

A Research Program for Promising Retrofit Technologies

Prepared for the
MIT Symposium on Retro-fitting of
Coal-Fired Power Plants for Carbon Capture

Howard Herzog

March 23, 2009

1. Background and Motivation

The commercialization of Carbon Capture and Storage (CCS) technologies is a significant challenge. It is a difficult enough task on new coal-fired plants, but even a greater challenge for retro-fitting existing plants. This is for several reasons, including:

- Availability of adequate space
- Restrictions caused by the existing plant layout
- Lower efficiency of older plants
- Difficulty in optimizing design, especially concerning the extraction of turbine steam

Today, the only proven CCS capture technology is amine scrubbing. In some ways it works very well – it is highly selective for CO₂ and has recovery rates above 90%. However, it is also very energy intensive. For a new plant, it will reduce the plant output by 25-30%. While this may be acceptable on a new high efficiency power plant, it makes retro-fitting older, less efficient plants very difficult. For example, an existing plant with 35% efficiency when retrofitted with CCS will have its efficiency reduced to 20-25%. This is a very expensive proposition.

If we are going to meet stated emission reduction goals of 50-80% by 2050, the emissions from existing coal plants must be addressed. While the first step may be efficiency improvements¹, this is not sufficient. In the long run, the existing coal plants will either have to be shut down or retrofitted with CCS if we are to meet the emissions targets stated above.

In summary, we cannot ignore emissions from the existing (and growing) coal fleet. If we want to continue to operate these plants, we must retrofit them with CCS. However, current technologies may extract too high a price. Therefore, it is an important research goal to develop new CCS technologies appropriate for retrofits. As discussed below, this is a very challenging goal.

There are two primary approaches to capturing CO₂ from existing plants. The first is post-combustion capture, which includes amine scrubbing. The second option is oxy combustion capture. They are each reviewed in the following two sections. The final section of this paper will address RD&D recommendations.

2. Post-Combustion Capture Technologies

Post-combustion capture technologies are reviewed in a White Paper prepared for the Clean Air Task Force under a grant from the Doris Duke Foundation (Herzog *et al.*, 2009). A brief summary follows.

¹ When doing CCS, efficiency improvements are an important first step. Reducing the amount of CO₂ per kWh reduces the cost of CCS.

At a coal-fired power plant, CO₂ is a component of the flue gas. The total pressure of the flue gas is 1 atm and the CO₂ concentration is typically 10-15%. The process of transforming this low pressure, low concentration CO₂ into a relatively pure CO₂ stream is referred to as post-combustion CO₂ capture. This capture step is typically followed by a compression step, where, for ease of transport (usually by pipeline) and storage, the CO₂ is compressed to 100 atm or more.

The only commercially available technology for post-combustion technologies is the amine chemical absorption process. All commercial amine processes can work with gas-fired power plants, but today only a subset can work on coal-fired power plants. A coal plant flue gas is more difficult to handle because of the pollutants it contains, primarily particulate matter and SO₂. Amine plants have been built to the scale of 1,000 tons of CO₂ per day. An additional order of magnitude scale-up would be required for typical coal-fired power plants, but this should pose no major technical hurdles.

The first amine processes were based on monoethanolamine (MEA) with inhibitors added to prevent degradation and corrosion. Some of the newer processes are based on mixed amines or hindered amines in an attempt to reduce the parasitic energy requirement of the capture process. One challenge is that solvents with lower the energy requirements generally exhibit slower absorption rates. Current research includes investigating the use of the additives like piperazine so one can use an amine mixture that lowers the energy requirement without significantly slowing down the CO₂ absorption rate.

Alternate chemical absorption processes are being investigated. The most prominent efforts are using an ammonia solvent. Compared to amines, ammonia may be able to significantly lower the parasitic energy requirement. However, it presents the challenge of lower absorption kinetics and the need to control the “ammonia slip” (ammonia vapor escaping the process either in the clean flue gas or the captured CO₂).

Membrane and pressure swing adsorption processes have also been suggested. However, in general, they cannot compete with amine scrubbing. The reason is that they rely on a partial pressure driving force. Since CO₂ in the flue gas of a coal-fired power plant has a partial pressure of 0.1-0.15 atm (10-15% concentration, total pressure of 1 atm), membrane and pressure swing adsorption processes are generally impractical. However, membrane technology has successfully been used in combination with chemical absorption processes, but these processes rely on absorption and not membranes to do the separation.

Biomimetic approaches take their cues from living systems that have evolved highly efficient systems for capturing and/or converting CO₂. These include the use of the enzyme carbonic anhydrase, an efficient catalyst of CO₂ reaction with water, as well as microalgae systems because *they consume* CO₂ in photosynthesis. Another approach that has been proposed is to cool the flue gas to low temperatures so that the CO₂ is separated as dry ice.

A relatively new area of investigation involves structured materials, possibly stimuli-responsive, that can have entropic (e.g., shape selective) rather than enthalpic interactions between the sorbate and the separations media. This could lead to a significant reduction of the parasitic energy requirement. These materials could work through the application of stimuli, e.g., an electric field, to modify the separation environment in order to release the captured solute (as opposed to temperature swing). These materials include specialized adsorbents with finely controlled structure (e.g., metal-organic frameworks and ZIFs), the functionalization of adsorbent surfaces (e.g., fibrous matrices, etc.), and liquid phase absorbents such as ionic liquids.

3. Oxy-Combustion Technologies

Because nitrogen is the major component of flue gas in power plants that burn coal in air (as all existing plants do), post-combustion capture is essentially a nitrogen-carbon dioxide separation. If there were no nitrogen, CO₂ capture from flue gas would be greatly simplified. This is the thinking behind oxy-combustion capture: instead of air, the power plant uses an oxygen stream ($\geq 95\%$ purity) for combustion of the coal. The oxygen is produced on-site in an air separation plant, which represents the largest cost component in the capture process.

For retrofit applications, there are three primary concerns:

- The production of oxygen
- The modification of the boiler to use oxygen instead of air. This is necessary to keep temperatures from going too high and to meet the radiative and convective heat transfer characteristics of the boiler. This is accomplished by recycling part of the flue gas to the boiler.
- The clean-up of the flue gas of criteria pollutants (SO₂, NO_x, particulates, mercury) and non-condensibles (O₂, N₂, Ar).

As with post-combustion capture, the resulting CO₂ stream is compressed. It is during compression that the water is removed. The oxy-combustion process is capable of recovery rates of 97% or greater.

It is useful to understand the sources of parasitic energy loss for both the post-combustion and the oxy-combustion processes (MIT, 2007). The percentages below assume a power plant operating at 38.5% HHV² efficiency before capture. These numbers are meant to be illustrative, as they may vary from plant to plant.

For post-combustion capture (based on monoethanolamine scrubbing):

- Losses associated with low pressure steam extraction from the turbine (in order to regenerate the amine solution) - 13%
- Power for pumps and fans for capture process - 2%

² High Heating Value

- Power for the CO₂ compressors - 9%

This yields a total of 24%

For oxy-combustion capture:

- Power for air separation plant - 17%
- Power for pumps, fans, etc.- 3%
- Power for the CO₂ compressors - 9%
- Efficiency *increase* in boiler – (8%)

This yields a total of 21%, but relies on taking credit for an efficiency increase in the boiler. This has been shown only on paper studies, not in practice. It may also be harder to realize on existing boilers as opposed to new boilers. The above analysis also shows the importance of oxygen production on the economics of oxy-combustion capture.

How does oxy-combustion compare to today's amine scrubbing process? McCauley *et al.* (2008) quote studies that claim oxy-combustion capture shows a 10-16% improvement in levelized costs over MEA. However, there is not enough experience to choose one approach over the other at this point. The largest oxy-combustion boilers are 30 MW_{th}, one at Babcock & Wilcox's Clean Environment Development Facility and one at Vattenfall's Schwarze Pumpe plant. The later pilot plant also includes an oxygen plant and flue gas purification.

Some technologies broadly considered under the oxy-combustion category, such as chemical looping, are not appropriate for retrofits and, therefore, will not be reviewed in this paper. The three critical areas for RD&D reviewed below are oxygen production, boiler modifications, and flue gas purification.

3.1. Oxygen Production

3.1.1 Cryogenic Oxygen Production

The standard technology for large-scale oxygen production is cryogenic fractionation of air. The temperature involves liquefying air and separation via distillation. Energy for refrigeration is provided by compressing the air (and cooling upon expansion). The largest cryogenic air separation units (ASU) today are about 4000 tons per day (tpd). However, it is feasible to go to about 10,000 tpd, which would provide enough oxygen for a 500 MW coal-fired power plant. Above that level, multiple trains would be necessary (Allam, 2008).

Designs of ASUs can vary significantly. Key parameters include what products one is interested in (i.e., oxygen, nitrogen, argon), their purity, their pressure, and the size of the ASU. For the oxy-combustion process, the design specifications include relatively low oxygen purity (95-97%), low pressure (1.3-1.7 bar), low power consumption, and large size (McCauley *et al.*, 2008).

R&D has already started in adapting ASUs to oxy-combustion. Air Liquide (Darde *et al.*, 2008) discuss design studies that show a 20% decrease in energy use over today's ASUs. They also suggest that another 10% savings is possible by integrating the ASU with the power cycle.

3.1.2. Ionic Transport Membranes

While the cryogenic process is today's state-of-the-art, the primary focus of R&D for the next generation of oxygen production is mixed metal oxide ceramic membranes, referred to as both ITM or OTM (Allam, 2008). These work at high temperatures (700 C) and require an oxygen partial pressure driving force. There are at least four major development efforts, Air Products, StatoilHydro, Praxair, and Linde/BOC. The Air Products effort is at a 5 tpd scale, with plans to go to 150 tpd and then 2000 tpd.

To operate ITMs as stand-alone units, one needs high temperature air (a pre-heater will be necessary for oxy-combustion), and recovery of energy from the depleted air (a turbine and heat recovery). This requires much more integration between the oxygen production and the power cycle compared to the current ASUs. One way to improve the process is to sweep the low pressure side of the membrane with flue gas because of its very low partial pressure of oxygen (Pfaff and Kather, 2008).

Some of the R&D challenges include sealing technology, chemical and mechanical stability of the different compositions envisioned, and reduction of high temperature creep (den Exter *et al.*, 2008). Even if these fundamental issues are resolved, it appears that for ITMs to be significantly better than cryogenic ASUs, they must highly integrate the ITMs into the power cycle.

3.2. Boiler Modifications

The most straightforward retrofits for oxy-combustion require no changes to the water and steam systems and minimum modifications to boiler. In the boiler, the temperature needs to be kept in a safe operating range and the heat transfer characteristics that the boiler was designed for must be maintained. This involves recycling a significant portion of the flue gas to perform the function of the nitrogen which was removed in the air separation unit. Research questions include at which point in the process to take the recycle stream from (before or after certain flue gas clean-up steps, does it require cooling, etc.) and how to combine it with the oxygen (Tigges *et al.*, 2008).

Another significant issue with the boiler retrofit is air leakage. Most boilers are designed to run just below atmospheric pressure for safety considerations, which encourages air leakage. Since the whole idea of oxy-combustion is to not feed air to the boiler, air leakage needs to be minimized. Proper sealing of the boiler and associated equipment will help minimize air leakage. Needless to say, this is one area that retrofits pose a much larger challenge than new plants.

The above approach can be termed the “synthetic air” approach. A more sophisticated approach can be termed the “oxy-burner” approach. Instead of mixing the recycled flue gas with the oxygen before entering the boiler, the boiler can be retrofitted with oxy-burners that introduce pure oxygen. This technology is commercially used in certain industries, such as glass, metals, cement, and waste treatment (Cieutat *et al.*, 2008). Some flue gas recycle is still required, but the flue gas is not pre-mixed with the oxygen. This approach will be used to retrofit a 30 MW_{th} boiler for Total’s Lacq CO₂ Project in France.

A more involved approach would be to replace the boiler entirely with a purposely designed oxy-combustion boiler. This would maximize the increase in steam cycle efficiency, decrease boiler size, and could eliminate the need for flue gas recycle. Design of these boilers is a major R&D task. Another approach to boiler design that seems very compatible with oxy-combustion is the use of Circulating Fluidized Bed (CFB) technology (Carbo *et al.*, 2008 and Suraniti *et al.*, 2008). Oxy-combustion can lead to small equipment sizes, control temperatures with circulating solids, and allow use of a wide range of low cost feedstocks.

3.3. Flue Gas Purification

The major impurities that need to be considered for removal from the flue gas are particulate matter (e.g., fly ash), criteria pollutants (e.g., SO₂, NO_x, mercury), non-condensable gases (e.g., Ar, N₂, O₂), and water. For retrofits, the CO₂ concentration in the flue gas exiting the boiler will generally be between 60-70%, with the above impurities making up the difference. The biggest reason for the range is the amount of air enleakage.

There are several strategies being suggested for flue gas purification. All the strategies have a few things in common. First, particulate matter must be removed using the same equipment in use on coal-fired power plants today. Some research may be needed on modifying the equipment for the new flue gas composition. The non-condensable gases and water will be removed during compression (water will be condensed, the non-condensable gases will be flashed).

This leaves the question about what to do with the criteria pollutants. There are at least three approaches:

- Do nothing. Let the SO₂ and NO_x remain with the CO₂ and co-sequester. This is the simplest and least expensive approach. However, it may cause complications for transport and storage (more regulatory and political as opposed to technical). This approach also yields the highest recovery rates for CO₂ (Darde *et al.*, 2008).
- Use the same equipment we do today to remove the NO_x (e.g., SCR - selective catalytic reduction) and SO₂ (FGD - flue gas desulfurization). Research will be needed to modify these approaches for the new flue gas composition.
- Eliminate the use of traditional SO₂ and NO_x control and simply remove them during compression by using a water wash. The SO₂ and NO_x will leave the

system as sulfuric and nitric acids. Air Products has done initial tests of this approach and report that it looks very promising (White *et al.*, 2008).

In general, there is a trade-off between CO₂ purity and CO₂ recovery. This is because as impurities are removed, some CO₂ will leave with them. Another research area is to find ways to maintain high purity with high recovery. This includes using distillation (instead of a simple flash) to remove the non-condensable gases and using membranes to recover CO₂ from the impurity streams.

4. RD&D Recommendations

In Herzog (2009), the RD&D recommendations centered around an RD&D pipeline. In the next section, we reproduce the proposed RD&D program for post-combustion capture. In the following section, we propose an RD&D program for oxy-combustion retrofit capture (additional RD&D funds will be needed for oxy-combustion technologies like chemical looping, which are beyond the scope of this paper).

4.1. Post-Combustion Capture

The cost estimate for an 8-10 year research program in Table 1 below. Note that this is total cost of program, including research funds from both the private and public sector. Also note that it for only post-combustion capture technology – a complete CCS budget would also need to address other capture approaches (i.e., pre-combustion, oxy-combustion), as well as transport and storage.

Table 1. Estimated cost of an 8-10 year US post-combustion research effort.

Component	# of projects	Cost per project (millions of \$)	Total Cost (millions of \$)
Demonstration	5	1000	5000
Pilot Plants	15	50 (25-100)	750
Proof of Concept	30	10	300
Exploratory Research	50	1	50
Simulation/analysis			100
Contingency			1200
TOTAL			7400

The basis for these estimates is as follows:

- **Demonstration project.** This cost per project number is an order of magnitude estimate for a demonstration plant based on estimates from the *The Future of Coal* (MIT, 2007) and experience of FutureGen. Of course, the exact details of what a demonstration looks like can vary widely. We envision power plants in the 200-300 MW range that captures about 60% of the CO₂ (to give the plant parity with emissions from a natural gas power plant).

- **Pilot plants.** Pilot plant activity today includes plants sized to process flue gas associated with 1-5 MW of electricity production, as well as plants sized to process flue gas associated with 10's of MW of electricity production. Many technologies have pilot plants built at both scales. Therefore, we anticipate the need for about 15 pilot plant tests. The cost range is attributed to the different size of pilot plants to be built.
- **Proof of Concept.** The cost of these projects will be variable – some may be only a few million, while others could be \$20 million or more. Our estimate is based on what a reasonable average cost might be.
- **Exploratory Research.** We feel it is important to cast a wide net, so we encourage funding many of these projects. After spending about \$1 million, enough information should be generated to decide whether it is worthwhile to move to the proof of concept stage.
- **Simulation/analysis.** The *Future of Coal Study* suggested \$50 million dollars per year on this task to cover all parts of CCS technology. Based on this estimate, we scaled it down to a level for post-combustion capture technologies only.
- **Contingency.** Because of the uncertainty in the estimates (and in future prices), we have included a 20% contingency.

4.2. Oxy-Combustion Capture

The cost estimate for an 8-10 year research program in Table 2 below. Note that this is total cost of program, including research funds from both the private and public sector. Also note that it for only oxy-combustion retrofit capture technology – a complete CCS budget would also need to address other capture approaches (i.e., pre-combustion, post-combustion, new oxy-combustion plants), as well as transport and storage.

Table 2. Estimated cost of an 8-10 year US oxy-combustion retrofit research effort.

Component	# of projects	Cost per project (millions of \$)	Total Cost (millions of \$)
Demonstration	3	1200	3600
Pilot Plants	10	100	1000
Proof of Concept	20	50	200
Exploratory Research	25	2	50
Simulation/analysis			100
Contingency			1000
TOTAL			5950

The basis for these estimates is as follows:

- **Demonstration project.** This cost per project number should be similar to post-combustion capture, if the capture efficiency were the same. However, for post-combustion capture, the estimate was based on 60% capture. By its nature, the oxy-combustion process will have capture rates over 90%, so it will be more expensive for similar sized plants (200-300 MW). Since oxy-combustion technology is more homogeneous than post-combustion capture technology, fewer demonstrations are required.
- **Pilot plants.** The cost of a pilot plant is based on Vattenfall's experience with their 30 MW_{th} plant (\$100 million). Pilot plants can be used to test boiler designs, purification technologies, and/or oxygen production technologies. As with the demonstration projects, fewer pilot plants are recommended for oxy-combustion compared to post-combustion.
- **Proof of Concept.** Compared to post-combustion capture, similar price, but fewer projects.
- **Exploratory Research.** Compared to post-combustion capture, fewer projects, but more dollars per project. It is harder to isolate a component in a oxy-combustion concept than in post-combustion capture, so the exploratory research will cost more per project.
- **Simulation/analysis.** Same as post-combustion capture.
- **Contingency.** A 20% contingency, same as post-combustion capture.

5. References

- Allam R., "Improved oxygen production technologies," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- Carbo, M.C., D. Jansen, C. Hendriks, E. de Visser, G.J. Ruijg and J. Davison, "Opportunities for CO₂ capture through oxygen conducting membranes at medium-scale oxyfuel coal boilers," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- Cieutat, D., I. Sanchez-Molinero, R. Tsiava, P. Recourt, N. Aimard and C. Prébendé, "The Oxy-combustion burner development for the CO₂ pilot at Lacq," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- Darde, A., R. Prabhakar, J-P. Tranierc and N. Perrin, "Air separation and flue gas compression and purification units for oxy-coal combustion systems," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- den Exter, M., J.F. Vente, D. Jansen and W.G. Haije, "Viability of mixed conducting membranes for oxygen production and oxyfuel processes in power production," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- Herzog, H. J., Meldon, J. and Hatton, A., "Advanced Post-Combustion CO₂ Capture", a White Paper prepared for the Clean Air Task Force under a grant from the Doris Duke Foundation (2009).
- McCauley K.J., H. Farzan, K.C. Alexander and D.K. McDonald, "Commercialization of oxy-coal combustion: applying results of a large 30MWth pilot project," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- MIT (Massachusetts Institute of Technology), The Future of Coal in a Carbon Constrained World, <http://mit.edu/coal>, (2007).
- Pfaff, I. and A. Kather, "Comparative thermodynamic analysis and integration issues of CCS steam power plants based on oxy-combustion with cryogenic or membrane based air separation," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- Suraniti, S.L., N. Nsakala and S.L. Darling, "Alstom oxyfuel CFB boilers: A promising option for CO₂ capture," Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).
- Tigges, K-D., F. Klauke, C. Bergins, K. Busekrus, J. Niesbach, M. Ehmann, C. Kuhr, F. Hoffmeister, B. Vollmer, T. Buddenberg, S. Wu and A. Kukoski, "Conversion of existing coal-fired power plants to oxyfuel combustion: Case study with experimental results and

CFD simulations,” Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).

White, V., L. Torrente-Murciano, D. Sturgeon and D. Chadwick, “Purification of Oxyfuel-Derived CO₂,” Proceedings of the 9th International Conference on Greenhouse Gas Control, in press, (2008).

