5'th INTERNATIONAL CO_2 CAPTURE TEST NETWORK

Capture And Separation Research In The Carbon Sequestration Science Focus Area

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Novel CO_2 Capture Technologies For Power Generation Point Sources

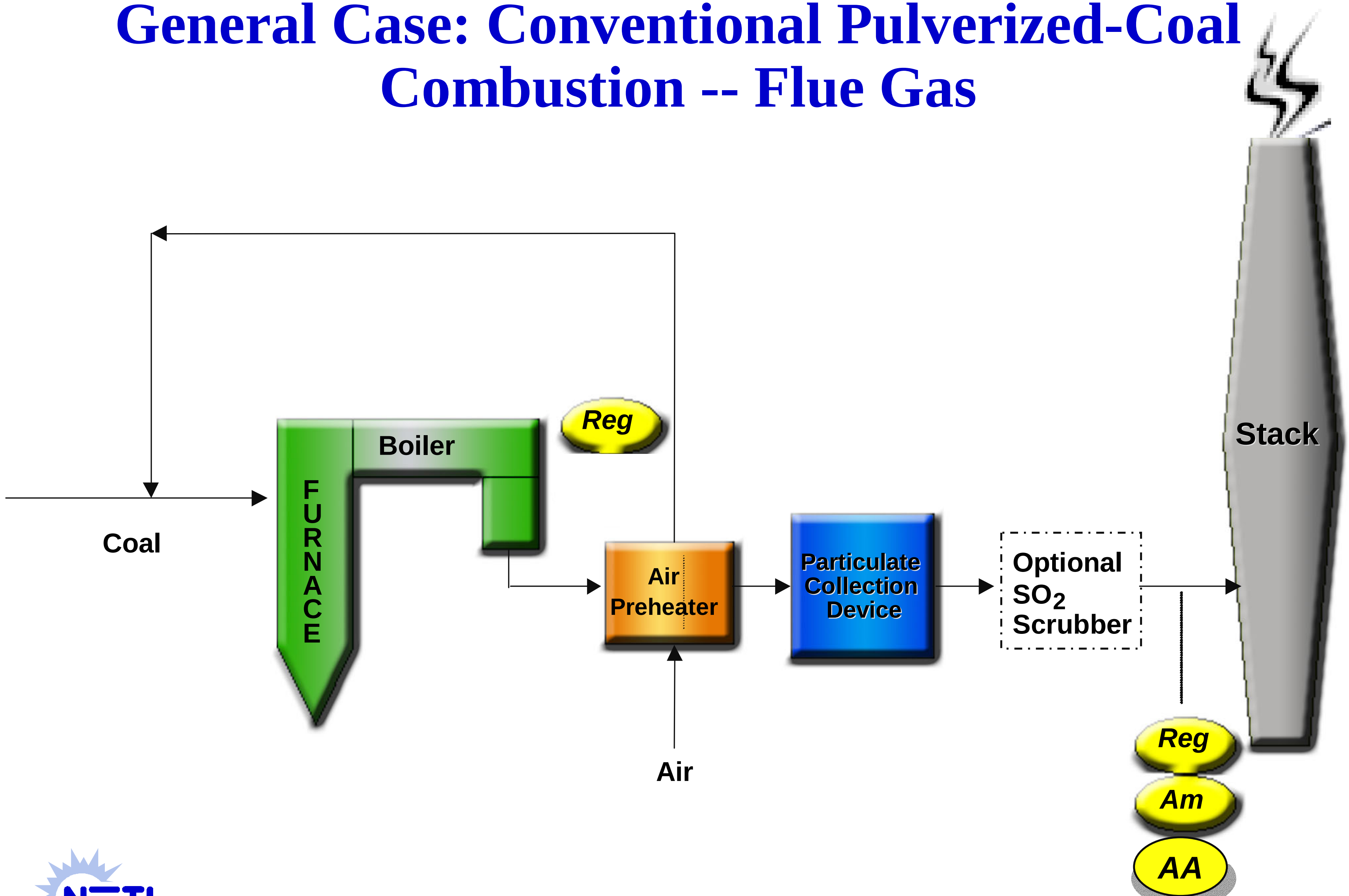
Scrubbing with Regenerable Sorbents Reg

Amine-Enriched Sorbents Am

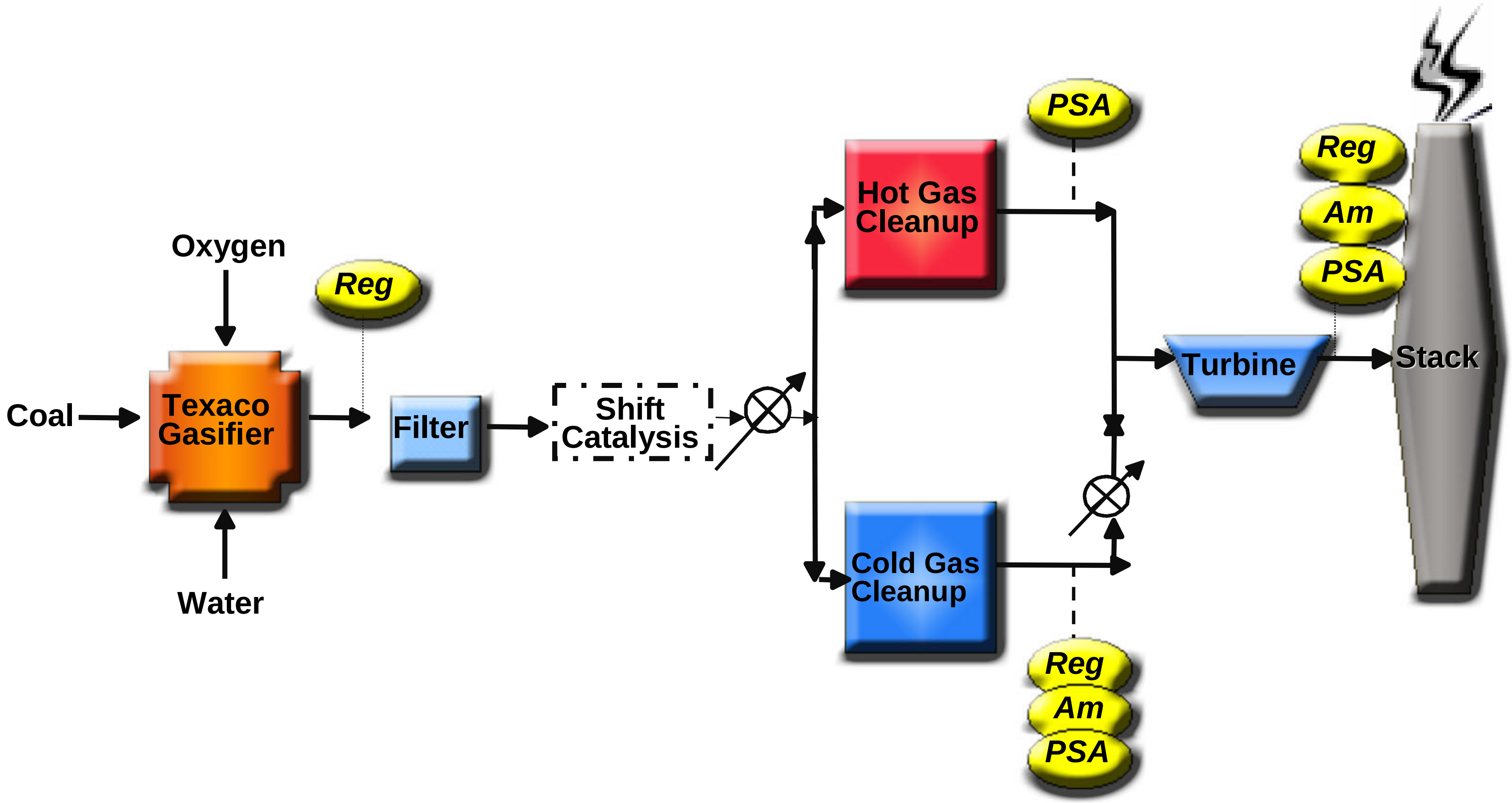
Sorbent Development for Pressure Swing/ Temperature Swing Adsorption PSA

Aqua Ammonia Process AA

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



General Case: Advanced Gasification/ IGCC -- Fuel (Synthesis) Gas



General Capture Issues Related To Carbon Sequestration

- Impact of other pollutants on capture scheme (multi-pollutant versus a la carte)
- Composition of final capture product and impact on capture/sequestration interface (pure CO_2, content of other major/minor components)
- Quantity of CO_2 captured

CO_2 Scrubbing With Regenerable Sorbents

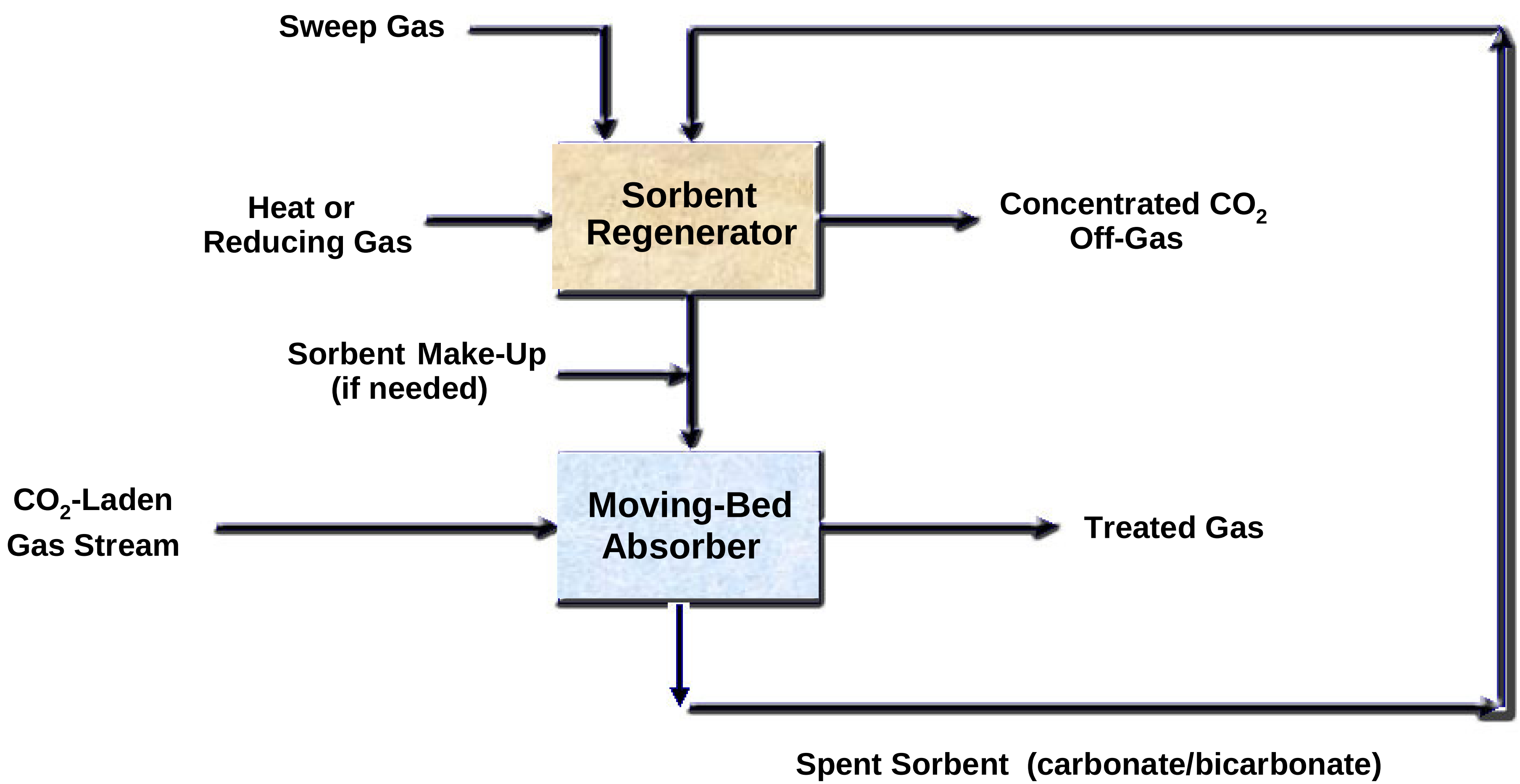
Technical Challenge

- **Provide experimental information with dry, regenerable sorbent processes for CO_2 removal from gas streams.**

Technical Approach

- **Thermodynamic analysis used to identify potential sorbents for CO_2 capture.**
- **Sorbents prepared using supports impregnated with alkali- or alkaline-earth metals.**
- **Lab-scale microbalance (TGA) study of absorption and regeneration chemistry of sorbents.**
- **Bench-scale packed-bed reactor study of absorption and regeneration chemistry of sorbents.**

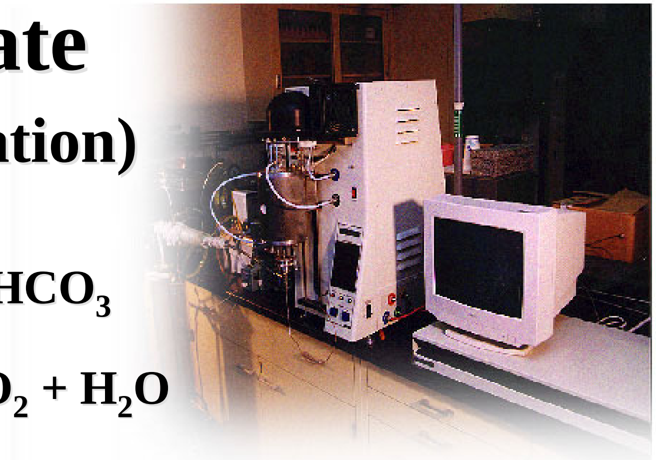
Conceptual Carbon Dioxide Removal Process



Regenerable CO_2 Capture Process Chemistry

Potassium Carbonate

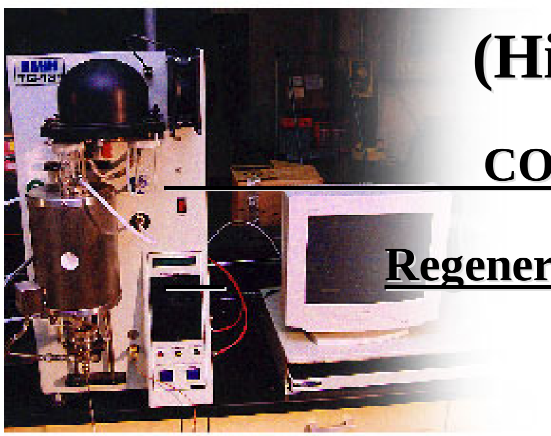
(Low Temperature Application)



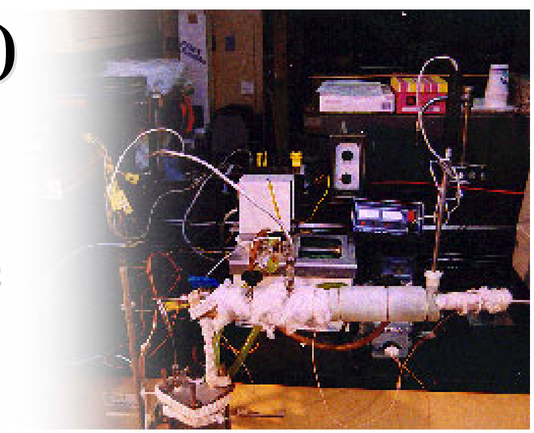
CO$_2$ Removal: $K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$

Regeneration: $2KHCO_3 + \text{Heat} \rightarrow K_2CO_3 + CO_2 + H_2O$

Calcium Oxide



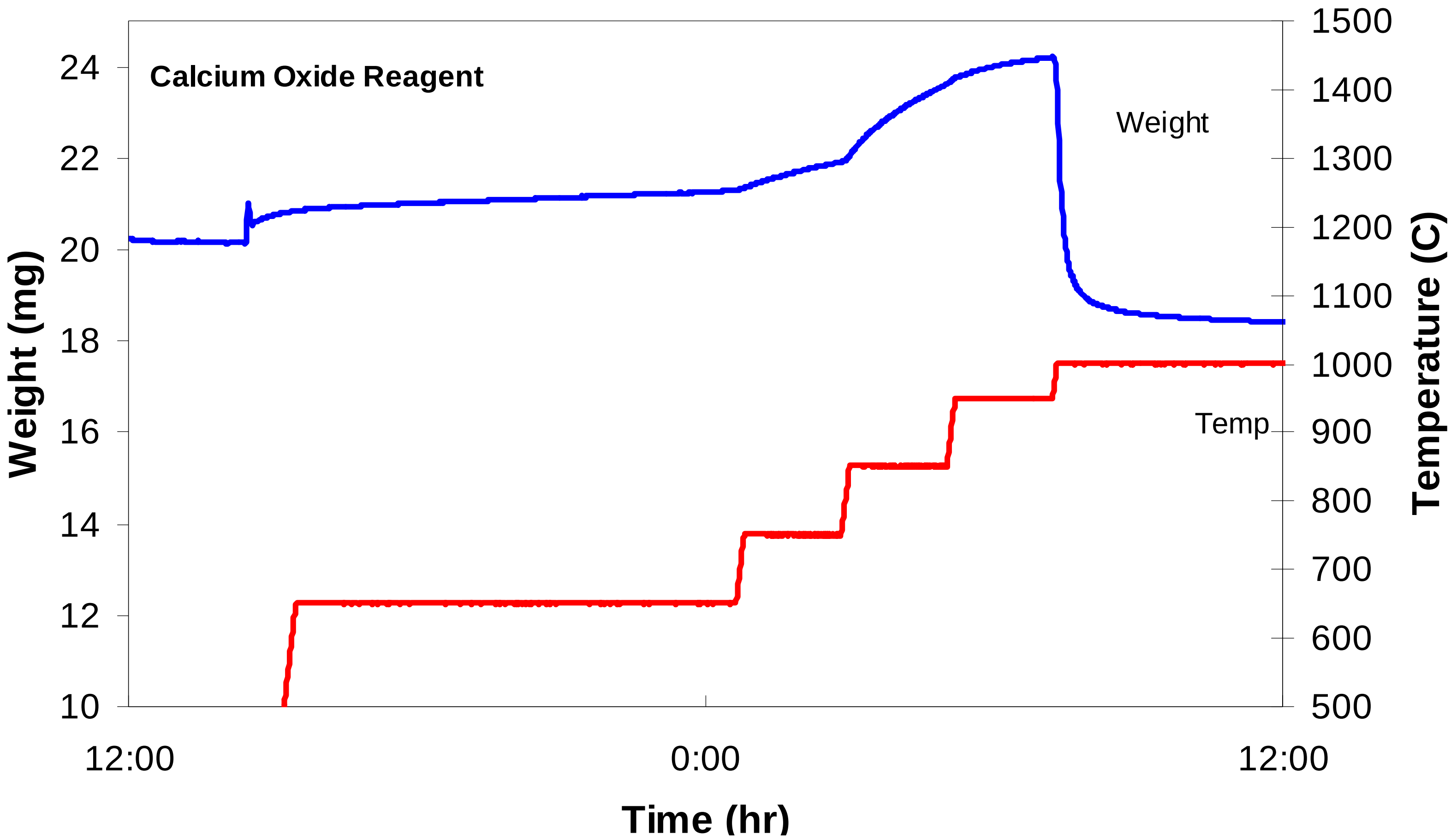
(High Temperature Application)



CO$_2$ Removal: $CaO + CO_2 \rightarrow CaCO_3$

Regeneration: $CaCO_3 + \text{Heat} \rightarrow CaO + CO_2$

Typical TGA Experiment
(Calcium oxide reagent @ 850C absorption)



Novel Amine-Enriched Sorbents for CO_2 Capture

- Objective
  - To develop novel solid sorbents for the capture of CO_2 from flue gas streams
- Technical Challenges
  - To reduce the energy intensity of current capture processes (e.g., MEA process)
  - To improve the capture capacity of sorbents
  - To produce affordable solid sorbents for the capture of CO_2
  - To improve the mass and heat transfer parameters
  - To increase the available contact surface
  - To reduce the corrosion problems

Technical Approach

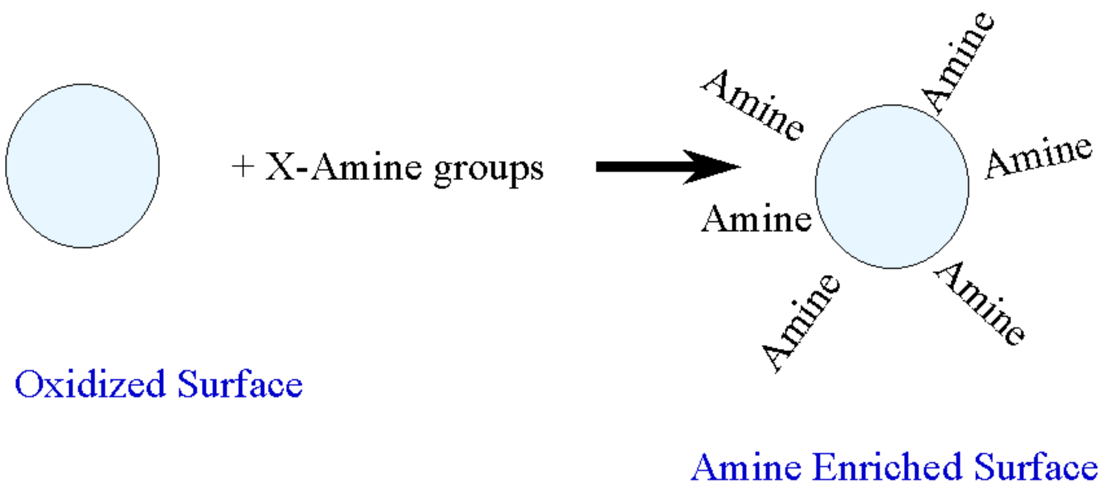
- A typical amine absorption process requires a large amount of liquid to capture a small quantity of gas. Gas/liquid contact surface can be increased by implanting the amine groups on a high surface area material. For example, activated carbon (2.3 g/cm^3 with 400 m^2/g) has a contact area of **9.19×10^8** m^2/m^3, whereas 1/4-inch ceramic intalox saddles have a contact area of **981** m^2/m^3.

- Chemically treat the high surface area materials with various amine compounds.

- Test the modified materials for CO_2 capture.

Current Solid Treatment

- NETL's chemical alteration of the solid substrate is a low cost technique.
- Performed in aqueous media with simple ionic reactions for the incorporation of the amine into solid matrix.
- Large selection of solid substrates, including waste fly ash, and large selection of amine based compounds.
- Resulting treatment produces a combined CO_2 capture coupling chemical absorption with physical adsorption.



Amine Sorbent Performance in CO_2/He/H_2O

Feed Materials	CO_2 Capture (umol/g) feed / treated	% CO_2 Capacity Enhancement
Treated NETL Fly Ash	24.4 / 174.6	615.5
Calgon Carbon (coal based)	8.0 / 48.7	608.2
Silica Gel	4.9 / 31.5	531.2
Sud Chemie Molecular Sieve 13X	13.6 / 15.8	16.1
Sud Chemie Carbon	92.0 / 54.4	(40.8)
Calgon Carbon (coconut based)	43.9 / 25.6	(41.6)

Sorbent Development for CO_2 Separation and Removal: *Pressure Swing and Temperature Swing Adsorption*

Objective

Development of regenerable sorbents for CO_2 adsorption in PSA/TSA processes in collaboration with industrial partners.

Technical Challenges

To apply the technique to both high and low temperature and pressure conditions.

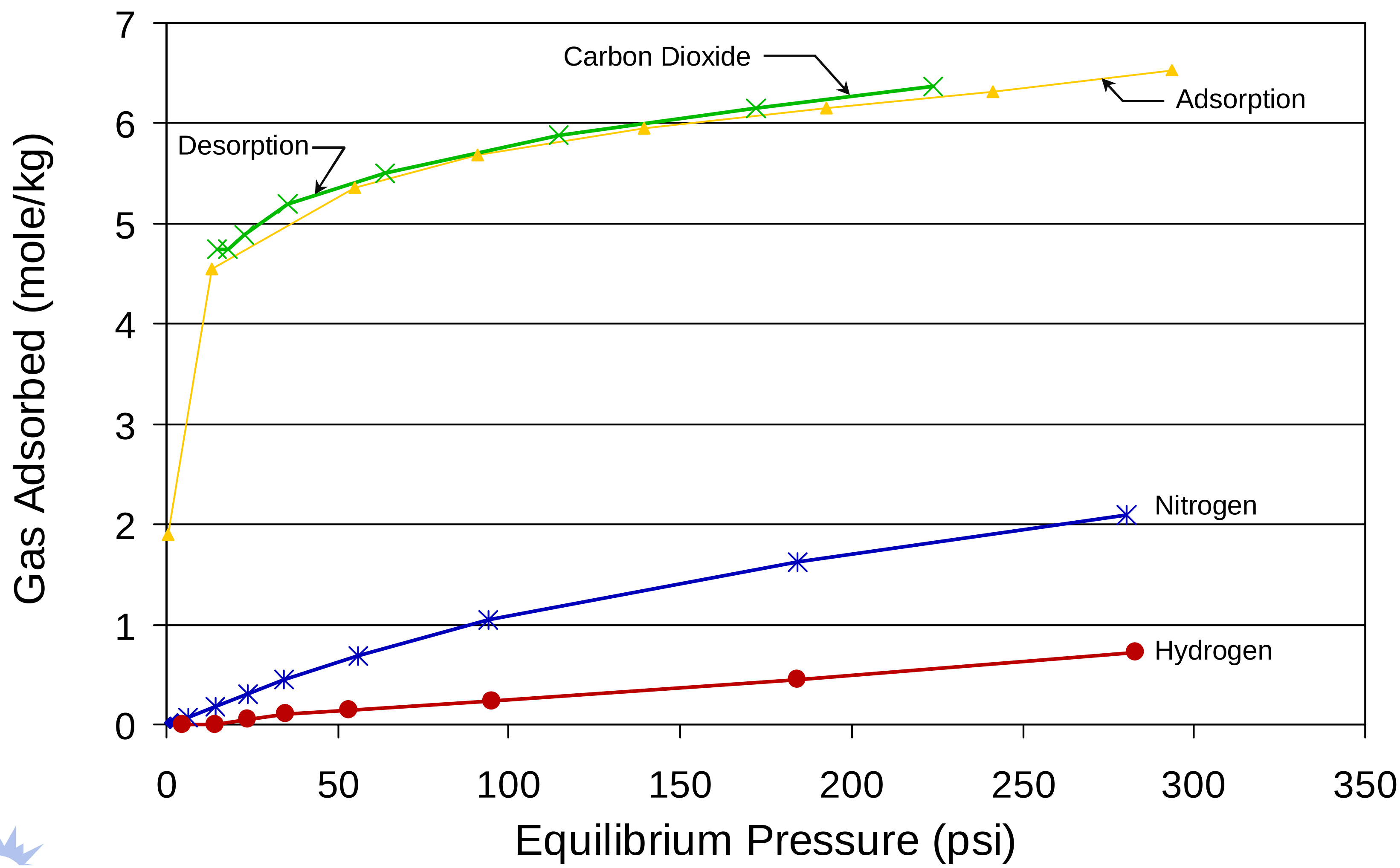
To reduce the energy penalties as defined in earlier PSA studies.

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

Technical Approach

- **Utilize prior experience in sorbent development and the expertise from the industrial partners to:**
  - Determine equilibrium adsorption/desorption capacity from volumetric adsorption.
  - Compare the competitive adsorption from gas mixtures using laboratory scale reactors.
- **Utilize molecular simulations to determine the impact of fundamental parameters, such as pore structure and chemical/physical interactions, on selective adsorption of CO_2.**
- **Construct models to optimize the process over a wide range of operating pressures.**

Sorption-Desorption Isotherms of Molecular Sieve 13X



Comparison of CO_2 Capture Capacities of Different Sorbents

Sorbents	Moles of CO_2/kg at 1 atm	Moles of CO_2/kg at 20 atm
MDEA Solution-Commercial	0.68	NA
Selexol Solvent-Commercial	NA	0.16
Synthetic Zeolite Z10-08	2.5 - 3	7 - 8
Synthetic Zeolite Z10-10	2.5 - 3	6 - 8
Natural Zeolites		
Na Alumino Silicate 1	1 - 1.5	4 - 5
Na Alumino Silicate 2	0.5 - 1	2 - 2.5
Ca K Alumino Silicate	0.1 - 0.2	1 - 1.5
NETL Sorbent	1.0-1.2	2.0-2.5

AQUA AMMONIA PROCESS TECHNICAL CHALLENGE

- There is a paucity of experimentally produced data for low temperature aqueous ammonia scrubbing of CO_2 from flue gas. Regeneration information is non-existent.

- Influence of SO_2 and NO_2 components on the ammonia/CO_2 scrubbing is unknown

- The impact of the experimental information on the proposed multi-component control process needs to be defined.

NETL

TECHNICAL APPROACH

- **Parametric study in a semi-batch reactor system.**
  - Absorption
    - Temperature
    - Ammonia concentration
    - CO_2, NO_x, SO_2 by themselves and collectively
  - Regeneration

- **Incorporate information into a mathematical model to be used for sensitivity studies and eventual scale-up of system.**

AQUA AMMONIA PROCESS CHEMISTRY (absorption)

- $2\ NH_3 + CO_2 \longrightarrow NH_2COONH_4$
- $NH_2COONH_4 + CO_2 + 2\ H_2O \longrightarrow 2\ NH_4HCO_3$
- $NH_2COONH_4 + H_2O \longrightarrow NH_4HCO_3 + NH_3$
- $NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$
- $2\ NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$
- $(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow 2\ NH_4HCO_3$

AQUA AMMONIA PROCESS CHEMISTRY
(regeneration)

- $2\ NH_4HCO_3(aq) \longrightarrow (NH_4)_2CO_3(aq) + CO_2(g) + H_2O$
- $NH_4HCO_3(aq) \longrightarrow NH_3(aq) + CO_2(g) + H_2O$
- $(NH_4)_2CO_3(aq) \longrightarrow 2\ NH_3(aq) + CO_2(g) + H_2O$

NETL

ADVANTAGES OF PROCESS

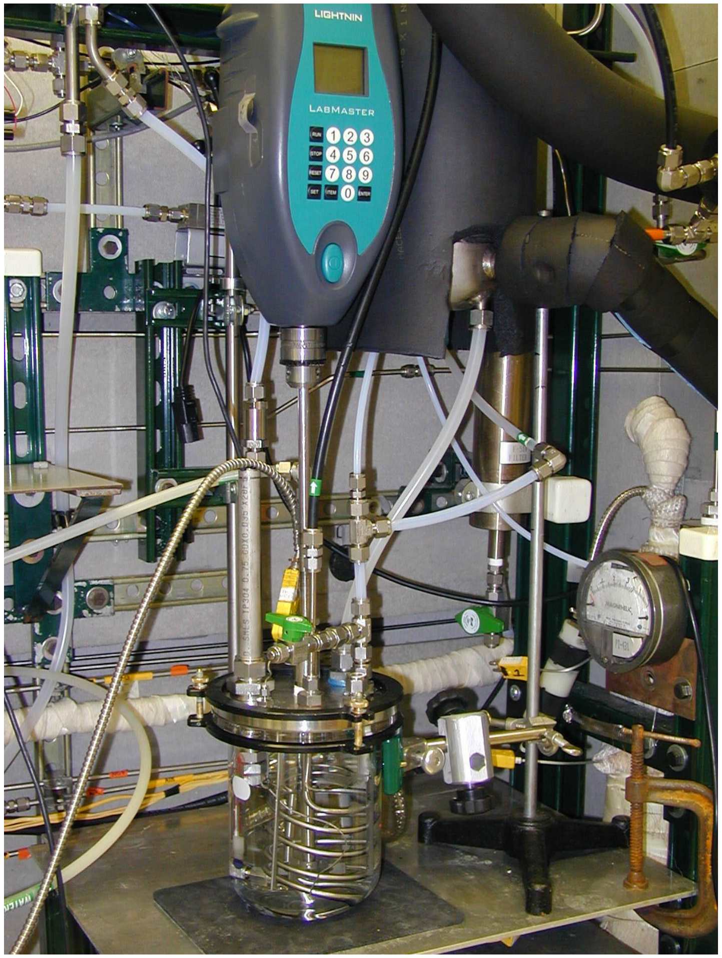
- Multi-component control of acid gases produced during coal combustion.
- Novel combination of oxidation step with ammonia wet scrubbing.
- Process is regenerable with respect to CO_2 scrubbing.
- Fabrication of a saleable commodity (fertilizer) out of waste materials (acid gases). Serendipitous to the process, the fertilizer may have an impact on terrestrial sequestration.
- Production of a pure CO_2 stream that can further be processed or sequestered.
- Can meet zero pollutant emissions.

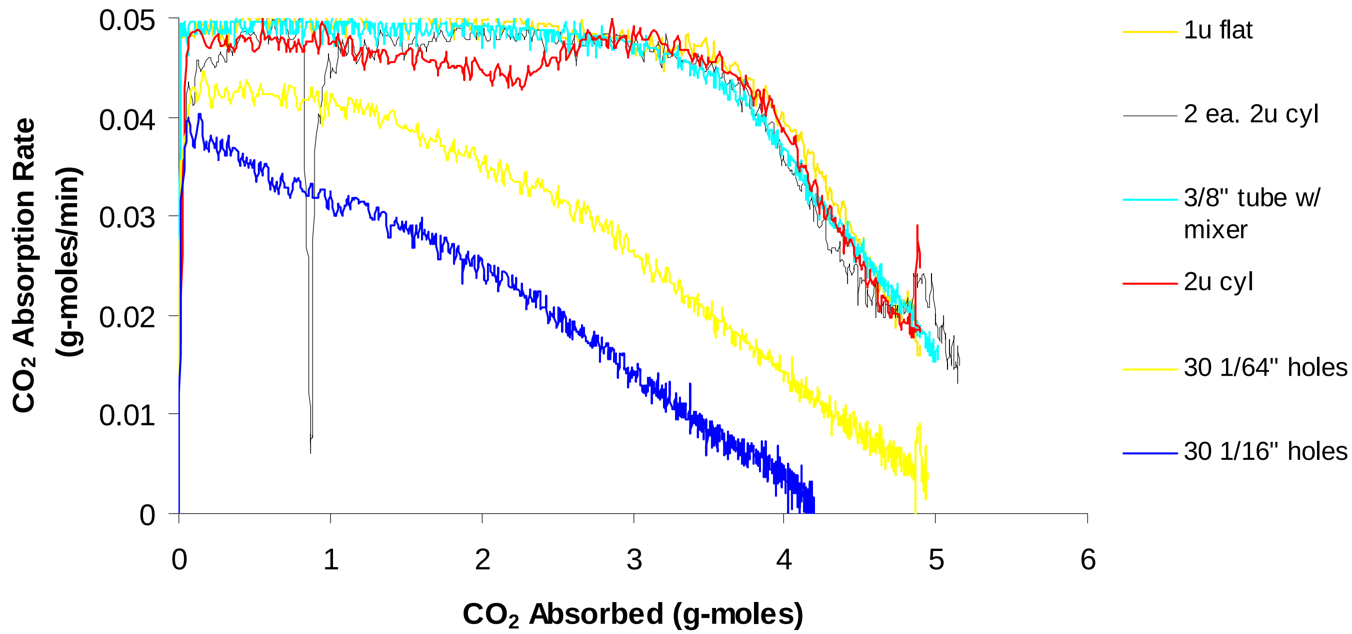
ADVANTAGES OF PROCESS

- **As compared to MEA scrubbing, the ammonia process :**
  - has a higher loading capacity
  - will not degrade in the presence of other flue gas components
  - has a lower parasitic power loss
  - will not corrode equipment

PARAMETRIC SCAN IN REACTOR SYSTEM

- Ammonia concentration: 7, 14, 21 wt%
- Temperature: 60, 80, 100 °F
- Reactor/solution volume: 3.0/1.5 liter
- Gas flow: 7500 sccm
- CO_2 concentration: 15 vol%
- Pressure: ambient



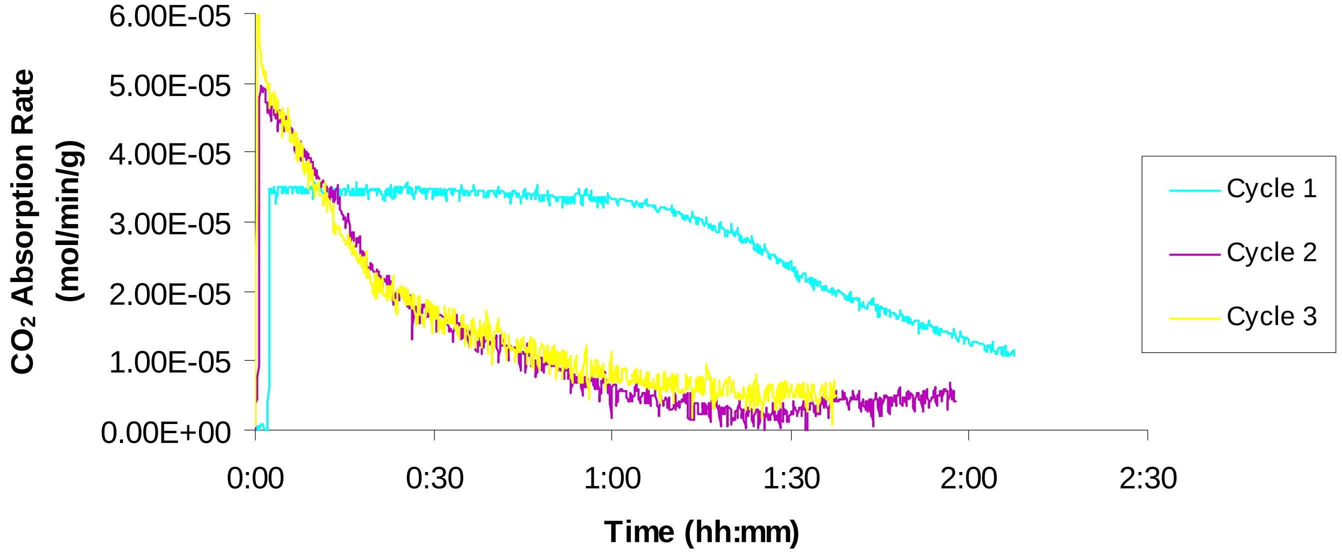


Effect of Sparger Types (CO_2 absorbed)

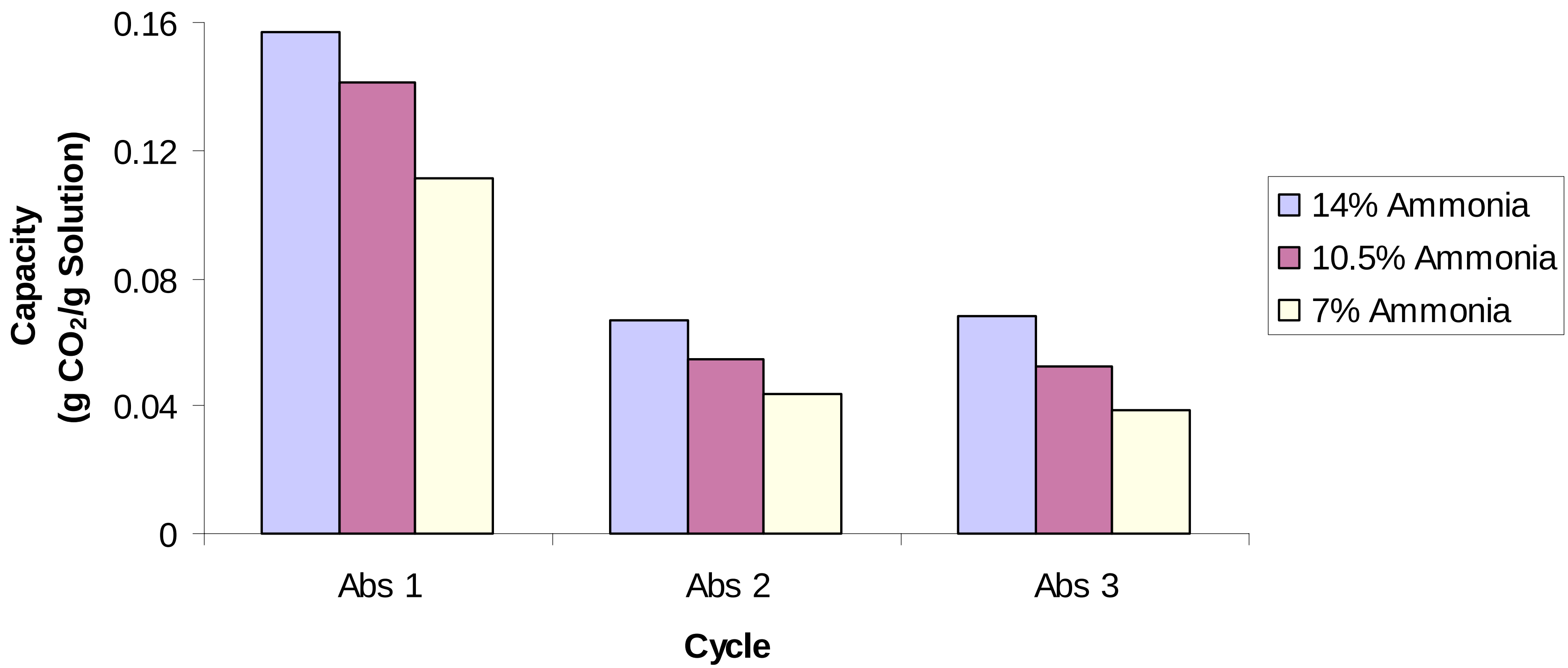
IMPACT OF TEMPERATURE

Temperature, ^oF	*Initial Rate, mole-CO_2 /min*	*Initial Conversion, mole %*	*CO_2 Loading, kg-CO_2/kg NH_3*
60	0.040	80.1	1.2
80	.048	96.1	1.1
100	.043	86.1	1.0

14% Ammonia Concentration



CO_2 Absorption Rate with 14% NH_3 Solution



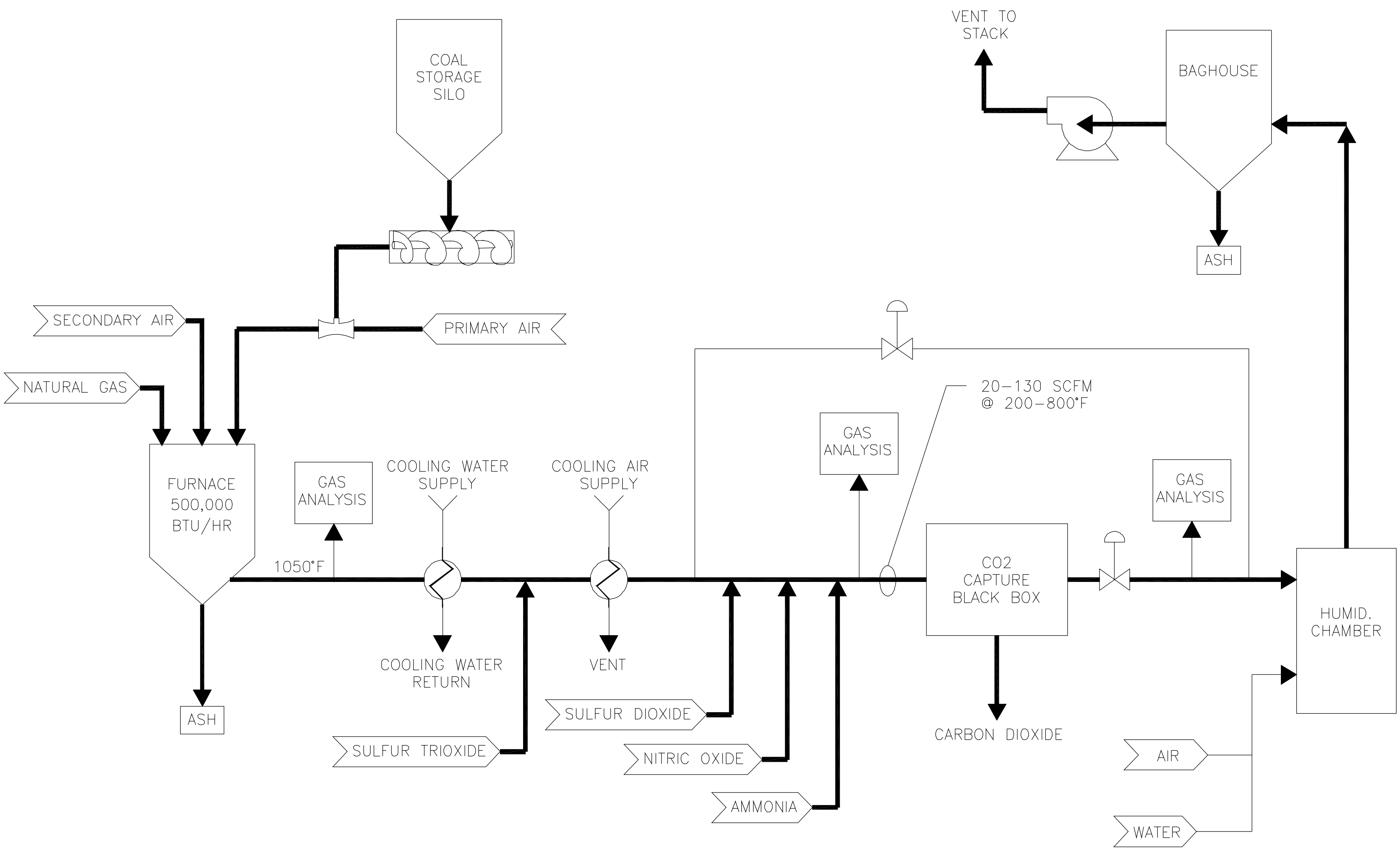
Effect of Cycling on CO_2 Absorption Capacity

SUMMARY

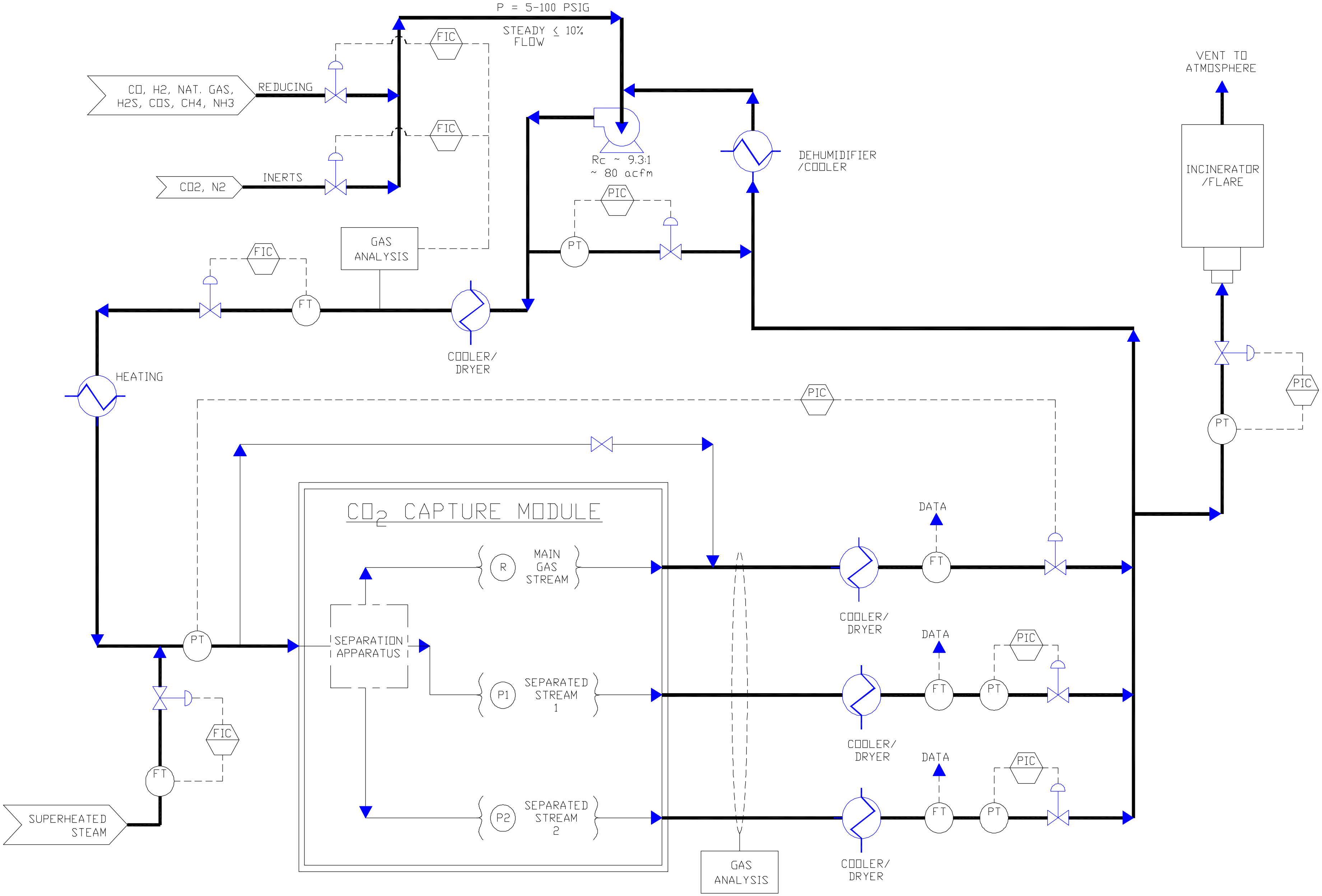
- Reaction rate information obtained on 7 %, 14%, and 21% ammonia solutions at 60^{o}F, 80^{o}F, and 100^{o}F.
- Thermal regeneration of ammonium bicarbonate and ammonium carbonate solutions demonstrated ability to release up to 60% of carbon in solutions.
- Regeneration energy reductions of >60% over current MEA technology were determined.
- Cycling tests determined the effective loading capacities of ammonia solutions after three absorption/regeneration cycles.

MCCF PAST HISTORY

- Timing appropriate in programmatic scheme of carbon sequestration
- Internal assessment
  - NETL experienced with flue gas and fuel gas cleanup
  - Facility existed in part
  - Air toxics sampling available
- In-house projects screened to determine process parameter ranges
- *Ad hoc* committee formed of personnel familiar with DOE-sponsored research and other outside capture development
- PFDs developed with “black box” technology for either flue gas or fuel gas applications



CO_2 Capture Facility – Flue Gas


P = 5-100 PSIG
STEADY ≤ 10% FLOW
FIC
FIC
CO, H2, NAT. GAS, H2S, COS, CH4, NH3
REDUCING
CO2, N2
INERTS
Rc ~ 9.3:1
~ 80 acfm
DEHUMIDIFIER /COOLER
VENT TO ATMOSPHERE
INCINERATOR /FLARE
PIC
PT
GAS ANALYSIS
FIC
FT
COOLER/ DRYER
HEATING
PIC
PIC
PT
CO2 CAPTURE MODULE
R
MAIN GAS STREAM
SEPARATION APPARATUS
P1
SEPARATED STREAM 1
P2
SEPARATED STREAM 2
PT
FIC
FT
SUPERHEATED STEAM
DATA
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COOLER/ DRYER
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GAS ANALYSIS

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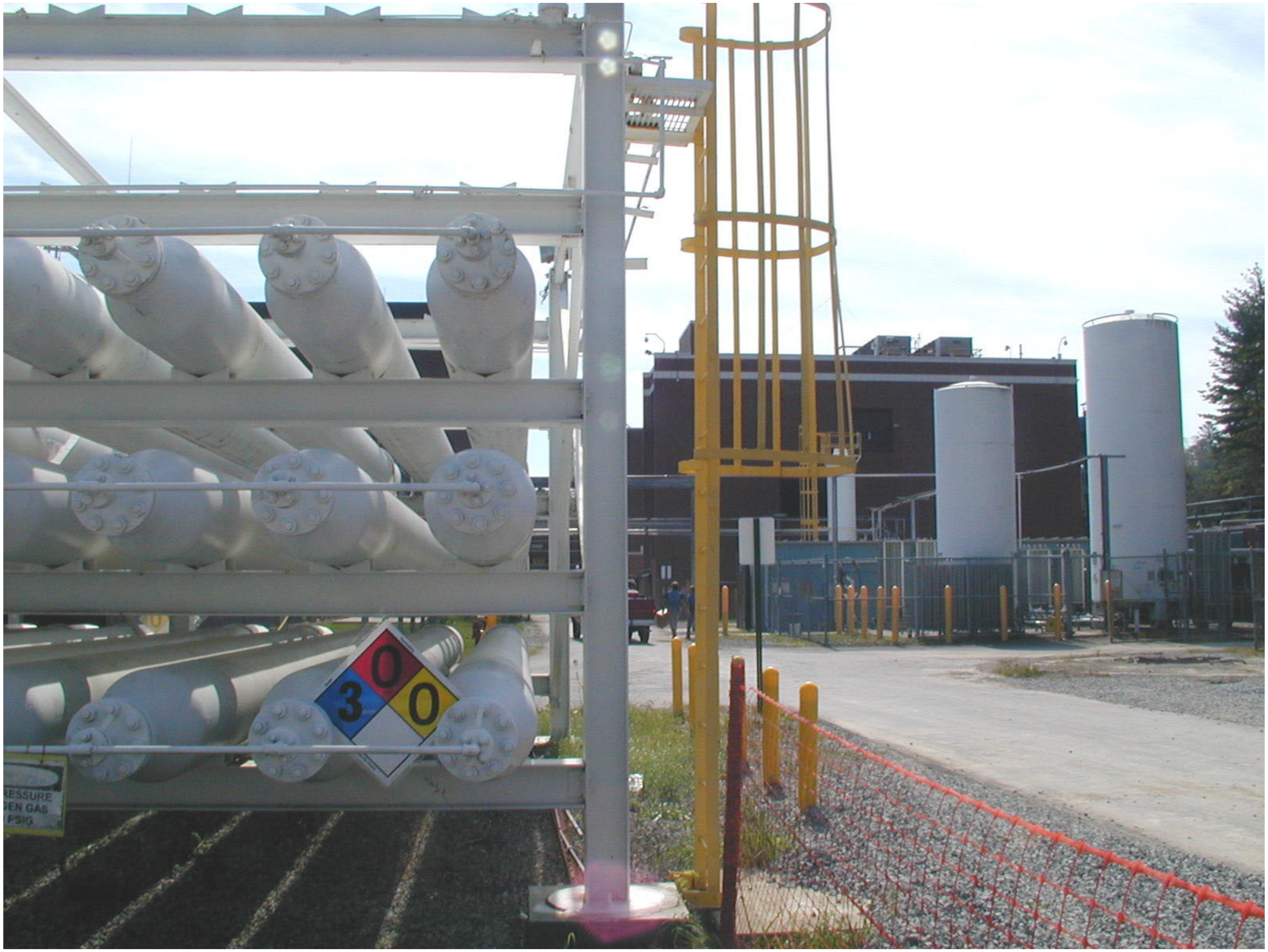

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