

March 6, 2012

Integrated Warm Gas Multicontaminant Cleanup Technologies for Coal-Derived Syngas

Final Technical Report

Period of Performance:
June 1, 2005 to September 30, 2010

Prepared for

U.S. Department of Energy
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DOE Cooperative Agreement No. DE-FC26-05NT42459

ACKNOWLEDGMENTS

This project was sponsored by the National Energy Technology Laboratory (NETL) of the U.S. Department of Energy (DOE) under Cooperative Agreement No. DE-FC26-05NT42459. This financial assistance from DOE/NETL is gratefully acknowledged.

To support the field demonstration and development of warm syngas cleanup for chemical applications, this project has worked in parallel toward multiple objectives for different aspects of RTI's warm syngas cleanup technologies. It would be difficult to name every individual who has contributed to this project. Nonetheless, we would like to attempt to recognize the individuals who contributed to the development of the warm CO₂ capture technologies.

- **DOE/NETL:** Gary Stiegel, Jenny Tennant, Kanwal Mahajan, David Lyons, Joseph Strakey, and Stewart Clayton (DOE/HQ)
- **Noblis:** David Gray and John Plunkett
- **RTI:** Gary Howe, Adesh Harle, Michael Levine, Jing-Ping Shen, Maruthi Pavani, Jason Trembly, and Luke Coleman

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ABSTRACT

One of the key obstacles for the introduction of commercial gasification technology for the production of power with Integrated Gasification Combined Cycle (IGCC) plants or the production of value added chemicals, transportation fuels, and hydrogen has been the cost of these systems. This situation is particularly challenging because the United States has ample coal resources available as raw materials and effective use of these raw materials could help us meet our energy and transportation fuel needs while significantly reducing our need to import oil. One component of the cost of these systems that faces strong challenges for continuous improvement is removing the undesirable components present in the syngas.

The need to limit the increase in cost of electricity to $< 35\%$ for new coal-based power plants which include CO_2 capture and sequestration addresses both the growing social concern for global climate change resulting from the emission of greenhouse gas and in particular CO_2 and the need to control cost increases to power production necessary to meet this social objective. Similar improvements to technologies for trace contaminants are getting similar pressure to reduce environmental emissions and reduce production costs for the syngas to enable production of chemicals from coal that is cost competitive with oil and natural gas.

RTI, with DOE/NETL support, has been developing sorbent technologies that enable capture of trace contaminants and CO_2 at temperatures above 400°F that achieve better capture performance, lower costs and higher thermal efficiency. This report describes the specific work of sorbent development for mercury (Hg), arsenic (As), selenium (Se), cadmium (Cd), and phosphorous (P) and CO_2 removal. Because the typical concentrations of Hg, As, Se, Cd, and P are less than 10 ppmv, the focus has been on single-use sorbents with sufficient capacity to ensure replacement costs are cost effective. The research in this report describes the development efforts which expand this sorbent development effort to include Se, Cd, and P as well as Hg and As. Additional research has focused on improving removal performance with the goal of achieving effluent concentrations that are suitable for chemical production applications.

By contrast, sorbent development for CO_2 capture has focused on regenerable sorbents that capture the CO_2 byproduct at higher CO_2 pressures. Previous research on CO_2 sorbents has demonstrated that the most challenging aspect of developing CO_2 sorbents is regeneration. The research documented in this report investigates options to improve regeneration of the CO_2 capture sorbents. This research includes effort on addressing existing regeneration limitations for sorbents previously developed and new approaches that focus initially on the regeneration performance of the sorbent.

EXECUTIVE SUMMARY

The primary objective of this project has been to develop syngas cleanup technologies that operate at temperatures > 400 °F with specific goals of reducing the cost of gasification technologies, improving the performance of the cleaning processes, and improving the thermal efficiency of syngas cleaning. The key driver for this research is the need to drive down the cost of commercial applications of coal gasification to make it competitive. This research has also focused on expanding RTI's syngas cleaning platform to address:

- A larger portfolio of contaminants, namely selenium (Se), cadmium (Cd), and phosphorous (P) as well as mercury (Hg) and arsenic (As)
- More stringent effluent concentrations that support chemical production as well as more stringent emission regulations
- The challenges of developing a cost effective CO₂ capture and sequestration process.

This research has resulted in two sorbent development programs. The first has worked towards the development of single-use sorbents for which their concentration in syngas is < 10 ppmv. At these concentrations, the utilization of the sorbent's capacity to capture contaminants can be slow enough that replacement costs are acceptable. To help expedite identification and development of sorbents for these applications, preferential selection criteria for candidate sorbent materials included commercially available materials and materials that demonstrated removal potential for multiple contaminants. In addition, the sorbent materials that were exposed to real coal-derived syngas during the Eastman field test (see Final Report for) were submitted for additional analysis for the contaminants in the expanded contaminant portfolio for this project to provide actual exposure information at operating conditions.

These criteria were selected to enable rapid transfer successful sorbent development and demonstration to actual commercial application. Available commercial materials were preferred because existing commercial production expertise would shorten or completely eliminate scale up production of this material for actual commercial application. The ability to effectively simultaneously remove multiple contaminants helps intensify the syngas cleaning process resulting in lower capital and operating costs which can accelerate implementation of a technology.

Three specialized laboratory reactor systems were used to screen and evaluate sorbent contaminant capacity. Testing in the laboratory reactor systems used a simulated syngas mixture for testing. The advantage of a simulated syngas mixture was the ability to carefully control the composition of the syngas and the concentration of the contaminants. This provided greater ability to investigate synergistic interactions between the primary syngas components, syngas and sorbent materials. However, the key disadvantage was the chemical composition of the contaminant was fixed. The selection of the contaminant chemical composition was selected based on the best available information, which is the thermodynamic equilibrium predictions based on chemical stability. Based on these thermodynamic predictions, the chemical composition of the contaminants was Hg vapor, arsine (AsH_3), hydrogen selenide (H_2Se), Cd vapor and phosphine (PH_3) for Hg, As, Se, Cd and P, respectively.

For the contaminants As, Se and P, at least one, but generally several sorbent materials were identified that had effective capture capacities of > 3 wt%. Modification of the testing protocol also enabled demonstrating that most promising sorbents could also effectively capture these contaminants at the DOE targets for these contaminants for chemical production. Another positive result from this development program was that several sorbent materials were identified that could effectively remove more than one contaminant. Unfortunately, there was not sorbent that effectively removed all of the targeted contaminants.

Mercury sorbent development attempted to address the limited capacity for Hg at operating temperatures > 400 °F. The results from analysis of the sorbent materials from the Eastman field test provided clues for a Hg sorbent with about 2 times the capacity for the of the mercury sorbent tested at Eastman. Additional research will be necessary to effectively integrate this new sorbent into the syngas cleanup technology platform.

The challenge for the Cd sorbent development task was generating a simulated syngas stream with a known and consistent concentration of Cd vapor. The approach attempted in this project involved using the vapor pressure of a heated sample of Cd metal to generate the Cd vapor. Unfortunately even at the outlet of the Cd vapor generator, the concentration of Cd vapor was significantly less than predicted based on thermodynamics and was not consistent. These results coupled with the Cd concentrations in the coal-derived syngas at Eastman warrant additional investigation of the importance of Cd as a contaminant in coal-derived syngas.

The second sorbent development program was devoted to regenerable sorbents for CO_2 capture. This program looked at a zeolite based CO_2 recovery process that exploited previous development of a lithium silicate-based sorbent material. The advantages of the Lithium silicate

material were exceptional CO₂ capture performance from syngas mixtures even in the presence of H₂S. The challenge was regeneration of this sorbent. In this project a number of zeolite materials were found that could effectively capture CO₂ at lower partial pressure and temperature and produce a pressurized CO₂ byproduct using a temperature swing desorption process. The problem was the effluent CO₂ concentration during regeneration of the lithium silicate-based sorbent was not sufficient to effectively use the zeolite sorbent for CO₂ recovery.

Using a modified screening process, which focused on high pressure regeneration, a novel magnesium oxide- (MgO-) based sorbent was identified. This sorbent had CO₂ capacities of > 40 wt% and could produce higher pressure CO₂ byproduct stream with a thermal swing. Process development of this process demonstrated that a pressure swing regeneration of this material was more acceptable than a thermal swing. However, even with a pressure swing, the CO₂ partial pressure was still very low and steam was needed. Techno-economic analysis of the process did not demonstrate significant thermal efficiency improvement over a conventional Selexol-based CO₂ capture process.

SECTION 1 INTRODUCTION

Although the large abundance and low cost of coal compared to other fossil fuels make coal an attractive fuel source, the use of gasification technology for the conversion of this fuel source into power through integrated gasification combined cycle (IGCC) systems or value-added chemicals—ranging from hydrogen to transportation fuels—has been limited. One limitation has been a cost-effective means of removing contaminants to meet specifications required for either power or chemical production. To address this limitation, RTI, with funding from the Department of Energy National Energy Technology Laboratory (DOE/NETL), has been actively developing a full syngas cleaning technology platform that operates at temperatures greater than 400 °F to optimize the overall thermal efficiency, reduce capital and operating costs, and enable tailoring contaminant removal performance for power and chemical applications.

Key components of this technology platform include the high-temperature desulfurization process (HTDP), the direct sulfur recovery process (DSRP), and sorbents for removal of trace components like hydrochloric acid (HCl), ammonia (NH₃), mercury (Hg), and arsenic (As). Pilot plant operation at Eastman Chemical Company in Kingsport, Tennessee with real coal-derived syngas successfully showed the technical capabilities of HTDP, DSRP, and sorbents for As and Hg. Independent techno-economic studies by Nexant and Noblis have used these pilot plant data to demonstrate that warm syngas cleanup both improves thermal efficiency and reduces capital cost of an IGCC system. Documentation of this technology development and the Eastman pilot plant testing can be found in a Final Topical Report entitled *Novel Technologies for Gaseous Contaminants Control*, submitted under DOE Contract No. DE-AC26-99FT40675.

This development and the Eastman pilot plant testing were exclusively focused on existing cleanup requirements for IGCC applications. In addition, the different technologies in the warm syngas cleaning platform were at different stages of development. To continue commercialization of this technology, the focus for the warm gas cleaning platform and this project were directed toward meeting syngas contaminant removal requirements for chemical production applications established by DOE/NETL and shown in Table 1-1. In addition to the requirements in Table 1-1, the project also focused on accelerating development of sorbent-based removal of trace contaminants and

Table 1-1. Warm Syngas Cleanup¹ – DOE Performance Goals

Contaminant	Maximum after Cleanup
S (total)	50 ppb
NH ₃	10 ppm
HCl	10 ppb
Hg	5 ppbw
Se	0.2 ppm
As	5 ppb
Cd	30 ppb
P	20 ppb
CO ₂	> 90%

¹ At pressure ≥600 psi; temperatures ≥400°F

sorbent-based CO₂ capture at temperatures above 400 °F. The goal was to ensure that these technologies would be available to help meet regulations being developed for new IGCC plants being built.

Development of these sorbent-based technologies for trace contaminant removal and CO₂ capture required very different developmental approaches to meet the specific removal constraints. An example of these differences is contaminant concentration in the syngas. Contaminants like Hg, As, selenium (Se), and cadmium (Cd) are typically present in concentrations of less than 1 ppmv. By contrast, CO₂ is typically present at > 5 vol% (50,000 ppmv). The cost-competitive solution for a sorbent-based approach for the high CO₂ concentrations requires a regenerable sorbent that permits multiple regenerations to reduce sorbent costs. For the trace contaminants, a single-use sorbent will be acceptable because the low concentration of the contaminant permits long periods of operation prior to the need to replace the sorbent. Therefore, distinct tasks were developed and implemented for sorbents for trace contaminant removal and high-temperature CO₂ capture.

1.1 Development of Trace Contaminant Sorbents

The previous development efforts for trace contaminants in DOE Contract No. DE-AC26-99FT40675 focused specifically on Hg and As with a goal of 90% capture of these contaminants. In this project, the list of contaminants has been expanded to include Se, Cd, and P. The analytic processes and equipment were also modified as necessary to ensure that the effluent concentrations of the contaminants could meet the specifications in Table 1-1 and enable chemical production with the clean syngas.

Table 1-1 provides a firm limit on the acceptable concentration for each target element for a clean syngas that is suitable for chemical production applications. However, Table 1-1 does not provide two key pieces of information about the concentration of contaminants in the original raw syngas. These are the specific composition of the contaminant species in the raw syngas and the concentration of these species. The complex interaction of the gasification reaction network, thermodynamic equilibrium constraints, and the high-temperature and high-pressure operating conditions makes evaluation of both the contaminant composition and the concentrations extremely challenging. At this time, the best information available is derived based on thermodynamic calculations to identify thermodynamically stable contaminant species and estimations of concentration based on the elemental analysis of typical coal feed stocks.

A summary of the available information on the stable thermodynamic contaminant species and estimated concentrations are provided in Tables 1-2 and 1-3, respectively. Based on

the information in Table 1-2, specific contaminant compounds were selected to effectively simulate contaminant-laden syngas. Similarly, the information in Table 1-3 was used to identify a typical concentration of these contaminants in the raw syngas mixture.

Table 1-2. Potential Species Present in Syngas for the Target Elemental Contaminants

Element	Species
S	H₂S, COS, CS₂
N	NH₃, HCN
Cl	HCl , metal chlorides
Hg	Hg (g)^{1,2} , Hg(CH ₃) ₂ ¹
As	As ₂ (g) ^{1,2} , As ₄ (g) ^{1,2} , AsH₃ (g)^{1,2} , AsS (g) ² , and other FeAs species ¹
Se	H₂Se (g)^{1,2}
Cd	Cd (g)¹ , CdS (condensed) ¹ , CdCl ₂ (g) ¹

¹ Equilibrium calculations by Diaz-Somoano (2003) at 572 to 932 °F

² Equilibrium calculations by Helble (1996) at 621 to 1341 °F

Bolded items identify the species chosen for simulated syngas testing.

Table 1-3. Contaminant Concentrations in Syngas

Species	Range of Concentrations in Coal	Range of Concentrations in Syngas
S	0.3 – 3.6 wt% ¹	750–7000 ppmv as H ₂ S and 25–200 ppmv as COS ₂
N	1.1 – 1.6 wt% ¹	50–800 ppmv as NH ₃ ₂
Cl	0.0032 – 0.37 wt% ³	170–830 ppmv as HCl ₂
Hg	0.02 – 1 µg/g ³	1.3–63 ppbv ⁴
As	0.5 – 80 µg/g ³	84–1300 ppbv ⁴
Se	0.2 – 1.6 µg/g ³	32–2600 ppbv ⁴
Cd	0.1 – 3 µg/g ³	11–340 ppbv ⁴

¹ Determined in Canadian feed-coals (Goodarzi, 2002)

² Data survey of four types of gasifiers conducted by Bakker (1998)

³ Typical concentrations in the world's coal as examined by Swaine (1990)

⁴ Calculated concentrations based on elemental concentration in coal and assuming complete vaporization

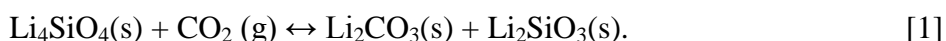
Material testing to identify and develop promising sorbents involved the use of specialized testing systems. For Hg, this testing system was developed as part of DOE Contract No. DE-AC26-99FT40675. A complete description of the Hg removal testing system, validation testing, sorbent screening, and initial capacity testing are included in the final report for the same DOE contract. The testing system developed for AsH₃ under that contract was modified to enable testing with other hydride contaminants (H₂Se and PH₃). Details on this system are provided in Section 2.3 in this report. Because the predicted stable thermodynamic for Cd was Cd vapor, a specialized testing system that attempted to generate Cd vapor from a gas flow through a temperature controlled bed of metallic Cd is described in Section 2.7.

In spite of the differences in the testing systems developed for each contaminant, the two consistent approaches for sorbent development were to preferentially look for commercial materials and maximize the value of a particular sorbent evaluating the potential for removing multiple contaminants. Preference was given to commercial materials, as these materials are generally able to rapidly move from laboratory testing to demonstration because no production scale-up issues are anticipated for a commercial material.

In an effort to maximize the information extracted from testing of trace contaminant sorbents during the Eastman Pilot Plant testing, analysis of the spent sorbent materials was expanded beyond As and Hg, which were required for the original project, to include Se, Cd, and P. The results from this analysis are discussed in Section 2.1.

1.2 Development of Lithium Silicate CO₂ Capture Sorbents

Funding under DOE Contract No. DE-AC26-99FT40675 also supported development of lithium silicate-based sorbents for high-temperature CO₂ capture from syngas. Lithium silicate was identified as an effective material to capture CO₂ using atmospheric thermogravimetric analysis (TGA) screening. TGA testing demonstrated that lithium silicate could effectively remove CO₂ from nitrogen and simulated syngas streams. Lithium silicate's ability to capture CO₂ was based on the reaction below:



The reaction between lithium silicate and CO₂ is exothermic, with a reaction enthalpy of $\Delta H^\circ_{298\text{K}}$ of -142 kJ/mol. Because reaction [1] is reversible, the sorbent releases CO₂ during regeneration. During TGA testing, the capacity and activity for CO₂ removal of the lithium silicate sorbent remained constant over multiple cycles based on either temperature or concentration swing regenerations.

To exploit this performance of lithium silicate materials, research and development (R&D) efforts focused on developing lithium silicate-based sorbents, including both fixed- and fluidized-bed formulations. The key challenge with the fluidized-bed formulation was that the lithium silicate became soft enough to enable the particles to agglomerate during the CO₂ capture and regeneration cycles. As a consequence, the fluidized-bed sorbent would fuse into a large solid mass that could not be fluidized. After multiple unsuccessful attempts to find a solution to this challenge, R&D efforts to develop a fluidized-bed sorbent formulation were halted, and efforts instead were concentrated on developing a fixed-bed sorbent formulation.

The challenge that thwarted efforts to develop a fluidized-bed sorbent formulation actually assisted the development of a fixed-bed formulation because the softening and fusing of the lithium silicate material effectively strengthened the sorbent formulation with each cycle. R&D efforts for a fixed-bed sorbent led to a promising formulation with sufficient physical strength, CO₂ capacity, and CO₂ reactivity.

Extensive testing of this fixed-bed sorbent formulation was conducted in RTI's bench-scale sorbent testing system, shown in Figure 1-1 on the following page. The sorbent was shown to effectively remove CO₂ from simulated syngas mixtures during 19 CO₂ adsorption and regeneration cycles. One significant advantage of this lithium silicate-based sorbent was that its CO₂ capture performance was enhanced in simulated syngas mixtures with sulfur species like hydrogen sulfide (H₂S) and carbonyl sulfide (COS). Furthermore, the lithium silicate sorbent also had some water gas shift activity. As shown in Figure 1-2, both the CO₂ and CO effluent concentrations at the start of the test were very low, and when the sorbent's CO₂ capacity was extinguished (at approximately 10 minutes), both the CO₂ and CO reached steady-state compositions different from those at the inlet of the reactor.

Based on the adsorption performance, lithium silicate-based sorbent appeared to be an ideal candidate for high-temperature CO₂ capture. Unfortunately, regeneration performance of this sorbent was not as promising. During atmospheric TGA testing, lithium silicate sorbent formulations could be easily regenerated with either a temperature swing or an inert gas. In RTI's bench-scale sorbent testing system, temperature swing regeneration could cause the thermal decomposition of lithium carbonate according to reaction [1], but the temperature required to fully regenerate the sorbent was >700 °C. This combination of high heat of reaction for thermal decomposition (142 kJ/mol) and high temperature for regeneration is not available in an IGCC system. In addition, the ability to transfer this heat at such a high temperature presents a technical challenge. Thus, temperature swing regeneration of lithium silicate-based sorbents is impractical.

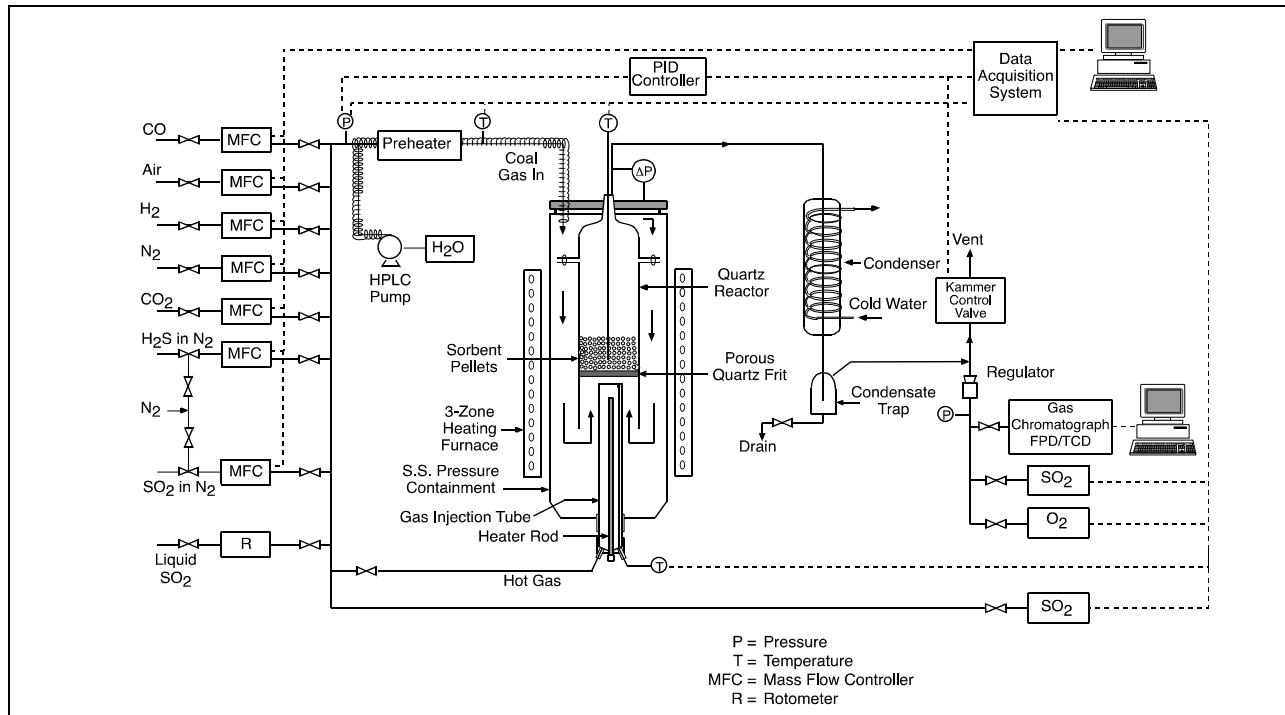


Figure 1-1. RTI's bench-scale sorbent testing system

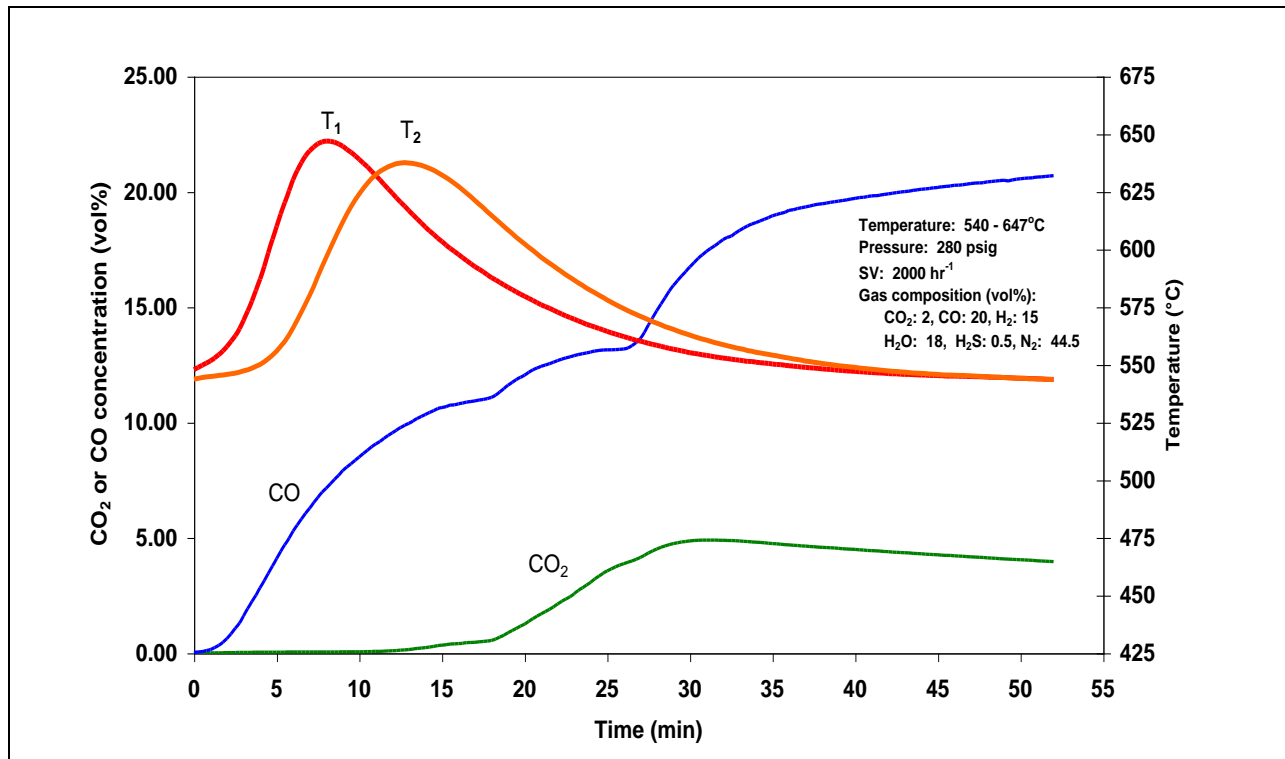


Figure 1-2. Profiles for adsorption process for lithium silicate for syngas containing 5,000 ppmv H₂S showing both CO₂ capture and water gas shift activity

The alternative option was to use a concentration swing to remove the CO₂ from the sorbent during regeneration. In TGA testing, the standard inert used was helium (He). Testing in RTI's bench-scale reactor system demonstrated that nitrogen (N₂) could also be used. Because using either He or N₂ as the inert to regenerate the sorbent resulted in a mixed gas product stream containing CO₂ with significant amounts of He or N₂, regeneration using a concentration swing based on these gases was not practical for generating a high-purity sequestration-ready CO₂ product.

The only promising gas that could be used was steam, which can be effectively separated yielding a relatively pure CO₂ stream for sequestration by condensation. Although operating RTI's bench-scale sorbent testing system with 100% steam was not possible, mixtures with up to 50% steam in N₂ were tested and clearly showed that steam could be used as an inert to regenerate lithium silicate-based sorbents. However, these laboratory data showed that steam-to-CO₂ ratios of >20 would be required to regenerate the lithium silicate-based sorbents. Preliminary techno-economic analysis showed that, for regeneration with steam-to-CO₂ ratios of >20, the energy penalty and amount of steam consumed by the regeneration would be economically prohibitive. Based on this analysis, the cost and energy requirements for regeneration of lithium silicate-based sorbent were determined to be prohibitive.

SECTION 2

DEVELOPMENT OF TRACE CONTAMINANT SORBENTS

2.1 Analysis of Sorbent Materials from Eastman Field Test

As part of the Eastman field test for DOE Contract No. DE-AC26-99FT40675, sorbents for mercury, arsenic, and ammonia were exposed to a coal-derived syngas stream at 200 °C and about 850 psig for roughly 500 hours. A simple process flow diagram of the multicontaminant skid for the exposure of these sorbents to coal-derived syngas is shown in Figure 2-1. Table 2-1 provides a list of the sorbents used in the multicontaminant skid. Pre- and post-test analyses of the mercury and arsenic sorbents were completed for mercury and arsenic and included in the final report for DOE Contract No. DE-AC26-99FT40675.

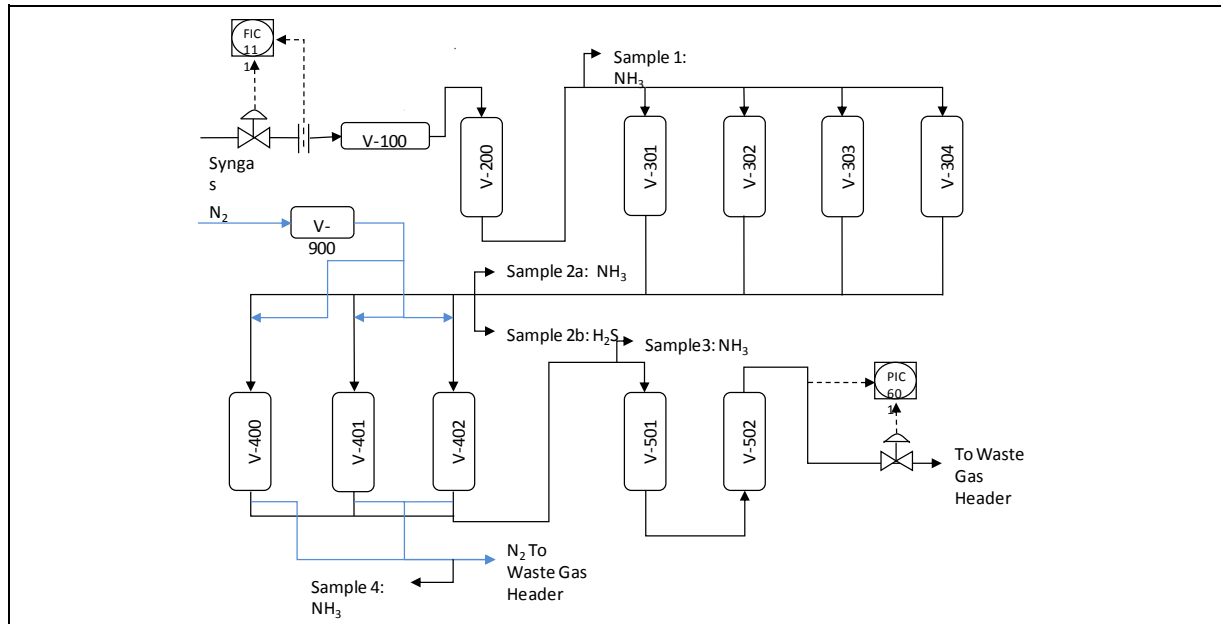


Figure 2-1. Block flow diagram for multicontaminant system

Table 2-1. List of Specific Materials Loaded in Vessels in Multicontaminant Skid

Vessel	Sorbent	Function
V-100	Lithium silicate	High-temperature CO ₂ removal
V-200	Commercial Sorbent A	Arsenic removal
V-301, V-302, V-303, V-304	G-72D	Bulk sulfur removal
V-400, V-401, V-402	CBV-712	Ammonia removal
V-501	G-72D	Polishing sulfur removal
V-502	Impregnated carbon	Mercury removal

However, during this field test, the sorbents from this multicontaminant skid were successfully exposed to the full contaminant matrix present in a coal-derived syngas for 500 hours. To fully explore the effects of contaminant-laden syngas on different sorbent

materials in the multicontaminant skid, all sorbents, which included the ammonia and commercial desulfurization sorbent in addition to the As and Hg sorbents, were analyzed for not only Hg and As, but also Se, Cd, and P. Because the sorbents were also carefully removed from the reactor vessels to preserve their relative position in the reactor vessel, analysis of the sorbent samples could provide information about the effect of the contaminant on the sorbent as the syngas moved through the sorbent bed. Samples of the RTI-3 sorbent removed from the high temperature desulfurization system after different operating periods were also included with the other sorbents for analyses. The results for the analyses of these sorbents are shown in Tables 2-2 through 2-6.

Table 2-2. Net Contaminant Concentrations for Commercial Sorbent A (Arsenic Sorbent)

Bed Position	Net element concentration in sorbent ¹ (µg/g)				
	Arsenic ²	Selenium ²	Cadmium ²	Phosphorous ²	Mercury ³
1 (top)	12700	1670	<1.25	<1.25	0.701
5	939	2.02	<1.25	<1.25	0.159
9	<1.25	<1.25	<1.25	12.7	0.043
13	1.66	<1.25	<1.25	<1.25	0.032
17	237	7.09	<1.25	1.77	0.035
21	27.4	<1.25	<1.25	<1.25	<0.020
25 (bottom)	249	14.6	<1.25	<1.25	0.044

¹ Net concentration refers to the difference in concentration between the post- and pre-sorbent samples.

² Elements recovered using Hydrogen fluoride (HF) dissolution and concentrations determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

³ Mercury concentration determined by DMA-80.

Table 2-3. Net Contaminant Concentrations for Commercial Sulfur Guard Bed Sorbent

Bed Position	Net Element Concentration in Sorbent ¹ (µg/g)				
	Arsenic ²	Selenium ²	Cadmium ²	Phosphorous ²	Mercury ³
1 (top)	5.11	<1.25	<1.25	2.31	0.054
4	5.58	<1.25	<1.25	3.14	0.075
8	8.94	<1.25	<1.25	3.33	0.145
12	7.25	<1.25	4.10	<1.25	0.060
16	3.56	<1.25	<1.25	3.73	0.022
20	4.41	<1.25	<1.25	3.60	0.151
24 (bottom)	4.35	<1.25	<1.25	3.66	0.146

¹ Net concentration refers to the difference in concentration between the post- and pre-sorbent samples.

² Elements recovered using HF dissolution and concentrations determined by ICP-OES.

³ Mercury concentration determined by DMA-80.

Table 2-4. Net Contaminant Concentrations for Ammonia Sorbent (CBV-712)

Bed Position	Net Element Concentration in Sorbent ¹ (µg/g)				
	Arsenic ²	Selenium ²	Cadmium ²	Phosphorous ²	Mercury ³
1 (top)	4.82	<1.25	<1.25	<1.25	< 0.020
3	4.93	<1.25	<1.25	<1.25	< 0.020
6	4.72	<1.25	<1.25	<1.25	< 0.020
9	4.76	<1.25	<1.25	<1.25	< 0.020
12	2.15	<1.25	<1.25	<1.25	< 0.020
15 (bottom)	2.32	<1.25	<1.25	<1.25	< 0.020

¹ Net concentration refers to the difference in concentration between the post- and pre-sorbent samples.

² Elements recovered using HF dissolution and concentrations determined by ICP-OES.

³ Mercury concentration determined by DMA-80.

Table 2-5. Net Contaminant Concentrations for Impregnated Carbon (Hg Sorbent)

Bed Position	Net Element Concentration in Sorbent ¹ (µg/g)				
	Arsenic ²	Selenium ²	Cadmium ²	Phosphorous ²	Mercury ³
2 (top)	181	<1.25	<1.25	41.0	< 0.020
4	205	<1.25	<1.25	<1.25	< 0.020
7	138	<1.25	<1.25	21.5	< 0.020
10	109	<1.25	<1.25	<1.25	< 0.020
13	102	<1.25	<1.25	<1.25	< 0.020
14 (bottom)	124	<1.25	<1.25	<1.25	< 0.020

¹ Net concentration refers to the difference in concentration between the post- and pre-sorbent samples.

² Elements recovered using HF dissolution and concentrations determined by ICP-OES.

³ Mercury concentration determined by DMA-80.

Table 2-6. Net Contaminant Concentrations for RTI-3 Sorbent

Sample Date	Net Element Concentration in Sorbent ¹ (µg/g)				
	Arsenic ²	Selenium ²	Cadmium ²	Phosphorous ²	Mercury ³
9/15/06	167	2.72	<1.25	<1.25	< 0.020
9/20/06	525	22.6	<1.25	<1.25	< 0.020
10/26/06	713	53.8	<1.25	<1.25	< 0.020
4/19/07 (1,500h)	1480	96.7	<1.25	<1.25	< 0.020
2/25/08 (3,000h)	686	47.5	<1.25	<1.25	< 0.020

¹ Net concentration refers to the difference in concentration between the post- and pre-sorbent samples.

² Elements recovered using HF dissolution and concentrations determined by ICP-OES.

³ Mercury concentration determined by DMA-80.

The analyses for the RTI-3 sorbent shows significant concentration increases for As and Se, but changes to the concentrations for Cd, P, and Hg remain below detection limits. These results are consistent with the results collected by URS Corporation during analysis of the syngas before and after the high-temperature desulfurization system during the field test (see final report for DOE Contract No. DE-AC26-99FT40675). Based on the

concentrations data collected by URS, the RTI-3 sorbent was removing about 97% of the As and 97% of the Se. Based on the URS's measurements of Hg concentration in the syngas, the Hg removed by RTI-3 was less than the experimental errors associated with Hg measurement. Although URS did attempt to measure the Cd concentration in the syngas, the results were consistently below the detection limit. URS did not perform any analysis to determine P concentration in the syngas.

The analyses for the different sorbents from the multicontaminant skid show some very interesting results. The absence of any increase or accumulation of Cd on any of the sorbents is consistent with URS's analysis of the syngas, which demonstrated that the Cd concentration in the syngas was below the detection limit. Commercial Sorbent A demonstrated significant concentration increases for As, Se, and Hg. The concentration of all three of these contaminants decreases rapidly along the length of the bed. Because the syngas was exposed to Commercial Sorbent A first, the expectation was that this sorbent would capture the As. The fact that the sorbent also captured Se and Hg was a positive observation.

Results for the commercial sulfur guard bed sorbent show an increase in the concentration of As, Hg, and P. Furthermore, the concentration profile for these contaminants was relatively constant across the entire length of the sorbent bed. This would suggest that the concentration of these contaminants was large enough to completely saturate the capacity of the sorbent. This was not expected, as the commercial sulfur guard bed sorbent was downstream of the bed containing Commercial Sorbent A. The high level of removal in the sorbent bed with Commercial Sorbent A should have significantly reduced the contaminant concentration in the syngas. The absence of any increase in the concentration of Se across the entire length of the sorbent bed with the commercial sulfur guard bed confirms that Commercial Sorbent A does remove the Se concentration in the syngas to essentially zero. However, Commercial Sorbent A does not seem to reduce the concentration of As and Hg to near zero.

The ammonia and Hg sorbent beds, which are the two subsequent beds through which the syngas passed, show no significant change in concentration for Se, Cd, and Hg. Both of these sorbents show a relatively consistent concentration increase in As along the length of the bed. The interesting feature is that the increase in As concentration in the Hg sorbent bed is greater than that of the ammonia sorbent, even though the Hg sorbent bed is downstream of the ammonia sorbent bed. During laboratory tests of the impregnated carbon with As, this sorbent showed very high capacity for arsine (>5 wt%). One potential

conclusion that can be drawn from the As concentration profile for the Hg sorbent bed is that As is present in the syngas as more than just an arsine species.

These results were extremely valuable in providing pertinent information about

- contaminant removal potential for a variety of different sorbents,
- demonstration and potential synergistic benefits of multicontaminant removal, and
- information about the actual chemical composition of the contaminant species present in coal-derived syngas.

2.2 Mercury Sorbent Development

2.2.1 Mercury Capacity

The field test results described in the previous section and the results from the previous laboratory testing program for Hg sorbent from warm syngas (see final report for DOE Contract No. DE-AC26-99FT40675) provide a strong foundation from which to continue Hg sorbent development. One of the key developmental goals for Hg sorbents for warm syngas applications is to increase Hg capacity in syngas at temperatures greater than 200 °C. Using the specialized testing system developed in DOE Contract No. DE-AC26-99FT40675, a series of potential sorbent candidates was tested to evaluate Hg capacity in simulated syngas mixtures at greater than 200 °C. The composition of these different syngas mixtures is provided in Table 2-7. The testing results are shown in Table 2-8.

Table 2-7. Typical Mercury Test Gas Compositions¹

Test Gas Designation	Composition (nominal vol%)				
	CO ₂	CO	H ₂	H ₂ S	Steam
Clean syngas	51.5	27.0	19.0	0.0	2.5
Dirty syngas	51.0	27.0	19.0	0.5	2.5
CO ₂ /N ₂	11.2	0.0	0.0	0.0	0.0

¹ Theoretical amount of mercury vapor in test gas stream was 280 ppbv.

Of all the materials tested in Table 2-8 below, only two showed higher Hg capacity than the impregnated carbon identified from the earlier testing program. One of these materials was a palladium- (Pd-) based sorbent developed by DOE/NETL's internal research program. This material demonstrated a Hg capacity of 0.353 wt% in dirty syngas (contains 0.5 vol% H₂S).

Table 2-8. Summary of Mercury Capacity Testing

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Capacity (wt. %)	Removal (%)
21	UND/EERC F2ZO	200	Dirty syngas	0.0033	94.3
26	UND/EERC F2ZO	200	Clean syngas	0.0014	67.5
22	UND/EERC F2BO	200	Dirty syngas	NC	-
23	UND/EERC F5BO	200	Dirty syngas	NC	-
24	CuO-Carbon	200	Dirty syngas	0.0018	99.6
25	Cu-O-MnO-Carbon	200	Dirty syngas	0.0005	93.2
28	Pd-Al ₂ O ₃	200	Dirty syngas	0.353	89.2
29	Commercial Sorbent A	200	Dirty syngas	NC	-
30	Commercial Sorbent A	200	Clean syngas	NC	-
34	Impregnated Carbon (Eastman)	200	Clean syngas	0.010	98.9
39	Impregnated Carbon (Commercial)	200	Clean syngas	0.17	90.0
41	Iodated Charcoal	200	Clean syngas	<0.04	-
42	Sud-Chemie Sample D	200	Clean syngas	NC	-
43	Sud-Chemie Sample D	200	Dirty syngas	0.0031	87.5
54	S-Carbon/Sud-Chemie Sample G	200	CO ₂ /N ₂	NC	-
57	S-Carbon/Sud-Chemie Sample G	200	Clean syngas	NC	-
58	Se-Commercial Sorbent A	200	Clean syngas	0.0069	96.5
62	As-Commercial Sorbent A	200	Clean syngas	NC	-
65	SeO ₂ -SiO ₂ -Al ₂ O ₃	30	Clean syngas	3.32	91.0
66	Ga-As Plates	200	Clean syngas	NC	-
67	SeO ₂ -SiO ₂ -Al ₂ O ₃ /Commercial Sorbent A	200	Clean syngas	NC	-
69	gamma-Al ₂ O ₃	200	Clean syngas	NC	-

NC = Not calculated. Analysis results from initial QC cartridge samples indicated that effluent concentration exceeded performance goal for cleaned syngas.

The second promising sorbent material was developed based on the results from analyses of the multicontaminant from the Eastman field test. One of the unexpected results from these analyses was the accumulation of Hg in the sorbent bed with Commercial Sorbent A. This was unexpected, because Commercial Sorbent A had failed to demonstrate sufficient Hg capture during its initial screening test. To confirm these results, the actual Hg capacity of this material was measured in both clean (sulfur-free) and dirty (contains 0.5 vol% H₂S) syngas mixtures. The results confirmed that the Hg capacity of Commercial Sorbent A was below the detection limit.

Because the simulated syngas mixtures did not increase the Hg capacity of Commercial Sorbent A, the other contaminants present in coal-derived syngas must be affecting its Hg capacity. Based on the analyses of Commercial Sorbent A, the two most promising contaminant candidates were As and Se. In a test with Commercial Sorbent A that had been exposed to As, no increase in Hg capacity was observed. Testing of Se sorbents at 200 °C is challenging because of the tendency for Se loss as Se vapor, which is then carried out of the reactor. To overcome this limitation, a Se-based sorbent was tested at

room temperature (where Se vapor loss is not a problem). During this test, the Se-based sorbent had a Hg capacity of about 3.32 wt%.

To demonstrate the potential of Se for Hg capture at 200 °C, a test was conducted with a mixed sorbent bed. This mixed sorbent bed consisted of a top layer of Se-based sorbent and a lower layer of Commercial Sorbent A. Commercial Sorbent A was chosen because the Eastman field test results showed almost complete retention of the Se. Although the results show that this sorbent combination did not reduce the effluent Hg concentration to less than 10% of its inlet concentration, it did remove 60% to 70% of the Hg for 4,560 minutes prior to terminating the test. This is equivalent to capturing approximately 0.5 wt% Hg in the Se-based sorbent.

One challenge in conducting the Eastman field test was procuring sufficient impregnated carbon for the Hg sorbent bed. At the time of the test, scale-up of this material was still being undertaken. Results from an initial scale-up batch prepared showed that the Hg capacity of this material (Set 34) was not the original test sample. Subsequent scale-up efforts were completed on this sorbent for other applications. Tests of a sample from a commercial batch of this sorbent have shown that this sorbent (see Set 39) can now be successfully produced for commercial applications.

2.2.2 Testing for Lower Mercury Effluent Concentration

With the focus of developing warm syngas cleaning technologies for chemical applications, acceptable levels of Hg concentration in the clean syngas were reduced to 5 ppbw for Hg. The sensitivity of the original test procedures developed with this mercury testing system had a detection limit equivalent to a concentration of 34 ppbw in the effluent syngas. Several modifications that were implemented reduced the detection limit for Hg sufficiently to demonstrate the ability to reduce Hg concentration in the syngas. The new testing protocol was used to demonstrate that the leading Hg sorbent was capable of meeting this Hg target.

In Table 2-9, the results from this test show that the impregnated carbon was able to reduce the inlet Hg concentration from 2016 ppbw in the pretreated simulated syngas to below 5 ppbw in the effluent syngas mixture. The Hg capacity for this sorbent at an effluent Hg concentration of < 5 ppbw was 0.14 wt%.

Table 2-9. Mercury Capacity at below 5 ppbw Hg Effluent

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Capacity (wt. %)	Removal (%)
70	Impregnated carbon (Commercial)	200	Clean syngas	0.14	100

2.3 Hydride Testing Program

In contrast to the mercury and cadmium contaminants, the primary contaminants for As, Se, and P are the hydride species, which are arsine (AsH₃), hydrogen selenide (H₂Se), and phosphine (PH₃). All of these hydride species are gases, which require a different testing system than for Hg. The toxic nature of the hydrides also requires similar specialized testing procedures to maintain a safe work environment. Because of these similarities, the same test system could be used with little modification for all three contaminants. To handle the volume of material required for the sorbent development program, two identical systems were built. A description of this testing system and procedures are provided below.

2.3.1 Candidate Hydride Material Preparation

Candidate materials for hydride removal were tested as received, except when the size of the material was reduced by grinding in a mortar and pestle to accommodate the exposure system reactor. The ground material was then sized using a No. 45 (Tyler equivalent 42 mesh) and No. 170 (Tyler equivalent mesh 170) standard test sieve before testing.

2.3.2 Metal Hydride Test System

A schematic of the hydride exposure system is shown in Figure 2-2. The main system components included the hydride gas mixture; a six-port, two-position valve (VICI, Inc.); an exposure chamber; and the backup QC cartridge sample. The hydride source gas mixture was supplied from a certified, compressed gas mixture containing nominal 50 ppm of the hydride in H₂ (Scott Specialty Gases, Inc.). The source gas was metered at 20 mL/min using a variable restrictor flow controller. Other simulated syngas components (CO and CO₂) were supplied by a second compressed gas mixture.

Flow from this mixture, metered at 80 mL/min with an upstream reference flow controller (Condyne, Inc.), was either blended directly with the hydride gas mixture stream or directed through two water-filled impingers maintained at room temperature and then blended with the hydride gas mixture before entering the six-port valve. Typical test gas compositions generated for the hydride exposure tests using this arrangement are shown in

Table 2-10. Dry nitrogen metered at 10 mL/min was supplied to the standby side of the valve to provide a sweep gas for purging the system during standby periods.

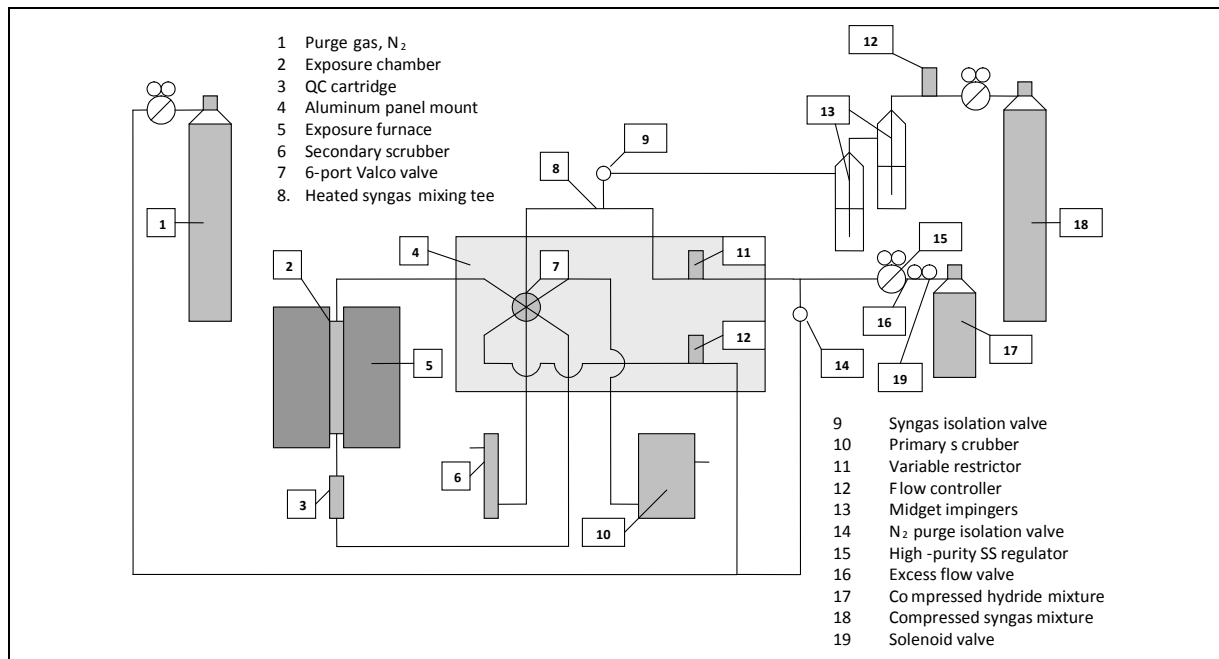


Figure 2-2. Hydride exposure test system

Table 2-10. Typical Hydride Test Gas Compositions¹

Test Gas Designation	Composition (nominal vol%)				
	CO ₂	CO	H ₂	H ₂ S	Steam
Clean syngas	51.5	27.0	19.0	0.0	2.5
Dirty syngas	51.0	27.0	19.0	0.5	2.5
Modified dirty syngas	11.2	38.5	47.0	0.8	2.5

¹ Theoretical amount of hydride in test gas stream was 10 ppm.

The six-port valve, configured with 0.125-in. ports, allowed the system to be placed in either exposure mode or standby mode without changing plumbing connections. Flow diagrams for the exposure and standby modes are shown in Figure 2-3. The valve was maintained at nominal 100 °C using a heated enclosure. All transfer lines leading into and out of the valve were constructed from 0.125-in.-O.D. stainless steel tubing. Like the valve, these lines were kept at nominal 100 °C using heat tapes.

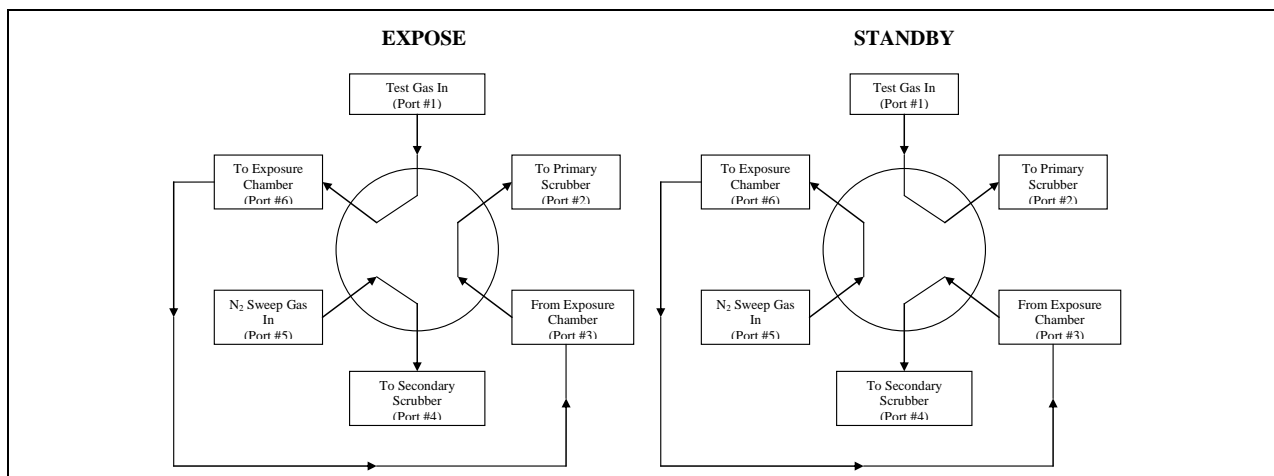


Figure 2-3. Six-port valve flow diagram on the hydride exposure test system

The exposure chamber holding the fixed bed of candidate sorbent during hydride exposures was constructed from stainless steel tubing (0.250 in. O.D. × 12 in. L). A tube furnace was used to maintain the chamber at the desired exposure temperature. Both tube furnace and exposure chamber were oriented vertically so that the simulated syngas containing the target hydride entered the top and exited the bottom of the chamber. Candidate sorbent beds were prepared by positioning a single quartz wool plug in the upper region of the chamber and adding enough sorbent on top of the quartz wool to produce a total bed length of 1 in. For most sorbents tested, this resulted in about 0.3–0.4 g of material, depending on the bulk density of the material.

To prepare the system for exposure tests, the six-port valve was placed in the standby position, and the flow of simulated syngas was started. The syngas flow was adjusted to 80 mL/min, as measured at the outlet of the primary scrubber. The flow of hydride/hydrogen was then started and adjusted to 20 mL/min, resulting in a total flow of 100 mL/min measured at the primary scrubber outlet. To start an exposure test, a backup QC cartridge sample was connected to the outlet of the exposure chamber containing the candidate sorbent, and this assembly was installed in the exposure test system. While the six-port valve remained in the standby position, the exposure chamber and QC cartridge were preheated for 30 min. Dry nitrogen supplied to the standby side of the valve was used to purge room air from the exposure chamber and QC cartridge while these components were being heated. After 30 minutes, the six-port valve position was switched from standby to exposure mode to direct the hydride-containing syngas flow through the exposure chamber and QC cartridge. The flow was measured at the primary scrubber outlet periodically during the exposure.

For safety reasons, the flows of simulated syngas and hydride/hydrogen were stopped at the end of each day. Dry nitrogen metered at 10 mL/min was introduced to the exposure side of the valve, and this flow, along with the house nitrogen supplied to the standby side of the valve, was used to keep all components of the system purged during overnight standby periods.

2.3.3 Hydride QC Cartridge Sampling and Analysis

The QC cartridge was constructed from 0.375 in. O.D \times 2 in L stainless steel tubing. Each QC cartridge was prepared immediately before use by positioning a quartz wool plug at the bottom of the cartridge, and then an appropriate amount of QC sorbent material was added to produce a sorbent bed length of approximately 1 in. The QC cartridge was sampled in the vertical position and preheated to a target operating temperature by heat tape before QC sample collection began. The QC cartridge sorbent and target operating temperature for each metal hydride studied are shown in Table 2-11.

Table 2-11. Hydride Quality Control Cartridge Configuration

Hydride	Sorbent Material	Operating Temperature °C
Arsine	Carulite	200
Hydrogen selenide	Impregnated carbon	60
Phosphine	CuO-Al ₂ O ₃	60

After a 30-minute sampling period, the six-port valve position was changed from exposure to standby, and the QC cartridge was cooled while being purged with nitrogen. Once purged, the QC sorbent was transferred from the cartridge to a 1-dram glass vial and stored in the glass vials at room temperature until analyzed.

2.3.4 Hydride Screening Study Procedure

To determine whether candidate sorbent materials retained the metal hydride, short-term screening studies were conducted by contacting the sorbent with the test gas containing the hydride in humidified, simulated syngas. The experimental exposure temperature ranged from 200 to 250 °C, and the typical exposure time was 30 minutes. After the 30-minute exposure, the system was purged with nitrogen, and the exposed candidate sorbent and QC sorbent were removed and transferred to separate 1-dram glass vials.

2.3.5 Hydride Capacity Study Procedure

Long-term metal hydride capacity studies were conducted at exposure temperatures between 30 and 430 °C. The capacity tests were started by installing the exposure chamber and a fresh QC cartridge in the exposure system and exposing the material to arsine-

containing syngas for 30 minutes. After this exposure time, the QC cartridge was cooled and removed using the nitrogen purge procedure previously described. The tube furnace, however, was allowed to remain around the exposure chamber at the target exposure temperature while the QC cartridge was cooled. (The candidate material was purged with dry nitrogen while heated during the 10-minute QC cartridge cooling period due to the fact that the six-port valve was maintained in the standby position.)

After the QC sorbent was removed, the empty QC cartridge (containing quartz wool only) was reinstalled in the exposure system and preheated. After approximately 10 minutes, the six-port valve position was changed from standby to exposure mode to expose the candidate sorbent to additional amounts of metal hydride. At the end of an exposure day, the six-port valve was switched to standby, and the syngas and hydride/hydrogen flows were stopped. The candidate sorbent was purged with dry nitrogen and maintained at the exposure temperature while in exposure mode during the overnight standby periods.

Additional QC cartridge samples were usually collected once per day to monitor for metal hydride breakthrough. Capacity test exposures were allowed to continue, with nominal exposure periods of approximately 8 hours per day, until the effluent concentration determined by QC cartridge measurements was $\leq 90\%$ of the feed concentration or sorbent capacity exceeded 5 wt%. At this point, a final backup QC cartridge was collected and the exposure test stopped. The exposed sorbent material and the sorbent from the final QC cartridge were transferred to separate 1-dram glass vials and were stored at room temperature until analyzed.

2.3.6 Metal Hydride Candidate Sorbent and QC Cartridge Analysis Procedure

To determine the amount of targeted metal hydride species retained on the candidate sorbent and QC cartridge materials, the entire sample amount was transferred from the 1-dram vial to a 50-mL centrifuge tube, and 10 drops of deionized water were added to the centrifuge tube, along with 2 mL of Unisolv and 0.5 mL of nitric acid. After digesting with heat, the final volume was adjusted with deionized water and the resulting solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the amount of metal retained on the QC sample.

2.4 Arsenic Sorbent Development

2.4.1 Arsenic Capacity

As with the Hg sorbents, one of the primary considerations for evaluating materials for As removal was their capacity. Preliminary economic analysis indicated that sorbents with a minimum As capacity of 2.35 wt% would be economically feasible. In order to facilitate commercialization of the promising sorbents, testing preference was given to existing commercial sorbents and sorbent that demonstrated the ability to capture multiple contaminants simultaneously. Results from testing a wide range of potential materials are provided in Table 2-12. Table 2-12 has a total of six materials that demonstrate an As capacity of > 2.35 wt%. Almost all of these materials also demonstrate an As capacity > 5 wt%.

To effectively identify the most promising sorbent candidates, additional testing of the sorbents was conducted to evaluate the reactivity of the sorbent with clean and dirty syngas. This reactivity toward syngas could be used to assist in rating the pool of promising sorbent, with the highest-ranking sorbents being the least reactive toward syngas. The test results showed that no sorbent material was without reactivity toward syngas. However, most of the activity occurred at the start, probably associated with either reduction or sulfidation of the different sorbent chemical components. Based on the As capacity and reactivity testing, the two most promising As candidates were the impregnated carbon and Commercial Sorbent A, respectively.

Because the Eastman field test of the high-temperature desulfurization system demonstrated that the RTI-3 sorbent had a significant capacity for As, additional testing was conducted to investigate the As capacity for this material. An RTI-3 sorbent sample removed after 1,500 hours of operation in coal-derived syngas was placed in the hydride test system and exposed to a simulated syngas mixture with 10 ppmv of arsine. The results show that the As concentration of RTI-3 at an effluent arsenic concentration of about 1400 ppbv was 0.56 wt% (or 5600 ppmw). Furthermore, the increase in effluent As concentration was relatively slow, indicating that RTI-3 could continue to remove significant amounts of the arsine in the syngas even at about 0.6 wt% loading.

Table 2-12. Summary of Arsine Capacity Testing

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Capacity (wt. %)	Removal (%)
250-3	Impregnated Carbon (Research)	250	Dirty syngas	>1.48	100
200-1	Impregnated Carbon (Research)	200	Dirty syngas	>7.96	100
200-2	Commercial Sorbent A	200	Dirty syngas	2.98	90.1
200-3	Sud-Chemie Sample A	200	Dirty syngas	>5.93	100
200-7	Commercial Sorbent C	200	Dirty syngas	>5.87	95.0
200-8	Sud-Chemie Sample B	200	Dirty syngas	>5.75	99.6
200-9	Pd-Al ₂ O ₃ (NETL)	200	Dirty syngas	>7.16 ¹	97.1
200-10	RTI-3	200	Dirty syngas	0.031 ¹	92.4
200-11	Impregnated Carbon (Commercial)	200	Dirty syngas	>5.76	99.9
200-12	Iodated Carbon	200	Dirty syngas	>8.07	99.7
200-14	Impregnated Carbon (Eastman)	200	Dirty syngas	>7.73	98.6
430-1	RTI-3 (1500 hr Absorber)	430	Dirty syngas	0.56 ¹	86.2

¹ Low material balance for this exposure

One of the more promising materials was the Pd-based sorbent provided by DOE/NETL and developed by their in-house research team. Although this material had a very high As capacity, the results from the capacity test are unique. During the first 4,000 minutes of As exposure, this Pd-based sorbent reduced the arsine concentration to essentially zero. However, at subsequently longer exposure periods, the effluent As concentration would exceed to inlet concentration for a brief period prior to dropping back down to near zero. Because of the uniqueness of this result, the test was continued until several of these brief periods of a high effluent As concentration could be observed. The objective of extending this test was to establish that the sampling and analytical procedures were not responsible for the unique performance.

Final analysis of the sorbent material demonstrated that the sorbent had only 5.5 wt% of As, when the expected amount based on the breakthrough profile should have been about 17 wt%. One potential explanation was that As was leaking out of the sorbent in the nitrogen flow used in hot overnight standby mode. Although testing of this hypothesis did demonstrate that a certain amount of As was removed with the nitrogen during the overnight standby mode, the amount of As removed was not sufficient to explain the large difference between the actual As concentration on the sorbent and the estimated concentration. The DOE/NETL research team was provided with a detailed report of testing with their Pd-based sorbents to help them continue development of these sorbent materials.

2.4.2 Testing for Lower Arsenic Effluent Concentration

Based on the shift in focus of this project to extend the warm syngas cleanup for chemical production applications, the target As concentration in the clean syngas was

lowered to 5 ppbv. The sensitivity of the original test procedure and analytical method would have been equivalent to about 250 ppbv. These sampling procedures and analytical methods were modified to enable achieving a detection limit below 5 ppbv in spite of the high inlet concentration (10,000 ppbv). The results of testing the two primary sorbent candidates with these new modified sampling and analytical methods are shown in Table 2-13. Neither of the two leading sorbent candidates was able to achieve the target As effluent concentration. These results along with the results from the Eastman field test with multicontaminant skid indicate that additional research is necessary to adequately identify an As sorbent for chemical production applications with coal-derived syngas.

Table 2-13. Modified As Testing for 5 ppbv Effluent Concentration

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Inlet concentration (ppbv)	Outlet concentration (ppbv)
200-15	Commercial Sorbent A	200	Dirty syngas	10,000	48.7
200-16	Impregnated Carbon (Eastman)	200	Dirty syngas	10,000	76.9
200-17	Impregnated Carbon (Eastman)	200	Low H ₂ S syngas	10,000	36.6

2.5 Hydrogen Selenide Sorbent Development

2.5.1 Hydrogen Selenide Sorbent Screening

The selection process for potential sorbents for hydrogen selenide focused initially on available commercial sorbents and especially those materials that had demonstrated potential for capturing more than one contaminant. The results of these initial screening tests are provided in Table 2-14. The results show that sorbent materials that have been tested for warm syngas cleanup for ammonia, HCl, and CO₂ as part of the warm syngas cleanup platform showed very limited removal of H₂Se. Other materials like Commercial Sorbent A and RTI-3 showed much higher removal of H₂Se.

Table 2-14. Results from Hydrogen Selenide Screening

Sorbent Material	Recovery (%)
RTI-3	85.6
Commercial Sorbent A	76.5
Trona T-50	12.7
RTI-9E (Li ₂ SiO ₃)	9.43
Sud-Chemie Sample G	84.4
CBV-712	4.07
Impregnated Carbon	52.7
Fe ₃ O ₄ -Al ₂ O ₃	66.4
Commercial Sorbent D	78.6

2.5.2 Hydrogen Selenide Capacity Testing

The promising sorbents identified during these screening tests were used to select a list of materials for capacity testing. Results for these capacity tests are shown in Table 2-15. A number of materials, which include Commercial Sorbent A, NiO-Al₂O₃, and Fe₃O₄-

Al₂O₃, had Se capacities of greater than 4.0 wt%. The results confirm the results obtained with Se capture on Commercial Sorbent A from the Eastman field test with the multicontaminant skid.

Table 2-15. Summary of Hydrogen Selenide Capacity Testing

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Capacity (wt. %)	Removal (%)
200-1	RTI-3	200	Dirty syngas	0.100	94.0
200-2	Impregnated Carbon (Research)	200	Dirty syngas	NC	-
200-3	Commercial Sorbent A	200	Dirty syngas	>5.23	96.1
200-4	Fe ₃ O ₄ -Al ₂ O ₃	200	Dirty syngas	>4.71 ¹	93.0
200-7	NiO-NiAl ₂ O ₄	200	Dirty syngas	>5.77	100
430-1	RTI-3	430	Dirty syngas	0.33 ¹	99.4

NC = Not calculated. Analysis results from initial QC cartridge samples indicated effluent concentration exceeded performance goal for cleaned syngas.

¹ Low material balance for this exposure

Interestingly, RTI-3 and the impregnated carbon did not show very large Se capacities. One potential explanation for the low removal by the RTI-3 sorbent was the 200 °C test temperature. A second test was performed with RTI-3, but at 430 °C, which is similar to the typical operating temperature of the high-temperature desulfurization system. The results show that the Se capacity did increase, but not significantly. The relative rate of increase on the effluent concentration as Se capacity increased was slow, indicating a long and slow breakthrough profile.

2.5.3 Testing for Lower Selenium Effluent Concentration

The target concentration for Se for chemical production is 200 ppbv. The initial configuration for the sampling and analytical procedures had a detection limit that was equivalent to about 240 ppbv. Several slight modifications were made to improve this detection limit. The results of a test with Commercial Sorbent A are shown in Table 2-16. During this test, Commercial Sorbent A effectively reduced an inlet concentration of 10,000 ppbv of H₂Se to about 25 ppbv at the start of the experiment. At the end of the test, the Se loading on the sorbent was 3.42 wt%, but the effluent Se concentration was only 153 ppbv.

Table 2-16. Modified Se Testing for 200 ppbv Effluent Concentration

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Capacity (wt. %)	Removal (%)
200-8	Commercial Sorbent A	200	Dirty syngas	3.42	98.5

2.6 Phosphine Sorbent Development

2.6.1 Material Selection for QC Cartridge

One of the key modifications of the hydride testing system required to enable testing sorbents for phosphine removal was identification of a suitable material for the QC cartridges. Identification of a suitable material was also a very challenging task. Multiple materials were rapidly identified that would capture phosphine. The problem was that these materials inevitably had high inherent concentrations of P. These high P backgrounds made accurate and consistent measurement of small differences in P concentration difficult to impossible. Attempts to prewash charcoal samples demonstrated that the P content of these materials could be reduced to acceptable background concentrations for analysis for low levels of phosphine capture, but this washing step changed the phosphine capture properties, and the change was not consistent even for identical washing conditions. After screening a number of materials, a copper-based material prepared by RTI with a low phosphorous background demonstrated retention of high concentrations of phosphine even in a simulated syngas containing 0.5 vol% H₂S. This copper-based material was used as the sorbent for the QC cartridges for phosphine testing.

2.6.2 Phosphine Sorbent Screening

The standard approach of preferentially screening commercial materials and materials with known multicontaminant capture capabilities was implemented for screening of potential phosphine sorbent materials. Because of the high inherent concentrations of P in the materials, the typical screening test was extended from 30 minutes to 120 minutes. This additional exposure time ensured that significant capture of P by a material could be effectively identified in spite of high P background concentrations. The results from these screening tests are provided in Table 2-17, which shows that four materials demonstrated greater than 85% retention of the P.

Table 2-17. Results from Phosphine Screening Studies

Sorbent Material	Recovery (%)
Commercial Sorbent A	30.3
CBV-712	13.0
Sud-Chemie Sample G	65.2
Commercial Sorbent D	87.1
Sud-Chemie Sample N	62.9
RTI-8	83.2
Sud-Chemie Sample M	79.4
Sud-Chemie Sample L	81.9
Sud-Chemie Sample E	89.0
Sud-Chemie Sample F	85.8
Sud-Chemie Sample A	81.3
Commercial Sorbent E	94.8

2.6.3 Phosphine Sorbent Capacity Testing

Results from the phosphine screening tests were used to select candidate sorbents for capacity testing. The standard phosphine concentration used for these capacity tests was

10 ppmv. However, for two specialized tests, the phosphine concentration in the simulated syngas was 1 ppmv rather than 10 ppmv. The results for capacity testing for phosphine are provided in Table 2-18. Based on these results, at least one material exists that can provide phosphine removal at 200 °C in dirty syngas at a P capacity of > 3 wt%.

Table 2-18. Summary of Phosphine Capacity Testing

Set #	Sorbent	Exposure Temp. (°C)	Matrix	Capacity (wt. %)	Removal (%)
200-1	CuO-Al ₂ O ₃	200	Dirty syngas ¹	>0.091	100
200-2	Commercial Sorbent D	200	Dirty syngas ¹	>0.259	88.3
200-3	RTI-8	200	Dirty syngas	0.40	43.7
200-4	Commercial Sorbent D	200	Dirty syngas ²	3.73	88.6
200-5	RTI-3	200	Dirty syngas	NC	-
200-6	Commercial Sorbent A	200	Dirty syngas	NC	-
200-7	Impregnated Carbon	200	Dirty syngas	NC	-

NC = Not calculated. Analysis results from initial QC cartridge samples indicated that effluent concentration exceeded performance goal for cleaned syngas.

¹ Phosphine challenge concentration was 1ppm instead of 10 ppm.

² Modified syngas matrix used for a portion of this exposure. Backup QC cartridge results indicated periodic spikes in the phosphine effluent concentration.

2.7 Cadmium Sorbent Development

2.7.1 Cadmium Test System

Based on thermodynamic calculations, the most stable Cd species in warm syngas is metallic Cd vapor. To effectively generate a simulated syngas mixture with Cd vapor, the design of the Cd test system needed to include a Cd vapor generator. The simplest design concept for this Cd vapor generator was to use a furnace to maintain a bed of Cd metal at a fixed temperature to generate a known vapor pressure of Cd and to continuously remove this Cd vapor with a sweep gas of CO₂.

A schematic of the cadmium exposure system is shown in Figure 2-4. The main components of the system included a cadmium vapor generator tube maintained at a constant temperature in a horizontally mounted tube furnace, an exposure chamber maintained at a constant temperature in a vertically mounted tube furnace, and a QC cartridge sample. The Cd vapor generator tube consisted of a bed of cadmium metal held at the center of a 0.25 in O.D. by 12 in. long stainless steel tube by two quarts wool plugs. The system was designed so that when heated, the Cd metal would vaporize and be carried downstream by a flow of CO₂ metered at 50 mL/min with an electronic mass flow controller. The cadmium vapor was then blended with a 60-mL/min flow of simulated

syngas supplied by a compressed gas mixture before entering the exposure chamber containing the candidate sorbent.

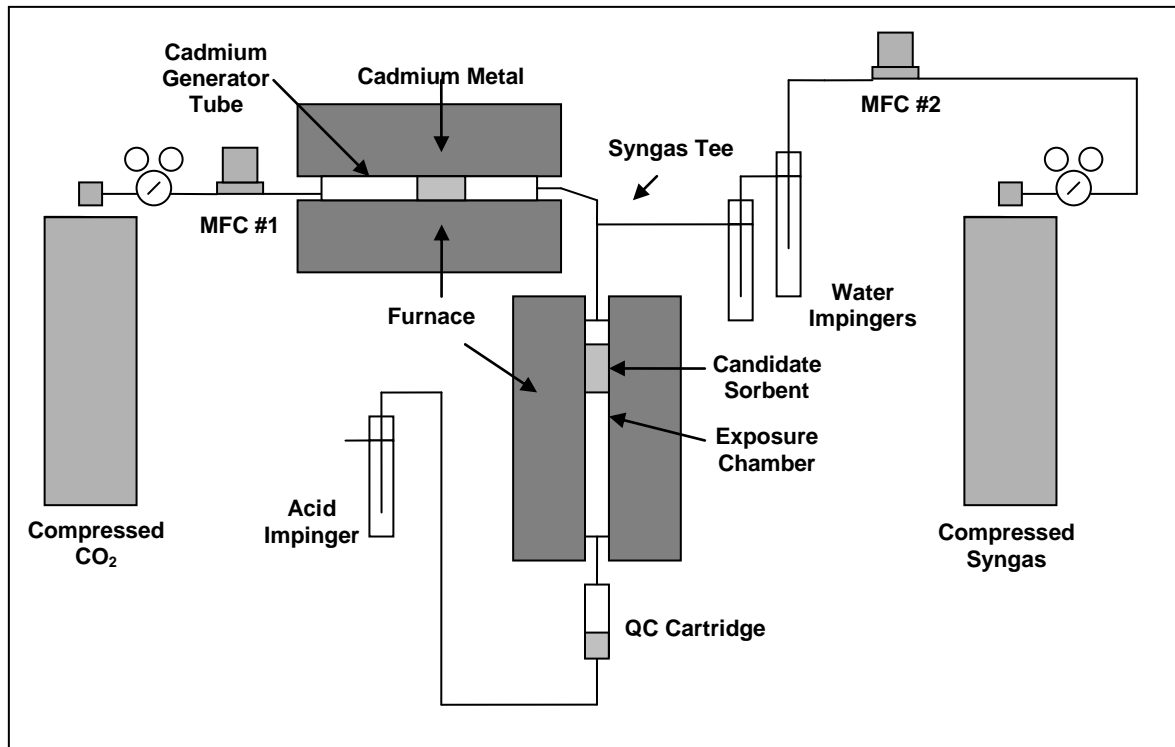


Figure 2-4. Cadmium Exposure System

Once the Cd exposure system was assembled, preliminary tests were conducted to demonstrate that the simulated syngas mixture did contain a known amount of Cd and that the concentration of Cd in the syngas was consistent. To effectively capture the Cd vapor, the syngas was forced through an impinger filled with an acidic solution. In the first tests, no Cd vapor was detected. Because of the potential for the system to accumulate Cd prior to becoming saturated, the acid impinger was moved directly to the outlet of the Cd vapor generator. Even at the outlet of the Cd vapor generator, no Cd vapor was detected.

A series of parametric tests was conducted to assist in defining the specific operating conditions necessary for consistently generating Cd vapor stream of known concentration. This series of parametric tests investigated

- operating temperatures up to a temperature within 10 °C of the melting point of Cd, replacing the original Cd metal with a fresh sample,
- using nitrogen as a sweep gas rather than CO₂, and
- pre-reduction treatments for the Cd metal to reduce or remove any potential surface oxide layer.

Although this parametric testing did manage to generate some Cd vapor, the concentration was significantly less than expected based on vapor pressure calculations and was not consistent.

Based on these results and the results from the Eastman field test, there is little evidence to suggest that CD vapor is a significant contaminant in coal-derived syngas.

SECTION 3 DEVELOPMENT OF WARM CO₂ CAPTURE TECHNOLOGY

3.1 Novel R&D Approach

3.1.1 Screening Criteria for Novel Sorbent Materials

Lithium silicate-based sorbents consistently demonstrated exceptional performance toward CO₂ capture from syngas. The challenge was specifically the regeneration. One of the primary reasons for this challenge is the low equilibrium partial pressure of CO₂ for lithium silicate at temperatures from 300 °C to 600 °C. However, this low CO₂ equilibrium partial pressure also makes lithium silicate a good sorbent for removing CO₂.

From this analysis, the ideal CO₂ sorbent for high-temperature application would be a material with a low equilibrium partial pressure between 200 °C and 400 °C and a significantly higher CO₂ equilibrium partial pressure at temperatures from 300 °C to 500 °C. For a fully shifted syngas stream in standard reference IGCC plants, the CO₂ partial pressure is approximately 300 psi. To achieve DOE's target CO₂ capture of 90%, the CO₂ partial pressure in the syngas must be reduced to roughly 30 psi. Alternatively, to effectively regenerate at system pressure, the equilibrium CO₂ partial pressure for regeneration would need to be >300 psi.

Using available thermodynamic properties, the equilibrium CO₂ partial pressure for a variety of different solids was calculated. Results of this effort, plotted in Figure 3-1, show that a number of different materials have equilibrium CO₂ partial pressure curves that fit the desired profile for an effective CO₂ sorbent. And, with this approach, the CO₂ product can be generated at high pressure, reducing the parasitic energy load for compression associated with capture and sequestration of CO₂.

Screening materials to demonstrate their ability to capture CO₂ at appropriate conditions requires testing at pressure. Unfortunately, the atmospheric TGA that was used in the original screening of sorbent materials would not be effective for testing at pressure. Therefore, our high-pressure TGA system was modified to enable sorbent screening. Because loading and unloading the high-pressure TGA was relatively time consuming, two additional high-pressure reactor systems were modified to assist in material screening tests. A description of these testing systems is provided in Section 3.2, Experimental Systems.

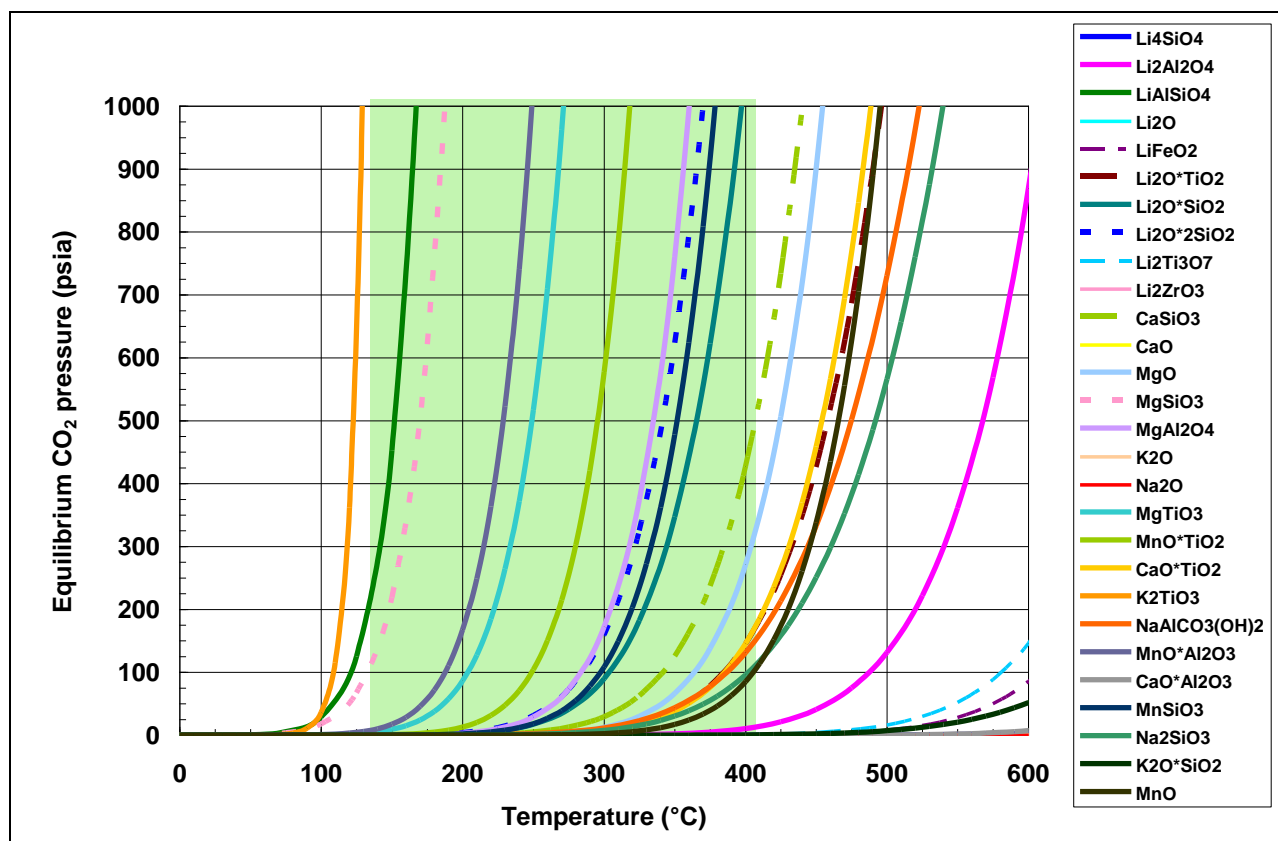


Figure 3-1. Thermodynamic equilibrium curves for CO₂ partial pressure with highlighted area showing materials meeting screening selection criteria

3.1.2 CO₂ Recovery for Lithium Silicate Regeneration

The existing body of data available for our lithium silicate-based sorbents had already demonstrated CO₂ adsorption performance from hot syngas during multicycle testing. The specific strengths of this adsorption performance were fast CO₂ adsorption kinetics, which allowed >90% removal, no reduction in CO₂ adsorption performance in the presence of high sulfur concentrations between 0.5 and 1 vol%, and performance stability over multiple adsorption and regeneration cycles.

The challenge lay in regeneration of the lithium silicate sorbent. Temperature swing was impractical because the very high temperature required consumes the high value heat and presents significant technical challenges in transferring the reaction enthalpy into the sorbent bed. Regeneration by concentration swing, although repetitively demonstrated in our bench-scale sorbent testing system, required too much steam for producing a high-purity CO₂ product or resulted in a dilute CO₂ product that cannot be used for sequestration.

A potential solution is to implement a CO₂ recovery process in which a second sorbent is used to effectively recover the dilute CO₂ from the regeneration effluent. This CO₂ recovery process was conceptualized based on the adsorption properties of zeolite materials. In this process, the dilute low-pressure effluent from lithium silicate regeneration is contacted with a sorbent. This sorbent selectively adsorbs the CO₂ at low temperature (<100°C). When saturated with CO₂, the sorbent is then pressurized with CO₂. After pressurization, the sorbent is heated. This heating results in a decrease in the adsorption capacity of the sorbent, which releases CO₂. The sorbent is then depressurized and cooled. At this point, the sorbent has been regenerated. The specific steps involved in the proposed CO₂ recovery process are shown in Figure 3-2.

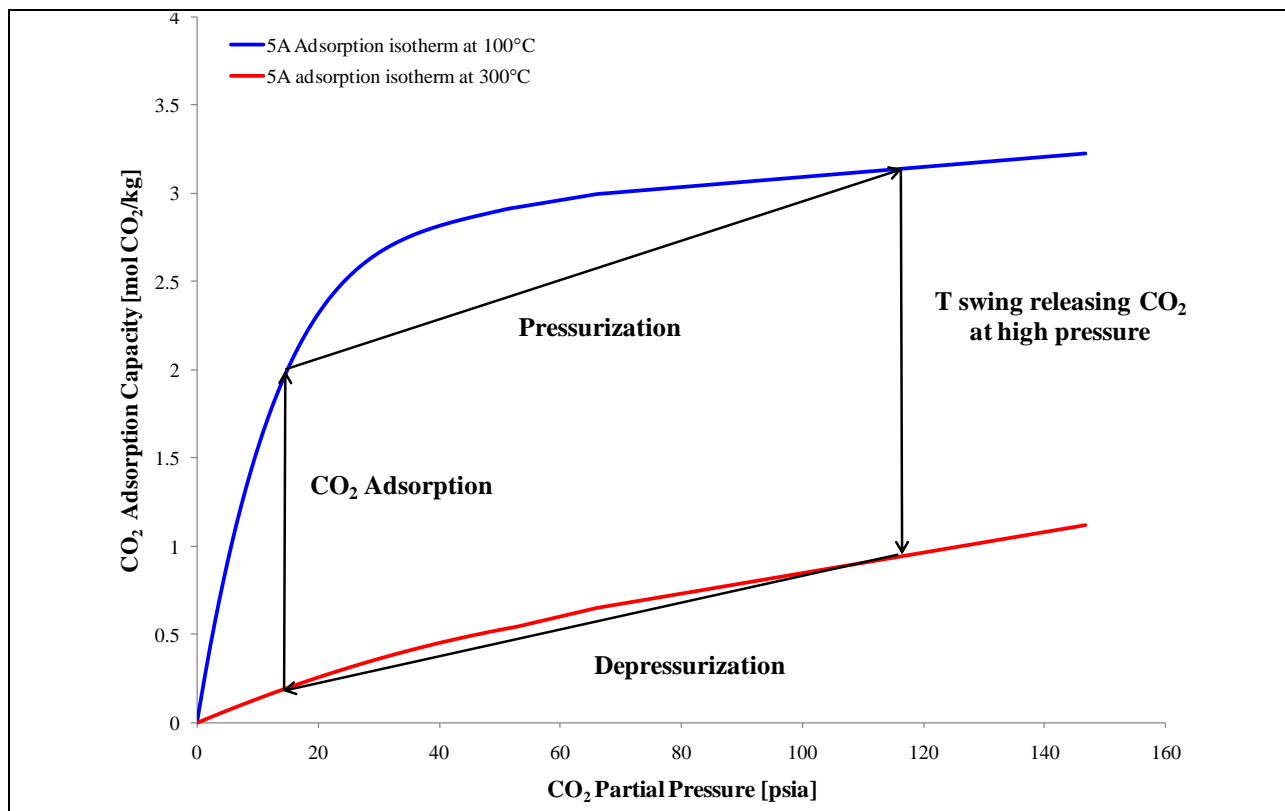


Figure 3-2. Processing steps in proposed CO₂ recovery process

Key performance criteria for the sorbent for the CO₂ recovery process are

- High CO₂ capacity at low CO₂ partial pressures
- High CO₂ capacity at low temperatures
- Low CO₂ capacity at higher temperatures (200 °C – 300 °C)
- Selective adsorption of CO₂ over water.

To effectively conduct R&D on this CO₂ recovery process, testing focused on evaluating the optimal regeneration conditions for the lithium silicate-based sorbent and developing the adsorption isotherms for promising zeolite materials over a temperature range of 100 °C to 300 °C.

3.2 Experimental Systems

High-pressure sorbent testing systems were required to effectively test at temperature and pressure conditions that would meet the target criteria for regeneration. Three existing reactor systems were modified for the specific purpose of testing sorbent materials for this project.

3.2.1 High-Pressure TGA

TGAs monitor the weight change of a solid sample in response to changes in gas composition and temperature. Specialized high-pressure TGAs (HP-TGAs) measure weight changes under high-pressure conditions. The CAHN TG-151 available at RTI has a reactor system suitable for testing at up to 800 °C and 600 psig. This TGA is pictured in Figure 3-3.

Specific CO₂ removal conditions were selected based on a typical General Electric syngas composition that has been shifted under optimal conditions to enable capture of >90% of the CO₂ from the syngas. Under these conditions, the CO₂ partial pressure should be approximately 300 psi. To achieve 90% removal of this CO₂, the effluent syngas stream must contain <30 psig of CO₂. For regeneration, the sorbent must be able to release the CO₂ to achieve a CO₂ partial pressure of >100 psig. One of the key parametric variables in regeneration is reaction temperature.

RTI's CAHN TGA was modified to facilitate materials screening tests under these conditions. These modifications also addressed technical challenges encountered during commissioning and initial operation. Table 3-1 lists the challenges encountered along with the solutions implemented.



Figure 3-3. RTI high-pressure TGA (HP TGA) modified for testing CO₂ sorbent materials

Table 3-1. Problems and Solutions Encountered with HP-TGA Testing

Problem	Solution
Control system crashing	The original control board was found to be faulty. A new control system was designed, installed, and validated.
Mass signal noise ($\pm 15\text{mg}$)	The noise in the mass signal was caused by the back pressure control valve. New control parameters were installed in the control software, reducing a significant portion of the noise.
Buoyancy (He-CO ₂)	The mass of the sample decreased (40%) upon the introduction of CO ₂ into He. The large buoyancy difference between the He and He/CO ₂ gas mixtures was determined to have caused the inconsistency. Helium was replaced with argon, reducing the buoyancy effect caused by gas composition.
Buoyancy (temperature)	The mass of the sample was found to linearly increase with temperature during the regeneration cycle. This increase is due to the decrease in the surrounding gas density with temperature. To reduce this effect, additional weight was added to the sample holder, reducing the buoyancy effect of the gas.

3.2.2 Automated Micro-reactor System

Although the HP-TGA proved successful for screening at optimal conditions for a regenerable CO₂ sorbent, a number of limitations inherent with the HP-TGA reduced its practical value as an effective screening tool. The two most important limitations were (1) the time required to effectively load and unload sorbent samples and (2) the specific data collected to monitor sorbent performance was weight change of the sorbent. To facilitate screening materials and promote the development of promising materials identified during screening, an existing reactor system equipped with two fully automated reactors was modified for screening and testing CO₂ sorbents. This system is shown in Figure 3-4.

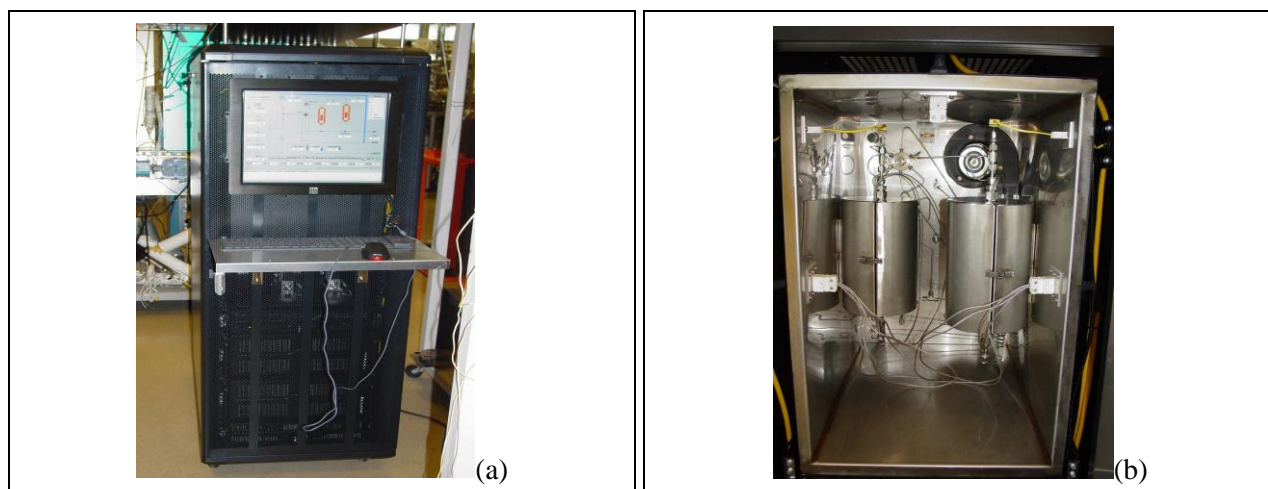


Figure 3-4. RTI's automated micro-reactor (AMR) system: (a) front view and (b) reactors

Because this system was automated and had two reactors, up to four cycles (CO₂ adsorption and regeneration) could be completed for two samples in a 24-h period, significantly

increasing the number of samples that could be tested. The reactors, shown in Figure 3-4(b), consisted of approximately 6-inch lengths of ½-inch stainless steel tubing. The volume of sorbent that could effectively be contained in these reactors was about 4 g. The system was capable of testing at a total pressure of 350 psig, temperatures up to 600 °C, and space velocities up to 9,000 h⁻¹ (at standard temperature and pressure [STP]). Test gases consisted of a CO₂/N₂ mixture for adsorption and N₂ for regeneration. The CO₂ concentration in effluent gas was monitored with a continuous CO₂ analyzer.

3.2.3 Micro-reactor System

The schematic for RTI’s micro-reactor system is shown in Figure 3-5. The reactor for this system consists of a 16-in length of ½-in SS tube that can hold between 1 and 10 g of sorbent material. The operating limits for this system are 700 °C and 500 psig. This gas feed system for this micro-reactor system was designed to enable testing of CO₂ adsorption in simulated syngas mixtures containing up to 60 vol% steam. As with the automated micro-reactor system, the CO and CO₂ reactor effluents were monitored with a continuous analyzer.

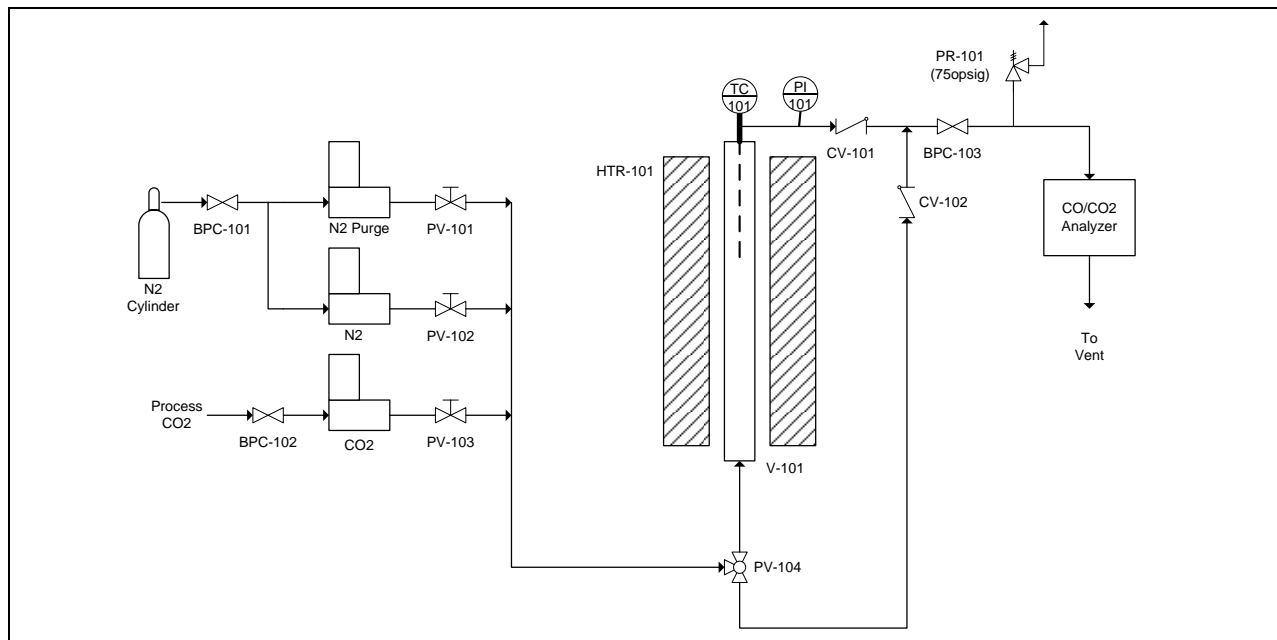


Figure 3-5. Schematic of RTI’s micro-reactor system as configured for CO₂ testing

3.3 Results

3.3.1 CO₂ Recovery Process

3.3.1.1 Zeolite Evaluation and Sorbent Development

An initial evaluation of potential sorbents that would meet the specifications required for a CO₂ recovery process indicated that the most promising sorbents were zeolites. A number of commercial samples of 5A and 13X zeolites were procured. Based on the recommendation of the zeolite vendor, a modified 13X (13X Z10 10ND) was also procured. The vendor indicated that their evaluation had shown this modified 13X zeolite had better CO₂ adsorption properties (over a wide range of CO₂ partial pressures).

Because a full adsorption isotherm was beneficial for the evaluation of these materials, the results from two different testing systems were combined to produce a full CO₂ isotherm from no CO₂ partial pressure (0 psi) to about 130 psi of CO₂ partial pressure. The atmospheric TGA was effectively used for adsorption below 14.7 psi of CO₂ partial pressure. The micro-reactor system was used to obtain the adsorption results at >14.7 psi of CO₂ partial pressure. Results from this testing are shown in Figure 3-6. Although both systems could provide results at close to 14.6 psi CO₂ partial pressure, the results from the reactor system were less accurate at this low CO₂ partial pressure, which explains the discontinuity in Figure 3-6 at 14.6 psi CO₂ partial pressure.

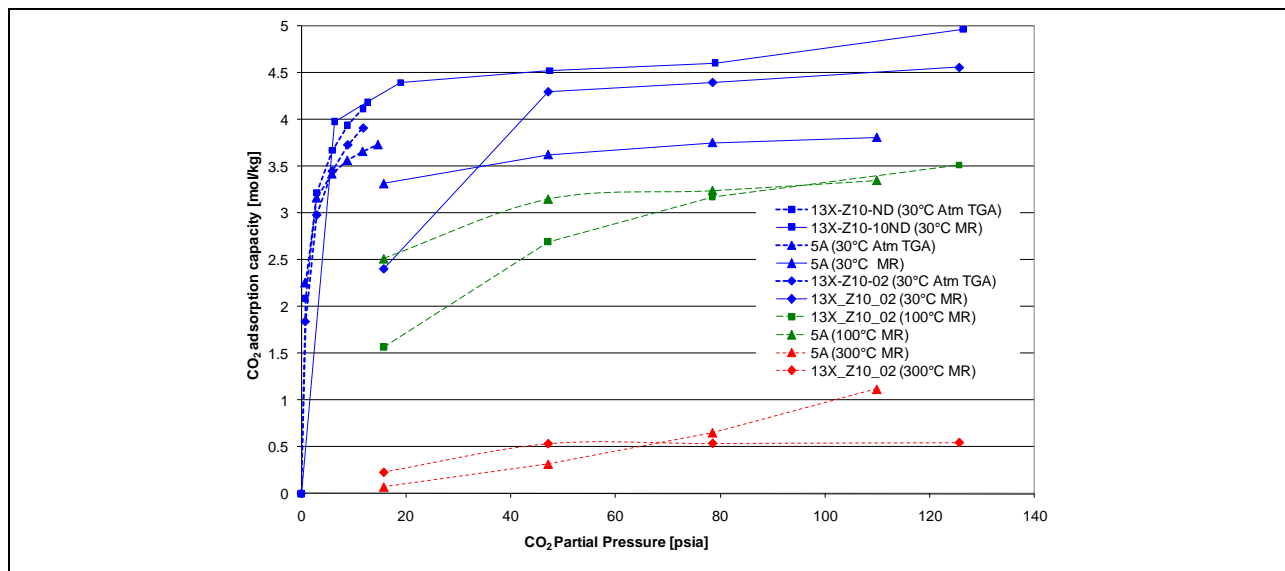


Figure 3-6. Adsorption profiles for 5A and 13X zeolites at different temperatures between 30 °C and 300 °C

As shown in Figure 3-6, at about 30 °C, the CO₂ adsorption ranged from about 3.5 mol of CO₂/kg of adsorbent for the 5A zeolite to about 4.5 mol of CO₂/kg of adsorbent for the 13X zeolite. At 300 °C, the CO₂ adsorption capacity for both zeolite materials decreased significantly and was roughly between 0.5 and 1 mol of CO₂/kg of adsorbent. The results for the 13X zeolite at 100 °C show a CO₂ adsorption capacity of between 2.5 and 3 mol of CO₂/kg of adsorbent. These results show that, if the CO₂ partial pressure in the off-gas from the lithium silicate regeneration is about 14.7 psia, the proposed CO₂ recovery process could be technically feasible.

The zeolites were tested with a mixture of CO₂ and steam to determine the selectivity of the zeolite material for CO₂ adsorption. These results, shown in Figure 3-7, indicate that the 5A zeolite material was more selective for CO₂ and that no significant difference in the CO₂ adsorption capacity was observed when steam was introduced. Therefore, if steam is used as an inert purge in the regeneration of lithium silicate, the CO₂ concentration in the regeneration off-gas stream can be increased by condensation of the steam. These results could be used to expand the potential operating window for the CO₂ recovery process.

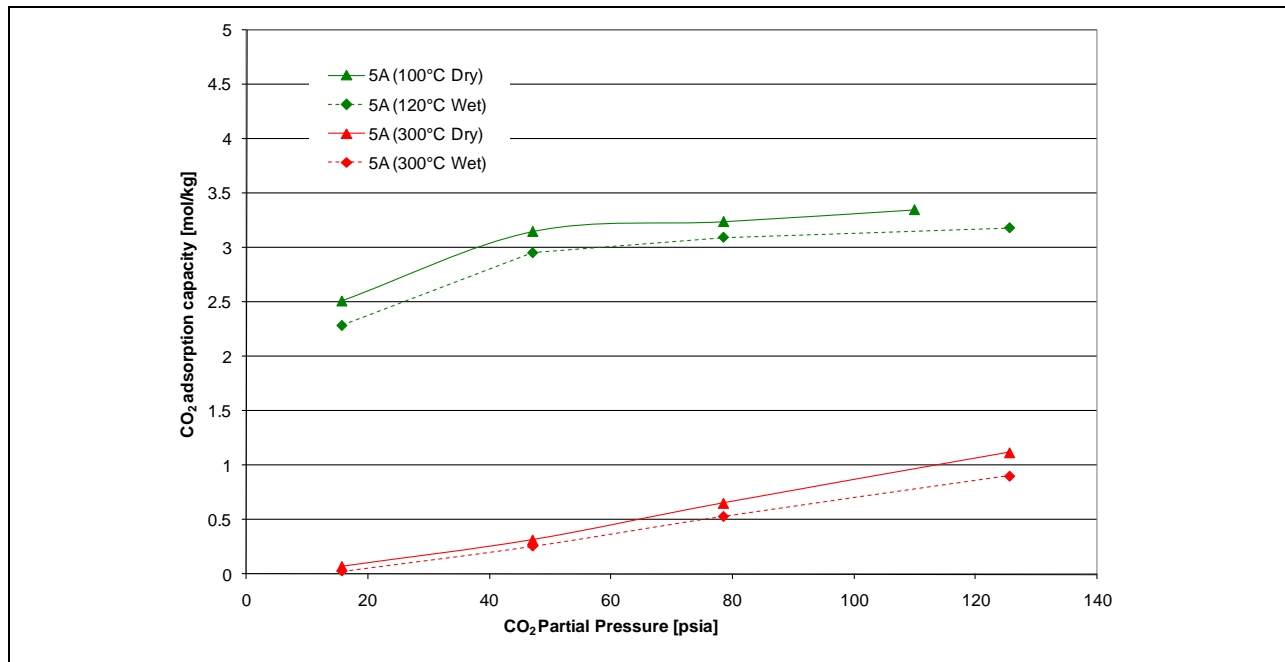


Figure 3-7. Effect of steam on CO₂ adsorption for Zeolite 5A

Because achieving the highest CO₂ adsorption capacity at the lowest partial pressure of CO₂ was an important feature for these zeolite materials in the CO₂ recovery process, the potential for improving the commercial zeolite adsorbents was investigated by modifying the zeolites by ion exchange. The CO₂ adsorption profiles for these modified sorbents are shown in Figures 3-8 and 3-9. For the 5A zeolites, two of the exchanged zeolites (B and D) showed

significantly lower CO₂ adsorption capacity. The CO₂ adsorption capacity for the other two ion-exchanged zeolites (A and C) was essentially identical to the original 5A zeolite.

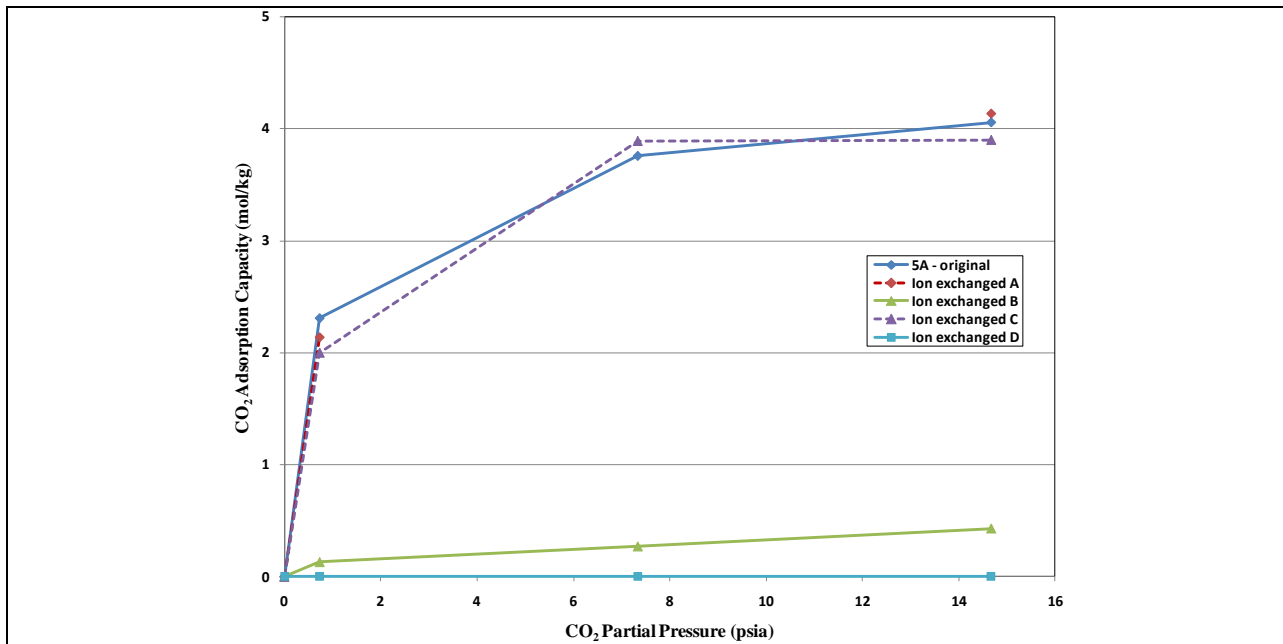


Figure 3-8. CO₂ adsorption capacities for ion-exchanged 5A zeolite samples

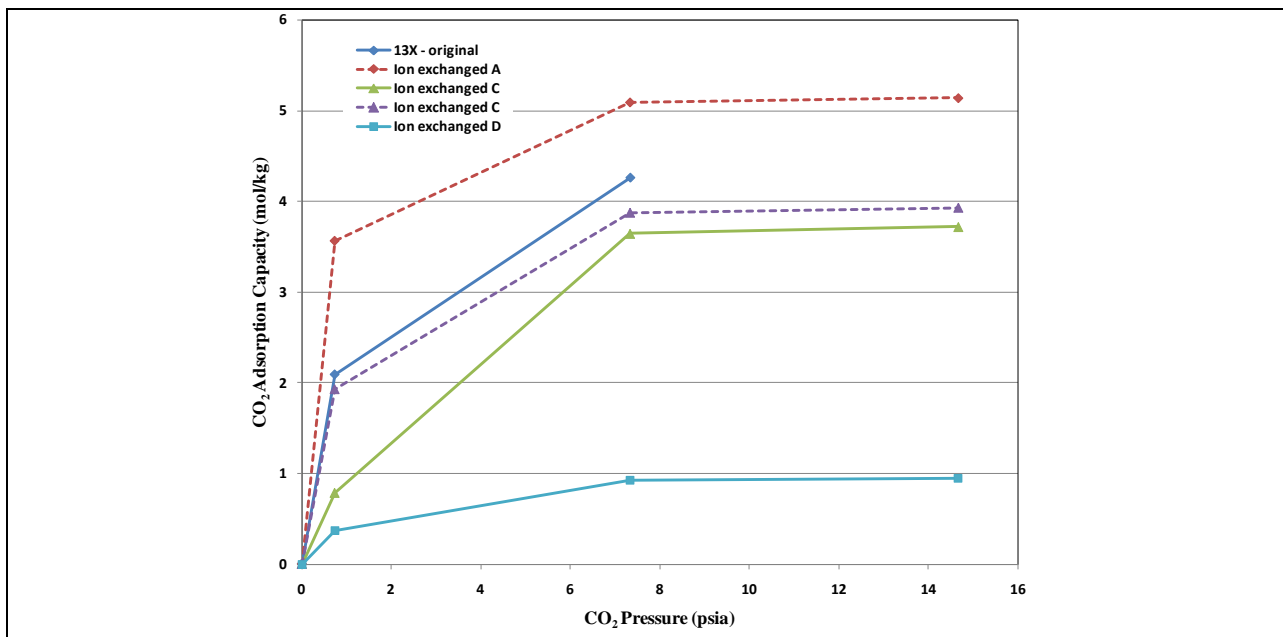


Figure 3-9. CO₂ adsorption capacities for ion-exchanged 13X zeolite samples

For the 13X zeolites, the ion-exchanged sample A had a higher CO₂ adsorption capacity than the original 13X, whereas exchanged zeolite D had a much lower CO₂ capacity than the

original 13X. Based on physical analysis of these materials, a correlation between the surface area, pore volume, and CO₂ adsorption capacity was identified.

3.3.1.2 Lithium Silicate Regeneration

In parallel with the work on the zeolite materials, lithium silicate sorbent testing was conducted to evaluate the ability to generate a suitable regeneration off-gas for the CO₂ recovery process. The primary objective was to obtain as high a CO₂ partial pressure in the regeneration off-gas as possible. The key operation parameters investigated were inert purge flow rate, using mixtures of N₂/steam as an inert, and the regeneration temperature.

The results from concentration swing-based regenerations with N₂ and N₂/steam mixtures at 600 °C are shown in Figures 3-10 and 3-11. The three most predominant results shown are (1) the CO₂ concentration in off-gas is very low (<1 vol%), (2) the CO₂ concentration in the off-gas is inversely proportional to flow, and (3) the time required for regeneration decreases significantly with increasing flow rate. The only effect of adding 15 vol% steam to the purge gas was a slight (<10%) increase in the CO₂ concentration in the off-gas. Thus, the shortest regeneration times occur at the highest purge rates and produce the lowest concentration of CO₂. These results confirm the result from previous testing that extremely high steam-to-CO₂ ratios would be required to effectively regenerate lithium silicate sorbents and produce a high-purity CO₂ byproduct.

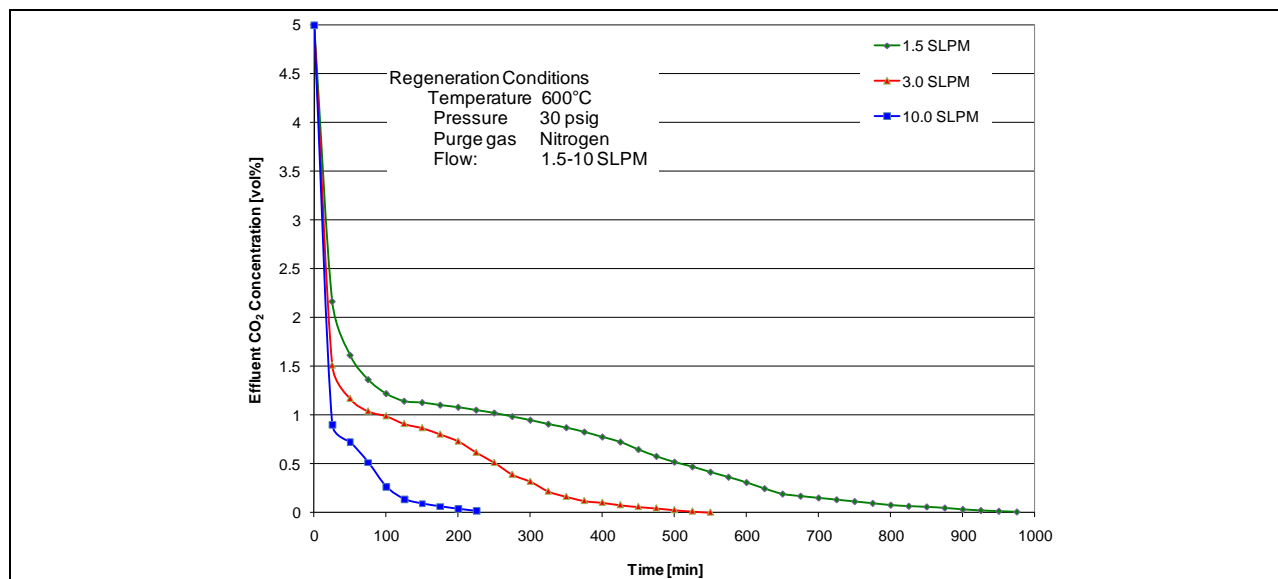


Figure 3-10. Effluent CO₂ concentration for regeneration by concentration swing at different nitrogen flow rates

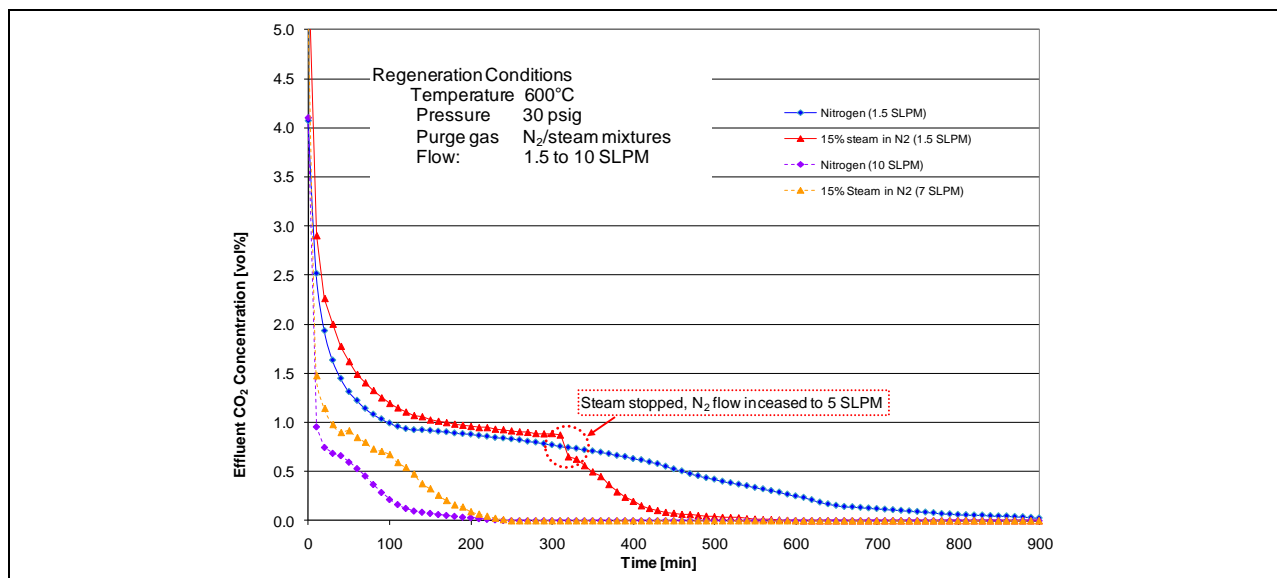


Figure 3-11. Effluent CO₂ concentrations during regeneration by concentration swing with N₂/steam mixtures

The results in Figures 3-10 and 3-11 were surprising because the CO₂ concentrations in the off-gas were significantly lower than expected based on thermodynamic equilibrium calculations. The regeneration profiles shown in Figures 5-5 and 5-6 suggest that mass transfer is limiting the regeneration. A theoretical explanation for this mass transfer limitation is that the promoter used to enhance the CO₂ capacity of the lithium silicate sorbents is responsible for mass transfer within the lithium silicate structure. For CO₂ capture, the promoter helps maximize the CO₂ capacity. However, during regeneration, transfer of the CO₂ from within the lithium silicate structure to the surface is facilitated by the promoter and can only proceed at a fixed rate.

Figure 3-12 shows results of several tests conducted at higher regeneration temperatures. The higher temperatures did result in higher CO₂ concentrations in the off-gas, but, even at a temperature of 750 °C, the CO₂ concentration in the off-gas was still only a fraction of the concentration necessary for effective integration with the zeolite-based CO₂ recovery process.

The general conclusion from testing conducted for the CO₂ recovery process was that zeolites could potentially be used for a CO₂ recovery process, but that generating an acceptable off-gas from concentration swing regeneration of lithium silicate was not practical using temperature or inert purge rates. For this reason, further testing and development for the CO₂ recovery process was discontinued.

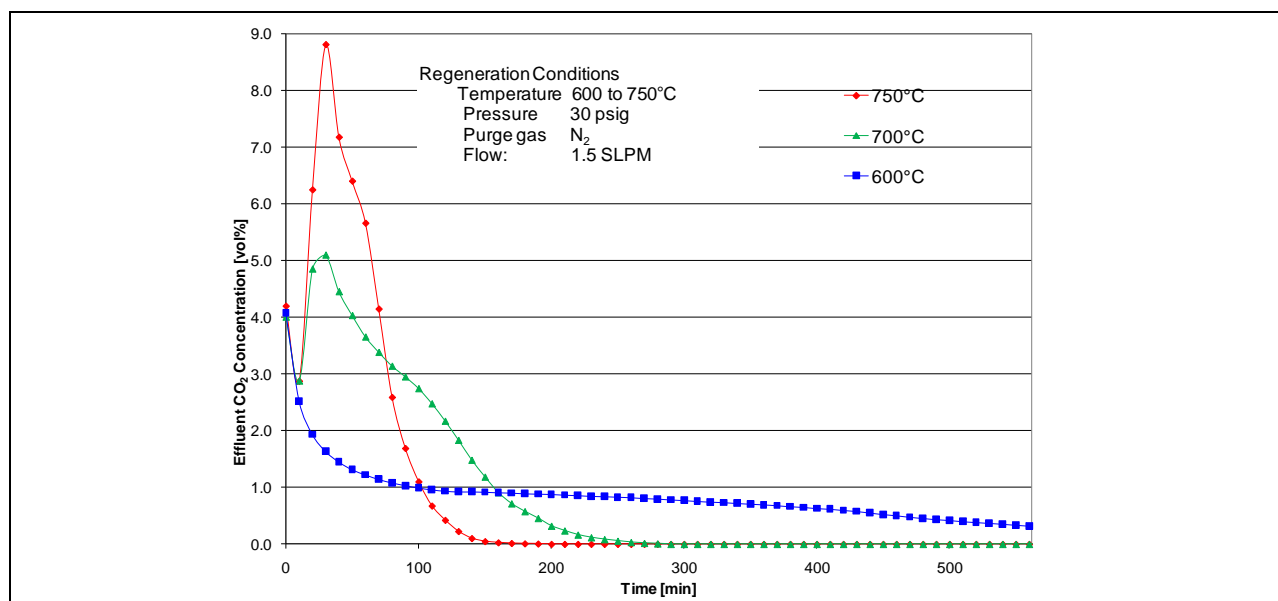


Figure 3-12. Effluent CO₂ concentration during regeneration by concentration swing at different temperatures

3.3.2 CO₂ Sorbent Development

3.3.2.1 Material Screening

A number of different materials were prepared and tested in either the HP-TGA or the AMR system. Table 3-2 presents results for some of the most promising materials. An Mg-Li-based material showed the most promising performance. Using the AMR system, testing of this material was expanded from the standard 3-cycle test to an 11-cycle test. During this test, this material showed consistent adsorption and regeneration performance producing a CO₂ byproduct during regeneration at pressures as high as 45 psig. This limit was imposed by the analytical system measuring the CO₂ in the micro-reactor effluent and not the material.

Table 3-2. CO₂ Test Results from Micro-Reactor System

Material	Temperature (°C)	CO ₂ Adsorption (wt%)
CaSiO ₃	200	0.23
CaSiO ₃	300	0.03
MgTiO ₃	250	0.41
Mg ₂ SiO ₄	250	0.24
MgAl ₂ O ₄	250	0.21
Mg-Li	250	4.49
MnO	250	0.14
Zn(OH) ₂	250	1.79
Mn(OH) ₂	250	1.19
MgO	300	2.03
Mg(OH) ₂	250	0.34

The screening tests with MgO and Mg(OH)₂ also indicated some promise for a CO₂ sorbent material. However, on a stoichiometric basis, the observed capacities were significantly below their theoretical values (110 wt% based on MgO and 76 % based on Mg(OH)₂). The low capacity of these samples was assumed to be a result of low reactivity with CO₂. Based on this

assumption, a series of MgO-based sorbents were prepared with the intention of making them significantly more reactive for CO₂ adsorption.

The results of an HP-TGA screening test for one of these materials are shown in Figure 3-13. During the first 60 minutes of the test, the MgO sample was exposed to a CO₂/N₂ mixture with a CO₂ partial pressure of 147 psig (total operating pressure 200 psig). The weight of the MgO was observed to increase rapidly, indicating that the MgO was reacting with the CO₂ to form MgCO₃. After 60 minutes, the MgO sample was heated to 500 °C. When the MgO sample reached 500 °C (about 80 minutes into the test), the MgO sample began to lose weight, indicating regeneration of the MgO by decomposition of the MgCO₃, which releases CO₂ and causes a weight decrease. Because the gas composition had not been changed, the MgO sample was regenerating at a CO₂ partial pressure of 147 psig. At about 160 minutes into the test, the CO₂ flow was stopped and the sample was purged with pure N₂. The MgO sample lost additional weight during this inert purge, returning to roughly the weight of the sample at the beginning of the test. With essentially no CO₂ partial pressure in the regeneration gas, any remaining MgCO₃ decomposed, releasing CO₂ and regenerating MgO.

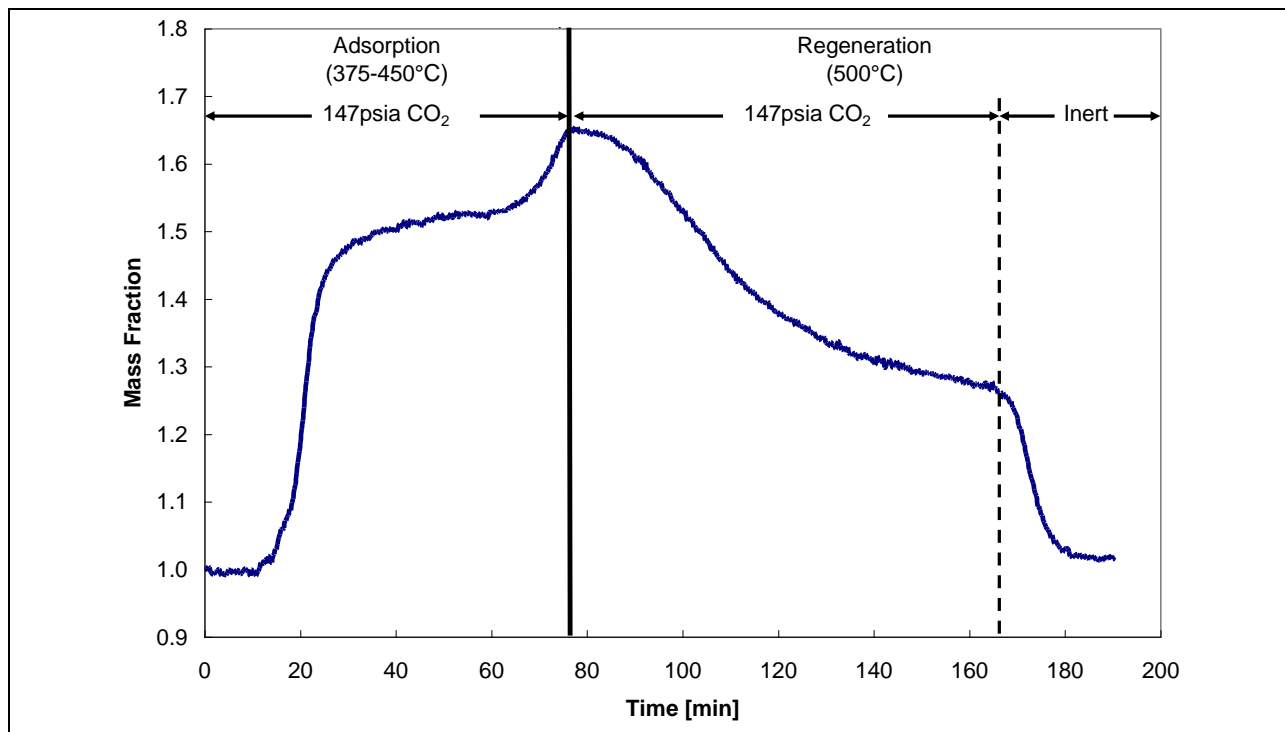


Figure 3-13. HP-TGA test of RTI-prepared “reactive” MgO sample

Based on analysis of the information in Figure 3-13, this MgO sample had a CO₂ capacity of roughly 56 wt%. Furthermore, the dynamic CO₂ capacity for regeneration producing a CO₂ byproduct with CO₂ pressure of 147 psig was about 30 wt%. The MgO sample also seemed to be fully regenerable based on the return to essentially the same initial starting weight after regeneration with an inert purge.

3.3.2.2 Promoter Screening and Evaluation

Additional investigation into the physical and chemical properties of these “reactive” MgO samples identified that small amounts of additional compounds were introduced into the MgO during preparation. These compounds acted as promoters for the reaction between MgO and CO₂. Additional investigation on promoter effects included chemical composition of the promoter, concentration of the promoter, and effect of the starting Mg compound. Analysis of the original active MgO materials indicated that the preparation method had introduced two components that could be active promoters. The results for testing with MgO materials made with specific amounts of these two promoters are shown in Figures 3-14 and 3-15.

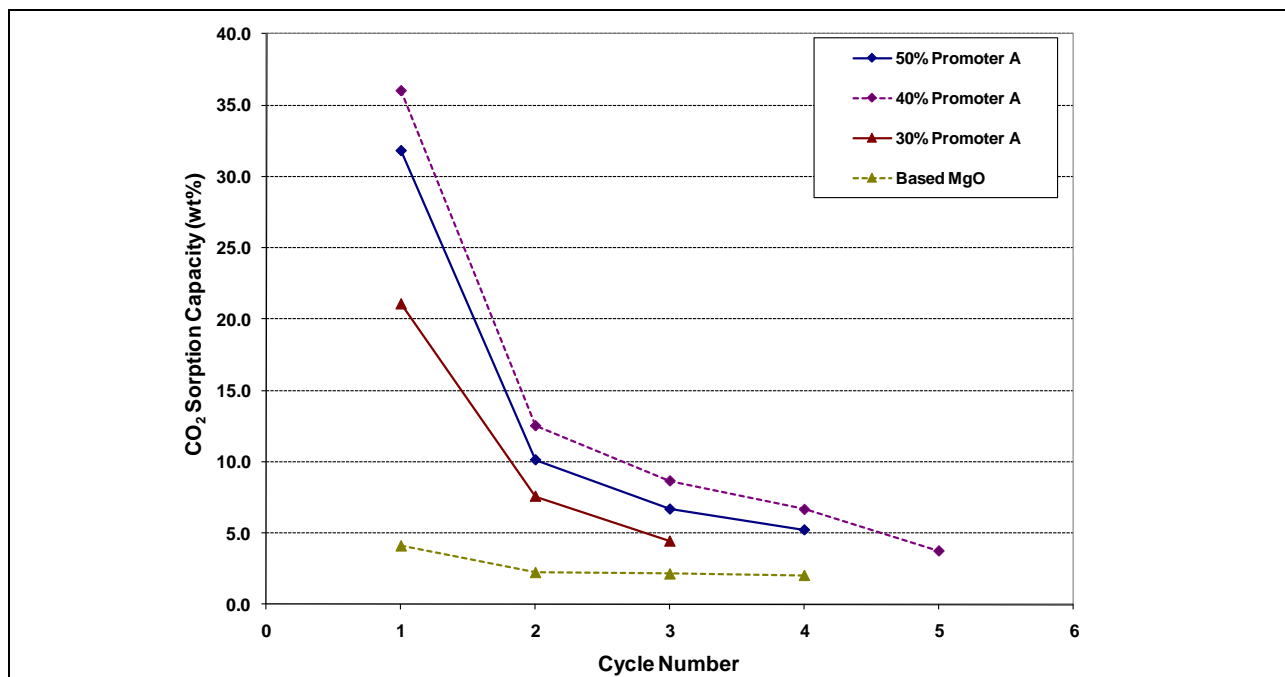


Figure 3-14. Parametric testing of Promoter A concentration on CO₂ capture performance for promoted MgO

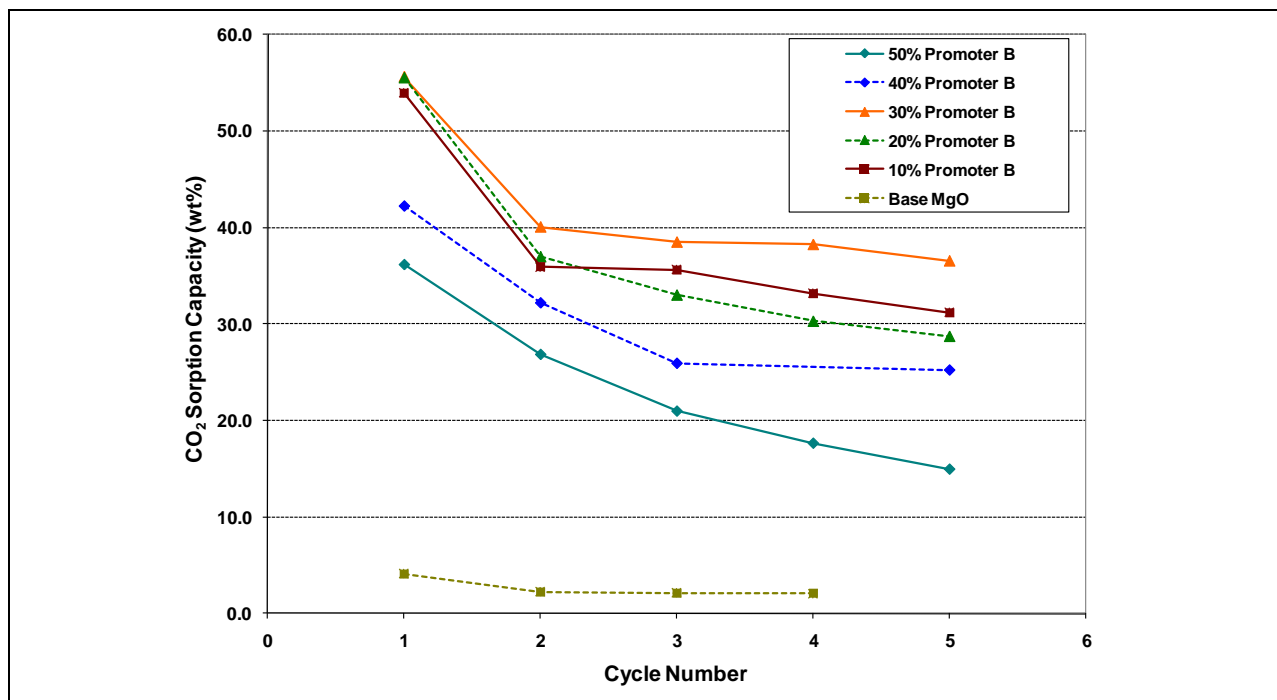


Figure 3-15. Parametric testing of Promoter B concentration for CO₂ capture performance on promoted MgO

Figure 3-14 shows that Promoter A has the strongest promoting effect during the first cycle. However, as more CO₂ capture and regeneration cycles are completed, the sorbent’s CO₂ capacity rapidly approaches capacities typical of the unpromoted material.

The results for MgO containing Promoter B, as shown in Figure 3-15, indicate a decrease in CO₂ capture capacity with increasing numbers of CO₂ capture and regeneration cycles; but, in most cases, the CO₂ capture capacity appears to be stabilizing at a significantly higher CO₂ value than the unpromoted MgO material. The CO₂ capture capacity also achieves a maximum at about 70 wt% MgO and 30 wt% Promoter B.

3.3.2.3 Evaluation of Promoting Commercial MgO-based Materials

A series of MgO samples with other potential promoters were prepared and tested. The results from these screening tests are shown in Figure 3-16. Based on these results, Promoters A, B, C, and D could be used to enhance the reactivity of MgO with CO₂.

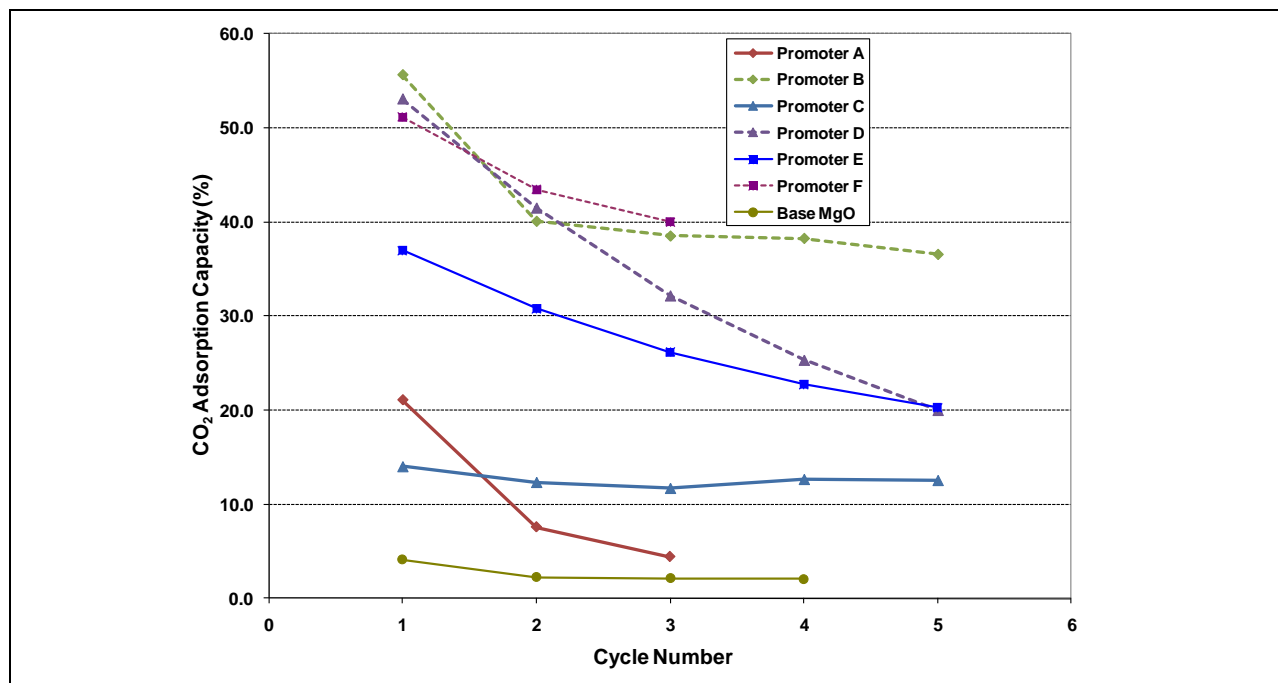


Figure 3-16. Parametric test results for CO₂ capture for MgO samples with different promoters

Because the promoters had such a significant effect on the CO₂ capacity of MgO materials prepared at RTI, the effect of adding these promoters to commercial Mg compounds that can readily be converted to MgO was investigated. Suitable Mg compounds include MgO, Mg(OH)₂, MgCO₃, and magnesium hydrate carbonate [(MgCO₃)₄.Mg(OH)₂.H₂O]. The test results for MgO, Mg(OH)₂, and MgCO₃ samples are shown in Figure 3-17 without any promoters. Figure 3-18 shows results of sorbent samples promoted with Promoter D. Figures 3-17 and 3-18 indicate that the promoter is the key ingredient required to activate the MgO material for CO₂ capture.

Promoting commercial MgO samples demonstrated that commercial sorbent materials of MgO, Mg(OH)₂, and MgCO₃ could achieve improved CO₂ capture capacity when impregnated with suitable promoters. If promoting commercially available MgO-based sorbent/catalyst was also successful, the R&D effort to develop a viable commercial CO₂ sorbent could be significantly reduced. The commercial fluid catalytic cracking (FCC) additive used to control SO₂ emissions from FCC regenerators, DeSO_x, which has all the fluidization, attrition resistance, and particle size distribution necessary, consists of a MgO/MgAl₂O₄ mixture. A sample of DeSO_x was obtained from the W. R. Grace Company. This catalyst has about 38 wt% MgO based on the available composition information. Testing of the original DeSO_x catalyst and promoted DeSO_x catalyst were completed. The results, along with the results from pure and promoted MgO, are presented in Figure 3-19, which shows that promoting the commercial

DeSO_x catalyst did result in improved CO₂ capacity of the material. Unfortunately, the improvement with promotion of the DeSO_x catalyst was not as large as observed with pure MgO, and the effect rapidly decreased with multiple cycles of operation.

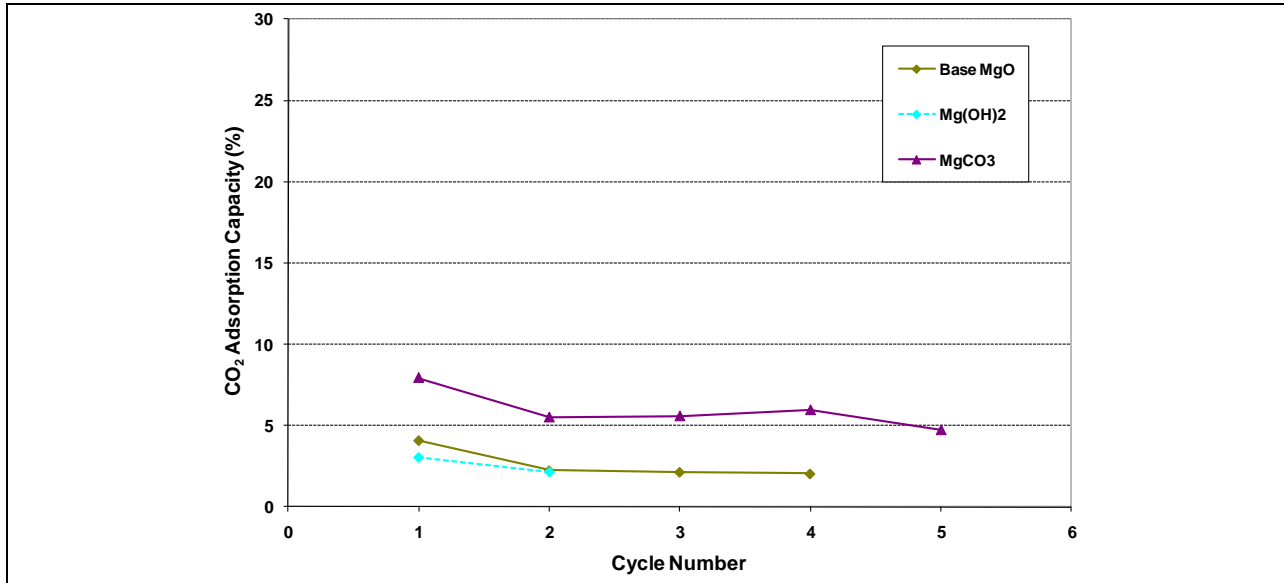


Figure 3-17. CO₂ capture performance for commercial samples of Mg compounds

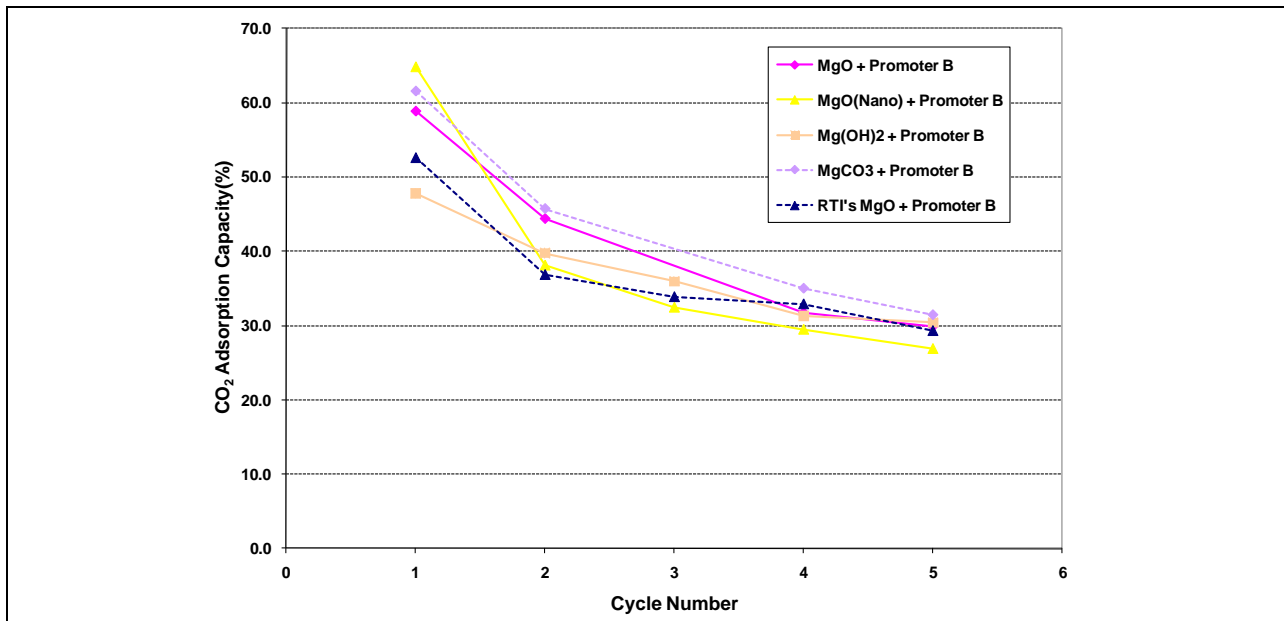


Figure 3-18. CO₂ capture performance of commercial samples of Mg compounds promoted with Promoter D

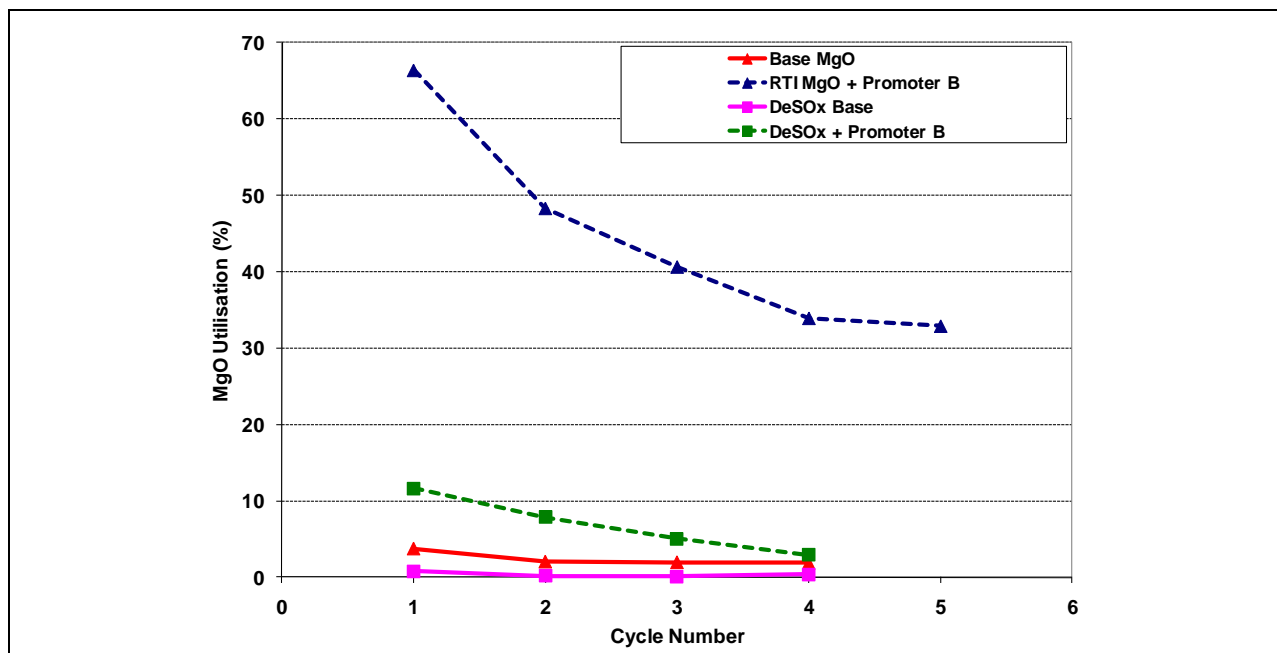


Figure 3-19. Comparison of MgO utilization for DeSO_x catalyst with and without Promoter B

Although the testing of promoted DeSO_x catalyst did not achieve the high level of CO₂ capture anticipated, this testing did show that strong commercial materials can be promoted and the key to effective sorbent development involves effectively optimizing and stabilizing the promoter effect.

3.3.2.4 Sorbent Development

With a strong understanding of the CO₂ capacity associated with different promoter/MgO mixtures, the focus of sorbent development became preparation of a sorbent formulation with suitable physical and mechanical strength. Although one of the primary functions of the support material is to provide suitable physical characteristics to the sorbent formulation, this support material must also serve as an acceptable foundation for the promoted MgO. The two key features that are required to make a material an acceptable foundation are to be chemically inert toward the active CO₂ capture species (MgO and promoters) and to provide structural support for the active species as the MgO is converted to MgCO₃ during CO₂ capture and back into MgO during regeneration. The latter requirement is critical to the long-term mechanical stability of the sorbent, while the former is more critical for chemical stability.

As an initial attempt at identifying suitable support materials, different candidate support materials were physically mixed with promoted MgO material. The results from testing these formulations in the AMR system are shown in Figure 3-20. These results indicate that magnesium aluminate and lithium aluminate are promising support materials.

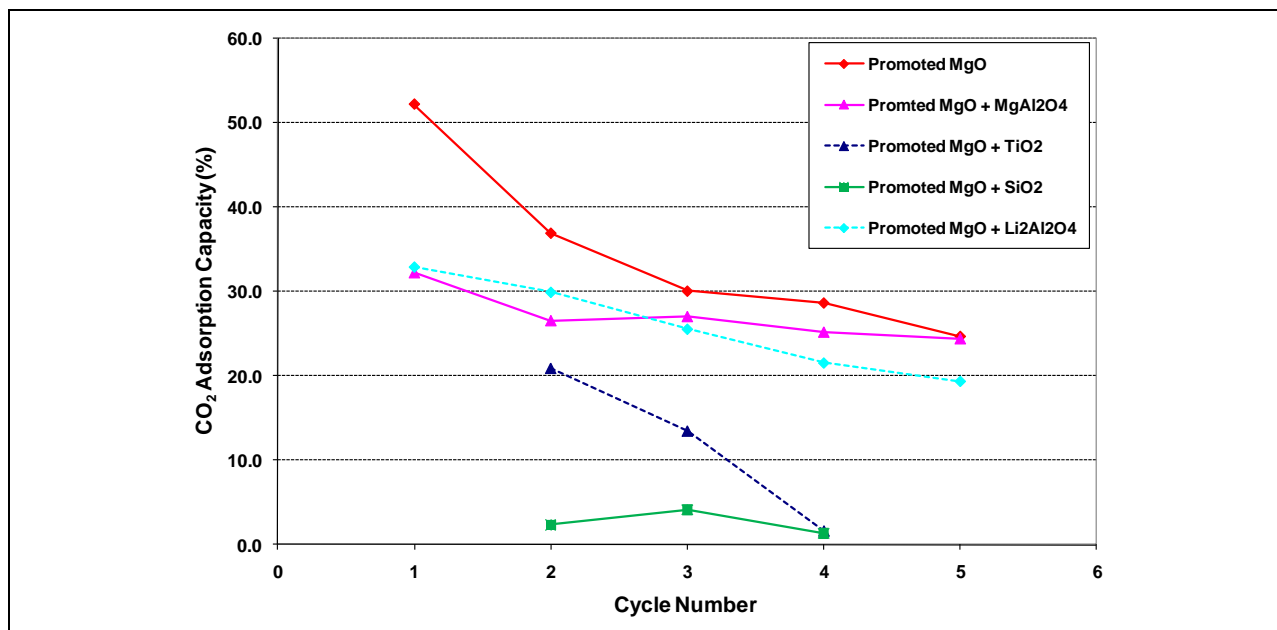


Figure 3-20. CO₂ capacity performance for physical mixtures of promoted MgO and support materials

Testing physical mixtures of the promoted MgO and support materials is an excellent screening tool to identify potential chemical interactions between the support and promoted MgO material. Unfortunately, it does not support development of a sorbent formulation that provides a structural foundation for the chemical transformations occurring between the CO₂ adsorption and regeneration cycles. Thus, support development was expanded to include incorporation of the support material as part of the sorbent formulation process. The first batch of sorbent formulation was prepared with sepiolite (a clay mineral that is a complex magnesium silicate, a typical formula for which is Mg₄Si₆O₁₅(OH)₂ • 6H₂O). This batch of materials was followed with a series of sorbent formulations based on alumina and bohemite.

The results from AMR testing of these two batches of sorbent formulations are shown in Figures 3-21 and 3-22. Both the results with sepiolite and alumina resulted in a significant decrease in MgO capacity. With bohemite, only limited loss of CO₂ capacity was observed at a calcination

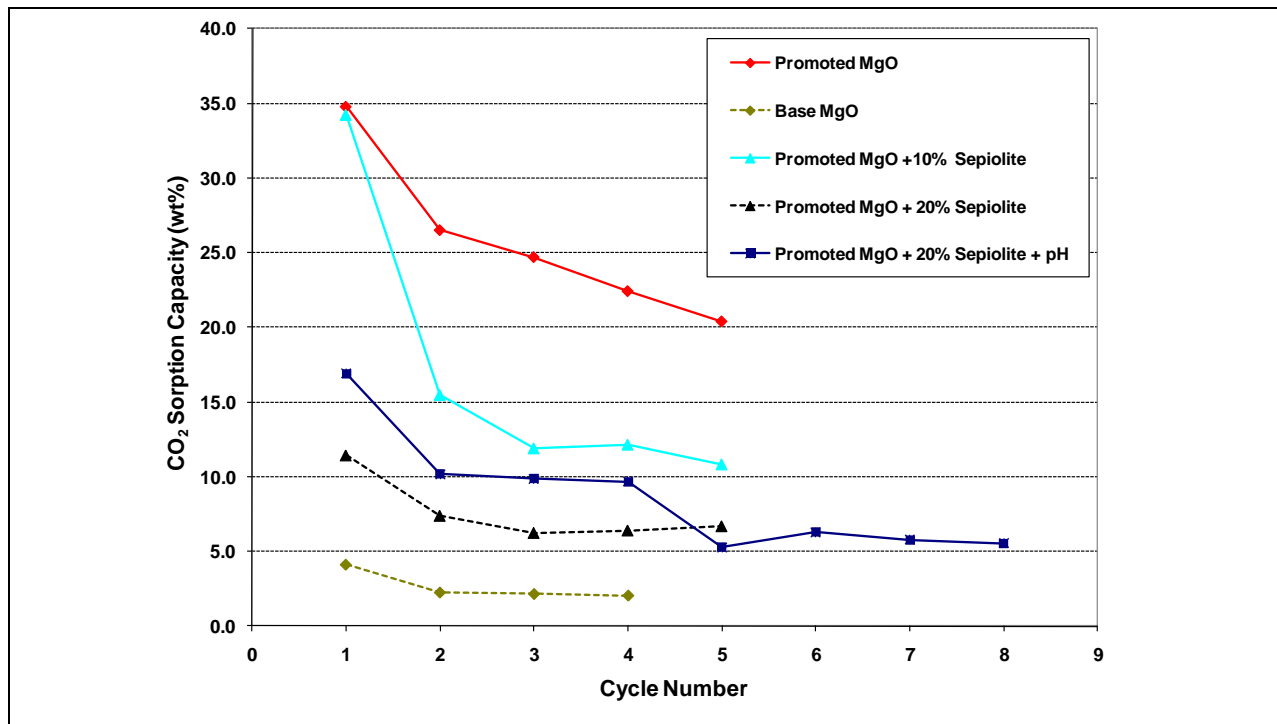


Figure 3-21. CO₂ capture performance for samples with sepiolite being used as a support material

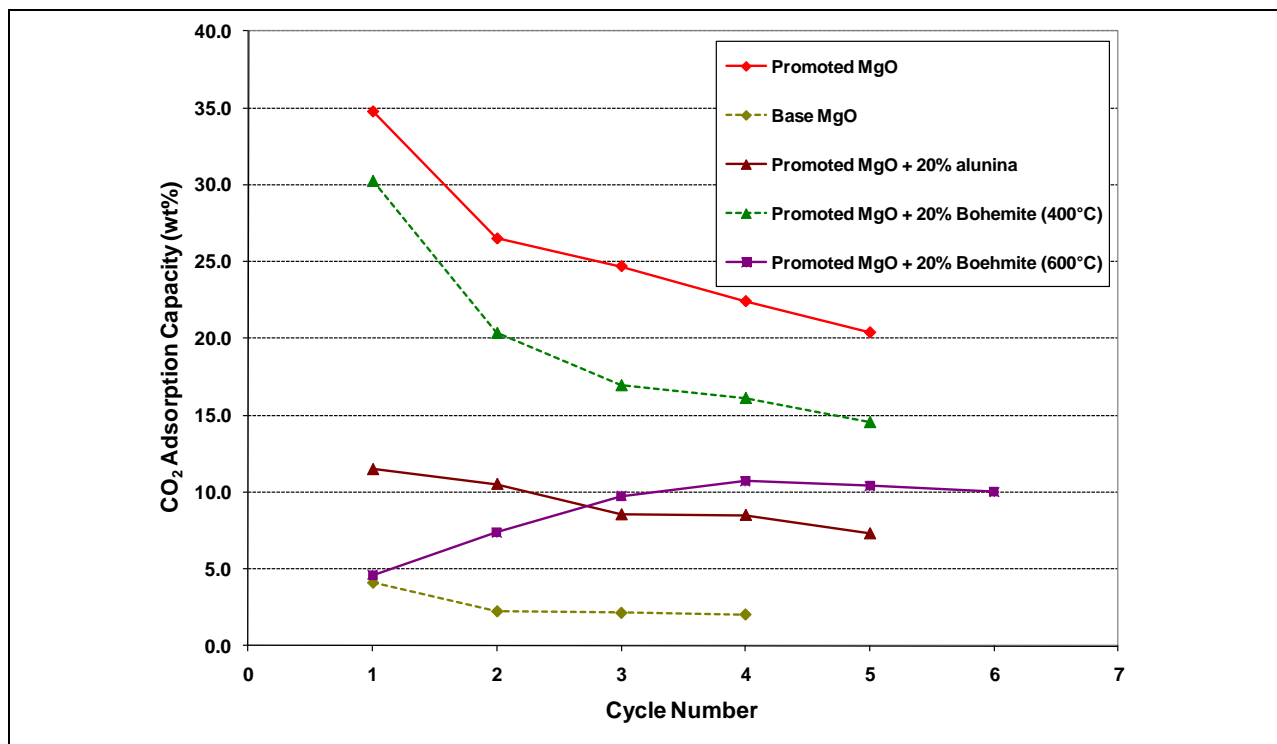


Figure 3-22. CO₂ capture performance for samples with alumina and bohemite being used as a support material

temperature of <400 °C. However, at higher calcination temperatures, the CO₂ capacity decreased and became essentially identical to the alumina samples.

As shown in Figure 3-22, magnesium aluminate was identified as a promising support material based on physical mixtures of magnesium aluminate and promoted MgO. The next step was to investigate preparation processes that incorporated magnesium aluminate during preparation of the MgO. A series of samples were prepared by co-precipitation of MgO and alumina. This mixture of MgO and alumina was converted to magnesium aluminate during calcination.

In the first series of samples prepared, the sorbent was prepared in a one-step process and subsequently calcined at temperatures from 400 °C to 600 °C. The CO₂ adsorption capacity for this series of samples is shown in Figure 3-23. For these samples, the maximum CO₂ capacity was observed at a calcination temperature of 400 °C. Any further increase in the calcination temperature resulted in a decrease in CO₂ capacity.

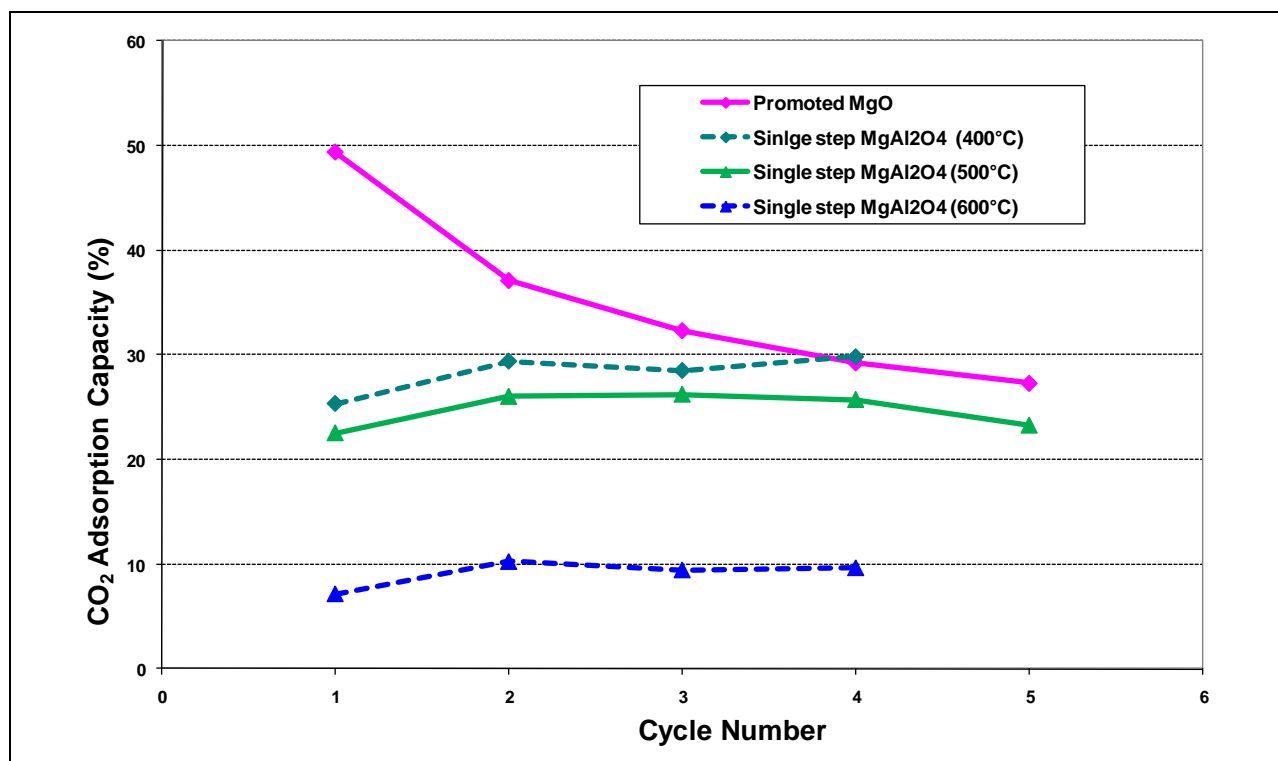


Figure 3-23. Comparison of CO₂ adsorption capacity for single-step formulations with magnesium aluminate calcined at different temperatures

In the next series of samples, the sorbent formulation was prepared, calcined, and subsequently promoted. The results for this second series of samples are shown in Figure 3-24. In contrast to the decrease in CO₂ capacity observed with increasing calcination temperature seen in Figure 3-23, the CO₂ capacity profiles show little or no effect of calcination temperature from 400 °C to 600 °C. Another interesting feature of the CO₂ capacity profiles for this series of sorbents is that, after the initial decrease in CO₂ capacity in the first cycle, subsequent decreases in CO₂ capacity were much smaller than observed for the base MgO promoted sample.

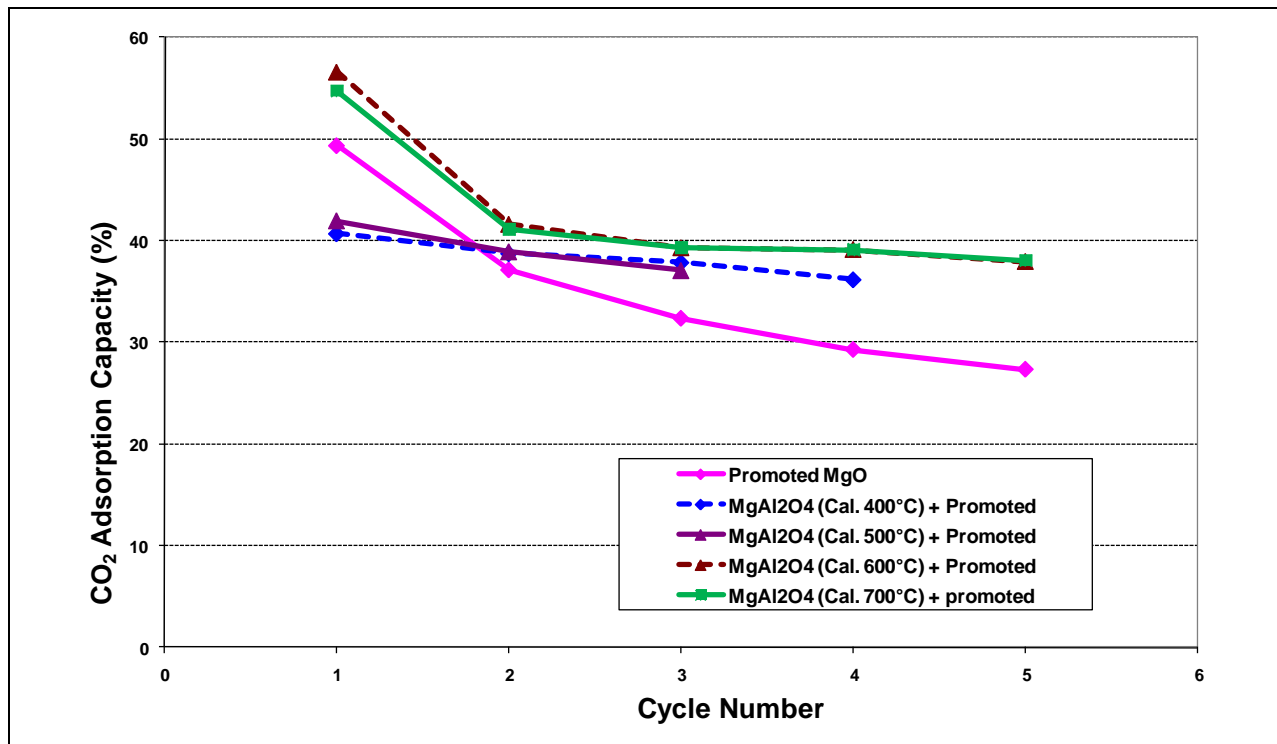


Figure 3-24. Comparison of CO₂ adsorption capacity for formulations with magnesium aluminate calcined at different temperatures prior to being promoted

Because calcium aluminate should have properties very similar to magnesium aluminate, a series of samples were prepared in which calcium oxide and alumina precursors were converted to calcium aluminate during calcination. The results for these series of samples are shown in Figure 3-25. The calcium aluminate sample with the highest CO₂ capacity was calcined at 400 °C. As the calcination temperature was increased, the CO₂ capacity for the calcium aluminate samples decreased, following the same trend observed for the magnesium aluminate samples. However, in general, the CO₂ adsorption capacity of the sorbent samples with calcium aluminate had lower CO₂ capacity than with magnesium aluminate.

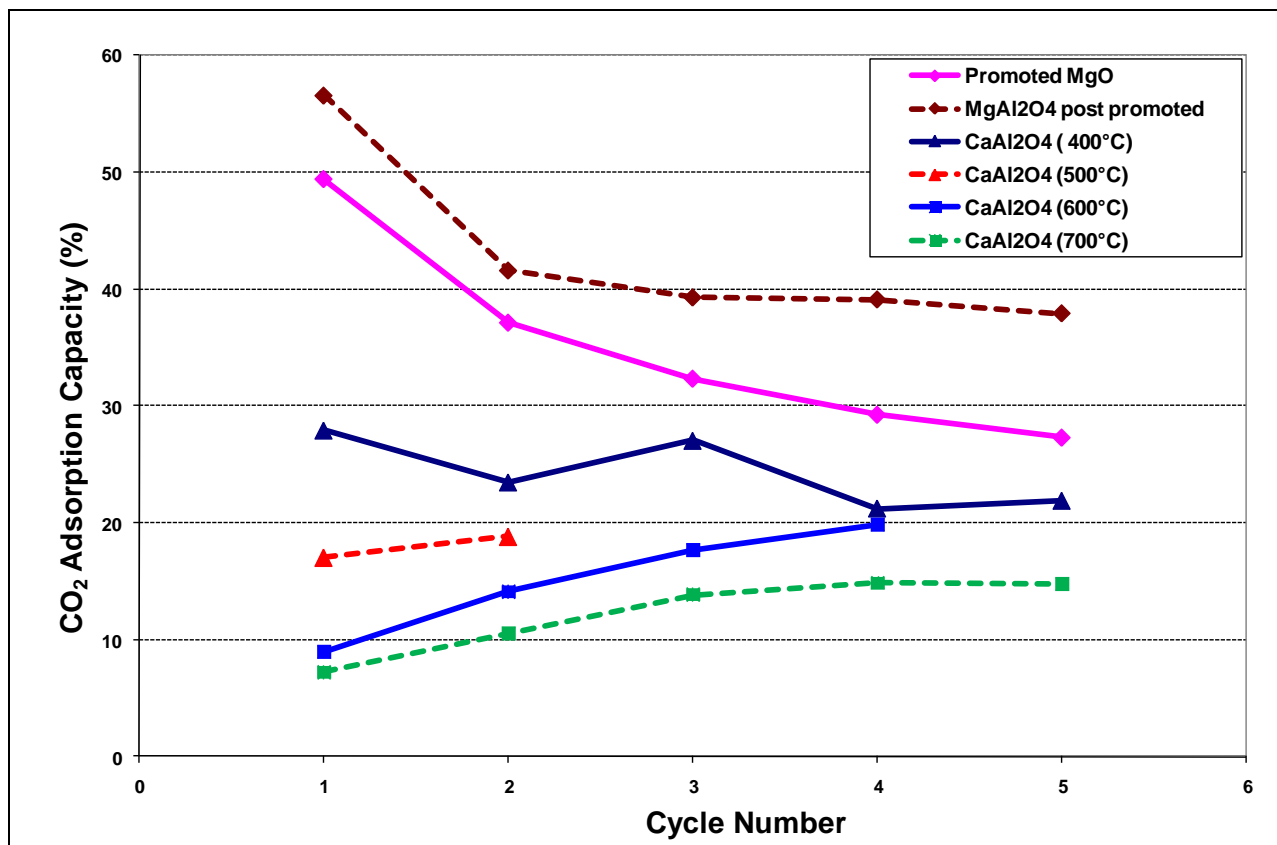


Figure 3-25. Comparison of CO₂ adsorption capacity for calcium aluminate-based formulations calcined at temperatures between 400°C and 700 °C

3.3.2.5 Syngas Testing

After modifications to the micro-reactor system were completed, which allowed testing in simulated syngas mixtures, a test was conducted with syngas containing 10 vol% steam. The results for this test, shown in Figure 3-26, indicate that the CO₂ capacity of the sorbent decreased from roughly 40 wt% to essentially zero in just four adsorption/regeneration cycles. To identify which specific component was responsible for this rapid decay in CO₂ capacity, several tests with CO₂/steam mixtures were conducted. The results from these tests are also shown in Figure 3-26. These results clearly show that the steam was responsible for this rapid decay in CO₂ capacity and that the rate of decay was faster with higher steam concentrations.

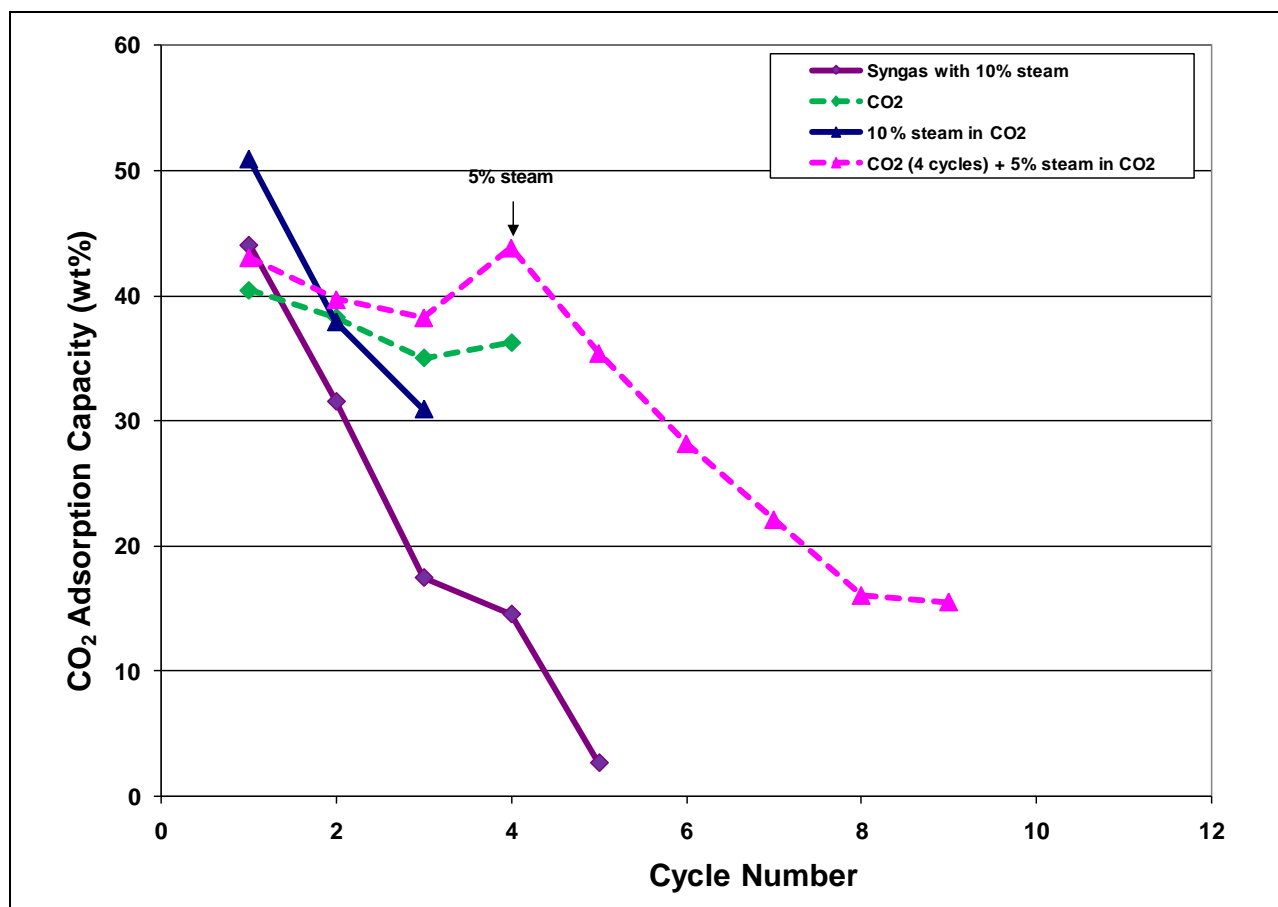


Figure 3-26. Effect of syngas and steam on CO₂ adsorption capacity of MgO sorbent promoted with Promoter B

Analysis of the chemical composition of the samples generated during testing with steam provided the evidence necessary to show that the steam was reacting with the promoter. The list of promoters previously identified was reevaluated to identify the promoters that were not anticipated to react with steam at typical operating conditions being used for the CO₂ capture process. A promoted MgO sample was made with Promoter F, which had the anticipated steam-resistant composition and achieved the highest CO₂ capacity in the original promoter screening tests. The results from testing this promoted MgO sample with steam concentrations of up to 60 vol% are shown in Figure 3-27. Figure 3-27 shows that steam did not result in rapid decay of the CO₂ capacity of this sorbent and, in fact, increased the CO₂ capacity of the sorbent. For steam concentrations up to 40 vol%, the CO₂ capacity for this promoted MgO sample remained relatively constant from cycle to cycle. At a concentration of 60 vol% steam, the CO₂ capacity was observed to decay for the final three cycles of the test, but this decay is significantly less than that observed for sorbent formulations made with Promoter B with as little as 5 vol% steam.

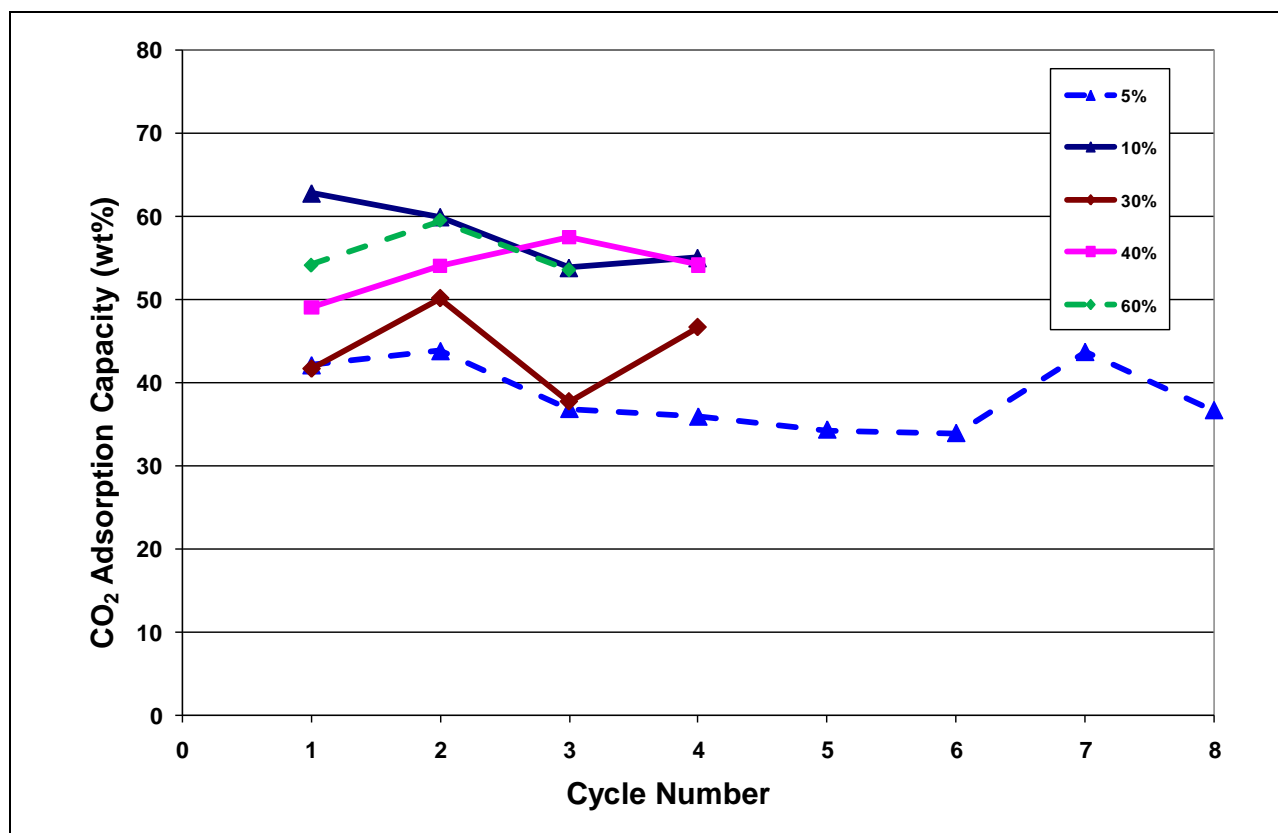


Figure 3-27. CO₂ adsorption capacity at different steam concentrations for MgO promoted with Promoter F.

3.3.3 Summary

Initial testing of 5A and 13X zeolite materials demonstrated that these materials had critical properties necessary for operation of a CO₂ recovery process from a dilute CO₂ stream that produces a high-pressure high-purity CO₂ product stream. These critical properties are

- High adsorption capacity at low temperature (<100 °C)
- Low adsorption capacity at high temperature (~300 °C)
- Minor competitive adsorption of water vapor at both high and low temperature
- Minimum CO₂ partial pressure of approximately 14.6 psi in dilute CO₂ stream.

For 5A zeolites, no specific improvements in CO₂ adsorption capacity were observed with ion exchange, but ion exchange of the 13X zeolites did show promise for improved CO₂ adsorption performance.

Attempts to identify operating conditions for regeneration of the lithium silicate sorbent that would produce a product stream with about 14.6 psi of CO₂ partial pressure were not

successful. These regeneration studies indicated that the typical effluent CO₂ concentration was <1.5 vol% (~ 0.15 psi). The only conditions under which higher CO₂ concentrations were observed was at temperatures of >700 °C. Because the CO₂ concentration in the lithium silicate regeneration effluent was too low for successful use of the CO₂ recovery process, these R&D activities were discontinued.

Based on the lessons learned during the screening of the lithium silicate sorbent, a new screening approach was implemented. This method identified several candidate materials. One of these materials is MgO. Although the theoretical capacity of MgO is high (~110 wt% based on MgO), the observed CO₂ capacity of commercially available MgO is <10 wt%. This discrepancy was believed to be the result of low reactivity of the MgO with CO₂. Through attempts to improve the CO₂ reactivity of MgO, a promoter material was identified that could achieve 20 wt% to > 60 wt% CO₂ adsorption capacity with MgO. Screening of other potential promoter agents identified at least four other materials. Development of the sorbent coupled with parametric testing has shown that

- Commercially available MgO precursors (MgO, Mg (OH)₂, MgCO₃) can be converted into CO₂ sorbents through addition of a promoter
- Magnesium aluminate is a good support that provides a stable foundation for the chemical transformations of CO₂ capture and regeneration and low reactivity with the active components
- Three of the six identified promoters have been demonstrated to be stable in syngas mixtures containing steam.

These results demonstrate the potential for developing an effective CO₂ sorbent for CO₂ capture at temperatures above 300 °C. In the next section, the testing focus shifts from material development to process development with the goal of demonstrating the technical feasibility of using MgO-based CO₂ capture sorbent for CO₂ capture in IGCC systems to achieve >90% CO₂ capture and high overall thermal efficiency and to minimize the increase in cost of electricity resulting from implementation of CO₂ capture and sequestration.

3.4 Process Development

3.4.1 Experimental Testing Supporting Process Development Feasibility

Based on the progress made with sorbent development, described in the previous sections, efforts to optimize integration of a regenerable sorbent-based warm CO₂ capture process in a thermally efficient and economically viable manner within an IGCC plant were initiated. To support this evaluation, micro-reactor testing was begun to explore the different

operating conditions to demonstrate the technical feasibility of these different process configurations.

The first series of tests investigated the effectiveness of regenerable CO₂ sorbents as a function of the partial pressure of CO₂. Figure 3-28 shows the results from this series of tests at adsorption temperatures of 325 °C and 375 °C. In Figure 3-28, the CO₂ capacity begins to significantly increase only at CO₂ partial pressures of >100 psi. As expected, higher adsorption temperatures (due to faster kinetics) result in higher CO₂ capacity.

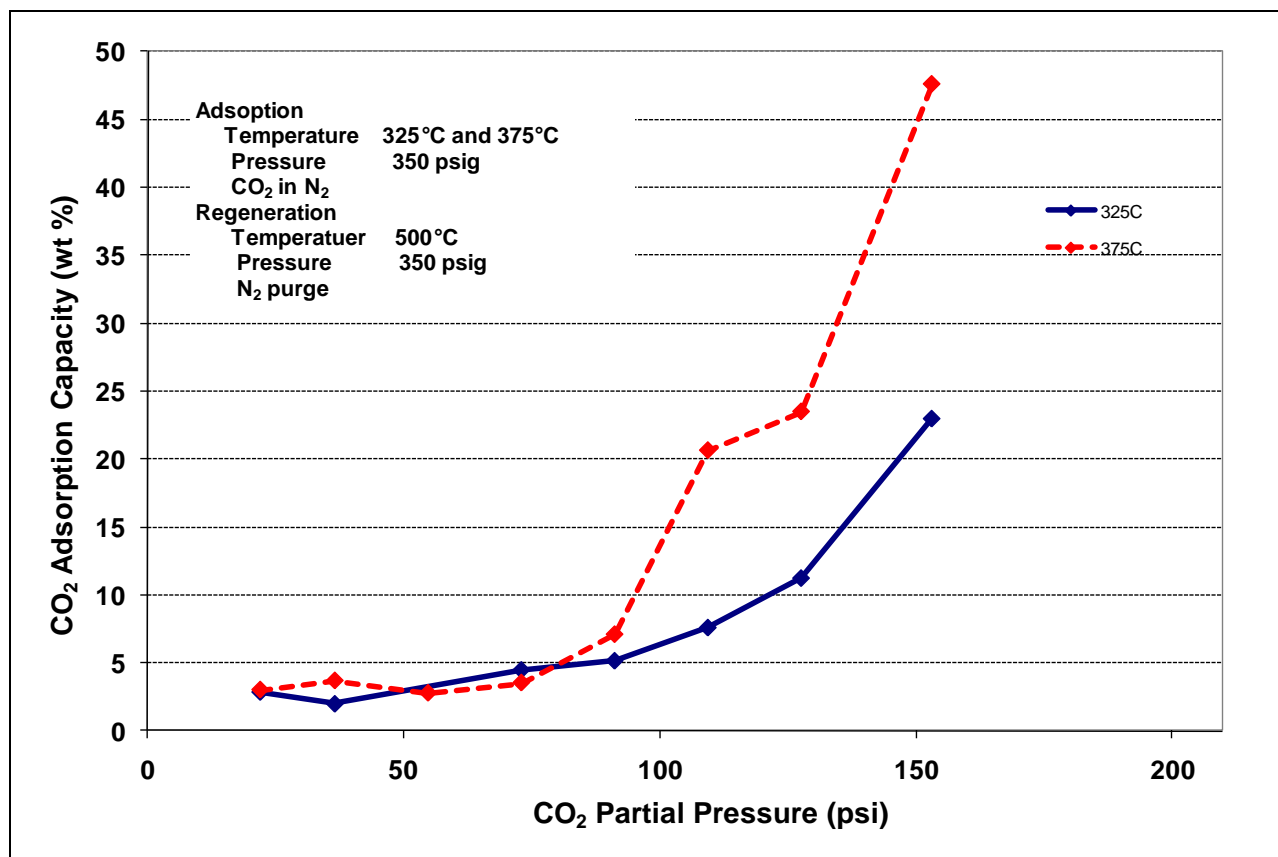


Figure 3-28. Effect of CO₂ partial pressure on CO₂ adsorption capacity

The next series of tests focused on exploring regeneration temperatures. During testing, the regeneration temperature was sequentially lowered from 500 °C to 375 °C in increments of 25 °C. As shown in Figure 3-29, stable consistent performance is maintained when the sorbent is regenerated between 400 °C and 475 °C. At regeneration temperatures >500 °C and <400 °C, the CO₂ capacity of the sorbent drops rapidly during the first two to three cycles, but appears to become more stable in subsequent cycles.

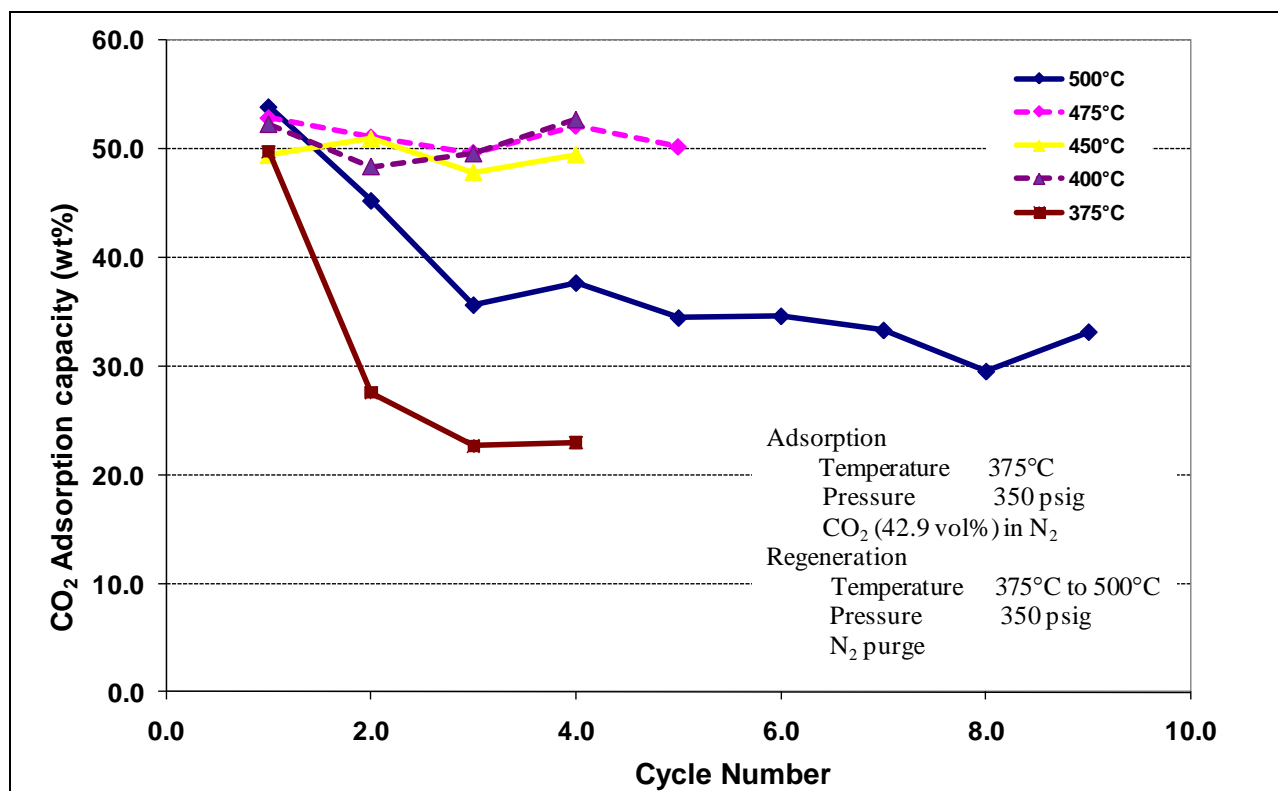


Figure 3-29. Effect of regeneration temperature on CO₂ adsorption capacity

The sorbent was also tested at different space velocities from 750 to 2,000 h⁻¹ at STP. The interesting result from this testing was that space velocity had little or no effect on the sorbent capacity, as shown in Figure 3-30.

A mixture of the sorbent and water gas shift (WGS) catalyst (8:1 sorbent to WGS catalyst) was tested to investigate potential benefits that could be derived from combining WGS and CO₂ capture. These potential benefits included a reduction in the steam needed by using CO₂ removal to help drive the shift reaction toward greater H₂ and CO₂ production and recovery of the exothermic WGS reaction enthalpy with the CO₂ adsorption enthalpy. The results, shown in Figure 3-31, indicate that this mixed bed was able to effectively convert CO into CO₂ and remove this CO₂.

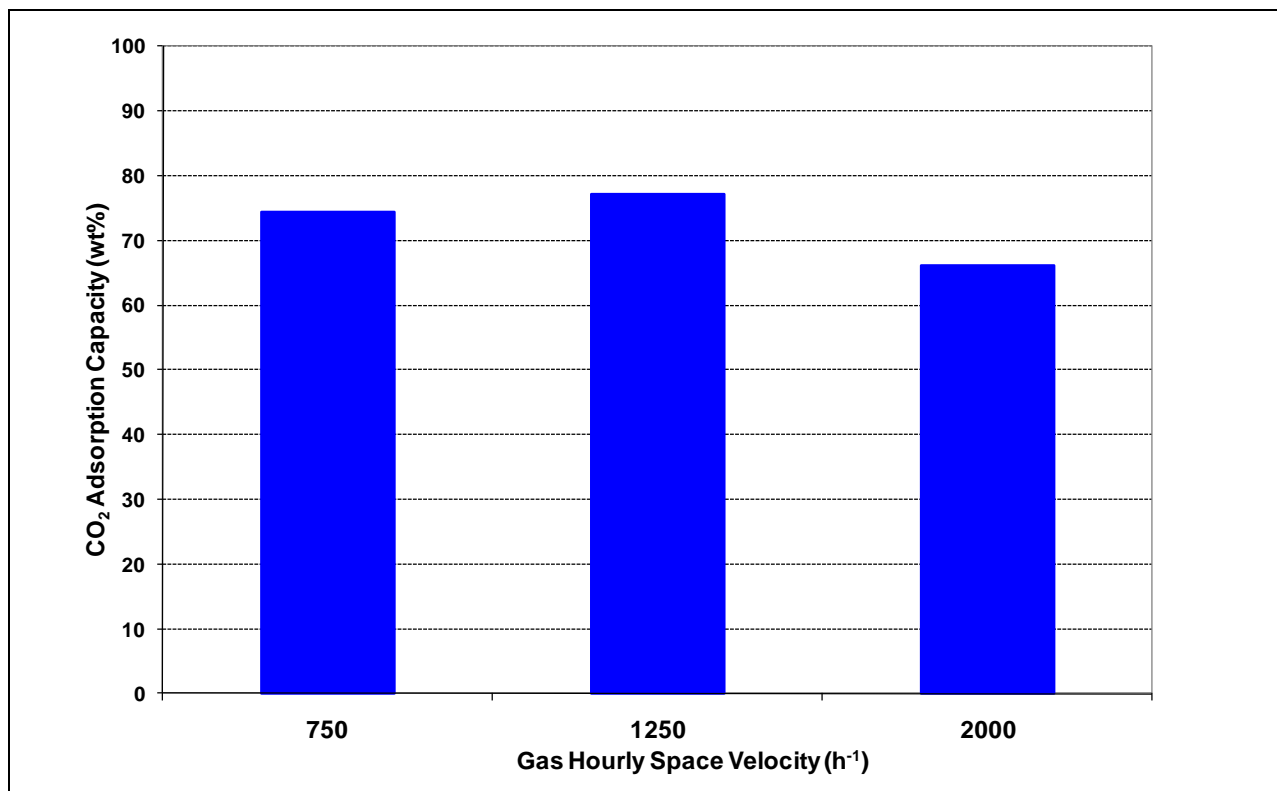


Figure 3-30. Effects of space velocity on CO₂ adsorption capacity

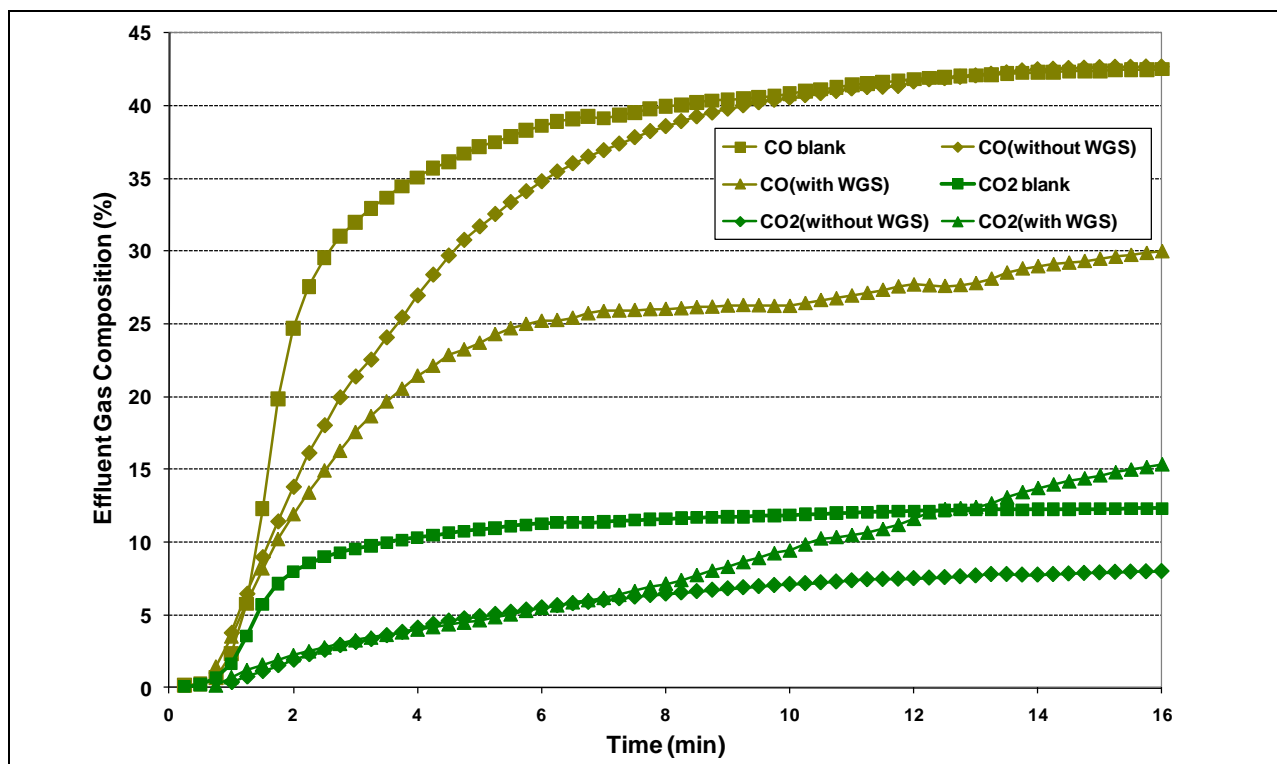


Figure 3-31. Effluent gas compositions for testing with and without WGS catalyst

Because most of the previous testing had been completed based on thermal swing regenerations, a series of tests were completed to demonstrate that the promoted MgO sorbents could also be effectively regenerated with a pressure swing. The temperature for this regeneration was selected to be lower than the adsorption temperature to facilitate using the heat release during adsorption to drive the endothermic regeneration reaction. Figure 3-32 shows that the promoted MgO sorbents developed can be regenerated with a pressure swing and with a regeneration operating temperature less than CO₂ adsorption. The cycle-to-cycle CO₂ capacity during the tests using pressure swing regeneration was almost identical to the results obtained with thermal swing regeneration.

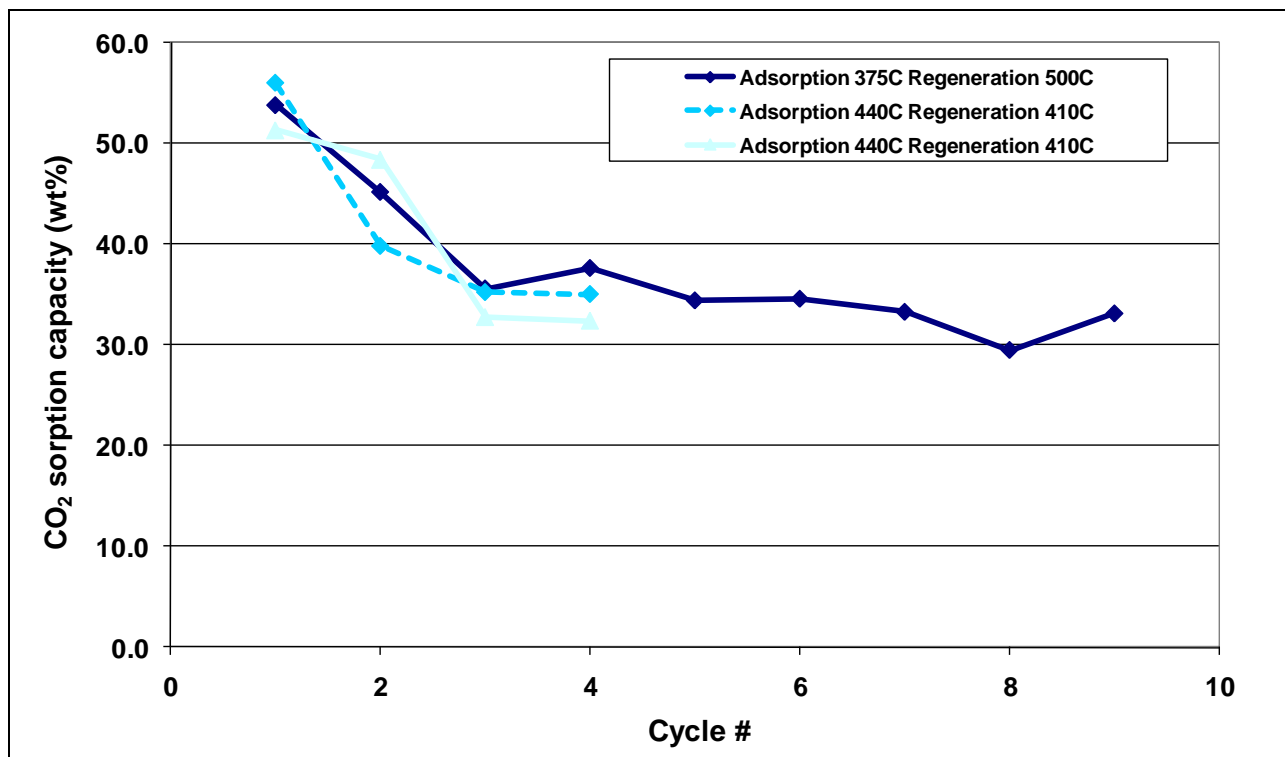


Figure 3-32. Test of new operating cycle for new process configuration

Because a key DOE programmatic goal is to achieve 90% CO₂ capture, a final series of experiments were conducted to demonstrate that a regenerable sorbent-based process using promoted MgO sorbent could effectively capture 90% of the CO₂ in the feed stream. Because all reactor systems have an inherent volume, a blank test was conducted to establish the CO₂ effluent profile for the reactor system without any CO₂ adsorption. Subsequently, parametric testing at different CO₂ partial pressures and adsorption temperatures was completed. Figure 3-33 shows the results at a CO₂ partial pressure of 225 psi and at three temperatures (300, 350 and 400 °C). As shown in Figure 3-33, the promoted MgO sorbent was able to reduce the effluent CO₂ concentration to <1 vol% CO₂ (detection limit for the equipment used in this particular test).

The length of time that the sorbent can achieve this high CO₂ capture decreased as the adsorption temperature increased. This high CO₂ capture was also observed at 150, 300, and 325 psi of CO₂ partial pressure. Figure 3-34 shows calculated CO₂ adsorption capacities for this high CO₂ capture at different adsorption temperatures and CO₂ partial pressures. Calculated CO₂ adsorption capacities associated with the high CO₂ capture ranged from almost no adsorption to about 60 wt%. As part of this additional testing, a different analytical system was used to monitor the effluent CO₂ concentration to significantly lower the detection limit. With this new analytical system, the effluent concentration at the conditions demonstrating >90% CO₂ capture was <100 ppmv.

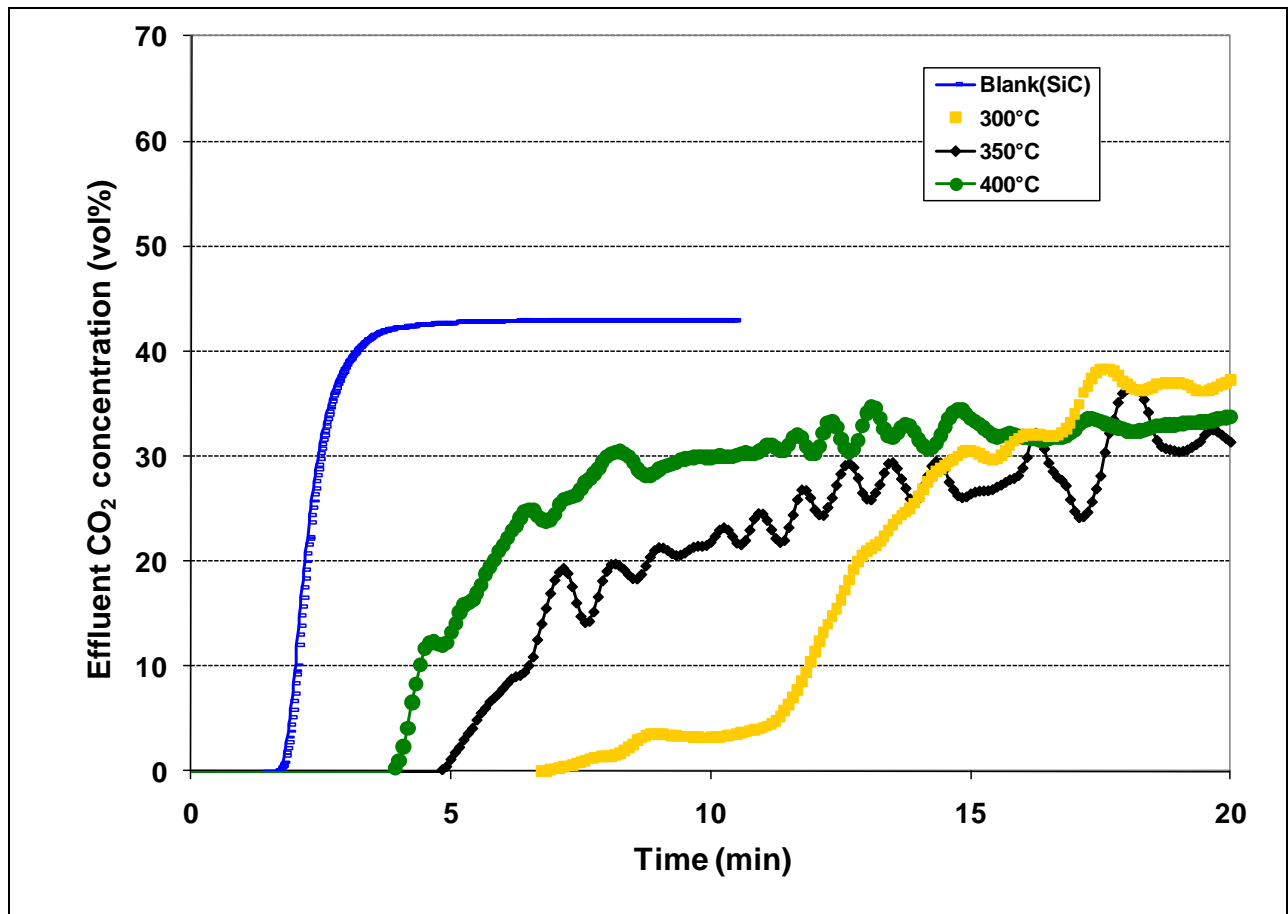


Figure 3-33. Temperature effects on MgO-based sorbents to achieve extremely low effluent CO₂ concentrations at 225 psi of CO₂ partial pressure

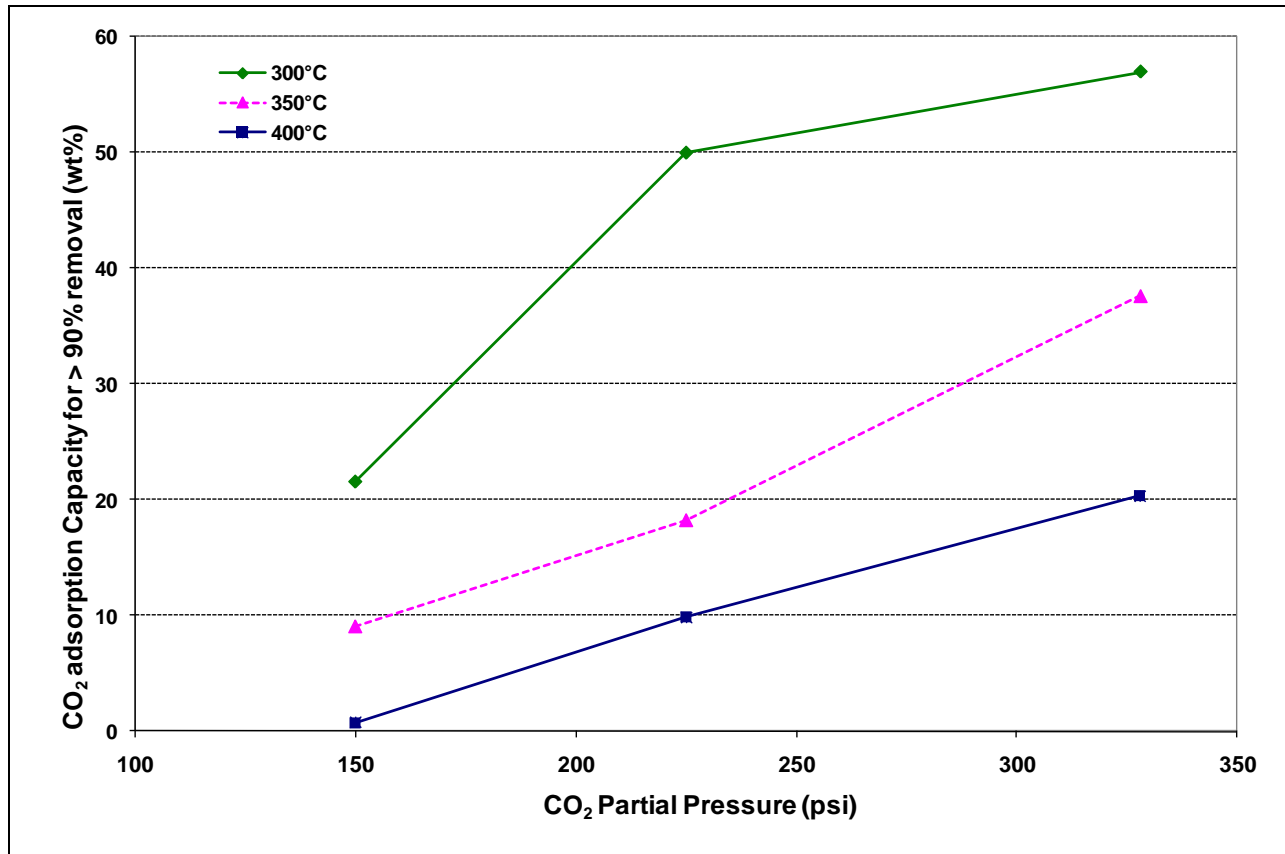


Figure 3-34. Calculated CO₂ adsorption capacities near 100% CO₂ capture for parametric testing of adsorption temperature and CO₂ partial pressure

3.4.2 Process Simulation

With the assistance of Noblis performing process simulation and analysis, RTI and Noblis evaluated a number of different process configurations. The simplified block flow diagram (BFD) of the generic IGCC system is shown in Figure 3-35. For this analysis, the goal was to evaluate and compare the thermal performance of different process configurations for the CO₂ capture and processing system. To fulfill this goal, the systems in the balance of the IGCC plant remained constant, while different process configurations for the CO₂ capture and processing system were evaluated. The specific processing required in the CO₂ capture and processing system included CO conversion to H₂ and CO₂, separation of the CO₂ from the H₂-rich syngas (>90% CO₂ capture), compression and conditioning of the CO₂ product for sequestration, and additional conditioning of the H₂-rich syngas. For the base case, the CO₂ capture and processing system included a water gas shift train, a cooling train, a Selexol separation process for the CO₂, and a compression train for the CO₂. The comparison case for the emerging technologies used Eltron's high-temperature H₂ membrane to separate the CO₂ from the H₂-rich syngas.

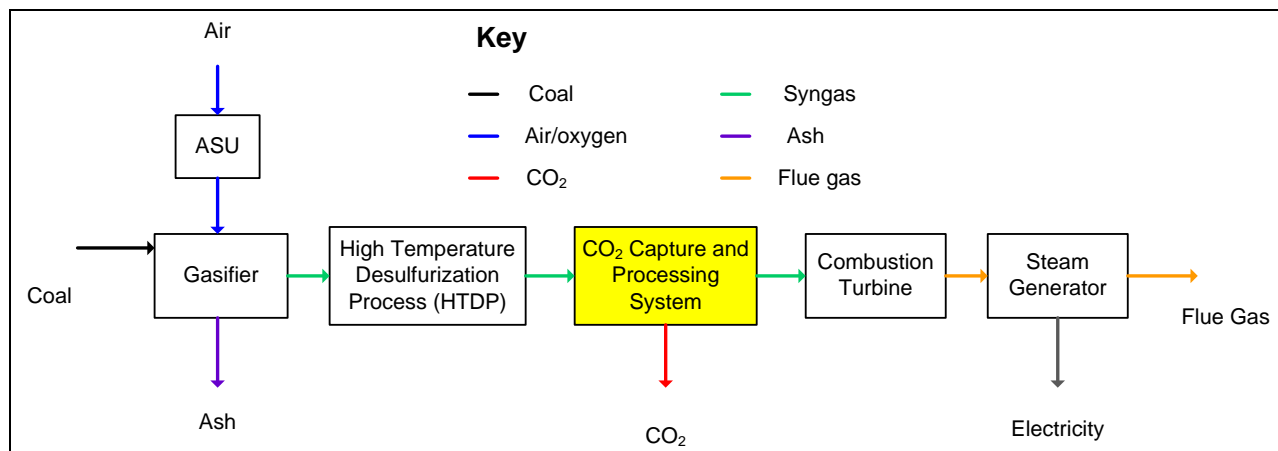


Figure 3-35. Block flow diagram of generic IGCC system

RTI evaluated a number of different configurations for the CO₂ capture and processing system that attempted to exploit the high-pressure regeneration, potential process intensification combining the CO₂ capture and the water gas shift reaction, and effective heat integration in the IGCC system. The most challenging was the heat integration. Because of the large amount of CO₂ involved, the key challenge encountered during heat integration process was not the quantity of heat, but the ability to use this heat for increasing net power generation. For the different configurations evaluated, the overall thermal efficiencies were comparable or slightly better than conventional CO₂ capture technologies. However, the overall efficiency improvements for these sorbent-based processes did not demonstrate the same level of thermal efficiency improvement that exists with other emerging technologies. Because the experimental results have demonstrated technical feasibility, RTI plans to continue to investigate and optimize thermal integration options for this technology.

SECTION 4 CONCLUSIONS

The overall objective for the Phase II work was to complete R&D supporting commercial deployment of the warm syngas cleaning technology platform for chemical/fuels production. The specific work to be accomplished in this phase is listed below:

- Provide technical support to facilitate successful scale-up of the warm syngas desulfurization process for a demonstration plant.
- Develop a warm syngas cleaning platform that will produce an effluent syngas product suitable for chemical/fuels production with the specification provided in Table 4-1.
- Develop a warm syngas CO₂ capture technology for both power and chemical production with a goal of 90% CO₂ removal and producing a sequestration-ready CO₂ stream.

Table 4-1. Warm Syngas Cleanup¹– DOE Performance Goals

Contaminant	Maximum after Cleanup
S (total)	50 ppb
NH ₃	10 ppm
HCl	10 ppb
Hg	5 ppbw
Se	0.2 ppm
As	5 ppb
P	20 ppb
CO ₂	> 90%

¹At pressure ≥600 psi; temperatures ≥400 °F

The first task has been added to the scope of work of DOE/NETL cooperative agreement DE-FE0000489 because these activities are critical to the successful design, construction, and operation of the precommercial syngas cleaning system.

4.1 Multicontaminant Technologies for Warm Syngas Cleanup Platform

Although the Eastman field test was specifically focused on Hg and As sorbents, this field test was the foundation from which the project was expected to continue and expand the multicontaminant technology development. To this end, the sorbents exposed during the Eastman field test were carefully analyzed to extract as much information about contaminant removal by these sorbents as possible. Through these analyses, multi-component capacity of Commercial Sorbent A was demonstrated. The observation of the trends for As capture by the different sorbent beds has provided evidence that more than one chemical species of As is present in the syngas. These other As species also have interacted differently with the sorbents, resulting in different removal capacities.

The Hg removal by Commercial Sorbent A during the Eastman field test was thoroughly investigated. The results of this investigation demonstrated that the Se capture by Commercial Sorbent A provided the sorbent with the potential to capture Hg. Additional testing of the Se-based sorbent has shown that Se has the potential for very high Hg capacities at higher temperatures, but these higher operating temperatures result in the loss of Se through vaporization. Experimentation with combination of multi-functional sorbents has shown promise in providing higher Hg removal capacities and limiting Se loss. Additional research will be necessary to fully develop and apply these multi-functional sorbent beds to optimize Hg capacity and removal.

Sorbent development for As, Se, and P was able to identify a number of candidate sorbents that demonstrated > 3.0 wt% capacity for these contaminants. With the primary selection process focusing on commercial materials and materials with the ability to remove multiple contaminants, the list of promising candidate sorbents is demonstration of successful acceleration of development and commercialization of these technologies.

Efforts to start testing for potential sorbents for Cd were hindered by the challenge of generating a consistent and known concentration of Cd vapor in a simulated syngas mixture. Even when the temperature of the Cd generator was maintained just 10 °C below its melting point, the effluent Cd vapor concentration was significantly less than thermodynamic predictions. This, coupled with the evidence from the Eastman field test that demonstrated a near-zero Cd concentration in actual coal-derived syngas, suggests that Cd may not be a serious contaminant in actual coal-derived syngas. These results warrant considering whether additional research in Cd removal technologies is necessary.

4.2 CO₂ Technology for Warm Syngas Cleanup Platform

One of the key objectives for developing the CO₂ capture technology under this project was to implement a modified version of our original screening process to identify materials that had the potential to regenerate at higher CO₂ partial pressures. The primary reason for this objective was to significantly reduce the amount of diluents necessary for sorbent regeneration, but this goal also presented a major opportunity for generating a high-pressure CO₂ by-product that could significantly reduce the parasitic energy demand for CO₂ compression. With this modified screening protocol, we were able to successfully demonstrate the ability to generate a high-pressure CO₂ product for both MgO-based materials and zeolite materials.

With two promising sorbent candidates, our next challenges were to develop a process to effectively exploit the promise of these two materials and to develop an acceptable formulation

for commercial production. For the zeolite sorbents, a key component of the process was to demonstrate that lithium silicate could produce a stream from which the zeolite material could effectively capture the CO₂. Unfortunately, efforts to demonstrate that the lithium silicate could produce a suitable product stream for CO₂ recovery with zeolites were not successful. At this point, all research efforts were reallocated to development of the MgO sorbent.

Although MgO has significant potential for CO₂ capture based on favorable thermodynamic equilibrium, actual experimental results with commercially available MgO-based materials did not support the thermodynamic results. Through efforts to increase the reactivity of the MgO for CO₂, we identified a total of six promoter mixtures that significantly increased the CO₂ capacity of MgO materials from <5 wt% to a range of 40 to 60 wt%. During testing with syngas, the most detrimental effect was associated with steam. Two of these promoters have been demonstrated to work in syngas mixtures with 10 vol% steam. The most promising promoter demonstrated that, up to a steam concentration of 60 vol%, the steam resulted in only a moderate increase in the CO₂ adsorption capacity.

As part of facilitating sorbent development, it was demonstrated that readily available commercial samples of MgO materials could be promoted with a significant increase in CO₂ adsorption capacity. This promotion was effective even with a commercial FCC catalyst material called DeSO_x, which had typical attrition resistance, particle size distribution, and fluidization properties suitable for fluid bed applications.

Based on the significant amount of CO₂ adsorbed by MgO, sorbent development focused on identifying a material that could provide the structural support for the repetitive transformation between MgO and MgCO₃ and would be essentially inert toward MgO and the various promoters. A number of different materials were screened, with magnesium aluminate being the most promising. In several preparations, calcination temperatures above 400 °C resulted in a significant reduction in CO₂ adsorption capacity. One preparation method in which promoters were added as the final preparation step demonstrated CO₂ adsorption capacity that was not adversely affected by calcination temperature and had reasonable cycle-to-cycle stability.

The final challenge was to incorporate the development completed for the MgO-based sorbent into a process with acceptable thermal integration in an IGCC system. The thermal integration for this process was probably the most challenging aspect of the project. Although a number of novel and creative approaches were considered, the net improvement in the overall thermal efficiency of the IGCC system was less than that for other emerging CO₂ capture

technologies being developed for IGCC systems. The key challenge encountered during our thermal integration process was not the quantity of heat, but the ability to use this heat for increasing net power generation. Because optimizing thermal integration is a challenge faced by all CO₂ capture technologies, we are continuing to examine approaches that can effectively result in an optimal integrated system with high thermal efficiency.