

# **SORBENT ENERGY TRANSFER SYSTEM (SETS) FOR CO<sub>2</sub> SEPARATION WITH HIGH EFFICIENCY**

Robert J. Copeland  
Gokhan Alptekin  
Mike Cesario  
Yevgenia Gershanovich  
TDA Research, Inc.  
12345 West 52<sup>nd</sup> Avenue  
Wheat Ridge, CO 80033-1916

## **1. ABSTRACT**

In a Chemical Looping Combustion (CLC) system a fossil fuel transfers its energy to reduce a metal oxide, producing CO<sub>2</sub> and water. The steam and CO<sub>2</sub> are cooled and the steam is condensed, producing a pure stream of CO<sub>2</sub> for sequestration. The metal is re-oxidized in air, heating high-pressure air in a gas turbine/combined cycle and/or fuel cell system. The oxidized metal is sent to the reducing reactor to repeat the cycle. The metal acts to transfer O<sub>2</sub> from the air to the fuel and the energy in the fuel to the air without carrying the CO<sub>2</sub> produced by the fuel with it.

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. In this paper we also show the application to gasified coal with 100% CO<sub>2</sub> capture.

## **2. INTRODUCTION**

Concern over global climate change has led to a need for new systems that produce electricity from fossil fuels and emit less CO<sub>2</sub>. The fundamental problem with current CO<sub>2</sub> separation systems is the need to separate dilute CO<sub>2</sub> and pressurize it for storage or sequestration. This is an energy-intensive process that can reduce plant efficiency by 9-37%, and CO<sub>2</sub> capture costs for projects reported to date can exceed \$70 per tonne of CO<sub>2</sub> (Herzog, Drake, and Adams 1997). The fundamental reason that CO<sub>2</sub> removal, compression and sequestration is so consumes such large amounts of energy and capital is that the CO<sub>2</sub> in 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 CO<sub>2</sub> through a pressure ratio of 100-1000.

In a Chemical Looping Combustion (CLC) system fossil fuel transfers its energy to reduce a metal oxide, producing CO<sub>2</sub> and water. The steam and CO<sub>2</sub> are cooled and the steam is condensed, producing a pure stream of CO<sub>2</sub> for sequestration. The metal is re-oxidized in air, heating high pressure air in a gas turbine/combined cycle. The oxidized metal is sent to the reducing reactor to repeat the cycle. The metal acts to transfer O<sub>2</sub> from the air to the fuel and the energy in the fuel to the air without carrying the CO<sub>2</sub> produced by the fuel with it.

### **2.1. Objective**

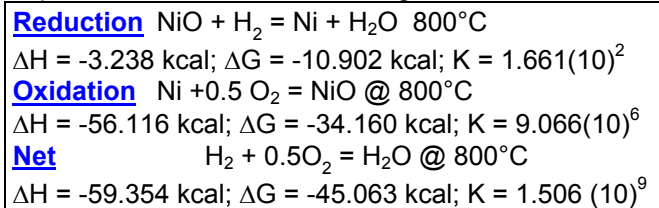
The objective of this project is to generate electricity from fossil fuels while capturing most or all of the CO<sub>2</sub>, and to do so with only a minimal impact on the conversion efficiency and the cost of electricity. To do this, TDA Research, Inc. (TDA) has identified a Novel CO<sub>2</sub> Separation 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 CO<sub>2</sub> and steam), and then the reduced metal oxide is reacted with hot, high pressure air to release its heat and drive a gas turbine. TDA's SETS is simply a type of a CLC; however, in our analyses we configure the process to make the minimum amount of changes to the power cycle, allowing the power cycle to operate in a very conventional manner.

## 2.2. Approach

To economically generate electricity and produce a high pressure, concentrated CO<sub>2</sub> 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 (CO<sub>2</sub> and water) separated from the hot, high pressure air used in the power cycle. Thus, the CO<sub>2</sub> 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 CO<sub>2</sub> and H<sub>2</sub>O 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 O<sub>2</sub> 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 large); the net reaction is simply the oxidation of hydrogen to water (similar results occur with CO and CH<sub>4</sub> with CuO and Fe<sub>2</sub>O<sub>3</sub>). 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.”

Equation 1. SETS reactions using Ni as O<sub>2</sub> sorbent.



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 of 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.

## 2.3. 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

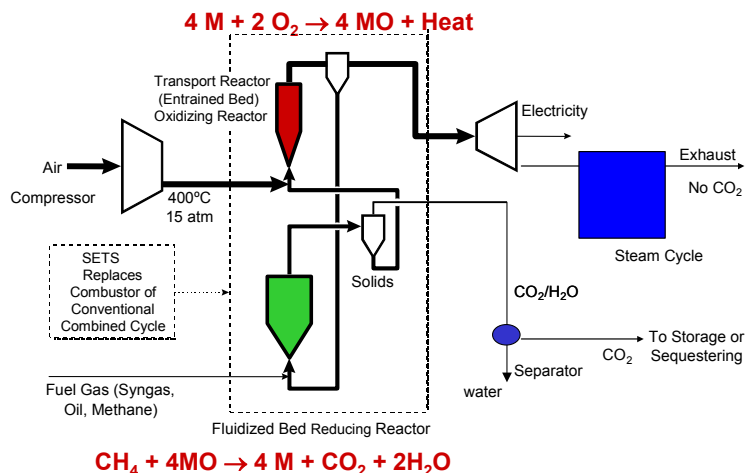


Figure 1. Sorbent energy transfer cycle schematic (M = metal).

UltraFuelCell), a very high efficiency conversion cycle in which the system can capture effectively all of the carbon emissions.

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<sub>4</sub>) to heat, which is stored in the reduced metal, and produces a stream, which consists of 33% CO<sub>2</sub> 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 CO<sub>2</sub>/H<sub>2</sub>O stream by condensing it and are now left with a stream of virtually 100% pure CO<sub>2</sub> at high pressure. The CO<sub>2</sub> (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<sub>4</sub> 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<sub>2</sub> and H<sub>2</sub>O. Natural gas is mixed with recycled CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>, CO, and CH<sub>4</sub> are left unreacted and sequestered with the CO<sub>2</sub>. 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.

For the gas turbine power generation cycle being illustrated here, air enters from the oxidation reactor from the compressor at ~400°C and we add in 3 mols of steam (extracted from the steam cycle) to replace the CO<sub>2</sub> + 2H<sub>2</sub>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 ~1,288°C (the standard design temperature of the turbine).

The CO<sub>2</sub> + 2H<sub>2</sub>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. Additional cooling condenses the water of combustion and the liquid is separated. We then compressed the 15 atm CO<sub>2</sub> to the delivery pressure, 35 atm (500 psig). In this work, we assume a nearby user for the CO<sub>2</sub> (e.g., Enhanced Oil Recovery (EOR)) and have therefore limited the maximum delivery pressure to sub-critical CO<sub>2</sub>. For long distance transport of the CO<sub>2</sub>, supercritical CO<sub>2</sub> (e.g., 103 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 at 800°C and higher. Our iron-based sorbent operates at 800°C (1,472°F) but our nickel based sorbent has long life even at an operating temperature of 1,050°C (1,922°F). When the temperature at the outlet of the oxidizing reactor limited to 800°C by the temperature limitations of our iron-based sorbent, the cycle will capture 38% of the CO<sub>2</sub> (the CO<sub>2</sub> 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 CO<sub>2</sub>, and at the 1050°C maximum operating temperature of the nickel sorbent, the cycle could capture 66% of the CO<sub>2</sub>.

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 CO<sub>2</sub> produced with SETS.

### 3. 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, Fe<sub>3</sub>O<sub>4</sub>, MnO, and Ni (in the reduced state) which convert to CuO, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, 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 Fe<sub>2</sub>O<sub>3</sub> to FeO by CH<sub>4</sub> will leave some unoxidized CO and H<sub>2</sub> in the reducing reactor outlet gas, reduction of CuO to Cu reacts virtually all of the fuel gases (<100 ppm CO+H<sub>2</sub> are sequestered with the CO<sub>2</sub>). Reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> and NiO to Ni also fully oxidizing the CH<sub>4</sub> (or any other fuel gas). The reduction reactions of Fe<sub>2</sub>O<sub>3</sub> and NiO with CH<sub>4</sub> 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 is 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 testing of these sorbents is described in the next section.

#### 3.1. 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- and nickel-based sorbents.

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 nation's 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). Oxygen loading was calculated based on the sorbent capacity at breakthrough, which we defined as the appearance of 1% H<sub>2</sub> (dry) in the reactor outlet. Pre-breakthrough levels of H<sub>2</sub> 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.

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)<sup>-6</sup> 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 million 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 our 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 (see Section 3.2) 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<sub>2</sub>, CO, CH<sub>4</sub> 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 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 an UltraFuelCell application. Figure 2 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 kinetics 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% H<sub>2</sub> (dry) in the outlet. Pre-breakthrough levels of H<sub>2</sub> and CO were below detectable limits in our instruments (i.e., < 0.1%).

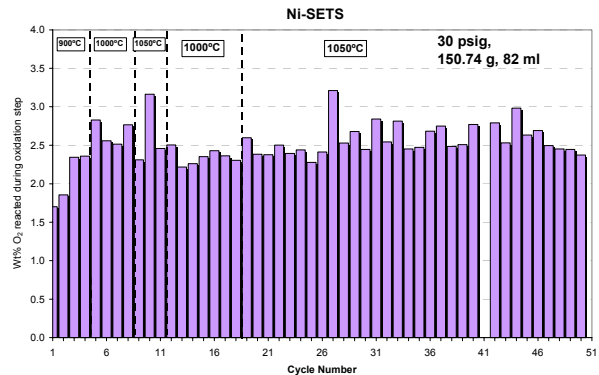


Figure 2. High temperature testing of Ni-SETS with full oxidation of fuel to CO<sub>2</sub> & H<sub>2</sub>O.

### 3.2. 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 CO<sub>2</sub> and H<sub>2</sub>O and to be regenerated for many cycles.

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..

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 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/ft<sup>3</sup>.

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

- Reduction of the sorbent with simulated syngas containing H<sub>2</sub> at a concentration varying from about 5% to 15% and a temperature range of ~780°C (1400°F to 1450°F) was very good. At the lowest space velocity studied, the leakage of H<sub>2</sub> in the outlet gas was very low (<90 ppm) when the inlet H<sub>2</sub> concentration was at 5%
- During sorbent reduction, greater than 80% of the available oxygen was consumed by the reducing gas before leakage of CO + H<sub>2</sub> exceeded 1% (dry). This leakage was reduced with an increase in inlet H<sub>2</sub> concentration.
- A temperature of 1350°F was adequate to oxidize the sorbent. Sorbent oxidation was very good with no O<sub>2</sub> leakage until near sorbent saturation.

- The oxidation of sorbent over 50 cycles was good, and the reproducible O<sub>2</sub> 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 ft<sup>3</sup> bed at 20 psia at the space velocity of our 50 cycle test, (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.

#### 4. APPLICATIONS

SETS can use any hydrocarbon fuel, including but not limited to Natural Gas (NG), oil, and gasified coal or biomass. Louisiana State University (LSU) and the DOE-National Energy Technology Laboratory (NETL), assisted us in these analyses. 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. The process operates with dual fluidized-bed or transport reactors to accomplish solid transfer and provide steady-state operation. CH<sub>4</sub> and the metal oxide (e.g., Fe<sub>2</sub>O<sub>3</sub>, NiO) are fed to the sorbent reducing reactor where reaction (1) occurs. A portion of the product gas, which contains only CO<sub>2</sub> and H<sub>2</sub>O, 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. H<sub>2</sub>O is separated by condensation, leaving pure CO<sub>2</sub>, 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 H<sub>2</sub>O and CO<sub>2</sub> 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 CH<sub>4</sub> to achieve the design gas turbine firing temperature. CO<sub>2</sub> 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 CO<sub>2</sub> 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 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture percent was small except in response to variations in SETS reactors temperatures. The CO<sub>2</sub> 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, CO<sub>2</sub> 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 CO<sub>2</sub> 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 (6,570 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 10<sup>6</sup> 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 Fe<sub>2</sub>O<sub>3</sub>-CuO-Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> sorbent compositions, respectively. The resulting CO<sub>2</sub> capture costs associated with SETS were \$15.82 per metric ton of CO<sub>2</sub> for the Fe<sub>2</sub>O<sub>3</sub>-CuO-Al<sub>2</sub>O<sub>3</sub> sorbent and \$18.33 per metric ton of CO<sub>2</sub> for the Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> 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 ±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 ±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<sup>5</sup> pounds of circulating sorbent more than doubled the estimated capture cost from \$15.82 to \$35.40 per metric ton of CO<sub>2</sub> using the Fe<sub>2</sub>O<sub>3</sub>-CuO-Al<sub>2</sub>O<sub>3</sub> sorbent.

The base case estimate of about \$15 to \$18 per metric ton of CO<sub>2</sub> captured with an increase in heat rate of less than 5% compares quite favorably with other CO<sub>2</sub> capture cost estimates. For example, Herzog (*The Economics of CO<sub>2</sub> Capture, in Greenhouse Gas Control Technologies, P. Rietem, B. Eliasson, and A. Wokaun, eds., Elsevier Science Ltd., 1999*) reports estimated capture costs ranging from \$18 to \$72

per metric ton of CO<sub>2</sub> 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<sub>2</sub> capture options.

Application of SETS to an UltraFuelCell with a Gas Turbine: 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 CO<sub>2</sub>. Previously, DOE/NETL had simulated and calculated the economics of several UltraFuelCell-based power plants without CO<sub>2</sub> capture. We analyzed cases for each of the two sorbents that we developed, Ni-SETS (nickel based) and TDASETS (iron based).

In the evaluation, we cooperated with Robert James of NETL/DOE. Robert James developed a simulation spreadsheet, which applied NiSETS 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<sub>e</sub> as the basis of plant capacity to carry out the simulation of SETS/UFC/Gas Turbine

There are two major causes for the decrease in efficiency in the system. The first one is directly related with the power requirement for the CO<sub>2</sub> compression. Even though SETS produces an essentially pure CO<sub>2</sub> stream at 3 atm, compression of the CO<sub>2</sub> from 3 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 CO<sub>2</sub> is also unavoidable in NiSETS/UFC/GT and any other CO<sub>2</sub> sequestration system as well. The other difference in the efficiency is associated with the low temperature of operation of the SETS reactor. The transport reactor effluent at 800°C in the FeSETS /UFC/GT system is expanded through a gas turbine. The expander inlet temperature in the FeSETS/UFC/GT is lower than that of the NiSETS/UFC/GT (1060°C), which reduces the amount of work recovered through the expansion, resulting a loss in the overall efficiency of the system. 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 CO<sub>2</sub> 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  $\Delta T_{lm}$ '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<sub>e</sub> 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 3 presents the cost for CO<sub>2</sub> 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 unimportant (i.e., at 1 million cycle life and higher, the cost for CO<sub>2</sub> capture is about \$10/ton with \$1/lb, or \$5/lb or \$10/lb sorbent); note that our measured sorbent life of over 1.8 million cycles is much better than this. At lower cycle lifetimes the replacement rate of sorbent become

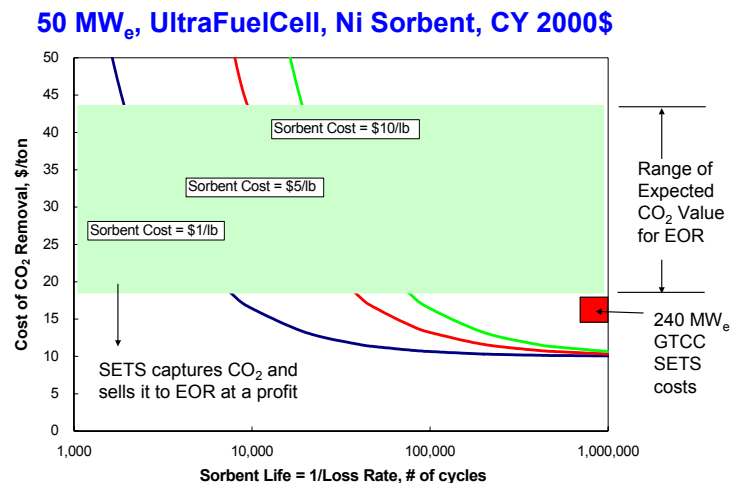


Figure 3. NiSETS/UFC/GT is low-cost with long-life sorbent.

significant, and can increase the cost of CO<sub>2</sub> 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 1 million cycles.

We also calculated the cost of removal of CO<sub>2</sub> while applying a credit for the sale of CO<sub>2</sub> to an EOR operator. Feinberg and Karpuk (1987) reported the value of CO<sub>2</sub> as \$10/tonne for merchant CO<sub>2</sub> 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 CO<sub>2</sub>. Both NiSETS and FeSETS have significant potential for sequestration of CO<sub>2</sub>. Because CO<sub>2</sub> has value and the cost of separating CO<sub>2</sub> is low, SETS could sell CO<sub>2</sub> at a price less than its value (i.e., actually make a profit of selling the greenhouse gas CO<sub>2</sub>).

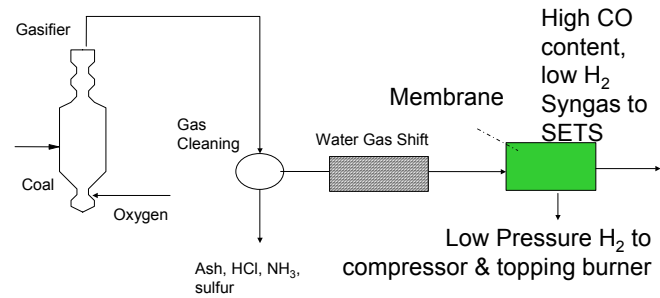


Figure 4. IGCC with SETS and H<sub>2</sub> topping for 100% CO<sub>2</sub> capture.

Application of SETS to Coal Gasification: TDA also considered the application of SETS to coal gasification and an Integrated Gasifier Combined Cycle (IGCC). Due to the temperature limitation of the known sorbents, SETS can not directly capture 100% of the CO<sub>2</sub>. However, by separating hydrogen (H<sub>2</sub>) from the gasified coal, one can burn that hydrogen to reach the peak temperature required in the gas turbine without emitting CO<sub>2</sub>.

IGCC requires gas cleaning to remove the ash, chloride, ammonia, sulfur, etc. Nominally, the gas cleaning is done at high temperature (most efficient) and then a Water Gas Shift (WGS) shifts most of the CO to H<sub>2</sub> and CO<sub>2</sub> using the water content of the gas stream.

Table 1 presents the gas compositions for a nominal Texaco gasifier following the WGS reactor. Note that the WGS is exothermic and 4.3% of the heat content of the gas stream is converted to heat, raising high pressure steam to be used in the steam cycle of the IGCC. While this is less efficient than the fuel in the gas turbine, the net loss is only about 2% of the power plant output.

TDA calculated the gas compositions into and out of the membrane assuming the WGS reactor was at equilibrium at 300°C. The high temperature (e.g., Pd) membrane was assumed to be selective to hydrogen. The hydrogen concentration entering and leaving the membrane separator are relatively high (44.3% in and 12.8% out). In comparison to other membrane systems we only capture ~55% of the energy in the gas stream as H<sub>2</sub>, since SETS delivers the balance of the heat by the combustion of CO and remaining H<sub>2</sub> to the combustion air. The net result is that the overall system minimizes the demands on the membrane (i.e., it is operating in regions of high fluxes and therefore minimum area/costs). This technology is an early stage of development; TDA made an approximate cost estimate for the cost of the high temperature membrane under this conditions.

Table 1. Gas compositions before and after H<sub>2</sub> removal.

Gas	Before H <sub>2</sub> removal	After H <sub>2</sub> removal
H <sub>2</sub>	44.3%	12.8%
CO <sub>2</sub>	29.7%	46.5%
CO	18.3%	28.6%
H <sub>2</sub> O	1.8%	2.8%
N <sub>2</sub>	5.9%	9.3%

Table 2 presents the cost for CO<sub>2</sub> capture (or CO<sub>2</sub> avoided when natural gas topping is used with an IGCC and SETS). When natural gas topping was used in the analysis we assumed that the natural gas cost was \$4.37/MMBtu (i.e., natural gas and syngas from coal gasification have the same costs). Based on our preliminary estimates for the high temperature membrane, this combination had both the highest CO<sub>2</sub> capture and the lowest cost for CO<sub>2</sub> capture (however, given the imprecision of that analysis we are not reporting the costs herein).

With a Ni-SETS IGCC plant and syngas topping, we capture 67% of the CO<sub>2</sub> produced in the plant. With an IGCC with SETS and natural gas (NG) topping, we reduce CO<sub>2</sub> emissions by 85%. Adding the low temperature membrane to separate H<sub>2</sub> from the syngas, and a H<sub>2</sub> topping, improves the CO<sub>2</sub> capture to 82%. Using water gas shift (WGS) and an amine plant to capture the CO<sub>2</sub> increases CO<sub>2</sub> capture to 90% (without any SETS). Of the above approaches, the lowest-cost approaches use the Ni-SETS.

SETS can reduce CO<sub>2</sub> emissions from an Integrated Gasifier Combined Cycle (IGCC) power plant as well as from a Natural Gas Combined Cycle (NGCC). Our previous work on SETS with a NGCC showed costs of \$18 to \$20/ton of CO<sub>2</sub> captured. In an IGCC with SETS, the cost for CO<sub>2</sub> capture can be reduced to less than \$9/ton CO<sub>2</sub> captured, due principally to the fact that coal has a higher carbon content than natural gas (i.e., the same equipment captures more CO<sub>2</sub> due to the higher carbon in the fuel).

## 5. CLOSURE

Presently the market for CO<sub>2</sub> in EOR and merchant uses is large and can pay more for the CO<sub>2</sub> than the cost to produce it. In summary, the SETS 1) reduces greenhouse gas emissions, 2) reduces the cost of electricity when there is a market for CO<sub>2</sub> 3) can reform natural gas to liquids and other chemicals and 4) increases owners' profits. After SETS is fully developed and demonstrated, owners would implement the SETS technology, with or without carbon emission taxes.

Given the expected cost of CO<sub>2</sub> capture and sequestration (\$15 and \$25/ton CO<sub>2</sub> 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.

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Table 2. Cost for CO<sub>2</sub> capture with IGCC.

High Temp. Membrane H <sub>2</sub> topping	
CO <sub>2</sub> capture	~100%
Cost per ton of CO <sub>2</sub>	\$ 5.37
Ni- SETS NG topping	
CO <sub>2</sub> capture	85%
Cost per ton of CO <sub>2</sub>	\$ 9.05
Low Temp. Membrane, H <sub>2</sub> topping	
CO <sub>2</sub> capture	82%
Cost per ton of CO <sub>2</sub>	\$ 12.48
Amine plant for CO <sub>2</sub> , H <sub>2</sub> topping	
CO <sub>2</sub> capture	90%
Cost per ton of CO <sub>2</sub>	\$ 10.04

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