

**OHIO COAL DEVELOPMENT OFFICE  
FINAL PROJECT ABSTRACT  
September 30, 2010**

**1. PROJECT SPONSOR:**

Ohio University ("Grantee")  
105 RTEC  
Ohio University  
Athens, OH 45701

**2. PROJECT MANAGER/TITLE:**

Thea Arocho  
Project Manager

**3. OCDO GRANT NO.**

OCRC AY08-09

**4. PHONE:** (740) 593-2856

**EMAIL:** [arocho@ohio.edu](mailto:arocho@ohio.edu)

**5. PROJECT TITLE:** "Ohio Coal Research Consortium AY07-08"

**6. PROJECT TERM FROM:** August 1, 2008 **TO:** September 31, 2010

**7. PROJECT UPDATE** \_\_\_\_ **--OR-- FINAL REPORT** \_\_\_X\_\_\_\_\_

**8. BUDGET:**

**CO-SPONSOR'S NAME**

OCDO  
Universities in the Consortium

**COST-SHARE**

\$ 1,900,473  
\$ 479,669

**TOTAL PROJECT VALUE:**

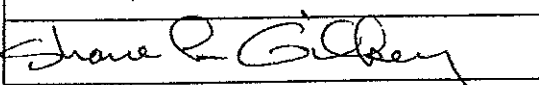
\$ 2,380,142

### Ohio Coal Research Consortium 2009 Projects

#	PI	Title	OCDO	University
<b>Goal B Projects -- Geologic Sequestration</b>				
<b>09-B2-C</b>	Dr. Nescic – OU	Determining the corrosive potential of transporting CO2 with impurities and development of mitigation strategies	\$160,000	\$41,592
<b>Goal C Projects -- Conversion of Coal to Power or Chemicals -- CO2 Ready for Sequestration</b>				
<b>09-C17-C</b>	Dr. Fan – OSU	Enhanced Coal to Liquid Technology Using Calcium Looping Process	\$160,000	\$53,994
<b>09-C24-N</b>	Dr. Verweij – OSU	Affordable CO2-selective membranes for post-combustion capture	160,000	\$40,008
<b>Goal C Projects -- Catalysts and Membrane Systems for Water Gas Shift of Syn-gas to Hydrogen</b>				
<b>09-C6-C</b>	Dr. Guliants – UC	Chemically and Thermally Stable Sodalite Membranes for Hydrogen and Carbon Dioxide Separation	\$160,000	\$51,495
<b>09-C9-C</b>	Drs. Guliants – UC and Verweij – OSU	Multi-Scale Catalytic Membrane Reactors for Hydrogen Production in Coal Gasification Systems	\$160,000	\$51,495
<b>Goal C Projects – Membranes for separation of O2 from Air</b>				
<b>09-C23-N</b>	Dr. Guliants – UC	Metal-Organic Framework-Based Membranes for Highly Selective Gas Separations	\$160,000	84,307

**Proposal Summary**

**OCDO ID# 2009 09-B2-C**

1. Project Title	Determining the corrosive potential of transporting CO2 with impurities and development of mitigation strategies		
2. Sponsoring University	Ohio University		
Address	105 Research and Technology Center		
City/State/Zip	Athens, OH 45701-2979		
Authorized Signature		Title	Assistant Vice President for Research
Co-sponsoring Agency			
Address			
City/State/Zip			
Authorized Signature		Title	
3. Principal Investigator	Srdjan Nestic	Title	Director, Institute for Corrosion and Multiphase Technology
Phone	(740) 593-9945	Fax	(740) 593-9949
E-mail	nesic@ohio.edu		
Co-Principal Investigator	David J. Bayless	Title	Director, Ohio Coal Research Center
Phone	(740) 331-4536	Fax	(740) 593-4902
E-mail	bayless@ohio.edu		
4. Project Location	Ohio University		
5. Continuation of #IV Year 3 Work?	<input type="checkbox"/> Yes	<input type="text" value="If yes, indicate Year 3 Project Number -- B2"/>	
6. Does the proposal contain proprietary or trade secret information?	<input checked="" type="checkbox"/> No	<input type="checkbox"/> Yes, proprietary or trade secret information contained on pages	

**Budget Summary**

Contributor	Dollar Contribution	Percentage of Total
OCDO	\$160,000	79%
Sponsoring University	\$41,592	21%
Co-sponsor #1		
Co-sponsor #2		
<b>Total Project Cost</b>	<b>\$201,592</b>	<b>100%</b>

## Determining the Corrosive Potential of Transporting CO<sub>2</sub> with Impurities and Development of Mitigation Strategies

### Executive summary

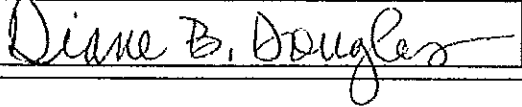
Emissions from fossil fuel-fired power plants represent a significant source of carbon dioxide (CO<sub>2</sub>) emissions, a known greenhouse gas. The capture and storage of CO<sub>2</sub> in geological reservoirs is now considered to be one of the main options for achieving deep reductions in greenhouse gas emissions. The CO<sub>2</sub> capture and storage process involves three stages: capture of the CO<sub>2</sub> from the power plant or industrial process, transmission of the CO<sub>2</sub> to the storage site followed by injection into the geological reservoir. The research activities are largely concentrating on development of the capture technology to reduce costs, and on assessing the technical feasibility of injecting and monitoring the CO<sub>2</sub> within the geological reservoirs themselves. Little of the research is being conducted on CO<sub>2</sub> transmission, but this remains a critical component that should not be overlooked.

In the period of 2007 ~ 2009, the Institute for Corrosion and Multiphase Technology (ICMT) and the Ohio Coal Research Center (OCRC) at Ohio University have conducted quantitative evaluation of thermodynamic and corrosion properties in both CO<sub>2</sub>-saturated water and water-saturated CO<sub>2</sub> phases to evaluate corrosion potential in CO<sub>2</sub> transport pipelines. In addition, the effect of impurities on high pressure CO<sub>2</sub> corrosion was also investigated by experimentation. The results indicated that corrosion rates are much higher if free water is present and the presence of impurities in CO<sub>2</sub> can increase the rate of corrosion of carbon steel in both CO<sub>2</sub>-saturated water and water-saturated CO<sub>2</sub> phases. Operating with very low level of water can inhibit the formation of free water which can reduce corrosion in CO<sub>2</sub> pipelines. However, recent studies as well as our results suggest that there still has a possibility of corrosion in CO<sub>2</sub>-rich phase with impurities, and it should not be neglected.

This work will be focused on addressing **Goal B: Evaluate CO<sub>2</sub> control methods which can be applied in Ohio.** Specifically, the corrosion of carbon steel in supercritical CO<sub>2</sub> with water and impurities (O<sub>2</sub>, SO<sub>2</sub>) will be studied under different conditions such as flow, pressure, temperature, water content, and impurities concentration. In addition, the guideline for pipeline safety of CO<sub>2</sub> pipeline will be established based on experimental data and pipeline information. It will be jointly undertaken by the ICMT and the OCRC in Ohio University. The OCRC has expertise on power plant and gasification plant operation, as well as funded research from the Department of Energy on CO<sub>2</sub> sequestration. The ICMT and the OCRC will visit American Electric Power (AEP), the USDOE/Albany Research Center, and ENCANA to obtain information on the water removal process, thermodynamic properties of mixtures and CO<sub>2</sub> transporting pipeline properties. The ICMT has conducted a large volume of research on CO<sub>2</sub> corrosion of mild steel which is complicated by many factors including multiphase flow, pressure, H<sub>2</sub>S, organic acids and other impurities and additives. Many of these factors have been investigated at ICMT covering a broad range of conditions seen both in downhole tubing as well as upstream piping. ICMT houses one of the world's largest facilities for testing CO<sub>2</sub> corrosion. It consists of an array of five single phase / multiphase flow loops as well as a battery of autoclaves which can work up to 2000 psi. Using these facilities realistic hydrodynamic and fluid chemistry conditions can be set up to study high pressure CO<sub>2</sub> corrosion with impurities. Advanced corrosion measuring techniques and analytical techniques will be deployed by ICMT to understand the effects of various impurities and flow on high pressure CO<sub>2</sub> corrosion mechanism. A guideline for safety of CO<sub>2</sub> pipelines will provide a database for the corrosion properties of carbon steel in supercritical CO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/SO<sub>2</sub> environments with all possible scenarios in CO<sub>2</sub> transport pipeline. It will also address a relationship between corrosion risk and lifetime of CO<sub>2</sub> transport pipelines under different conditions as well as mitigation strategies for corrosive potential of CO<sub>2</sub> transport pipeline.

**Proposal Summary**

**OCDO ID# 2009 09-C6-C**

1. Project Title	Chemically and Thermally Stable Sodalite Membranes for Hydrogen and Carbon Dioxide Separation		
2. Sponsoring University	University of Cincinnati		
Address	51 Goodman Drive, Suite 530 University Hall		
City/State/Zip	Cincinnati, Ohio 45221-0222		
Authorized Signature		Title	Sr. Grants Admin, Sponsored Research Services
Co-sponsoring Agency			
Address			
City/State/Zip			
Authorized Signature		Title	
3. Principal Investigator	Vadim Gullants	Title	Professor
Phone	(513) 556-0203	Fax	(513) 556-3443
E-mail	vgullant@alpha.che.uc.edu		
Co-Principal Investigator		Title	
Phone	( )	Fax	( )
E-mail			
4. Project Location	Cincinnati, Ohio		
5. Continuation of #IV Year 3 Work?	<input checked="" type="checkbox"/> YES	If yes, indicate Year 3 Project Number -- OCRC-AY08-09-C6	
6. Does the proposal contain proprietary or trade secret information?	<input checked="" type="checkbox"/> No	Yes, proprietary or trade secret information contained on _____ pages	

**Budget Summary**

Contributor	Dollar Contribution	Percentage of Total
OCDO	\$160,000	76%
Sponsoring University	\$ 51,495	24%
Co-sponsor #1		
Co-sponsor #2		
<b>Total Project Cost</b>	<b>\$211,495</b>	<b>100%</b>

## EXECUTIVE SUMMARY

Chemically and thermally stable zeolite membranes that possess small intracrystalline pores of molecular dimensions are highly desirable for H<sub>2</sub> separation from coal gasification products, such as syngas. However, the currently investigated zeolite membranes, such as *silicalite-1* (MFI) and *zeolite Y* (FAU), possess significantly larger pore sizes than the sizes of H<sub>2</sub>, CO<sub>2</sub> and CO molecules. The lack of suitable zeolite membranes represents a major obstacle in the development of novel inorganic membrane technology for hydrogen separation. In this on-going project C6 we successfully demonstrated that thin and essentially defect-free small-pore zeolite membranes grown on lab-made disk-shaped supports with unoptimized mass-transfer resistance showed the H<sub>2</sub> permeance of  $\sim 2 \cdot 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> and  $\alpha(\text{H}_2/\text{CO}_2) \sim 40\text{-}80$  in binary gas permeation tests. These membranes are thermally and chemically stable exhibiting no change in separation characteristics when tested in 3 vol. % moisture-containing gas stream at 450°C for 48h. However, for practical applications, these membranes will be fabricated on commercial tubular supports with pore structure optimized to provide enhanced H<sub>2</sub> permeance greater than  $5 \cdot 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> required for the target applications. Therefore, the two-year objective of this work is as follows:

- Develop chemically and thermally stable tubular zeolite membranes which exhibit in pilot-scale tests the H<sub>2</sub> permeance  $\geq 5 \cdot 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> and  $\alpha(\text{H}_2/\text{CO}) > 100$ , thereby lowering reforming costs for H<sub>2</sub> production to < \$0.40/kg

In this two-year program, the zeolite membranes will be fabricated initially on short sections of several types of commercial tubular supports obtained from Pall Corp. and screened for quality at the University of Cincinnati. Following these initial tests, longer sections of best tubular zeolite membranes will be fabricated and tested on pilot scale for the target H<sub>2</sub> separations from (1) coal syngas, (2) SMR and (3) refinery offgas streams as part of collaborations with NETL (1) and APCI (2 and 3). We will conduct one-month durability tests of the best membranes under typical process conditions in the above streams containing H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and hydrocarbons (up to C<sub>6</sub>). Lastly, we will conduct preliminary process design and economic analysis of H<sub>2</sub> separation processes employing novel zeolite membranes integrated with coal gasification, SMR and refinery processes in collaboration with NETL, APCI and Pall Corp. We anticipate that these tubular membranes will be thermally (700°C), chemically and mechanically (200 atm ΔP) stable under typical process conditions for over 1 month and provide >90% H<sub>2</sub> for utility power generation, 98% H<sub>2</sub> competitively with polymeric membranes, and 99.9% H<sub>2</sub> competitively with PSA.

Whereas this proposed work will focus on the development of small-pore zeolite membranes for H<sub>2</sub> separation from several process streams, the science underlying the synthesis of these membranes is the subject of a concept paper being submitted by the PI to US DOE ARPA-E DE 0000065 for funding.

## EXPANDED DISCUSSION ON KEY POINTS

*No concerns were raised by reviewers of this pre-proposal.* Therefore, we highlight here the key point related to long-term stability testing of optimized tubular zeolite membranes of this project. The long-term targets for H<sub>2</sub> selective membranes have been recently defined ("Hydrogen from Coal", Research, Development and Demonstration Plan for the Period 2004 through 2015, US DOE, Office of Fossil Energy, Dec. 26, 2005, 69 pp.) call for <50% change in the above H<sub>2</sub>-permselective properties over >10,000 h operation with >10 start/stop cycles under WGS and steam reforming conditions. Therefore, in the 30 day-long test proposed for Year 2, this test will include thermal cycling. For example, the membranes will be tested for about 200 hours and then allowed to cool to ambient temperature. This on/off cycle will be then repeated from four to six times resulting in an accumulative 30 days of operation.

## EXPANDED DETAILS ON THE SOW

This project represents a collaboration between the University of Cincinnati, NETL, APCI and Pall Corporation focused on the scaleup of microporous zeolite membranes for hydrogen separation developed in project C6. Please note that these collaborators will provide significant in-kind and in-cash

**Proposal Summary**

**OCDO ID# 2009 09-C9-C**

1. Project Title	Multi-Scale Catalytic Membrane Reactors for Hydrogen Production in Coal Gasification Systems		
2. Sponsoring University	University of Cincinnati		
Address	51 Goodman Drive, Suite 530 University Hall		
City/State/Zip	Cincinnati, Ohio 45221-0222		
Authorized Signature	<i>Diane B. Douglas</i>	Title	Sr. Grants Admin, Sponsored Research Services
Co-sponsoring Agency			
Address			
City/State/Zip			
Authorized Signature		Title	
3. Principal Investigator	Vadim Gullants	Title	Professor
Phone	(513) 556-0203	Fax	(513) 556-3443
E-mail	vgulliant@alpha.che.uc.edu		
Co-Principal Investigator		Title	
Phone	( )	Fax	( )
E-mail			
4. Project Location	Cincinnati, Ohio		
5. Continuation of #IV Year 3 Work?	<input checked="" type="checkbox"/> YES	If yes, indicate Year 3 Project Number -- OCRC-AY08-09-C9	
6. Does the proposal contain proprietary or trade secret information?	<input checked="" type="checkbox"/> No	Yes, proprietary or trade secret information contained on pages	

**Budget Summary**

Contributor	Dollar Contribution	Percentage of Total
OCDO	\$160,000	76%
Sponsoring University	\$ 51,495	24%
Co-sponsor #1		
Co-sponsor #2		
<b>Total Project Cost</b>	<b>\$211,495</b>	<b>100%</b>

## EXECUTIVE SUMMARY

This two-year project is aimed at developing new sulfur-resistant, chemically and thermally stable membrane reactors (CMRs) for hydrogen production and separation from coal syngas, which overcome the stability, catalytic activity and H<sub>2</sub> separation selectivity limitations of current CMRs based on Cu water-gas-shift (WGS) catalysts and *silicalite-1* membranes. The development of novel nanostructured Cu/Ni WGS catalysts, which display enhanced activity in a low temperature WGS process and improved stability, represents the major focus of this work. Accordingly, the overall objective of this two-year project is as follows:

- The two-year objective is to develop new sulfur-resistant, chemically and thermally stable membrane reactors employing novel Cu/Ni WGS catalysts with H<sub>2</sub> permeance  $>5 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  and H<sub>2</sub>/CO<sub>x</sub> selectivity  $>50$ , to enable lowering reforming costs for H<sub>2</sub> production to  $< \$0.40/\text{kg}$

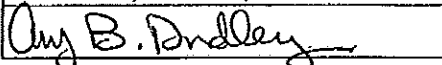
The novel Cu/Ni catalysts containing Cu/Ni alloy nanoparticles (ca. 3-10 nm) supported on commercial oxide supports will be obtained by 3 promising synthesis methods: (1) in reverse micelles; (2) by polyol process; and (3) by dendrimer-assisted synthesis. The Cu/Ni nanoparticle size distribution and morphology will be characterized by TEM and SEM. Their phases and surface compositions will be characterized by XRD and X-ray photoelectron spectroscopy (XPS). XPS will also shed light on the chemical state of surface Cu and Ni species as a function of processing and WGS reaction conditions. Temperature programmed reduction (TPR) in H<sub>2</sub> will yield information on the metal-metal and metal-support interactions. The specific Cu and Ni surface areas in these catalysts will be characterized by H<sub>2</sub>, CO and N<sub>2</sub>O adsorption.

The WGS activity will be tested using a microreactor equipped with a TCD/FID GC and a simulated coal syngas of 55% CO, 31% H<sub>2</sub>, 4% CO<sub>2</sub>, 5% CH<sub>4</sub> and 5% N<sub>2</sub> (dry basis) diluted with appropriate amount of steam. The reaction rates for the Cu/Ni catalysts will be compared with those of other low temperature WGS catalysts and the sulfur sensitivity of the best Cu/Ni catalysts (promoted with ZnO and Sn) will be investigated by exposing them to 500 ppm of H<sub>2</sub>S in the model WGS feed. It is anticipated that this work will lead to identification of novel Cu/Ni alloy catalysts with significantly improved WGS activity and stability that are dependent on their chemical composition, the size of Cu/Ni alloy nanoparticles, their shape and the nature of oxide support.

These novel WGS catalysts will be tested with two kinds of H<sub>2</sub>-permeable membranes, (1) zeolitic membranes being developed by the PI at the University of Cincinnati (UC) in project C6, and (2) amorphous silica membranes in development by Prof. Verweij at OSU. The best disk-shaped zeolitic membranes synthesized at UC display the binary H<sub>2</sub>/CO<sub>2</sub> selectivity of 50-80 and steady-state H<sub>2</sub> permeance  $\sim 2 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  at 1 atm and 400°C. Their H<sub>2</sub> permeance is expected to be further increased to  $\geq 5 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  in the next two years through the use of commercial tubular supports with optimized mass-transfer characteristics as described in the project C6 proposal submitted to OCDO for funding. It is expected that the requested OCDO support will enable this UC/OSU team to obtain critical experimental data and pursue DOE funding in CMRs for H<sub>2</sub> separation.

Proposal Summary

OCDO ID# 2009 09-C17-C

1. Project Title	Enhanced Coal to Liquid Technology Using Calcium Looping Process		
2. Sponsoring University	The Ohio State University Research Foundation		
Address	1960 Kenny Road		
City/State/Zip	Columbus, Ohio 43210		
Authorized Signature		Title	Sr. Sponsored Program Officer
Co-sponsoring Agency			
Address			
City/State/Zip			
Authorized Signature		Title	
3. Principal Investigator	Dr. Jacques Zakin	Title	Professor
Phone	(614) 688-4113	Fax	(614) 292-3769
E-mail	zakin.1@osu.edu		
Co-Principal Investigator	Dr. L.S. Fan	Title	Distinguished University Professor
Phone	(614) 688-3262	Fax	(614) 292-3769
E-mail	fan.1@osu.edu		
4. Project Location	Koffolt Laboratory		
5. Continuation of #IV Year 3 Work?	<input checked="" type="checkbox"/> Yes	If yes, indicate Year 3 Project Number - C17	
6. Does the proposal contain proprietary or trade secret information?	<input checked="" type="checkbox"/> Yes	Yes, proprietary or trade secret information contained on pages 2, 3, 5, 6	

Contributor	Dollar Contribution	Percentage of Total
OCDO	\$160,000	75%
Sponsoring University	\$53,994	25%
Co-sponsor #1		
Co-sponsor #2		
<b>Total Project Cost</b>	<b>\$213,994</b>	<b>100%</b>

## ENHANCED COAL TO LIQUID TECHNOLOGY USING CALCIUM LOOPING PROCESS

### Executive Summary

The increasing energy demand and the necessity for energy independence have brought coal to liquid (CTL) technologies, which have the capability of near term implementation due to their compatibility with the existing infrastructure, to the forefront. The United States has 494 billion tons of coal reserves, within which the state of Ohio has 5% or 24 billion tons of reserves and hence the development of an energy efficient coal to liquid technology will be very beneficial. Coal derived liquids are high quality, ultraclean fuels which result in lower particulate, sulfur and NO<sub>x</sub> emissions when compared to the petroleum derived fuels. Currently, the indirect production of coal derived liquid fuels is through the coal gasification and Fischer Tropsch (FT) process using multistage gas clean up, water gas shift reactors(WGSR) to adjust the syngas composition, PSA to produce H<sub>2</sub> for the product upgrader and syngas recycle through the FT reactor. It has been estimated that the carbon foot print of the coal to liquids process is at least 150 – 175% higher than petroleum based fuels. By the implementation of carbon capture and sequestration, the life cycle CO<sub>2</sub> emissions for the coal to liquids process can be reduced by 20% compared to conventional fuel.

The addition of CO<sub>2</sub> capture to the coal to liquids process will further add units to reform the C1-C4 hydrocarbons produced in the off gases from the FT reactor and CO<sub>2</sub> capture units, making the over all process very energy intensive. In contrast, the Calcium Looping Process (CLP) utilizes the principles of process intensification, combining the reaction and separation steps in a single unit and improving the energy efficiency and economics of the over all process. It is capable of producing a sequestration ready CO<sub>2</sub> stream by capturing all the CO<sub>2</sub> emitted during the coal to liquids process. In addition to achieving carbon capture, the CLP improves the efficiency of the coal to liquids process by conversion of the Fischer Tropsch reactor's off gases to hydrogen which is used to adjust the H<sub>2</sub>:CO ratio of the FT feed and for the product upgrader. The CLP is capable of reforming the hydrocarbons and shifting the unreacted syngas in the FT offgases in the presence of a calcium based sorbent and reforming catalyst while simultaneously capturing the CO<sub>2</sub>. It integrates the reforming of hydrocarbons, water gas shift (WGS) reaction and in-situ carbon dioxide (CO<sub>2</sub>) removal at high temperatures in a single reactor while eliminating the need for excess steam addition, WGS reactor and catalyst, CO<sub>2</sub> scrubber and a hydrogen purification system and reduces the overall foot print of the hydrogen production process. The CLP comprises of two reactors; the carbonation reactor where the thermodynamic constraint of the reforming and WGS reaction is overcome by the incessant removal of the CO<sub>2</sub> product and high-purity H<sub>2</sub> is produced and the calciner where the calcium sorbent is regenerated and a sequestration-ready CO<sub>2</sub> stream is produced. The purity of H<sub>2</sub> and the conversion of hydrocarbons are increased by a large extent when the carbonation reaction is integrated with the WGS reaction. The exothermic carbonation and WGSR convert the highly endothermic reforming of hydrocarbons into a heat neutral process thus simplifying the reforming process and reducing the temperature of reforming from >900C to 650C. Experiments conducted in a bench scale facility have revealed that high purity H<sub>2</sub> of >97% purity can be produced by the CLP with integrated CO<sub>2</sub> capture.

The overall objective of this project is to combine various unit operations (reforming of hydrocarbon FT offgases, WGS, CO<sub>2</sub> capture, sulfur capture and H<sub>2</sub> production for the upgrader) into a single stage reactor and improve the over all efficiency and footprint of the CTL process by using the CLP. The specific objectives are to a) adjust the syngas feed to the FT reactor into a 2:1 H<sub>2</sub>:CO stream without a catalyst, convert all the C1-C4 hydrocarbons and unconverted syngas in the FT offgases thus removing the recycle and achieve simultaneous CO<sub>2</sub> and H<sub>2</sub>S capture at high temperatures to ppb levels in a single stage reactor, b)produce H<sub>2</sub> for the product upgrader, c)produce a sequestration ready CO<sub>2</sub> stream, d)reduce the excess steam requirement e)produce more liquid fuel than the conventional process, for the same amount of coal consumed by using the FT offgases. During the first year, the combined reforming, WGS, CO<sub>2</sub> and sulfur removal reaction will be investigated in simulated fuel gas streams containing the offgases from the FT reactor in the presence of various catalysts and optimizing the conditions of operation. Recyclability of the sorbent and multicyclic reaction and regeneration will be studied in a bench scale reactor. ASPEN efficiency analysis will also be conducted throughout the length of the project. The second project year will involve subpilot scale testing of the CLP for CTL process and overall preliminary technoeconomic and lifecycle analyses.

**Proposal Summary**

**OCDO ID# 2009 09-C23-N**

1. Project Title	Metal-Organic Framework-Based Membranes for Highly Selective Gas Separations		
2. Sponsoring University	University of Cincinnati		
Address	51 Goodman Drive, Suite 530 University Hall		
City/State/Zip	Cincinnati, Ohio 45221-0222		
Authorized Signature	<i>Diane B. Douglas</i>	Title	Sr. Grants Admin, Sponsored Research Services
Co-sponsoring Agency			
Address			
City/State/Zip			
Authorized Signature		Title	
3. Principal Investigator	Vadim Gullants	Title	Professor
Phone	(513) 556-0203	Fax	(513) 556-3443
E-mail	vgullant@alpha.che.uc.edu		
Co-Principal Investigator		Title	
Phone	( )	Fax	( )
E-mail			
4. Project Location	Cincinnati, Ohio		
5. Continuation of #IV Year 3 Work?	<input type="checkbox"/> NO	If yes, indicate Year 3 Project Number --	
6. Does the proposal contain proprietary or trade secret information?	<input checked="" type="radio"/> (No)	Yes, proprietary or trade secret information contained on pages	

**Budget Summary**

Contributor	Dollar Contribution	Percentage of Total
OCDO	\$160,000	65%
Sponsoring University	\$ 84,307	35%
Co-sponsor #1		
Co-sponsor #2		
<b>Total Project Cost</b>	<b>\$244,307</b>	<b>100%</b>

## EXECUTIVE SUMMARY

Zeolites have been under intense investigation over the past 70 years as adsorbents for industrial gas separations and, more recently, as inorganic and mixed matrix membranes. They are attractive for gas separation applications because of their adsorption and molecular sieving properties owing to the presence of micropores with sizes precisely defined by their crystal structures. Zeolites are highly desirable as adsorbents and membrane materials for three highly important gas separations which will produce CO<sub>2</sub>-rich waste streams suitable for sequestration: (1) CO<sub>2</sub> separation from N<sub>2</sub> present in flue gas; (2) air separation for oxycombustion to produce CO<sub>2</sub>-rich flue gas; and (3) CO<sub>2</sub> separation from H<sub>2</sub>-rich coal syngas (and delivery of the H<sub>2</sub> product). However, the currently investigated *zeolite Y* (FAU) and *silicalite-1* (MFI) membranes and adsorbents suffer from low (perm)selectivities in the above separations due to large pore sizes and the lack of discriminating intermolecular interactions for the relevant gases.

Therefore, the development of these gas separation applications is strongly coupled to the rate of the discovery of new zeolite structures with suitable framework chemistries and pore sizes. While the discovery of new synthetic zeolites has slowed down significantly in recent decades, the field of microporous *metal-organic* (MOF) and *zeolitic imidazolate* (ZIF) frameworks first reported several years ago has been undergoing rapid development. In this 2-year project several promising ZIFs and MOFs will be synthesized and their gas separation properties as adsorbents and membranes will be explored in binary gas adsorption and permeation tests. Accordingly, the major project objectives are the following:

- Demonstrate the proof of concept for ZIFs and MOF to separate (1) CO<sub>2</sub> from N<sub>2</sub> with binary adsorption selectivities > 50 at r.t.-200°C and 0.2-40 atm; (2) air; and (3) H<sub>2</sub> from coal syngas manifested in binary adsorption H<sub>2</sub>/CO<sub>2</sub> (and H<sub>2</sub>/CO) selectivities > 50 at r.t.-350°C and 1-30 atm
- Demonstrate the proof of concept for initial membranes made from the best ZIFs and MOF identified in Year 1 which display the permselectivities >40 and permeances of selectively permeating gas species >5·10<sup>-8</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>

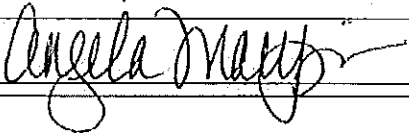
Several promising ZIFs and MOF structures will be synthesized by reported methods and characterized by XRD (phase purity and thermal stability), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> atmospheres (thermal and chemical stability), N<sub>2</sub> adsorption at 77K (pore volumes and sizes). Single-component CO<sub>2</sub>, CO, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> and binary CO<sub>2</sub>/N<sub>2</sub>, N<sub>2</sub>/O<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and CO/H<sub>2</sub> adsorption tests will be conducted at r.t.-100°C, total pressures of 0-50 atm and several gas compositions in order to fully characterize the potential of the novel ZIFs and MOFs for the target gas separation applications. In the case of ZIFs, we will aim to elucidate the process conditions for the H<sub>2</sub> size-selective adsorption behavior of these small-pore frameworks.

Chemical stability of the best ZIFs and MOF identified in the binary adsorption tests will be studied in the presence of typical gas impurities present in relevant process streams, e.g., SO<sub>2</sub> and NO saturated with H<sub>2</sub>O at 50°C and 1 atm typical of flue gas after a wet scrubber; H<sub>2</sub>S and H<sub>2</sub>O at 50-350°C and 1-5 atm typical for coal syngas in the case of ZIFs for H<sub>2</sub> separation. These ZIF and MOF samples will be examined by the XRD, N<sub>2</sub> porosimetry and gas adsorption to determine their chemical stability in the presence of typical flue and coal syngas impurities.

The mixed-matrix membranes containing the best ZIFs/MOF and several glassy and rubbery commercial polymers will be fabricated by reported methods. The gas solubility in these membranes will be characterized as a function of the ZIF/MOF loading employing adsorption microbalance. The viscoelasticity and modulus of the membrane will be determined by dynamic mechanical analysis, whereas the tensile strength will be measured using the Instron. This information will aid in understanding the effect of ZIF/MOF on the membrane strength. SEM and TEM will provide information about the membrane morphology, the uniformity of ZIF/MOF dispersion in the matrix, and the crystal size. Gas permeation studies will be conducted employing available steady-/unsteady-state setup and CO<sub>2</sub>, CO, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> as well as their relevant binary mixtures at feed pressures up to 40 atm at r.t.-100°C. These experiments will aim at establishing the structure-property relationships for the ZIFs and MOFs and engineer the mixed-matrix membranes for the target gas separations.

**Proposal Summary**

**OCDO ID# 2009 09-C24-N**

1. Project Title	Affordable CO <sub>2</sub> -selective membranes for post-combustion capture		
2. Sponsoring University	The Ohio State University Research Foundation		
Address	1960 Kenny Road		
City/State/Zip	Columbus, OH 43210-1163		
Authorized Signature		Title	Sr. Sponsored Program Officer
Co-sponsoring Agency			
Address			
City/State/Zip			
Authorized Signature		Title	
3. Principal Investigator	Hendrik Verweij	Title	Professor
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Co-Principal Investigator	N/A	Title	
Phone	( )	Fax	( )
E-mail			
4. Project Location			
5. Continuation of #IV Year 3 Work?	<input type="checkbox"/> No		
6. Does the proposal contain proprietary or trade secret information?	<input type="checkbox"/> No		

**Budget Summary**

Contributor	Dollar Contribution	Percentage of Total
OCDO	\$160,000	80%
Sponsoring University	\$40,008	20%
Co-sponsor #1		
Co-sponsor #2		
<b>Total Project Cost</b>	<b>\$200,008</b>	<b>100%</b>

# Affordable CO<sub>2</sub>-selective membranes for post-combustion capture

## 2. Executive Summary

### *Project goal*

The overall goal of the proposed project is to realize practical CO<sub>2</sub>-selective inorganic (ceramic) membranes, primarily for post-combustion capture. These membranes have high molar permeance of  $f_{\text{CO}_2}^a > 10^{-6}$  [mol/(m<sup>2</sup>s·Pa)]<sup>\*</sup>, and a selectivity >20 with respect to N<sub>2</sub> and H<sub>2</sub>O. The operation temperature can range from room temperature to 400°C; the pressure difference across membrane is up to 10 Bar for both flat and tubular geometries. The overall membrane performance is expected to be stable for >5 years, with <50% degradation in permeance while maintaining the selectivity. In addition, polymer supports will be applied to replace conventional inorganic supports, and rapid thermal processing will be developed to reduce the synthesis time from >5 days to <2 hours. These two approaches will lead to a significant reduction of membrane fabrication costs from unacceptable current >\$500/m<sup>2</sup> to viable <\$50/m<sup>2</sup>. The separation function will be provided by a thin micro-porous inorganic membrane. The three most promising compositions are, zeolite Y, γ-alumina and amorphous silica. All have been tested in our lab and show optimum performance in distinct operational regimes with temperatures, <100°C, <200°C and <400°C respectively.

### *Anticipated achievements*

Microporous, zeolite Y, γ-Al<sub>2</sub>O<sub>3</sub> and amorphous silica will be synthesized as thin membranes on a commercially available polysulfone support. The membrane structure will be formed by colloidal dip-deposition, additive removal by reactive ion etching, and consolidation by rapid thermal processing. The latter will enable forming of high-temperature phases on polymer supports with limited thermal stability. The membrane thickness will be <500 nm to obtain a high permeance, and to avoid cracking or delamination of the membrane by flexing the support. A top thin layer of poly-di-methyl-siloxane (PDMS) will be applied for mechanical protection and to suppress the adverse defects of membrane defects on intrinsic membrane selectivity. The operation conditions will be chosen such that the feed side of the membrane becomes >50% saturated with CO<sub>2</sub>. This leads to transport mechanism, known as "Type II", that provides high flux and selectivity for CO<sub>2</sub>. Studies on single gas and mixture permeation will be carried out as a function of conditions to optimize performance and confirm "Type II" separation.

### *Justification for the work*

Current emissions of CO<sub>2</sub> in power plants waste (flue) gas streams constitute about one third of the total CO<sub>2</sub> emissions from human sources in the U.S. It has also become the largest factor in the U.S. contribution to unacceptable global climate change due to the greenhouse effect. Addressing this problem requires energy efficient, and hence cost effective, separation of CO<sub>2</sub> from other flue gas molecules. Membranes offer the best potential to achieve this goal since they operate isothermally and, ideally, do not require any external work. Membranes that approach the ideal limit have a high-selectivity combined with a high flux. A low cost price and high operational stability ensure that the external work input during manufacturing is much less than the equivalent amount of work produced in the power plant. Inorganic membranes are generally more selective and stable in harsh conditions, and up to higher temperatures. The PDMS "defect cover" layer is stable up to 400°C; the polysulfone support is stable up to 160°C which is sufficient for the target application. Other organic polymer support materials that allow higher temperatures are in development. Recently our group demonstrated, for the first time, the feasibility and use in membrane fabrication of rapid processing techniques use in the semi-conductor industry, such as high-intensity infra-red illumination and reactive ion etching. This will lead to better membrane properties and, especially reduction of the fabrication cost and time.

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\*  $f_{\text{CO}_2}^a$  can vary non-linear with CO<sub>2</sub> pressure, this number is for typical, relevant conditions.