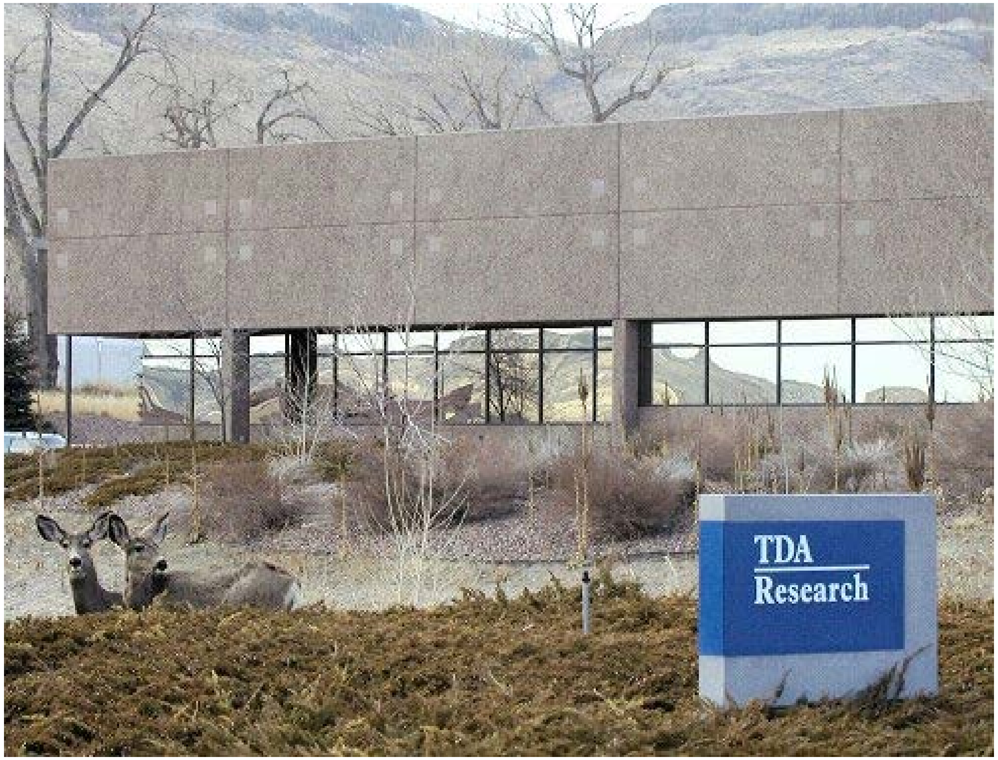
Oxy-Combustion System Process Optimization
(Contract No. DE-FE-0029090)



Gökhan Alptekin, PhD

Ambal Jayaraman, PhD

Mike Bonnema

Jerrod Hohman

Freya Kugler

Mike Ware

2018 CO_2 Capture Technology Meeting

August 14, 2018

TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

Project Summary

- **The objective is to optimize the Pressurized Oxy-Combustion (POxC) process to minimize the Cost of Electricity (COE)**
  - System analysis and design work to optimize POxC process, including thermal management, heat integration, power cycle optimization using process design and modeling supported with Aspen Plus® process simulations
  - Develop a new chemical absorbent-based CO_2 purification system to remove the residual oxygen that contaminates the recovered CO_2
- **Major Project Tasks**
  - Sorbent Optimization and Evaluation
    - Performance validation via long-term cycling tests
  - Process, System Design and Modeling
  - Techno-economic analysis
    - Various configurations with different ASU and O_2 removal options
    - High fidelity engineering analysis and process simulation

Project Partners

<u>Project Duration</u>

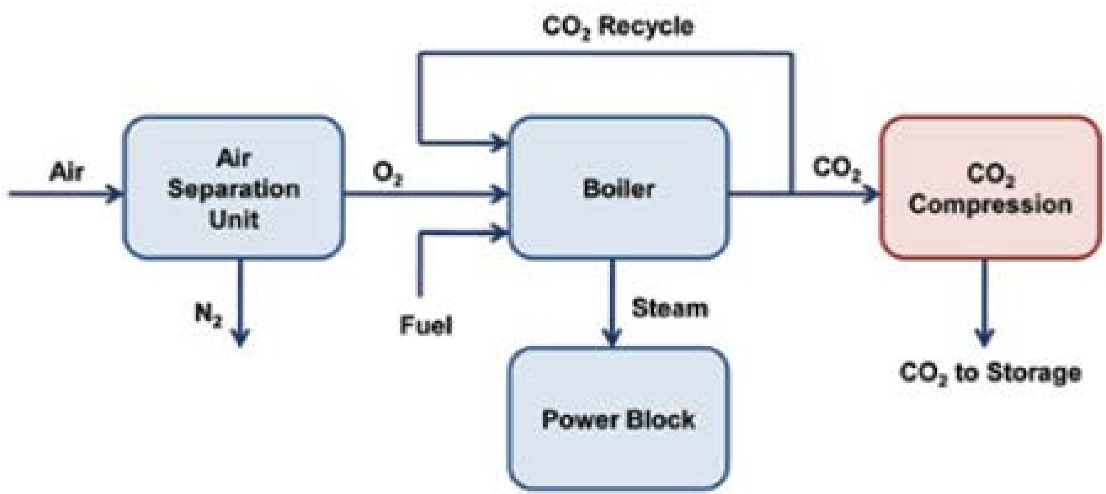
- **Start Date = October 1, 2016**
- **End Date = September 30, 2019**

<u>Budget</u>

- **Project Cost = $1,375,042**
- **DOE Share = $1,099,998**
- **TDA and UCI = $275,044**

Oxy-Combustion & Carbon Capture

- **In oxy-combustion fuels is burned in O_2 instead of air, which results in a flue gas of primarily CO_2 with trace levels of impurities**
- **POxC reduces energy and capital costs of the equipment used to purify and compress the CO_2**
- **DOE/NETL objective is to optimize the POxC process to limit the COE increase to less than 20% over the no-capture case**
- **The main cost contributors POxC process includes:**
  - **Air Separation Unit**
  - **CO_2 Purification system**



	COE ($/MWh)	Increase in COE(%)*
NETL Non-Capture Ref., Air-fired SC w/o CCS	58.90	--
NETL Base Case Current Technology	91.07	54.6
NETL Cumulative Technology Case	78.15	32.7
Proposed Goal	70.68	20.0

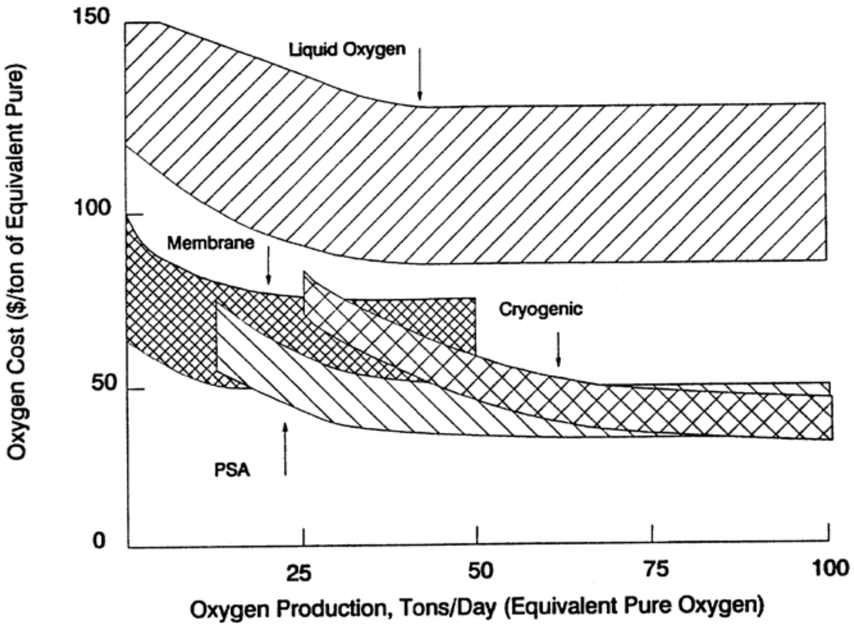
**Relative to the non-capture case*

Source: Cost of Electricity for Low Pressure Oxy-Combustion Technologies (NETL 2012).

Air Separation Options

- **ASU is one of the largest cost contributors to oxy-combustion (consumes over 5% of plant power and constitutes ~20% of plant cost)**
- **Cryogenic air separation is the choice of technology at large-scale**
  - 600 MW plant requires ~170 ton O_2/day
- **Cryo-separation is highly energy intensive due to the thermal inefficiencies inherent in the low operating temperatures**
- **Alternatives**
  - Ion Transport Membranes
    - High TRL
  - Sorbent-Based Air Separation System (TDA Technology developed under DE-FE0026142)
    - Low TRL

Source: Air Products and Chemicals, Inc.



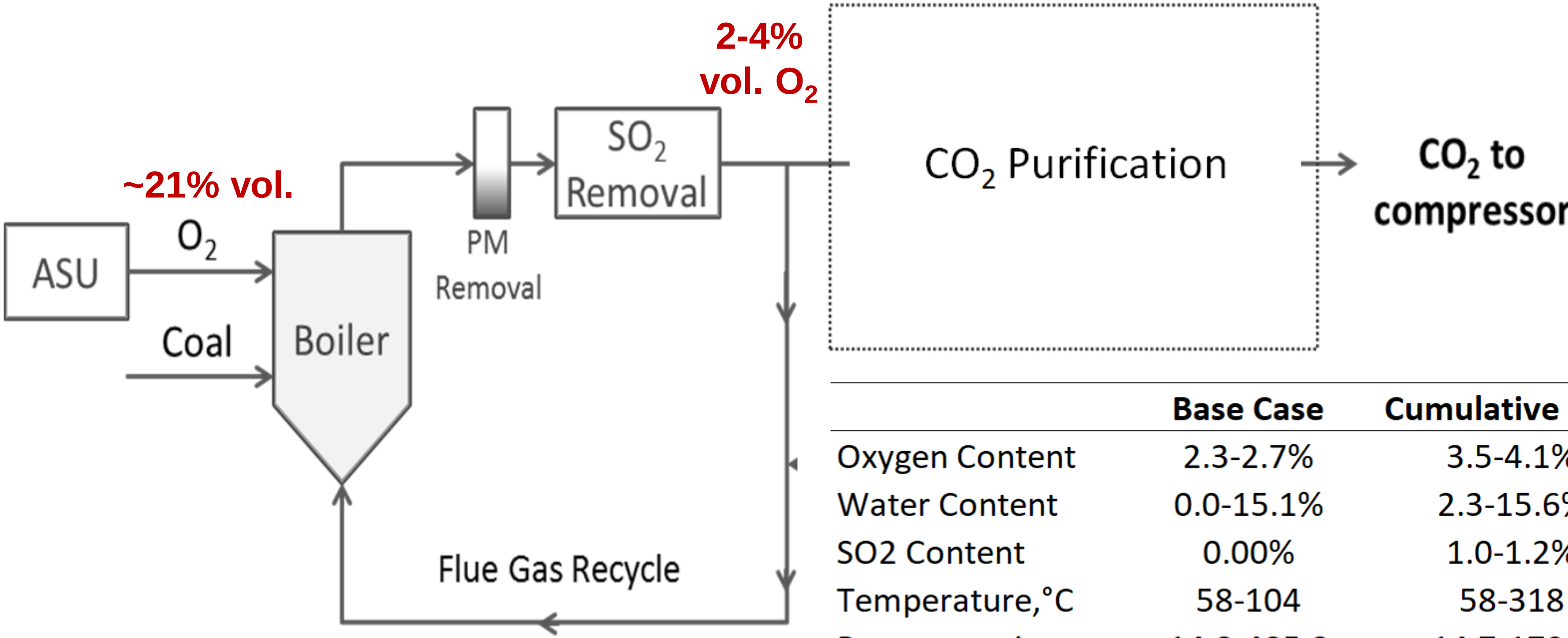
Source: Kobayashi, 2002

Process Optimization Case Matrix

Case	Power Cycle psig/°F/°F	Subsystem Concept Evaluated	Oxidant	Sulfur Removal
1 (Base)	Supercritical Steam 3500/1110/1150	Current ASU	95% O_2 Cryogenic ASU	Wet FGD
2	Supercritical Steam	Advanced O_2 Membrane w/ Preheat in Boiler	~100% Advanced O_2 Membrane (Ion Transport)	Wet FGD
3	Supercritical Steam	Advanced O_2 Membrane w/ Preheat by Natural Gas Firing	~100% Advanced O_2 Membrane (Ion Transport)	Wet FGD
4	Supercritical Steam	Advanced O_2 Sorbent (TDA) w/ Preheat in Boiler	95%+ Advanced O_2 Sorbent (TDA)	Wet FGD
5	Supercritical Steam	Advanced O_2 Sorbent (TDA) w Preheat by Natural Gas Firing	95%+Advanced O_2 Sorbent (TDA)	Wet FGD
6	Supercritical Steam	CO_2 Purification by Catalytic De-oxidation with Natural Gas	Two cases chosen from Case 1 through Case 5 (e.g., one TDA & one Ion Transport)	Wet FGD
7	Supercritical Steam	CO_2 Purification by Chemical Looping	Two cases chosen from Case 1 through Case 5 (e.g., one TDA & one Ion Transport)	Wet FGD
8	Supercritical Steam	Advanced CO_2 & ASU Compression	Two cases chosen from above (one TDA & one Ion Transport)	Wet FGD
9	Ultra-supercritical Steam 4000/1350/1400	Ultra-supercritical Steam Cycle with Advanced Materials	Same as Case 8 except steam cycle (one TDA & one Ion Transport)	Wet FGD
10	Ultra-supercritical Steam	Co-sequestration	Same as Case 9 without CO_2 Purification (TDA & Ion Transport)	Co-capture with CO_2
11	Supercritical CO_2 Conditions: TBD	Supercritical CO_2 Cycle with Advanced Materials	Same as Case 8 except working fluid (one TDA & one Ion Transport)	Wet FGD

Research

CO_2 Purification Need in POxC



	Base Case	Cumulative Case
Oxygen Content	2.3-2.7%	3.5-4.1%
Water Content	0.0-15.1%	2.3-15.6%
SO2 Content	0.00%	1.0-1.2%
Temperature,°C	58-104	58-318
Pressure, psia	14.8-485.8	14.7-179.9

Source: Cost of Electricity for Low Pressure Oxy-Combustion Technologies (NETL 2012).

- **The oxygen content in the CO_2 product has to be reduced to less than 1,000 ppmv prior to CO_2 compression**
- **Heat integration/optimization is critical**
  - **10-15% of plant's energy output**

CO_2 Purity Specifications

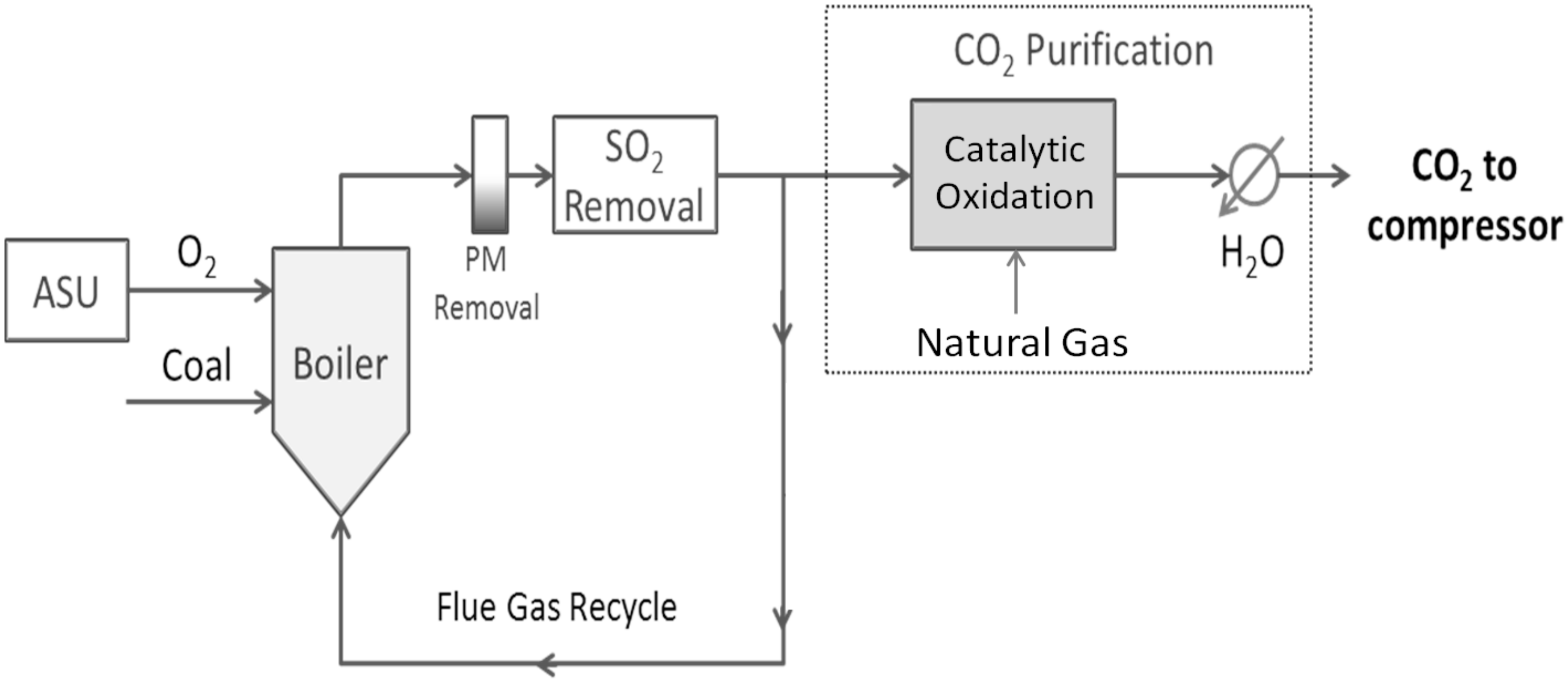
Component	Unit	Carbon Steel Pipeline		Enhanced Oil Recovery		Saline Reservoir Sequestration		Saline Reservoir CO_2 & H_2S Co-sequestration	
	(Max unless Otherwise noted)	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature
CO_2	vol% (Min)	95	90-99.8	95	90-99.8	95	90-99.8	95	20 – 99.8
H_2O	ppmv	500	20 - 650	500	20 - 650	500	20 - 650	500	20 - 650
N_2	vol%	4	0.01 - 7	1	0.01 - 2	4	0.01 - 7	4	0.01 – 7
O_2	vol%	0.001	0.001 – 4	0.001	0.001– 1.3	0.001	0.001– 4	0.001	0.001 – 4
Ar	vol%	4	0.01 – 4	1	0.01 – 1	4	0.01 – 4	4	0.01 – 4
CH_4	vol%	4	0.01 – 4	1	0.01 – 2	4	0.01 – 4	4	0.01 – 4
H_2	vol%	4	0.01 - 4	1	0.01 – 1	4	0.01 – 4	4	0.02 – 4
CO	ppmv	35	10 - 5000	35	10 - 5000	35	10 - 5000	35	10 - 5000
H_2S	vol%	0.01	0.002 – 1.3	0.01	0.002 – 1.3	0.01	0.002 – 1.3	75	10 - 77
SO_2	ppmv	100	10 - 50000	100	10 - 50000	100	10 - 50000	50	10 - 100
NO_x	ppmv	100	20 - 2500	100	20 - 2500	100	20 - 2500	100	20 - 2500
NH_3	ppmv	50	0 - 50	50	0 - 50	50	0 - 50	50	0 - 50
COS	ppmv	trace	trace	5	0 - 5	trace	trace	trace	trace
C_2H_6	vol%	1	0 - 1	1	0 - 1	1	0 - 1	1	0 - 1
C_3+	vol%	<1	0 - 1	<1	0 - 1	<1	0 - 1	<1	0 - 1
Particulates	ppmv	1	0 - 1	1	0 - 1	1	0 - 1	1	0 - 1
HCN	ppmv	trace	trace	trace	trace	trace	trace	trace	trace
Glycol	ppbv	46	0 - 174	46	0 - 174	46	0 - 174	46	0 - 174

* Not enough information is available to determine the maximum allowable amount for HCl, HF, Hg, MEA and Selexol solvent.

- **Stringent requirements for O_2 (and other contaminants) in compressed CO_2**
  - **<0.001% vol. O_2**

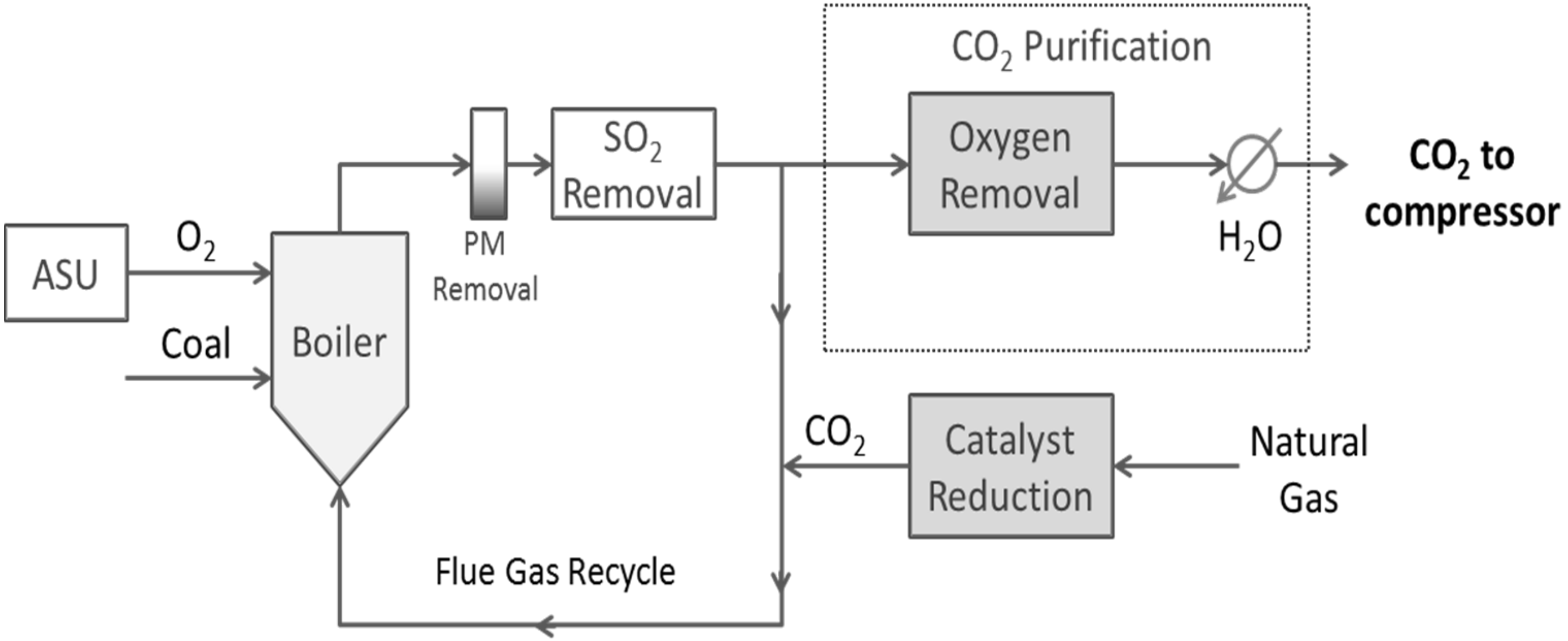
TDA RESEARCH

CO_2 Purification via Catalytic Oxidation



- **Catalytic oxidation is mature technology**
- **Challenges with catalytic oxidation**
  - **To meet the O_2 concentration requirements, natural gas has to be used in greater quantities than required by the reaction stoichiometry**
  - **Excess natural gas ending in the CO_2 will reduce system efficiency**
  - **Limit on CH_4 is high (1% vol.) but tighter on heavier HCs**

TDA's CO_2 Purification System

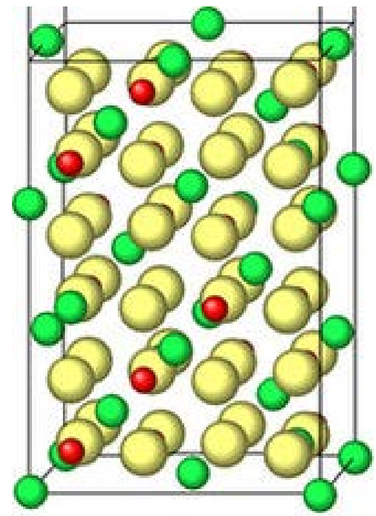


- TDA proposes a chemical absorbent-based oxygen removal system
  - Low O_2 concentration in the treated CO_2 can be readily achieved
  - Excess natural gas can be recycled back to the boiler
- Does not use precious metal catalysts; low cost metal oxide catalyst could polish off impurities

TDA RESEARCH

TDA's Sorbent

- **TDA sorbent consists of a high surface area (>100 m^2/g) mixed metal oxide $A_xB_yO_z$ phase that selectively reacts with the oxygen in the compressed CO_2 at moderate temperatures (<200 to 500°C)**

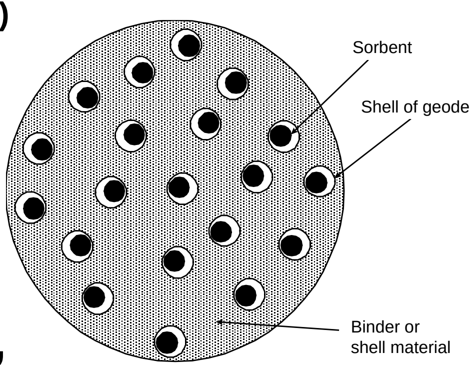


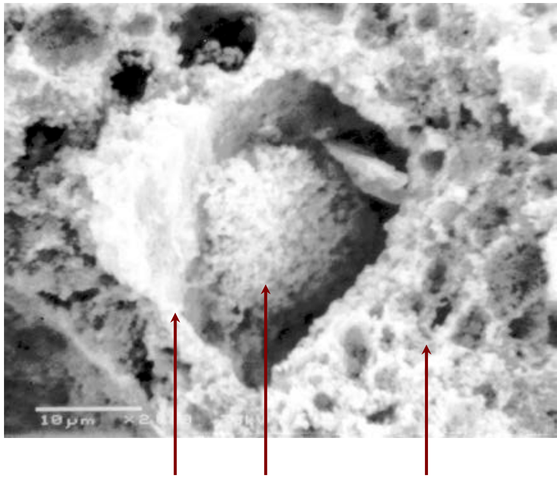
Crystal model for $A_xB_yO_z$

$$2M + O_{2(g)} = 2MO$$

$$4MO + CH_{4(g)} = 4M + CO_{2(g)} + 2H_2O_{(g)}$$

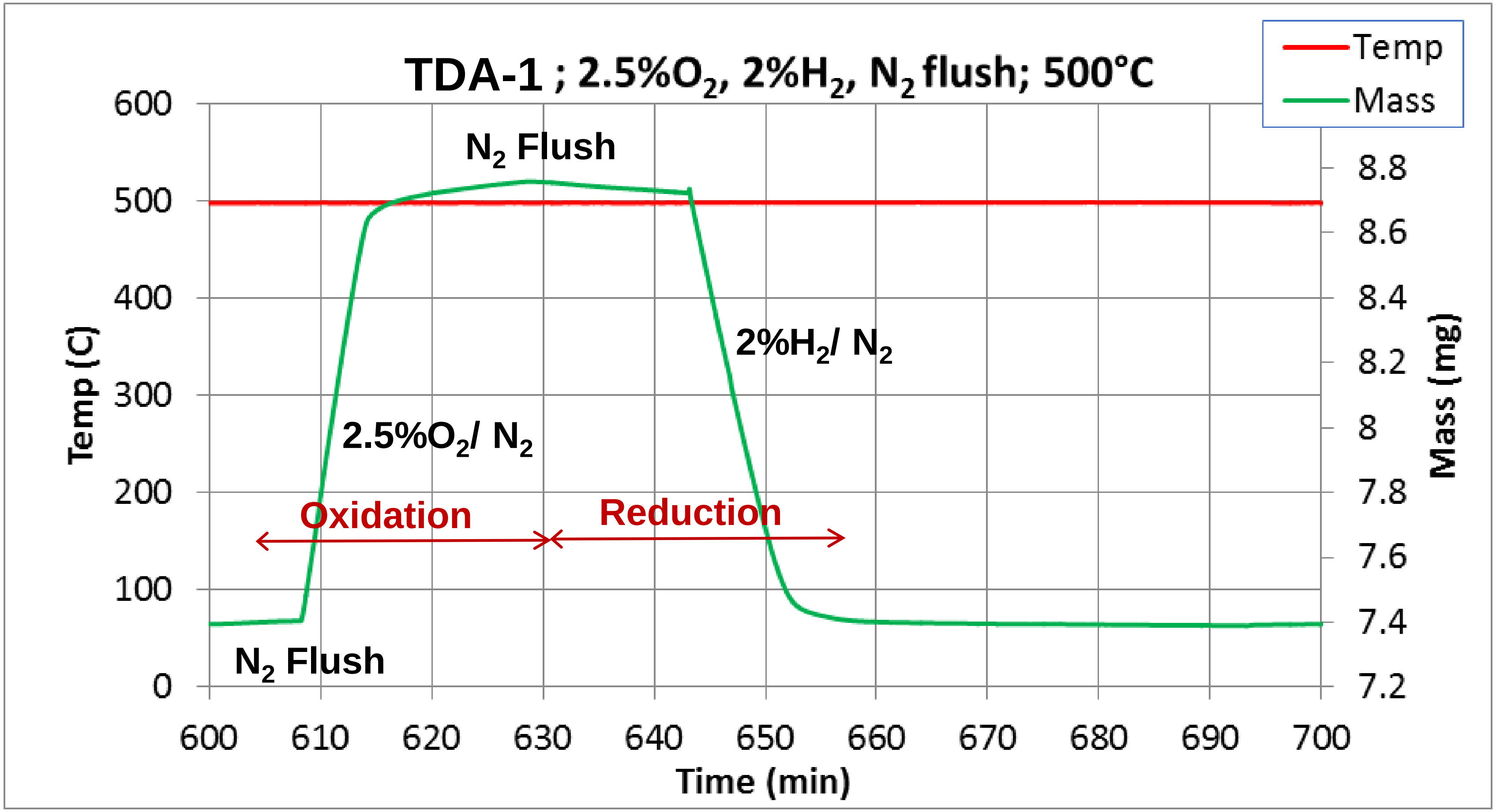
- **Sorbent can effectively reduce O_2 content to less than 100 ppmv**
  - **No equilibrium limitations**
- **TDA's sorbent uses a unique structure referred to as a "geode"**
  - **High mechanical integrity**
  - **High chemical stability**
  - **High surface area**





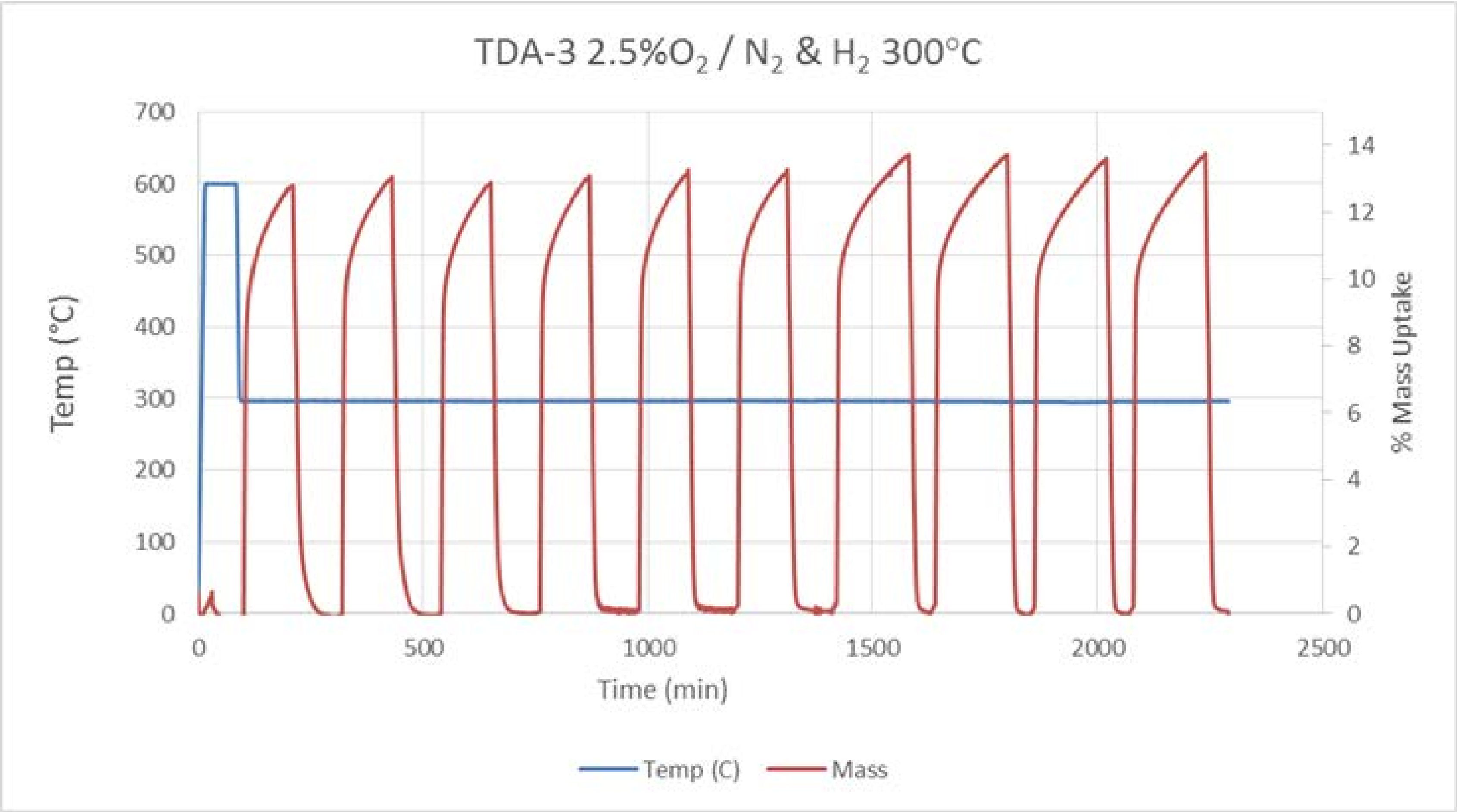
TDA's geode sorbent structure as seen in SEM

Typical RedOx Cycle - TGA Tests



- **Fast oxidation/reduction kinetics at 500°C**
- **18-20% O_2 uptake capacity (kg O_2 removed per kg sorbent)**

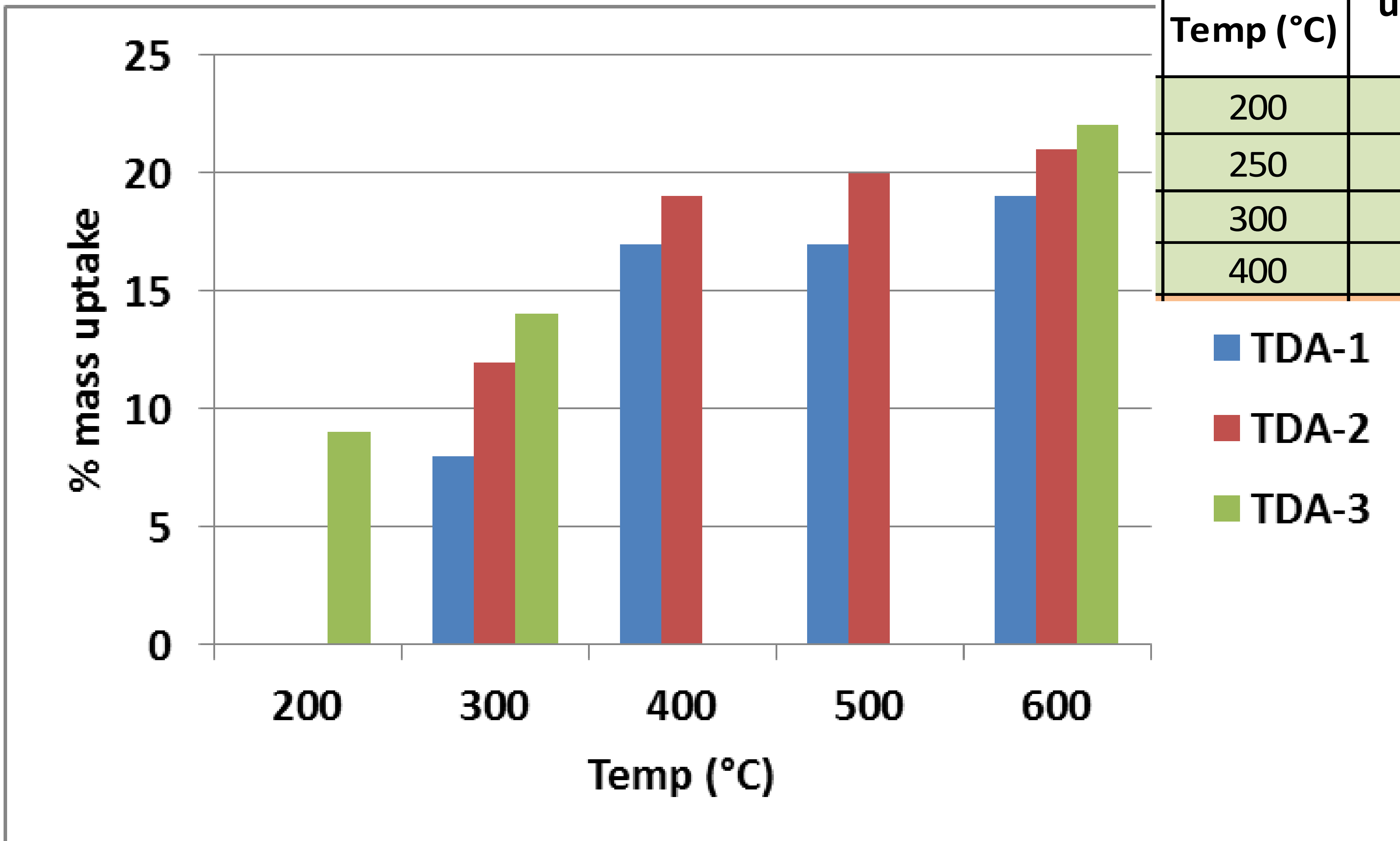
TGA Cycles at 300ºC



- **Formulations were modified using promoters to improve kinetics and oxygen uptake at lower temperatures**
- **Modified samples showed high capacity (12+% wt. O_2) at 300ºC**

Impact of Temperature

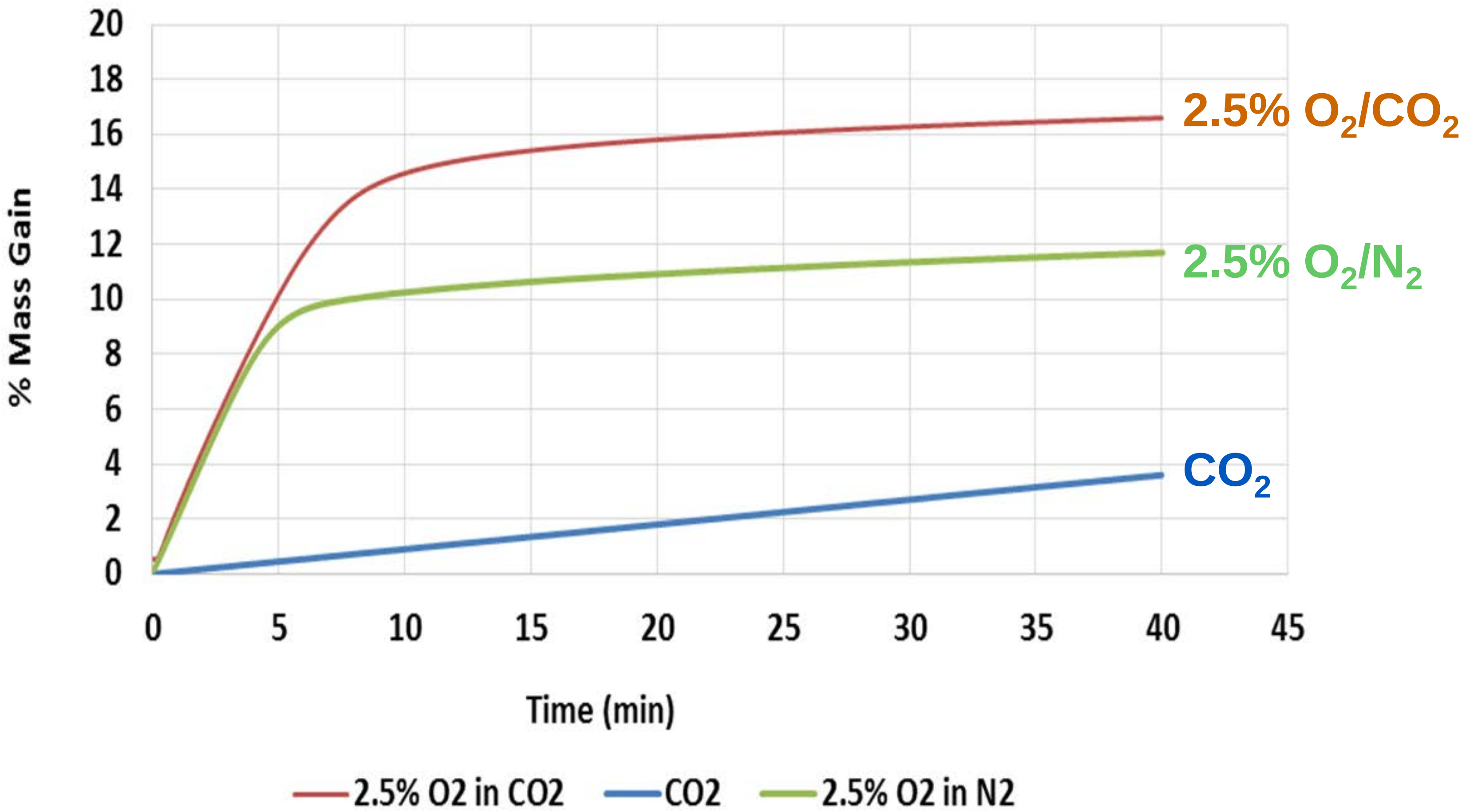
Gases: 2.5%O_2 /N_2 & 2% H_2/N_2



Cycle Temp (°C)	% oxygen uptake (by mass)
200	6.0
250	12.5
300	17.3
400	20.5

- **TDA-3 showed better oxygen uptakes at all temperatures**

O_2 Uptake in the Presence of CO_2



- **Some metal oxide carbonation was evident**
- **Oxidation is much faster than carbonation (from CO_2 reaction)**

TDA RESEARCH

Fixed Bed Reactor Tests

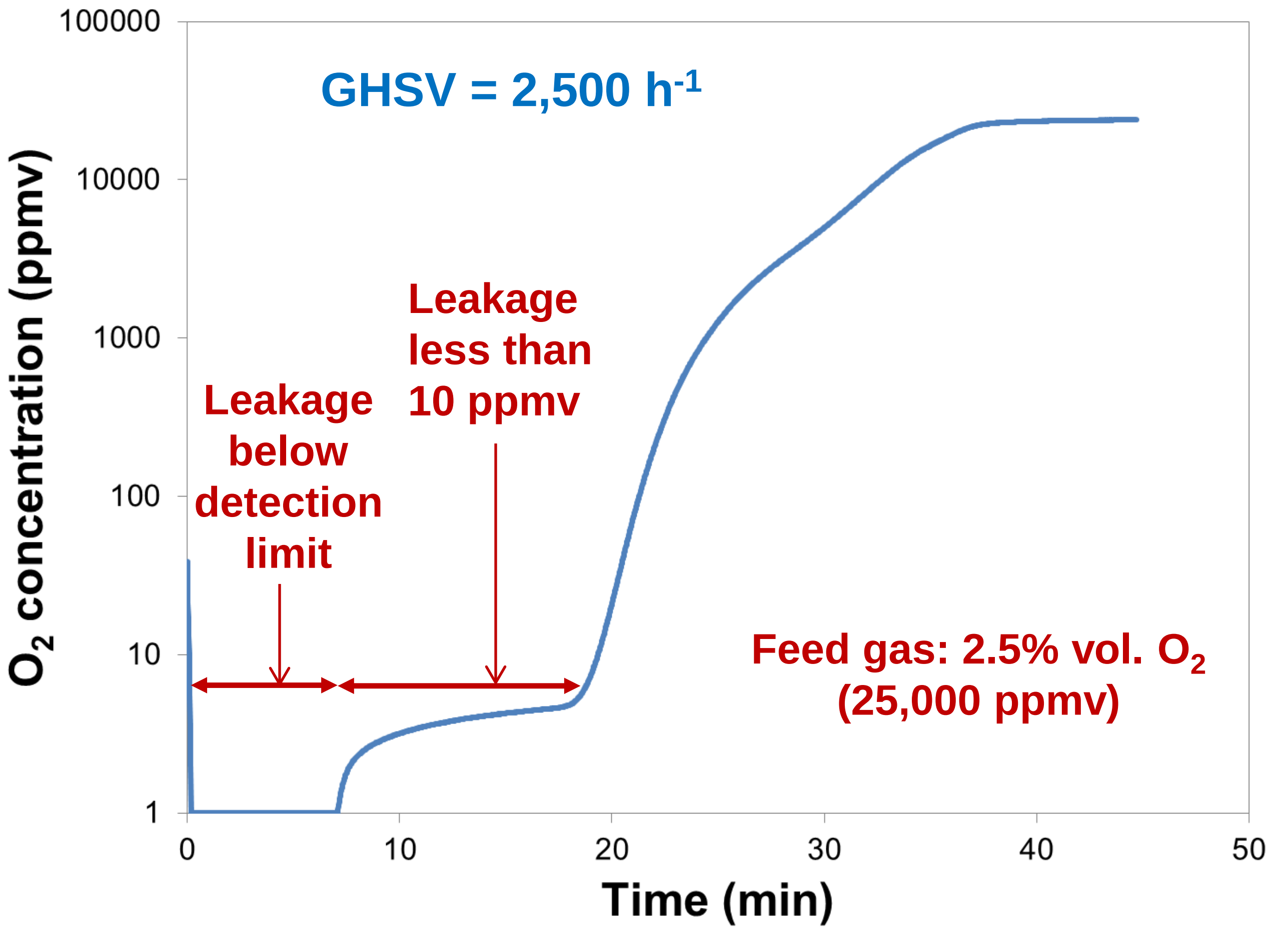
Test Capabilities

- Breakthrough tests
- Life cycle tests

Variables

- Temp. 200-550°C
- Space velocity = 500-10,000 h^{-1}
- Pressure = 1-20 bar
- Absorption: 0.1-5% O_2/CO_2
- Regeneration: 0.1-100% H_2 or CH_4
- An electro-chemical O_2 analyzer (ZR800 Zirconia Oxygen Analyzer) with 1 ppmv O_2 detection capability was used to measure the O_2 concentration
- California Analytical NDIR analyzer for CO_2, CO, CH_4 measurements

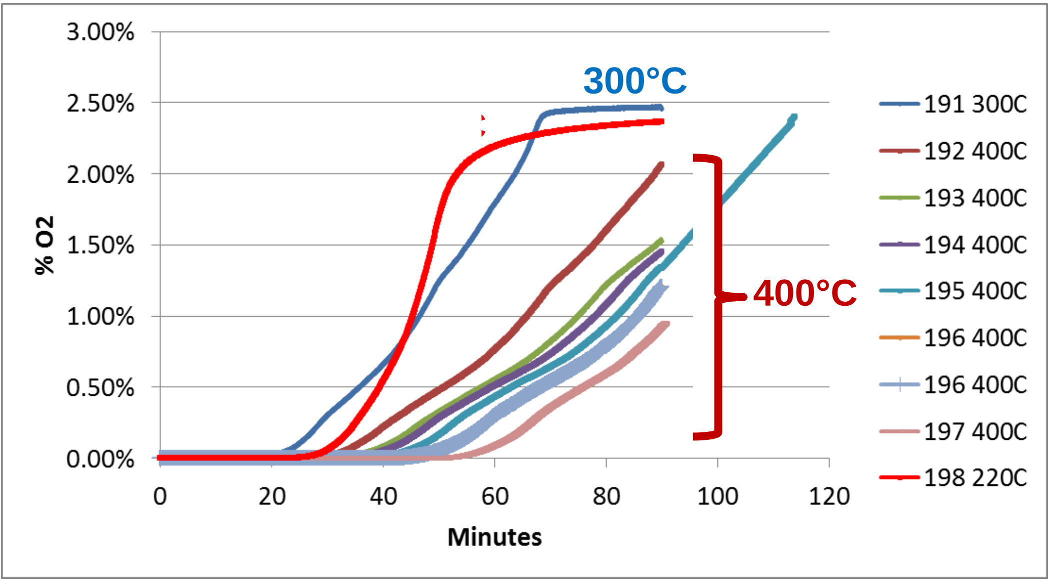
Breakthrough Tests

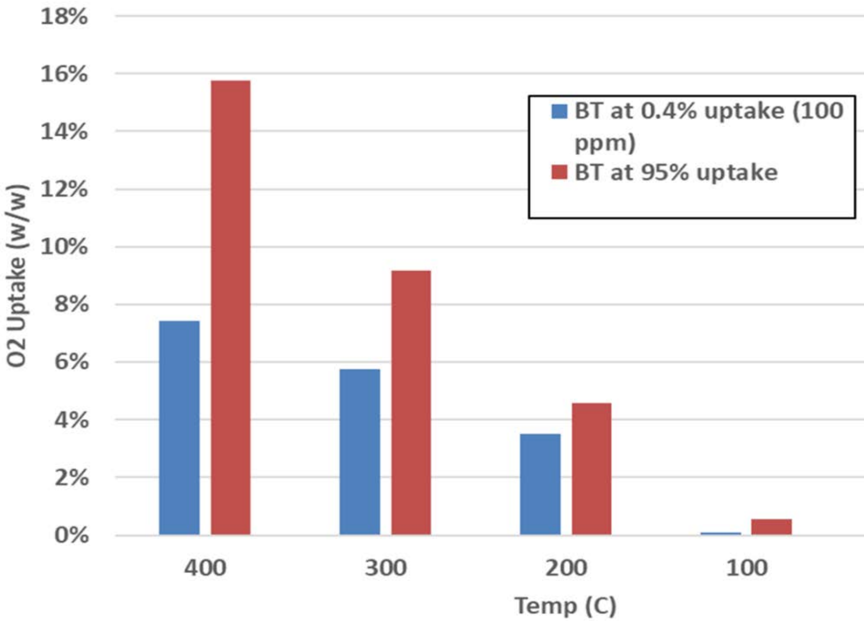


- Breakthrough tests confirmed very high oxygen removal efficiency
- O_2 concentration in treated gas can be lowered to <10 ppmv

Multiple Cycle Tests

Cycle # 191 – 198: 400°C



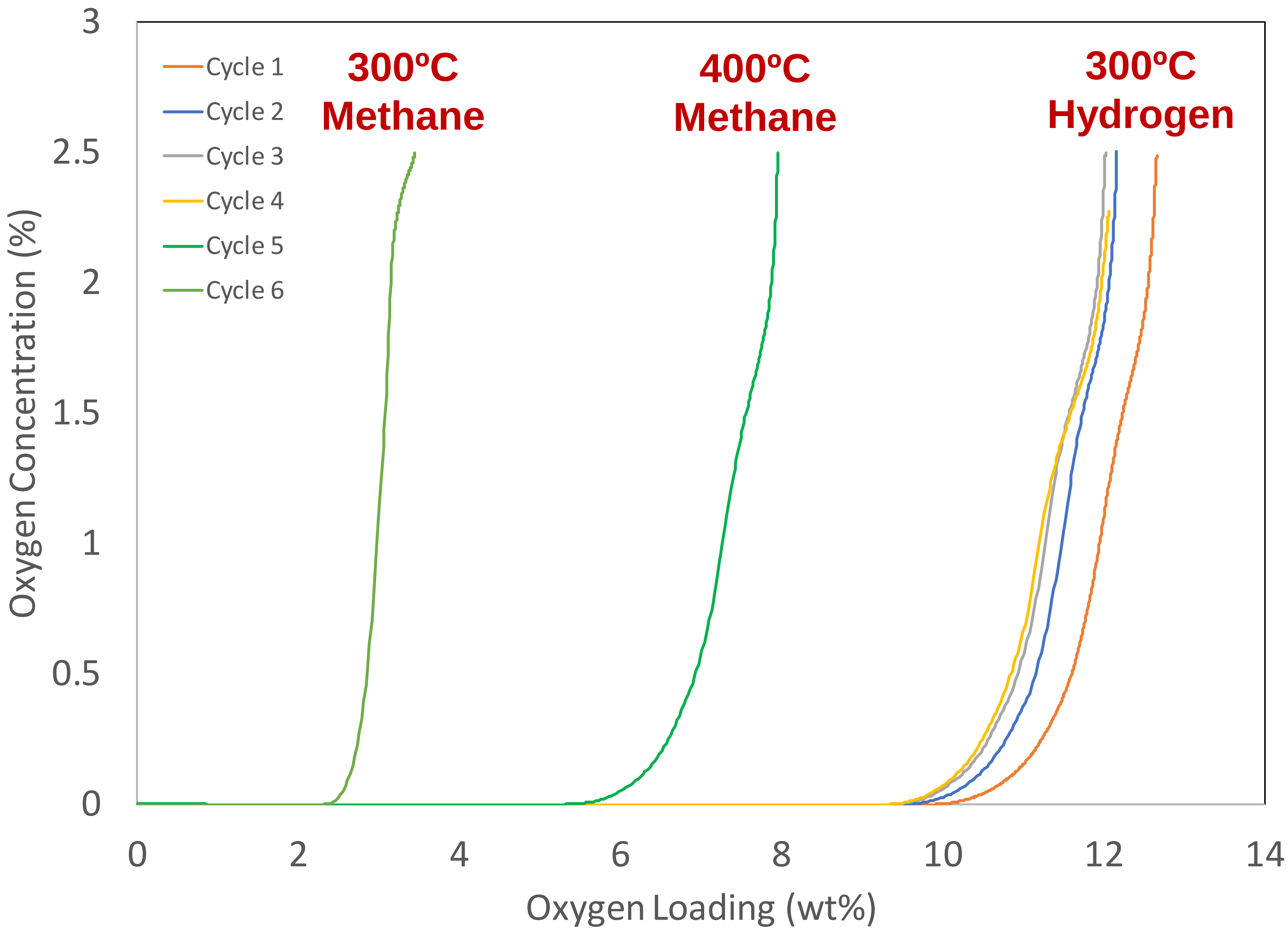


- **Stable performance was observed over 300 cycles; both isothermal and TSA cycles in 200-500ºC range**
  - **At 400ºC ~7.4%wt. O_2 capacity at 100 ppmv breakthrough**
  - **15.77% wt. O_2 capacity at 95% O_2 uptake**

Temp (˚C)	100 ppm BT (0.4% O_2 uptake)	Saturation BT (95% O_2 uptake)
400	7.42%	15.77%
300	5.75%	9.18%
200	3.50%	4.59%
100	0.09%	0.54%
50	0.03%	0.06%

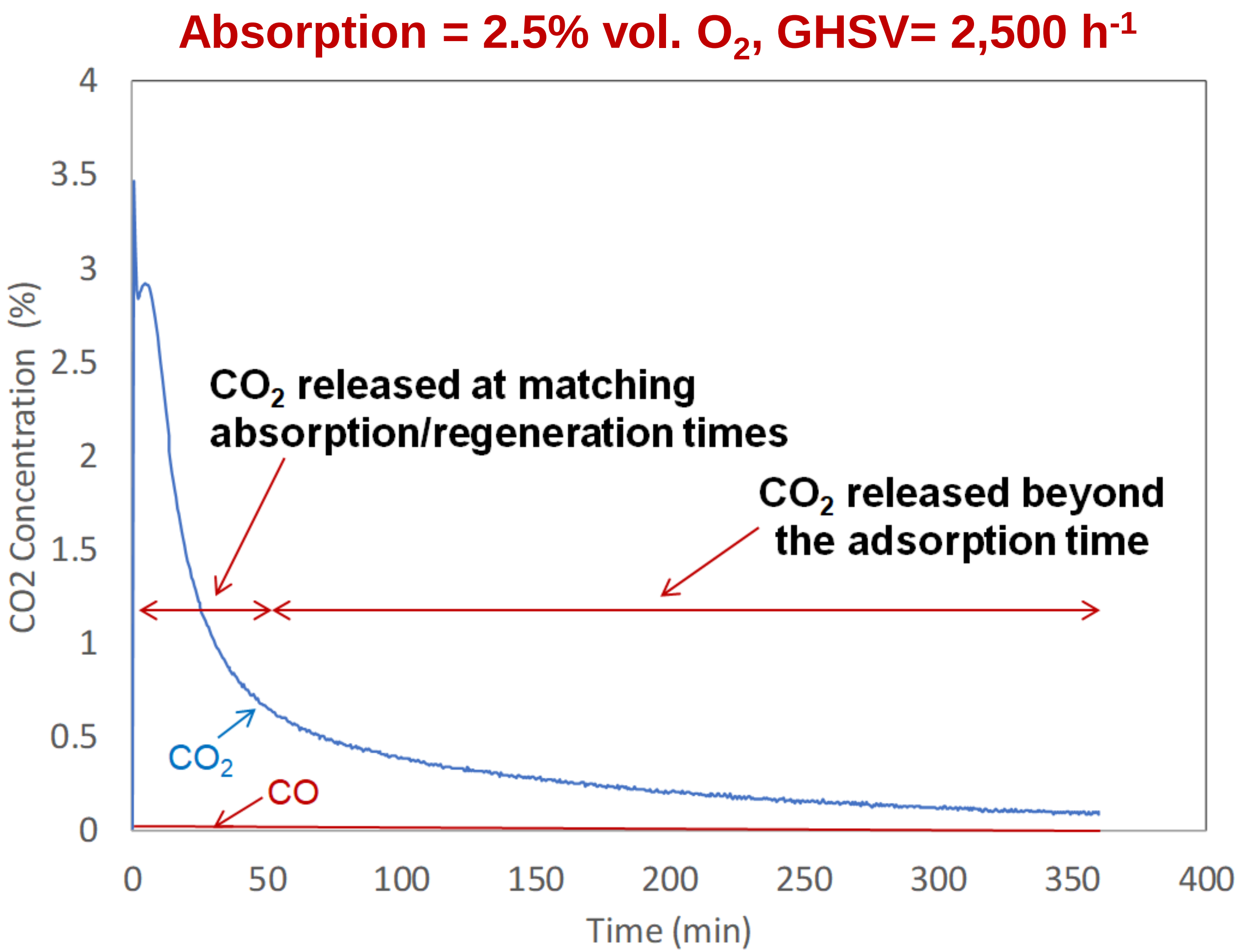
TDA RESEARCH

Using Methane as Reduction Gas



- **When CH_4 is used instead of hydrogen the oxygen uptake decreased due to incomplete regenerations (lower reduction rates with CH_4)**

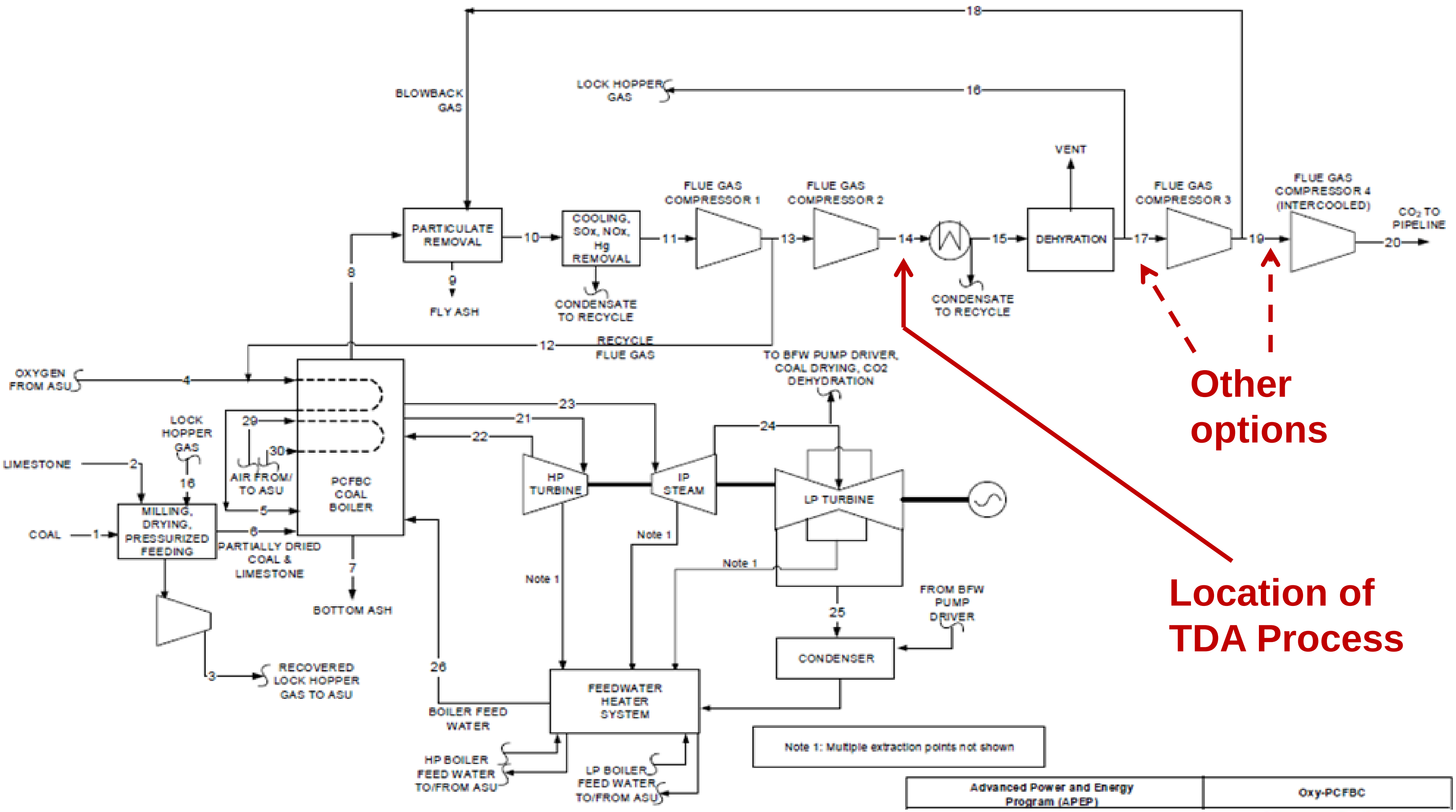
Reaction Products - 400ºC CH_4 Reduction



- **Longer regenerations are needed for full reduction**
- **CH_4 reduction primarily generated CO_2 (<50 ppm CO was observed)**

RESEARCH

CO_2 Purification Process Design



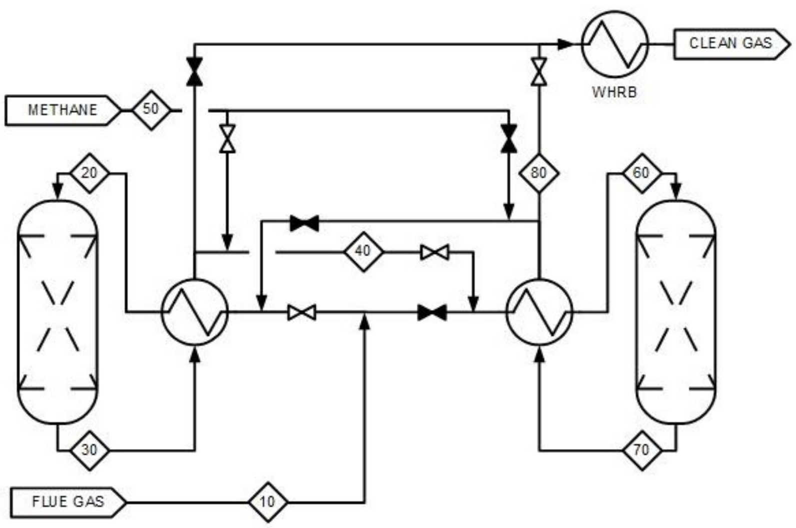
System Integration

- **Both absorption and regeneration processes are exothermic**
- **Absorption**

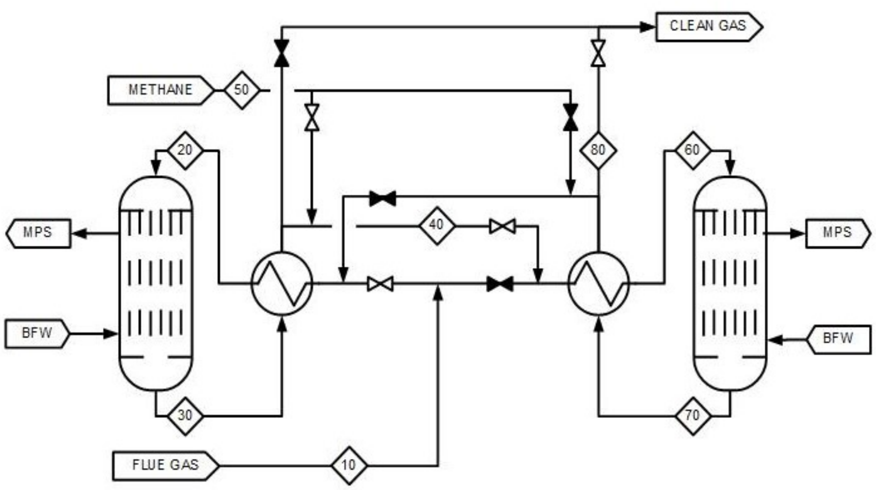
  $4M + 2O_2 \rightarrow 4MO$ **$\Delta H_{rxn} = -140\text{-}150$ kcal/mole**
- **Regeneration**

  $4MO + CH_4 \rightarrow CO_2 + 2H_2O + 4M$ **$\Delta H_{rxn} = -40\text{-}50$ kcal/mole**

- **Various heat removal options have been investigated**

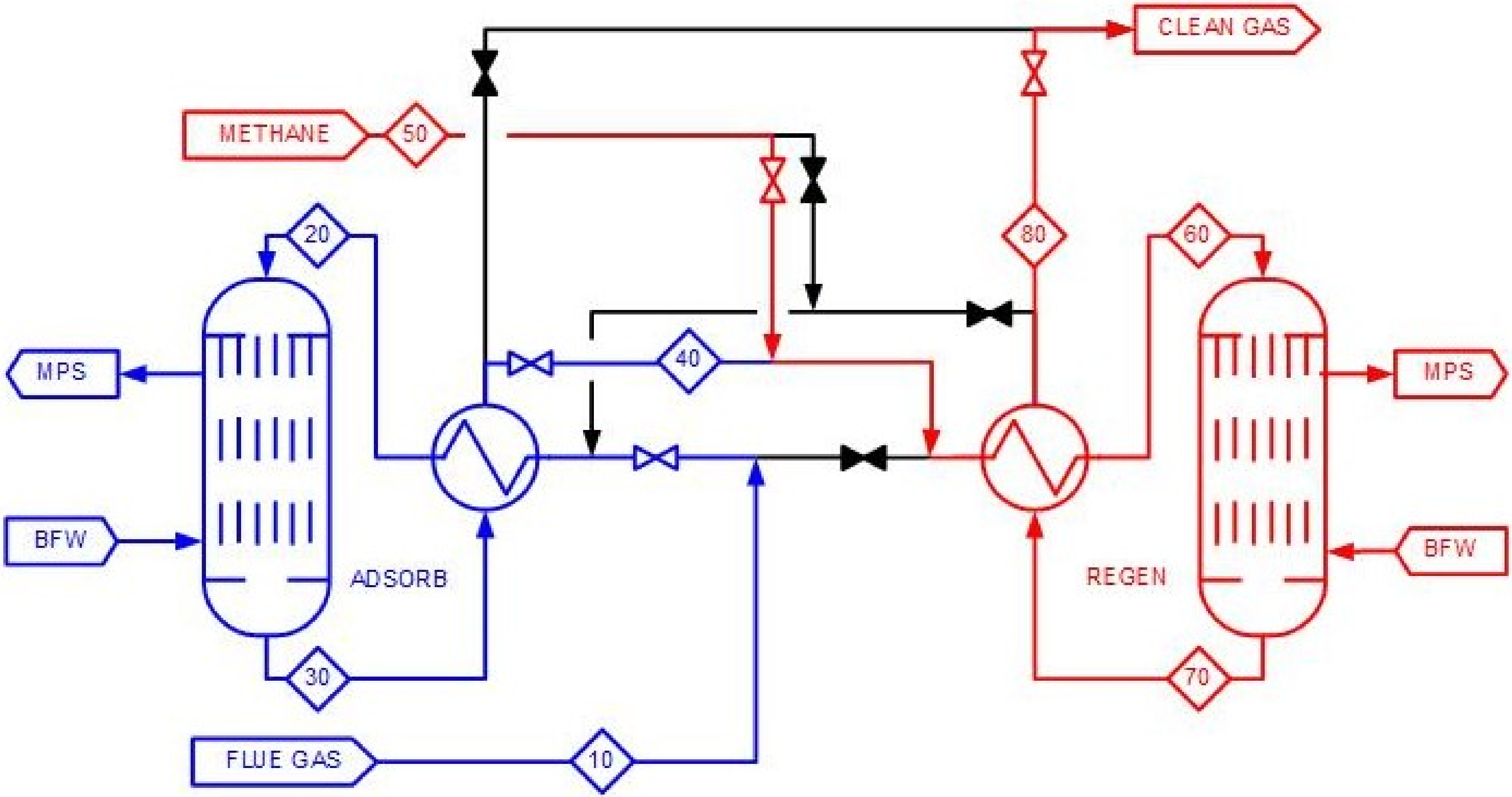


Adiabatic Design



Isothermal Design

Isothermal Design



- **Reactors operating in series provides good flow match between the oxidation and reduction steps**

Isothermal Reactors

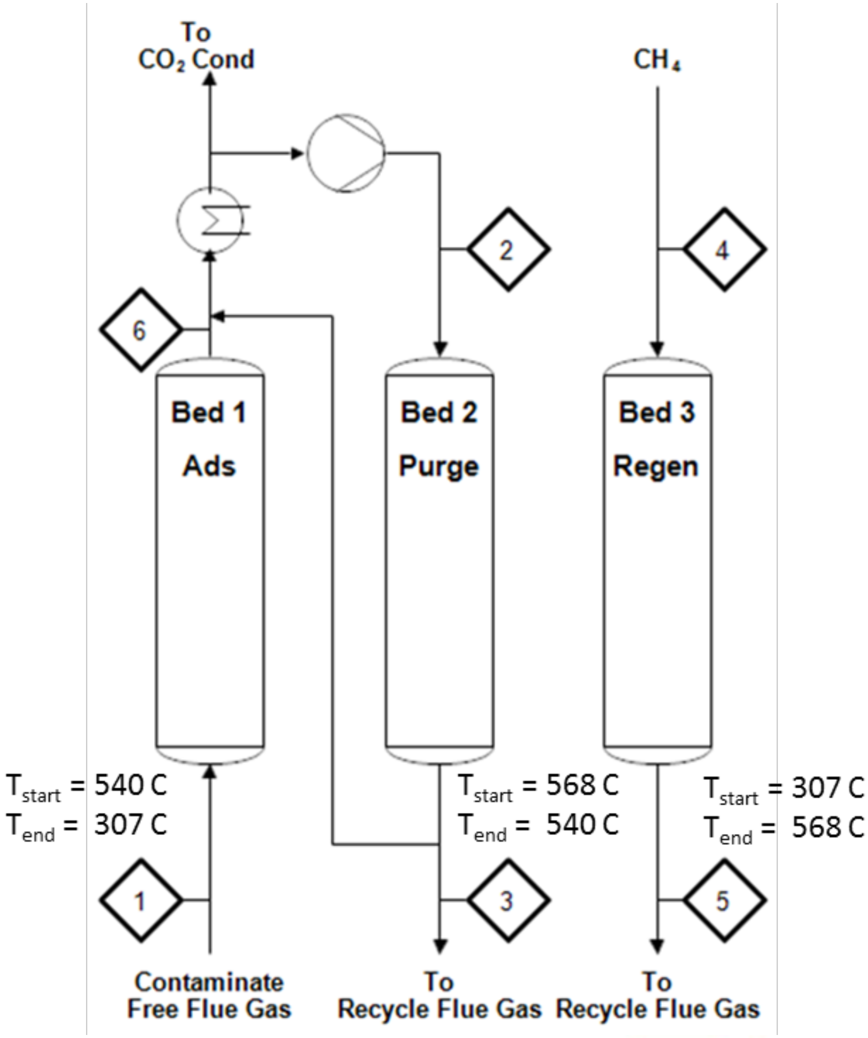
- **Two reactors operate in series to remove O_2 from the flue gas**
  - The first reactor receives flue gas from the compressor and the sorbent adsorbs the oxygen in the flue gas
  - The second reactor receives the clean flue gas spiked with methane to regenerate the sorbent
- **Isothermal reactors are packed tube, steam is raised using the heat generated by reaction exotherm**
- **Both reactors are equipped with feed-product heat exchangers to heat the incoming flue gas to the reaction temperature**

Stream ID	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**
Temperature (°C)	78	400	425	99	50	407	425	126
Pressure (bar)	23.9	23.9	22.9	22.9	22.1	22.1	22	22
Flow (10^6 Sm^3/day)	9	9	8.8	8.8	0.2	9	9.2	9.2
N2	2.60%	2.60%	2.70%	2.70%	0.00%	2.60%	2.60%	2.60%
O2	2.70%	2.70%	**0.00%**	0.00%	0.00%	0.00%	0.00%	0.00%
Ar	4.00%	4.00%	4.10%	4.10%	0.00%	4.00%	3.90%	3.90%
CH4	0.00%	0.00%	0.00%	0.00%	100%	2.10%	**0.10%**	0.10%
CO2	90.50%	90.50%	93.00%	93.00%	0.00%	91.10%	90.60%	90.60%
H2O	0.20%	0.20%	0.20%	0.20%	0.00%	0.20%	2.80%	2.80%

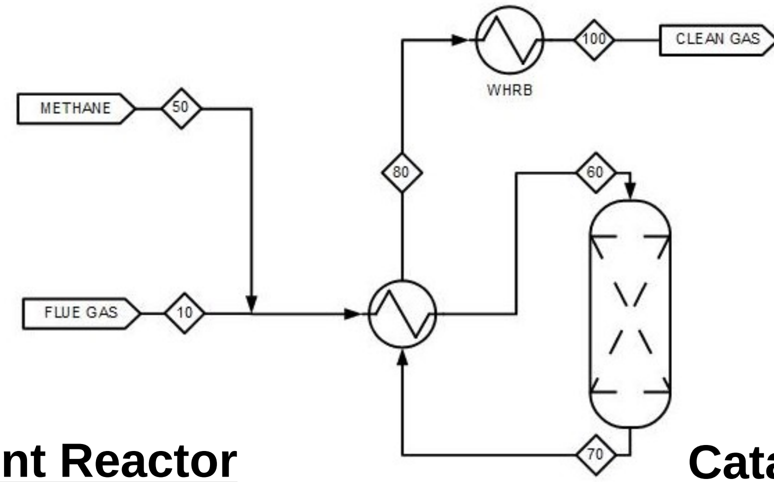
Cycle Sequence Optimization

- In a multi-step cycle sequence, a purge step is added to purge any CH_4 from the bed
- At the end of the reduction step, the void spaces in the bed will be filled with CH_4 (2% vol. max) mixed with CO_2 which could be transferred into the CO_2 stream
- Using a small amount of the oxygen-free CO_2 and purge the bed into the flue gas recycle
- Any residual CH_4 will be combusted in the boiler

	Stage 1	Stage 2	Stage 3
Time (min)	2	2	2
Bed 1	Abs	Regen	Purge
Bed 2	Purge	Abs	Regen
Bed 3	Regen	Purge	Abs



CatOx vs. Sorbent-Based O_2 Removal



Isothermal Sorbent Reactor

Reactor Type – 2 x Packed Tube Feed-Product Exchangers

- Adsorber – 63 MW_{th} /Regen – 61 MW_{th}

Operating Temperatures

- Absorber Bed – 425°C
- Regeneration Bed – 425°C
- Outlet Flue Gas – 126°C

Heat Recovery – 39 MW_{th} from the shell side of the reactors

- Steam Generated – 59,640 kg/hr @ 45 bar (medium pressure)

Catalytic Reactor

Reactor Type – Single Fixed Bed Feed-Product Exchangers

- Reactor – 44 MW_{th}

Operating Temperatures

- Catalyst Bed – 520°C
- Outlet Flue Gas – 165°C

Heat Recovery – 31 MW_{th} from waste heat recovery boiler

- Steam Generated – 48,400 kg/hr @ 45 bar (medium pressure)

Plant Performance Summary

Case #	1	2	3	4	5
GROSS POWER GENERATED (AT GENERATOR TERMINALS) (KWE)					
STEAM TURBINE	785,587	791,313	781,468	723,700	715,557
DEPLETED AIR EXPANDER	-	214,779	212,201	80,118	80,714
TOTAL GENERATED (KWE)	785,587	1,006,092	993,669	803,818	796,271
TOTAL AUXILIARIES (KWE)	235,587	456,091	443,669	253,818	246,271
NET POWER (KWE)	550,000	550,000	550,000	550,000	550,000
NET PLANT EFFICIENCY (% HHV)	31.24	31.01	31.23	32.61	33.00
THERMAL INPUT					
COAL KWT HHV	1,760,447	1,773,645	1,679,498	1,686,511	1,569,989
NATURAL GAS KWT HHV	-	-	81,458	-	96,584
TOTAL KWT HHV	1,760,447	1,773,645	1,760,956	1,686,511	1,666,573
CARBON CAPTURED (%)	99.5	99.5	97.0	99.5	99.5

Case	Power Cycle psig/°F/°F	Subsystem Concept Evaluated	Oxidant
1 (Base)	Supercritical Steam 3500/1110/1150	Current air separation unit (ASU)	95% O_2 Cryogenic ASU
2	Supercritical Steam 3500/1110/1150	Advanced O_2 Membrane with Preheat in Boiler	~100% Advanced O_2 Membrane (Ion Transport)
3	Supercritical Steam 3500/1110/1150	Advanced O_2 Membrane with Preheat by Nat. Gas Combustion	~100% Advanced O_2 Membrane (Ion Transport)
4	Supercritical Steam 3500/1110/1150	Advanced O_2 Sorbent (TDA) with Boiler Heat	95%+ Advanced O_2 Sorbent (TDA)
5	Supercritical Steam 3500/1110/1150	Advanced O_2 Sorbent (TDA) with Nat. Gas Combustion Heat	95%+Advanced O_2 Sorbent (TDA)

Acknowledgements

- **DOE/NETL funding under the DE-FE-0029090 project is greatly appreciated**
- **DOE Project Manager, Diane R. Madden**
- **Dr. Ashok Rao, UCI**