OPTIMIZING REFINERY AMINE SYSTEM PERFORMANCE WITHOUT CAPITAL

Why U.S. Refineries have turned to MDEA formulations for clean diesel related expansions and increased sulfur crude slates.

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Abstract:

With expansion of refineries for cleaner fuels, many amine systems faced additional large capital expenditures for the amine regeneration equipment. Upgrading the amine solvent to formulated Methyldiethanol-amine (MDEA) products allowed these additional treating units to fit within the existing amine regeneration equipment. We will look at several case studies and approaches to both maximize amine circuit efficiency with solvent and operation approaches. We will also explore customer treating goals for refineries and the conversion approaches taken when moving from MEA, DGA, DIPA, or DEA to higher efficient MDEA formulations.

Background:

The first decade of the 21st century saw large changes in the United States refineries. Environmental regulations governing diesel fuel changed, requiring the Ultra-Low Sulfur Diesel (ULSD) specification to be met by U.S. refiners. In current production this meant hydrogenation and amine treating expansions for these products. Engineering groups within the refiners and engineering companies went to work with ULSD unit designs, fabrications and installations.

From these design efforts the first consideration was to determine if there was adequate capacity in the existing amine systems present in the refinery to handle circulation and acid gas from these additional treating units. For many refineries the answer was no. Increases in production, sulfur content, and unit expansions had used all the available amine circulation, regeneration capacity, and/or sulfur unit (Claus) capacity. Large expansions of the amine circuits and more costly expansions of the sulfur plant were required to move these refineries to the new fuel specifications on existing operating solutions.

An alternate approach was relief through changes in amine chemistry. The goal was simply to fit the additional capacity needs into the existing circulation, energies, and Claus plant present in the current equipment. To accomplish this efficiency improvement new chemistry was needed. Historically refinery main system operated on MEA or Diethanol-amine (DEA) designs. The aqueous weak base allowed high acid gas capacity in each gallon of amine circulated and steam stripping regeneration to recover the acid gas and re-use the chemical. The amine treating process has been the most efficient approach to acid gas removal from gas and liquid stream since its development in the 1930's. Improvements in equipment and chemistry have advanced the process but it remains much the same as when it was first implemented.

$$H_2S + \text{Amine} \rightleftharpoons \text{AmH}^+ + HS^-$$

Chemistry:

Monoethanol-amine (MEA) is a stronger base primary amine used in general amine treating. With specific advantages in low pressure treatment to low specification due to the strong base properties of a primary amine there remains some applications where MEA is still favored. It also allows thermal reclamation in atmospheric distillation equipment as the amine will boil overhead prior to thermal degradation temperatures. Processes like landfill gas and coke oven gas in steel production rely on the thermal reclaiming ability for these high contamination systems.

Solvent	Carbon Steel Corrosion, MPY
30 Wt% MEA	**32**
50 Wt% DEA	**25**
15 Wt% MEA	**13**
20 Wt% DEA	**8**
50 Wt% GAS/SPEC™ SS™	**4**

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The MEA, however, does have disadvantages that lead to a less efficient amine treating loop in refineries. The MEA becomes increasingly corrosive above the recommended 15-18 Wt. % operating concentrations. The rich loadings are also limited typically to 0.30 – 0.35 m/m for corrosion risk management. From these two corrosion considerations for carbon steel piping the capacity of a gallon of MEA solution can be increased by ~83% or more with a GAS/SPEC™[1] MDEA formulation.

The stronger primary and secondary amines will also remove essentially all of the CO2 present in streams being treated. This is an additional acid gas load on the amine solution and regeneration requirement for the stripping tower and heat duties. The reaction energy between MEA and the acid gasses forming and separating salts in solution are relatively high, requiring regeneration energies in the reboiler of 650 BTU/Lb of H2S and higher stripping steam rates to drive the H2S out of the amine solutions, i.e. 3-3.5 Steam to Acid Gas molar ratios versus 1.2-1.5 for MDEA products. MEA plant designs therefore have large circulations and energy duties associated with the limited efficiency of this amine molecule choice.

More recent amine plant designs or systems that moved from MEA to an amine with higher efficiency operate using DEA. The weak base chemistry is still the technology in use with the amine in aqueous solution reacting with H2S and CO2 to form as disassociated salt in solution allowing for high acid gas carrying capacity in each gallon of circulated solution versus any physical solvent approach. The Di-ethanolamine (DEA) is a secondary amine, meaning two substitutions of ethanol have been made to the ammonia base molecule. DEA solutions are operated up to 30-32 Wt. % before an elevated corrosion risk to carbon steel limits their efficiency. DEA as a larger molecule cannot be reclaimed at atmospheric pressure as the boiling point is now greater than the thermal degradation temperature of the amine. Systems with high contamination use alternate reclaiming approaches to manage solution quality. The molecule has both lower reaction energy with the acid gases reacted to salts in solution and will remove a little less CO2 from the streams being contacted. Thus conversions of capacity limiting MEA systems to DEA have occurred in many refineries over the last 40 years. This was an early low capital approach to gaining acid gas removal capacity when MEA circulation and/or regeneration were limiting. This approach was taken with previous refinery expansions, unit additions, or increased sulfur feed stock blends.

Solvent / Loading	Relative Capacity
18wt% MEA / 0.35m/m	1.00
40wt% DIPA / 0.40m/m	1.17
35wt% DEA / 0.40m/m	1.29
50wt% GAS/SPEC SS / 0.45m/m	1.83

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[1] GAS/SPEC is a trademark of INEOS

DGA[2] and DIPA amines are also used in a small number of refineries driven by similar need for capacity increases beyond what MEA could provide without expansion equipment. The DGA is a primary amine but allows operation up to 40 Wt. % before corrosion concerns limit its capacity. It is also disadvantaged in energy improvements with heats of reactions higher than MEA. DIPA is a secondary amine alternate to DEA, but also at a higher energy cost. It is similarly managed as DEA in strength and loadings operated.

So this again became a step-wise improvement in refinery capacity without capital construction for amine and sulfur plants with these new refinery treating additions. The Methyl-diethanol amine (MDEA) provides another step in solution capacity within the same equipment. MDEA is a tertiary amine (all 3 hydrogen atoms substituted on the ammonia molecule). The chemistry at work in all these amines is the same with weak acid-base reaction to salt in solution to maximize acid gas loading per gallon of solution. The regeneration reverses the process with drop in pressure and increase in temperature to drive the acid gas out of the salt form in solution. However, the MDEA molecule provides some significant improvements to acid gas capacity per gallon of solution; reduction in corrosion risk, reduction in regeneration energy, and the ability to allow CO2 to slip through absorbers and not increase regeneration and Claus plant volume. MDEA has long been the preferred approach to tail gas unit operation due to the CO2 slip to avoid large inert recycle to the Claus plants. Similarly, refineries with significant Coking and Cracking operations can unload the CO2 traffic or treat to specific CO2 goals with MDEA or specialty formulations of MDEA. The lack of hydrogen on the nitrogen in MDEA allows amine concentrations to be operating up to and beyond 50 Wt. %, restricted now by viscosity and surface tension limits on solution hydraulics and not actual corrosion.

Solvent	**Avg. H2S Heat of Reaction BTU/Lb.**
GAS/SPEC SS	450
MEA	650
DGA[1]	674
DIPA	530
DEA	493

[1] DGA is trademark of Huntsman

So the choice of amine molecule basically allows capacity expansion without capital equipment expansion when these limits are reached for a refinery.

What checks are then required when moving from a stronger base amine to the higher efficiency MDEA formulations? Predominantly system evaluations must focus on the mass transfer and hydraulic considerations of the refinery amine system. The two areas of concern are liquid turndown for absorbers and the stages of mass transfer provided for in historical designs of the plant.

Whenever a vintage system is moved from historical design to new high efficiency chemistry the current operation is likely very different from that original design. Inlet H2S concentrations are often greatly increased and environmental restrictions have tightened. A choice of a 6 or 8 tray absorber design in the 1960's and 70's may have been correct, but today's Mayan crude and tighter emissions are taxing the operation of that 6 tray tower. Operations may be over circulating amine to the tower to accomplish the treatment but expectations of reducing circulation with a chemistry change may not be met as the mass transfer is limiting. Each absorber should be evaluated for current conditions in the refinery and any expected scenarios for these mass transfer limitations. In numerous conversions over the last 10 years a few re-piping modifications have been found where lower loaded rich amine from a nearby absorber has been introduced into a mid-point of towers with mass transfer limitations to improve acid gas polish with more circulation and lower average loadings. In one

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[2] DGA is a trademark of Huntsman

case this was actually a detriment to the absorption as the current operation had this introduction of amine at higher rich content than the amine dropping onto the tray from above. Re-locating the feed to the bottom of the tower corrected the mass transfer and allowed conversion to MDEA.

The second issue is turn-down. The MDEA solutions operated at 40 – 50 Wt. % concentration provide capacity much greater than comparable 18 Wt. % MEA circulation. Therefore, reduction in amine circulation is immediately achievable based on the chemistry of the amine process. However, the actual tower needs to be evaluated as turndown to the lower amine circulation may not be hydraulically possible in the given equipment. Again, with numerous conversions circulation turndown has been limited by sieve tray flow minimums, valve trims, pump minimums and packing wetting minimums well before the actual amine chemistry loading maximums are reached.

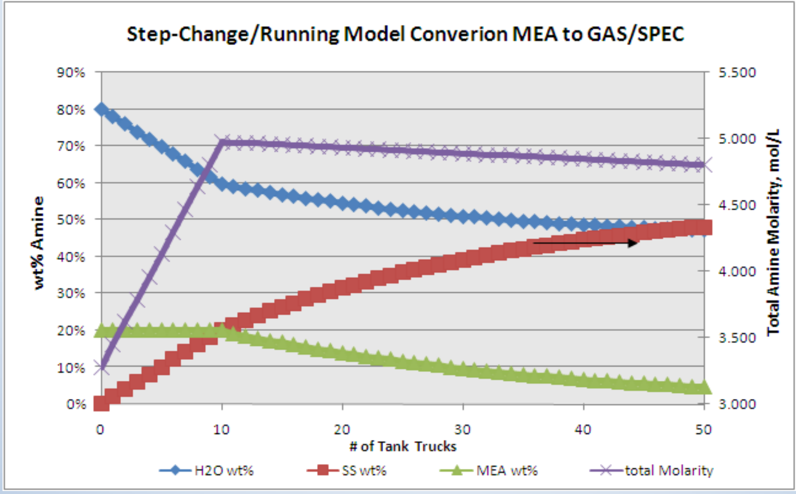
How is this evaluation made and what is needed? First, accurate flow, composition, temperature, and pressure conditions for each stream being treated by the amine are required. These seem straightforward but many refinery systems have little idea about the actual composition and even flow of streams being treated by the amine. It is more often the case that the amine circulation is set high for worst case crude blends or historical operating of the absorber and left in the low efficiency mode. This is understandable as measurement and analysis of the absorber feed streams are often not a part of the plant operations and the outlet treat may also be lost in blend with other streams of much later evaluation of H2S or SO2 emissions on the larger system. Therefore a specific tower with elevated outlet H2S may be difficult to identify in some systems and the approach becomes assurance of treat through over circulation in all cases.

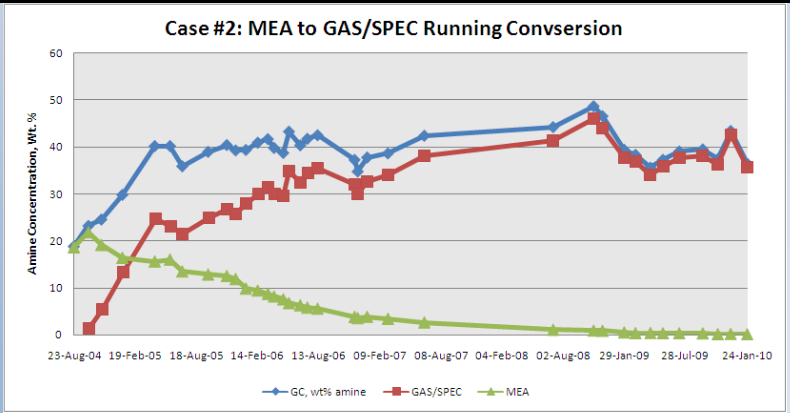
Alternately, rich loadings are often tested to infer the inlet stream content. I take issue with this approach generally for efficiency as the rich loading measurements are often H2S only and in the process of taking the sample for titration significant H2S is lost. Therefore pushing for higher amine rich loadings based on this measurement can walk a plant into overloaded rich amine operation and acid gas pitting corrosion of rich equipment. The rich measurement is fine for a general idea of how loaded a specific absorber is when no other stream data is available to material balance the absorber, but does not adequately provide accurate data to push to maximize loadings and manage corrosion risk from the acid gas release.

I will discuss the conversion analysis issue from two perspectives. As an engineer, my first choice would be to get accurate data on the streams being treated to optimize both current amine operation and future MDEA operation through simulation/modeling to maximize the efficiency of current amine operation and future increased capacity operation. Ideally, the amine system could follow rates and compositions operating in the refinery and be tuned for the lowest energy approach. However, stream information is often generalized or assumed but the limitation on current MEA, DEA, DGA, or DIPA solution is real. As concentrations are increased, circulation is supplemented sending line velocities beyond guidelines, and finally regeneration energy and Claus capacity limiting refinery production rates. The MDEA solution buys the refinery capacity and relief from these operating “out of bounds” risks being taken for production capacity. The higher capacity allows the system to be backed down and provides room for the ULDS system and/or other equipment or load increases. The most optimal MDEA cycle operation is often not reached as the circulation is set for the worst case sulfur load or the highest stream rate scenario. Though not “optimal” this is a large step change improvement over previous amine operating cycles. Taking the second approach provides immediate capacity and energy relief with additional efficiencies to be sought through KPI tool analyses, improved measurements and improved control of the operation.

Case Study 1 & 2:

The first studies looks at two refineries that walked up capacity production with debottlenecking projects and add-on coking and cracking projects until the limit of the MEA system had been reached. The MEA was operating typically in both systems at 22-26 Wt. % to provide enough amine to the absorbers to carry the acid gas away in the required treating for the units. The rich loadings also well exceeded recommended industry guidelines, approaching and exceeding 0.5 m/m in some absorbers. The piping velocities had increased from historic design as new expanded pumping was implemented with equipment additions over the years but line size on long runs were left as originally specified. The resulting operation was easily foreseen with repeated leaks in the rich amine piping via erosion and corrosion.

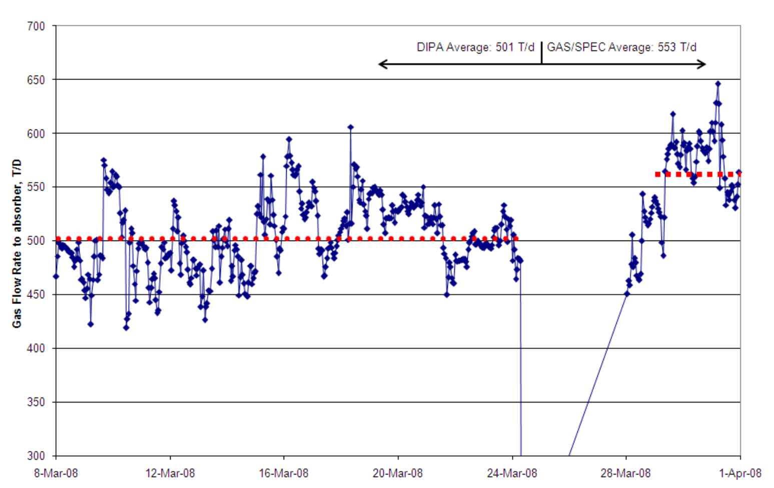




Rich piping corrosion can have many contributors. The corrosivity of the amine itself adds to issues at the areas where iron sulfide passivation cannot protect the piping. High piping velocities coupled with any solids in solution act as an abrasive to scour through any passivation layer protection on the carbon steel. The rich loading overload can cause have early release of the acid gas back into a vapor phase. The large expansion of volume further increases line velocity for the erosion issue, while the acid gas release is typically CO2 first and creates localized carbonic acid concentrations. The carbonic acid then causes pitting corrosion. The typical failure mechanism in rich piping is localized pitting corrosion through the carbon steel. The location is often after a change in direction of flow or after a throttling location. Heat affected zones from manufacture where stress relieving of the carbon steel was not accomplished are also predominant areas of localized corrosion. These heat affected zones are more susceptible to the pitting or localized cracking corrosion risks as stresses in the iron grain boundaries are more easily attacked for iron loss. In case two, the operations had frequent rich piping failures and very large consumption of MEA occurring yearly due to the operation moving beyond the capacity provided by the MEA. I did not include the affect of heat stable salts on the corrosion issue in this discussion as it was not a factor in either MEA system with the very high amine losses being experienced. The large physical losses from the systems were a natural purge for strong acid contaminants. Both sites avoided even running thermal reclaiming equipment with the large losses and replacement occurring on the MEA solvents.

The MDEA conversions on these two refineries main systems allowed the solution capacity increase to mitigate each of the issues causing failures to the rich piping. The case one system operates at 40 Wt.% amine as several liquid treating absorbers are in the circuit without water wash equipment for soluble amine recovery. Consumption of amine is less than half of the previous MEA consumption and energy cost savings go directly to the site's bottom line economics. The case two main system does not have liquid treating so operation is possible at 45 Wt. % with the ability to push to 50%. A liquid treating absorber is part of future plant expansion Coker addition but will have water wash allowing flexibility in amine chemistry and concentration without solubility losses with the treated hydrocarbon liquids.

Case 4: Complete Conversion (Diisopropanolamine) to formulated MDEA solvent.



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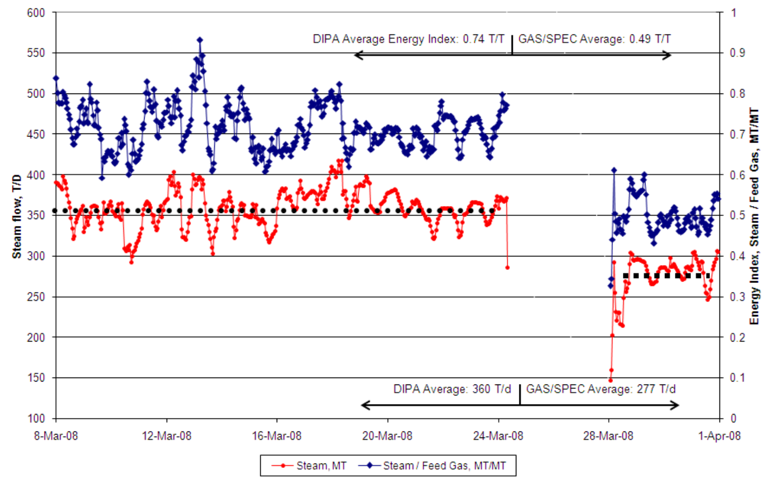


Case 3 & 4:

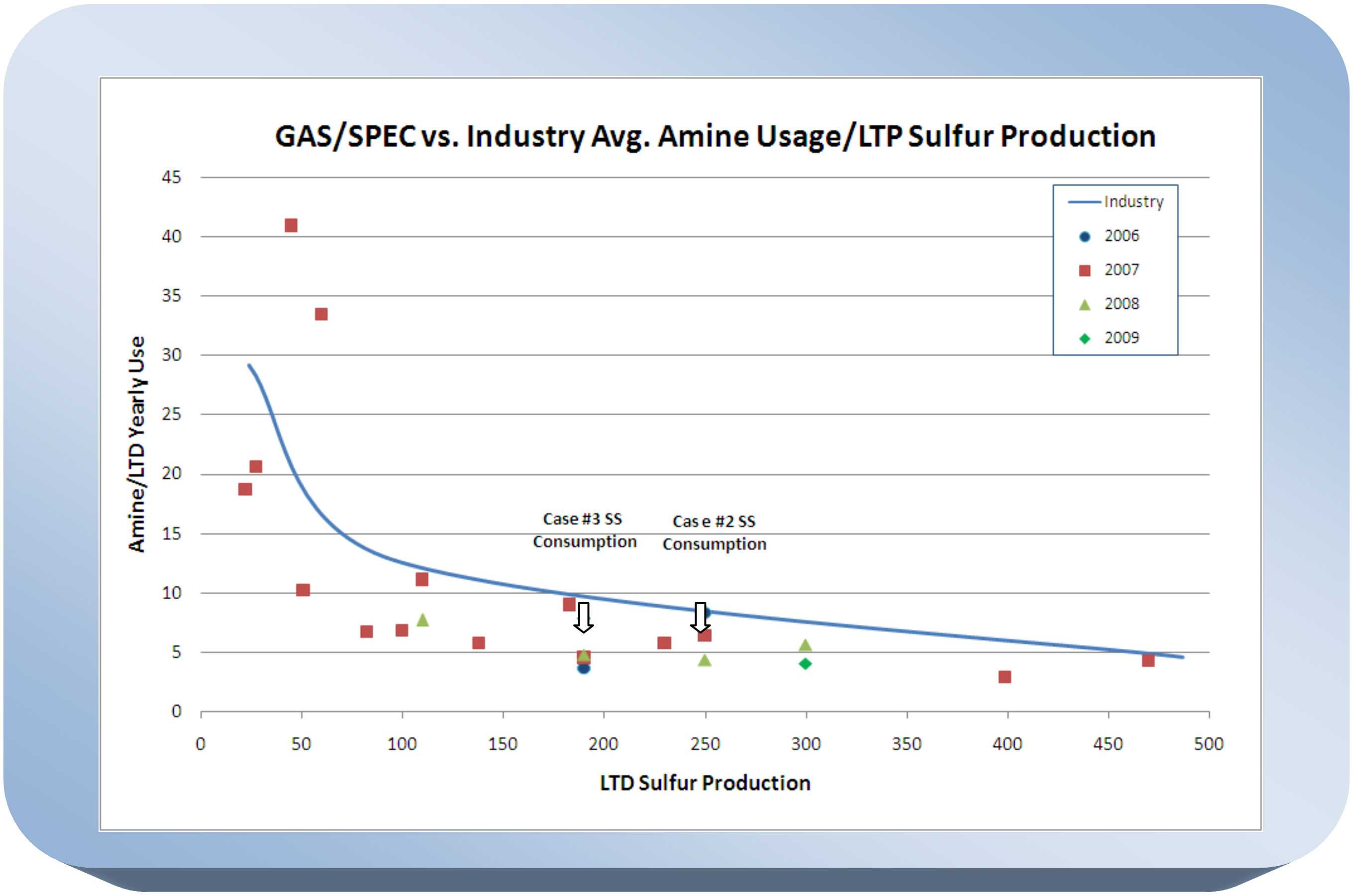
While DEA and DIPA offer higher capacity than MEA operation, conversions in these systems to MDEA have been just as numerous largely because of energy and capacity improvements as the systems reached the limit of the secondary amine capacity. These two cases were also converted more quickly to MDEA chemistry with two different conversion approaches.

Conversions:

There are a number of options in approaches to convert refineries to new amine chemistry. While the preference to remove previous solvent, clean, inspect, and repair the amine system is ideal, loss of production, operation, or even just refinery expense for the maintenance required steers decision making to "on the fly" type conversions of the chemistry. In the cases sited here two types of conversions were accomplished. The first two cases sited were through a running conversion of the chemistry to MDEA solvent. Initially the MDEA content can be boosted to a combined operating concentration that does not increase corrosion potential from the MEA. In fact, from the start the MEA content is dropping, improving the solution corrosivity. The jump in amine molarity in solution drops the acid gas loading, further moving, the system away from the rich loading and amine strength corrosion contributors. The final immediate benefit is circulation reduction within loading guidelines for the now higher molarity solution. In each case the corrosivity failures reduced and stopped as MEA content fell below 10 wt. %. With this reversal in failure rate the amine consumption dropped to normal expectations for refinery operations. As expected this extends the timing on fully converting to MDEA as the active purge of solution is eliminated.

The next energy benefits was seen as the MEA depleted past 10 to below 5 wt. %. Lean loadings trend down with MEA content as the MDEA is much easier to strip and the reaction energy average for the amine solution drops with increased MDEA content. New operating thought processes were implemented in both units as the high stripping rates were no longer needed to achieve target lean loadings and absorber performances throughout the site. The system with larger CO2 content streams noted improved Claus operation as the H2S content increased in the acid gas and inert CO2 content reduced.

The conversion in Case 3 was also completed as running conversions but the approach was a plug flow replacement of chemistry. Pre-diluted MDEA formulation was staged to be added into the lean pumps and regenerated lean solution purged in "once through" replacement of chemistry. The system was lined up with minimal auxiliary equipment operating and the change-out initiated. The amount of fill exceeded the plant volume slightly to accomplish the chemistry change with low level of residual chemistry present from any back mixing in volume areas of the amine circuit. The advantage of this approach was removal of contaminants as well as progressing to full advantages of the capacity, energy, and low corrosion benefits of MDEA immediately for the plant operation. In case #3 the conversion coincided with



the start-up of new UDS systems. Finally, the case four DIPA to MDEA conversion was a dump and fill timed with the outage of the refinery allowing equipment cleaning, inspection, and repair prior to operation on the new MDEA solvent.

Conclusions:

MDEA is now the predominant amine used in U.S. refining. Systems are operating at high efficiency and reduced losses. Active contaminant management has become the technical requirement for maintaining quality of the amines as the "purge and replace" mentality of high loss systems has faded. The GAS/SPEC Technology Group monitors operation, quality, and consumption with KPI tools for customers. The refinery systems on formulated MDEA clearly lead the way in operating efficiency; dropping energy use, increasing capacity, and lowering amine consumption across the board in refining from sweet crude units to the sourest systems in the Americas. These efficiencies allow the sweetening of these gas and liquid streams while improving the bottom line and meeting expansion needs with little or no capital to the amine and sulfur plant systems.

The author

Erik Stewart is Technical Manager for INEOS Oxides in the Americas. He joined the GAS/SPEC Technology group in 1988 and has developed a number of environmental technologies, for H_2S, SO_2 and NO_x removal. He has U.S. and World Patents in Chlorohydrin production technology and holds a Bachelors of Science degree in chemical engineering from the University of Washington, Seattle WA 1988.

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