Overview of Proven and Emerging CO_2 Purification Processes for CCUS

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Presentation Roadmap

- Sources and Contaminants
- Sequence (Timing) of Purification Steps
- Dehydration
- Distillation
- Catalysts
- SO_2 / Other Sulfur Species
- NO_X
- Others: Aerosols, Salts, Mercury…

High Purity Sources: Ethanol, Fertilizer, Amine Regen.

- ≥ 95 %v. CO_2 (dry) basis
- Saturated with Water Vapor
- ~Atmospheric Pressure

→ **Compress and Dehydrate**

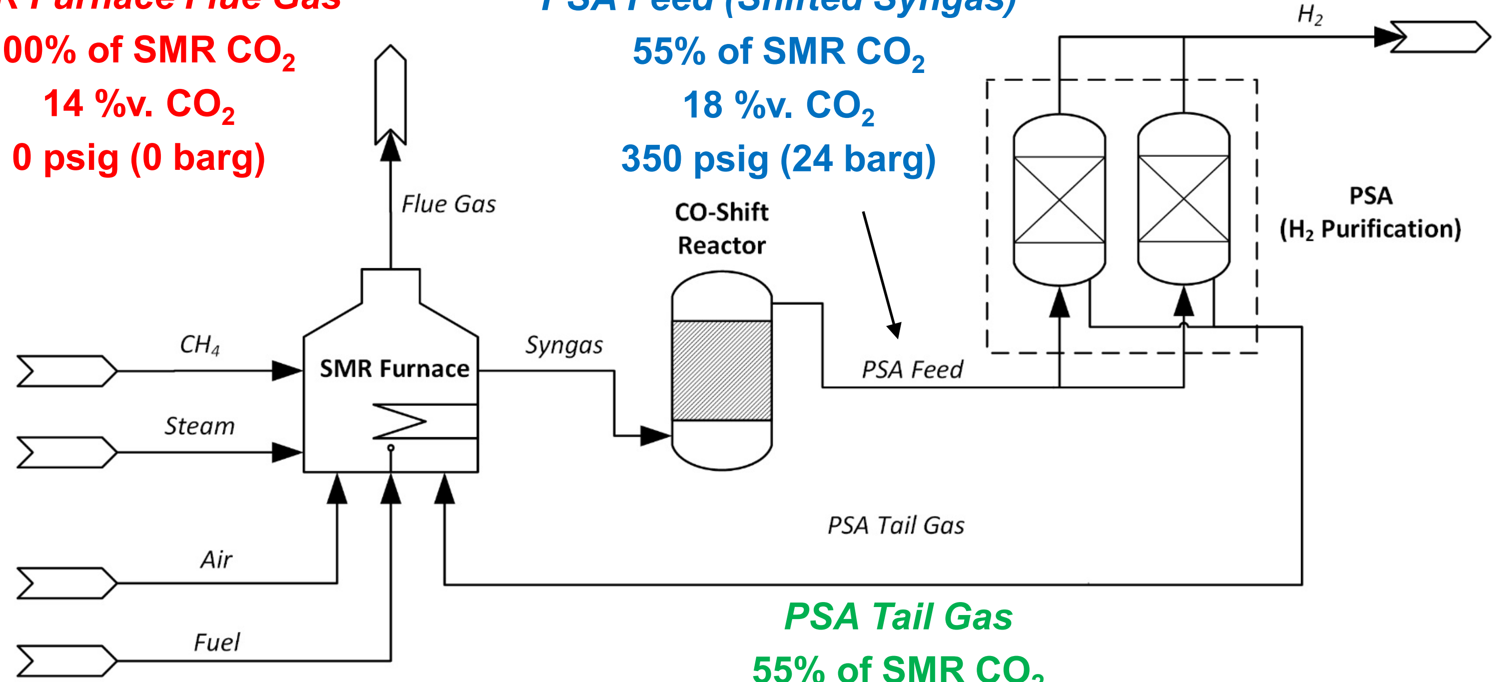
- High Oxygen Spikes (~10,000 ppmv) Common in Ethanol Plant CO_2

→ **Distillation**

Intermediate Purity Source: Hydrogen Production

SMR Furnace Flue Gas
100% of SMR CO_2
14 %v. CO_2
0 psig (0 barg)

PSA Feed (Shifted Syngas)
55% of SMR CO_2
18 %v. CO_2
350 psig (24 barg)



PSA Tail Gas
55% of SMR CO_2
40 %v. CO_2
5 psig (0.4 barg)

SMR = Steam Methane Reformer

Lower Purity Sources: Flue Gas

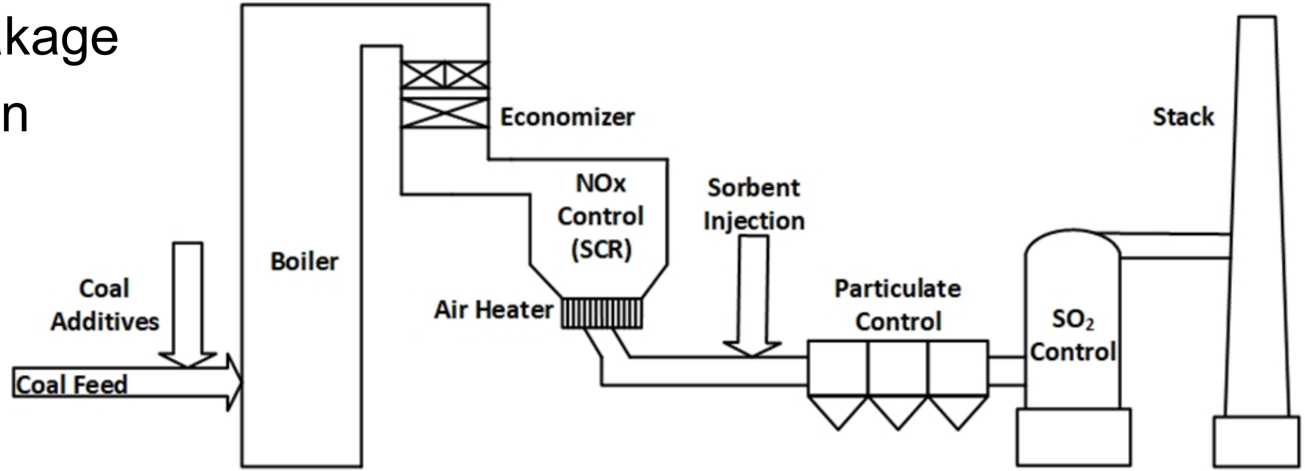
- ~Atmospheric Pressure, Water Saturated
- Too Hot for Capture Technologies
- **Contaminant Issues**:

  SO_2, H_2S, NO_X, PM, Aerosols, Hg

Fuel / Process	Flue Gas ~%v.CO_2
Natural Gas	4
Coal	12
FCC	15
Cement	21
Steel	26

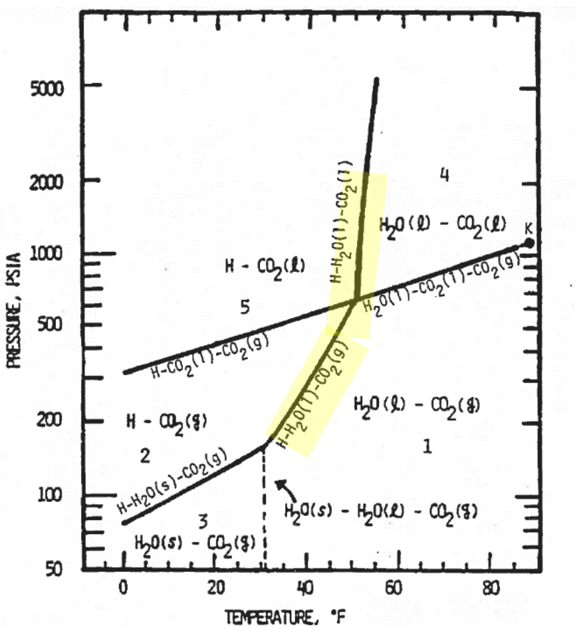
Countermeasures Before Capture:

- Reduce Air In-Leakage
- Maximize Emission Controls →
- Quench and SO_2 Polishing



Reasons for Dehydration of CO_2

- Prevent Water Ice in CO_2 processed below 32°F (0°C).
- Prevent CO_2–H_2O Solid Hydrates → (Clathrates) above 32°F (0°C).
- CO_2 Corrodes Carbon Steel When Liquid Water Phase is Present.



CO_2-H_2O Hydrate Figure
Courtesy of Gas Processors Association.
GPA Research Report RR-99

Corrosion of Carbon Steel Tube Sheet in Wet CO_2, Water Condensing Service at 400 psig (28 barg).

CO_2 Dehydration Process: TEG Absorption

- Typical performance ~ 150 ppmv H_2O.
- Water Absorbed from CO_2 into TEG in Contactor.
- Heating TEG to 370°F (188°C) in Regeneration Skid Strips Water out of TEG.
- Suitable for Many Projects with only Compression Needed After Capture

Concerns:

- Glycol Carryover in Dry CO_2
- VOC/HAP Emissions in Vent Streams

Contactor

Regeneration Skid

CO_2 Dehydration Process: Mole Sieve Adsorption

- Typical performance ~1 ppmv H_2O.
- Process Gas Flows Top Down in Drying Bed Cycles.
- Heated Gas (400°F [204°C]) Flows up in Regeneration Bed Cycles.
- Capital and Operating costs ~1.5 times TEG Absorption.

Concerns:

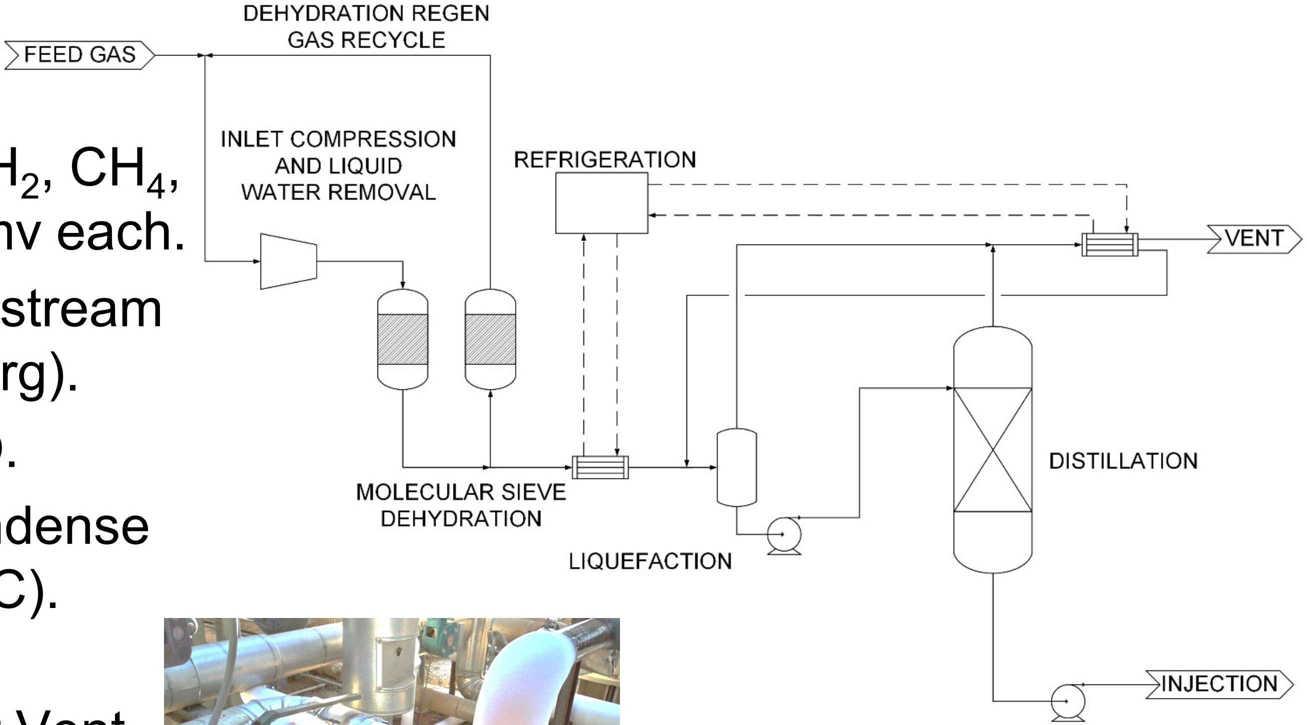
- Media Must be Kept Free of <u>Any</u> Liquids (Water, Oil, etc.).
- Media Replaced ~Every 3 Years.

Impacts of Oxygen in CO_2

- Oxygen makes mixtures of CO_2 and water more corrosive.
  (Remember the picture of the heat exchanger tube sheet on slide 6 ?!)
- Oxygen can oxidize TEG leading to faster solvent degradation.
- Oxygen can lead to biological growth in underground formations.
- Oxygen can react with H_2S under certain conditions to form elemental sulfur, sulfuric acid, and / or other sulfur compounds.

Liquefaction and Distillation of CO_2

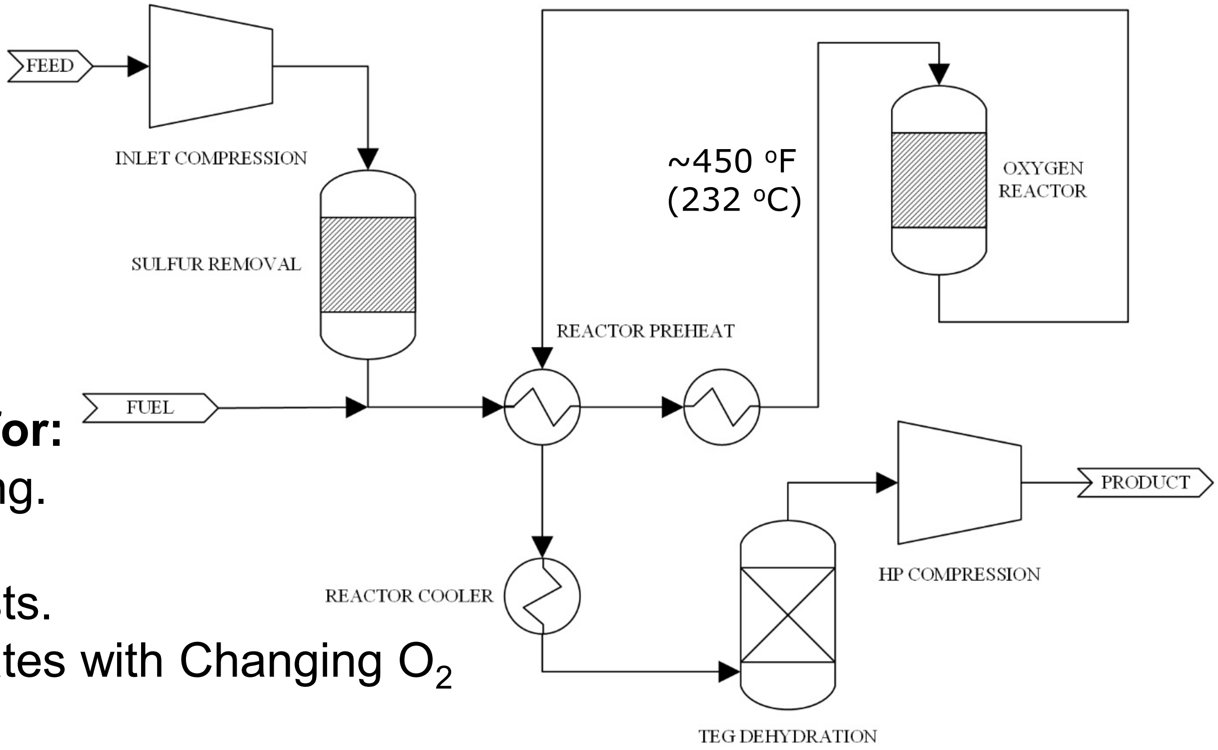
- Removes Lighter Impurities: O_2, N_2, H_2, CH_4, CO, NO to <10 ppmv each.
- Compress CO_2 rich stream to ~ 350 psig (24 barg).
- Dry to ~1 ppmv H_2O.
- Refrigeration to Condense CO_2 at ~10°F (–12°C).
- Lower Boiling Point Compounds Go Out Vent.



Water Vapor from the Air Freezes on Pipe Before Insulation is Installed.

Emerging Option: Catalytic Reduction for Oxygen Removal from CO_2

- Proposed for meeting 10 ppmv limit in CO_2.
- Trimeric hasn't found any commercial applications.
- Demonstrated in other applications.

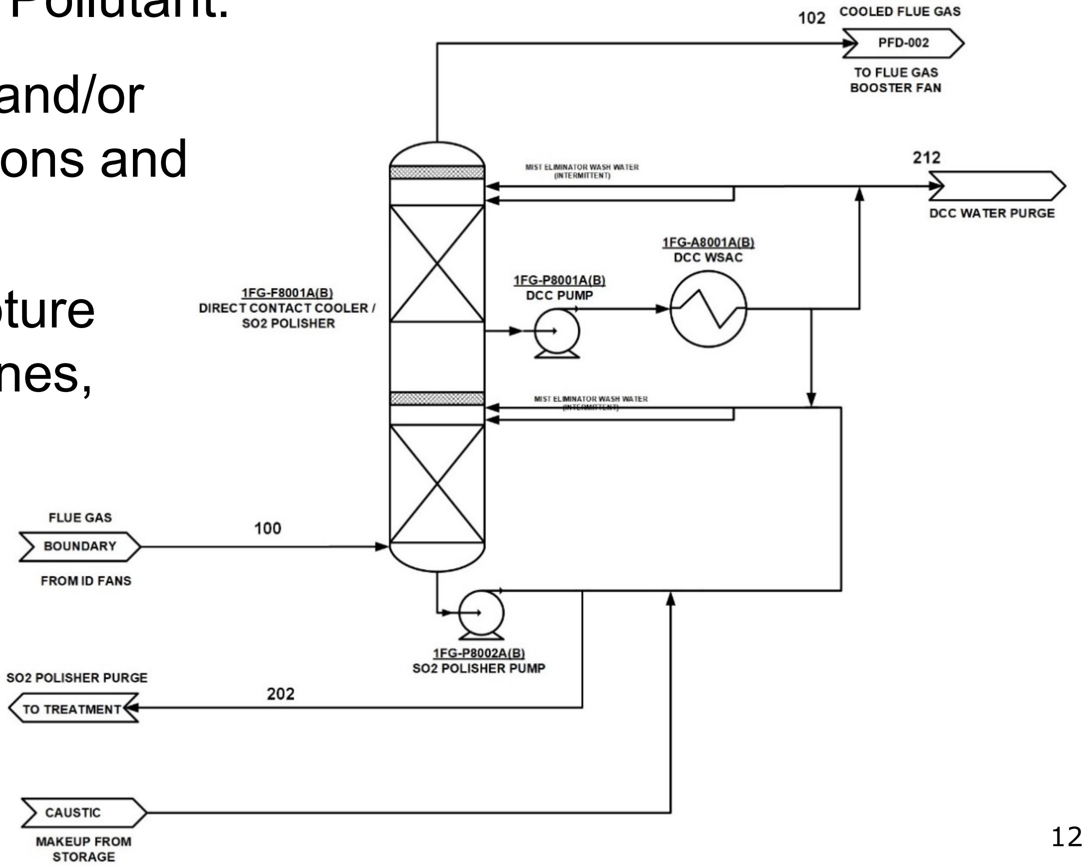


Careful Evaluation Needed for:

- Catalyst Fouling and Coking.
- Catalyst Life and Sparing.
- Catalyst Replacement Costs.
- Matching Fuel Injection Rates with Changing O_2 concentrations in Feed.
- CO ppmv in Product vs. Spec Limits.

Direct Contact Cooler / SO_2 Polisher (Caustic Scrubbing)

- SO_2 is Toxic and is a Criteria Pollutant.
- SO_2 can be Oxidized to SO_3 and/or H_2SO_4 Causing Other Emissions and Corrosion.
- At the Front End of Most Capture Processes: Amines, Membranes, Sorbents
- Downstream of FGD unit, SO_2 Polisher can get down to 1 or 2 ppmv.



H_2S Removal Options for CO_2 Conditioning

- H_2S is Toxic and Corrosive.
- Technology Selection for removal from CO_2 depends on:
  - Feed Stream: Flow Rate, Pressure, Composition.
  - Treated Gas Specification.
  - Emission Limits for H_2S and SO_2.

Scale	Sulfur Loading (approx.) lb/day	tonne/day	Common Treatment Options
Small	300	0.15	Scavengers
Medium	13,000	6	Liquid Redox
Large	45,000	20	Selective Amine, Claus

NO_X – General Background

- NO_X = Nitric Oxide (NO) + Nitrogen Dioxide (NO_2).
- NO_X is a Criteria Pollutant, NO and NO_2 are Toxic and Corrosive.
- Present in Flue Gas Streams.
  - Coal-Fired Power Plant w/ SCR ~ 40 ppmv.
  - Gas-Fired Turbine Unabated ~ 100's of ppmv.
  - NO to NO_2 Ratio ~ 90 / 10.
- NO_X may Lead to Specific Corrosion Risks in CO_2 Transport.
- NO_X Must be Characterized in Detail for Each Source, Capture, and Purification Method.
  - (Example Next Slide).

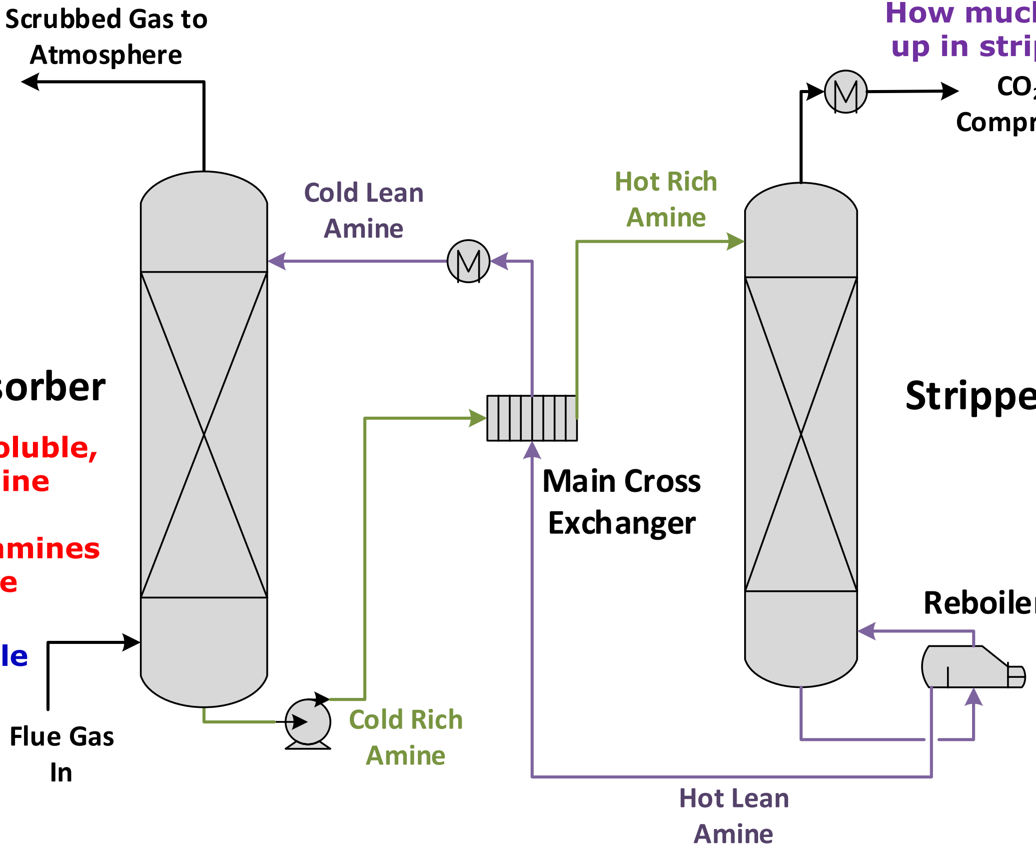
NO_X in Flue Gas Example Case

NO can oxidize to **NO_2** (w/ O_2 + sufficient residence time)

NO_2: Readily soluble, <u>reacts</u> with amine (products may include Nitrosamines and Heat Stable Salts)

NO: Less soluble

NO_X in flue gas



How much NO_X ends up in stripped CO_2 ?

What happens to NO_X in Compression and Purification ?

Flue Gas NO_X – Manage Before Capture

Technology	Minimum Treated NO_X Level	Challenges	Maturity
Water/Steam Injection	25 ppmv	Impact on turbine performance, high purity water needed	Commercially Proven
Dry Low NO_X (DLN) Combustor Ultra Low NO_X (ULN) Combustor	DLN: 9 - 15 ppmv ULN: 4 ppmv	Increased turbine cost/footprint, turndown challenges	Commercially Proven
Selective Catalytic Reduction (SCR)	~90% Reduction 5 ppmv	Ammonia slip, difficult to retrofit, catalyst management	Commercially Proven
NO_X Scrubbing	Limited Use in This Application	Large liquid waste stream with nitrates/other chemicals, chemical costs	Developmental

NO_X – **Manage During** CO_2 Purification

Technology	Description	Key Challenges	Maturity
Distillation	NO Exits in Overhead Stream and NO_2 Exits in Bottoms Stream	Removal of both NO and NO_2 Requires 2 Columns. Lower CO2 Recovery. NO in Vent Stream. Disposal of Liquid Streams Containing Nitrate Species.	NO Stripping – Proven NO_2 Removal – Developmental
NO_X Scrubbing	Chemical scrubbing solution (e.g., peroxide, ozone, potassium permanganate) to remove NO_2 from CO_2	Chemical cost, disposal of liquid waste stream	Developmental

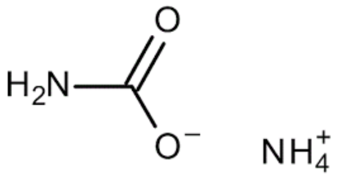
NO_X – Incidental Removal During CO_2 Purification

Process	Reported NO_X Removal*	Key Challenges
NO_X Removal in Compressor Condensate	Minimal at 10 psig (0.7 barg). ~ 60% at 216 psig (15 barg).	Limited by what dissolves in the water. NO_2 can be converted to NO and Nitric Acid in the Condensate and NO Can Desorb Back into the Gas.
NO_X Removal in Dryer Beds	~ 15%.	NO_X ends up in Regeneration Gas (Sometimes Recycled, Sometimes Vented)
NO_X Removal in Compressor Oil	High Acid Number in Oil after 850 Hours of Operation.	Increased Oil Monitoring Requirements. Could Impact Oil Consumption and Compressor Reliability

*Reference: Final Scientific Report, DOE award number: DE-FE0013163

Other Contaminants Seen in CCUS (1 of 3)

- Corn Oil and Other Impurities in Ethanol Plant CO_2 Can Solidify with Changes in Pressure and Temperature.
- Compressor Oil in CO_2 and Produced Water (Condensate)
- Glycol Carry Over in CO_2 from TEG Dehydration Unit.
- Free Ammonia Gas can React with CO_2 to form ammonium carbamate salts.



Ammonium Carbamate$_{(s)}$

Sulfur-containing Solid on liquid CO_2 pump impeller in Distillation Plant.

Other Contaminants Seen in CCUS (2 of 3)

- SO_2 Oxidizes to SO_3 and forms Liquid H_2SO_4 Droplets (Aerosol) in DCC.
- SO_3 can act as Nucleation Site other Aerosol Formation.
- Aerosols are Very Difficult to Remove.
- Technology Options:
  - Alkaline Sorbent Injection Upstream of PM Control Removes up to 99% of H_2SO_4.
  - Wet ESP removes sulfuric acid and non-sulfuric acid aerosols (90% one field, 99% two fields).
  - Absorber Water Wash Design for Improved Aerosol Removal
  - Combinations of the above technologies.

Other Contaminants Seen in CCUS (3 of 3)

- Mercury (Hg) found in Coal-Fired Flue Gas is a Hazardous Air Pollutant.
- Mercury is Very Detrimental to Brazed Aluminum Used in "Cold Box" Heat Exchangers.

Removal Options

- "Co-Benefits" Removal: SCR and FGD systems reduce Hg Concentrations.
- Activated Carbon Injection upstream of PM removal device.
- Halogen addition to the coal to oxidize mercury and remove in FGD.

Team Acknowledgement

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