

A Novel CO₂ Separation System

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Project Summary

NEED Concern over global climate change has led to a need to reduce CO₂ emissions from power plants. Unfortunately, current CO₂ capture processes reduce the efficiency with which fuel can be converted to electricity by 9-37%, and CO₂ capture costs can exceed \$70 per tonne¹ of CO₂ (Herzog, Drake, and Adams 1997).

OBJECTIVE To generate electricity with little reduction in conversion efficiency while emitting little or no CO₂ to the atmosphere, TDA Research, Inc. (TDA) is developing a Novel CO₂ Separation System, which we call a Sorbent Energy Transfer System (SETS).

APPROACH TDA's SETS reacts fuel with a metal oxide sorbent in a fluidized bed, storing energy in the sorbent by reducing the metal oxide to a metal while fully oxidizing the fuel (e.g., natural gas, oil, and/or gasified coal) to CO₂ and steam. After condensing the steam, the CO₂ (which is not diluted by nitrogen) is further compressed and sent to sequestration. The chemical energy in the reduced sorbent is then liberated by re-oxidizing (burning) the sorbent with high-pressure air in a transport reactor, and the resulting hot, high-pressure air is then used to drive a gas turbine and generate power. To be economically competitive, the process needs low-cost, highly reactive sorbents that absorb and release oxygen in seconds and can be cycled without degradation for a million or more cycles, and high throughput, low cost reactors for oxidizing and reducing the sorbent.

TECHNOLOGY TDA has developed both iron and nickel based oxygen sorbents that have the properties that we need for the SETS process to be economical. We first developed lower cost iron based sorbents that were strong, attrition resistance, and had enough oxygen capacity to fully oxidized fuel to CO₂ and steam. TDA produced a large batch of the iron-based sorbents (called TDASETS), which were then tested by Kellogg, Brown, and Root, Inc. (KBR) in a scalable fluidized bed reactor at conditions simulating the SETS process. The sorbent fully oxidized fuel to CO₂ and steam. Measurements of the attrition rate carried out at both TDA and KBR showed that TDA's iron based sorbents will last for more than 1,000,000 cycles. However, testing also

¹ 1 tonne = 2,205 lbs.

demonstrated that the iron based sorbents could not be used for extend period at temperatures above 800°C because the iron sinters into larger, less reactive crystallites. This temperature limitation in turn limits the efficiency of the power cycle, because modern, high efficiency gas turbines generally have expander inlet temperatures of ~1200°C.

To operate at higher temperatures, where the power cycle and CO₂ capture are even more efficient, we than developed a nickel based sorbent (Ni-SETS) and tested it in our small scale fluidized bed. In these tests the Ni-SETS sorbent had excellent activity, strength, attrition resistance, and the ability of fully oxidize fuel (CH₄) to CO₂ and steam at 1,050°C without sintering. We also tested the Ni-SETS sorbent as a reforming catalyst at 830 to 950°C, where it also demonstrated excellent performance as a partial oxidation sorbent and reforming catalyst that could be used to convert methane (CH₄) to syngas (CO + 1.8H₂) that could then used as the feedstock for a Gas to Liquids (GTL) (i.e., chemicals and ultra-clean fuels) process.

COSTS Because the sorbents we have developed have very high surface areas and are small and porous to reduce mass transfer resistance, they can be fully oxidized in three seconds and reduced in less than 18 seconds. Thus, the SETS process can be carried out in small, high throughput (transport and fluidized bed) reactors. Because the reactors are small, internally insulated and do not require exotic materials, the capital cost of the system is very low.

SETS utilizes the full chemical potential of combustion of the fuel, even though the net reaction is carried out in two steps. However, as a result of the two-step process, no additional energy is needed to separate CO₂ from the combustion products, and the concentrated CO₂ stream produced can be further compressed for sequestration with very little additional energy.

TDA worked with two evaluators who independently analyzed the cost of CO₂ capture (Louisiana State University, LSU, and the Department of Energy, DOE, National Energy Technology Laboratory, NETL). LSU estimated the cost impact for CO₂ capture on a Natural Gas Combined Cycle (NGCC) power generation system to be \$15 to 20/ton (CY 1998\$). DOE NETL analyzed the cost and efficiency impact of SETS integrated into an 80% efficient UltraFuelCell system. With ~100% CO₂ capture, SETS causes only a 2% loss of efficiency. The cost of electricity increases only 14% at 4 MW plant (James 2000) and 10% for a 50 MW plant. Based on the 50MW UltraFuelCell case, the cost for CO₂ capture was only \$10/ton (CY 1998\$).

APPLICATIONS The application of the SETS process is to produce electrical power from fossil fuels without emitting any greenhouse gases. In the near term, the use of SETS to generate power and a high pressure CO₂ stream is very attractive because the SETS system would produce power for no more than the cost of current systems and the value of the CO₂ stream is greater than the cost of producing it; the CO₂ stream could be sold at a profit and the cost of producing electricity would actually be lowered by the presence of the CO₂ capture process. If the large markets for CO₂ (such as Enhanced Oil Recovery) are saturated or the users too remote, then the CO₂ produced can be further compressed and sequestered. In this case, the cost of CO₂ recovery using the SETS process is \$10 to \$20 per ton, with an additional \$5 to \$15 per ton expense for further compressing the CO₂ from SETS process pressure (3-20 atm) to pipeline or sequestration pressure (35 to 100 atm); total costs for sequestration would therefore range from \$15 to \$35 per

ton CO₂. Proposed carbon taxes are estimated to be on the order of \$45 to 100 per ton of CO₂, and hence sequestration using SETS should be preferable than paying proposed carbon taxes.

IMPACT Near-term applications that integrate power production with the sale of CO₂ could capture as a product. Since SETS can be sited at any location with a nearby CO₂ user, SETS could effectively sell the captured CO₂ to EOR (45 to 160 million tonne/yr) and merchant CO₂ (8.2 million tonne/year, 1986). This corresponds to an electrical output of 60,000 MW. While this is not a very large fraction of the total generating market, it will provide a powerful impetus for the early adoption of the technology. Once the CO₂ markets are saturated, SETS could be incorporated into virtually all new generating capacity, although we are basing our design on a natural gas feed (the fuel of choice for virtually all new power plants), SETS is adaptable with relatively minor changes to any fossil fuel. The U.S. power market is growing at approximately 2% per year (approximately 20,000 MW of capacity installed per year). Each years installed capacity accounts for 51 million tons/year of CO₂ which could be economically sequestered.

Scientific/Technical Innovation

Concern over global climate change has led to a need for new systems that produce electricity from fossil fuels and emit less CO₂. The fundamental problem with current CO₂ separation systems is the need to separate dilute CO₂ and pressurize it for storage or sequestration. This is an energy intensive process that can reduce plant efficiency by 9-37%, and CO₂ capture costs for projects reported to date can exceed \$70 per tonne of CO₂ (Herzog, Drake, and Adams 1997). The fundamental reason that CO₂ removal, compression and sequestration consumes such large amounts of energy and capital is that the CO₂ is power plant exhausts is diluted by large amounts of nitrogen that are present in the air used to burn the fuel, and any disposal must essentially concentrate and compress the CO₂ through a pressure ratio of 100-1000. The process that we are developing inherently reacts the oxygen and fuel without the bringing along the nitrogen, and therefore produces an exhaust stream that contains only water and CO₂. After the water is removed by condensation we are left with an almost pure, high pressure CO₂ stream that can be either sold or inexpensively sequestered.

Objective

The objective of this project is to generate electricity from fossil fuels while capturing most or all of the CO₂, and to do so with only a minimal impact on the conversion efficiency and the cost of electricity. To do this, TDA Research, Inc. (TDA) has identified a Novel CO₂ Separation System that we call a Sorbent Energy Transfer System (SETS). Our system fully oxidizes a fossil fuel in two stages. First, the fuel is used to reduce a metal oxide sorbent (producing a stream of concentrated CO₂ and steam), and then the reduced metal oxide is reacted with hot, high pressure air to release its heat and drive a gas turbine.

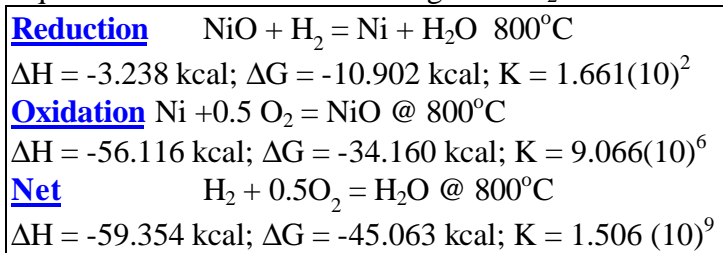
Approach

To economically generate electricity and produce a high pressure, concentrated CO₂ stream, the SETS process transfers the energy of the fuel to a high pressure air stream that drives a gas turbine, but does so through an intermediate solid sorbent stream which allows us to keep the combustion

products (CO₂ and water) separated from the hot, high pressure air used in the power cycle. Thus, the CO₂ is kept at high pressure and never diluted with nitrogen. The SETS process oxidizes the fuel (gasified coal, petroleum fuels or natural gas) at pressure by reacting the with a metal oxide such as copper or iron or nickel,. The fuel is oxidized to CO₂ and H₂O and the metal oxide is reduced, producing a metal (or a lower valance metal oxide). Essentially, the energy content of the fuel (a reduced form of carbon) is used to produce a high energy form of the metal oxide. The reduced form of the metal oxide is then contacted with a stream of intermediate temperature (400°C), high-pressure (10 atm) air from the compressor stages of a gas turbine. The reduced form of the metal is re-oxidized by the hot pressurized air, heating the air to roughly 900°C and liberating the energy that was stored when the fuel reduced the metal oxide. In effect, the heating value of the fuel is transferred to the air by the sorbent, which in turn simultaneously transfers O₂ from the air to the fuel without also transferring nitrogen that could dilute the combustion products.

Equation 1 illustrates the reactions that occur between Ni/NiO and hydrogen in the SETS cycle (hydrogen should be considered as a model reducing gas molecule, similar equations can be written for methane or CO). All of the reactions are favorable (i.e., ΔG is negative and the equilibrium constant is

Equation 1. SETS reactions using Ni as O₂ sorbent.



large); the net reaction is simply the oxidation of hydrogen to water (similar results occur with CO and CH₄ with CuO and Fe₂O₃). The free energy and heat of reaction for combustion is driving force for this process, we simply use that energy in two steps so that we keep the CO₂ separate from the nitrogen that would dilute it if we simply burned the fuel in an air stream. Therefore we do not have to use any additional energy to separate the CO₂ from the combustion products, since SETS replaces part or all of the combustor in a conventional system. The key feature is that the carbon in the fuel is never allowed to mix with and be diluted by the “combustion air.”

A second major advantage of the SETS system is that it does not require that any new hardware be developed. The power generation cycle is essentially a standard combined cycle, except that the combustor is replaced by a fluidized bed and a transport reactor (the SETS), one of which uses fuel to reduce the particulate metal oxide and one which oxidizes the metal to heat the air entering the turbine. Thus, as long as the sorbent works as planned (the sorbent is the only new item other than the system design), the technical risk is relatively low because all of the processes are carried out in standard process equipment.

The SETS Cycle

There are many variations on the SETS cycle; it can be used with different fuels (natural gas, oil, or gasified coal or biomass) and with either gas turbines, gas turbine combined cycles or fuel cell/combined cycles. We will first illustrate how the system can be integrated into a Gas Turbine Combined Cycle (GTCC) using natural gas as the fuel (this is also known as a Natural Gas Combined Cycle (NGCC) (see Figure 1). Later we will describe the application of the system to a fuel cell (e.g., an UltraFuelCell), a very high efficiency conversion cycle in which the system can capture effectively all of the carbon emissions.

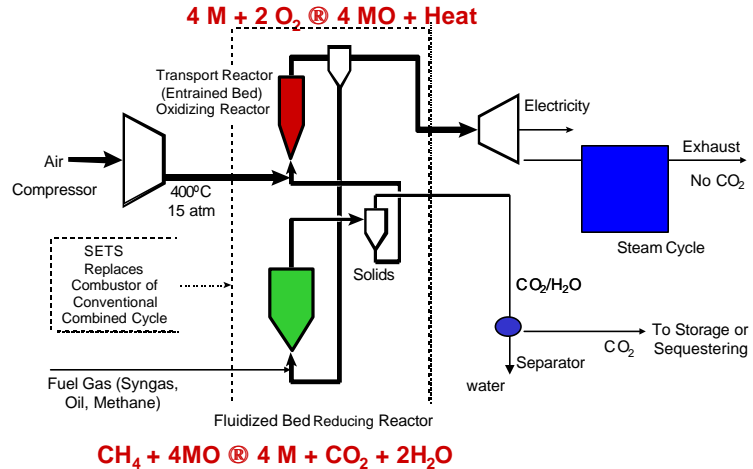
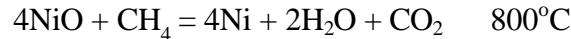


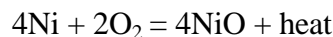
Figure 1. Sorbent energy transfer cycle schematic (M = metal).

The first step in the SETS process is to reduce a metal oxide to a metal (or a metal oxide to a lower valence metal oxide).



The metal (oxygen sorbent) is supported on or contained within an inert support (such as alumina), which provides a high surface area for reaction and good physical properties such as crush strength and attrition resistance. Reducing the metal oxide converts the energy in the fuel (e.g., CH_4) to heat, which is stored in the reduced metal, and produces a stream, which consists of 33% CO_2 and 67% water. We carry this step out at high pressure; we carry out the reduction at the pressure of the air leaving the compression section of the gas turbine so that we do not have to move the solid particles through a substantial pressure difference (which is a mechanically difficult and expensive process). For example, in the case we are illustrating, the air stream exiting the compressor of the General Electric Frame 7A gas turbine is at 13.5 atmospheres, so both the oxidation and reduction steps are carried out at this pressure. We then remove the water from the $\text{CO}_2/\text{H}_2\text{O}$ stream by condensing it and are now left with a stream of virtually 100% pure CO_2 at high pressure. The CO_2 (still at 13.5 atm) is then sold or sent to a storage or sequestration process with little additional compression energy required.

The reduced metal or lower valence state metal oxide now contains virtually all of the chemical energy in the original fuel gas (all of the energy from the reduction (combustion) of the CH_4 is now stored as chemical energy in the reduced metal oxide). The reduced particles enter a second reactor (also run at 13.5 atm) where they are re-oxidized with air, producing large amounts of heat and heating the air to the temperatures needed to drive a gas turbine-combined cycle (900°C or greater).



From an overall perspective, the sorbent transfers the energy content of the fuel to the air while also transferring oxygen from the air to the reducing reactor where it fully oxidizes the fuel to CO_2 and H_2O .

Figure 2 shows the major components of the SETS. Natural gas is mixed with recycled CO_2 and steam to minimize the production of coke in the reducing reactor. While coke production would not be an operating problem because any coke produced would burn off in the oxidizing reactor, we prevent CO_2 from being released to the environment as a result of coke burn-off. During the Phase II project, we found that the reducing reactor performed best when it was run as a fluidized bed reactor. This provided the longer residence times (10-20 seconds) needed to run the reduction reaction to completion so that only very small amounts (ppm levels) of H_2 , CO , and CH_4 are left unreacted and sequestered with the CO_2 . A transport reactor was selected for the oxidation side of SETS, where only 3 second residence times are needed for the oxidation reaction to take place.

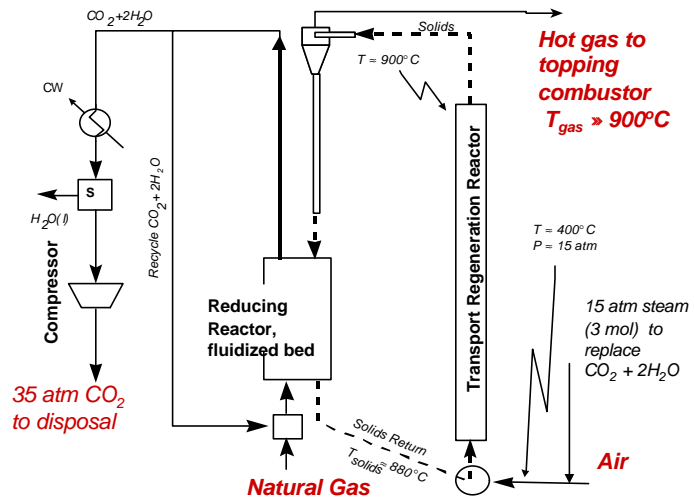


Figure 2. SETS components (natural gas as CH_4).

For the gas turbine power generation cycle being illustrated here, air enters from the oxidation reactor from the compressor at $\sim 400^\circ\text{C}$ and we add in 3 mols of steam (extracted from a steam cycle) to replace the $\text{CO}_2 + 2\text{H}_2\text{O}$ loss from the gas turbine. Air and reduced solid sorbent are mixed in the transport regeneration reactor. The air oxidizes the metal or metal oxide to a higher valence state and both are heated to a nominal 900°C . The hot vitiated air then goes to the topping combustor when additional natural gas heats the air entering the turbine inlet to $\sim 1,288^\circ\text{C}$ (the standard design temperature of the turbine).

The $\text{CO}_2 + 2\text{H}_2\text{O}$ leaving the reducing reactor are cooled, and the heat is used to generate low pressure steam which is delivered to the steam bottoming cycle. Addition cooling condenses the water of combustion and the liquid is separated. We then compressed the 15 atm CO_2 to the delivery pressure, $35 \text{ atm (500 psig)}$. In this work, we assume a nearby user for the CO_2 (e.g., Enhanced Oil Recovery (EOR) and have therefore limited the maximum delivery pressure to sub-critical CO_2 . For long distance transport of the CO_2 , supercritical CO_2 (e.g., $103 \text{ atm, 1,500 psig}$) would be needed, but modest amounts of additional equipment and power would then be necessary.

In this Phase II project, TDA has developed iron and nickel based sorbents that can operate in at 800°C and higher. Our iron based sorbent operates at 800°C ($1,472^\circ\text{F}$) but our nickel based sorbent has long life even at an operating temperature of $1,050^\circ\text{C}$ ($1,922^\circ\text{F}$). When the temperature at the outlet of the oxidizing oxidizing reactor limited to 800°C by the temperature limitations of our iron based sorbent, the cycle will capture 38% of the CO_2 (the CO_2 produced when added

natural gas is burned to boost the air temperature from 800 to 1,288°C is not captured). For a conservative 900°C nominal outlet temperature and a nickel based sorbent SETS captures 49% of the CO₂, and at the 1050°C maximum operating temperature of the nickel sorbent, the cycle could capture 66% of the CO₂.

The more complicated, higher efficiency Ultra Fuel Cell based cycles described latter are capable of fuel to electrical energy generation efficiencies of 80% and can capture all of the CO₂ produced.

Technology

Although any transition metal oxide could be used in the SETS process, we want a sorbent that is inexpensive, stable at high temperatures (does not sinter) and has good oxygen capacity. We reviewed the costs and properties of many sorbents, and selected four that looked like they offered the best combination of cost and performance: Cu, FeO, Fe₃O₄, MnO, and Ni (in the reduced state) which convert to CuO, Fe₂O₃, Mn₂O₃, and NiO when they are oxidized. Of these, iron and copper have the lowest costs and have very good oxygen capacities. We evaluated Cu and FeO during the Phase I project. While the reduction of Fe₂O₃ to FeO by CH₄ will leave some unoxidized CO and H₂ in the reducing reactor outlet gas, reduction of CuO to Cu react virtually all of the fuel gases (<100 ppm CO+H₂ are sequestered with the CO₂). Reduction of Fe₂O₃ to Fe₃O₄ and NiO to Ni also fully oxidizing the CH₄ (or any other fuel gas). The reduction reactions of Fe₂O₃ and NiO with CH₄ are slightly endothermic, but the endotherm is small enough that the sensible heat of the sorbent can be used to provide the small amount of heat required (in order to avoid the need for extremely expensive high alloy heart exchangers, we need the sorbent reduction reactions to be either thermoneutral or only slightly endothermic).

Initially in our Phase II project, we made and tested sorbents that contained copper, whose reduction reactions are exothermic for all of the potential fuel gases (hydrogen, carbon monoxide and methane). Unfortunately, while copper sorbents could be repeatedly between CuO ↔ Cu, the sorbents agglomerated when tested in a fluidized bed. We therefore eliminated copper as a potential sorbent.

During the rest of our Phase II project we worked with iron- and nickel-based sorbents. Although we had initially stayed away from these materials because the reaction of the sorbent and fuel gas was endothermic, the endotherm is small enough that the sensible heat of the active sorbent and its support can supply the necessary heat. In fact, the required heat easily provided by utilizing a small temperature swing (~20°C) between the oxidation and reduction reactors. During Phase II we successfully made both iron and nickel based sorbents with good capacity, activity, and attrition resistance. The development and testing of these sorbents is described in the next section.

Multiple Cycle Testing of SETS Sorbents at TDA

During Phase II, TDA first worked to improve the sorbents that we had originally developed in Phase I. We made stronger, more attrition resistant sorbents and tested them to demonstrate their durability. The first tests were carried out in a Thermo Gravimetric Analyzer (TGA) which allowed us to rapidly run the sorbent through many cycles to test their chemical stability. We then tested the sorbents in a small scale fluidized bed. While the copper and copper/iron sorbents demonstrated excellent chemical stability, all of the copper containing sorbents agglomerated when tested in TDA's small scale fluidized bed. We then focused our attention on the development of iron based and nickel based sorbents.

Figure 3 shows TDA's small-scale fluidized bed reactor. The reactor is a 3" Inconel pressure vessel with a 24" tall Inconel insert which has a 1.5" ID. Typically we loaded the reactor with sorbent to a depth of 2.8 inches. The reactor is capable of operating up to 100 psig @ 1050°C and has an automated feed system which uses mass flow meters to control the feed flow of H₂, CO, CO₂, CH₄, N₂, and air while water is supplied through a metering pump. We have continuous on-line monitors for O₂, CO, CO₂, CH₄, GC analysis for N₂ and H₂ and computerized data acquisition, storage and analysis.



Figure 3. TDA's small-scale fluidized bed apparatus.

Iron-Based Sorbents

After screening a large number of sorbent formulations to eliminate those with insufficient strength or chemical stability, we spray dried small quantities of several of our best formulas at a nearby CoorsTek facility (CoorsTek is the nations largest manufacturer of technical ceramics). We fired these sprayed dried materials at several different temperatures, conducted attrition tests in our ASTM attrition tester and repeated our TGA tests on the strongest sorbents to verify that they remained chemically active. We selected two iron based sorbent formulations/firing conditions for multiple cycle testing and ultimately selected one (which is reported on here).

We first tested our iron based sorbent at 900°C in the fluidized bed reactor. The sorbent demonstrated a slow loss of chemical activity in the tests. When we removed the sorbent from the reactor, we found that it had formed many large particles, i.e., the iron based sorbent had agglomerated like the copper, but at a slower rate. We concluded that at 900°C the agglomeration would continue and make the sorbent unusable, long before it failed chemically or wore out by attrition.

We then loaded a fresh batch of the iron-based sorbent and tested with the reduction reaction carried out at 720°C and the auto-thermal oxidation heating the sorbent to 800°C (i.e., we allow the very exothermic oxidation reaction to heat the sorbent from 720°C to 800°C, without changing

the oven temperature). Figure 4 shows the results of 59 cycles of testing under those conditions, which are representative of a Gas Turbine or GTCC application. Oxygen loading was calculated based on the sorbent capacity at breakthrough, which we defined as the appearance of 1% H₂ (dry) in the reactor outlet. Pre-breakthrough levels of H₂ and CO were below detectable limits in our instruments (i.e., < 0.1%). The sorbent has excellent chemical stability and no loss of activity with cycling.

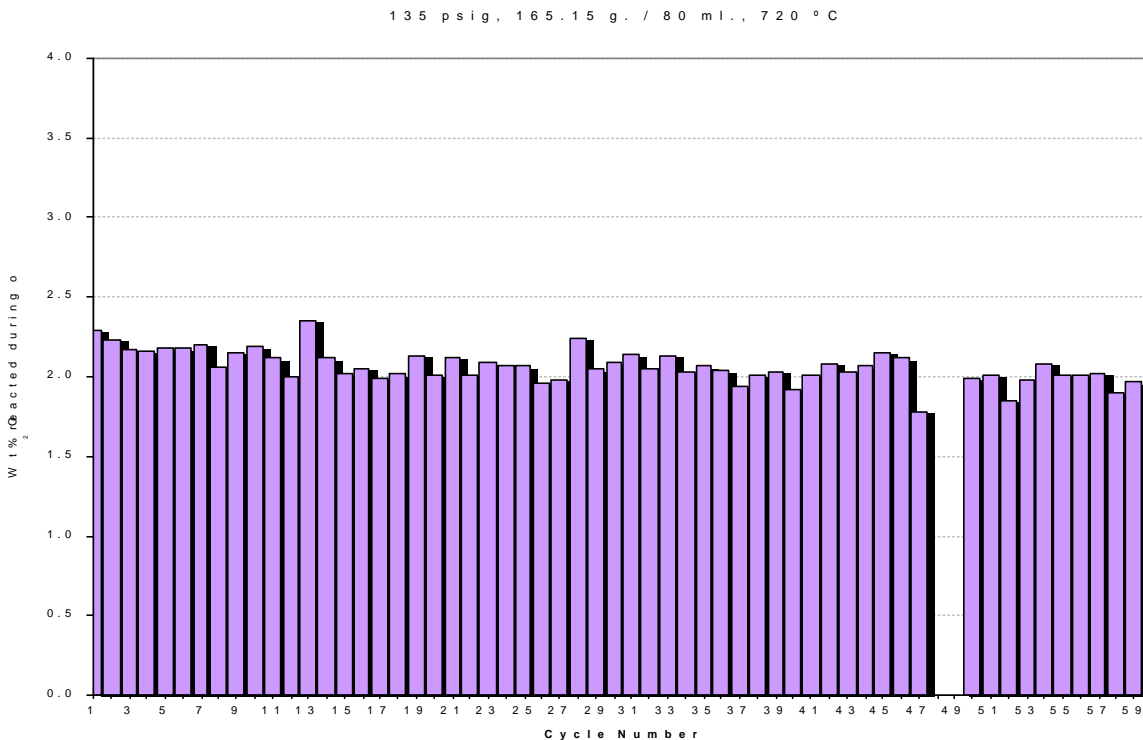


Figure 4. Multiple cycle tests of our iron-based sorbent, Lot 080800 (precursor to TDASETS).

After completing the 59 cycle test we carried out an accelerated attrition test on this same batch of sorbent. In TDA’s ASTM attrition tester, the Attrition Index (AI) was only 0.64%/h and the bulk density was 2.16 g/cc. We sent the sorbent to Kellogg, Brown, and Root, Inc. (KBR) for Davison Index (DI) testing. KBR measured a DI of 1 (the lowest DI rating that KBR has ever measured for any material) for the cycled material (this is even better than their results on a previous TDA hot gas cleanup sorbent, which they had tested and whose lifetime they had estimated at 1.8 million cycles {0.55(10)⁻⁶ lb loss per lb circulated}). While these data indicate that the sorbent could have a lifetime of more than 1.8 million cycles, in the economic analysis we report later, we conservatively estimate the sorbent life is only 1,000,000 cycles.

TDA then spray dried a large batch (~100 lbs, 45 kg) of the same iron based formulation described above, which we called TDASETS. Unfortunately, TDASETS was not as dense as the precursor (bulk density 1.8 g/cc versus 2.16 g/cc for Lot 080800) and the attrition index (AI) was 2.5%/h (versus 0.64%/h in Lot 080800). Although we used the same firing conditions to make both

sorbents, the density of the TDASETS was lower than that of the first batch due to a change in the spray drying (which we did not discover until after the sorbent was sent to KBR for multiple cycle testing in their large scale and scalable fluidized bed reactor). Given that the problem was discovered too late to re-manufacture the sorbent and still meet project schedule requirement, we decided to continue testing of TDASETS, even though we recognized that it was not nearly as attrition resistant as it could be.

Fortunately, even though TDASETS was manufactured improperly, it still had adequate attrition resistance for use in a fluidized bed. The tests at KBR (below) showed that TDASETS had a long life (i.e., low loss rate to attrition), is chemically stable (has stable oxygen loading), and is also active (i.e., removes H_2 , CO , CH_4 to very low levels).

Ni-SETS

Given the temperature limitations of the iron based sorbent, we started developing a nickel based sorbent for SETS. We first tested nickel impregnated on alumina and found that it would be active at much higher temperatures than the iron. However, we observed a slow loss of chemical activity (i.e., oxygen loading decreased with cycling), probably due to the formation of nickel aluminate.

We next made geodes of nickel-based sorbents using several binders in the support phase that would not form nickel aluminate. We again screened many sorbents and selected one, which we called Ni-SETS. We then conducted multiple cycle testing at SETS conditions, representative of

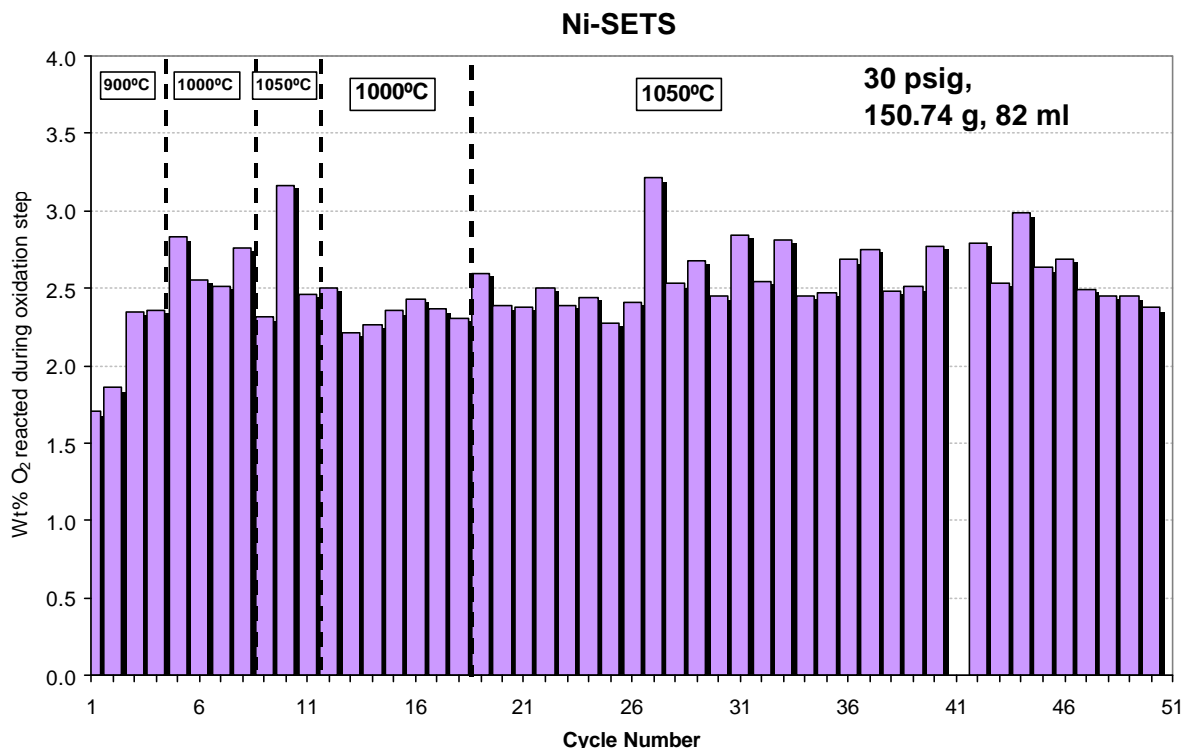


Figure 5. High temperature testing of Ni-SETS with full oxidation of fuel to CO_2 & H_2O .

an UltraFuelCell application. Figure 5 presents the results of the multiple cycle testing. In our initial tests at 900°C the capacity of the Ni-SETS increased with time, and in our tests at 1000°C the loading was even slightly higher (probably due to the improved kinetic at higher temperatures). We then conducted further tests at 1050°C, and again found a slight increase in capacity over the 1000°C case. Finally, we conducted a long series of tests at constant conditions where the sorbent demonstrate very stable oxygen loading with cycling. The oxygen loading was calculated at breakthrough, again defined as 1% H₂ (dry) in the outlet. Pre-breakthrough levels of H₂ and CO were below detectable limits in our instruments (i.e., < 0.1%).

Testing of TDASETS at KBR

Kellogg Brown & Root, Inc. is one of the largest designers and constructors of fluidized bed process equipment, the licenser of the Texaco gasifier, and a leading constructor of chemical process, refinery and power generation facilities. We have an excellent working relationship with KBR, and have previously had “geode” based zinc oxide based hot gas cleanup sorbents tested in their Transport Reactor Test Unit (TRTU) at the Kellogg Brown and Root Technology Center (KBRTC) and qualified for use in their High Temperature Gas Desulfurization process.. The experience gained during this process development was applied to testing new sorbent(s) proposed for the SETS applications.

The objective of the testing was to study the reduction, oxidation and attrition characteristics of our TDASETS sorbent in their pilot scale reactors. The particular objectives were to determine the suitability of the sorbent to fully oxidize fuel to CO₂ and H₂O and to be regenerated for many cycles.

Description of Research

Sorbent reduction and oxidation tests were conducted sequentially in a pilot-scale fluidized bed reactor facility that provides data that is directly scaleable to a commercial reactor. The test conditions were selected to simulate the environment expected in a low-pressure fuel cell application. In addition to this, a fluid bed reactor appears to be the best type of reactor to conduct the sorbent reduction, which from a cost and performance point of view is the most important step in the application. Figure 6 shows the 6 inch ID by 8 ft tall fluidized bed reactor used in these tests.

Scouting and parametric tests were conducted primarily at 20 psia (~5 psig) operating pressure in the fluidized bed reactor to determine the optimum operating conditions, and these were followed by a 50-cycle test at the same conditions. The velocity in the fluidized bed was varied from 0.06 to 0.18 ft/sec



Figure 6. KBR fluidized bed reactor.

over a temperature range of 1400°F to 1450°F. For most of the tests, the velocity was maintained at about 0.12 ft/s. The density in the fluidized bed was about 94 lb/ft³.

KBR Research Findings

The results of KBR's study of the reduction and oxidation steps are:

- Reduction of the sorbent with simulated syngas containing H₂ was very good at concentrations varying from about 5% to 15% and a temperature range of 1400°F to 1450°F. At the lowest space velocity studied, the leakage of H₂ in the outlet gas was very low (<90 ppm) when the inlet H₂ concentration was at 5%.
- During sorbent reduction, greater than 80% of the available oxygen was consumed by the reducing gas before leakage of CO + H₂ exceeded 1% (dry). This leakage was reduced with an increase in inlet H₂ concentration.
- A temperature of 1350°F was adequate to oxidize the sorbent. Sorbent oxidation was very good with no O₂ leakage until near sorbent saturation.
- The oxidation of sorbent over 50 cycles was good, and the reproducible O₂ breakthrough concentrations and temperature exotherms indicated that there was no deterioration in performance.
- No significant sorbent attrition was observed from the fines content determined from the particle size distributions measured before and after the multi-cycle test (50 cycles). The attrition rate in a commercial fluidized bed reactor was estimated to be 1.1 lb/hr in a 3,000 ft³ bed at 20 psia at the space velocity of our 50 cycle test, (with fines defined as particles with diameters of less than 40 microns).
- Sorbent performance after the multi-cycle test was found to be as good as that of the fresh sorbent (after conditioning).

KBR's tests with the iron-based SETS sorbent were excellent. The sorbent had no loss of activity and the attrition was extremely low, at about the same rate as we estimated previously and that we use in our economics analysis.

Applications

SETS can use any hydrocarbon fuel, including but not limited to Natural Gas (NG), oil, and gasified coal or biomass. However, to simplify our analyses, we limited our economic analysis to the use of natural gas as the fuel and analyzed the impact of SETS in two applications:

- 1) A Natural Gas fired Combined Cycle (NGCC): *LSU*
- 2) An UltraFuelCell with Gas Turbine: *NETL*

We were assisted in these analyses by from Louisiana State University (LSU) and the DOE-National Energy Technology Laboratory (NETL). Each application is discussed in the following sections.

Application of SETS to a Natural Gas Fired Combined Cycle (NGCC)

The simplest, nearest term and least risk application of SETS to power generation is to integrate it into a gas turbine or Natural Gas Fired Combined Cycle (NGCC). The analysis of the SETS-NGCC combination was carried out by LSU under subcontract. LSU prepared an Aspen model of the SETS process in which the sorbent was limited to a nominal maximum temperature of 900°C. A schematic diagram of the SETS process integrated with a natural gas-fired combined cycle (NGCC) for power generation is shown in Figure 7. The process operates with dual fluidized-bed or transport reactors to accomplish solid transfer and provide steady-state operation. CH₄ and the metal oxide (e.g., Fe₂O₃, NiO) are fed to the sorbent reducing reactor where reaction (1) occurs. A portion of the product gas, which contains only CO₂ and H₂O, is recycled to control carbon deposition and to provide sufficient gas for solids transport. Energy removed from the remaining reactor product gases is used to generate low-pressure steam in HRSG1. H₂O is separated by condensation, leaving pure CO₂ which is compressed for transport to a suitable sequestration site. The low-pressure steam is fed to the steam turbine to replace intermediate pressure steam extracted from the steam turbine and fed to the sorbent oxidizing reactor. Reduced sorbent is re-oxidized according to reaction (2) in the sorbent oxidizing reactor using excess air and intermediate pressure steam extracted from the steam turbine. The quantity of intermediate pressure steam is equal to the amount of H₂O and CO₂ removed in the sorbent reducing reactor and is used to avoid reducing gas flow rate through the gas turbine. The combustor feed consists of gas product from the sorbent oxidation reactor supplemented with sufficient CH₄ to achieve the design gas turbine firing temperature. CO₂ formed in the combustor is discharged directly to the atmosphere as in the standard NGCC process. Power is generated in the gas turbine and the thermal energy in the turbine exhaust gas is used to generate steam in HRSG2 which in turn produces additional power generation in the bottoming steam turbine. The percentage CO₂ capture depends primarily on the operating temperatures of the SETS reactors as the quantity of supplemental fuel decreases as the temperatures of the SETS reactors increase and approach the turbine firing temperature.

Using Aspen Plus, we simulated a standard NGCC process using a General Electric MS7001FA gas turbine (the baseline system) as well as SETS-NGCC processes using the GE turbine and sorbent formulations. We first simulated the standard NGCC plant. When possible, the actual operating conditions associated with the GE MS7001FA combined cycle were used. When actual conditions were not available, reasonable conditions were selected so that the overall simulated

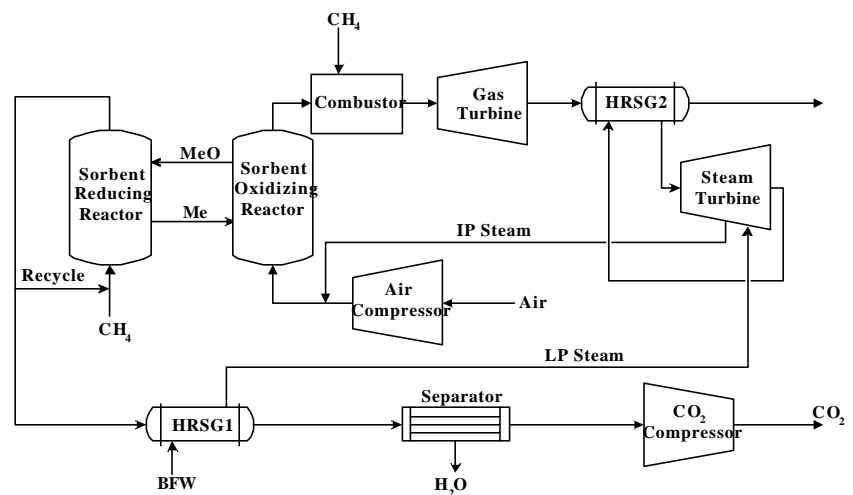


Figure 7. Schematic diagram of the SETS-NGCC process.

performance closely matched published performance data for an actual plant. For example, the net generating capacity of 247 MWe and 55.7% lower heating value (LHV) efficiency from the simulation were quite close to the published GE values of 242 MWe and 55.6% LHV efficiency.

These base case simulation results show that overall performance of the SETS-NGCC process is effectively independent of sorbent composition and that CO₂ emissions can be reduced by almost 50% with a corresponding LHV efficiency loss of less than 5% with a 900°C sorbent temperature. The sensitivity of the SETS-NGCC process to variations in sorbent composition, sorbent circulation rate, product gas recycle ratio, and SETS reactor temperatures were examined. The variation in the LHV efficiency was quite small in all cases, and ranged from a minimum of 51.1% to a maximum of 53.1%. Similarly, the variation in CO₂ capture percent was small except in response to variations in SETS reactors temperatures. The CO₂ capture was between 49.1% and 49.2% for a variety of assumptions regarding sorbent composition, sorbent circulation rate and product gas recycle ratio. However, CO₂ capture increased dramatically with an increase in SETS reactors temperatures, from 49.1% at reactor temperatures of 900°C to 61.8% at 1000°C and to 100% at 1288°C. No supplemental fuel is required when the SETS reactors operate at the gas turbine firing temperature, and all the CO₂ produced can be captured.

Purchased equipment costs were then estimated using standard literature correlations and converted to 1999 values using the Chemical Engineering cost index. The total capital cost of the SETS addition to the NGCC plant was estimated (using standard “textbook” cost factors) to be about \$11 million. This is an increase of approximately 10% over the total capital cost of the NGCC plant without SETS.

Annual incremental costs associated with the increased capital cost, slightly higher consumption of natural gas, sorbent replacement, and boiler feed water were estimated and normalized to a unit kWh basis to account for the differences in LHV efficiency. All annual costs were based on a 75% on-stream factor (6570 operating hours per year). Incremental capital cost was based on an annual capital recovery of 10%, while the base case unit costs of natural gas, sorbent, and boiler feed water were taken to be \$4.00 per million Btu, \$6.50 per pound, and \$0.83 per thousand gallons, respectively. The base case sorbent replacement rate was taken to be 1 pound per 10⁶ pounds circulated in each reactor pass, based conservatively on attrition data obtained at TDA and KBR. With this approach, the cost of electricity from the standard NGCC plant was estimated to be 31.5 mills per kWh, with incremental costs of 2.9 and 3.4 mills per kWh associated with the SETS process using Fe₂O₃-CuO-Al₂O₃ and Fe₂O₃-Al₂O₃ sorbent compositions, respectively. The resulting CO₂ capture costs associated with SETS were \$15.82 per metric ton of CO₂ for the Fe₂O₃-CuO-Al₂O₃ sorbent and \$18.33 per metric ton of CO₂ for the Fe₂O₃-Al₂O₃ sorbent. The increased demand for natural gas caused by the small efficiency penalty was the most important factor in the incremental cost of electricity followed, in order, by capital cost, sorbent replacement, and boiler feed water.

Because cost estimates at this stage of process development are very approximate, we carried out a cost sensitivity analysis by varying the capital cost estimate, the natural gas unit cost, the boiler feed water cost, and the sorbent unit cost and replacement rate. The factored capital cost estimation method is generally considered to be correct within ±30% (although case to case comparisons are much more accurate), and the base case estimate was varied within this range.

The natural gas unit price may fluctuate with location and time, and the sensitivity analysis considered a $\pm 50\%$ variation. Boiler feed water cost, while variable, does not contribute significantly to the overall cost. The sorbent unit cost and particularly the sorbent replacement rate are subject to significant uncertainty, since the sorbent is currently under development. Sorbent unit cost was varied between \$4.00 and \$9.00 per pound, or $\pm 38.5\%$ of the base cost. While sorbent replacement cost is only the third most important incremental cost contributor under base case conditions, it could quickly become a dominant cost if the target replacement rate is not achieved. For example, increasing the sorbent replacement rate by a factor of 10 to 1 pound per 10^5 pounds of circulating sorbent more than doubled the estimated capture cost from \$15.82 to \$35.40 per metric ton of CO_2 using the $\text{Fe}_2\text{O}_3\text{-CuO-Al}_2\text{O}_3$ sorbent.

The base case estimate of about \$15 to \$18 per metric ton of CO_2 captured with an energy penalty of less than 5% compares quite favorably with other CO_2 capture cost estimates. For example, Herzog (*The Economics of CO_2 Capture, in Greenhouse Gas Control Technologies*, P. Riemet, B. Eliasson, and A. Wokaun, eds., Elsevier Science Ltd., 1999) reports estimated capture costs ranging from \$18 to \$72 per metric ton of CO_2 with energy penalties ranging from 9% to 34%. These estimates were from a variety of sources and apply to a range of power generation and CO_2 capture options.

Application of SETS to an UltraFuelCell with a Gas Turbine

The DOE-NETL is developing a power system of remarkable efficiency called an UltraFuelCell which consists of a multistage solid oxide fuel cell and a gas turbine, nominally fueled by natural gas. The key to this high efficiency (over 80% of the LHV of natural gas can be delivered as electricity) is the use of several fuel cells each operating at progressively higher temperatures. Compressed air and fuel are delivered a moderate temperature (e.g. 500°C) to the first of a series of fuel cells. As the fuel is converted to electricity, the waste heat created by the resistive losses in the cell heat the fuel and air, which then flow into another cell operated at higher temperatures where further fuel is converted and the air and fuel heated again. The process repeats multiple times until the concentration of $\text{H}_2/\text{CO}/\text{CH}_4$ in the fuel is reduced to low levels (e.g., 94% fuel conversion in the fuel cells). The remaining fuel is burned in the hot air leaving the fuel cell; that combustion raises the temperature further (e.g., to $1,050^\circ\text{C}$). The hot, high pressure combustion products then are expanded in a gas turbine, driving the compressor and generating net power to be delivered to the electric grid. Thus, all of the fuel is burned and the waste heat of the fuel cell is also used to generate power in the gas turbine portion of the UltraFuelCell. This multistage fuel cell design concept opens the temperature window around the fuel cell and solves heat-management problems found in other fuel cell systems, allowing most of the fuel to be consumed in the fuel cell and allowing the use of for relatively low air flowrates while still providing heat management within the fuel cell.

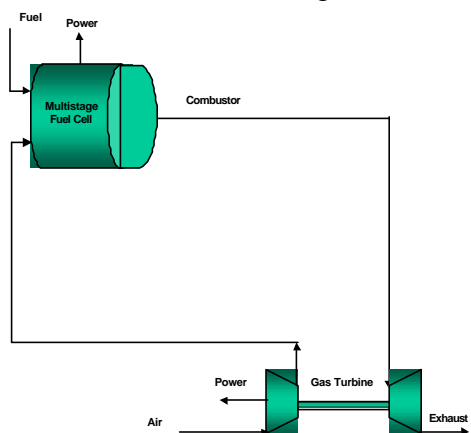


Figure 8. Simplified schematic of an UltraFuelCell and Gas Turbine.

DOE (James and George 2000) have analyzed the UltraFuelCell in several configurations. The most efficient configuration uses a combination of a gas turbine and UltraFuelCell. Figure 8 presents a simplified diagram of this system; although heat exchangers are needed to generate steam, recuperative heat the inlet air, pre-heat the steam for the pre-reformer, and may be used to recover water, those items are not shown for simplicity.

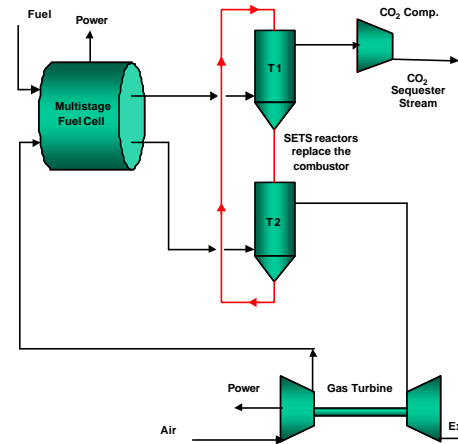


Figure 9. Schematic of an UltraFuelCell and gas turbine integrated with a SETS cycle.

Figure 9 shows the UltraFuelCell/gas turbine from above combined with the primary SETS components. Basically the SETS replaces the combustor of the UltraFuelCell with the SETS oxidizing and reducing reactors. A CO₂ compressor is added to compress the captured CO₂ (e.g., at 3 atm) to pipeline pressures. Again in the interest of simplicity, we have omitted several heat exchangers, including the condenser that removes the water before the CO₂ is compressed.

With the assistance of DOE-NETL, TDA integrated the SETS system into an UltraFuelCell (UFC) power plant, an integrated system in which SETS can potentially capture 100% of the CO₂. Previously, DOE/NETL had simulated and calculated the economics of several UltraFuelCell-based power plants without CO₂ capture. We analyzed cases for each of the two sorbents that we developed, Ni-SETS (nickel based) and TDASETS (iron based).

- 1) NiSETS/UFC/GT with a 1,060°C maximum temperature with Ni-SETS
- 2) FeSETS/UFC/GT with a 800°C maximum temperature with TDASETS

In the evaluation, we cooperated with Robert James of NETL/DOE. Robert James developed a simulation spreadsheet, which applied SETS to an UltraFuelCell combined with a gas turbine cycle. The previous NETL simulation work indicated that the UFC/GT system benefits from the economies of scale and higher generating capacities enable a more competitive system. Thus, we selected 50 MW_e as the basis of plant capacity to carry out the simulation of SETS/UFC/Gas Turbine. Table 1 presents a comparison of UFC/Gas Turbine combinations with and without SETS.

Table 1. Comparison of cost parameters with and without CO₂ capture in a 50 MW plant.

	UFC/GT	NiSETS/UFC/GT	FeSETS/UFC/GT
Fuel Conversion Efficiency (%)	79.9	78.0	74.5
Capital Investment (\$/kW)	742	834	881
Operational Expenses* (\$ 1,000)	7,988	8,489	8,508
Cost of Electricity** (cents/kWh)	3.07	3.38	3.55
Cost of Removing CO ₂ ** (\$/ton)	N/A	10.01	15.47

* For a 50 MW system

** Cost of Energy = \$3/MMBtu

There are two major causes for the slight decrease in efficiency in the system when SETS is added. The first one is directly related with the power requirement for the CO₂ compression.

Even though SETS produces an essentially pure CO₂ stream at 3 atm, compression of the CO₂ from 3 atm to 35 atm drained 64 kW of power from the net output of the plant, resulting in a 1.6% decrease in the fuel conversion efficiency. The efficiency drop due to the compression of CO₂ is also unavoidable in NiSETS/UFC/GT and any other CO₂ sequestration system as well. The other difference in the efficiency is associated with the fact that the SETS system operates at a lower temperature than a standard combustor. The transport reactor effluent at 800°C in the FeSETS/UFC/GT system is sent directly to the gas turbine (and its temperature is not further increased by burning additional natural gas). This insures that we capture all of the produced, but slightly lowers the efficiency of the gas turbine, the turbine inlet temperature with FeSETS/UFC/GT is 800°C, and that of the NiSETS/UFC/GT is 1060°C. The parasitic power loss in the FeSETS/UFC/GT is also slightly higher than that of the NiSETS/UFC/GT system mainly due to the pressure drop associated with the increased number of components (two additional heat exchangers and a catalytic reactor).

The capital cost for the FeSETS/UFC/GT and NiSETS/UFC/GT systems are about the same. Although FeSETS/UFC/GT system uses two additional heat exchangers, the overall cost of heat exchange equipment is not considerably higher than the system using Ni-sorbents. This is mainly because incorporation of those additional heat exchangers reduced the load on the existing ones (since the heat needs to be conserved, to cool off the fuel cell effluent stream from 970°C to 55°C before the CO₂ compressor, the heat duty applied through the heat exchange process is same whether we use 3 or 4 heat exchangers). We actually experienced a slight decrease in the costs of overall heat exchange equipment due to slightly higher ΔT_{lm} 's that can be achieved with the FeSETS configuration. The largest capital cost increase for the FeSETS system was due to the increase in the cost of the fuel cell unit, which requires larger cells (or more number of cells) to compensate the losses in the efficiency (since the system operates at a lower efficiency, it requires a bigger fuel cell to generate 50 MW_e of power). Because the fuel cell is the most expensive component of the system, the need for larger fuel cells increased the capital cost of the system.

Figure 10 presents the cost for CO₂ capture as a function of the sorbent cost and cycle life (i.e., the reciprocal of the loss rate per cycle). With a high cycle life the cost of the sorbent is relatively un-important (i.e., at 1,000,000 cycle life and higher, the cost for CO₂ capture is about \$10/ton with \$1/lb, or \$5/lb or \$10/lb sorbent); note that our measured sorbent life of over 1,800,000 cycles is much better than this. At lower cycle lifetimes the replacement rate of sorbent become significant, and can increase the cost of CO₂ to \$50/ton or more.

Fortunately, our TDASETS sorbent predecessor has a very low DI and a cycle life, which is anticipated to be significantly greater than one million cycles.

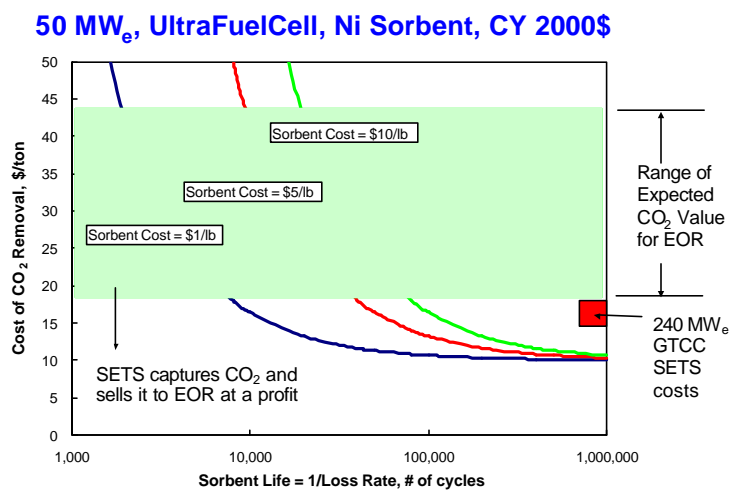


Figure 10. NiSETS/UFC/GT is low cost with long-life sorbent.

The reason that the cost of CO₂ recovery is largest in the iron based system and varies with fuel cost is that the cost of CO₂ recovery here is defined as the additional operating costs and capital costs for the SETS system compared to the non-SETS system. In order to achieve the same level of power generation capacity, the natural gas consumption will be much higher for the iron based system than for the system based on Ni-sorbents. As illustrated in Figure 11, an increase in the cost of natural gas has a much higher negative effect in the cost of removal of CO₂ with the FeSETS//UFC/GT system than on the NiSETS/UFC/GT.

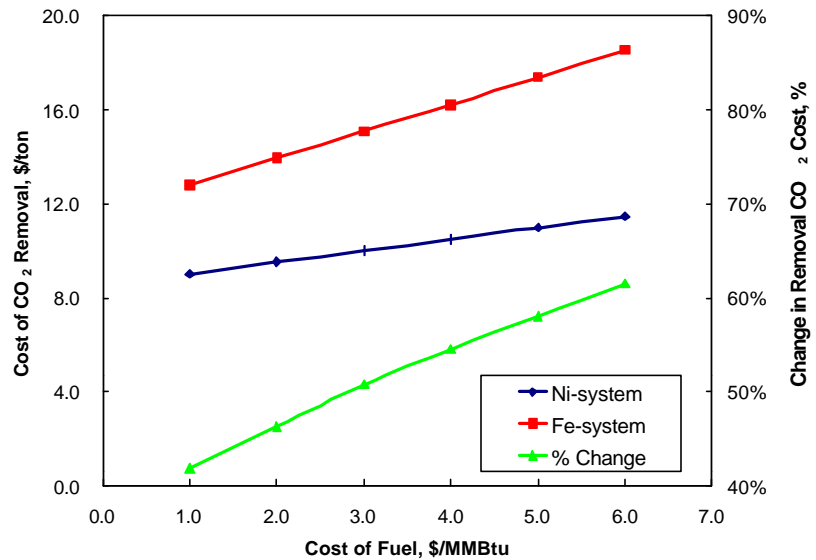


Figure 11. Cost of removal of CO₂ with FeSETS and NiSETS.

As illustrated in Figure 11, an increase in the cost of natural gas has a much higher negative effect in the cost of removal of CO₂ with the FeSETS//UFC/GT system than on the NiSETS/UFC/GT.

We also calculated the cost of removal of CO₂ while applying a credit for the sale of CO₂ to an EOR operator. Feinberg and Karpuk (1987) reported the value of CO₂ as \$10/tonne for merchant CO₂ but \$15 to \$40/tonne for Enhanced Oil Recovery (EOR). We converted these values to 2000 dollars, using the chemical engineering price index conversion (as 323.4 and 392.6 for the year 1987 and 2000, respectively); range of \$12.1/ton to \$44/ton of CO₂. Table 2 presents the cost of CO₂ and carbon removal with or without sales credit for 50 MW NiSETS/UFC/GT and 50 MW FeSETS/UFC/GT plant. Both NiSETS and FeSETS have significant potential for sequestration of CO₂. Because CO₂ has value and the cost of separating CO₂ is low, SETS could sell CO₂ at a price less than its value (i.e., actually make a profit of selling the greenhouse gas CO₂).

Table 2. Cost of CO₂ and carbon separation with and without CO₂ sales credit).

Plant Size/Type	Separation Cost	Sequestration Cost	
	(no sales credit) \$/ton CO ₂	(with \$12.1/ton sales credit) \$/ton CO ₂	(with \$44/ton sales credit) \$/ton C
50 MW NiSETS/UFC/GT	10.01	(2.09)	(34.00)
50 MW FeSETS/UFC/GT	15.47	3.46	(28.57)

(Numbers in parentheses) indicate a negative cost; therefore a profit from the sale of CO₂.

Impact

While a number of processes for separation and compression of CO₂ from stack gases have been studied, all are extremely costly and add significantly to the overall energy demand (Smelser and

Booras, 1991). Herzog (1997) summarized a number of current and advanced systems for removing CO₂ from power plant flue gases. Although removing CO₂ from conventional oil or gas fired plants requires less energy than from conventional coal plants (because the carbon/hydrogen ratio of coal is higher than that of either oil or gas), the energy penalty is severe, 13-37% for current technologies and 9-15% for future systems.

SETS efficiently uses the chemical potential of the fuel to transfer the fuel energy by reducing a metal oxide. The reduced solid is then moved into a high-pressure air stream that oxidizes the metal sorbent (i.e., “burns” the transferred fuel energy) to heat the air in a combined cycle power plant. Since the energy required to separate the solids from the air is very low, little of the power cycle’s work is lost in this separation. Similarly, since reducing the sorbents fully oxidize the fuel to CO₂ and H₂O, which are also easily separated by condensing the water and recovering the CO₂ as a high-pressure gas, only a very small amount of additional power is required to deliver high pressure (e.g., 35 atm) CO₂ to the sequestration system. The net result is about a 5% increase in the fuel usage for the same net power delivered to the utility grid, compared to an energy penalty of 13 to 37% for current CO₂ separations system. Thus, SETS represents a substantial improvement in CO₂ capture technology.

SETS with a CO₂ Co-Product

CO₂ has value as an inert gas and as a chemical feedstock. For example, Enhanced Oil Recovery (EOR) uses CO₂ to increase oil production from existing fields. The value of CO₂ in EOR was estimated by Feinberg and Karpuk (1987) as \$18 to \$44/ton (CY 2000 \$). CO₂ also has value in a number of commercial applications (e.g., dry ice, urea production, etc.). The value of CO₂ for these applications is highly variable, and depending on market conditions can range from \$10 to \$100/ton.

Since the value of CO₂ is often greater than the cost of CO₂ capture with SETS, SETS can be used profitably in some near term applications. By selling the CO₂ into existing markets such as EOR, a plant operator can sell the CO₂ and make a profit while at the same time effectively sequestering the CO₂. Since the SETS could be sited at any location where there is a nearby market for the carbon content, the captured CO₂ could be effectively sold into the EOR (45 to 160 million tonne/yr) and the merchant CO₂ markets (8.2 million tonne/year, 1986). At the end of five years, the SETS could potentially have sequestered up to 840 million tons of CO₂, totally eliminating the CO₂ emissions from 60,000 MW of electrical production (6% of the total U.S. electrical production).

SETS with CO₂ Sequestration

SETS can capture CO₂ for sequestration. Costs are on the order of \$10/ton to \$20/ton for separation and compression to pipeline pressures. Assuming the CO₂ market is either saturated or that the SETS plant is too far from the potential users for shipment of the CO₂ to be economic, the CO₂ could be sequestered at an additional cost of \$5 to \$15/ton (Herzog, Drake, and Adams 1997). Thus, the total cost is for CO₂ capture and sequestration is \$15 to \$25/ton with SETS integrated into an UltraFuelCell system. Plants designed for CO₂ sequestration instead of CO₂ sales could be sited in almost any location, and would therefore be applicable to most or all of the

new generating capacity; it is much easier to install SETS (or any other process) on new units than to retrofit it to existing units. The U.S. electrical capacity is growing at approximately 2% per year, accounting for 20,000 MW of new installed capacity each year.

In the long term, CO₂ capture and disposal must be lower than the anticipated CO₂ emissions taxes. In Norway the CO₂ emissions taxes are \$50/tonne = \$45.4/ton; in Sweden a similar tax is of \$35-40/ton CO₂ imposed (in Swedish currency, 380 SEK/ton CO₂). Literature estimates of carbon emission taxes to stabilize CO₂ concentrations are over \$100/ton (Kim and Edmonds 2000). Taking into consideration anticipated storage costs, SETS based sequestration will cost between \$15 and \$25/ton CO₂, even when the high value CO₂ markets are not close-at-hand or have been saturated. Thus, SETS clearly offers a substantial economic advantage over other known CO₂ sequestration approaches in a climate-constrained world.

The installed base of electrical generation capacity in the U.S. is 762,408 MW (1994). While it is impossible to accurately forecast growth rates for electrical generation capacity one to three decades in the future, if we assume a 2% annual growth rate and implementation beginning 15 years from now, the total annual market for new generation technology in the U.S. (and therefore the potential annual U.S. market for SETS/Combined Cycle systems) will be 20,000 MW/year.

One year's worth of this electric growth represents about 51 million tons per year of CO₂ if we conservatively assume that the capacity is supplied by 50% LHV natural gas fired combined cycles (i.e., the lowest carbon content fossil fuel). If the growth occurred all in coal-fired generation, the potential savings (or emissions) would be about 90 million tons of CO₂ per year. After 10 years of growth, the cumulative greenhouse gas savings are 2,500 million tons of CO₂ assuming all natural gas fueled generation (4,400 million tons savings with coal).

Closure

In summary, the SETS 1) economically reduces greenhouse gas emissions, 2) reduces the cost of electricity when there is a market for CO₂ and 3) increases owners' profits. After SETS is fully developed and demonstrated, owners would in many cases (where CO₂ markets exist) profitably implement the SETS technology, with or without carbon emission taxes.

Given that the expected cost of CO₂ capture and sequestration (\$15 and \$25/ton CO₂ for NiSETS/UFC/GT) is significantly less than carbon emission taxes (\$35 / \$50/ton currently in Sweden/Norway), SETS can minimize the cost of environmental controls on electric production, allowing the continued use of the USA's abundant fossil energy resources even in a climate constrained world.

Future Activities

TDA plans to continue the development of low cost and better performing nickel based sorbents and then to transfer the sorbent technology to Saint-Gobain NorPro (NorPro), who has the capability to produce the sorbent in large scale for commercial use. We will test nickel-based sorbents made by NorPro in a scalable fluidized bed reactor. Under subcontract to TDA, KBR will design, fabricate and checkout a small SETS system. The test system will operate with a

fluidized bed in the reducing side and a transport reactor in the oxidizing side. Sorbent will circulate between the two reactors and we will test NorPro sorbent at the design operating conditions and will generate data which can be scaled. TDA will conduct revised analyses to evaluate the impact of the SETS based on the data generated by the KBR small-scale SETS system.

References

- Albanese A.S. and M. Steinberg, *Environmental Control Technology for Atmospheric Carbon Dioxide*, DOE/EV-0079, Brookhaven National Laboratory, Brookhaven, NY (1980).
- Baumeister, T., Avallone, E.A., and Baumeister III, T., (1978) *Mark's Standard Handbook for Mechanical Engineers*, 8th ed., McGraw Hill.
- Blok, K., Williams, R., Katofsky, R., and Hendriks, C. (1997) Hydrogen production from natural gas, sequestration of recovered CO₂ in depleted gas wells and enhanced natural gas recovery, *Energy* **22**, 161-168.
- Cullity, B.D. (1956) *Elements of X-Ray Diffraction*, Addison-Wesley Publishing.
- Eggersted, P.M. (1995). "Lightweight Ceramic Filter Components: Evaluation and Application" in *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Morgantown, West Virginia: U.S. Department of Energy Morgantown Energy Technology Center, Report No. DOE/METC-95/1018 (DE95009732).
- Feinberg, D.A. and M.E. Karpuk (1989). *CO₂ Sources for Methane Synthesis*, Topical Report No. 1, prepared by TDA Research, Inc.: Wheat Ridge, CO for Gas Research Institute, contract No. 5087-260-1543, report No. GRI/89-0055, March.
- Freund, P. (1998) Abatement and mitigation of carbon dioxide emissions from power generation. *Power-gen 98 conference, Milan, June* (<http://www.ieagreen.org.uk/pge98.htm>)
- Froment, G.F. and Bischoff, K.B. (1990) *Chemical Reactor Analysis and Design*, 2nd ed. Wiley.
- Hatanaka, T., Matsuda, S., and Hatano, H. (1997) A new-concept gas-solid combustion system "MERIT" for high combustion efficiency and low emissions. *Proc. Intersoc. Energy Conversion Eng. Conf.* **30**, 944-948.
- Herzog H., E. Drake, J. Tester and R. Rosenthal, *A Research Needs Assessment for the Capture, Utilization, and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants*, DOE/ER-30194, U.S. Department of Energy, Washington, DC (1993).
- Herzog H.J. and E.M. Drake, *Long-Term Advanced CO₂ Capture Options*, IEA/93/0E6, IEA Greenhouse Gas R&D Programme, Cheltenham, UK (1993).
- Herzog H.J., E. Adams, D. Auerbach and J Caulfield, *Technology Assessment of CO₂ Ocean Disposal*, Report 95-001, MIT Energy Laboratory, Cambridge, MA (1995).
- Herzog, H. et al. (1996), *Energy Conv. Magmt.* **37**, 999.
- Herzog, H., E. Drake, and E. Adams (1997). *CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change*, Energy laboratory, Massachusetts Institute of Technology, Cambridge, MA, DOE Order No. DE-AF22-96PC01257, January.
- Herzog, H., Eliasson, B., and Kaarstad, O. (2000) Capturing greenhouse gases. *Scientific American* **282**(2):72-79.
- Ishida, M. et al. (1987). *Energy*, **20**, 147.
- Ishida, M., and Jin, H. (1994) A novel combustor based on chemical-looping reactions and its reaction kinetics. *J. Chem. Eng. Japan* **27**, 296-301.

- Ishida, M. and H. Jin (1995) *Chemical-Looping Combustion Power Generation Plant System*, U.S. Patent number 5,447,024, Sept. 5.
- Ishida, M., Jin, H., and Okamoto, T. (1996) A fundamental study of a new kind of medium material for chemical-looping combustion. *Energy & Fuels* **10**, 958-963.
- Ishida, M., and Jin, H. (1996) Novel chemical-looping combustor without NO_x formation. *Ind. Eng. Chem. Res.* **35**, 2469-2472.
- Ishida, M., Jin, H., and Okamoto, T. (1998) Kinetic behaviour of solid particle in chemical-looping combustion: suppressing carbon deposition in reduction. *Energy & Fuels* **12**, 223-229.
- Ishida, M., Yamamoto, M., and Saito, Y. (1999) Experimental works on innovative chemical-looping combustor. *ECOS'99, International Conference on Efficiency, Costs, Optimization, Simulation and Environmental Aspects of Energy Systems*, Tokyo, June 8-10, 306-310.
- James, R.E. III, (2000). *Multistage, Solid State, Fuel Cell Plant with Gas Turbine and CO₂ Sequestration: A Concept Audit*, U.S. DOE NETL Process Engineering Report No. OSPS-PED-REJ-2000-4, November
- James, R.E. III, and T.J. George (2000). *1st Revision, Advanced high Temperature Fuel cell System (Compilation of NETL Internal Process & Cost Analyses)*, U.S. DOE NETL Process Engineering Report No.s OSPS-PED-REJ-2000-1, February, PE1998.01, PE1998.02, PE1998.03, OSPS-PED-REJ-2000-2, PE1998.05, PE1999.01, PE1999.02, and OSPS-PED-REJ-2000-1,
- Jin, H., Okamoto, T., and Ishida, M. (1998) "Development of a novel chemical-looping combustion: synthesis of a looping material with a double metal oxide of CoO-NiO". *Energy & Fuels* **12**, 1272-1277.
- Jin, H., Okamoto, T., and Ishida, M. (1999) "Development of a novel chemical-looping combustion: synthesis of a solid looping material of NiO/NiAl₂O₄." *Ind. Eng. Chem. Res* **38**, 126-132.
- Kim, S.H., and J.A. Edmonds (2000). *Potential for Advanced Carbon capture and Sequestration technologies in a Climate Constrained World*, Report no. PNNL-13095 prepared for the U.S. Department of Energy Under Contract DE-AC06-76LO 1830, February
- Kirkpatrick, M. and R. Pike (1994). *AIChE Symposium Series*, Vol. 90, No. 298.
- Kunii, D. and Levenspiel, O. (1991) Fluidization Engineering, 2nd ed. Butterworth-Heinemann.
- Lippert, T.D., G.J. Bruck, Z.N. Sanjana, and R.A. Newby. (1995). "Westinghouse Advanced Particle Filter System" in *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Morgantown, West Virginia: U.S. Department of Energy Morgantown Energy Technology Center, Report No. DOE/METC-95/1018 (DE95009732).
- Lyngfelt, A., B. Leckner, and T. Mattisson (2000). "A fluidized-bed combustion process with inherent CO₂ separation; Application of chemical-looping combustion" by Anders Lyngfelt, Bo Leckner and Tobias Mattisson, Dept. of Energy Conversion, Chalmers University of Technology, 412 96 Göteborg, Sweden Accepted (2000) for publication in *Chemical Engineering Science*. Marchetti C, "On Geoengineering and the CO₂ Problem", *Climatic Change* 1(1), pp. 59-68 (1977).
- Matsen, J.M., Rossetti, S.J. and Halow, J.S. (1985) "Fluidized Beds and Gas Particle Systems," in Encyclopedia of Chemical Processing and Design, vol 23, Marcel Dekker.
- Mimura T., H. Simayoshi, T. Suda, M. Iijima and S. Mituoka, "Development of Energy Saving Technology for Flue Gas Carbon Dioxide Recovery by Chemical Absorption Method and Steam System in Power Plant", *Energy Convers. Mgmt.*, in press (1997).

- Misra, C. (1986) Industrial Alumina Chemicals, ACS Monograph 184, American Chemical Society.
- Mudd, M.J. and J.D. Huffman (1993). "Initial Operation of the Tidd PFBC Hot Gas Clean Up Filter, *Advanced Coal-Fired Power Systems '93 Review Meeting*, Morgantown, WV: U.S. Department of Energy Morgantown Energy Technology Center, Report No. DOE/METC-93/6131 (DE93000289).
- Nakano, Y., Iwamoto, S., Maeda, T., Ishida, M., and Akehata, T. (1986) Characteristics of reduction and oxidization cyclic process by use of Fe_2O_3 medium. *Iron & Steel Journal of Japan* **72**, 1521-1527.
- Perry, R.H., Green, D.W. and Maloney, J.O eds. (1984) Perry's Chemical Engineers' Handbook, 6th ed. McGraw Hill.
- Reichele, D., B. Kane, J. Houghton, J. Ekmann, et al. (1999). *Carbon Sequestration State of the Science*, Office of Science, Office of Fossil Energy, U.S. Department of Energy, A Working Paper for *roadmapping* future carbon sequestration R&D, February.
- Reid, R.C., Prausnitz, J.M., and Poling, B.E. (1987) The Properties of Liquids and Gases, 4th ed. McGraw Hill.
- Richter, H., and Knoche, K. (1983) Reversibility of combustion processes. In *Efficiency and Costing*, ACS Symposium Series. Ser **235**, 71-86.
- Sadeghbeigi, R. (1995) Fluid Catalytic Cracking Handbook, Gulf Publishing.
- Smelser, S. and G. Booras (1991). *Energy* **16**, 1295.
- Steinberg M., "Production of Hydrogen and Methanol from Natural Gas with Reduced CO Emission", *Hydrogen Energy Progress XI*, Proc. of the 11th World Hydrogen Energy Conf., Stuttgart, 1, pp. 499-510 (1996).
- Steinberg M., *An Analysis of Concepts for Controlling Atmospheric Carbon Dioxide*, Weast (1981) Handbook of Chemistry and Physics, 62nd ed., CRC Press.
- Zheng, D., Y. Uchiyama, and M Ishida (1986). *Energy*, **11**, 631.

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