DEVELOPMENT OF AN ENERGY-EFFICIENT, ENVIRONMENTALLY FRIENDLY SOLVENT FOR THE CAPTURE OF CO_2

primary project goals

This Babcock & Wilcox Power Generation Group, Inc., (B&W) project focuses on identifying concentrated piperazine (PZ)-based solvent formulations that improve overall solvent and system performance.

technical goals

- Improve system operability and reliability.
- Minimize environmental impacts.
- Reduce corrosion potential.
- Maximize solvent durability.

technical content

B&W is characterizing and optimizing the formulation of a novel solvent for the capture of carbon dioxide (CO_2) at coal-fired utility plants. The solvent of interest has been identified through a 5-year solvent development program conducted at B&W. The solvent formulations of interest comprise concentrated solutions of a cyclic diamine, PZ. Testing at B&W indicates that blends of concentrated PZ with other compounds have the potential to perform substantially better than PZ itself. The objective is to lower the total cost of solvent-based CO_2 capture systems by identifying formulations that improve overall solvent and system performance.

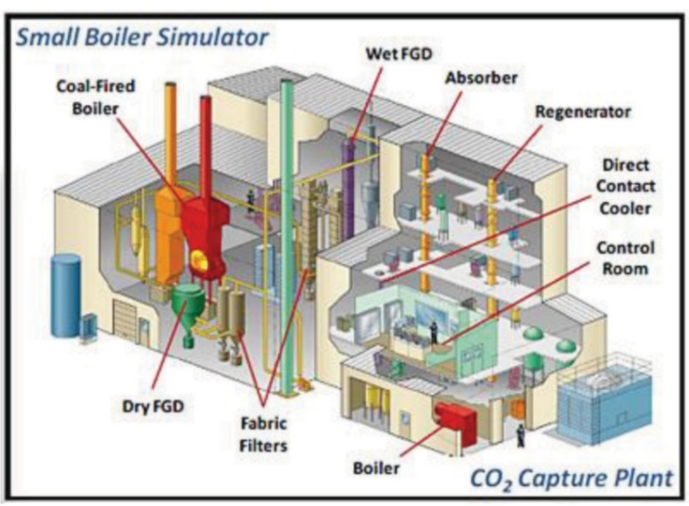

Figure 1: B&W 7-Ton/Day Pilot Facility

technology maturity:
Bench-Scale, Simulated and Actual Flue Gas

project focus:
Optimized Solvent Formulation

participant:
Babcock & Wilcox

project number:
FE0007716

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performance period:
10/1/11 – 4/30/14

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The CO_2-reactive species (there may be other non-reactive species) in the solvent formulation may include amines, carbonates, or amino acid salts in combination with concentrated PZ. Amine solvents are grouped according to their molecular structure. Carbonate and amine reactions with CO_2 can be summarized as follows:

Carbonates: $CO_3^{=} + CO_2 + H_2O \leftrightarrow 2\ HCO_3^-$

Hindered and tertiary amines: $CO_2 + R_3N + H_2O \leftrightarrow HCO_3^- + R_3NH^+$

Primary and secondary amines: $CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH_2^+$

Solvent Contaminant Resistance – Amine solvents chemically degrade in a variety of ways (thermal degradation due to exposure to the high temperatures of the regeneration process, oxidative degradation due the presence of oxygen in the flue gas, carbamate polymerization, etc.). Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals (possibly originating with the coal fly ash). Minimizing solvent degradation and the attendant production of potentially hazardous chemical species is a central objective of this project.

Flue Gas Pretreatment Requirements – Flue gas supplied to the CO_2 capture system must be cooled to approximately 40°C and relatively free of contaminants. Concentrations of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) must be less than about 10 parts per million (ppm)—preferably around 1 ppm.

Solvent Makeup Requirements – Solvent makeup is required to offset solvent losses due to volatility, degradation, the formation of heat stable salts, etc. PZ-based solvents are expected to minimize such losses due to the lower volatility and better resistance to thermal degradation exhibited by PZ relative to solvents such as monoethanolamine (MEA). This project is focused on minimizing solvent losses in the system.

Waste Streams Generated – Waste streams generated by the process will be similar to those generated by convention amine processes, including reclaimer waste solids, spent carbon and particulate filter cake from solvent filtration equipment, and potentially waste water. It is an objective of this project to minimize the environmental impact of these streams through careful selection of the solvent formulation and operating conditions.

Process Design Concept – The CO_2 capture process, illustrated in Figure 2, comprises a relatively conventional absorption/stripping process.

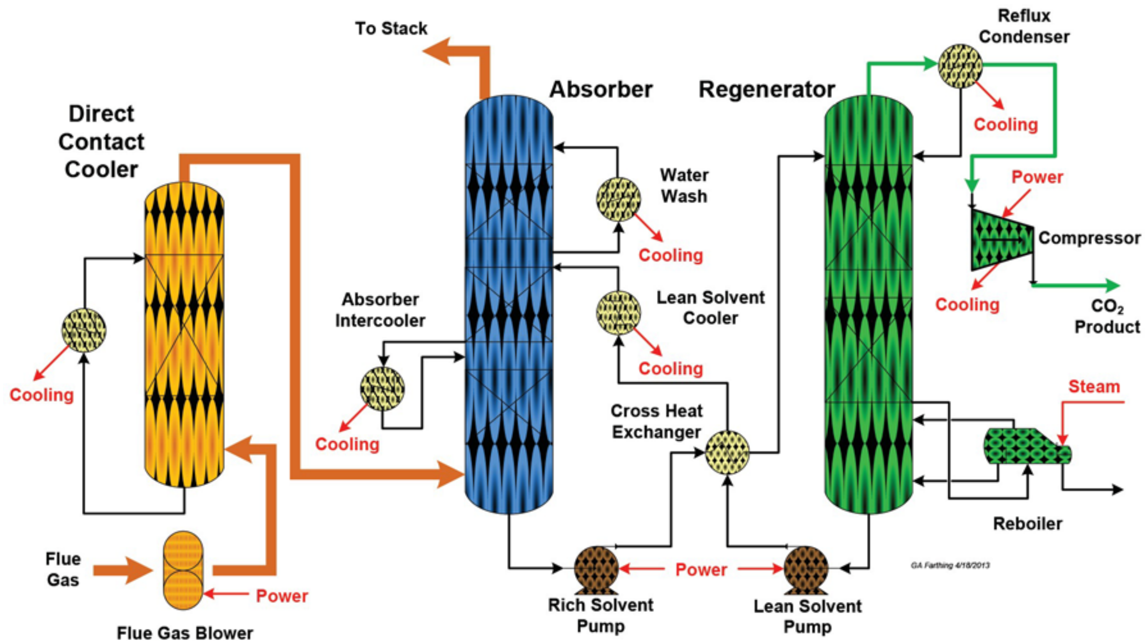

Figure 2: Schematic of Solvent-Based CO_2 Capture Process

technology advantages

Piperazine, used alone, has demonstrated high rates of absorption and low regeneration energy. Recent testing at B&W indicates that blends of concentrated PZ with other organic compounds may perform substantially better than PZ alone.

R&D challenges

- Selection of a solvent formulation involves compromises that seek to optimally balance competing effects. Using limited and potentially non-representative data generated in laboratory-scale equipment is extremely challenging. Previous solvent development work supports correlation of laboratory results with pilot-scale performance estimation to optimize solvent formulation.
- Goals include improved system operability and reliability, minimizing environmental impacts, reducing corrosion potential, and maximizing solvent durability.

results to date/accomplishments

- A list of candidate solvent formulations was developed and refined. This work comprised evaluations regarding overall solvent performance criteria, identification of primary active components, and verification of wet chemistry analytical techniques for CO_2 loading and alkalinity.
- Several modeling approaches were identified. Tools considered include equilibrium models, semi-empirical rate-based models, and rigorous rate-based models. Tools for the prediction of process economics were also evaluated.
- Characterization tests in B&W's wetted-wall column (WWC) were completed on a baseline concentrated PZ solvent and 12 candidate solvent formulations. The liquid film mass transfer coefficient (kg), as well as equilibrium partial pressure of CO_2 (P_{CO2}*), were obtained from each WWC test. Other parameters, such as heat of absorption and CO_2 working capacity, were also derived from these experimental data. Preliminary solvent formulation performance was then estimated with in-house, semi-empirical models.
- Solvent volatility and solubility testing was performed on several candidate formulations of concentrated PZ solutions containing salts of amino acids, carbonates, and other amines. Also evaluated were organic additives designed to improve the solubility of PZ and its carbamates. In addition, it was found necessary to characterize candidate formulations with respect to their viscosities in order to ensure good mass transfer performance and acceptable operability.
- Installation of the bench-scale continuous solvent degradation system (CSDS) was completed. The CSDS will enable comprehensive investigations of proposed solvent formulation degradation under representative operating conditions. It is intended to simulate key features of industrial CO_2 capture processes, including cyclical absorption and regeneration process conditions. The CSDS is designed for continuous, unattended operation for tests lasting 100 to 1,000 hours or more.

next steps

This project ended on April 30, 2013.

available reports/technical papers/presentations

Final Report, "Optimized Solvent for Energy-Efficient, Environmentally Friendly Capture of CO_2 at Coal-Fired Power Plants," June 2014. *http://www.osti.gov/scitech/servlets/purl/1136527*.

Farthing, G., "Optimized Solvent for Energy-Efficient, Environmentally Friendly Capture of CO_2 at Coal-Fired Power Plants," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.