**Technical Report**

**September 1998**

**Title:** *A Novel $CO_2$ Separation System*

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**Sponsor:** U.S. Department of Energy

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## PROJECT DESCRIPTION

### Introduction

Because of concern over global climate change, new systems are needed that produce electricity from fossil fuels and emit less $CO_2$. The fundamental problem with current systems which recover and concentrate $CO_2$ from flue gases is the need to separate dilute $CO_2$ and pressurize it to roughly 35 atm for storage or sequestration. This is an energy intensive process that can reduce plant efficiency by 9-37% and double the cost of electricity.

There are two fundamental reasons for the current high costs of power consumption, $CO_2$ removal, and concentration systems: 1) most disposal, storage and sequestering systems require high pressure $CO_2$ (at roughly 35 atm). Thus, assuming 90% removal of the $CO_2$ from a typical atmospheric pressure flue gas that contains 10% $CO_2$, the $CO_2$ is essentially being compressed from 0.01 atm to 35 atm (a pressure ratio of 3,500). This is a very energy intensive process. 2) The absorption-based (amine) separation processes that are used to remove the $CO_2$ from the flue gas and compress it to 1 atm consume approximately 10 times as much energy as the theoretical work of compression because they are heat driven cycles working over a very low temperature difference. Thus, to avoid the problems of current systems, we need a power cycle in which the $CO_2$ produced by the oxidation of the fuel is not diluted with a large excess of nitrogen, a power cycle which would allow us to eliminate the very inefficient thermally driven absorption/desorption step. In addition, we would want the $CO_2$ to be naturally available at high pressure (approximately 3 to 6 atmospheres), which would allow us to greatly reduce the compression ratio between generation and storage (from roughly 3,500 to approximately 8).

To meet this objective, we propose a power generation system in which a fossil fuel (gasified coal, petroleum fuels or natural gas) at pressure is used to reduce a metal oxide, producing metal (or a lower valance metal oxide), $CO_2$ and water (Figure 1). The water is condensed and its energy used to raise steam, leaving behind a stream of pure $CO_2$ at 3 to 6 atmospheres that can be readily stored or sequestered. The metal oxide is then "burned" or re-oxidized in air from the compressor section of a gas turbine, producing a hot high pressure stream of air which is used to drive a gas turbine. The exhaust can in turn be used to drive a steam bottoming cycle. The oxidized particles are then recycled to the first reactor to be reduced again and repeat the cycle. The system which transfers the energy of the fuel to the air without bringing the carbon along is called a Sorbent Energy Transfer System (SETS). The cycle can be run on any fuel gas (gasified coal, oil or natural gas) and does not require the development of new hardware. The power generation cycle is essentially a standard combined cycle, except that the combustor is replaced by two fluidized beds (the SETS), one which uses fuel to reduce the particulate oxide and one which oxidizes it and heats the air entering the turbine. The system is described below using methane as the fuel (because it is simplest to explain).

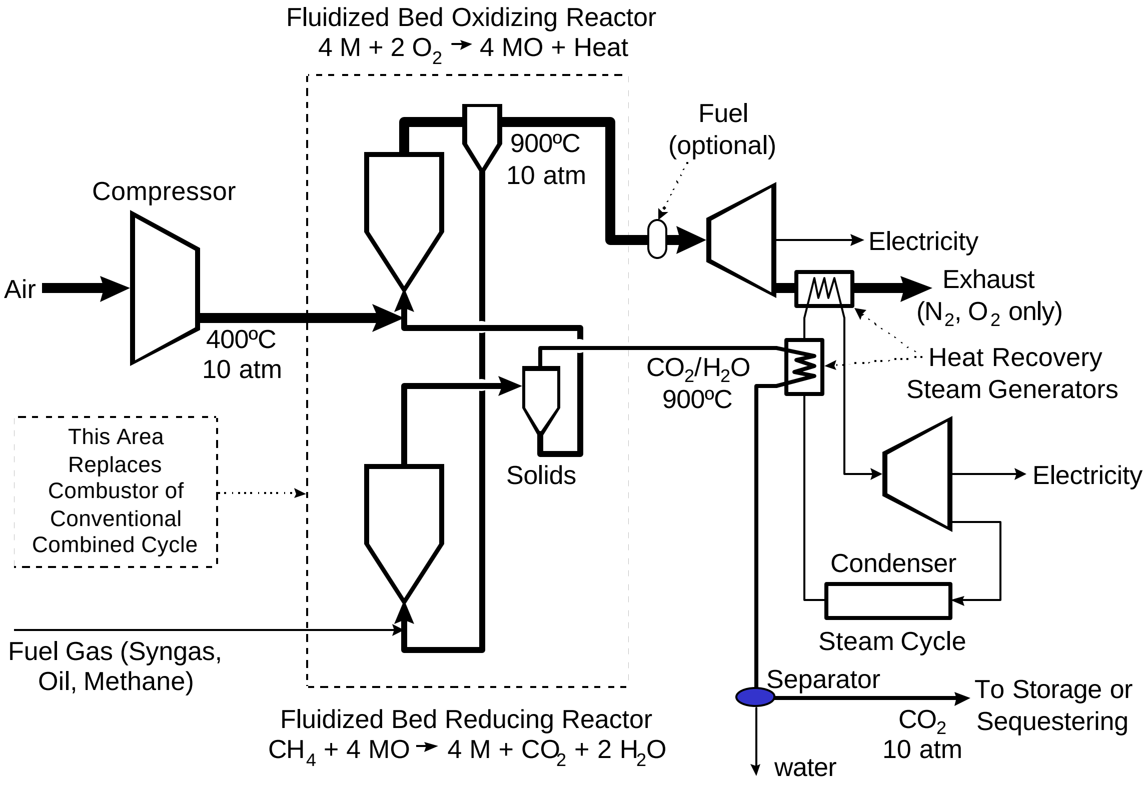

Figure 1. Sorbent energy transfer cycle schematic (M = metal).

The first step in the SETS process is to reduce a metal oxide to a metal (or a metal oxide to a lower valance metal oxide). In general, the metal (oxygen sorbent) would be supported on, or contained within, an inert support (such as alumina) which would provide a high surface area for reaction and good physical properties such as crush strength and attrition resistance. For example, if copper were the metal oxide the formula would be:

$$CH_4 + 4\ CuO \rightarrow CO_2 + 2\ H_2O + 4\ Cu$$

In this way, we convert the energy in the fuel to energy which is stored in the reduced metal, and produce a stream which consists of 33% $CO_2$ and water. We carry this out at pressure (10 atmospheres, for example) in a fluidized bed reactor, and remove the steam from the $CO_2$ by condensing it (producing valuable mid-pressure steam which can be used to generate electricity in the steam turbine of a combined cycle) and a stream of virtually 100% pure $CO_2$ at 10 atm. The $CO_2$ is sent to a storage or sequestering process with little additional compression energy.
Virtually all of the chemical energy in the original fuel gas is now incorporated into a new fuel (small particles of copper on an inert support). The reduced copper particles enter a second fluidized bed (also run at 10 atm) and 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 (900ºC or greater).

$$4\,Cu + 2\,O_2 \rightarrow 4\,CuO$$

The air entering the oxidizing bed is the hot (400°C) high pressure (10 atm) air leaving the compressor stages of a standard gas turbine. The only $CO_2$ emissions from such a system would be produced if we burned some additional fuel to further boost the temperature of the high pressure air just before it entered the expander stages of the turbine. The copper/alumina particles would then be returned to the reducing reactor and the cycle repeated.

This power cycle requires no new hardware; it is essentially a standard combined cycle in which the combustor is replaced by the fluidized bed oxidation and reduction reactors. The system can dramatically reduce or eliminate $CO_2$ emissions. The degree of $CO_2$ removal is limited only by the performance of the filters used to protect the turbine. With current 900°C filters the cycle would reduce the $CO_2$ emissions of a coal gasifier combined cycle by 83% while suffering only a 1.5 - 4% efficiency penalty. With the advanced filters currently under development, $CO_2$ emissions could be totally eliminated with no additional efficiency penalty. Since the power cycle uses only standard combined cycle generating equipment and two circulating fluidized bed reactors, the major research needs are further design, sorbent development, pilot scale testing and detailed engineering and cost analyses.

## Geodes for a Long Life Sorbent

To make a sorbent pellet that can hold large amounts of sorbent without being destroyed by the absorption-regeneration process, TDA has developed a new sorbent structure, which we call a geode (Figure 2). Like the geode that you buy at a gift shop, our geode has a hollow shell. The sorbent is loosely contained in, but does not fill, the hole(s) in the center. Thus, the sorbent can expand and contract indefinitely without destroying the pellet structure that surrounds it. Unlike the gem shop geode that has a single hole in the middle, our geode sorbent contains hundreds or thousands of holes in a structure that looks like a conventional catalyst support pellet on the outside. The interior structure of the geode is like a sponge, a sponge that is partially filled with the chemically active material, zinc titanate ($Zn_2TiO_4$ for the fluidized bed desulfurization).

To make the very small (e.g., 100 µ) particles required by fluidized bed and transport reactors, TDA has modified our previous methods of making the geode. The geode is made by mixing the ZnO sorbent with water, titania, a low cost silica-containing material (e.g., bentonite or other natural clays or minerals), and other additives. The mixture is formed by spray drying or extruding and then firing. After firing, the water and some additives evaporate and/or burn, leaving behind a complex porous structure.

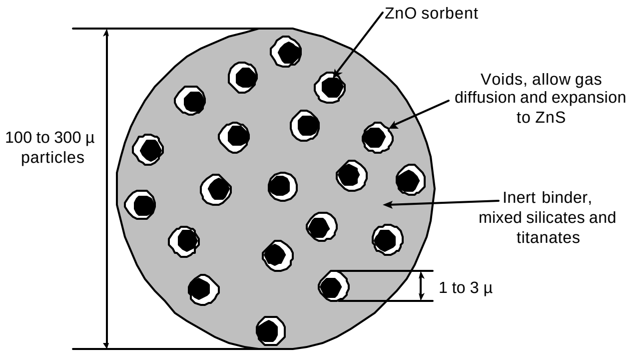

Figure 2. Structure of TDA's "geode."

Due to the nature of this mixture, it separates upon firing into two different phases which are each thermodynamically stable: titanates and silicates. Data from both published phase diagrams and our independent measurements show that the phases are physically separate. The size of each chemically active region of the geode (i.e., 1-3 µm) is controlled by the selection of the starting materials.

In the geode structure there are voids in both the mixed silicate and the zinc titanate phases. The matrix of mixed silicates (i.e., the binder) is a continuous porous structure filled with extremely small pores (0.1 to 1 µm). This structure holds the sorbent in place. Because of the porosity left behind as the water evaporates, the $H_2S$ can easily diffuse in from the exterior of the pellet to the tiny pockets of sorbent. The geode structure: 1) is very strong because there is a continuous support phase, 2) effectively contains the sorbent inside small holes in the interior of the pellet, 3) allows the sorbent to expand and contract freely without disrupting the pellet structure, 4) allows the $H_2S$ to diffuse quickly into the interior of the pellet, and 5) can hold large quantities of sorbent and absorb large quantities of sulfur. In addition, the process that we use to produce the geode is inherently low in cost. The geode is formed by mixed metal oxide techniques, yet the geode has the continuous inert structure associated with catalyst supports, which have high strength and long life.

## TECHNICAL OBJECTIVES

The Phase I research will carry out preliminary proof of concept experiments to determine whether the geode structure can be used to make a low-cost, long life, redox metal oxide based sorbent for use in the SETS cycle. The specific goal of the Phase I work is to optimize the formulation of the geode in order to obtain the following properties:

- Less than 10 lbs of oxygen per 100 lbs of fresh sorbent,
- An 80 to 300 micron particle size,
- Reduction @ 700ºC (1292ºF) with oxidation initiated with 400ºC (752ºF) air, and
- Costs of less than $8/lb when produced at 50,000 lbs/year.

## Technical Approach

In order to bring our new power cycle from a concept to a commercial reality we need a team with a variety of skills. Specifically, in this three phase program we need to:

1) Carry out the conceptual and thermodynamic analyses necessary to better define the cycle and optimize the reaction conditions,
2) Develop a sorbent with suitable physical and chemical properties,
3) Test the sorbent at the laboratory and pilot scale,
4) Engineer the oxidation and reduction reactors,
5) Prepare detailed engineering designs to predict the total cycle performance and cost.

To provide the necessary skills, we have assembled a team which includes TDA Research (TDA), M.W. Kellogg (Kellogg) and Louisiana State University (LSU) (Figure 3). TDA invented the new system design. TDA will manage the project, carry out the conceptual engineering and thermodynamic analysis to define the process, and develop the sorbent. Kellogg will review the initial conceptual designs, carry out detailed engineering analyses, and test the sorbent in their circulating fluidized bed pilot facility. LSU will aid in the thermodynamic analyses. Kellogg, one of the largest U.S. engineering and construction contractors (with particular experience in fluidized bed design and construction) has the ability to provide complete commercial scale facilities.

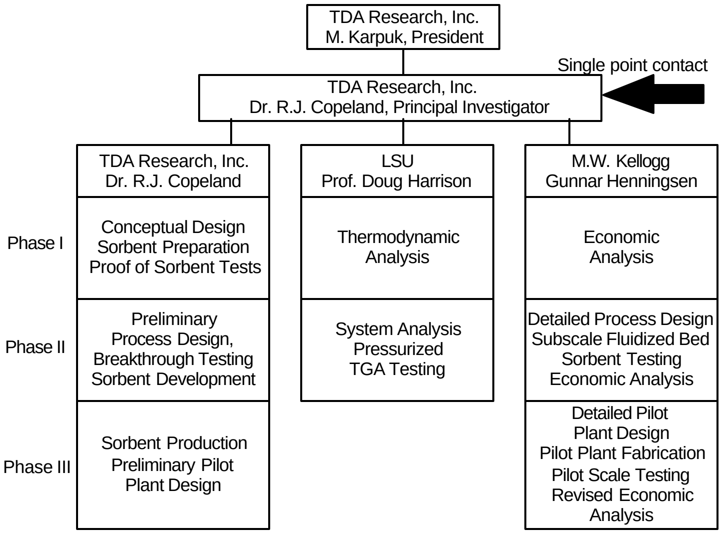

Figure 3. Project organization.

## SUMMARY

During this period, TDA screened the list of potential redox metal oxides and revised the SETS oxidation/reduction system. We selected four redox metal oxides--copper, iron, manganese, and nickel--all of which are exothermic on oxidation. However, only copper and manganese are exothermic oxidizers of methane.

## PROGRESS

Dr. Doug Harrison of LSU, TDA's consultant, screened 77 potential redox metal oxides and identified 13 which could potentially meet the thermodynamic requirements. His results are reported in Appendix A.

Based upon Dr. Harrison's results, TDA conducted a first order cost of sorbent assessment. Table 1 presents this data which 1) identifies the oxidized and reduced states of the SETS sorbent, 2) calculates the theoretical loading of each redox metal oxide, 3) reports the cost of the raw material, and 4) calculates the theoretical cost for transferring oxygen. (Since two moles of $O_2$ are required to fully oxidize one mole of $CH_4$, the theoretical cost is equivalent to the relative cost of transferring energy). Five sorbents were identified with a cost of less than \$20/lb of $O_2$ capacity. Those marked with a √ were selected for further study. Although the price of vanadium is comparable to nickel, vanadium requires an additional hazardous disposal cost. In addition, nickel is catalytic to the reforming of methane.

Table 1. Raw material costs for redox metal oxides.
Costs from Chemical Market Report of March 10, 1997, excepted as noted

| Oxidized State | Reduced State | Loadings wt | Cost \$/lb | \$/lb $O_2$ | |
|---|---|---|---|---|---|
| CeO2 | Ce2O3 | 4.65% | 1.21 | \$ 26.03 | assigned same as CuO |
| Cr2O3 | CrO | 10.52% | 16.5 | \$156.77 | |
| Co2O3 | CoO | 9.65% | 28.22 | \$292.54 | |
| CuO | Cu | 20.12% | 1.21 | \$ 6.02 | √ |
| IrO2 | Ir2O3 | 3.57% | 30 | \$840.75 | \$30/lb assumed |
| Fe2O3 | FeO | 10.02% | 0.295 | \$ 2.94 | √ |
| Mn2O3 | MnO | 10.13% | 1.04 | \$ 10.26 | √ |
| MoO3 | MoO2 | 5.56% | 16.5 | \$296.88 | |
| NiO | Ni | 21.42% | 3.93 | \$ 18.35 | √ Reforming catalyst |
| RhO2 | Rh2O3 | 6.81% | 30 | \$440.51 | \$30/lb assumed |
| Ru2O3 | RuO | 6.40% | 30 | \$469.01 | \$30/lb assumed |
| WO3 | WO2 | 6.90% | 5 | \$ 72.46 | |
| VO3 | VO | 38.58% | 6 | \$ 15.55 | |

Two of the selected sorbents are exothermic with the reducing reactors (CuO and $Mn_2O_3$) and two are endothermic (NiO and $Fe_2O_3$). By selecting the proper quantities of each, we can produce a reactor which is thermally neutral or slightly endothermic or exothermic.

As shown in Table 2, the source can influence the net cost per pound of $O_2$. However, the primary difference is expected to be in the loading. Based on the available data, the preferred combinations are expected to be copper or manganese with iron. Because it is costly, the use of nickel should be limited to a catalytic role unless iron oxides are not suitable. Both CuO and $Mn_2O_3$ are relatively low cost; they are exothermic and they fully oxidize fuel gases (< 100 ppm $H_2$ + CO). CuO can release some $O_2$ into the $CO_2$ at very high temperatures (i.e., $>900^{o}$C).

Table 2. Cost of selected redox metal oxides with consideration of sources.

| | | |
|---|---|---|
| • NiO | | \$3.93/lb |
| • CuO | | \$1.21/lb |
| • $MnO_2$ | | |
| ● >90% $MnO_2$ | | \$1.04/lb |
| ● Natural African > 74% $MnO_2$ | | \$0.10/lb |
| • Iron oxides | | |
| ● FeO | Black, Synthetic | \$0.82/lb |
| ● $Fe_2O_3$ | Red, Natural | \$0.295/lb |

Source: Chemical Marketing Report March 10, 1997

Unfortunately, iron like nickel, will not fully oxidize all of the fuel; at 900$^oC$ 4.45% of the exit gas will be ($H_2$ + CO), even with an excess of $Fe_2O_3$. While copper or manganese will fully oxide the fuel gases, in a single stage fluidized bed, CuO or $Mn_2O_3$ would be reduced before the iron oxides (or NiO), leaving the iron or nickel equilibrium level of $H_2$ and CO in the dry $CO_2$ going to disposal. That effect both increases the cost of disposal and increases the relative fuel costs to replace the caloric value of the hydrogen and carbon monoxide.

To solve the problem of residual reducing gases in the effluent, TDA selected a two stage reducing reactor as illustrated in Figure 4. In this version of the SETS, air is compressed to ~ 10 ATM, which heats the air to ~ 400$^oC$. The reduced sorbents (e.g., copper and iron, since they are the lowest cost exothermic/endothermic combination) and air are mixed in a transport reactor where the sorbent is oxidized. The oxidization heats the sorbent and air to ~ 900$^oC$ and the two are separated (i.e., in the cyclone).

In Reactor 2, the sorbents (at 900$^oC$) enter the top of a fluidized bed reactor and partially oxidized gases leaving Reactor 1 at ~500$^oC$ and 67% to 90% oxidized (i.e., most of the oxidation occurs in Reactor 1). Since Reactor 2 has a great excess of oxidation potential and CuO has the greatest reduction potential, only some of the copper oxide is reduced to copper while fully oxidizing all of the fuel gases to $CO_2$ and $H_2O$; the $Fe_2O_3$, due to the small quantity of $H_2$, CO, and $CH_4$ entering Reactor 2. Due to the high flow rate of cooler gases (i.e., 500$^oC$) and limited reaction occurring in Reactor 2 (are active cooling by generating steam or reforming of the $CH_4$), the solids are maintain at temperatures less than 900$^oC$ to inhibit loss of oxygen for the sorbents and the solids leave Reactor 2 at 600$^o$ to 700$^oC$.

The solids leaving Reactor 2, as slightly depleted in oxygen (as oxides) and drop into Reactor 1, which is also a flulidized bed. Recycled gases from the effluent of Reactor 2 are mixed with natural gas (primarily $CH_4$) and flow into the fluidized bed (Reactor 1). This Reactor (#1) has an excess of reducing gas so that both sorbents are fully reduced to maximize the oxygen transfer form the oxidizing (Transport regeneration reactor) to the reducing side of the SETS. Due to the endothermic reforming the solids leave Reactor 1 at ~ 500$^oC$.

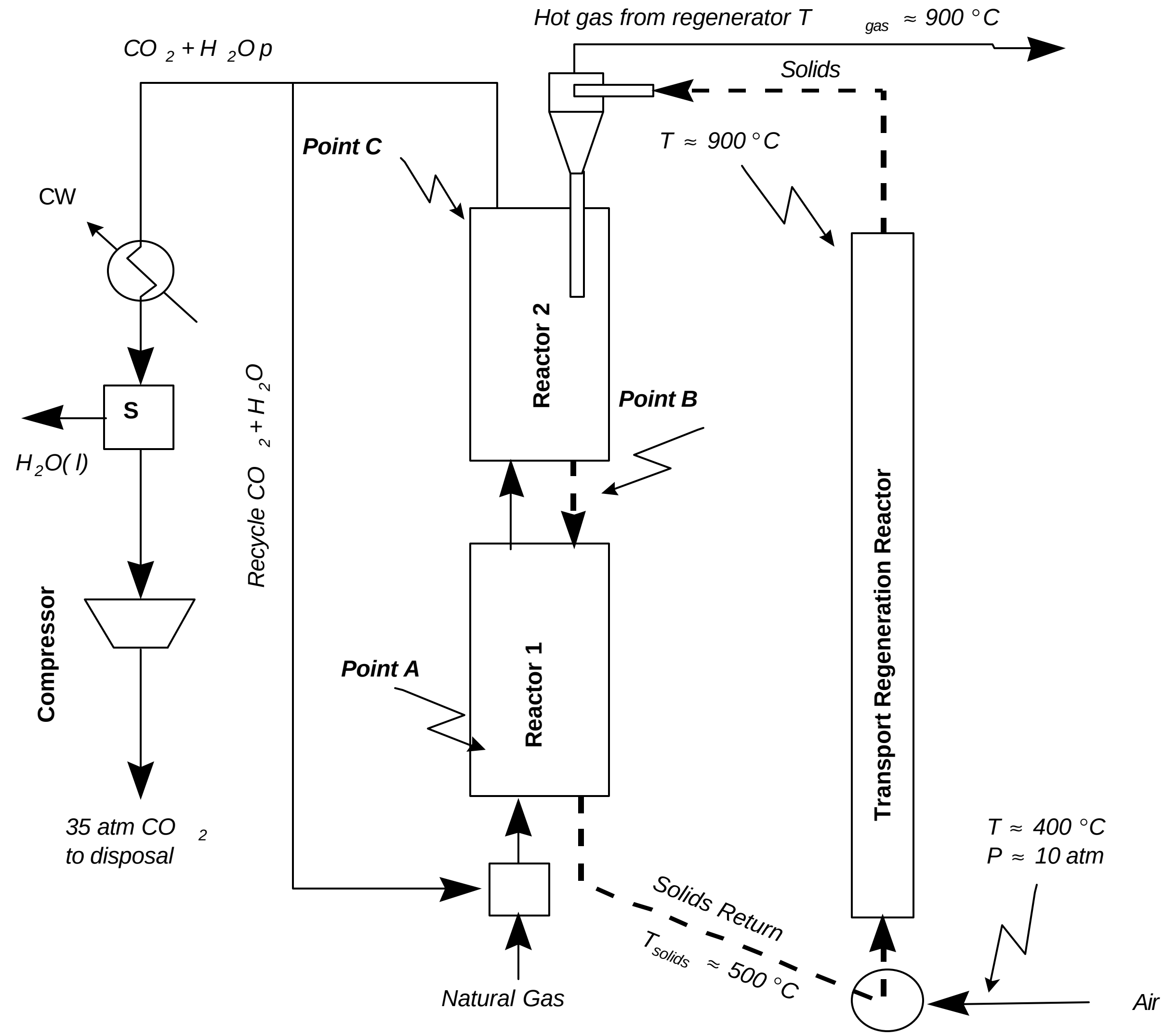

Figure 4. SETS system.

Figure 5 identifies the temperatures and pressures expected in the nominal SETS, and the nominal reactions occurring in each reactor. When the recycling $900^{o}C$ $H_2O$ and $CO_2$ mix and react with the natural gas, some reforming of the $CH_4$ to CO and $H_2$ occurs. The mixed gas temperature is around $400^{o}C$. The partially reformed gas enters Reactor 1 which has 600 to $700^{o}C$ solids entering from the top. Due to the endothermic and exothermic reactions, the reactor will operate at ~ $500^{o}C$.

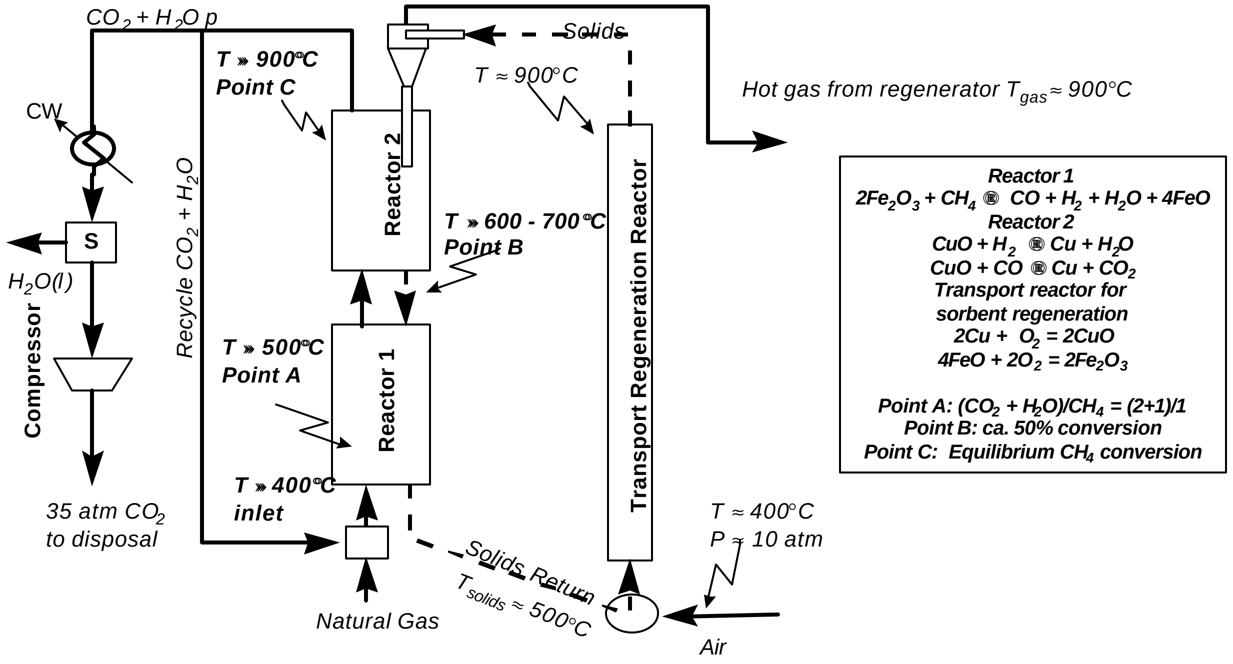

Figure 5. SETS nominal operating points.

The hot Reactor 2 effluent is ~ 99% $CO_2$ + $H_2O$, with the greatest impurities being the $N_2$ which was in the natural gas and trace amounts of $H_2$/CO or $O_2$. Part of that effluent recycles to the inlet of Reactor 1 to begin the reforming process and provide a high $H_2O$ + $CO_2$ to $CH_4$ ratio. The high $H_2O$ + $CO_2$ to $CH_4$ ratio minimizes the formation of coke which is oxidized to $CO_2$ in the regeneration reactor and released to the atmosphere.

The balance of the Reactor 2 effluent is cooled, generating steam which is used in the combined cycle. Since the steam is condensed at high pressure and comprises 67% of the gases (i.e., $CH_4$ + 4 "O" *(from oxides)* = $CO_2$ + 2 $H_2O$), the condensing of the steam with $CO_2$ can be used to generate pure steam at low pressure. The pure steam can then be used at ~ 8% efficiency in the steam cycle. Given that the difference between the higher and lower heating value is 9.25% of the latter, additional heat can be delivered to the power generating system. TDA estimates a 1 to 4% overall efficiency loss for the system or a nominal 3%.

Based on cost data supplied by The M.W. Kellogg Co., TDA estimated the overall cost for $CO_2$ separation. The energy efficiency penalty in this cycle is small, on the order of 1.5 - 4.0% (3% is assumed as a nominal value). Assuming a cost of \$3/MMBtu for natural gas, the efficiency is a moderate cost of 0.614 mill/$kWh_e$. Assuming a cost of \$50/$kW_t$ = \$100/$kW_e$ for the SETS equipment and another 2.28 mills/$kWh_e$ to run it, the cost of the equipment is much higher. The total cost for the capital and efficiency penalty is ~ \$11/ton of $CO_2$ separated.

Due to the uncertainty of the base cost for the SETS sorbent, its life, and its loading capacity, the replacement sorbent cost is estimated at between \$5 and \$20/ton of $CO_2$ separated (equivalent to 1.32 to 5.26 mills/$kWh_e$). The total cost for $CO_2$ separation is \$16 to \$31/ton (4.21 to 8.16 mills/$kWh_e$).

Table 3. Cost for CO$_2$ separation.

- Capital costs, similar to FCC units, ~ \$50/kW$_t$ or \$100/kW$_e$ @ 50% combined cycle
- For natural gas, CO$_2$ separation costs
  - \$3/MMBtu 3% efficiency penalty = 0.614 mill/kWh$_e$
  - 75% CF, 15% Fixed charge rate =2.28 mills/kWh$_e$
- **Sorbent Cost = TBD ~ \$(5 to 20)/ton CO$_2$**
- **Overall ~ \$16 to \$31/ton of CO$_2$**

## Future Activities

In the next reporting period we will start fabricating geodes in copper, iron, nickel, and manganese oxides using an alumina support mixed with natural clays. Since nickel may be needed as a catalyst, we will also investigate catalyst carriers.

## Actual Costs

Total expenses chargeable to DOE at the end of September 1998 were $14,121.

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