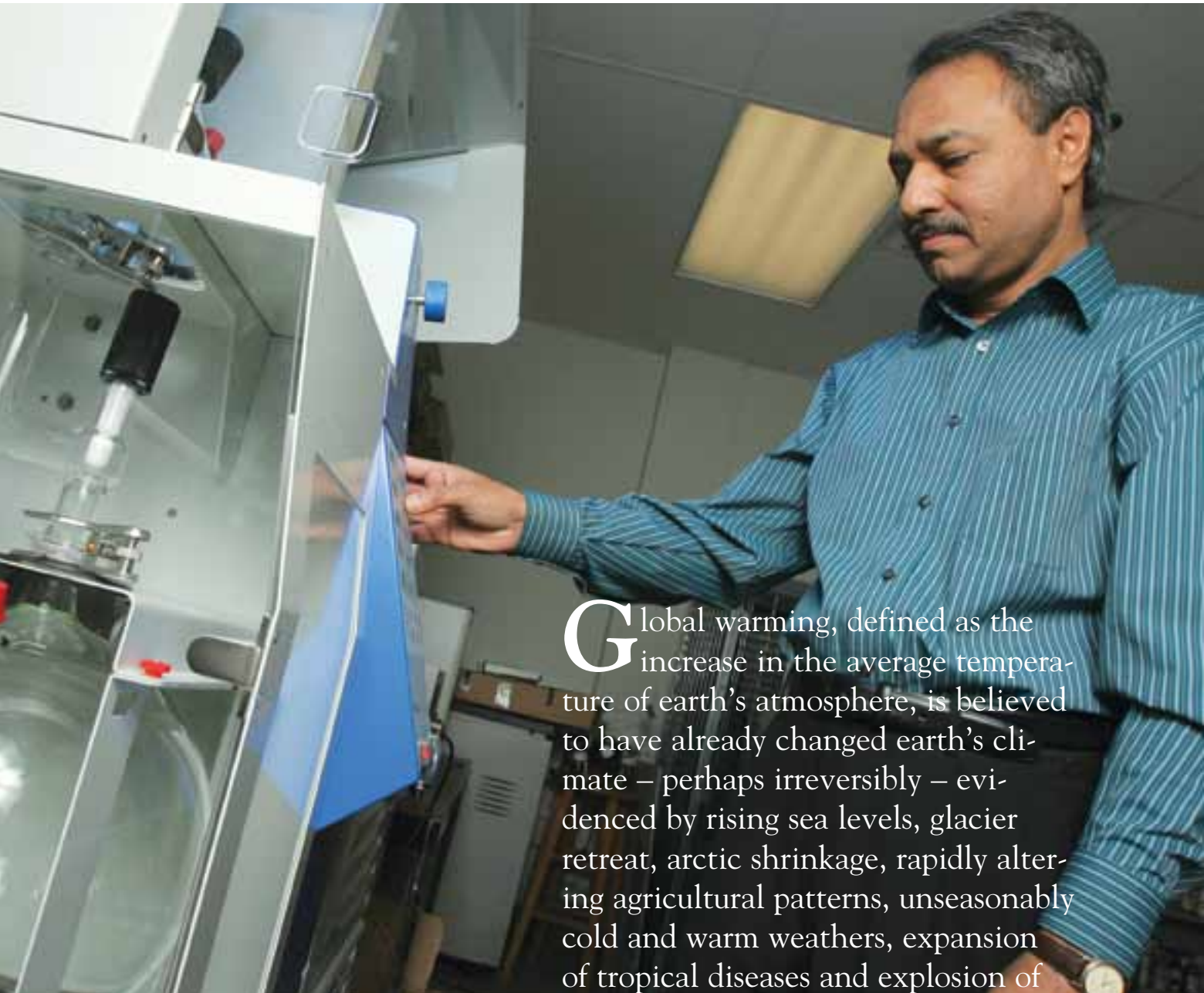
Novomer Inc. Working with Ablemarle Corp. and Eastman Kodak, Novomer is using a novel catalyst to get CO₂ to react with petrochemical epoxides to create polycarbonate products for the packaging industry.

McGill University Researchers at the school are working with the 3H Company to integrate a self-concentrating absorption technology into a curing process for the precast concrete industry using CO₂ as a reactant.

PhosphorTech Corp. Investigators are demonstrating a light-harvesting catalyst to reform CO₂ into methane gas and other products.

Utilization *not* sequestration: A novel paradigm in greenhouse gas mitigation

University of Toledo researchers offer radical alternative to CO₂ storage.



Global warming, defined as the increase in the average temperature of earth's atmosphere, is believed to have already changed earth's climate – perhaps irreversibly – evidenced by rising sea levels, glacier retreat, arctic shrinkage, rapidly altering agricultural patterns, unseasonably cold and warm weathers, expansion of tropical diseases and explosion of forest fires. This poses a great threat to the quality of life on this planet. Irrespective of the origin and modality of its use, the ultimate chemical fate of conventional fossil fuel combustion is always CO₂ and H₂O. Both these species

By Abdul-Majeed Azad (in lab, above), Desikan Sundararajan, Sirhan Al-Batty and Eric McDaniel

are well-known greenhouse gases and are responsible for contributing considerably to global warming, a subject of contentious political, social and technical debate. As a result of constant increase in their concentration and retention, scientific projections estimate that the average global temperature will rise between 1.4°C and 5.8°C by the year 2100. In 2007, the global level of CO₂ was 30 billion metric tons and is projected to be 43 billion metric tons by 2030. The United States contributes the largest – 22.2 percent – toward global CO₂ emission.^{1,2}

It is less known that water vapor is a naturally occurring greenhouse gas and accounts for the largest percentage of the greenhouse effect (36–66 percent) in terms of radiation absorbance. Water vapor concentrations fluctuate regionally. However, unlike in the case of CO₂, human activity does not directly affect water vapor concentrations except at local scales (e.g., near irrigated fields). Water vapor is approximately 80 percent of all greenhouse gases by mass and about 90 percent by volume. However, the radiative importance of water vapor is less than that of CO₂, CH₄ and N₂O. Moreover, the lifetime of water vapor in the environment is about nine days compared with thousands of years for CO₂.³

The efforts to diminish the influence of carbon footprints on the way energy is produced and used today will be the most visible legacy of the technological developments of the 21st century. Catalytic (using bimetal- or trimetal-supported alumina matrices) and noncatalytic schemes of direct thermal cracking of natural gas (methane) leading to CO₂-free H₂ generation at high temperatures have been demonstrated on a laboratory scale.^{4,5} Several nonfossil approaches are also being actively pursued. One of those alternative pathways is biofuels, but even biofuels, including those derived from waste biomass, involve the logistic burden of and energy for harvesting, processing, separation, purification and delivery. However, their use, too, ultimately leads to the generation and accumulation of CO₂ and water vapor in the atmosphere.

In the mean time, solutions must evolve – without the problems associated with greenhouse gases – using the nation's available energy resources. The two approaches however, are not mutually exclusive, because no fossil fuel use could avoid greenhouse gas generation. Hence, it is relevant and prudent to have a technology that separates CO₂ in the flue gas stream without expending additional energy. The resulting CO₂ must be ready for compression and transport to a storage facility.

There is a frantic race to control, combat and counter the menace of global warming, albeit with very limited success. For example, the National Energy Technological Laboratory

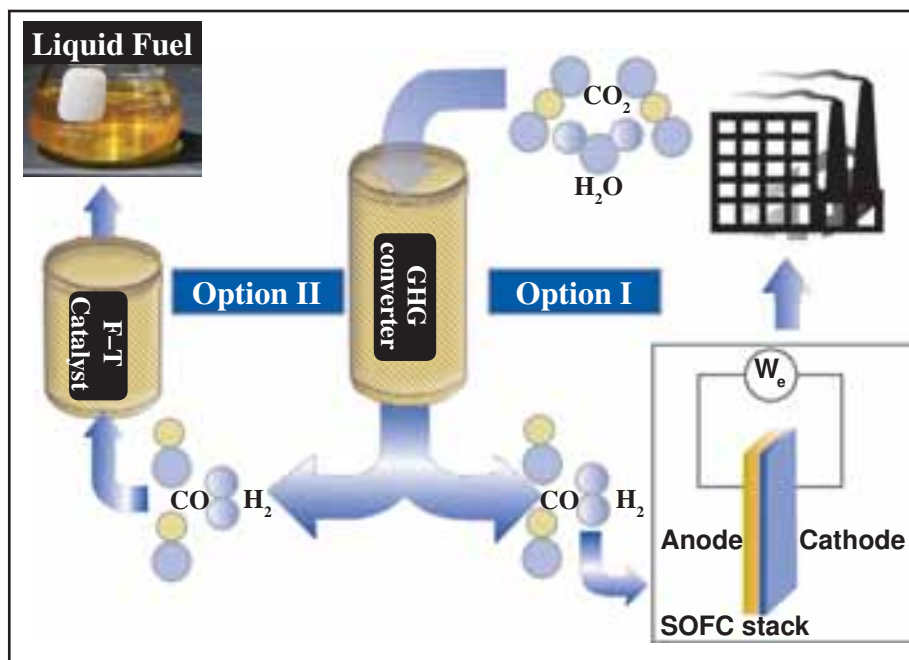


Fig. 1. Schematic pathways of the proposed CO₂ mitigation technology.

under the auspices of the Department of Energy has been working to develop a range of carbon capture and storage technologies.⁶ In July 2008, it awarded 15 new cooperative agreements to R&D projects focused on development, testing and demonstration of oxy-combustion, chemical looping, membranes, solvents and sorbents for postcombustion CO₂ capture.⁷

Chalmers introduces CLOU

In this connection, the on-going efforts of the Lyngfelt group at Chalmers University of Technology in Sweden are significant. This group has developed a novel approach to separate CO₂ by using the benign redox capability and thermochemical aspects of a host of solid-oxide carriers in a fluidized bed mode.⁸⁻¹⁰ It has coined the acronym CLOU – *chemical looping with oxygen uncoupling* – to describe the process.

CLOU is essentially an extension of the chemical-looping combustion concept, itself based on a 55-year-old patent by Lewis and Gilliland¹¹ describing the production of high-purity CO₂ by circulating a solid-oxide carrier between two fluidized bed reactors: an air reactor and a fuel reactor. The fuel is introduced in a fuel reactor containing a solid-oxide carrier (M_xO_y), wherein it is oxidized to CO₂ and H₂O. The reduced oxygen carrier (M_xO_{y-1}) is transported to the air reactor where it is reoxidized. After water removal by simple condensation, CO₂ is separated with no direct loss in efficiency, because the fuel does not encounter air.

Recently, the Lyngfelt group showed that the methodology is applicable to solid fuel, such as coal, as well.^{12,13} This broader scope of capturing CO₂ by the CLOU process is of tremendous interest, of course, because there is an abundance of coal and similar solid fuels (including biomass) worldwide.

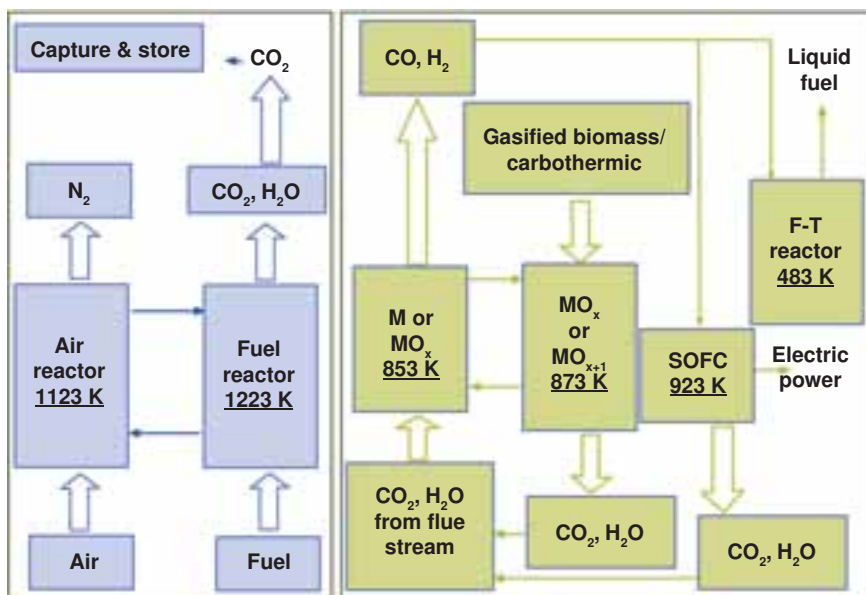


Fig. 2. Overall summary of the chemical looping combustion process (left) for CO₂ capture and the proposed greenhouse gas beneficiation technique (right).

Researchers have also successfully employed a number of unsupported – as well as supported – oxides of the first *d*-group of transition metals (notably Mn, Fe, Co, Ni and Cu) amenable to facile redox transformation. Some, recently, have used compositions containing two metals (Fe–Mn or Fe–Ni) and perovskites endowed with tailored stoichiometric defects (CaMn_{0.875}Ti_{0.125}O₃).¹⁰ In some cases, inert zirconia¹⁴ and silica¹⁵ supports also have been used. During the 238th American Chemical Society’s annual meeting, several approaches were presented in the symposium on “Advances in CO₂ Conversion and Utilization.”¹⁶ The methodologies presented in 15 papers ranged from catalytic to electrochemical, photochemical and thermochemical, using stand-alone or supported systems. These methodologies lead to a variety of end-products, such as CO, formaldehyde, formic acid, methanol and methane.

With such extensive efforts dedicated toward mitigating greenhouse gas effect, in general, and lowering the carbon footprints, in particular, an energy revolution could be initiated by developing a methodology and demonstrating its practical implications, wherein CO₂ and water vapor could be catalytically or photocatalytically converted into syngas (CO + H₂). This value-added calorific commodity could then be used in high-end applications, including the synthesis of value-added liquid hydrocarbons by the Fischer–Tropsch process¹⁷ or generating electricity by fuel cells. A visual of the greenhouse gas beneficiation concept is shown in Fig. 1.

Innovation

In contrast, the CLOU process, we have developed a technique that, in essence, causes targeted and quantitative conversion of CO₂ and H₂O to CO and H₂, respectively, through a simple heterogeneous gas/solid redox process.¹⁸ This is based

on the simple fact that any reducing reaction must be accompanied by a concurrent oxidation process and vice versa. Thus, the reduction of CO₂ and H₂O must be accompanied by a concomitant oxidation of another species elsewhere in the system. In that sense, this methodology is in fact CLOU operating in reverse (Fig. 2), albeit with more attractive features, such as less energy intensiveness, less expense and added beneficiation rather than sequestration.

Whereas the CLOU process obviates the separation step by using a solid oxidizer in lieu of air, the greenhouse gas beneficiation paradigm offers several self-evident advantages. For example, at much lower temperatures, it converts the two greenhouse gases to syngas for generating electrical power via fuel cells or for liquid fuel via an F–T process. Moreover, the spent reactant is regenerated easily by using inferior quality syngas gas, such as from biomass. Finally, the exit streams of the fuel cell, as well as

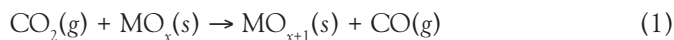
the regenerator, are CO₂ and H₂O that can again be fed into the cycle with no processing or additional cleanup.

Below, we detail our strategy of converting CO₂ to CO, of water vapors into hydrogen, and a mixture of carbon dioxide and water vapor to syngas (CO + H₂), via innovative heterogeneous reaction with a simple metal or metal oxide under very mild experimental conditions (580°C; 1 atmosphere). When fed into an IT-SOFC at 650°C, these streams create an open-circuit voltage comparable with running the same SOFC with H₂ (ideal fuel) or CO.

The metal and metal oxide that mediate the conversion of CO₂ to CO, of water into hydrogen or the CO₂ + H₂O mixture into syngas (CO + H₂), are, in turn, converted to an oxide with enhanced magnetic characteristics. The spent oxide could be either regenerated or used for manufacturing a variety of ceramic magnets (spinel ferrites of the general formula A^{II}B^{III}O₄),¹⁹ a product that has an annual market value of about \$5.4 billion. The regeneration of the spent oxide could be conducted either carbothermally or with gasified biomass that can serve as a low-quality substitute for conventional reductant under mild experimental conditions.

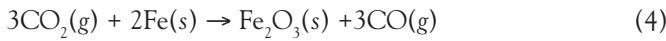
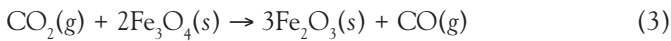
Theoretical rationale

We consider the following gas–solid redox reactions:



In our work, the greenhouse gas interacts with iron oxide (magnetite, Fe₃O₄) in one case, and with elemental iron in the other. The reduction of CO₂ to CO results in formation

of Fe₂O₃ because of the oxidation of Fe₃O₄ and Fe:



The numerical value of the overall equilibrium constant for a stoichiometric reaction is a measure of the occurrence propensity of the said reaction. It is also a strong function of temperature and, at a given temperature, K is unique for a particular reaction. In stoichiometry calculations, we assume the reaction runs to completion. However, by definition, K is the ratio of the concentration of the reactants and the products at equilibrium. Therefore, at a given temperature, a large K value (>1) implies that the fraction of product(s) is larger than the reactant(s) and that the equilibrium lies to the right, whereas, a small K value shifts the reaction to the left. Finally, the equilibrium constant is related to the Gibbs energy of the reaction, which dictates its thermodynamic feasibility.

The overall equilibrium constant is given by²⁰

$$K = K_0 \cdot K_1 \cdot K_2 \quad (5)$$

where,

$$K_0 = \exp\left(\frac{-\Delta G_0^\circ}{RT_0}\right)$$

$$K_1 = \exp\left[\frac{\Delta H_0^\circ}{RT_0} \left(1 - \frac{T_0}{T}\right)\right]$$

$$K_2 = \exp\left(-\frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT + \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}\right) \quad (6)$$

K_0 is the equilibrium constant at the reference temperature T_0 (298 K), K_1 is a multiplier that contributes toward the temperature effect when the heat of reaction is independent of temperature, and K_2 accounts for the change in heat of reaction with temperature. In most of the instances, K_2 is small (approximately equal to 1). When we use reliable thermodynamic data for various components,²¹ the net equilibrium constant for reaction (3) at 580°C (853 K) was computed to be

$$K = K_0 \cdot K_1 \cdot K_2 = (5.76 \times 10^{10})(4.144 \times 10^{-6})(1) = 2.387 \times 10^5$$

Clearly the equilibrium constant of the reaction is far greater than 1, and this accounts for the fact that the equilibrium lies to the right. Accordingly, the reduction of CO₂ to CO with magnetite is feasible.

In addition, the thermodynamic equilibrium oxygen partial pressure (p_{O_2}) in the biphasic mixture of Fe₃O₄ and Fe₂O₃ could be computed to be 1.82×10^{-15} atmosphere at 853 K. At p_{O_2} values greater than 1.82×10^{-15} atmosphere, the oxidation of Fe₃O₄ to Fe₂O₃ will occur. Similar analysis yields a value of 1.41×10^{-26} atmosphere for the equilibrium

p_{O_2} needed for the oxidation of Fe to Fe₂O₃.²¹ Therefore, at p_{O_2} greater than 1.41×10^{-26} atmosphere, oxidation of Fe to Fe₂O₃ will take place.

The reactions in Eqs. (3) and (4) show that the oxidation of Fe or Fe₃O₄ to Fe₂O₃ is attended by the reduction of CO₂ to CO. The p_{O_2} caused by the coexistence of CO₂ and CO by virtue of the reaction:



could be computed from the following equation:

$$p_{\text{O}_2} = \left(\frac{p_{\text{CO}_2}}{p_{\text{CO}}}\right)^2 \cdot \left(\frac{1}{e^{\frac{-\Delta G_0^\circ}{RT}}}\right)^2 \quad (8)$$

According to Eq. (8), it is possible to control the p_{O_2} at a given temperature very precisely by controlling the ratio of the concentration of CO₂ and CO in the mixture. The p_{O_2} values computed at 853 K in some CO₂/CO mixtures are shown in Table I.

Table I. Equilibrium p_{O_2} values at 853 K in some representative CO₂/CO and H₂O/H₂ mixtures.

Mixture	p_{O_2} (atm)	Mixture	p_{O_2} (atm)
CO ₂ – 100 ppm CO	1.445×10^{-18}	H ₂ O – 100 ppm H ₂	4.6×10^{-19}
CO ₂ – 10 ppm CO	1.445×10^{-16}	H ₂ O – 100 ppm H ₂	4.6×10^{-17}
CO ₂ – 1 ppm CO	1.445×10^{-14}	H ₂ O – 1 ppm H ₂	4.6×10^{-15}
CO ₂ – 0.1 ppm CO	1.445×10^{-12}	H ₂ O – 0.1 ppm H ₂ [†]	4.6×10^{-13}

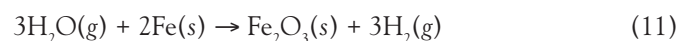
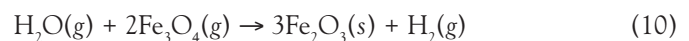
As stated above, at 853 K, the equilibrium p_{O_2} values for the individual Fe₃O₄/Fe₂O₃ and Fe/Fe₂O₃ coexistences is 1.82×10^{-15} and 1.41×10^{-26} atmosphere, respectively. Both these values must be exceeded to oxidize Fe₃O₄ or Fe to Fe₂O₃. Table I figures indicate that the p_{O_2} generated by the CO₂–CO mixture in the last row (a practically pure CO₂ stream) exceeds both these values by several orders of magnitude. Therefore, it is reasonable for us to believe that pure CO₂ is capable of oxidizing Fe₃O₄ and Fe to Fe₂O₃, while, as seen from Eq. (3) and Eq. (4), CO₂ is reduced to CO.

Likewise, to demonstrate the feasibility of the reaction between water vapor and the solid metal or metal oxide, the p_{O_2} values at 853 K for various H₂O/H₂ mixtures were computed for the reaction



Some typical values in the H₂O/H₂ mixtures are also summarized in Table I.

The p_{O_2} value in the H₂O – 0.1 ppm H₂ mixture (almost pure H₂O stream) is also more than several orders of magnitude higher than that required theoretically for the oxidation of Fe₃O₄ or Fe to Fe₂O₃ as per the reactions



Utilization *not* sequestration

Therefore, water vapor, like CO_2 , is capable of oxidizing Fe_3O_4 and Fe to Fe_2O_3 . As with CO_2 , H_2O is reduced to H_2 .

Thus, the proposed technology offers two feasible pathways to utilize the syngas thus produced:

- A direct feed to a solid oxide fuel cell; and
- Conversion to liquid fuels, such as hydrocarbons, ethanol and butanol via Fischer-Tropsch synthesis.

These pathways are depicted in Fig. 1.

Experimental details

We obtained commercial-grade steel-mill waste powder (particle size less than 45 micrometers, hereafter referred to as “mill scale”) and two types of iron powders (purity ~99 percent; average particle size 1–3 and 80 micrometers). In some cases, we also used nanoscale iron powder produced by the solvothermal conversion of mill scale in an autoclave by a method one of us developed.²² All the samples were systematically characterized for their phase and morphological features before and after the conversion reactions using XRD, SEM/EDS and VSM.

The powder then was packed into a stainless-steel filter with 5-micrometer-sized size pores, which was placed in the center of a quartz reactor located in the uniform temperature zone of a furnace. The sample was first heated up to 580°C in high-purity nitrogen and then switched to pure CO_2 flowing at 100 standard cubic centimeters per minute. In the case of experiments involving water vapor, CO_2 was bubbled through a water bath prior to entry into the reactor. The moisture content was varied by controlling the temperature of the water bath. The sample size was varied from 2 to 15 grams.

We quantified the conversion yield of the gaseous species in the exit stream of the reactor using a gas chromatograph. We assessed the quality and quantity of the product by measuring the performance of a single-button SOFC (Ni-GDC||YSZ||LSM-GDC), monitoring the open-circuit voltage using the CO , H_2 and a combination of the two gases. We compared this with the open-circuit voltage



Fig. 3. Experimental setup used for the validation of the concept using exhaust from an internal combustion engine as feed.

obtained when we ran the fuel cell with pure H_2 and CO under identical conditions.

To further evaluate the validity of the concept in real-world-like conditions, we fed the exhaust of a 600 cubic centimeter internal combustion engine into a reactor packed with the magnetite powder. The exit stream was led into the anode of a single-button SOFC operated at 650°C . The experimental setup used for this evaluation is shown in Fig. 3.

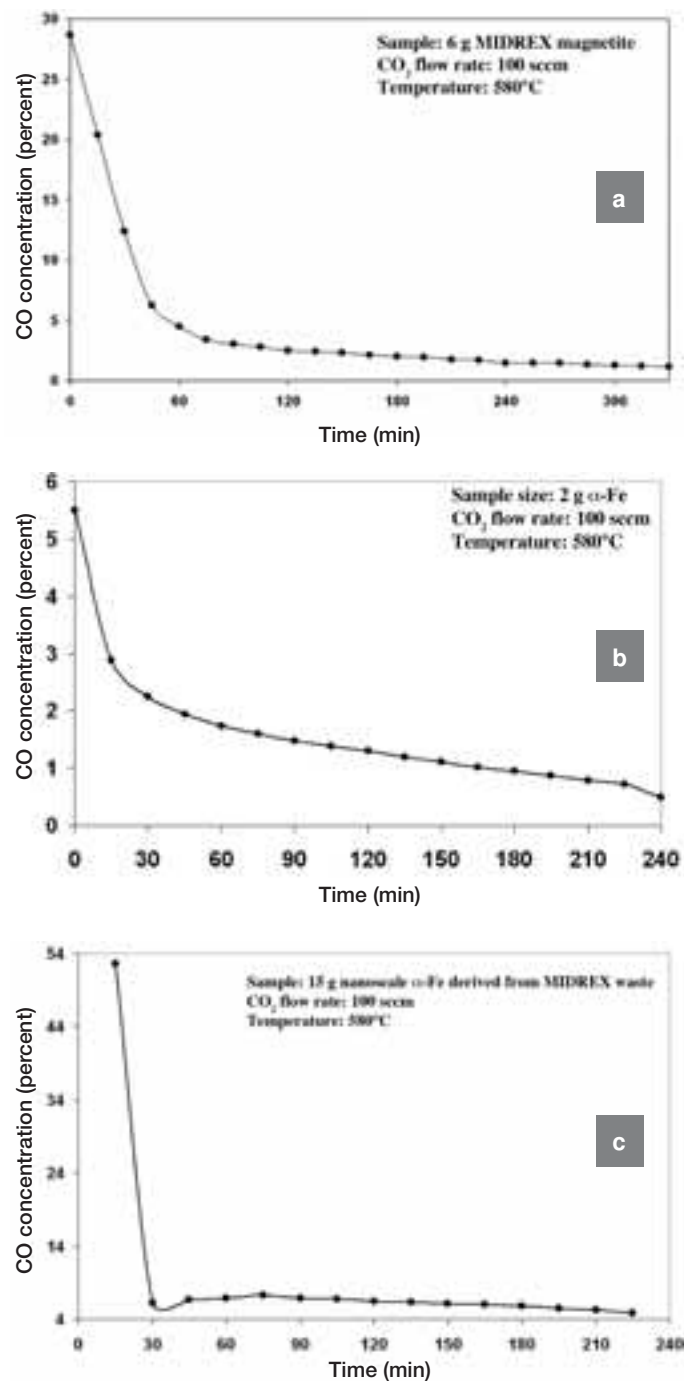


Fig. 4. Time dependence of CO generation from CO_2 with (a) Fe_3O_4 , (b) commercial microscale Fe and (c) nanoscale Fe powder.

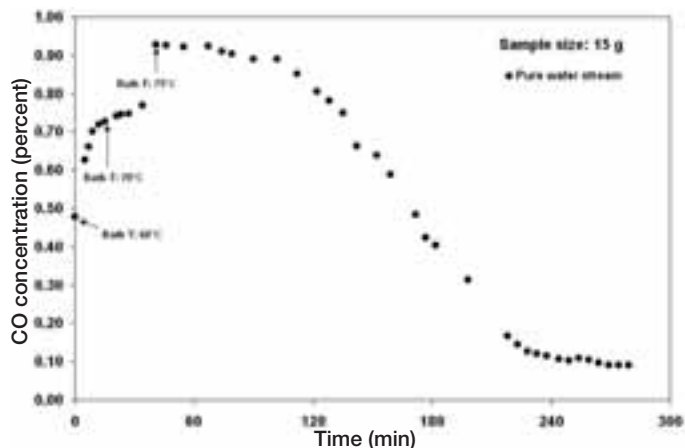


Fig. 5. Evidence of H_2 generation from pure water stream in contact with the magnetite.

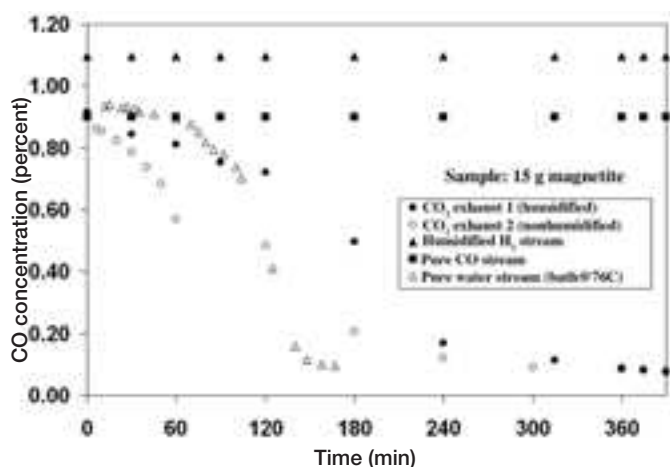


Fig. 6. Comparison of a single-button fuel cell output with different feeds upon interaction of CO_2 with magnetite.

Results and discussion

Literature is abundant with suggestions for CO_2 storage (also known as sequestration). The sequestration ideas related to storage in geologic formations and terrestrial ecosystems are most widely discussed.

In the first, proponents envisage that CO_2 is stored under pressure between porous rock layers, capped by a layer or multiple layers of nonporous rocks. In the second, proponents envisage increased CO_2 uptake by plants through tree-planting, no-till farming, forest preservation and understanding and deciphering the genomes of carbon-storing soil microbes.

Other possibilities that have been looked at and pursued to a great degree are the dissolution of CO_2 in brine²³ and reaction with alkali or alkaline-earth minerals to form solid carbonates.²⁴ Other interesting concepts for CO_2 sequestration are through self-assembled organic nanochannels,²⁵ zeolites²⁶ or MCM-41 materials,²⁷ or its reduction to CO in the presence of hydrogen and methane over magnesia.²⁸

The photoreduction of CO_2 with water vapor over titania dispersed on silica and zeolites also has been reported,²⁹ but

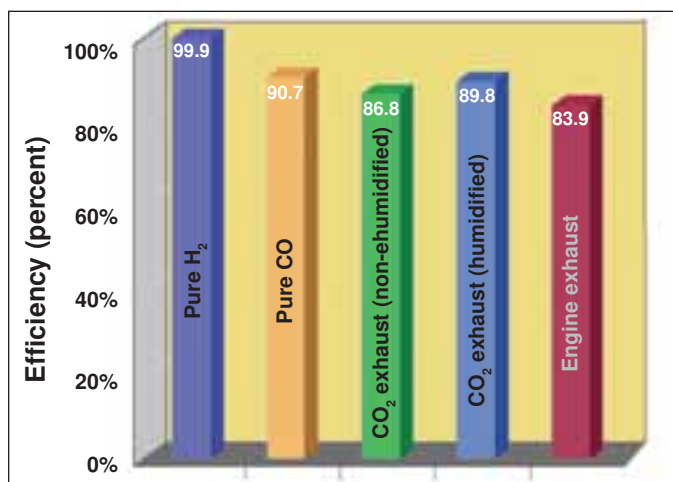


Fig. 7. Comparison of the efficiency of a single-button fuel cell at $650^\circ C$ on various feeds. The efficiency is defined as the ratio of $OCV_{(GHG-fuel)}$ to $OCV_{(H_2)}$ *

with very low activity. The evolution rate of the products (in this case methane and methanol) per hour was a few nanomoles per gram of catalyst. Moreover, in all these instances, the end products were, most of the time, methanol, formaldehyde, formic acid and methanol that require elaborate separation protocols, not syngas.

Also, Bidrawn et al.,³⁰ have reported the reduction of CO_2 at $800^\circ C$ in a solid-oxide electrolyzer, by operating an SOFC in reverse using CO– CO_2 mixture as the fuel and chromium-substituted LSM ($La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_3$) in conjunction with (yttria + zirconia)-doped ceria and palladium as the redox stable anode. The problem here, evidently, is that the fabrication of this complex electrolyzer is quite elaborate.

In contrast, Fig. 4 shows the evidence of CO_2 conversion to CO we monitored by the online GC signals with 6 grams of magnetite, 2 grams of commercial iron and 15 grams of nanoscale iron. The CO yield in all these cases was very close to the theoretical value as per Eqs. (3) and (4), within the permissible experimental errors. Several subsequent runs under identical experimental conditions yielded similar

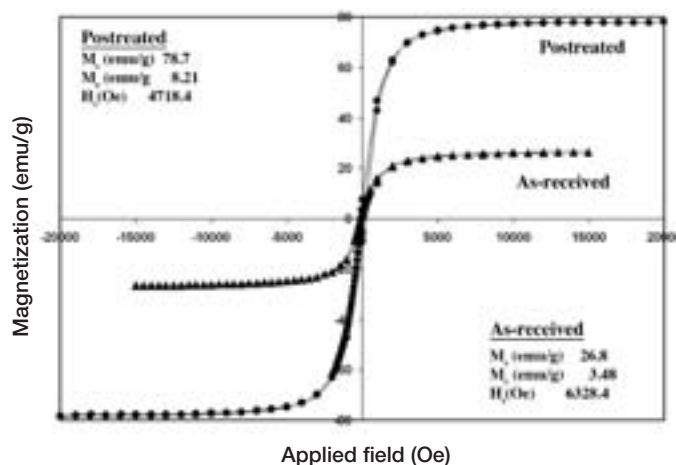


Fig. 8. Fe_3O_4 magnetization curve before and after exposure to CO_2 gas at $580^\circ C$ for 4 hours.

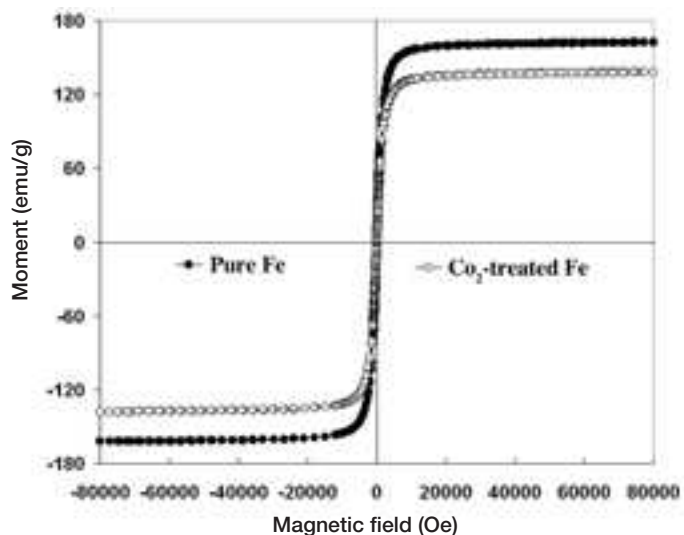


Fig. 9. Magnetization curve of iron before and after exposure to CO₂ gas at 580°C for 4 hours.

results, bolstering the theoretical concept outlined above.

The monotonic CO concentration decrease over time is simply caused by the gradual depletion of the active component (Fe or Fe₃O₄) with the progress of the reaction.

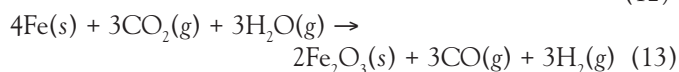
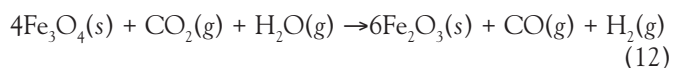
We found direct evidence of the propensity of water vapor reduction to hydrogen, per Eq. (10), in the functionality of a solid-oxide button fuel cell (Fig. 5). As we expected, we saw that the open-circuit voltage responded sharply to the increase in temperature of the water bath. Simply put, as the vaporization and, hence, steam content of the stream increased steadily with rise in the bath temperature, the hydrogen level also increased.

The steady decline in the cell output with time is caused by the constant consumption of the magnetite. Elsewhere, we have also amply demonstrated this generation of hydrogen via metal–steam reforming reaction.^{31–33}

We further verified that CO₂ was indeed converted to CO by connecting the exit stream to an SOFC at 650°C. This is shown in Fig. 6 for dry and humidified CO₂ streams.

In all the above cases, we continuously monitored the fuel cell response under the open-circuit voltage “no load” condition. Our results show a good correlation with the operational efficiency of the reactant. In the case of humidified CO₂ stream, the higher open-circuit voltage can be attributed to the reduction of water vapor. The presence of H₂ in the gas stream, although in small concentration, accentuated the cell performance.

Thus, it is reasonable to conclude that a mixture of CO₂ and H₂O (both of which are potent greenhouse gases and are the final products of a combustion process) could be converted to syngas through the reactions



The syngas stream could be either used as a combined feed for SOFC or catalyzed to liquid fuel via Fischer–Tropsch synthesis. We are currently investigating the latter option in our laboratory.

An unexpected byproduct

It should be pointed out that as per Eqs. (3), (4), (10), (11), (12) and (13), Fe₃O₄ and Fe theoretically transform to Fe₂O₃ upon interaction with CO₂, H₂O and their mixtures.

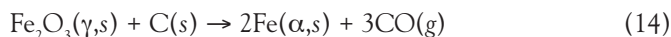
Intuitively, this could be hematite. However, a comparison of the magnetic measurements before and after CO₂ reduction in this work showed that this was not the case. In fact, we found that the reaction formed maghemite (γ-Fe₂O₃), not hematite. This discovery can be seen from the pronounced behavior of the postreduced sample from the magnetization vs. applied magnetic field curves shown in Figs. 8 and 9. (Similar curves were obtained for water-treated samples as well.)

The formation of maghemite makes sense. Because metal oxides tend to be crystalline substances, the reactions they undergo are either reconstructive or topotactic. In reconstructive reactions, native crystals disassociate, react and crystallize again. In topotactic reactions, the crystal structure of each particle remains intact throughout the reaction.

Maghemite is ferrimagnetic and isostructural with spinel magnetite and it has a cationic deficiency at the octahedral B-site in the lattice. It is also known to form by the topotactic transformation of magnetite attended by internal atomic displacements and defect formation, so that the initial and final lattices are in coherence.³⁴ Diffusion studies with radioactive iron tracers in magnetite particles have been used at high temperatures and relatively low *p*_{O₂} to confirm this.³⁵

This observation correlates the changes in the diffusion coefficients because of the changes in *p*_{O₂} values with reactions that involve the formation of vacancies in the octahedral lattice.³⁶ Formation of these vacancies is important for diffusion³⁷ and oxidation because it electrically compensates for the conversion of Fe²⁺ to Fe³⁺. We believe the experimental conditions we employed in this work are conducive to the observed effect.

Carbothermic reduction, according to the following stoichiometric reaction with graphite powder at 600°C, converts the highly magnetic maghemite into elemental iron:



The XRD patterns of the sample before and after the reduction provide evidence of this conversion (Fig. 10).

Conclusion

We have identified two inexpensive precursors – a metal and an oxide – that are capable of converting CO₂ and H₂O to CO and H₂, respectively, on a 1:1 molar basis, at a mild temperature of 580°C and 1-atmosphere pressure. The importance is that this is a beneficiation of the two major greenhouse gases.

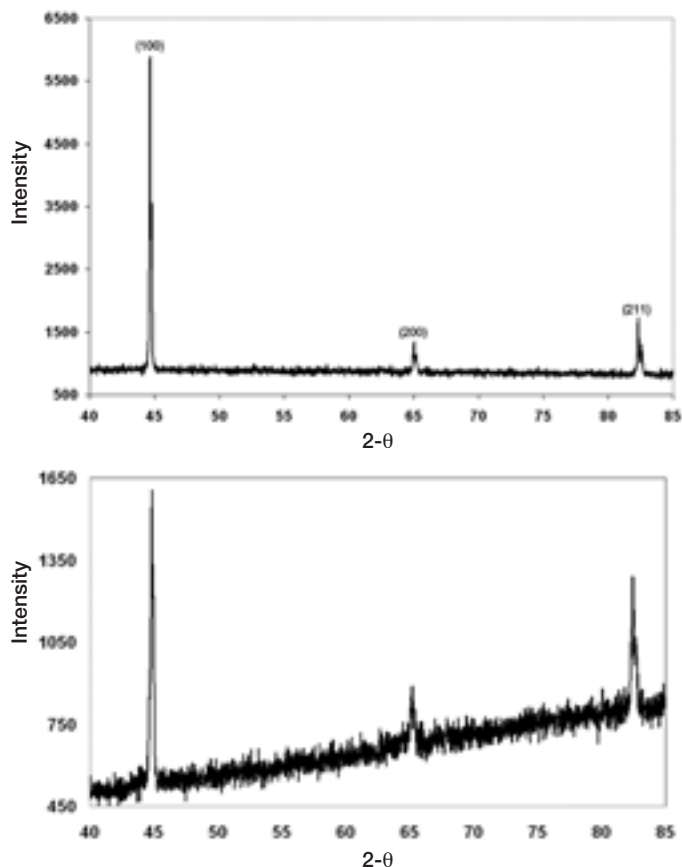


Fig. 10. Structural evidence of reconversion of maghemite to iron via carbothermic reduction.

We demonstrated that these streams, after they have been reduced, can be fed into a SOFC at 650°C to create an open-circuit voltage comparable with the performance of the ideal fuel, pure H₂. We believe the energy sector can benefit from this approach because it would provide a means of curbing the carbon footprints from fossil fuels in an innovative way.

Alternatively, the streams can be used to make syngas, a precursor to other fuels and materials. For example, NASA is currently looking at nonpetroleum-based jet fuels in the pursuit of alternatives to power commercial jets and address rising oil costs. A greenhouse-gas-derived Fischer–Tropsch fuel could respond to that quest. We currently have experiments in progress to explore this option.

We believe our concept will advance the state-of-the-art in the pursuit of carbon capture and sequestration in two ways:

- As mentioned above, although several methodologies have been proposed, none of them seem capable of selectively and quantitatively converting CO₂ to CO – one of the two valuable precursors for F–T synthesis. Therefore, the theoretical concept and experimental results shown here are perhaps the first of their kind that ensure selective, quantitative and targeted conversion of CO₂ to CO.
- The reduction of the CO₂ provides a “green” envi-

ronmentally benign process of combating the ever-increasing greenhouse gas effect. Furthermore, it shows a waste product of steel industry can be employed as an effective agent for the envisaged conversion. Almost 20 million metric tons of mill-scale waste is produced annually by the steel industry worldwide. The U.S. share of this waste generation is 1.5 million metric tons per year. Thus, a remediation of this industrial waste, alone, provides great value because more than 80 percent of it is currently landfill destined.

Calculations based on the stoichiometry of Eq. (3) indicate that at the current level of mill-scale available worldwide, about 2 million metric tons of CO₂ could be converted into 1.2 million metric tons of CO annually. In the case where elemental iron (available in essentially an unlimited supply) is used, every 1 million metric tons of metal would remediate 1.2 million metric tons of CO₂, producing 0.754 million metric tons of CO.

In either case, the spent oxide could be regenerated by carbothermic reduction under mild experimental conditions or by using low-quality gasified biomass. Alternatively, the maghemite product could be valuable in the manufacturing of ferrite (MFe₂O₄) components, because of its highly magnetic behavior. ■

About the authors

Abdul-Majeed Azad is a professor in chemical engineering at the University of Toledo. He recently was selected for a Fulbright Distinguished Chair Award in Alternative Energy Technology (see page 20).

Desikan Sundararajan obtained his Ph.D. (2009) from UT’s Chemical Engineering Department and currently works as a project engineer with Total Compliance LLC in Hilliard, Ohio.

Sirhan Al-Batty obtained his bachelor’s and master’s degrees in chemical engineering from UT. He is currently pursuing his Ph.D. and will graduate in 2012.

Eric McDaniel is an undergraduate student in chemical engineering at UT. He worked in the Azad Research Group for two semesters as a co-op intern, assisting graduate students in the CO₂ beneficiation project. He will graduate in 2012.



The authors, from left: Desikan Sundararajan, Abdul-Majeed Azad and Sirhan Al-Batty. Not pictured is Eric McDaniel.

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