Acid Gas Treating

Chapter 10
Based on presentation by Prof. Art Kidnay
Plant Block Schematic

Adapted from Figure 7.1, *Fundamentals of Natural Gas Processing*, 2nd ed. Kidnay, Parrish, & McCartney
Topics

Chemical Absorption Processes
Physical Absorption
Adsorption
Cryogenic Fractionation
Membranes
Nonregenerable H2S Scavengers
Biological Processes
Safety and Environmental Considerations
Gas treating

Gas treating involves removing contaminants to sufficiently low levels to meet specifications

- Primary focus on removing “acid gases”
  - Carbon dioxide (CO$_2$)
  - Hydrogen sulfide (H$_2$S)
  - Plus other sulfur species
- Other contaminants
  - Mercury
  - Ammonia
  - Elemental sulfur
  - Arsenic

The acid gas problem

- H$_2$S is highly toxic
- H$_2$S combustion gives SO$_2$ – toxic & leads to acid rain
- CO$_2$ is a diluent in natural gas – corrosive in presence of H$_2$O

Purification levels

- H$_2$S: Pipeline quality gas requires 0.25 grains/100 scf (4 ppmv)
- CO$_2$: pipeline quality gas may allow up to 4 mole%
  - Cryogenic applications need less than 50 ppmv
Two step process

Two steps

- **Remove** the acid gases from natural gas
- **Dispose** of the acid gases

Disposition

- **CO$_2$**
  - Vent to atmosphere
  - EOR – Enhanced Oil Recovery
  - Sequestration

- **H$_2$S**
  - Incineration or venting (trace amounts)
  - React with scavengers (e.g. iron sponge)
  - Convert to elemental sulfur
  - Injection into suitable underground formation
CO2 Capture and Sequestration

Power Station/Industrial Facility

CO2 Stored in Saline Formation

CO2 Replaces Methane Trapped in Coal

Enhanced Oil Recovery (CO2 Displaces Oil)

IMPERMEABLE CAP-ROCK

SALINE RESERVOIR

CO2 Captured and Sequestered

500 m

1000 m

1500 m

OIL

CH4

CO

CO

CO

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Processes for acid gas removal

Acid Gas Removal Processes

Solvent Absorption

Physical
- Selexol
- Rectisol
- Sulfinol

Chemical
- MEA
- Benfield
- Giammarco
- Vetrocoke

Hybrid
- Ifpexol
- Celisolv

Solid Adsorption
- Amisol
- Iron sponge
- Zinc oxide

Membranes
- Cellulose acetate
- Polyimide
- Polysulfone

Direct Conversion
- Stretford
- Lo Cat

Cryogenic Fractionation
- Ryan-Holmes

Figure 10.1, *Fundamentals of Natural Gas Processing*, 2nd ed., Kidnay, Parrish, & McCartney, 2011
Selecting a process

Factors for selecting process

▪ Type & concentration of impurities
▪ Hydrocarbon composition of the gas
▪ Pressure & temperature of the gas
▪ Specifications for outlet gas
▪ Volume of gas to be processed

Four possible scenarios

▪ Only CO$_2$
▪ Only H$_2$S
▪ Both CO$_2$ and H$_2$S
▪ Both CO$_2$ and H$_2$S present but selectively remove H$_2$S
  ▪ Allow CO$_2$ slip
Selecting a process

Figure 10.2, *Fundamentals of Natural Gas Processing*, 2nd ed., Kidnay, Parrish, & McCartney, 2011
Chemical Absorption Processes
Physical vs. Chemical Absorption

(Examples: carbonated water, soft drinks, champagne)

\[ \text{CO}_2 \]

\text{gas}

\text{liquid}

\text{water}

high P, low T = absorption

low P, high T = desorption

\[ \text{H}_2\text{S} \]

\text{gas}

\text{liquid (amine + water)}

\[ \text{H}_2\text{S} + \text{R}_1\text{R}_2\text{R}_3\text{N} = \text{R}_1\text{R}_2\text{R}_3\text{NH}^+\text{S} \]  
(soluble salt)

reversible exothermic reaction
Amine Chemistry

Gas treating amines are:
- Weak Lewis Bases
- $H^+$ from weak acids react with the electrons on N:

ABC substituents influence:
- How fast acids react with N:
- Temperature bulge in absorber
- Energy required in regenerator
- Chemical Stability
- Unwanted reactions

Dow Oil & Gas – Gas Treating Technology
Presentation to URS Washington Division, August 2009
Rich Ackman – ackmanrb@dow.com
Sterically hindered amines – selective H$_2$S absorbers

Diisopropanolamine (DIPA)  2-amino,2-methyl,1-propanol (AMP)
Amines

Amines remove $H_2S$ and $CO_2$ in two step process:

- Gas dissolves in solvent (physical absorption)
- Dissolved gas (a weak acid) reacts with weakly basic amines

$H_2S$ reaction

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+HS^-$$

$CO_2$ reacts two ways with amine:

- With water
  $$CO_2 + H_2O + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+ HCO_3^-$$
  - Much slower than $H_2S$ reaction

- Without water
  $$CO_2 + 2 R_1R_2NH \leftrightarrow R_1R_2NH_2 + R_1R_2NCOO^-$$
  - Faster but requires one H attached to the N
  - Use tertiary amines to “slip” $CO_2$
## Comparison of acid gas removal solvents

<table>
<thead>
<tr>
<th>Process</th>
<th>Capable of meeting H₂S spec?</th>
<th>Removes COS, CS₂, &amp; mercaptans</th>
<th>Selective H₂S removal</th>
<th>Minimum CO₂ level obtainable</th>
<th>Solution subject to degradation? (degrading species)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>Yes</td>
<td>Partial</td>
<td>No</td>
<td>100 ppmv at low to moderate pressures</td>
<td>Yes (COS, CO₂, CS₂, SO₂, SO₃ and mercaptans)</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>Yes</td>
<td>Partial</td>
<td>No</td>
<td>50 ppmv in SNEA-DEA process</td>
<td>Some (COS, CO₂, CS₂, HCN and mercaptans)</td>
</tr>
<tr>
<td>Triethanolamine (TEA)</td>
<td>No</td>
<td>Slight</td>
<td>No</td>
<td>Minimum partial pressure of 0.5 psia (3 kPa)</td>
<td>Slight (COS, CS₂ and mercaptans)</td>
</tr>
<tr>
<td>Methyl-diethanolamine (MDEA)</td>
<td>Yes</td>
<td>Slight</td>
<td>Some</td>
<td>Bulk removal only</td>
<td>No</td>
</tr>
</tbody>
</table>

### Representative operating parameters

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>DEA</th>
<th>DGA</th>
<th>MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight % amine</td>
<td>15 to 25</td>
<td>30 to 40</td>
<td>50 to 60</td>
<td>40 to 50</td>
</tr>
<tr>
<td>Rich amine acid gas loading</td>
<td>0.45 to 0.52</td>
<td>0.21 to 0.81</td>
<td>0.35 to 0.44</td>
<td>0.20 to 0.81</td>
</tr>
<tr>
<td>Acid gas pickup</td>
<td>0.33 to 0.40</td>
<td>0.20 to 0.80</td>
<td>0.25 to 0.38</td>
<td>0.20 to 0.80</td>
</tr>
<tr>
<td>Lean solution residual acid gas</td>
<td>~0.12</td>
<td>~0.01</td>
<td>~0.06</td>
<td>0.005 to 0.01</td>
</tr>
</tbody>
</table>

Gas Treating Amines

Generic Amines

- **MEA** (monoethanolamine)
  - 15 – 18% wt. (5 – 6.1% mol)
- **DEA** (diethanolamine)
  - 25 – 30% wt. (5.4 – 6.8% mol)
- **DIPA** (diisopropanolamine)
  - 30% - 50% wt. (5.5 – 11.9% mol)
- **MDEA** (methyldiethanolamine)
  - 35% - 50% wt. (7.5 – 13.1% mol)

<table>
<thead>
<tr>
<th></th>
<th>Wt%</th>
<th>Mol%</th>
<th>Load Range</th>
<th>Relative Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>18%</td>
<td>6.1%</td>
<td>0.35</td>
<td>1</td>
</tr>
<tr>
<td>DGA</td>
<td>50%</td>
<td>14.6%</td>
<td>0.45</td>
<td>3.09</td>
</tr>
<tr>
<td>DEA</td>
<td>28%</td>
<td>6.3%</td>
<td>0.48</td>
<td>1.41</td>
</tr>
<tr>
<td>MDEA</td>
<td>50%</td>
<td>13.1%</td>
<td>0.49</td>
<td>3.02</td>
</tr>
<tr>
<td>CompSol 20</td>
<td>50%</td>
<td>10.4%</td>
<td>0.485</td>
<td>2.37</td>
</tr>
<tr>
<td>CR 402</td>
<td>50%</td>
<td>14.7%</td>
<td>0.49</td>
<td>3.38</td>
</tr>
<tr>
<td>AP 814</td>
<td>50%</td>
<td>13.9%</td>
<td>0.485</td>
<td>3.16</td>
</tr>
</tbody>
</table>

*Dow Oil & Gas – Gas Treating Technology*

Presentation to URS Washington Division, August 2009
Rich Ackman – ackmanrb@dow.com
Amine Solution Densities

Lean amine composition will dictate volumetric circulation rate & pumping power required

- Need to determine density/volumetric flow at actual pumping temperature

\[ W_{\text{BHP}} = \frac{\dot{m}(\Delta P)}{\rho \eta_{\text{pump}}} = \frac{\dot{V}(\Delta P)}{\eta_{\text{pump}}} = \frac{\dot{V}\rho gH}{\eta_{\text{pump}}} \]

*GPSA Engineering Data Book, 13th ed.*
Amine Solution Densities


Updated: January 4, 2019
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Typical Amine Treating Plant

 Typical plant configuration

- Broad range of treating applications
- Low to intermediate specifications
- Selective treating, low H₂S
- Low installed cost
Amine Tower Parameters

Tower Design Considerations

- Gas Composition
- Trays
  - System Factor Bubble Area
    - MEA/DEA – 0.75 abs (0.85 reg)
    - MDEA & Formulated Solvents – 0.70 abs (0.85 reg)
  - System Factor Downcomer
    - MEA/DEA – 0.73 abs (0.85 reg)
    - MDEA & Formulated Solvents – 0.70 abs (0.85 reg)
  - Standard Cross Flow vs. High Capacity
    - Calming Section, MD Trays
- Packings
  - Random Packing
  - Capacity vs. efficiency, GPDC overlay
  - Structured Packing

Dow Oil & Gas – Gas Treating Technology
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Amine Tower Parameters

Absorber design considerations

- Pinch points limit
  - Top of tower lean pinch
  - Temperature bulge maximum
  - Bottom of tower rich pinch
  - Confidence level in VLE
- Temperature profile indicator

Absorber Temperature Profiles
Liquid Phase

Stage

Temperature [°F]

C-1 Conservative
C-2 Controlled Efficient
C-3 Intercooler
## Amine Approximate Guidelines

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>DEA</th>
<th>DGA</th>
<th>MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas pickup, scf/gal @ 100°F</td>
<td>3.1 – 4.3</td>
<td>6.7 – 7.5</td>
<td>4.7 – 7.3</td>
<td>3 – 7.5</td>
</tr>
<tr>
<td>Acid gas pickup, mols/mol amine</td>
<td>0.33 – 0.40</td>
<td>0.20 – 0.80</td>
<td>0.25 – 0.38</td>
<td>0.20 – 0.80</td>
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<td>Lean solution residual acid gas, mol/mol amine</td>
<td>~ 0.12</td>
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<td>Rich solution acid gas loading, mol/mol amine</td>
<td>0.45 – 0.52</td>
<td>0.21 – 0.81</td>
<td>0.35 – 0.44</td>
<td>0.20 – 0.81</td>
</tr>
<tr>
<td>Max. solution concentration, wt%</td>
<td>25</td>
<td>40</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>Approximate reboiler heat duty, Btu/gal lean solution</td>
<td>1,000 – 1,200</td>
<td>840 – 1,000</td>
<td>1,100 – 1,300</td>
<td>800 – 900</td>
</tr>
<tr>
<td>Steam heated ave. heat flux in reboiler, Btu/hr ft²</td>
<td>9,000 – 10,000</td>
<td>6,300 – 7,400</td>
<td>9,000 – 10,000</td>
<td>6,300 – 7,400</td>
</tr>
<tr>
<td>Heats of reaction (approximate)</td>
<td>Btu/lb H₂S</td>
<td>Btu/lb CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Btu/lb H₂S</td>
<td>610</td>
<td>555</td>
<td>674</td>
<td>530</td>
</tr>
<tr>
<td>Btu/lb CO₂</td>
<td>825</td>
<td>730</td>
<td>850</td>
<td>610</td>
</tr>
</tbody>
</table>

*GPSA Engineering Data Book, 14th ed.*, portion of Figure 21-4
Amine System Initial Design

Amine solvent considerations

- Lean amine concentration (wt% amine in water)
- Rich & lean amine loadings (mole acid gas per mole amine) – difference is the allowed amine pick-up

Determine amount of acid gas to be absorbed

- Difference between what can be contained in the treated gas & what is in the feed gas

Determine rate of lean amine to the absorber

- Molar rate amine based on the allowed pick-up
- Total mass rate amine+water based on the allowed lean amine concentration
- Total volumetric flowrate (standard conditions) based on lean amine concentration

Determine the reboiler duty for regeneration

- Based on heat of regeneration for each amine & acid gas (CO₂ & H₂S)
Operating issues with amine units

Corrosion – caused by:
- High amine concentrations
- Rich amine loadings
- Oxygen
- Heat stable salts (HSS)

Foaming – caused by
- Suspended solids
- Surface active agents
- Liquid hydrocarbons
- Amine degradation products (heat stable salts)
HYSYS Example Simulation

The absorber and regenerator columns in this flowsheet are operating in "Efficiency" mode for faster performance and rigorous rate-based distillation of H2S and CO2 based on column geometries in the "Railing" lab. "Advanced Modelling" mode is available for rigorous rate-based distillation of all components.

To configure acid gas column parameters and calibrate to plant data, open the absorber/regenerator column and navigate to Parameters | Acid Gas.
Hot potassium carbonate process (Hot Pot)

Major reactions

\[
K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2 KHC\text{O}_3
\]

\[
K_2CO_3 + H_2S \rightleftharpoons KHS + KHCO_3
\]
Physical Absorption
Characteristics of physical absorption processes

Most efficient at high partial pressures

Heavy hydrocarbons strongly absorbed by solvents used

Solvents can be chosen for selective removal of sulfur compounds

Regeneration requirements low compared to amines & Hot Pot

Can be carried out at near-ambient temperatures

Partial dehydration occurs along with acid gas removal

Figure from UOP Selexol™ Technology for Acid Gas Removal, UOP, 2009
## Comparison of chemical and physical solvents

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Solvent</strong> (e.g., amines, hot potassium carbonate)</td>
<td>Relatively insensitive to $\text{H}_2\text{S}$ and $\text{CO}_2$ partial pressure</td>
<td>High energy requirements for regeneration of solvent</td>
</tr>
<tr>
<td></td>
<td>Can reduce $\text{H}_2\text{S}$ and $\text{CO}_2$ to ppm levels</td>
<td>Generally not selective between $\text{CO}_2$ and $\text{H}_2\text{S}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amines are in a water solution and thus the treated gas leaves saturated with water</td>
</tr>
<tr>
<td><strong>Physical solvents</strong> (e.g., Selexol, Rectisol)</td>
<td>Low energy requirements for regeneration</td>
<td>May be difficult to meet $\text{H}_2\text{S}$ specifications</td>
</tr>
<tr>
<td></td>
<td>Can be selective between $\text{H}_2\text{S}$ and $\text{CO}_2$</td>
<td>Very sensitive to acid gas partial pressure</td>
</tr>
</tbody>
</table>
Physical Solvents – Selexol

Characteristics

- Poly (Ethylene Glycol) Dimethyl Ether
  \[ CH_3 \cdot O \cdot (CH_2 \cdot CH_2 \cdot O)_n \cdot CH_3 \text{ where } n \text{ is from 3 to 10} \]
- Selexol is a mixture of homologues so the physical properties are approximate
- Clear fluid that looks like tinted water

Capabilities

- \( \text{H}_2\text{S} \) selective or non selective removal – very low spec. - 4 ppm
- \( \text{CO}_2 \) selective or non selective removal – 2% to 0.1%
- Water dew point control
- Hydrocarbon dew point control
  - See relative solubilities; more efficient to remove hydrocarbon vs. refrigeration
- Organic sulfur removal – mercaptans, disulfides, COS
Selexol Processes

Physical solvent which favors high pressure & high partial pressure

Configurations

- $\text{H}_2\text{S}$ & organic sulfur removal
  - Steam stripping for regeneration
- $\text{CO}_2$ removal
  - Flash regeneration
  - Chiller for low $\text{CO}_2$

Special applications

- Siloxanes are removed from landfill gas
- Metal carbonyl are removed from gasifier gas
Solubility in Selexol at 70°F (21°C)

Figure 10.6, *Fundamentals of Natural Gas Processing*, 2nd ed., Kidnay, Parrish, & McCartney, 2011
Selexol process – CO$_2$ separation

**Absorber**

**CO$_2$**

**Lean Solution Filter**

**Treated Gas**

**Feed Gas**

*UOP Selexol™ Technology for Acid Gas Removal, UOP, 2009*

Selexol process – sulfur removal & CO₂ capture

UOP Selexol™ Technology for Acid Gas Removal, UOP, 2009
Membranes
Membrane systems

Based on Fick’s law of diffusion through the membrane

\[ J_i = \frac{S_i D_i (\Delta p_i)}{L} \]

where:  
- \( J_i \) is the molar flux of component \( i \) through the membrane  
- \( S_i \) is the solubility term  
- \( D_i \) is the diffusion coefficient  
- \( \Delta p_i \) is the partial pressure difference across the membrane  
- \( L \) is the thickness of the membrane

The permeability combines the properties of solubility & diffusion

- Differs for each compound  
- Provides selectivity

\[ y_{i,\text{permeate}} \propto \left( \frac{P_{\text{feed}}}{P_{\text{permeate}}} \right) y_{i,\text{feed}} \]
Module configurations – hollow fiber

Approximately 70% of membrane systems are hollow fiber

Courtesy MTR
Module configurations – spiral wound

Continued Development of Gas Separation Membranes for Highly Sour Service, Cnop, Dormndt, & schott, UOP
Module configurations – spiral wound
Membrane module flow schemes

No moving parts
Simple, reliable operation
Low hydrocarbon recovery

Allows for greater CO₂ removal
High hydrocarbon recovery
Requires recycle compressor
Feed with high CO₂
Intermediate hydrocarbon recovery
Reduced compression

_UOP Separex™ Membrane Technology_, UOP, 2009
Retrieved March 2016 from _http://www.slideshare.net/hungtv511/uop-separex-membrane-technology_
**CO₂/CH₄ Separation Example**

Two stage process (non-optimized)
# CO₂/CH₄ Separation Example

![Diagram showing CO₂/CH₄ separation process]

<table>
<thead>
<tr>
<th>Composition [mol%]</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>93.0</td>
<td>98.0</td>
<td>63.3</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>7.0</td>
<td>2.0</td>
<td>36.7</td>
</tr>
<tr>
<td>Flowrate [MMscf]</td>
<td>20.00</td>
<td>17.12</td>
<td>2.88</td>
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<tr>
<td>Separation Factors</td>
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<tr>
<td>Methane</td>
<td>90.2%</td>
<td>9.8%</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>24.4%</td>
<td>75.6%</td>
<td></td>
</tr>
<tr>
<td>Pressure [psig]</td>
<td>850</td>
<td>835</td>
<td>10</td>
</tr>
<tr>
<td>Methane Recovery</td>
<td>90.2%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Removal</td>
<td></td>
<td></td>
<td>75.6%</td>
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</table>

<table>
<thead>
<tr>
<th>Composition [mol%]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>93.0</td>
<td>97.8</td>
<td>16.6</td>
<td>60.6</td>
<td>85.1</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>7.0</td>
<td>2.2</td>
<td>83.4</td>
<td>39.4</td>
<td>14.9</td>
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<tr>
<td>Flowrate [MMscf]</td>
<td>20.00</td>
<td>18.82</td>
<td>1.18</td>
<td>3.30</td>
<td>2.12</td>
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<tr>
<td>Separation Factors</td>
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</tr>
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<td></td>
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</tr>
<tr>
<td>Pressure [psig]</td>
<td>850</td>
<td>835</td>
<td>10</td>
<td>835</td>
<td>10</td>
</tr>
<tr>
<td>Methane Recovery</td>
<td></td>
<td></td>
<td></td>
<td>98.9%</td>
<td></td>
</tr>
<tr>
<td>CO₂ Removal</td>
<td></td>
<td></td>
<td></td>
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<td>70.1%</td>
</tr>
</tbody>
</table>

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Adsorption
Acid gas removal by adsorption (mole sieves)

Figure 10.10, *Fundamentals of Natural Gas Processing*, 2nd ed., Kidnay, Parrish, & McCartney, 2011
Nonregenerable $\text{H}_2\text{S}$ Scavengers
Nonregenerable H$_2$S scavengers

<table>
<thead>
<tr>
<th>Process Phase</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-based processes</td>
<td>Iron oxides</td>
</tr>
<tr>
<td></td>
<td>Zinc oxides</td>
</tr>
<tr>
<td>Liquid-based processes</td>
<td>Amine-aldehyde condensates</td>
</tr>
<tr>
<td></td>
<td>Caustic</td>
</tr>
<tr>
<td></td>
<td>Aldehydes</td>
</tr>
<tr>
<td></td>
<td>Oxidizers</td>
</tr>
<tr>
<td></td>
<td>Metal-oxide slurries</td>
</tr>
</tbody>
</table>

Summary
Summary

Appropriate technology based on...

- Amount of acid gas to be removed
- Concentration of acid gas in feed gas
- Pressure of feed gas

Very typical to find an amine treating system to remove $\text{H}_2\text{S}$ and/or $\text{CO}_2$

- May be able to “slip” CO2 into treated gas depending on the final specs
Supplemental Slides
"Study places CO2 capture cost between $34 and $61/ton"
*Oil & Gas Journal*, Oct. 12, 2009