

Carbon Dioxide Capture And Separation Techniques For Power Generation Point Sources

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POINT SOURCES OF INTEREST

- **Fossil-fuel power generation plants contribute about 1/3 of anthropogenic CO₂ emissions**
- **Power generation point sources**
 - Pulverized-coal combustion plants
 - Advanced power systems
- **CO₂ concentration from large sources (fossil fueled power plants) typically low**
- **Capture step**
 - Post-combustion
 - Pre-combustion
- **Storage step in carbon sequestration requires concentrated CO₂**



Novel CO₂ Capture Technologies For Power Generation Point Sources

- Aqua Ammonia Process for Multicomponent Removal 

- Hybrid Membranes for CO₂ Separation 

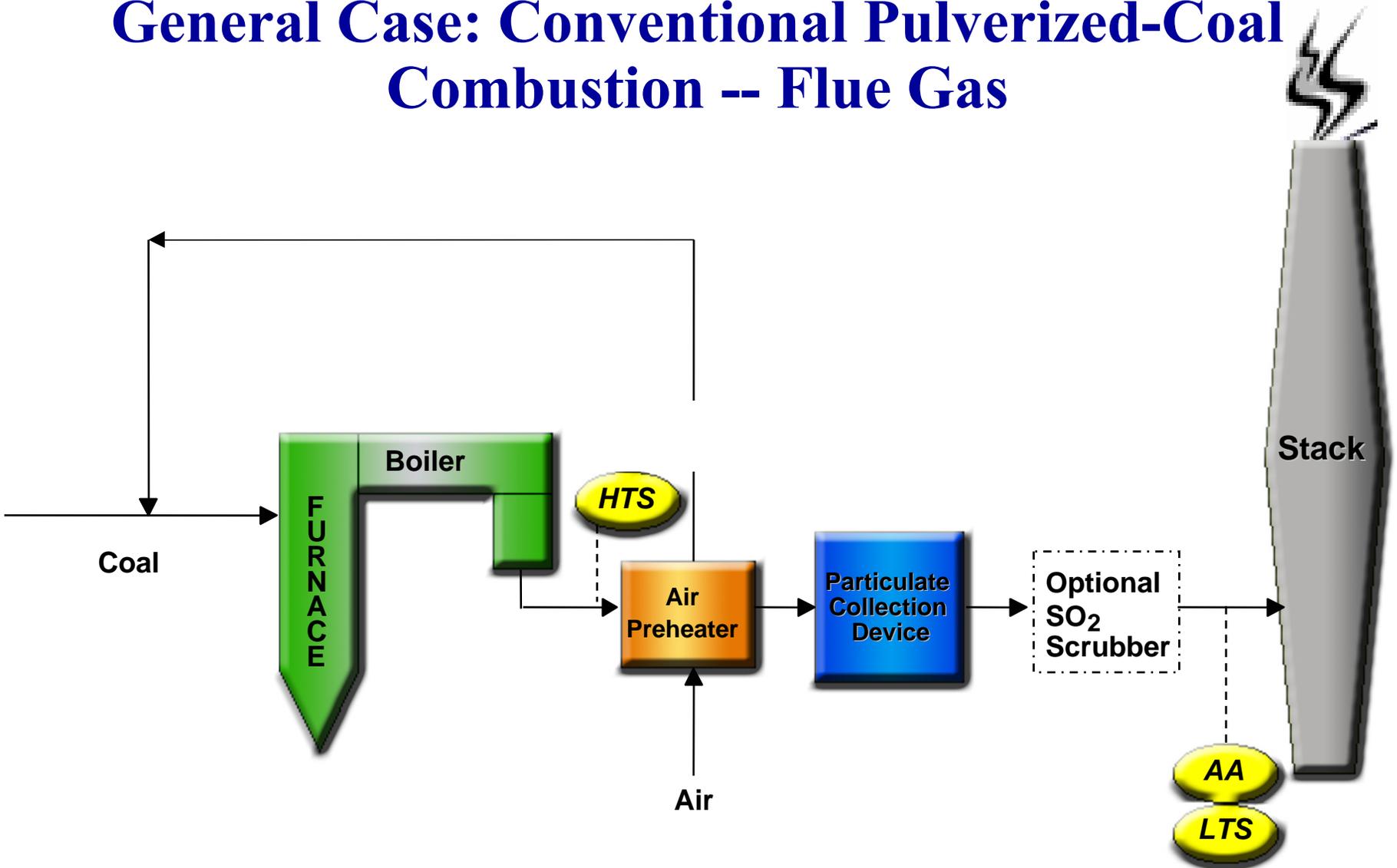
- Solvents for CO₂ Capture 

- Regenerable Sorbent Capture Techniques

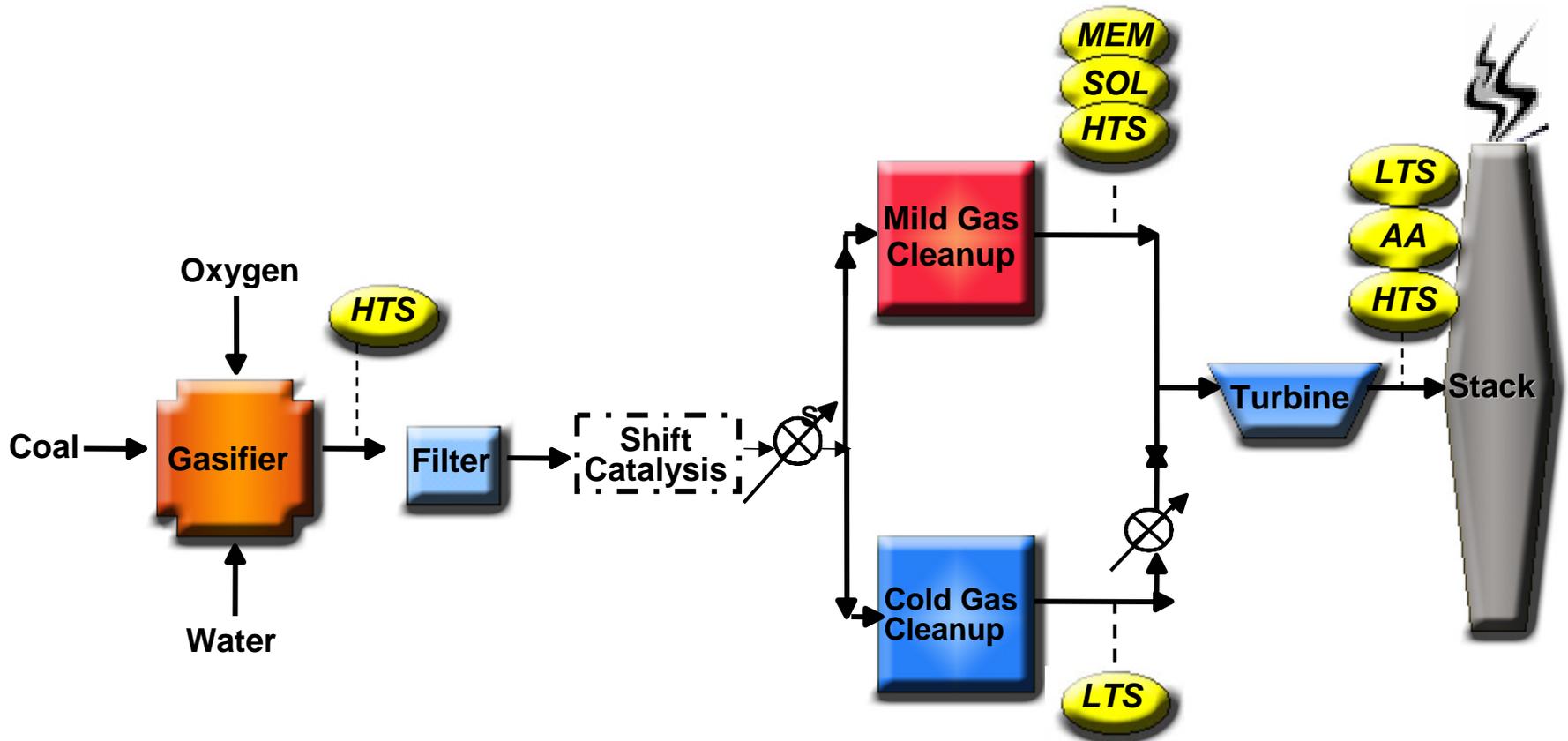
- Low temperature (<300°F) 

- High temperature (>300°F) 

General Case: Conventional Pulverized-Coal Combustion -- Flue Gas



General Case: Advanced Gasification/ IGCC -- Fuel Gas



AQUA AMMONIA PROCESS FOR MULTICOMPONENT REMOVAL

•Objective

–To develop a knowledge/data base to determine whether an ammonia scrubbing process is a viable regenerable-capture technique that can remove carbon dioxide and potentially sulfur dioxide, nitric oxides, and trace pollutants from flue gas.

•Technical Challenges

–The parasitic energy requirement needs reduced as compared to the current amine-based wet scrubbing system.

–There is a lack of experimentally produced data for low temperature aqueous ammonia scrubbing of CO₂ from flue gas in a cycling mode. Regeneration information is non-existent.

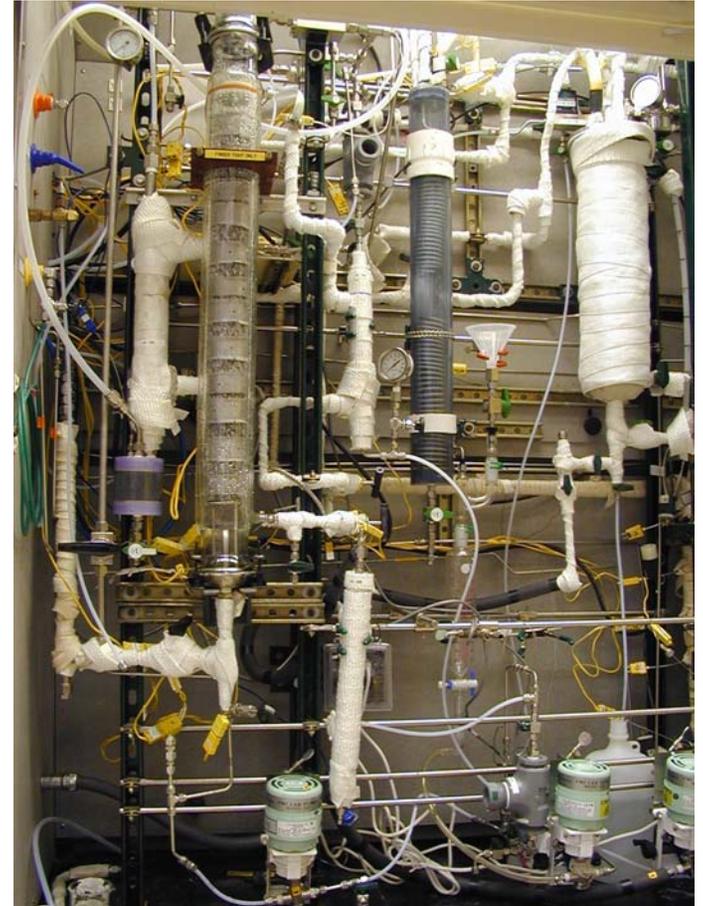
–Influence of SO₂ and NO₂ components on the ammonia/CO₂ scrubbing is unknown.

–Ammonia vapor loss needs characterized.



TECHNICAL APPROACH

- **Results of semi-batch reactor system used as basis for continuous flow unit design coupling absorption and regeneration**
- **Perform parametric study**
 - Gas and liquid residence times in absorber and regenerator
 - Absorber and regenerator temperatures
 - Initial ammonia concentration
 - CO₂ concentration
 - Available mass transfer area
 - SO₂ and NO_x effects
- **Identify species present**
- **Utilize expertise of CRADA partner**
- **Update current systems analysis**



Regeneration Heat Requirements for a 14% Aqueous Ammonia Solution Compared to Current MEA Technology

Process	ΔH_{rx} (kcal/mol)	Sensible Heat (kcal/mol)	Heat of vaporization (kcal/mol)	Total (kcal/mol)	% Reduction from MEA process
MEA	20.0	52.9	18.9	91.8	0
ABC → AC	6.4	36.0	0	42.4	54
ABC → NH ₃	15.3	36.0	0	51.3	44
AC → NH ₃	24.1	36.0	0	60.1	35

Aqua Ammonia Continuous Unit

Preliminary Regenerator Residence Time Results at Steady State

Test	1	2	3
Start Solution Mass	2000	3000	4000
Absorber			
Inlet CO ₂ Flow (sccm)	3520	3520	3520
Inlet CO ₂ Concentration (%)	14.9	14.9	14.9
Mean Inlet Gas Temperature (°F)	79	80	80
Flow CO ₂ Out (sccm)	2640	2460	2250
Outlet CO ₂ Concentration (%)	11.4	10.7	9.9
CO ₂ Removal Efficiency (%)	25.1	30.2	36.2
Number of Cycles	16	11	14
Inlet pH	9.3	9.4	9.4
Outlet pH	9.0	9.0	9.0
Bicarbonate/Carbonate Mass Ratio	0.28	0.24	0.29
Regenerator			
Exit Gas Flow (sccm)	956	930	--
Temperature (°F)	170	170	170
CO ₂ Concentration (%)	97.8	99.2	--
Bicarbonate/Carbonate Mass Ratio	0.07	0.04	0.01



HYBRID MEMBRANES FOR CO₂ SEPARATION

•Objective

–To prepare hybrid CO₂-selective membranes with properties desirable for “pre-combustion decarbonization” and ultimately lower the capital cost and energy penalty associated with separating/capturing CO₂ from large point sources.

•Technical Challenges

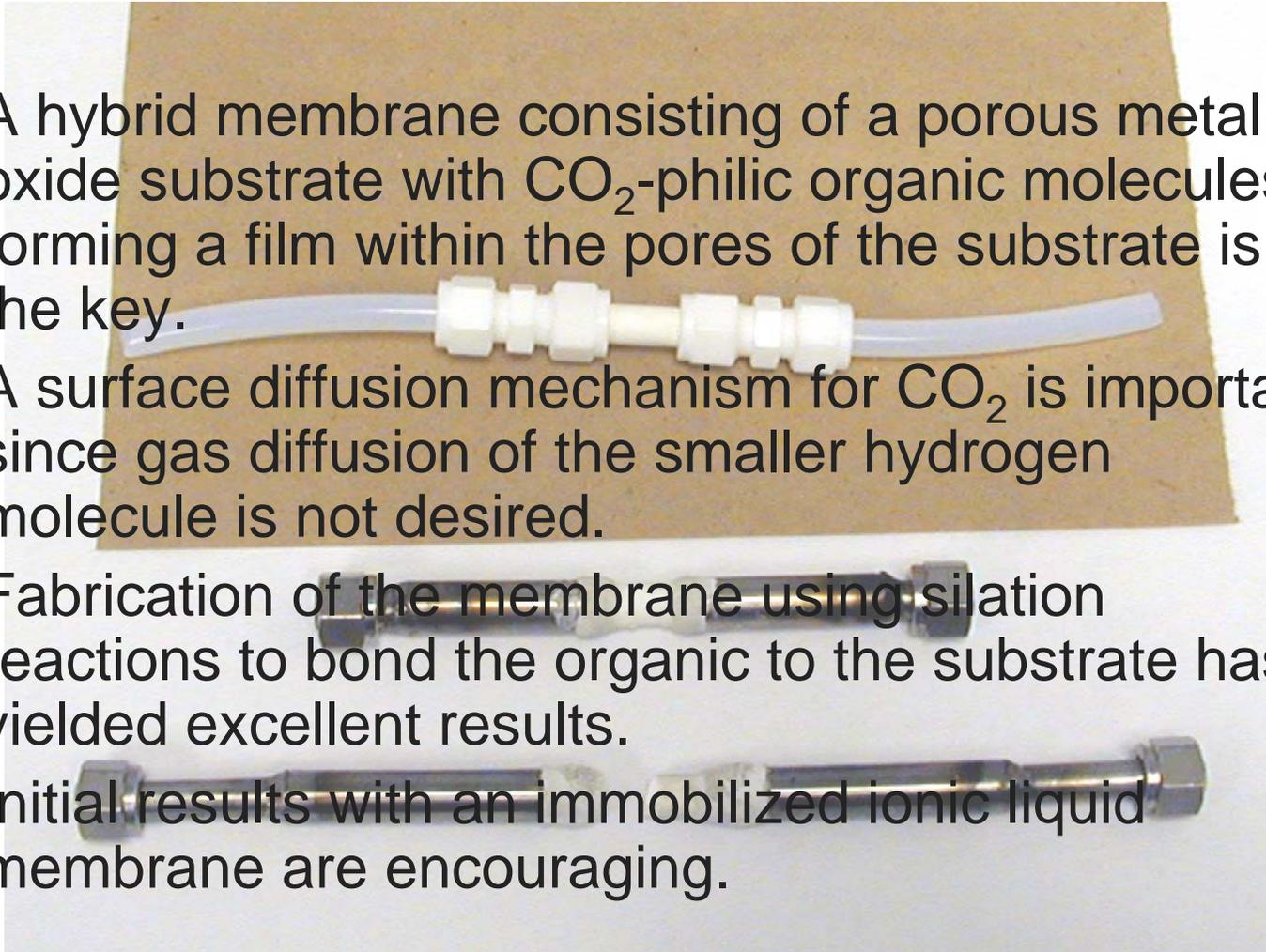
–The membrane must have the following characteristics to be relevant:

- Physically robust and chemically stable to withstand harsh gasification conditions in a reducing environment
- Thermally stable to 150°C and higher
- Highly permeable: 10^{-6} mol/Pa/m²/s
- Highly selective toward CO₂ (13:1)

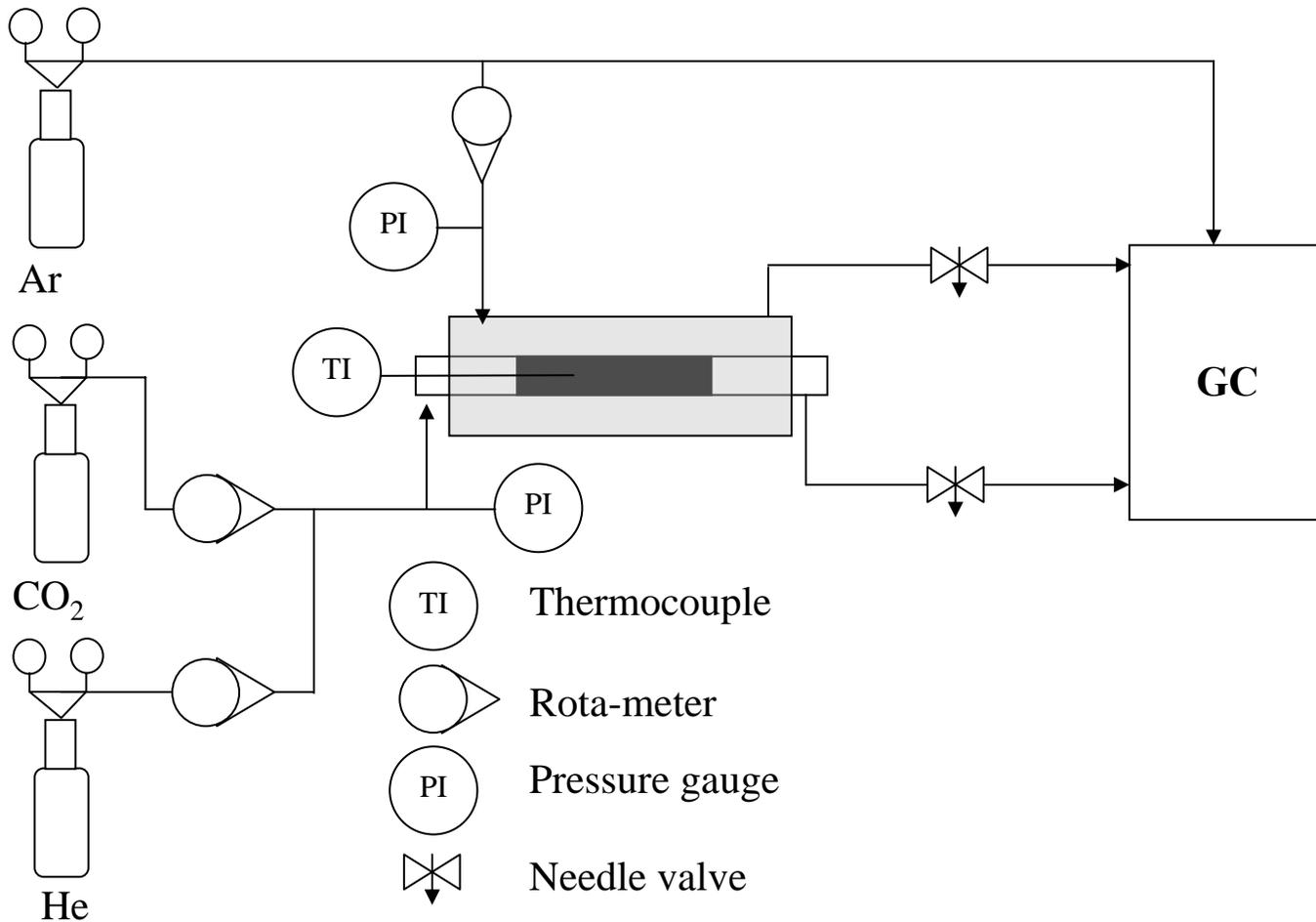


TECHNICAL APPROACH

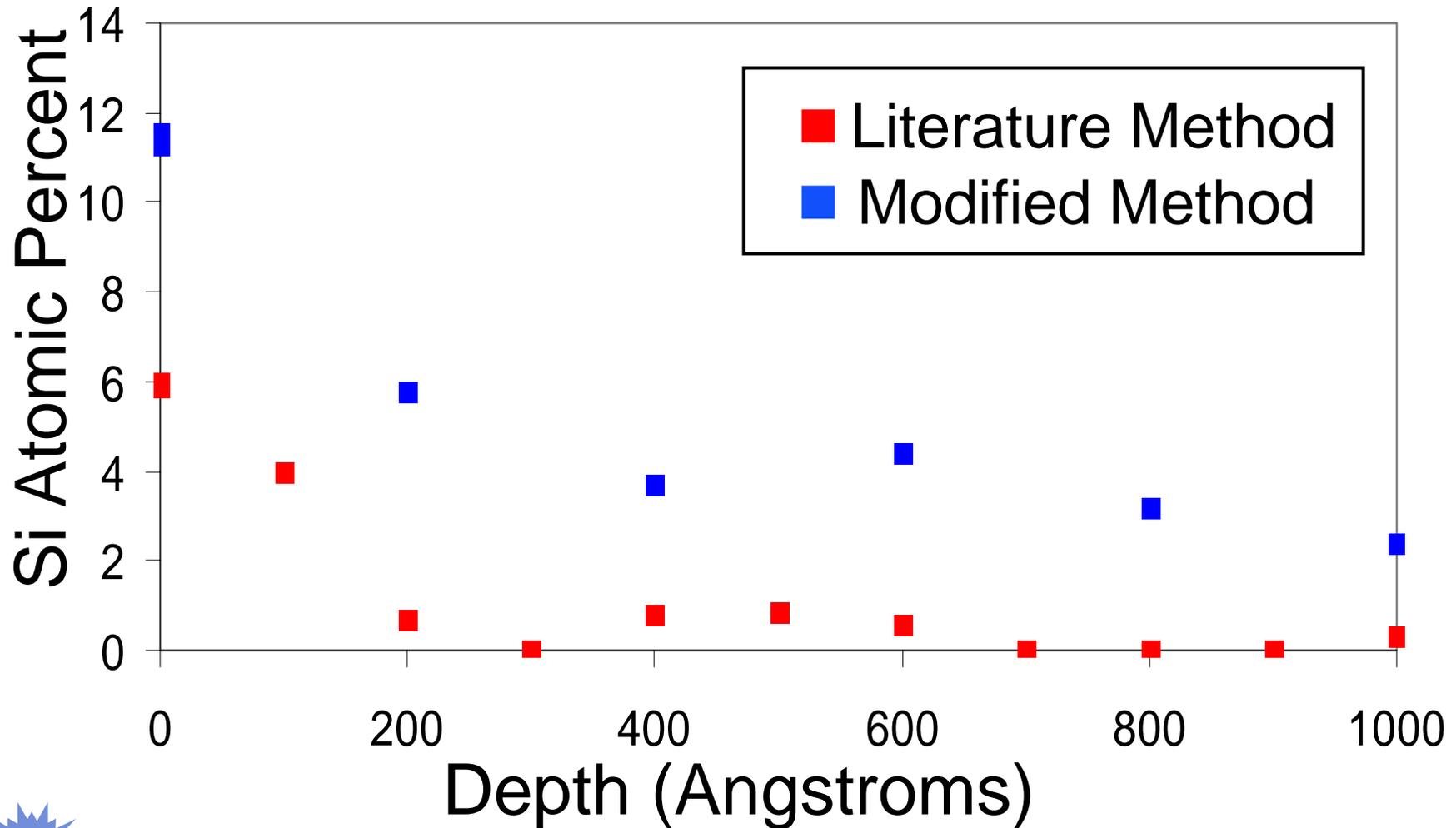
- A hybrid membrane consisting of a porous metal oxide substrate with CO₂-philic organic molecules forming a film within the pores of the substrate is the key.
- A surface diffusion mechanism for CO₂ is important since gas diffusion of the smaller hydrogen molecule is not desired.
- Fabrication of the membrane using silation reactions to bond the organic to the substrate has yielded excellent results.
- Initial results with an immobilized ionic liquid membrane are encouraging.



Membrane Test Assembly



Pore Penetration As Determined By XPS For a Silated Membrane



SOLVENTS FOR CO₂ CAPTURE

•Objective

To test and develop new physical solvents to selectively capture CO₂ from fuel gas streams, particularly those containing CO₂, CO, H₂S, H₂O, and H₂ in amounts typically found in coal gasification streams. The tests will be conducted under operating pressures and temperatures found in the gasification system.

•Technical Challenges

The physical solvents should selectively dissolve CO₂ from gaseous streams within the IGCC system and preferably after the shift reactor. The solvent must be extremely chemically stable, inert, and have low vapor pressure.

The effect of other constituents in the fuel gas on the integrity of the CO₂ solvation properties of the solvents must be negligible.

The solvent must operate at elevated temperature to maintain a higher overall IGCC thermal efficiency as compared to low temperature physical solvents.

The cost of the process should be lower than conventional scrubbing techniques.

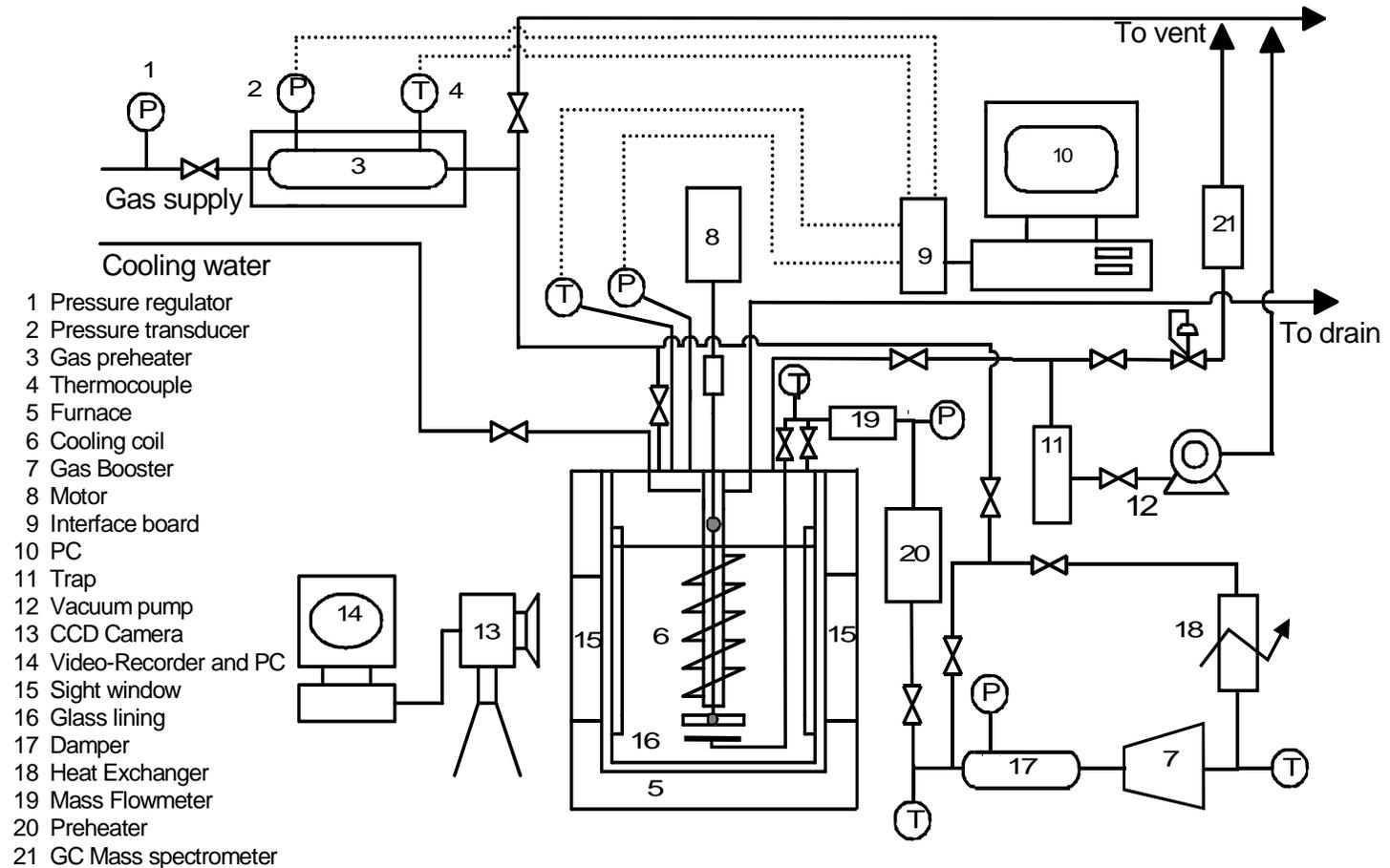


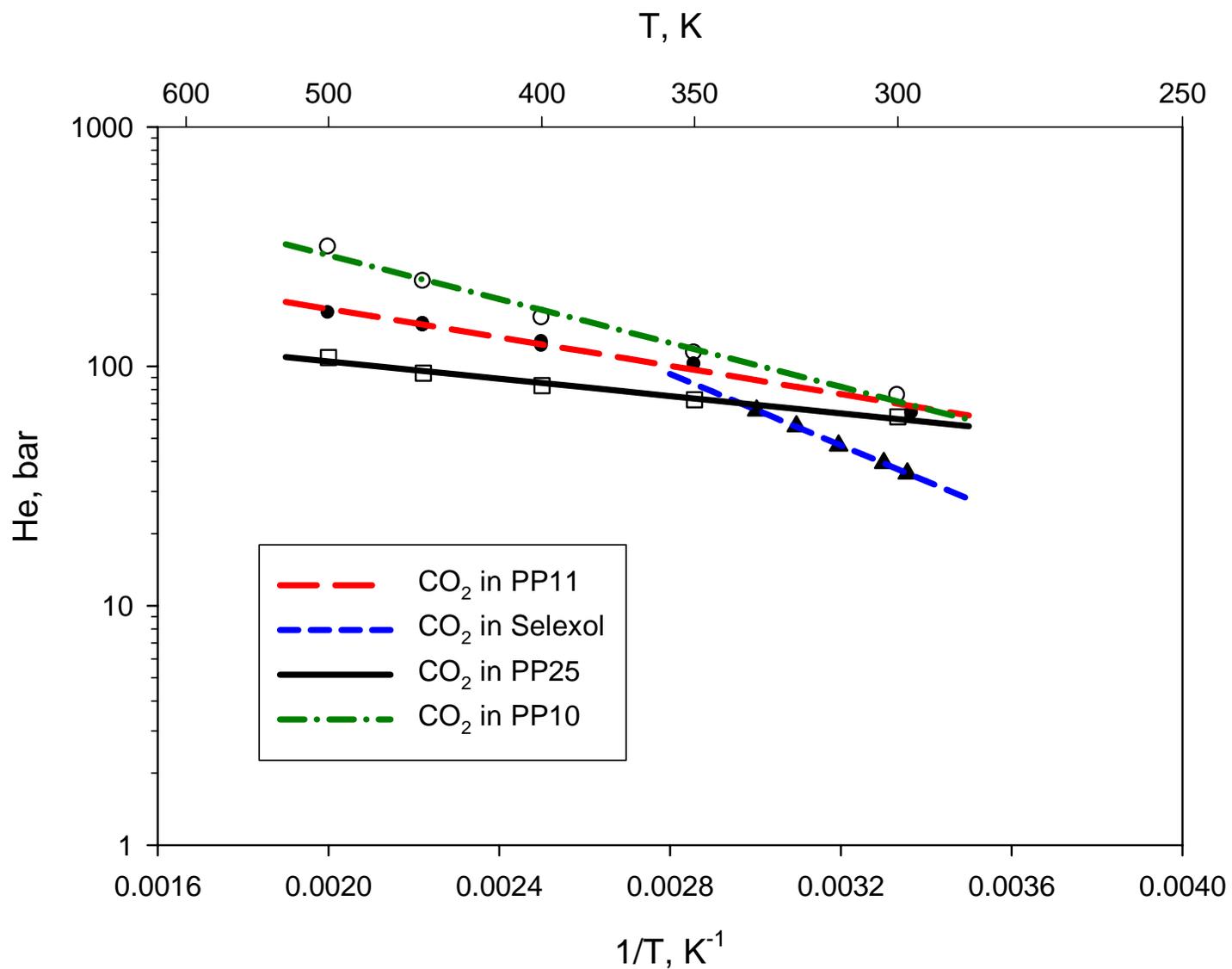
TECHNICAL APPROACH

- **CO₂ typically displays much higher solubility in fluorinated compounds than in their corresponding hydrocarbons. These perfluorinated compounds have been chosen for investigation:**
 - Fluorinated compounds are extremely thermally stable. The C-F bond is very high energy, allowing them to be routinely used in very high temperature applications, such as Teflon's use in cooking ware.
 - Fluorinated compounds are extremely chemically stable. It is not expected for them to be chemically degraded by either the high operating temperatures or the presence of reactive compounds.
 - Fluorinated compounds have extremely low vapor pressures, minimizing solvent losses.
- **In collaboration with the University of Pittsburgh, tests in a well-instrumented high temperature, high pressure reactor are conducted to obtain solubilities and mass transfer information. The effect of gaseous components other than CO₂ on the performance of the solvents will also be studied.**
- **Based on relevant experimental information, a systems analysis comparing the fluorinated solvent process with the benchmark (Selexol) process will be conducted.**



STIRRED AUTOCLAVE





Henry's Law Constant as a Function of Temperature: **Comparison with Selexol process**



Regenerable Sorbent Capture Techniques

•Objective

–To develop novel solid, regenerable sorbents for the adsorption/absorption of CO₂ from gas streams with temperature-swing and/or pressure-swing operational modes for regeneration.

•Technical Challenges

–To produce affordable solid sorbents for the capture of CO₂.

–To reduce the energy intensity and penalties of earlier or more conventional capture processes.

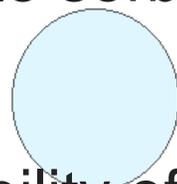
–To subject the sorbent to a high or low temperature and high or low pressure environment. Flue gas or fuel gas applications may apply.

–To identify and quantify the sorbent adsorption capacity, adsorption/desorption rate, durability, selectivity, and sensitivity to possible contaminants.

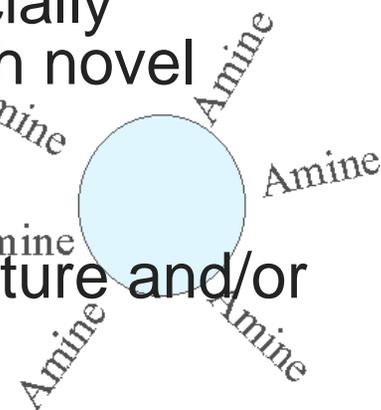


Technical Approach

- Prepare sorbents containing supported or unsupported alkali-or alkaline-earth metals to be tested in simulated mild/high temperature fuel or flue gas streams.
- Chemically treat certain high surface area materials with various amine compounds. Immobilized amine sorbents will capture CO₂ in low temperature flue or fuel gas applications.
- Develop baseline information with commercially available zeolite sorbent for comparison with novel sorbents.
- Test regenerability of sorbents in a temperature and/or pressure swing mode.



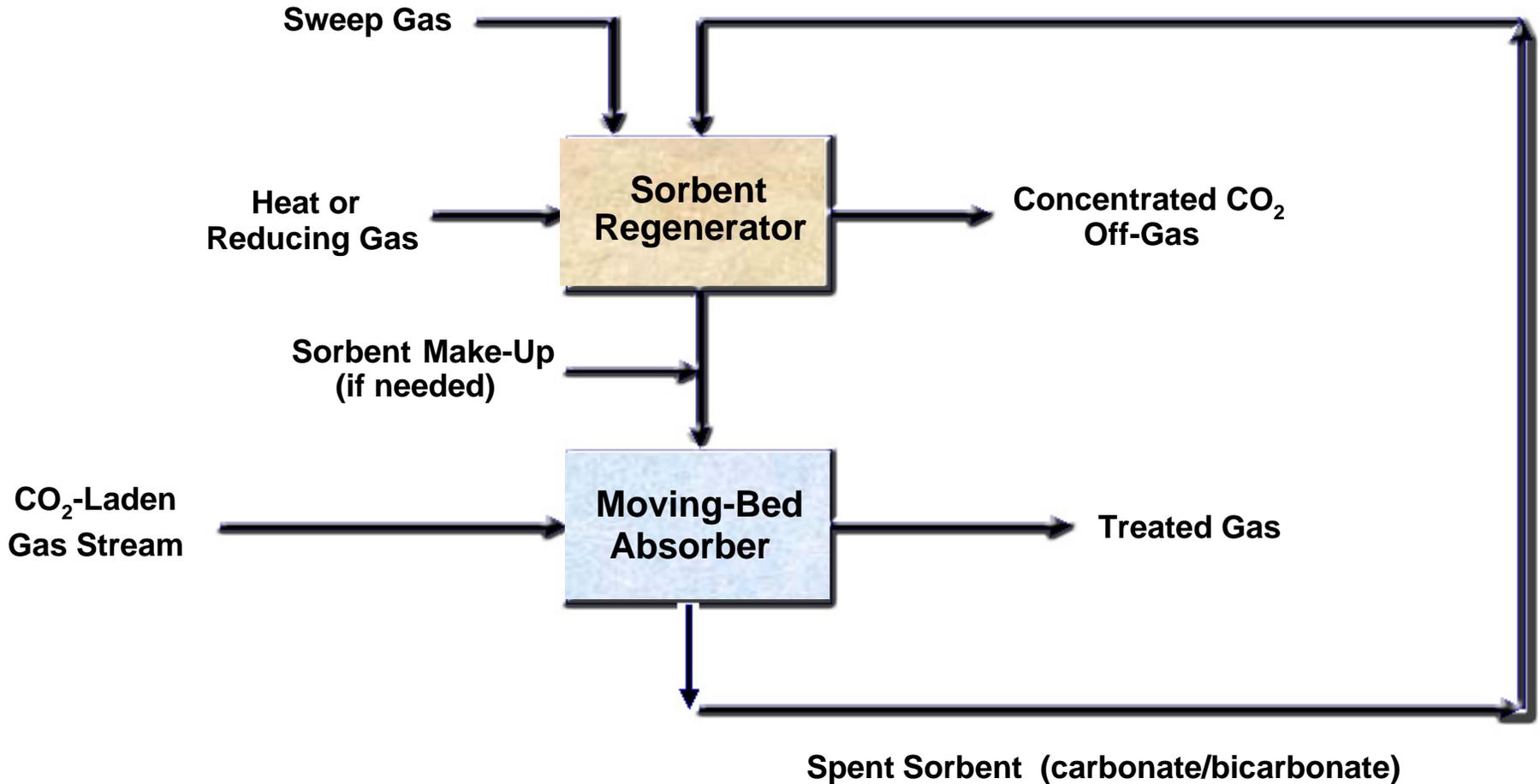
+ X-Amine groups



Oxidized Surface

Amine Enriched Surface

Conceptual Carbon Dioxide Removal Process



Comparison of CO₂ Capture Capacities of Different Sorbents

Sorbents	Moles of CO₂/kg at 1 atm	Moles of CO₂/kg at 20 atm
MEA Solution-Commercial	1.2	NA
Selexol Solvent-Commercial	NA	0.38
Synthetic Zeolite Z10-08	2.5 - 3	7 - 8
Natural Zeolite -- Na Alumino Silicate	1 - 1.5	4 - 5
Sodium-Based NETL Sorbent	4 - 6	---
NETL Immobilized Amine Sorbent	3 - 6	---



CO₂ CAPTURE STUDIES IN NETL'S MODULAR CO₂ CAPTURE FACILITY

Objective

To facilitate commercial readiness of advanced, cost-effective capture and separation technologies. Technologies range from conceptual to verification at large scale.

Technical Challenges

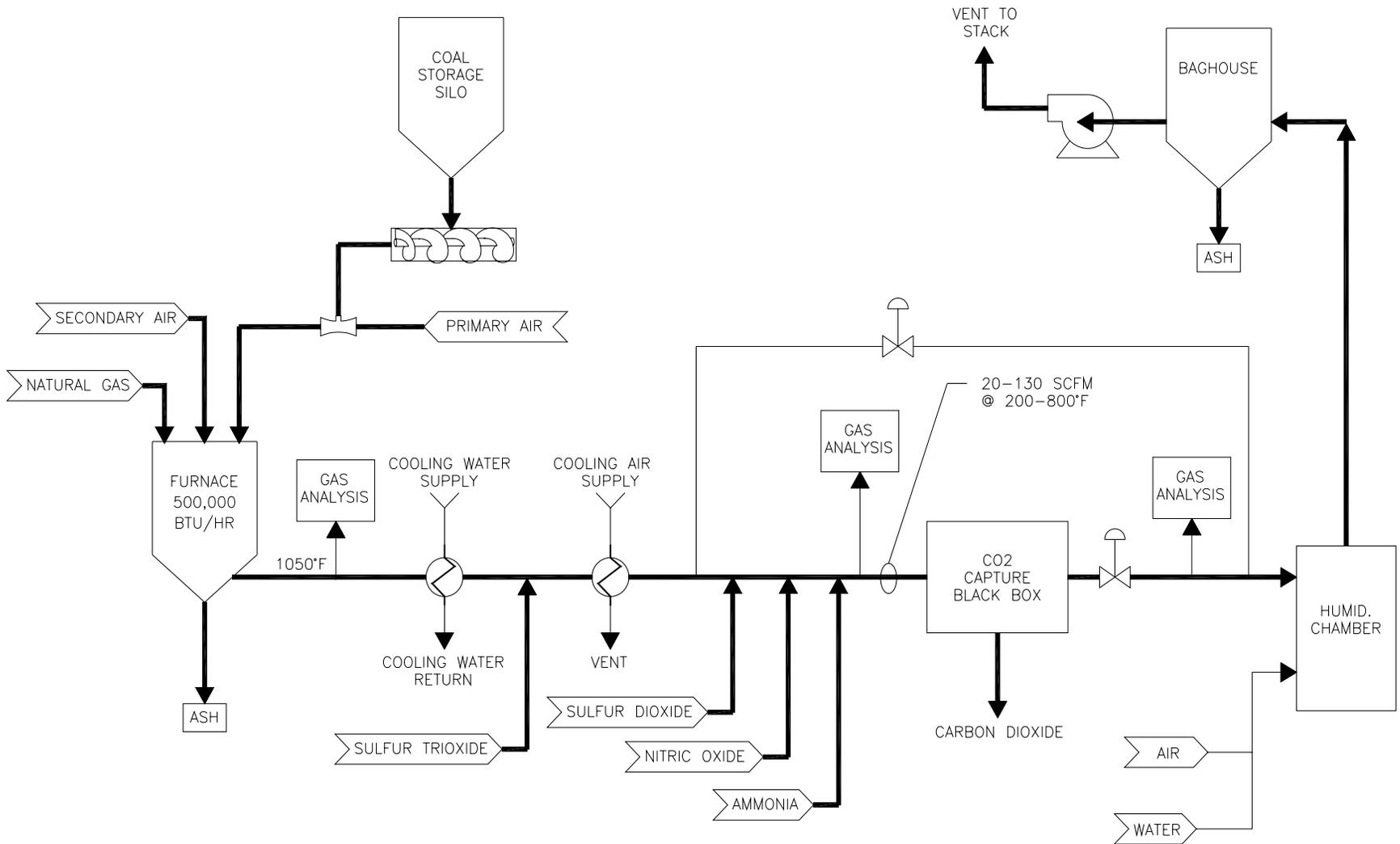
To utilize a modular facility capable of investigating various capture technologies.

To select candidate technologies for investigation.

To ultimately provide experimental information from which further engineering scale-up decisions can be made.



CO₂ Capture Facility – Flue Gas



First Campaign With Zeolite 13X

- Zeochem Molecular Sieve consists of spherical pellets (8 x 12 mesh) obtained from Sud Chemie.
- Molecular sieve composed mainly of sodium aluminosilicate with 10 angstrom average pore diameter.



MCCF Zeolite Experimental Summary

- Molecular sieve 13X was able to adsorb CO₂ from flue gas at baseline conditions (40°C at atmospheric pressure).
- CO₂ breakthrough time is related to molar flux, but little difference in CO₂ capacity (1.3-1.7 mol CO₂/kg sorbent).
- Moisture impacts adsorption.
- A high temperature of regeneration (350°C for 3 hr) is required after adsorption of CO₂ from moisture containing flue gas.
- Nitric oxides produced from combustion are adsorbed on sorbent. Sulfur dioxide deleteriously impacts sorbent.
- Combination of PSA with TSA may be optimal mode of regeneration for this technology.

