DOE/ARC-2003-005

Capture of CO_2 from Recirculating Flue Gas Boilers

Thomas L. Ochs
USDOE/Albany Research Center (ARC)
ochs@alrc.doe.gov

The possible need for an economical method for the separation of CO_2 from flue gas adds a new set of challenges to power plant design, construction, operation, and maintenance. Many of the new requirements of CO_2 separation are similar in nature to those addressed by the mature chemical engineering processes used in petroleum refining and industrial chemical production. Chemical engineering processes are regularly used to separate heterogeneous vapors in processes such as the fractionation of hydrocarbons or the separation of the components of air. This paper addresses the application of chemical engineering processes to the mixtures of gases and vapors found in the flue gas of recirculating boilers. Adaptation of these techniques can lead to a reduction in the energy required to capture CO_2.

INTRODUCTION:

There are a number of proposed methods for separating CO_2 from flue gas and sequestering that flue gas. At this time (2003) there is no general consensus on which method or methods will prove to be most cost effective if the need for CO_2 sequestration arises. There is, however, no question that CO_2 can be removed from power plant flue gas and sequestered using a number of approaches. The only real questions are the cost of separation of the combustion product components and the cost of the methods for sequestration of those components identified as pollutants. Any capture and sequestration technology will require capital investment, increase operating costs, and reduce plant efficiency. Engineering research is presently underway in many organizations to determine how to best capture and sequester CO_2 with a minimum impact on the cost of electricity. Among the methods being investigated for separation are:

- Chemical reaction of the CO_2,
- Absorption of the CO_2,
- Membrane separation, and
- Separation by condensation.

In all four of these approaches the flue gas stream can be either a dilute CO_2 stream, as presently found in conventional power plants, or a concentrated stream. It is the process of separation by condensation from a concentrated stream that the research reported here addresses. The method of concentration used in this paper is the recirculation of flue gas and the injection of oxygen into that flue gas stream to support combustion (“recirculating combustion” or “recycling combustion”).

Our research uses computer modeling to characterize the composition of the combustion products in a recirculating combustion system, and a combination of computer modeling and experimentation to identify the processes best suited for separating the components of those combustion products. A simplified view of a computer model of a power plant with flue gas recirculation, oxygen injection, and condensation separation with compression is shown in Figure 1. The operations labeled "compression" and "compressed gas separation" are the areas for the research reported in this paper. What looks relatively simple in this figure has proven to be richly complex with opportunities for both energy conservation and increased energy consumption.

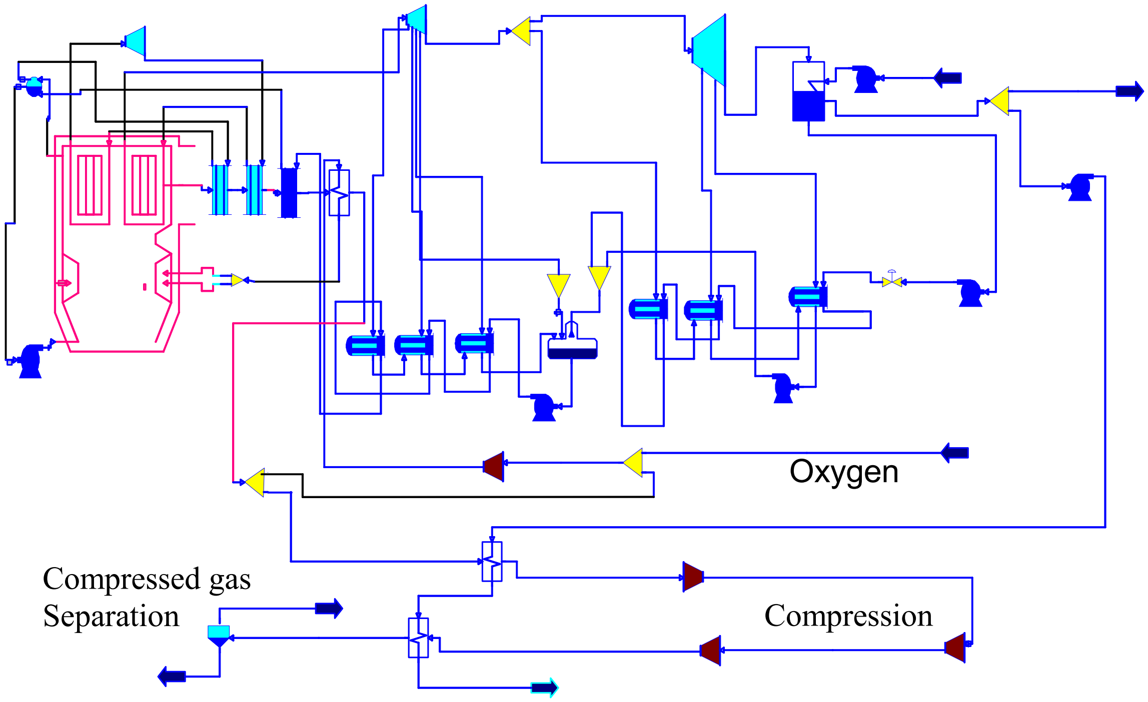

Figure 1: Subcritical power plant with flue gas recirculation and condensation[1].

In our research, we have assumed an integrated approach can be used to address the introduction of specific targets for emissions of selected pollutants, including reduced levels of SO_2 and NO_x as well as targets for CO_2, Pm2.5, and Hg. These five pollutants are anticipated to have the greatest impact on the methods for fossil fueled power generation over the next 20 years.

This project evolved from the conjunction of two precursor projects: CO_2 Sequestration by Mineral Carbonation, an effort undertaken by the Albany Research Center(ARC)[1] and partner organizations, and a Participating Agency Service Agreement (PASA) between USDOE and USAID (United States Agency for International Development)[2]. The PASA was designed to help the Government of Indonesia improve the performance of its power plants. In the method being explored by ARC for CO_2 sequestration (mineral carbonation) it is necessary to concentrate, compress, and heat the CO_2. ARC is combining the performance improving techniques applied in the PASA to improve the effectiveness of methods for separation of CO_2 and the simultaneous capture of multiple pollutants.

Initial studies at ARC identified the enabling technologies necessary to implement integrated pollution removal using the condensation of compressed vapors (Figure 2). Research is presently being pursued by other organizations in many of the areas related to these enabling technologies, including oxygen supply, flue gas recirculation, water treatment, and to a lesser extent, wet compression and expansion heat recovery. We are concentrating our efforts in the area of wet heat exchange.

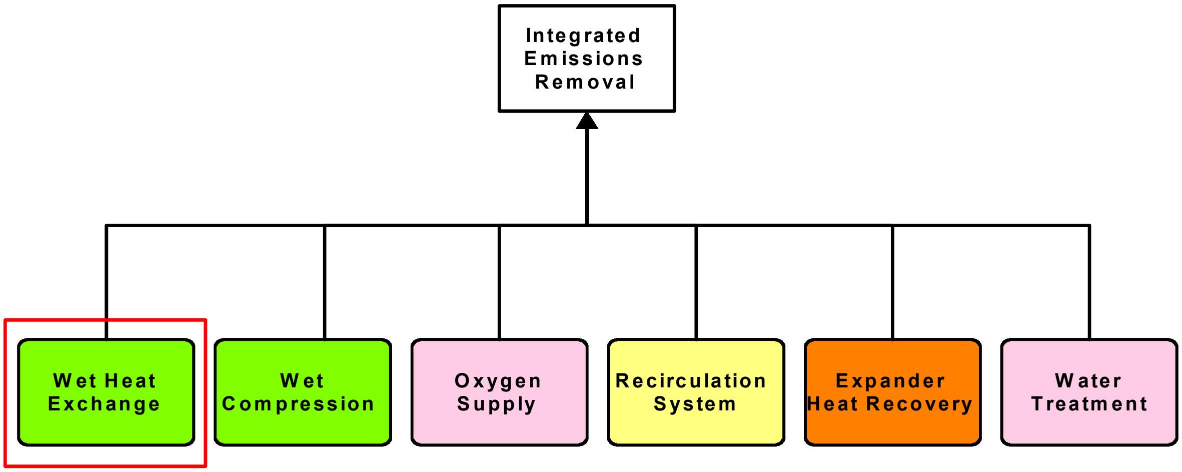

Figure 2: Enabling technologies

Background:

The Albany Research Center has been modeling characteristics of power generation systems using GE GateCycle® software[a,3]. The system examined in this paper is a 400 MW, mildly supercritical, double reheat, 3,500 psi (24.13 MPa), 1050°F (566°C), 1050°F, 1050°F power-generation unit. The power plants were modeled using "wet flue gas recirculation." In wet recirculation, moisture is retained in the recirculated portion of the flue gas and the temperatures throughout the recirculation system are kept above the dew point. In the models, condenser pressure was maintained at 1 psia (6.89 kPa) and ambient temperature was kept constant at 59°F (15°C).

The composition of the flue gas in both a power generating system using flue gas recirculation and a standard "once-through" combustion system are shown in Table 1. The table represents modeled input in the form of chemical thermal power (3.57×10^9 BTU/hr (1,046 MW)) and fuel type (Illinois #6 seam, Old Ben Mine #26). The choice of fuel (coal) was made to maintain consistency with other modeling efforts[4], to reflect the use of our most abundant fossil fuel source, and to demonstrate application of the technology on a carbon rich fuel source. The input chemical power (in the form of fuel flow) is kept constant in these models as the technology of the power plant is varied. Maintaining constant fuel flow keeps the oxygen flow constant, when oxygen injection is used, and therefore the power required to produce oxygen is constant for each case

---

[a] The USDOE neither endorses nor recommends specific products. References to product names are for information purposes only and should not be interpreted as endorsement or recommendation.

studied (assuming the use of the same oxygen generation technology). In these models the source of oxygen is assumed to be a cryogenic air separation unit (ASU) producing approximately 330 ton/hr (299 tonne/hr) of 98% pure O_2 consuming approximately 0.25 MWh/ton for a constant additional auxiliary load of 82.5 MW. The fuel feed rate (and therefore the oxygen flow rate) was determined for a conventional pulverized coal power plant with single reheat and a net rating of approximately 400 MW at a flue gas O_2 concentration of 3.5% on a wet basis. The O_2 content of the recycling flue gas was kept at approximately 21% by volume after O_2 injection.

DISCUSSION:

Chemistry of the Recirculation Stream:

In the recirculation system examined, the greatest mass of combustion products is recirculated for oxygen injection and reuse as the oxygen source to support combustion. This results in significantly different chemistry in the flue gas (Table 1). Recirculation (in contrast to combusting the fuel directly in pure oxygen) dilutes the oxygen to reduce the reaction rate and combustion product temperature to levels that can be contained by conventional materials. If oxygen is allowed to increase significantly above atmospheric levels, the combustion system and the heat exchange surfaces have to be redesigned. During the recirculation of the flue gas, the moisture is retained in the combustion products (no condensation of the recirculated water vapor) which makes this a wet recirculation system.

Table 1: Comparison of combustion products leaving the boiler with and without flue-gas recirculation[3].

	Flue gas without recirculation	Flue gas with recirculation
Flow (lb/hr)	3,539,738	4,154,215
CO_2 (vol)	0.1368	0.6085
O_2 (vol)	0.0350	0.0350
N_2 (vol)	0.7345	0.0206
H_2O (vol)	0.0829	0.3269
SO_2 (vol)	0.0020	0.0090
Ar (vol)	0.0088	0.0000

Six things, shown by Table 1, make the handling of this recirculated gas stream different from the handling of the once-through flue gas stream.

1. There is a higher mass flow in the recirculating flue gas system due to the higher effective molecular weight of the recirculated gas. Fans moving the gas stream will perform more work in a recirculation system than in a comparable once-though system.

2. There is nearly 33% water vapor in the recirculating flue gas (4 times the water vapor in non-recirculated flue gas).
    a. All portions of the system must remain above the dew point to avoid condensation of acid species
    b. Dropping the temperature of the bleed stream at ambient pressure will condense a good portion of the water vapor, removing a significant fraction of the mass of the flue gas, and dissolving and entraining SO_2, CO_2, and particulates. This condensation is shown as the "H_2O Condensation" block of Figure 3 and as the first condensation of Figure 4, and removes 73 tons of water from the modeled bleed stream.
3. The concentration of CO_2 increases from approximately 14% in a once-through flue gas stream to approximately 61% of the gas stream in a recirculating flue gas system. In the system examined, this CO_2 is also considered condensable at high partial pressure and ambient temperature.
4. Combining the CO_2 and the H_2O in the recirculating system, nearly 94% of the flue gas is condensable. Thus, the non-recirculated portion of the flue gas stream is small (25.85 ton/hr), as shown in Figure 4.
5. The concentration of N_2 in the recirculation system has been reduced from approximately 73% in the once-through system to approximately 3% in the recirculating system. NOx will consequently be dramatically reduced (although the actual concentration of NOx is related to temperatures and chemistry of the fuel/air combustion process). In fact, NOx reduction was the driving force for the development of recirculating flue gas systems.
6. The concentration of SO_2 in the recirculating model is approximately 4 times the concentration of SO_2 in the once-through model.

A bleed stream of combustion products (approximately 22.5% of the total in this model) is extracted from the system and treated to remove pollutants. It is the treatment of this bleed stream that we are investigating. Figure 3 and Figure 4 summarize some elements of the treatment.

Condensation Stages:

In the process of treatment of the wet flue gas bleed stream, there are three separate sets of conditions, as seen in Figure 3. The first stage is condensation of water vapor at ambient pressure. The second and third stages involve condensation of CO_2 at moderate (< 1,000 psi) and high pressures (> 1,000 psi). During the moderate pressure stage, the remaining water vapor and part of the CO_2 are condensed. At the higher pressures, the condensate is predominantly CO_2.

Thermodynamics is useful in determining equilibrium compositions of the fluids involved in wet heat exchange, however, the conditions found in actual wet heat exchangers can be far from equilibrium, depending on the rates of flow. The present experimental investigations at ARC involve the first stage of condensation (ambient pressure) as noted in the red box in Figure 3 while ongoing modeling efforts are examining all three stages.

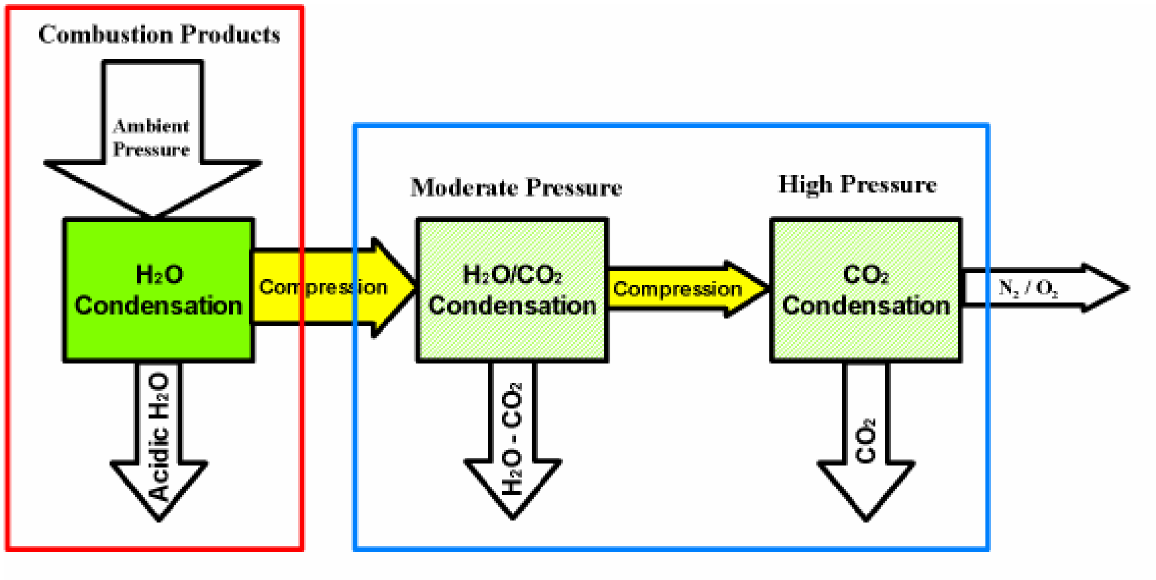

Figure 3: Stages of condensation

Reduction of Mass Along the Bleed Stream Path:

The bleed stream can be viewed as diminishing in both volume and mass, as condensation occurs and the remaining gases are pressurized (which reduces the remaining volume). The change in mass is shown in Figure 4 for a specific four-stage compression system. The reduced volume and mass result in reduced capital costs, reduced operating costs, and a reduced footprint for the equipment involved. However, increased pressure serves to increase the capital cost of the downstream equipment.

While the system depicted in Figure 4 is uncommon in the power sector, it is a common process stream from the chemical process industry. Similar process diagrams can be found in the petrochemical industry, for liquid fuels production, and in many inorganic chemical processes. The determination of partitioning of components in the various streams is a common problem for distillation engineers. There is a large reservoir of information that can be used to approximate the behavior of large-scale systems using similar processes.

The mass, composition, and pressure of each flow stream in Figure 4 are shown in Table 2. The flue gas bleed stream starts at either ambient pressure or slightly above ambient pressure. Initial condensation takes place at approximately ambient temperature (below the critical temperature of CO_2) for each of these streams except for the fifth and final one. The fifth stream condenses below the freezing point of water due to controlled turbo-expansion of high pressure gas. Gas pressure is reduced from approximately 5,000 psi to approximately 2,000 psi to regain compression energy and further cool the stream, condensing more of the CO_2.

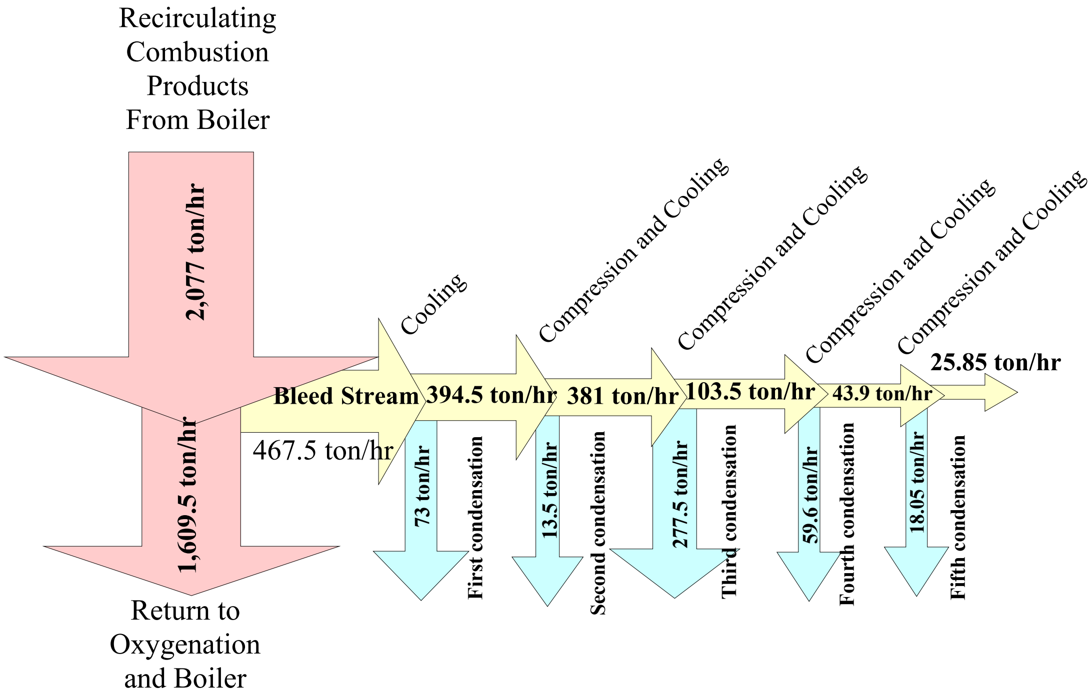

Figure 4: Diminishing mass flows of flue gas bleed stream due to condensation

Table 2: Mass flow, composition, and pressure of the bleed stream after each condensation.

	Flue gas bleed	After first condensation	After second condensation	After third condensation	After fourth condensation	After fifth condensation
Mass (ton/hr)	467.5	394.5	381	103.5	43.9	25.85
CO_2 (vol.)	0.6085	0.8711	0.9143	0.71	0.39	0.085
O_2 (vol.)	0.035	0.0501	0.0526	0.1821	0.383	0.5765
N_2 (vol.)	0.0206	0.0294	0.0309	0.1069	0.2249	0.3384
H_2O (vol.)	0.3269	0.0365	0.0022	0.001	0.0021	0.0001
SO_2 (vol.)	0.009	0.0129	0.0000	0.0000	0.0000	0.0000
Pressure (psia)	15	15	180	1,200	2,500	5,000 to 2,000

Control of Multicomponent Condensation:

The simplified situations shown in Figure 4 and Table 2 belie the underlying complexity of multi-component, multi-phase separation. Generally, experimental data are not available for each mixture of combustion components so we rely on thermodynamics and chemistry to approximate the compositions and flows in our initial estimates and to limit the boundary conditions for follow-on experimental work. Control of this complex system of components and phases will fall to the operators and engineers at power plants where such a method is implemented. As we know from experience with existing power plants, the most difficult control problems occur during start-up, shut-down, and rapid transitions or upsets. What happens to our complex system of condensing vapors as we go through these transitions? Suddenly the steady state system is a moving target and the operators will need tools to assist them in making the transitions without causing severe problems in the system.

Similar problems in controlling complex condensing systems can be found in the petroleum and chemical industries[5,6,7]. Generally, the condensations we will be interested in are non-reactive, which simplifies the problems faced in calculating conditions found in the condensing systems. The partial pressure and temperature influence on condensation are similar in nature to the existing steam systems in power plants (where the condensation is of a pure substance). However, the existence of multiple components and interactions between those components can make control of these condensing systems difficult.

Complexity varies in a condensing system as follows (from least complex to most complex):

1. Pure substance
2. Multiple immiscible components
3. Multiple miscible components
4. Multiple miscible components with reactions

Systems of combustion products from flue gases are on the third level of complexity, multiple miscible components (with entrained particulates in the early parts of the system). Transient events in the system, including startup and shut-down, also increase the complexity of the system.

CONCLUSION:

Initial modeling indicates that condensation of components in a recirculating combustion system is feasible for conventional power plants. The control strategies for these proposed systems are similar in nature to those found in the petroleum and chemical processes industries. Multi-component condensation systems will require new areas of training and experience in processes that are unfamiliar to both operators and engineers at power plants. Techniques used in the chemical and petroleum industries to efficiently control production can be directly applied to control of condensing bleed streams in recirculating boilers.

REFERENCES:

1 O'Connor, et. al., CO_2 Storage in Solid Form: A Study of Direct Mineral Carbonation, Proceedings of the 5th International Conference on Greenhouse Gas Technologies, Cairns Australia, August, 2001.

2 Ochs, Thomas and Young, Sheila, "Improved Plant Performance: Integrating Computer Modeling, Inspections, and Measurements," PowerGen International, Nov 11-13, 2001, Las Vegas, NV.

3 Ochs, Thomas, Energy Recovery as a Key Component in Low Emission Power Plants, Proceedings of the 27th International Conference on Coal Utilization and Fuel Systems, March 4-7, 2002, Clearwater, Florida.
4 Owens, W., Buchanan, T., DeLallo, M., Schoff, R., White, J., Wolk, R., Evaluation of Innovative Power Plants With CO_2 Removal, Sponsored by USDOE/EPRI Report 1000316, Prepared by Parsons Energy and Chemicals Group Inc. and Wolk Integrated Technical Services, http://www.netl.doe.gov/coalpower/gasification/30_publications.htm.
5 Himmelblau, David M., Basic Principles and Calculations in Chemical Engineering, 6th Ed., Prentice Hall PTR, Upper Saddle River, NJ, 1996.
6 Kister, Henry Z., Distillation Design, McGraw Hill, 1992.
7 Leffler, William L., Petroleum Refining in Nontechnical Language, PenWell Corporation, Tulsa Oklahoma, 2000.