U.S. DEPARTMENT OF
ENERGY

PNNL-23167

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

CAS-NETL-PNNL CEP Program Final Report

DL King
KA Spies
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March 2014

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Contents

Task 3.3 - Warm Syngas Cleanup and Catalytic Processes for Syngas Conversion to Fuels

Subtask 2: Integrated Warm Syngas Cleanup and CO_2 Capture System

This collaborative joint research project is in the area of advanced gasification and conversion, within the Chinese Academy of Sciences (CAS)-National Energy Technology Laboratory (NETL)-Pacific Northwest National Laboratory (PNNL) Memorandum of Understanding. The goal is the development and testing of an integrated warm syngas cleanup process. This effort is focused on an advanced, integrated system for capture and removal of alkali, sulfur, PH_3, AsH_3, chloride, and CO_2, leading to a future process demonstration at a CAS gasification facility. Syngas produced by gasification can be used for production of fuels (Fischer-Tropsch, SNG, mixed alcohols), chemicals (MeOH, NH_3), and hydrogen for fuel cells and Integrated Gasification Combined Cycle IGCC. To employ this syngas, especially for synthesis reactions, contained impurities must be removed to sub-ppmv levels [1]. Commercially available approaches to remove contaminant species suffer from inefficiencies, employing solvents at ambient or lower temperature along with backup sacrificial sorbents, whereas syngas utilization occurs at higher temperatures. The efficiency and economics syngas utilization can be significantly improved if all the contaminants and CO_2 are removed at temperatures higher than the chemical synthesis reaction temperatures (>250°C) [2].

Due to lack of third year funding support for the project, research activities were curtailed prior to reaching the final deliverables. This report documents work completed with the available funding, and meets the request of the NETL office for project closeout.

1.0 Research objectives

This project had as its primary objectives:

- Cleanup all catalyst-poisoning contaminants from warm coal or biomass-derived syngas in the warm temperature range (300-500°C).
- Remove CO_2 from the purified, warm syngas, in conjunction with water gas shift, to produce hydrogen or syngas with the appropriate H_2/CO ratio for chemical or fuel synthesis.

These objectives can be seen in Figure 1, and were met with the funding provided.

- Demonstrate an integrated process for hydrogen production at a CAS site at the end of this 3-year project.

This objective, a demonstration at the CAS facility in China, was not met due to loss of third year project funding.

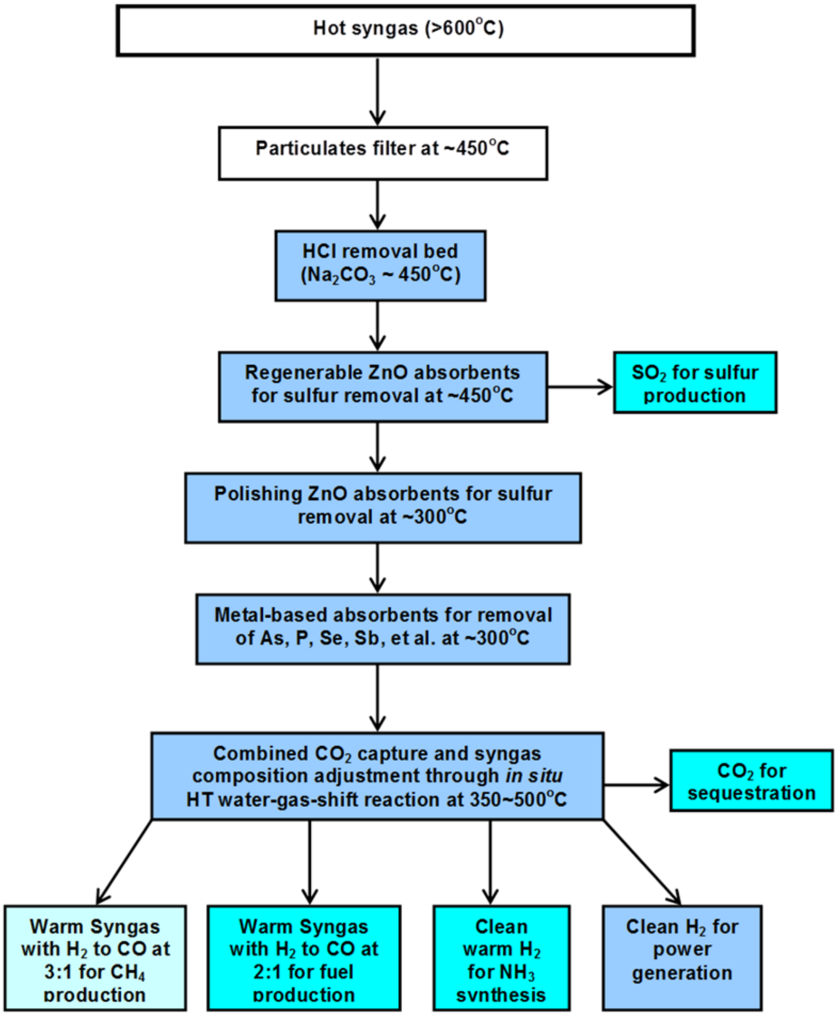


Figure 1. Warm gas cleanup and CO_2 capture, representing the PNNL part of the collaboration. The boxes in the last row show the options for use of syngas depending upon H_2/CO ratio.

1.1 Research and development activities

The following activities were carried out with support from the CAS-NETL-PNNL joint project.

1.1.1 Chloride Removal

Through the use of a packed fixed bed of sodium carbonate (Na_2CO_3), chloride (as HCl) was removed through the formation of NaCl: $2HCl + Na_2CO_3 \rightarrow 2\ NaCl + CO_2 + H_2O$, which is thermodynamically favorable. Figure 2 shows the results of tests for chloride removal, showing essentially quantitative removal, and that significant capacity toward chloride can be obtained at 450°C at space velocity as high as 80,000 hr^{-1}, although maximum chloride capacity of 50 wt.% was obtained at 20,000 hr^{-1}.

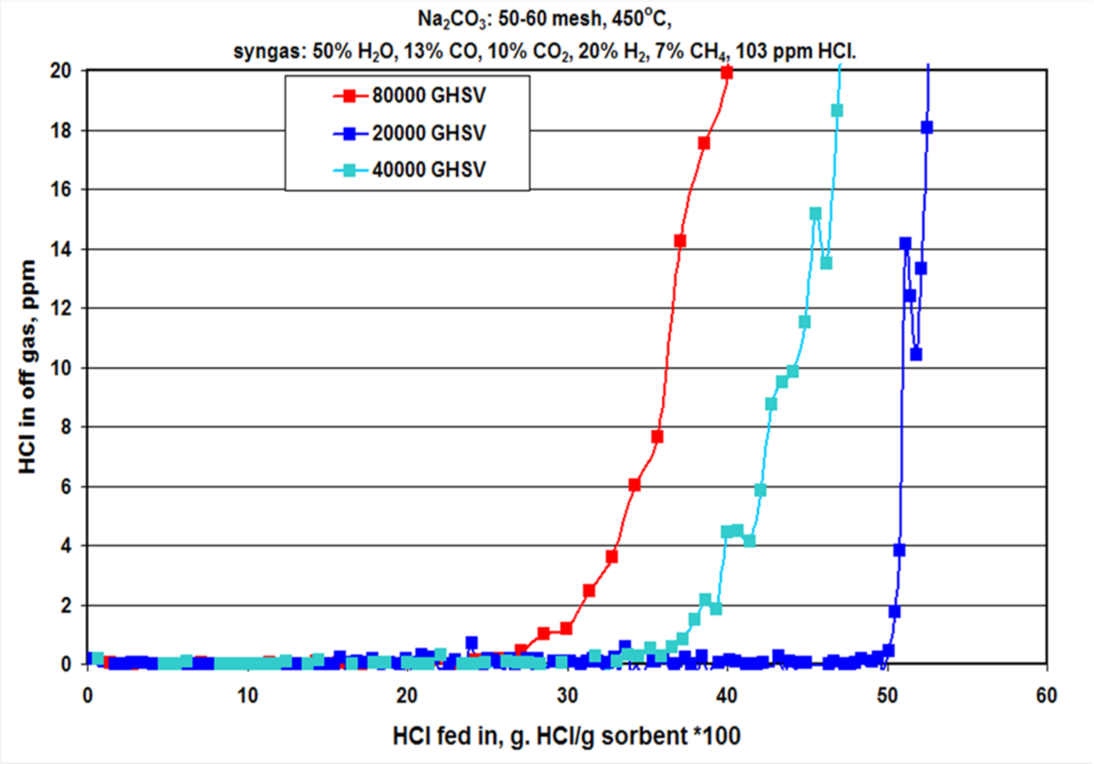


Figure 2. Effect of space velocity on absorption capacity for HCl by a solid bed of Na_2CO_3, operating at 450°C, with a wet syngas feed.

1.1.2 Sulfur Gas Removal

Our work focused on development of sulfur gas removal based on a ZnO-based absorbent. There are various forms of modified ZnO, with many focusing on addition of TiO_2 or other additives to allow ZnO to function more effectively at elevated temperatures (≥500°C) without loss of Zn via reduction [3,4]. The ZnO absorbent we selected was provided by Sud Chemie (now Clariant), and contains ~10 wt.% Al_2O_3. Despite the large amount of available literature, there was little to guide us in selection of operating parameters for our selected ZnO absorbent. This is, in part, the result of variations found in H_2S concentration in the feed, the water content, the absorbent composition and particle size, space velocity, and operating temperature in reported studies [5-7]. Moreover, in many cases information was not sufficiently detailed regarding sulfur gas slip and its identity (H_2S or COS), when that slip was in the few ppmv range. These considerations guided the focus of this work.

Our efforts focused on identifying preferred operating conditions for adsorption of both of the sulfur gases (H_2S and COS) with ZnO-based absorbents under warm temperature conditions. There has been a substantial amount of work published on H_2S absorption by ZnO, although much less so with COS. References indicate that COS first hydrolyzes to H_2S and is then absorbed by ZnO, hence the need for H_2O to be in the feed when COS is present; otherwise COS is not well captured by ZnO [8,9]. Literature also describes the role of acidic additives such as Al_2O_3 added to the ZnO to facilitate the conversion of COS to H_2S in the presence of water [10]. A significant effort was expended to determine the fate of COS in the presence of the Al_2O_3-modified ZnO. We examined performance of the absorbent with both H_2S and COS, on fresh and regenerated ZnO, with and without water in the feed, and with and without syngas as a co-feed.

Operating at 450°C, we carried out absorption experiments with COS, with either syngas or N_2 as the primary gas, with either H_2O present or absent in the feed. Under dry feed conditions with N_2 as carrier gas, COS is completely absorbed by ZnO at 450°C, as shown in Figure 3, with performance very comparable to H_2S absorption. We went to elaborate lengths to exclude water from the system. Therefore, we have no evidence that COS must be catalytically converted to H_2S prior to absorption, rather the opposite appears to be true with this absorbent.

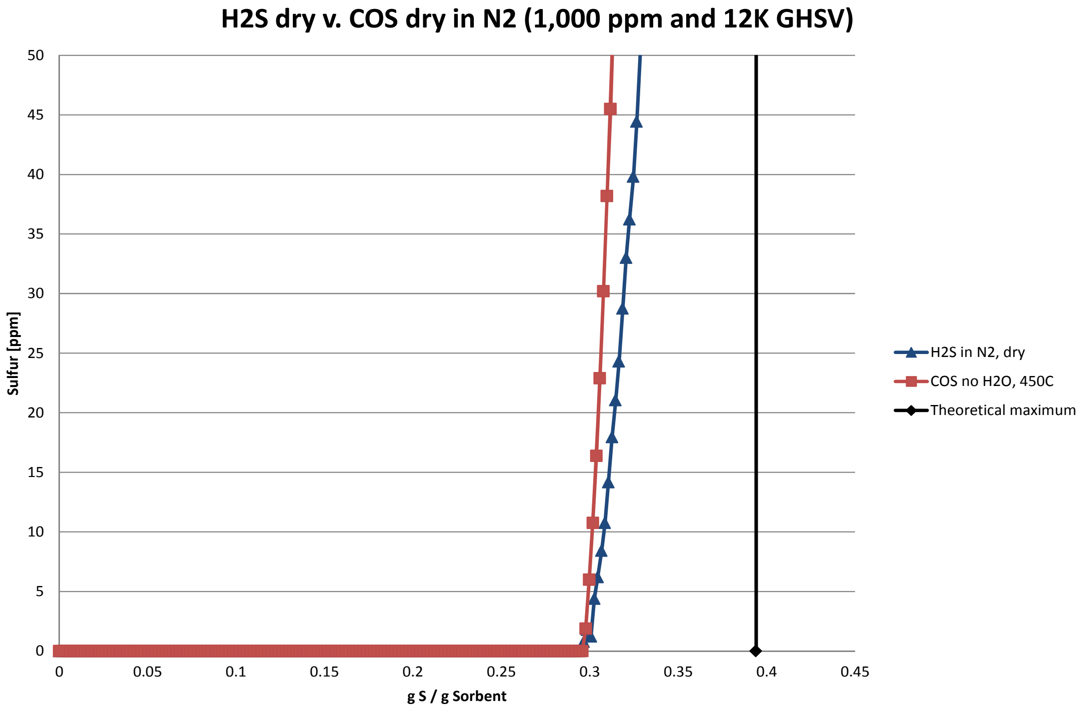


Figure 3. Comparative absorption behavior of ZnO toward H_2S and COS. Conditions: 1000 ppmv sulfur gas (H_2S or COS) in N_2, dry, GHSV = 12,000. Horizontal axis is g S absorbed/g ZnO initial.

On the other hand, we have seen that COS absorption is quite temperature dependent. Thus, although good performance is observed at 450°C, whereas performance is poor at 200°C, as shown in Figure 4. At these lower temperatures, COS hydrolysis most likely becomes the primary means COS removal because H_2S is effectively removed at 200°C.

We also examined performance of ZnO following regeneration, and compared it with fresh ZnO. Uniformly, we found that regenerated ZnO (by oxidation in 2% O_2/98%N_2 at 600°C) had good capacity toward H_2S, but the sulfur slip was generally in the 3 to 5ppmv range. Capacity of the regenerated sample is reduced by about one third. Only in the case of fresh ZnO were we able to reach levels sulfur gas levels <100ppbv, as shown below in Figure 5. This confirms that an approach in which bulk H_2S is absorbed over regenerated ZnO, with the small sulfur slip handled by a downstream polishing bed of fresh zinc oxide. [Note: the high S signal near t = 0 we have verified to be an artifact due to H_2S releasing from the walls of the stainless steel reactor.]

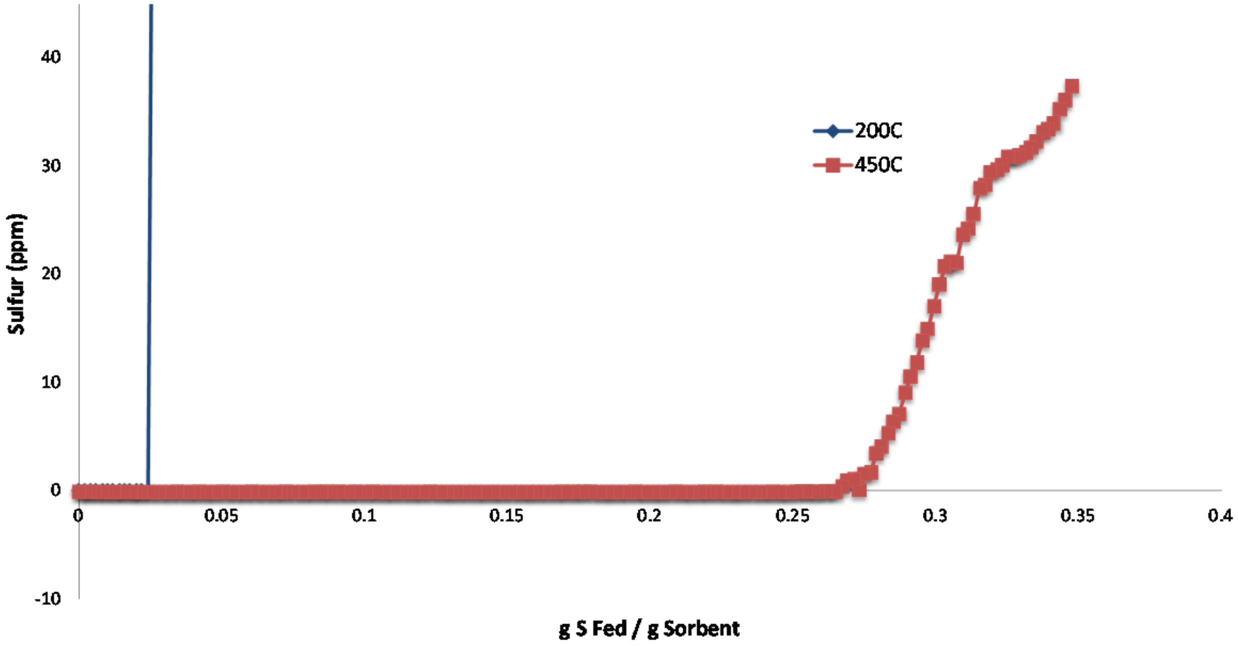


Figure 4. Effect of temperature on COS absorption over ZnO, inert dry gas carrier, 24,000 GHSV, 500ppmv H_2S.

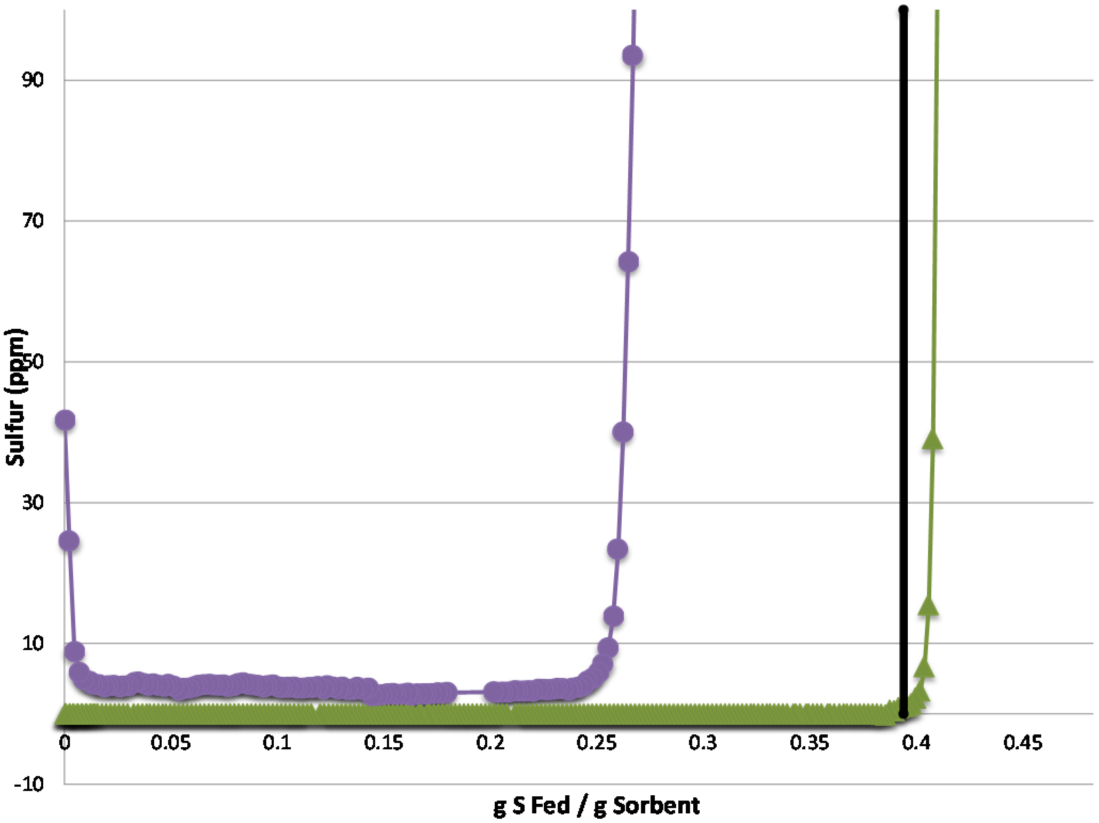


Figure 5. ZnO with H_2S (1,000 ppm) in Syngas (45% CO, 28% H_2, 14% CO_2), 20% H_2O, 12K GHSV, 450°C. Green: fresh absorbent; blue; 1x regenerated absorbent.

1.1.3 CO_2 Removal

Previously, we described the regenerable absorption of CO_2 by MgO-Na_2CO_3, in the presence of $NaNO_3$, which is a molten salt at the operating temperature of the experiment shown below (400°C) [11]. The first absorption cycle in Figure 6 shows a capacity of approximately 30 wt%, while each of the subsequent cycles show a capacity of about 16.5 wt%. XRD evidence has shown that during the first cycle, $MgCO_3$ is formed, while in subsequent cycles only the double salt $MgCO_3$-Na_2CO_3 is formed. The important detail to understand is that CO_2 absorption occurs during the first cycle primarily during the heating up phase (i.e., at temperature below 400°C. At 400°C, $MgCO_3$ decomposes to MgO and CO_2 (regardless of the surrounding gas), whereas at 400°C the double salt is stable in CO_2, but not in N_2 (hence the effectiveness of a pressure swing approach). Although the high capacity through $MgCO_3$ formation could not be sustained in this experiment, nevertheless it highlighted the fact that MgO can also absorb CO_2 efficiently at temperatures <400°C if a molten salt is present. This suggested that we study the system $MgO + NaNO_3 + CO_2$, without the presence of the alkali carbonate component.

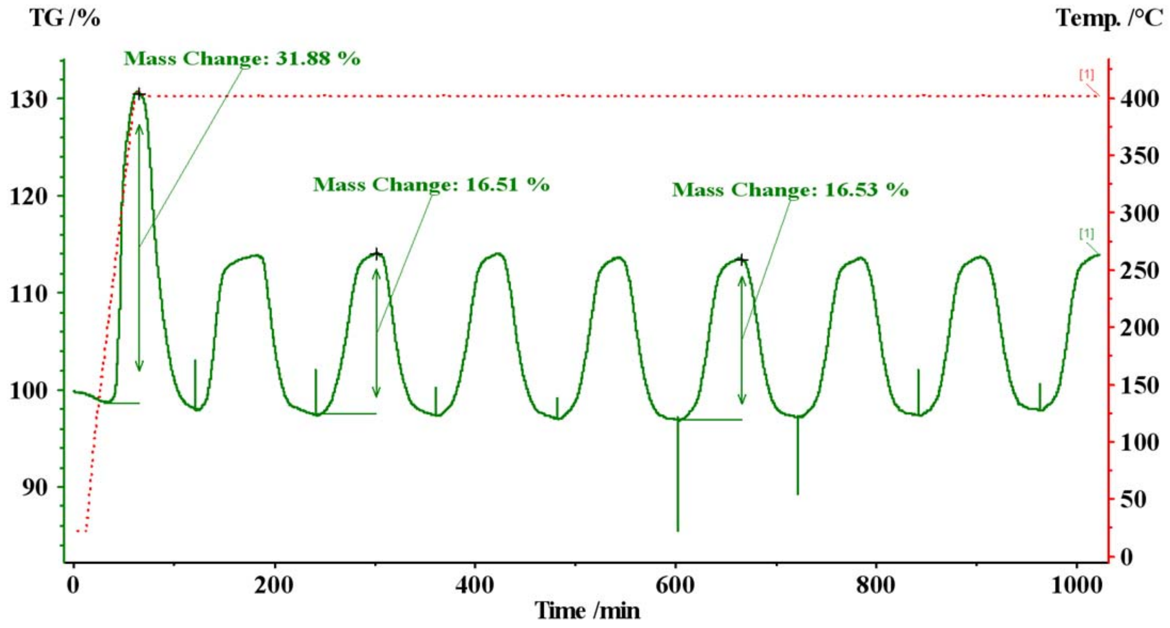


Figure 6. Multiple regeneration cycles of double salt (MgO-Na_2CO_3) with CO_2, pressure swing (absorption—100% CO_2; desorption—100% N_2) at 400°C. The first absorption peak includes MgO conversion to $MgCO_3$.

Absorption-desorption curves for $MgO + NaNO_3$ are shown in Figure 7. The operation in this case was a combined temperature-pressure swing. A first cycle absorption shows conversion of greater than 70% of the MgO to $MgCO_3$. Subsequent cycles show decreasing capacity, which appears to line out at about 30% MgO conversion. We have tried various conditions for absorption and regeneration of MgO-$MgCO_3$, but have not been able to find an absorbent that consistent converts 70% of MgO over multiple regeneration cycles. We do not know the cause, but suspect this may be related to the changing interaction between MgO-$MgCO_3$ and $NaNO_3$ as the material particle properties change (sintering occurs).

1.1.3.1 Effect of other molten salts

Due to the fact that absorption of CO_2 appears to occur over MgO once the $NaNO_3$ melts, we examined the effect of using other salt mixtures and salt eutectic mixtures in place of $NaNO_3$. In the experiment, the salt was first melted and cooled to re-solidify, and then MgO was placed physically on top of the salt. A Thermogravimetric TGA experiment was carried out in flowing CO_2, in which the uptake of CO_2 was recorded as a function of temperature. It can be seen in Figure 8 below that CO_2 absorption begins at different temperatures with the different salt mixtures, in all cases coinciding with its melting point. Thus, we have found that very high conversion of MgO to $MgCO_3$ can be obtained at temperatures below 200°C. We note, however, that regeneration does not undergo a similar decrease in temperature, as that is limited by thermodynamics and T>400°C is required to regenerate $MgCO_3$.

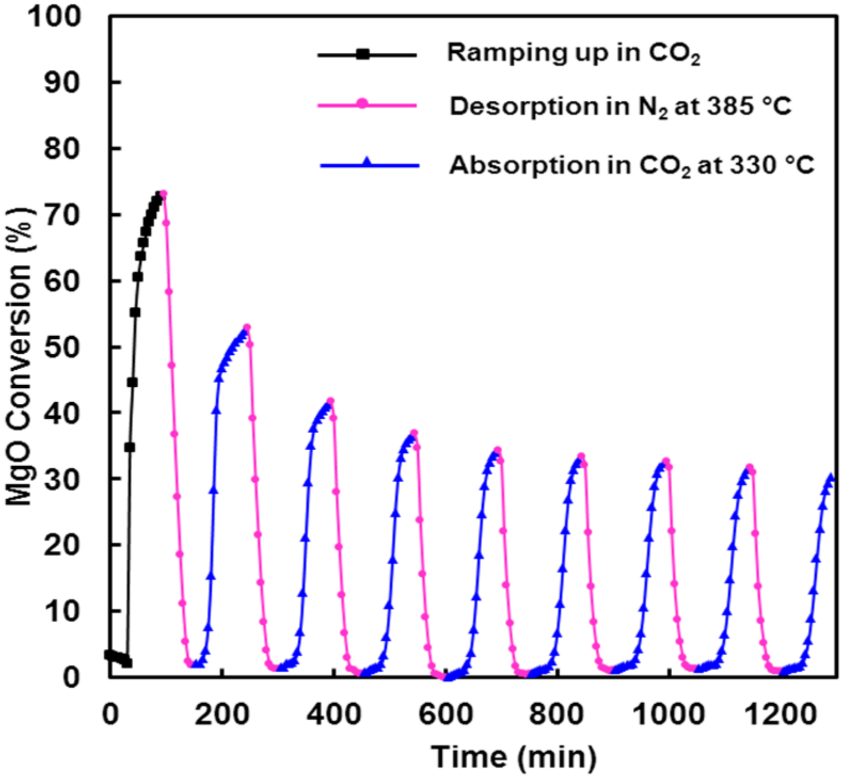


Figure 7. Cyclic CO_2 absorption test of 20%$NaNO_3$ + 80%MgO through temperature-pressure combined swing: 330°C in CO_2 and 385°C in N_2.

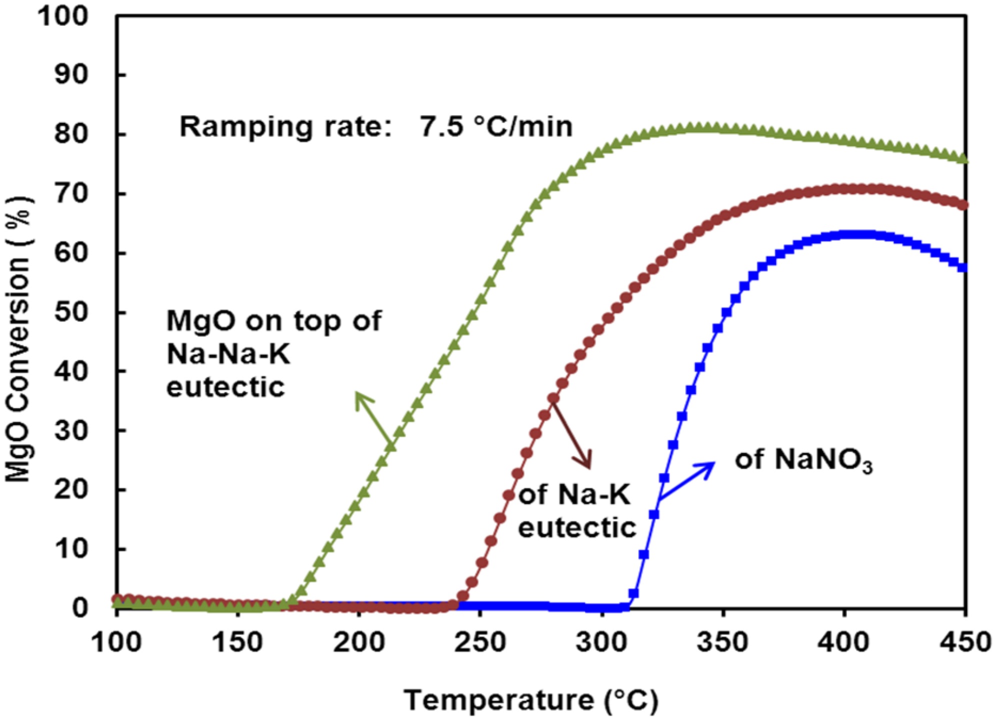


Figure 8. CO_2 absorption on MgO with various nitrate, nitrate-nitrate, and nitrate-nitrite eutectic salts during non-isothermal heating in CO_2.

1.1.3.2 Fixed bed absorption tests

Although initial studies utilized TGA to demonstrate uptake and release of CO_2, it is important that performance be demonstrated in fixed bed tests. Figure 9 shows a schematic of the conceptual experiment, carried out with pressurized syngas containing CO_2. The absorbent was MgO-Na_2CO_3 + $NaNO_3$ double salt, carried out under pressure swing conditions at 400°C.

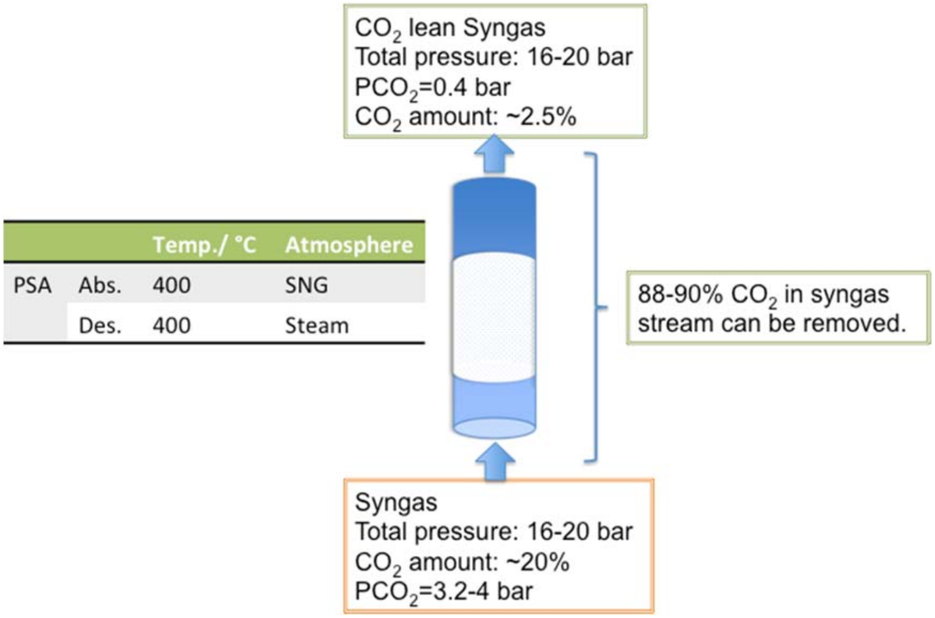


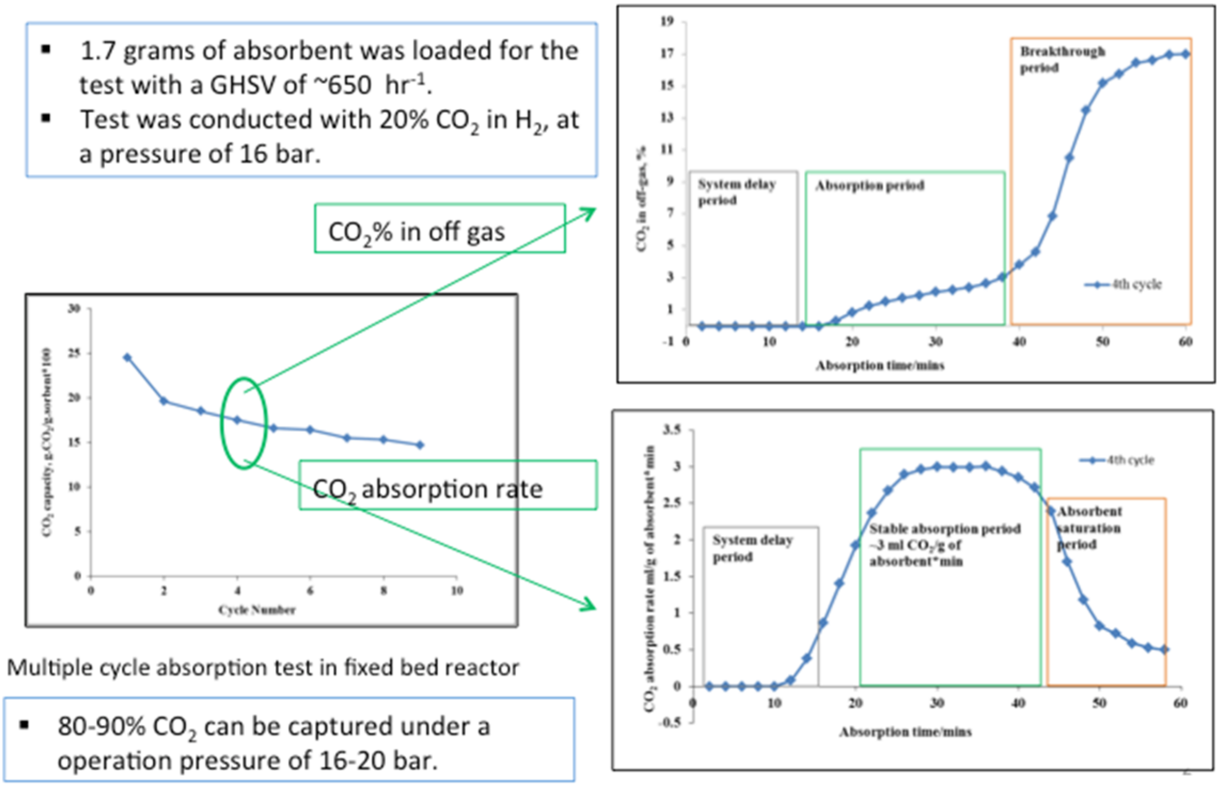
Figure 9. Schematic of fixed bed CO_2 absorption tests.

The experimental details and results are shown in Figure 10. In this case, CO_2 was separated from H_2 (rather than syngas).

1.1.4 Collaborative Activities

1.1.4.1 Collaborations with CAS

In searching for an inexpensive capture material for CO2, CAS was interested in dolomite, a cheap mineral with composition $MgCa(CO_3)_2$. This material can be decomposed at elevated temperatures, to MgO-$CaCO_3$, but this material does not absorb CO_2 over the temperature range 200 to 400°C. Similar to the MgO-Na_2CO_3 double salt, MgO-$CaCO_3$ was also found to absorb CO_2 when a molten salt was added to the mixture. With this information and guidance, CAS was able to continue carrying out work on CO_2 capture with that material, and also identified certain benefits in terms of increased kinetics, especially for decomposition of $MgCa(CO_3)_2$, by the presence of steam. We collaborated with CAS in demonstrating the efficacy of the $NaNO_3$ addition, and also shared data on the effect of pressure on CO_2 absorption. CAS published a paper based on their work on the dolomite system [12].



- 1.7 grams of absorbent was loaded for the test with a GHSV of ~650 hr^{-1}.
- Test was conducted with 20% CO_2 in H_2, at a pressure of 16 bar.

Multiple cycle absorption test in fixed bed reactor

- 80-90% CO_2 can be captured under a operation pressure of 16-20 bar.

Figure 10. Demonstration of CO2 capture in fixed bed operation.

1.1.4.2 Collaborations with NETL

The collaborative work with NETL was primarily carried out with Dr. Yuhua Duan, who contributed to the overall knowledge of these systems through computational work. This included determining the thermodynamics (ΔH and ΔG) of formation of $MgNa_2(CO_3)_2$ relative to $MgCO_3$ + Na_2CO_3. This was essential to our understanding of the operation of the double salt system for CO_2 capture, and understanding why the MgO component did not also participate in CO_2 absorption. Separately, Dr. Duan carried out calculations helping to interpret the role of $NaNO_3$ in facilitating CO_2 capture with MgO. This resulted in several published papers, including two joint papers.

1.1.5 Lessons Learned

We have found working with CAS to be a positive experience. We were able to share CO_2 absorption-desorption data on the dolomite system, with CAS providing capabilities to carry out TGA measurements at pressure and in the presence of steam, a capability which we did not have at PNNL. We also applied to a Funding Opportunity Announcement on CO_2 capture in FY2013, and CAS was selected as a partner in the proposal along with the University of Connecticut. The proposal was not funded. We were careful to apply for patent coverage prior to sharing technical information on the role of nitrate salts with CAS. As expected, once CAS understood the importance of molten salts on CO_2 capture with dolomite, they proceeded to carry out much of their work independently, leading to subsequent independent publications.

In the case of NETL, we learned the importance of personal interactions. Although he was not funded directly through the CAS-NETL-PNNL agreement, Dr. Duan collaborated with us to provide a theoretical underpinning of the CO_2 capture with double salt, based on thermodynamic calculations. He also collaborated with us to understand and quantify the energetic advantage of the use of molten salt on CO_2 capture with MgO. Several publications have come from this collaboration. Aside from Dr. Duan, our interactions with NETL on this project were minimal. Despite significant efforts, we were unable to generate any enthusiasm on the part of NETL for our work. It is likely that more effort on our part to share the excitement and discovery on this project might have generated greater interest.

2.0 Technical accomplishments

2.1 Publications

1. K. Zhang, X. Li, Y. Duan, D. L King, P. Singh, L. Li.; Roles of Double Salt Formation and $NaNO_3$ in Na_2CO_3-Promoted MgO Absorbent for Intermediate Temperature CO_2 Removal. Int. J. Greenhouse Gas Control, 12 (2013) 351–358.
2. K. Zhang, X. Li, W-Z. Li, A. Rohatgi, Y. Duan, P. Singh, L. Li, D. L. King; Phase Transfer-Catalyzed Fast CO_2 Absorption by MgO-Based Absorbents with High Cycling Capacity. Submitted to Advanced Materials Interfaces.
3. Y. Duan, K. Zhang, X. Li, D. L. King, B. Li, L. Zhao, Y. Xiao; ab initio Thermodynamic Study of the CO_2 Capture Properties of M_2CO_3 (M = Na, K)- and $CaCO_3$-Promoted MgO Sorbents Towards Forming Double Salts. Aerosol and Air Quality Research, doi: 10.4209/aaqr.2013.05.0178

2.2 Patents

1. Li, Liyu; King, David L.; Liu, Jun; Huo, Qisheng. Methods, systems, and devices for deep desulfurization of fuel gases. U.S. Patent 8,158,545 (2012).
2. K. Zhang, D. L. King, X. Li, L. Li, A. Rohatgi, P. Singh. System, Sorbents, and Processes for Capture and Release of CO_2. Filed March, 2013.

2.3 Presentations

1. Keling Zhang, Xiaohong Shari Li, Wei-Zhen Li, Yuhua Duan, Aashish Rohatgi, Prabhakar Singh, David L. King; Phase Transfer-Catalyzed Fast CO_2 Absorption by MgO-Based Absorbents with High Cycling Capacity. Poster presentation at the Philadelphia Catalysis Club, October 2013.
2. David L. King, Keling Zhang, X. Shari Li, Aashish Rohatgi; Warm CO_2 Capture by MgO-Based Double Salts: Facilitation by Molten Alkali Nitrate Salts. Presented at the Clearwater Coal Conference, Clearwater, FL, June 2013.
3. Yuhua Duan, Dan Sorescu, David Lubke, Bingyun Li,, Keling Zhang, David King; Theoretical Screening of Mixed Solid Sorbents for CO_2 Capture, 12th Ann. Conf. on Carbon Capture, Use, and Storage May 15, 2013, Pittsburgh, PA.

4. Keling Zhang, David King, Xiaohong Shari Li, Yuhua Duan, Aashish Rohatgi, Prabhakar Singh; The Role of $NaNO_3$ in Facilitating the Capture of CO_2 by MgO-based Oxides: An In Situ Examination of Surface and Interfacial Chemistry. Presented at the MRS 2013 Spring Conference.
5. K. Zhang, X. S. Li, R. Dagle, R. Xing, D. L. King, Y. Duan, P Singh; Carbon Capture-Promoted Syngas Utilization for Production of Fuels and Chemicals. Presented at the 2012 International Pittsburgh Coal Conference, Pittsburgh, PA; October 15-18, 2012.
6. X. S. Li, K. Zhang, L. Li, H. Chen, Y. Duan, P. Singh, D. L. King. MgO-$CaCO_3$ Double Salt Absorbents for CO_2 Removal at 300-500°C. Presented at the 2012 International Pittsburgh Coal Conference, Pittsburgh, PA; October 15-18, 2012.
7. David King, Keling Zhang, Liyu Li, Haobo Chen, Yuhua Duan, Shari Li, Prabhakar Singh; Carbon Capture-Promoted Syngas Utilization for Production of Fuels and Chemicals. Presented orally at the Eleventh Annual Conference on Carbon Capture, Utilization & Sequestration, Pittsburgh, PA, May 2, 2012.
8. Liyu Li, Chris J. Howard, Baowei Chen, Shari X. Li, Haobo Chen, David L. King. Direct Hydrogen Production from Warm Coal and Biomass Syngas. Presented orally at the 28th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 13, 2011.
9. Prabhakar Singh, Keling Zhang, Liyu Li, David L. King. Role of Double Salt Structure and Formulation on arm Temperature CO_2 Capture. Presented orally at the 28th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 15, 2011.

2.4 Demonstrated technical results

In parallel with the CAS-NETL-PNNL project, PNNL had obtained funding from the State of Wyoming to demonstrate syngas cleanup and CO_2 capture-assisted methanation. This has been done in collaboration with the Western Research Institute, the organization that provided the gasifier for the demonstration, using a western (sub-bituminous) coal. In April, 2013, we demonstrated all the steps of the gas cleanup but not the CO_2 capture-enhanced methanation. This was documented in a semiannual report, submitted to the State of Wyoming in June 2013. The latter unit operation, CO_2 capture-enhanced methanation, will be added in a final demonstration, scheduled for April 2014.

3.0 Recommended Next Steps, Collaborative Work

Significant work remains in the development of the CO_2 capture technology. Although CO_2 capture is effective with either the Na_2CO_3-MgO or $CaCO_3$-MgO systems plus $NaNO_3$, the nitrate salt is oxidizing and corrosive. This is evidenced by corrosion spots appearing on the walls of the tubing in contact with the material. This occurs with stainless steel and even to some extent with Hastelloy C. This situation is alleviated working with alumina tubes; hence, the ultimate solution may be to operate with ceramic-lined fixed bed reactors. In addition, CO_2 capture-assisted water gas shift or methanation requires a co-mingling of the capture material plus the metal catalyst. It is possible that the nitrate will oxidize the metal catalyst. Even if the oxidized metal catalyst is re-reduced, loss of $NaNO_3$ will be the end result. Work to identify alternatives to molten nitrate salts needs to be supported and carried out, to determine their effectiveness, operating conditions, and other information. Collaborative work investigating fluid bed operation for the CO_2 capture and release, rather than fixed bed operation, also needs to be examined as an option to deal with the significant temperature rise that can been encountered in the absorbent bed following CO_2 absorption.

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[12] X. Yang, L. Zhao, Y. Xiao; Effect of NaNO3 on MgO−$CaCO_3$ Absorbent for CO_2 Capture at Warm Temperature; Energy Fuels 2013, 27, 7645−7653.

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