Gas Sweetening

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Webinar Part One

Introduction

- GPAC is a non-profit organization formed to promote the interaction and exchange of ideas and technology to those involved in the hydrocarbon processing industry.

- GPAC has many exciting things planned for 2021 including 12 technical webinars

- GPAC has operated in Alberta since 1959 because of the support of our membership and generous sponsors. A big thank you to:

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Mike Sheilan

Mike was the co-founder of Amine Experts in 1999 and is currently Senior Principal Engineer for Amine Experts and Dehydration Experts. For 40 years Mike has provided expert advice, training and consulting services in the area of hydrate control, gas dehydration, gas and liquid sweetening, hydrocarbon recovery and sulphur plant operations.

Mike is an authority on gas processing and has been published in the Oil and Gas Journal, Hydrocarbon Processing Magazine, LNG Industry Magazine, Petroleum Technology Quarterly, Sulphur Magazine and Chemical Engineering Magazine and has presented at various conferences, including the LRGCC, GPAC, GPA-Midstream, NACE, SOGAT and AFPM. He is also a Senior advisor to the Laurance Reid Gas Conditioning Conference in Norman, Oklahoma.

He previously worked for Brenntag Chemicals (Travis Chemicals) as Technical Service Engineer and then Technical Service Manager from 1981 to 1999, where he provided technical support for the gas processing industry in North America.

Mike has a BSc. in Chemical Engineering from the University of Calgary. He is a member of APEGA, NACE and GPAC.

amine eXperts

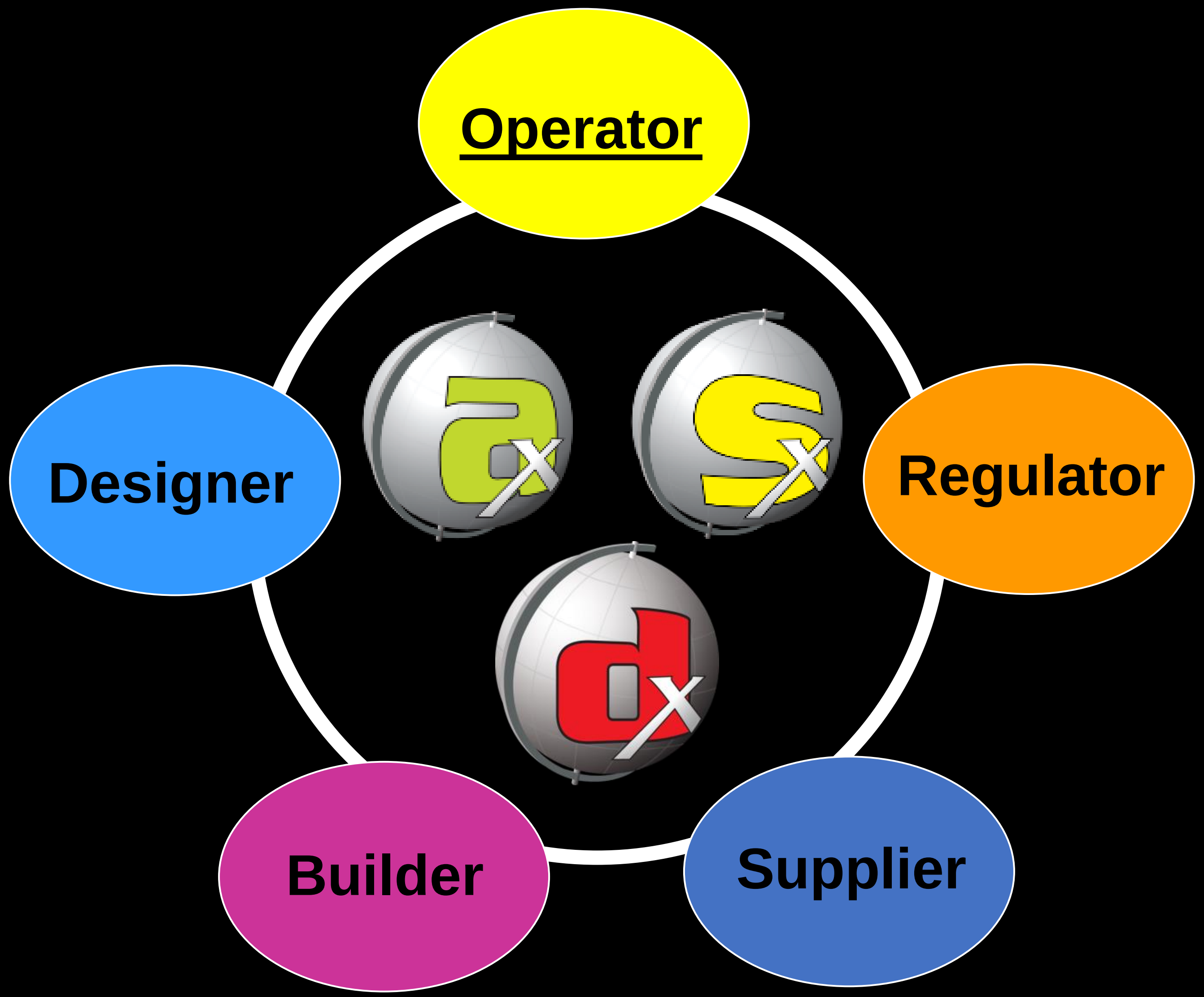
Sulphur eXperts

- Headquartered in Calgary, Alberta
- over 3000 projects in over 60 countries
  - 285 Amine and Sulphur projects in 2019
- senior staff has over 350 years combined experience
- employees have authored more than 70 papers
- provide technical support to every major oil and gas company in the world
- provide technical support to all major process licensors

amine eXperts

Sulphur eXperts

dehydration eXperts



amine eXperts

Sulphur eXperts

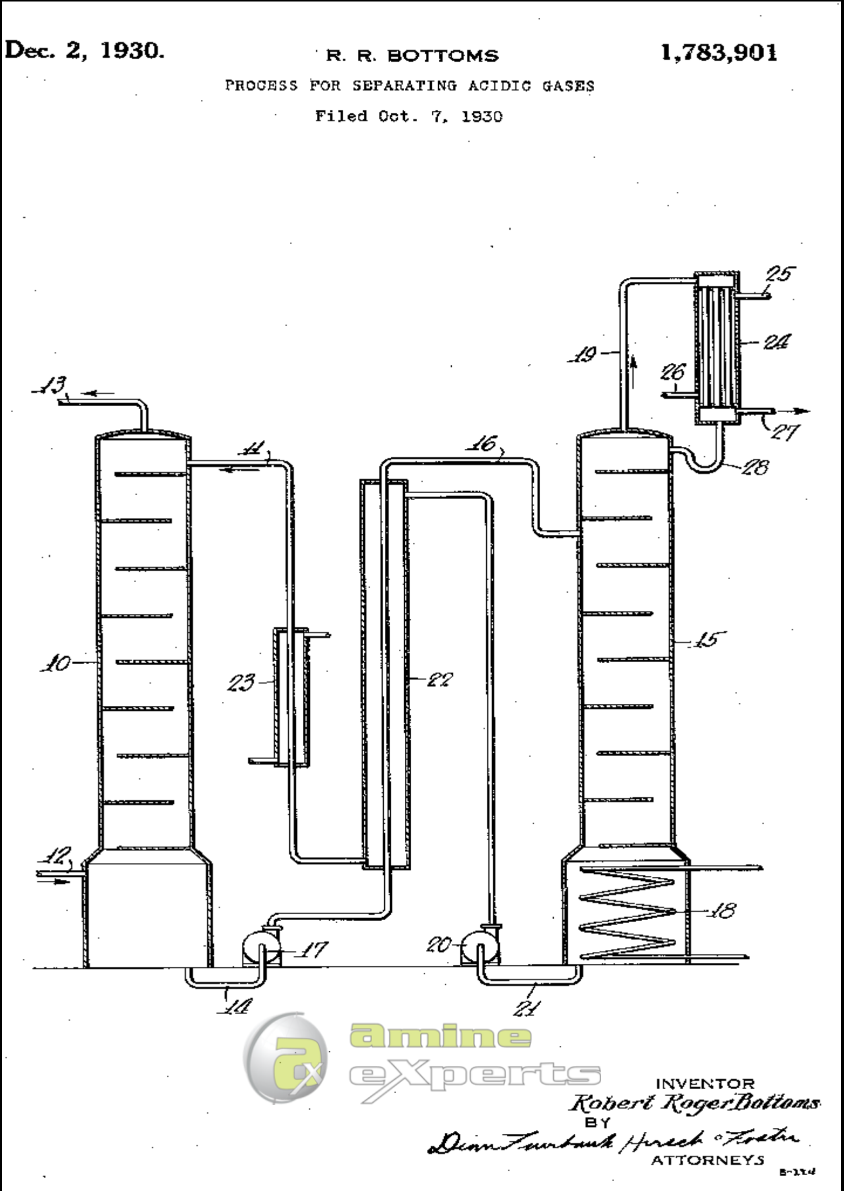
dehydration eXperts

Primary Areas of Assistance

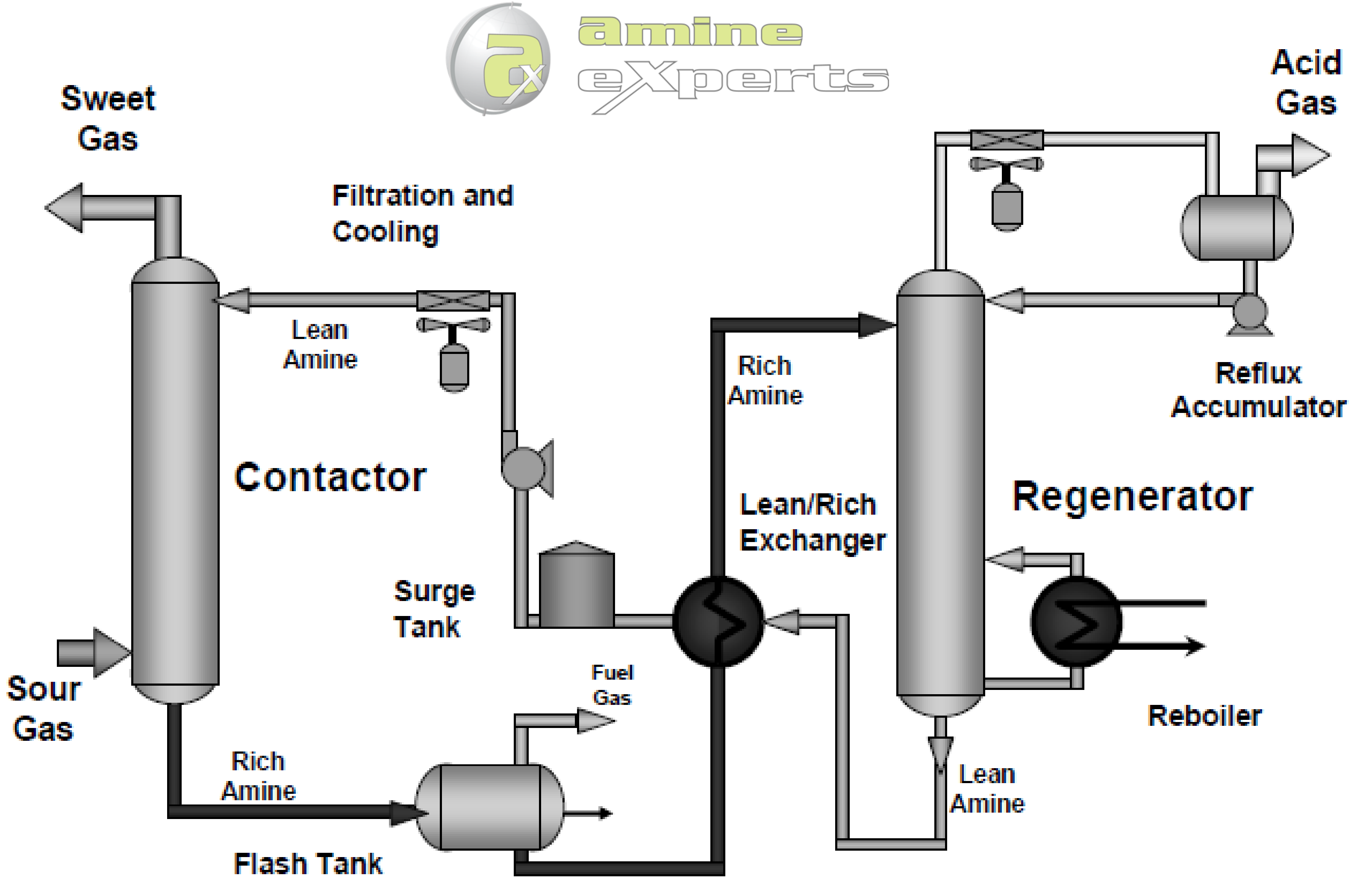
- gas, liquid sampling and analysis
- training seminars
- on-site technical assistance
- engineering studies

Types of Sweetening Processes

- Absorption
  - Physical, Chemical and Hybrid
  - (**Amines**, Potassium Carbonate, Caustic, etc.)
- Adsorption
  - Physical and Chemical
  - (Molecular Sieves, Iron Sponge, Zinc Oxide, etc.)
- Changes in P & T
  - Membranes, Fractionation/Distillation



Amine Plant Flowsheet



CONTACTOR CHEMISTRY

- acid gases react with weak liquid bases to form thermally regenerable salts

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{heat}$$

$$\left.\begin{matrix} H_2S \\ \\ CO_2 \end{matrix}\right] + \text{lean amine} \longrightarrow \text{rich amine} + \text{heat}$$

REGENERATOR CHEMISTRY

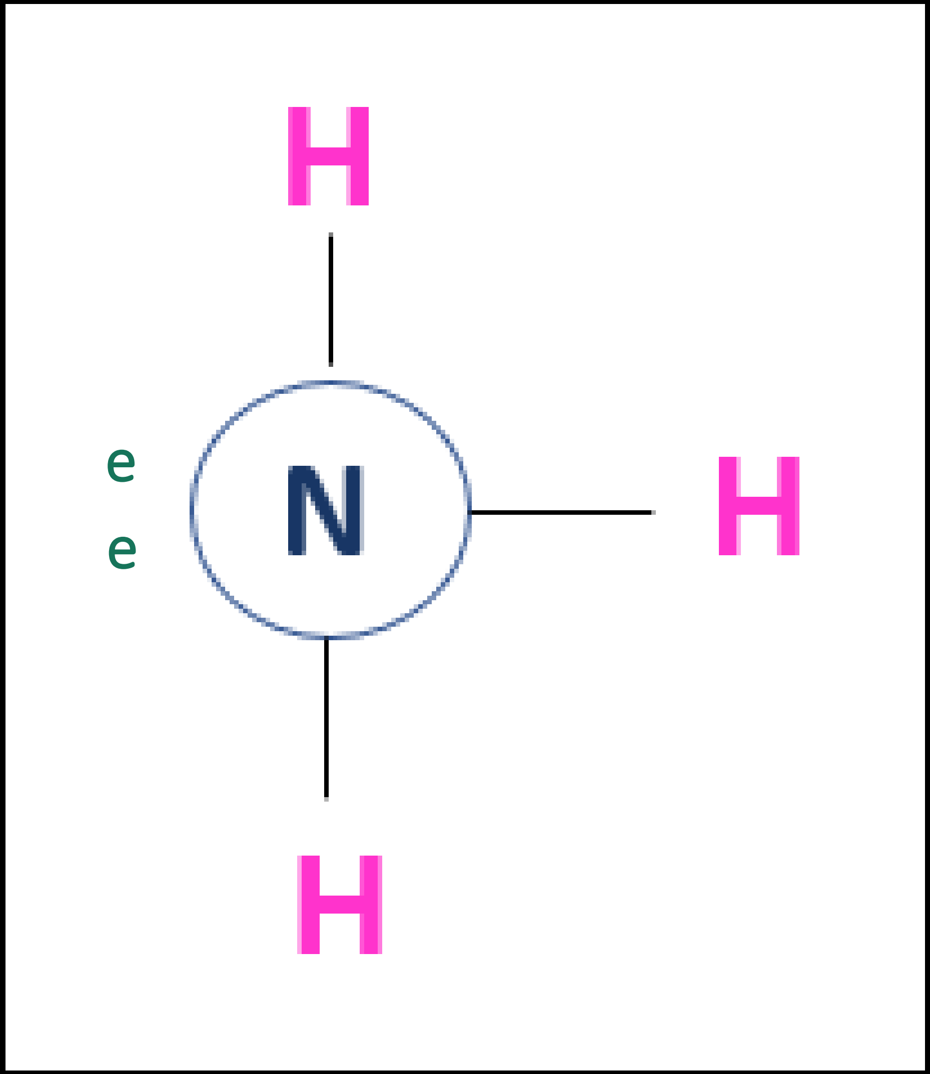
- adding energy (heat) to the salts reverses the reaction to form the original bases and acids

$$\text{acid} + \text{base} \longleftarrow \text{salt} + \text{heat}$$

$$\left.\begin{array}{l} H_2S \\ \\ CO_2 \end{array}\right] + \text{lean amine} \longleftarrow \text{rich amine} + \text{heat}$$

Molecular Structures of Amines

- **AMMONIA**
  - building block for amines
- all amines react instantaneously with H_2S
- what changes between amines is how reactive they are with CO_2



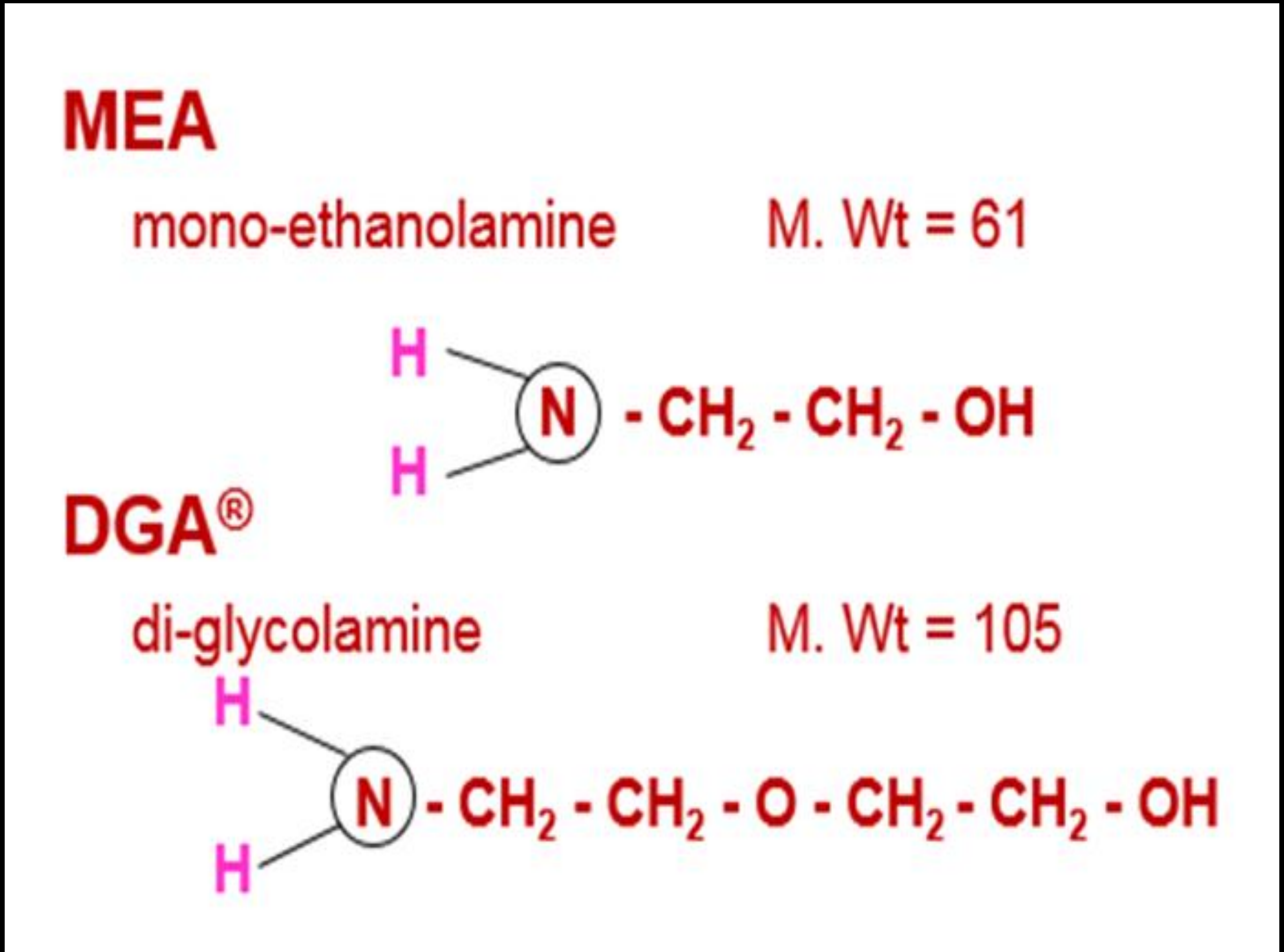
Primary Amines

MEA

- primarily in refineries; high capacity per circulation volume (high molarity); **max concentration only about 20 wt%**
- strong base, deep CO_2 and H_2S removal; good COS & CS_2 removal
- high energy consumer; high degradation (CO_2, O_2, COS); reclaimable

DGA (same as MEA; plus)

- **max concentration closer to 50 wt%;** thus high overall molarity/capacity
- high H_2S removal capability at very high temperatures; effective solvent when plant has lean amine cooling problems
- high COS reactivity; reclaiming converts degradation products back to DGA



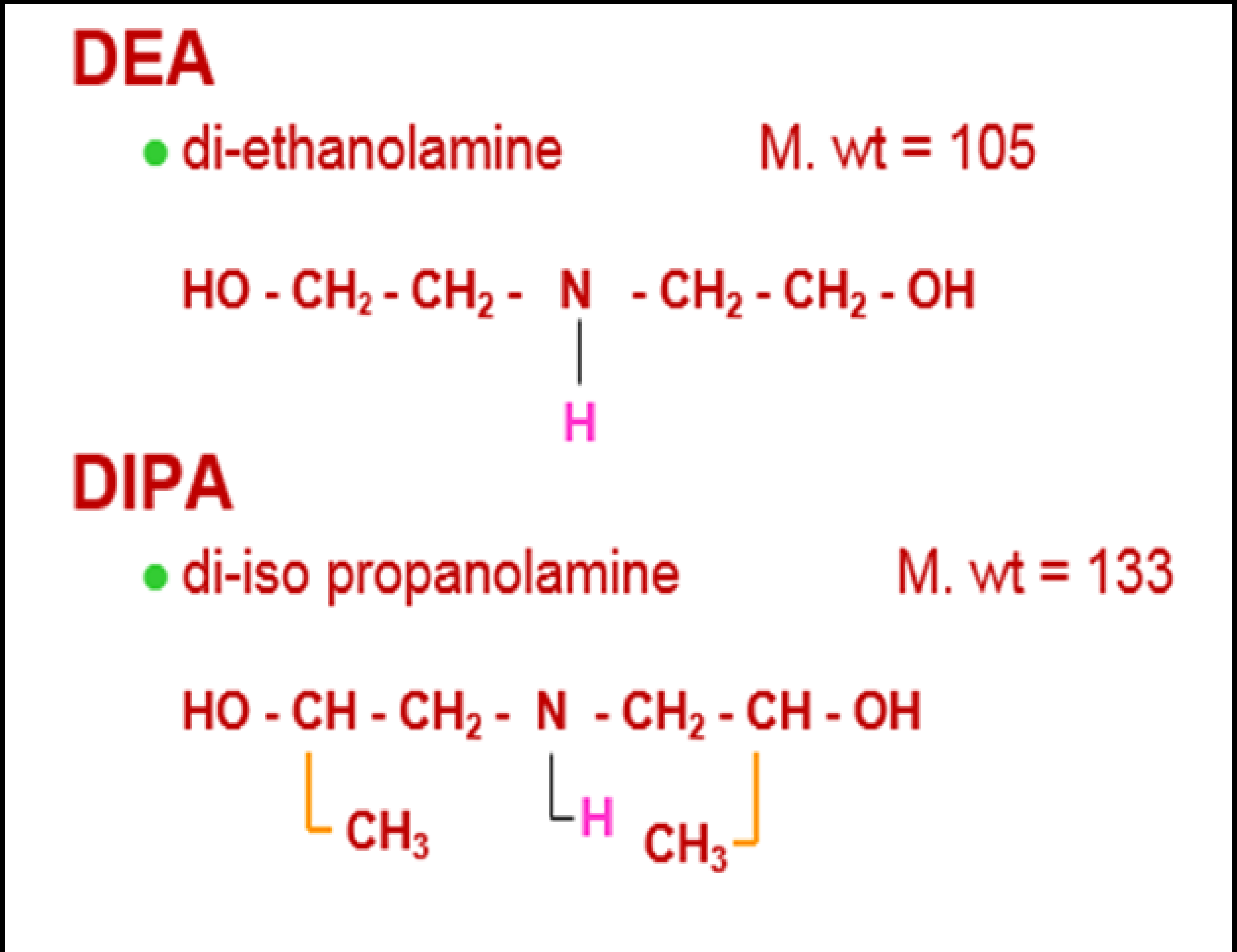
Secondary Amines

DEA

- high use solvent; strong H_2S and CO_2 removal capability
- **typical max strength around 35 - 37 wt%**
- lower reboiler duty than primary amines; less degradation; requires vacuum distillation reclamation

DIPA (same as DEA; plus)

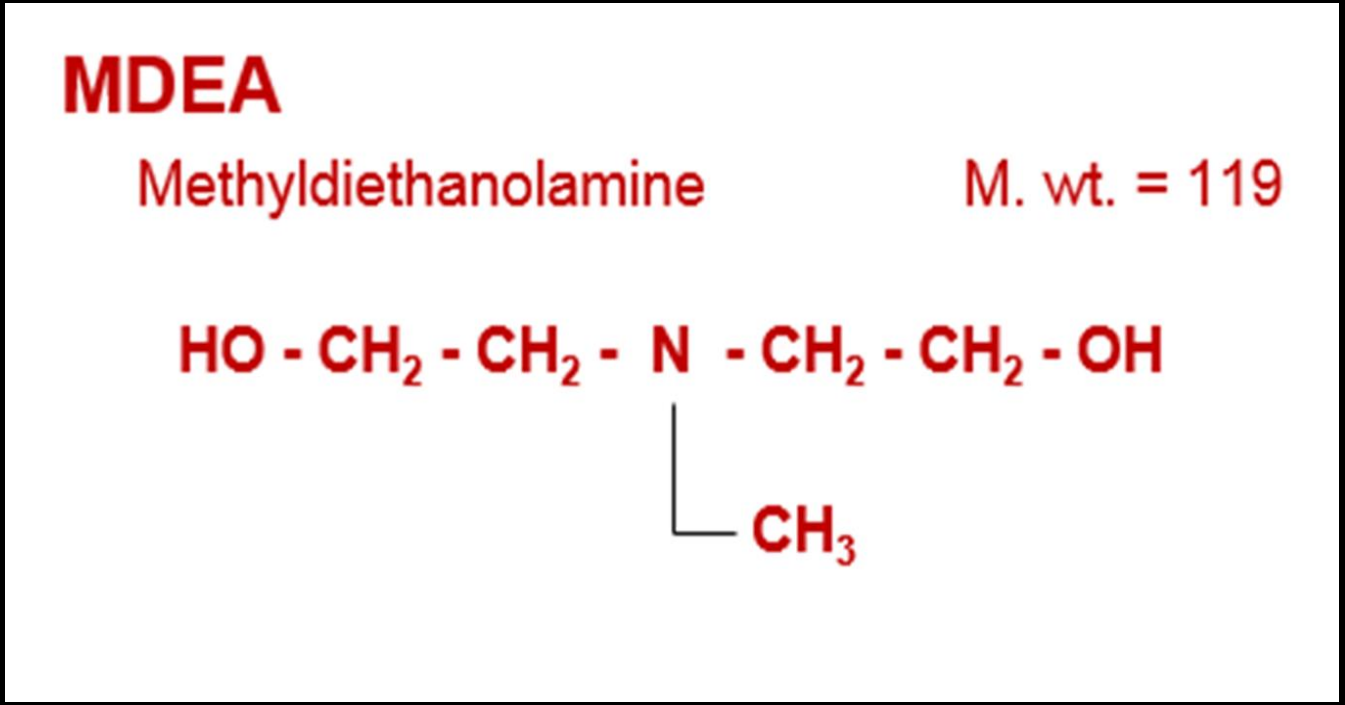
- **maximum concentration ~ 45 - 55 wt%**
- higher hydrocarbon solubility
- good CO_2 slip characteristics in TGTU applications
- reclaimable with atmospheric distillation unit



Tertiary Amines

MDEA

- no direct reactivity with CO_2
- two step reaction mechanism (slow dissolution in water to form acid followed by rapid reaction with basic amine) allows for slipping of CO_2 into treated gas
- low regeneration energy
- high capacity; minimal CO_2-related degradation; lower inherent corrosive tendencies
- works very well as base solvent for formulated amines
- **typical strength is 40-50 wt%.**



Reaction Mechanisms

- H_2S reactions (proton transfer)

  - all amines

$$[R_1R_2NR_3] + H_2S \longleftrightarrow [R_1R_2NR_3]H^+ + HS^-$$

(hydrogen bisulfide, <u>instantaneous</u>)

Reaction Mechanisms

- CO_2 reactions (**primary and secondary amines**) - carbamate formation

$$2[R_1R_2NH] + CO_2 \Longleftrightarrow [R_1R_2NH]H^+ + [R_1R_2N\text{-}COO]^-$$

(fast)

"carbamate reaction"

Reaction Mechanisms

- CO_2 (**primary and secondary**)

  acid-base reaction (slow)

$CO_2 + H_2O \Longleftrightarrow H_2CO_3$ **(carbonic acid)**

$H_2CO_3 \Longleftrightarrow H^+ + HCO_3^-$ **(bicarbonate)**

$H^+ + R_1R_2NH \Longleftrightarrow R_1R_2NH_2^+$

$CO_2 + H_2O + R_1R_2NH \Longleftrightarrow R_1R_2NH_2^+ + HCO_3^-$

Reaction Mechanisms

CO_2 reactions

- Tertiary Amines

$$CO_2 + H_2O \underset{\text{(slow)}}{\longleftrightarrow} H_2CO_3$$

$$[R_1R_2NR_3] + H_2CO_3 \underset{\text{(fast)}}{\longleftrightarrow} [R_1R_2NR_3]H^+ + HCO_3^-$$

FORMULATED AMINES

(Ucarsol; Gas/Spec; JeffTreat; AdvAmine, etc.)

- most contain components that increase CO_2 absorption properties
- some formulations show improved LP treated gas H_2S specification; very good solvents for Acid Gas Enrichment (AGE) and Tail Gas Treating Units (TGTU)
- tailor-made outlet CO_2 concentration
- more available “vendor-supplied” technical service

ACTIVATED AMINES

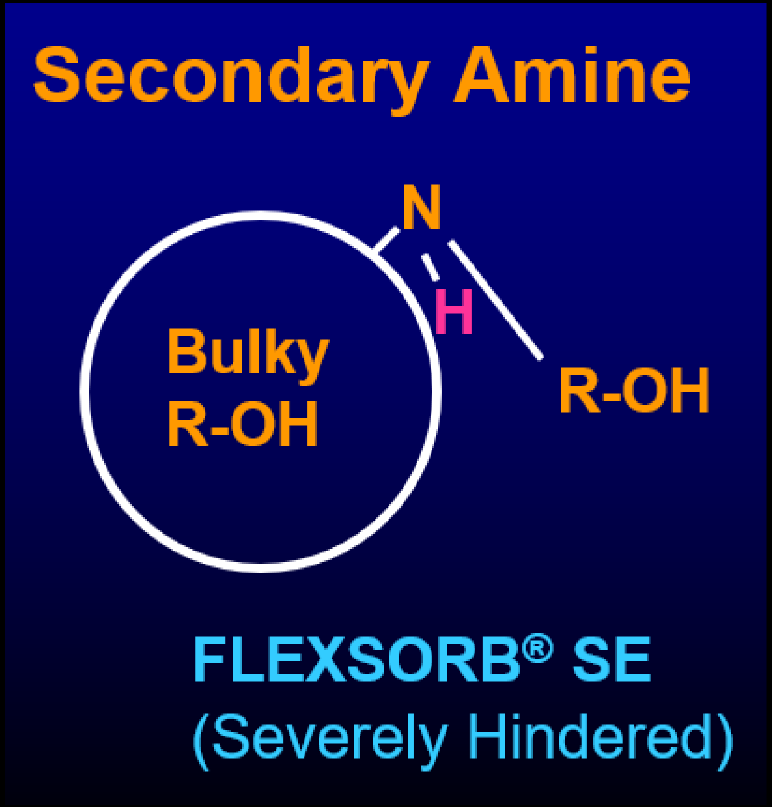
(aMDEA [BASF OASE]; AP800 series; etc.)

- MDEA-based solvents with an activator / energizer (piperazine) that greatly enhances the CO_2 removal capabilities of the solvent
- primarily used in CO_2-only removal facilities (used extensively in shale gas treatment facilities; LNG; fertilizer plants)
- high capacity; low corrosion; low degradation in the presence of CO_2

HINDERED AMINES

(Flexsorb; SCOT Ultra)

- solvent formulations containing a bulky side group that reduces the CO_2 shuttle rate and reduces the carbamate formation for exceptionally good CO_2 slip
- best-in-class acid gas enrichment and tail gas treating
- high loading capacity; low regeneration energy; low circulation rates
- very expensive solvent – 4 to 5 times more than MDEA



MIXED SOLVENTS

(Sulfinol D/M/X, etc.)

- combination chemical and physical solvent formulations (chemical / physical / water)
- high capacity, reduced regeneration energy because part of solvent simply regenerated by flash pressure reduction
- extended sulphur species removal possible (solvent of choice for mercaptan removal)
- much higher hydrocarbon co-absorption than chemical solvents
- work better at high acid gas partial pressures

GENERAL DESIGN CRITERIA

TREATED GAS SPECIFICATION

Gas Plants (all amines)

- less than 2 mol% CO_2; 4-16 ppmv H_2S

Refineries (all amines)

- generally, less than 50 ppmv H_2S; no CO_2 spec

Tail Gas Treating Units (DIPA, MDEA, Flexsorb, SCOT Ultra)

- <10 ppmv up to around 250 ppmv H_2S

Carbon Capture (MEA, MDEA)

- < 1 mole% CO_2

LNG Production (activated MDEA equivalent)

- < 50 ppmv CO_2 (-160°C; volume shrinks by a factor of about 600)

GENERAL DESIGN CRITERIA – Important Factors

- **Partial Pressure of H_2S and CO_2**
  - higher partial pressure improves efficiency / capacity

$$pp_i = x_i \bullet P$$

- **Lean Loading**
  - driven by regeneration conditions (higher energy or solvent choice)
- **Rich Loading**
  - limited by corrosion, temperature bulge, partial pressure, equilibrium

GENERAL DESIGN CRITERIA – Column Design

- **Number and Type of Trays / Height and Type of Packing**
  - normally around 20 trays (or equivalent height of packing)
  - more trays if extended sulphur species removal required (weaker acid sulphur species are not touched until almost all the H_2S and CO_2 have already been removed)
  - less trays for tail gas units (need to minimize contact stages for improved CO_2 slip); also design with multiple feed tray locations for optimal slip

GENERAL DESIGN CRITERIA

- **Energy Consumption Reduction**
  - lower circulation rates
  - move to solvent that requires less reboiler duty
  - additional hot flash

- **Hydrocarbon Co-absorption**
  - reduced circulation rates; higher rich loadings; higher absorber temperatures
  - amine dependent (**MEA<DEA<DGA<MDEA<DIPA**)

OPERATING ISSUES

- Meeting Specification
- Heat Stable Amine Salts
- Degradation
- **Corrosion**
- **Feed Preparation**
- **Foaming**
- **Filtration**

Next Webinar

MEETING SPECIFICATION

- quality of the treated gas (specification) is set by the quality of the lean amine (lean loading and temperature)
- regenerate the solvent well (as required for application)
- keep lean amine temperatures as cool as possible but still warmer than the feed gas temperature
- reduce foaming and fouling in the absorber
- have sufficient contact stages in the absorber
- maintain sufficient circulation rate to control absorber bulge temperature

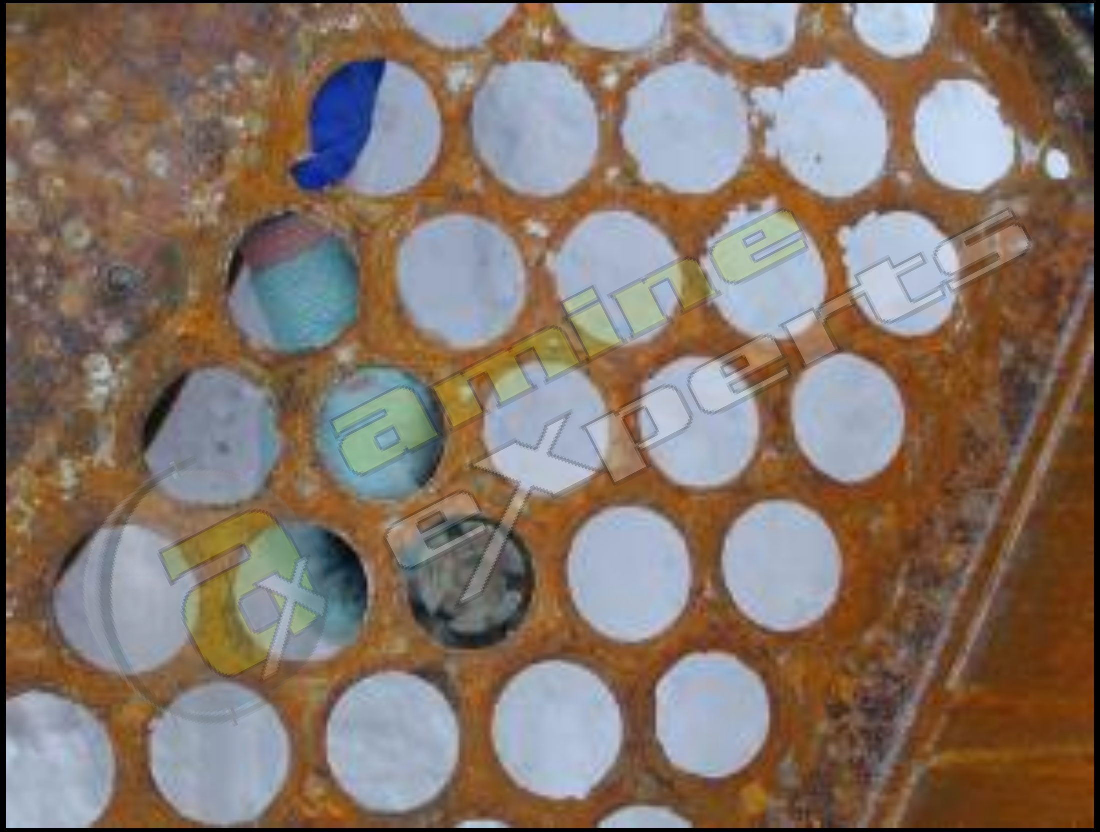
HEAT STABLE AMINE SALTS

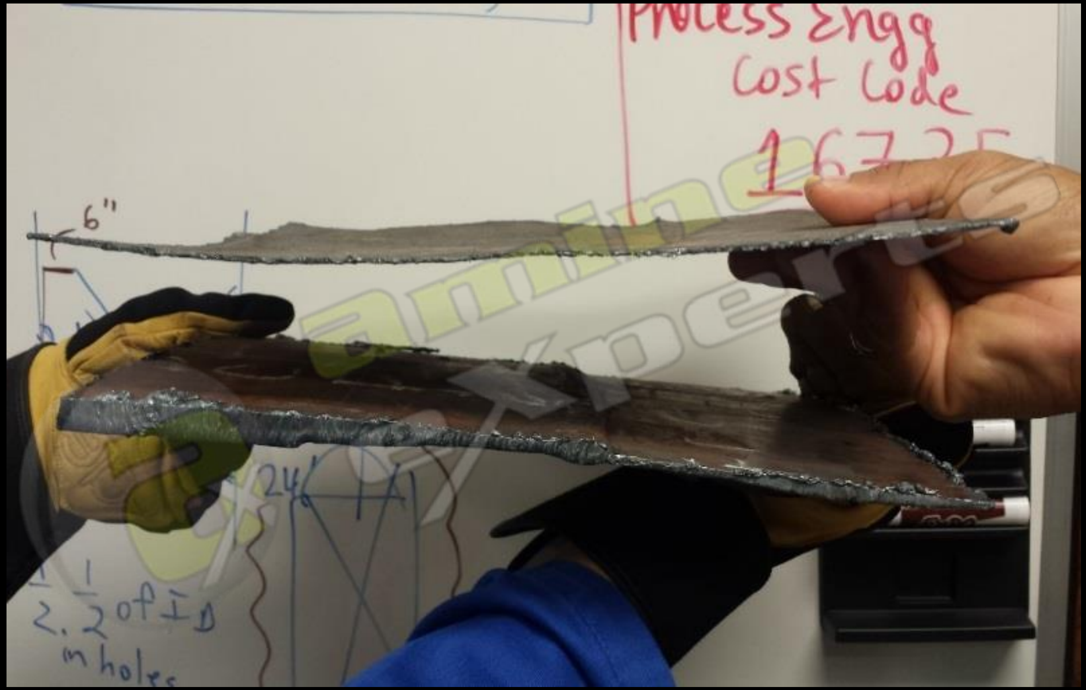
- formed by the reaction of amines with acids stronger than H_2S or $CO_{2;}$; build up in systems because they do not regenerate at normal regeneration conditions
- tend to increase solution corrosivity (especially in the reboiler and lower regenerator)
- can affect both acid gas absorption (reduces) and regeneration of the amine (improves)
- controlled by ion exchange; vacuum distillation; electrodialysis or ‘bleed and feed’

DEGRADATION

- primarily caused by CO_2, COS and oxygen
- thermal degradation also a possibility (watch reboiler temps and heat flux)
- breaks down amine molecule into components that may not have the same acid gas carrying capacity; are corrosive and also promote foaming
- in TGTU service, with MDEA, can be catastrophic for CO_2 slip, as primary / secondary amines are formed by the breakdown of the MDEA molecule.
- removed via vacuum distillation or atmospheric distillation if the solvent allows for it

CORROSION!





CORROSION CONTROL

Recommendations:

- make sure the lean solution is well regenerated; do regeneration in the column and not the reboiler
- don't exceed recommended maximum strengths
- max total rich loading: 0.45 to 0.55 mol acid gas / mol amine (depending on the type of amine; CO_2 content)
- minimize heat stable amine salts (maximum 2-3 wt%)
- maximum amine pipe velocity: 2 m/s (6 ft/s); 1 m/s in exchanger tubes
- control temperatures in absorber and regenerator
- post-weld heat-treat all amine plant replacement work; proper metallurgy

FEED PREPARATION, FOAMING and FILTRATION

GPAC

Webinar Part two

Why Amine Systems Fail?

amine eXperts

Thank You GPAC
Any Questions!

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