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## Successful MDEA conversion

MDEA conversion illustrated by a series of case studies

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### INEOS LLC

As part of a Federal Trade Commission mandated remedy to the merger of The Dow Chemical Company and the Union Carbide Corporation, INEOS plc was able to purchase both Dow's Ethanolamines and GAS/SPEC MDEA-based specialty amine businesses. This purchase became effective on February 12, 2001.

INEOS LLC was set up as the newly acquired company, which includes the GAS/SPEC Technology Group. All the key Ethanolamines and GAS/SPEC personnel were retained by INEOS LLC. All GAS/SPEC products, technology and know-how became the exclusive property of INEOS on a global basis.

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# Successful MDEA conversion

Shelby Oostwouder, The Dow Chemical Company, USA, discusses MDEA conversion, illustrated by a series of case studies.

A recent inquiry for conversion from a methyldiethanolamine (MDEA) product to a product supplied by The Dow Chemical Company, began 'Due to changes from the original design basis for the gas plant, additional CO<sub>2</sub> removal capacity is required from the existing MDEA system. To accomplish this, a solvent capable of continuous rich amine loading of 0.75 mol CO<sub>2</sub>/mol amine is required.' The letter went on to specify that there should be no major equipment modifications, the overall corrosion rate had to be guaranteed not to exceed 2 mm/yr, and the product had to be added on top of the current product. Meeting all of these expectations was not possible in this situation. However, the customer expectations were clearly identified to start with so that a dialogue between the plant and the MDEA provider could quickly focus on what would be the difficulties in achieving successful plant operation.

The majority of projects evaluating the conversion of an existing plant to a MDEA product are usually focused on one thing: to increase the gas throughput of the plant. The switch to the MDEA product will usually meet this objective, but it can be other existing or potential conditions in the plant that ultimately determines the overall success of a conversion. Some problems which arise after a conversion to MDEA are not possible to predict, but full communication between the plant and the amine supplier before the conversion occurs will allow many problems to be predicted and mitigated. One of the first steps is to identify all of the problems in the current amine system operation.

## Study current system operation

Problems in amine systems usually fall into one of four categories:

- 1 Failure to meet specification.
- 1 Foaming.
- 1 Amine losses.
- 1 Corrosion.

Each of these problems can be the result of a single factor or several factors working in conjunction. It is valuable to know the cause of the existing problems before the amine changeout occurs<sup>1</sup>. Some problems can be eliminated with the changeout, others will not. Solutions that require physical modification of the plant can be completed while the plant is shut-down for a change of amine rather than after it is back in operation.

## Case study one

A large gas plant converted from diethanolamine (DEA) to a formulated MDEA to increase CO<sub>2</sub> removal. Soon after start-up the absorber column began foaming. Gas chromatograph analyses run on the flash gas and acid gas revealed both contained hydrocarbon species, C<sub>6</sub>+. The glycol dehydration unit downstream operated at a cooler temperature and had historically captured a considerable amount of hydrocarbons. Finally, it was discovered that a parallel DEA system historically required continuous antifoam with a back-up system for upset control. The foaming problems were caused by continuous heavy hydrocarbon absorption into the amine solution.

This plant will require ongoing antifoam use as long as the heavy hydrocarbons are present in the inlet gas. Additional recommendations for this plant included maintaining an active carbon bed to remove hydrocarbons and periodic purges of the acid gas condensate to provide another path for the hydrocarbons to escape the amine system.

An operating practice of the plant was to cut the amine rate during a foaming upset. This practice was stopped as it can contribute to foaming in a couple of ways. Decreasing circulation without adjusting the lean amine cooling fans, manual controlled, was decreasing lean amine temperature and increasing the amount of heavy hydrocarbons condensing into the amine at the top of the tower. The lower circulation rate was also causing a higher rich amine CO<sub>2</sub> loading and a higher amine temperature in the bottom of the tower, increasing the conditions for CO<sub>2</sub> degassing, and again increasing the foaming incident.

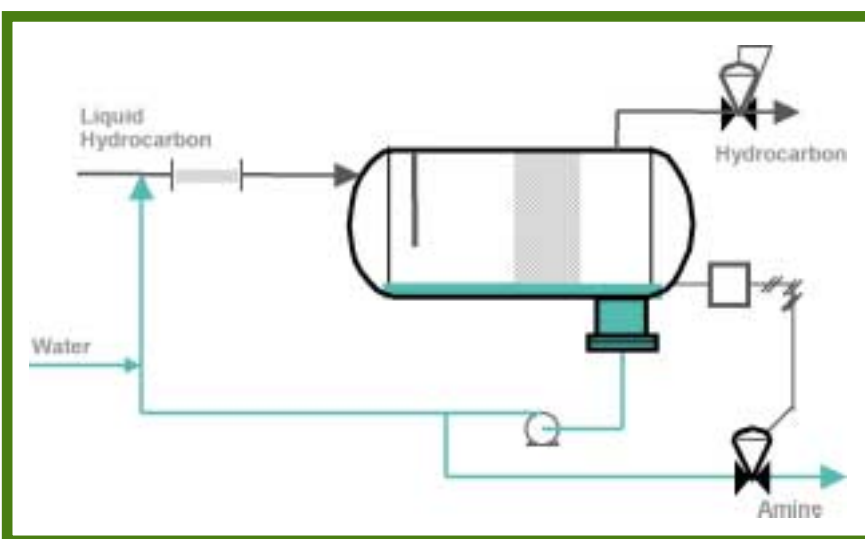


Figure 1. Water wash system for liquid hydrocarbon treater.

### Case study two

This integrated refinery system has multiple gas absorbers and a liquid-treating unit<sup>2</sup>. Historical amine losses with monoethanolamine (MEA) and MDEA were both in excess of 600 000 lb/yr (272 156 kg/yr). Further conversion to MDEA increased the operating cost associated with this high level of amine loss.

Ranking of the current amine loss areas, identified entrainment for both liquid and gas treaters as the largest loss category. Mist eliminators were placed in each absorber and a water-wash system was installed on the treated liquid stream. A typical water-wash system is shown

in Figure 1. The loss rate was reduced from 640 000 lb/yr (290 300 kg/yr) to 175 000 lb/yr (79 400 kg/yr). The water wash recovered much of the amine loss due to solubility in the liquid hydrocarbon stream.

### Evaluate future operating requirements

When plants are being converted to an MDEA based product, one of the key tools for determining how the plant will run in the future is the use of an amine process simulator<sup>3</sup>. Many simulators are available in the industry to complete detailed engineering design. The formulated MDEA vendors offer detailed simulations to predict product performance and provide design options. Dow uses a kinetic based absorber model that has been proven to be very accurate for performance predictions, including the temperature profile across for the absorber. This is often the key criterion for setting the plant design or operating capacity. With accurate prediction of the solvent performance and determination of the rich loading and temperature profile of the absorber, an optimised plant design, minimum circulation, minimum energy duty, and maximum capacity can be determined for existing or planned equipment.

Another critical aspect of evaluating the potential performance with the new amine product is having accurate information on the details and condition of the equipment. Besides providing process flow sheets, all the available details of vessel and tray drawings and exchanger specification sheets can be very important. Information

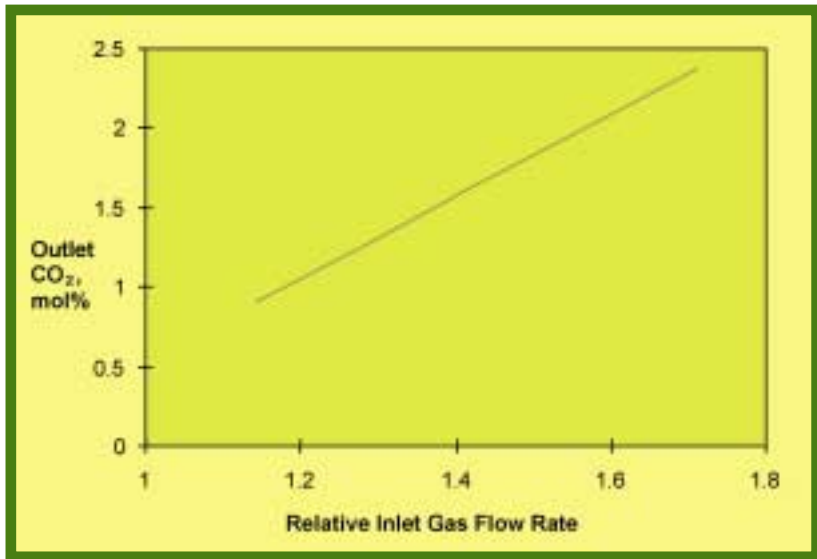


Figure 2. Effect of increased gas flow rate on outlet CO<sub>2</sub>.

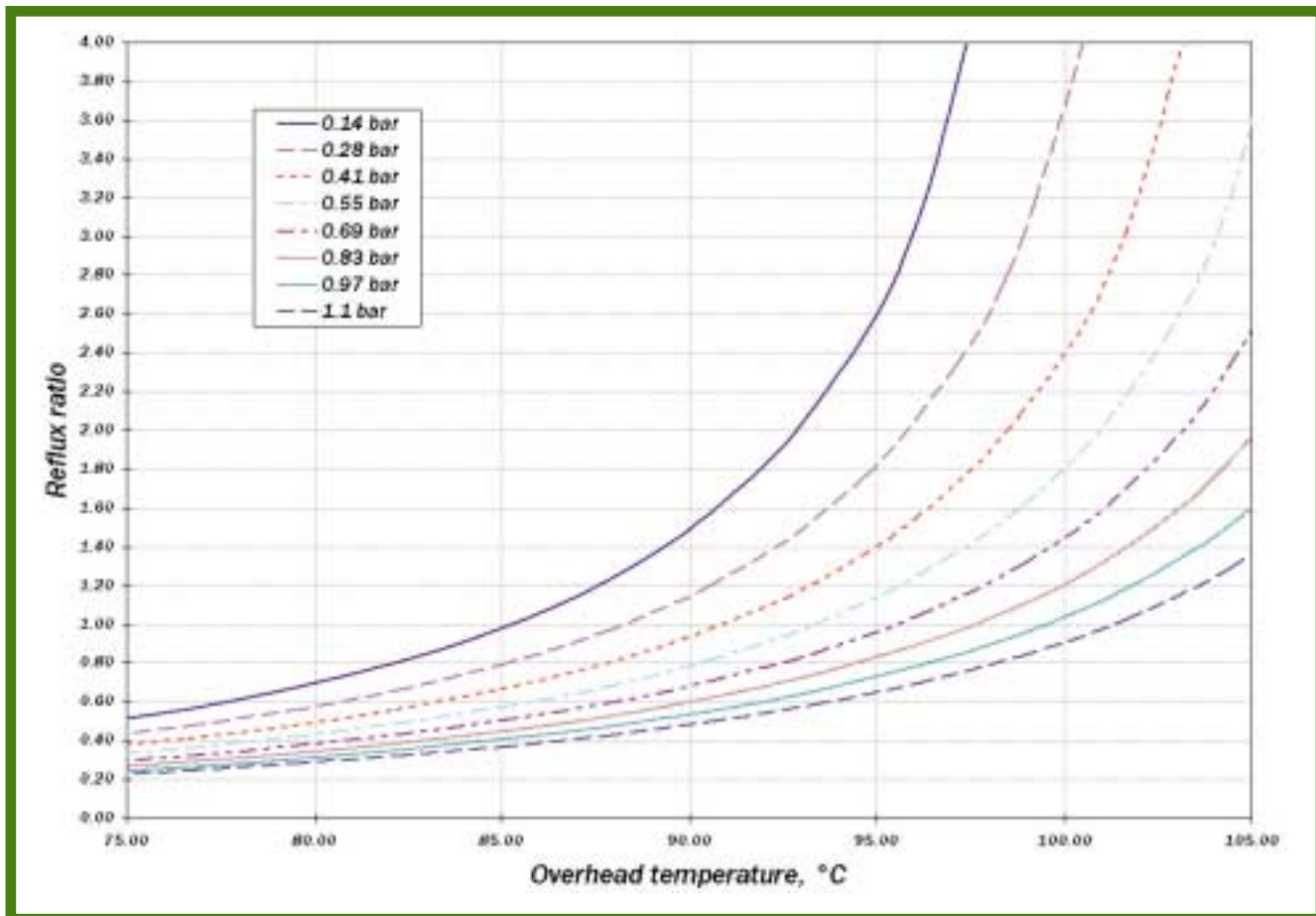


Figure 3. Regenerator overhead temperature correlation.

from past inspections of the equipment or process details indicating potential equipment damage can also be very valuable in knowing what maintenance to prepare for during the shutdown for conversion.

### Case study three

A CO<sub>2</sub> removal unit was constructed in front of a deep ethane recovery cryogenic system<sup>4</sup>. The absorber design includes 30 trays with 3 in. weir heights to maximise mass transfer while utilising a minimum CO<sub>2</sub> energy solvent to meet a tight CO<sub>2</sub> specification. The plant was originally designed with the 30 tray absorber to use generic MDEA to reduce the 3.3% inlet CO<sub>2</sub> to a 50 ppmv CO<sub>2</sub> specification in the treated gas. It was later determined the commercial simulator results were erroneous and the generic MDEA would not meet the tight CO<sub>2</sub> specification.

Dow provided simulations showing performance of formulated MDEA in the equipment. The operating plant achieved well under the 50 ppmv CO<sub>2</sub> specification. There was unused regeneration capacity in the regeneration design, so a second absorber was installed to treat additional gas, increasing the production capacity at the site.

### Case study four

An old Sulfinol<sup>5</sup> unit was relocated to be used for CO<sub>2</sub> removal from coal seam gas. This coal seam gas generally contains over 10% CO<sub>2</sub> and virtually no H<sub>2</sub>S in a methane stream. The treated gas can contain up to 1% CO<sub>2</sub> but maximum throughput is emphasised.

The original plant consisted of a 20 tray absorber and a 15 tray regenerator. Detailed tray evaluation indicated the high gas throughput was expected to challenge the efficiency of the trays. Under these conditions, additional sections were added to both the absorber and regenerator to ensure the most optimal mass transfer design for the tower diameter. The modified absorber has a carbon steel shell with 31 carbon steel trays and stainless valves. The modified stripper has a carbon steel shell with 20 stainless trays.

The MDEA formulation was adjusted to deliver the specific removal requirements. The plant now maximises gas throughput at the expense of reduced tray efficiency. Figure 2 describes the mass transfer relationship that allows optimisation of gas throughput with the high CO<sub>2</sub> kinetics of this formulated MDEA product.

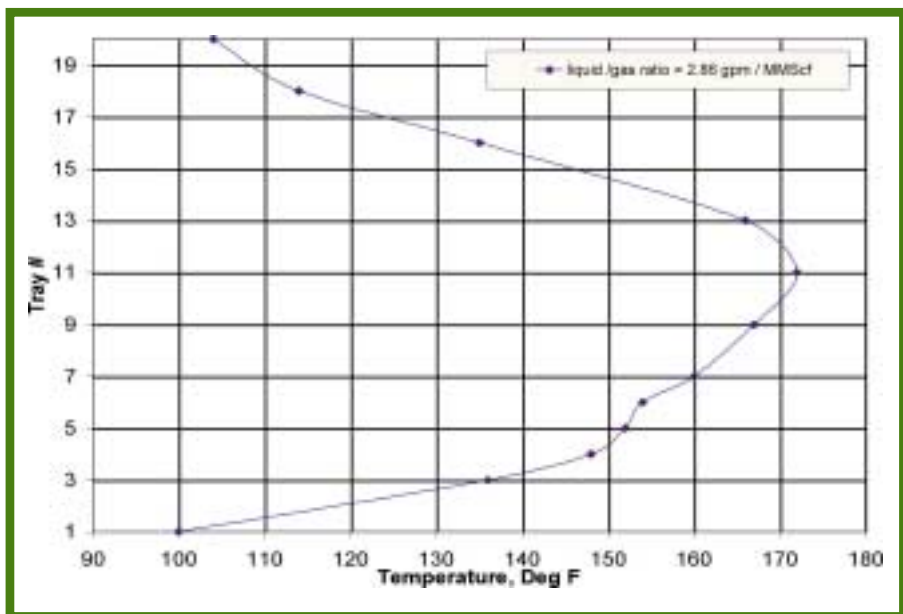


Figure 4. MDEA absorber temperature scan.

### Follow operating guidelines

After a conversion to a new amine product has occurred there can be inefficiencies caused by not operating the unit in accordance with the directions provided with the new solvent. This usually occurs when operations have established process variable set points that were optimal for the previous product. However, often the process variables should be maintained quite differently for operation with an MDEA based material. For example, if a plant switches from DEA to MDEA to achieve selective H<sub>2</sub>S removal and reduced CO<sub>2</sub> pickup, the guidelines for operating the regeneration system are different.

### Case study five

A large gas plant converted from DEA to an MDEA formulation. This plant had percentage amounts of both H<sub>2</sub>S and CO<sub>2</sub> in the inlet gas, which needed to be reduced to low levels. The main criteria set for the conversion were a 10% increase in throughput, a 20% decrease in circulation rate, and a 15% energy saving. These goals were met except the energy savings were only 7% initially.

The additional energy savings available by lowering the reflux ratio required to strip the new solvent had not been realised. Moving the plant down from a 2.0 (moles steam/mole amine) reflux ratio to a 1.2 reflux ratio achieved the additional energy savings. The previous DEA solvent had required higher steam rates to achieve guideline lean loadings.

### Case study six

A CO<sub>2</sub> removal unit constructed almost exclusively of carbon steel was converted from an inhibited MEA solution to an MDEA product<sup>6</sup>. While on MEA, the plant typically had about 10 ppm dissolved Fe in their solution. After converting to MDEA, the iron concentration in solution increased to a 200 ppm average. General corrosion did not seem to be an issue because the total iron in solution corresponded to less than 0.1 ml per year (mpy) based on the carbon steel surface area of the plant.

Operation of the plant with higher than recommended lean CO<sub>2</sub> loadings and a closer cross exchanger approach temperature, resulted in CO<sub>2</sub> flashing and localised corrosion in the carbon steel cross exchanger. The flashing and corrosion led to FeCO<sub>3</sub> deposition in the rich line leading to the stripper and on the top stripper trays.

The recommendations to the plant were to replace the cross exchanger with 304 SS and to limit the rich CO<sub>2</sub> loading to 0.45 M/M for this service and the lean CO<sub>2</sub> loading at 0.015 - 0.020 M/M. The plant replaced the failed equipment with 304 SS and subsequently the Fe concentration in solution was reduced to below 20 ppm. Based upon pressure drop readings across the exchanger, it appears that the FeCO<sub>3</sub> problem has almost disappeared. With the MDEA conversion the energy performance of the exchanger was greatly improved and CO<sub>2</sub> flashing was occurring prior to the stripping column. Reducing the cross-exchanger approach or change in metallurgy was required to either stop the flashing or control the CO<sub>2</sub> attack on the equipment.

## Work closely with the supplier

No matter how much review and planning occurs before a conversion to MDEA, often treating needs can change over time. A plant may suddenly encounter new impurities such as oxygen as new wells are brought online<sup>7</sup>, need greater selectivity<sup>8</sup>, or increased capacity. When these situations occur, often the best solutions to meet the new challenge come from a good team effort between the plant and the product supplier.

### Case study seven

A gas plant converted one of its two DEA units to a MDEA product. The MDEA unit had reached a gas rate of 131 MM SCFD (146 251 Nm<sup>3</sup>/hr) and was close to the capacity limit of the equipment design. The operating company found more gas to treat and needed to debottleneck the plant to raise the treating capacity to 145 MM SCFD (161 888 Nm<sup>3</sup>/hr).

One of the signs that the plant is at capacity is that it is experiencing elevated treated gas temperature out of the absorber ranging from 10 to 20 °F (-12 to -6 °C) above the lean amine temperature. Figure 4 is a temperature scan of the tower. It shows the temperature bulge is in the middle of the tower and more elongated than it should be. Generally, increasing the circulation rate is the best way to lower the temperature bulge in the tower and plans are to increase circulation by 25%. Lowering the lean amine temperature is not an option because a 10 °F (-12 °C) temperature differential must be maintained between the lean amine and inlet gas to prevent hydrocarbon condensation.

For comparison of what a more normal bulge temperature looks like the scan of the DEA system at the site is given in Figure 5. This profile shows a lower and more defined temperature bulge because the DEA unit operates with a liquid/gas ratio of 4.32 gpm/MMscf (36.5 (m<sup>3</sup>/hr)/MMNm<sup>3</sup>) while the MDEA unit operates at 2.86 gpm/MMscf (24.2 (m<sup>3</sup>/hr)/MMNm<sup>3</sup>).

### Case study eight

This plant processes natural gas derived from coal seams<sup>9</sup>. The plant was originally designed around 35 wt% concentration of DEA to achieve maximum CO<sub>2</sub> removal. Increased natural gas demand forced the company to investigate methods to achieve greater production. Since building an additional processing train represents a fairly large capital investment, the company looked first at additional ways of achieving increased throughput with the existing facilities, including mechanical equipment changes, revised operating parameters, and the use of a formulated MDEA.

A ten month pilot plant study was undertaken that evaluated different absorber internals and a wide variety of commercially available solvents. As a result of the study, DEA was replaced by an MDEA product which showed a throughput increase to 120%. The residual CO<sub>2</sub> levels in the treated gas dropped from 1.5% with DEA to under 0.6% with the new product. This enabled the plant to further increase production by increasing the amount of gas bypassed around the plant.

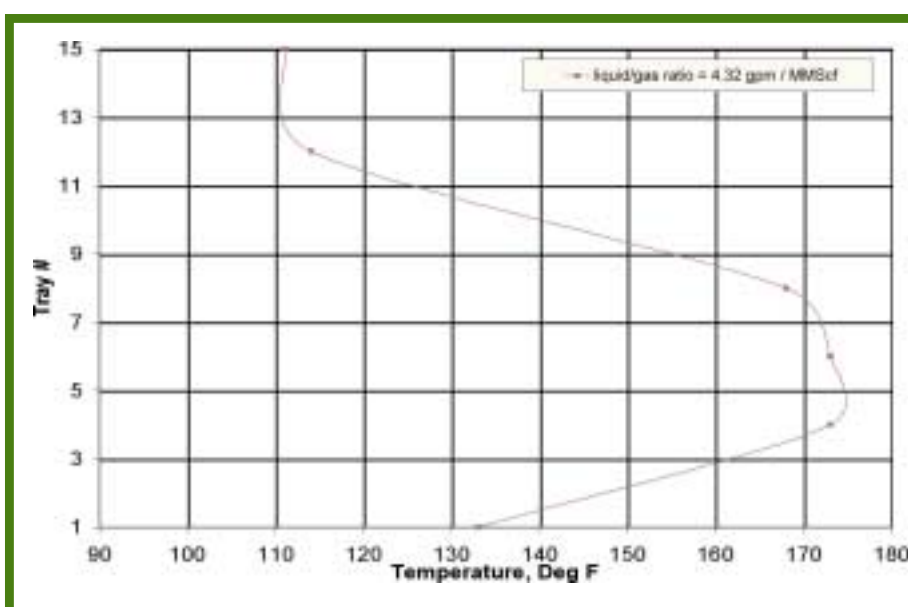


Figure 5. DEA absorber temperature scan.

Since the complete gas processing plant consisted of four trains, converting solvents in all units yielded an increase in productivity equivalent to adding another train, at less than a tenth of the cost. Utilising a joint solvent vendor/end-user team several amine unit operating problems were solved. These included coal fines and traces of pipeline compressor lubricant entering the inlet gas stream, improper installation of vessel internals, over dosage of antifoam, and various other problems.

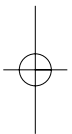
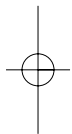
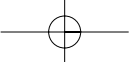
A fifth train was subsequently erected and placed on line to add even greater capacity. The MDEA product in all five trains now generates a daily saving of nearly US\$ 200 000 in bypassed gas, which helped justify the capital cost of the newest train.

## Conclusion

MDEA products have improved performance in many amine systems. The most successful conversions are those which analysed the operation of the existing plant, consider the future needs, and optimise the plant operation based on the new amine. Though unexpected challenges can always arise even in the best planned situation, coordinated efforts by both the plant and solvent supplier will stand the best chance of finding the best solution.

## References

1. ABRY RGF and DUPART MS, Amine plant troubleshooting and optimization, *Hydrocarbon Processing*, August 1995.
2. STEWART EJ and LANNING RA, Reduce amine plant solvent losses Part 2, *Hydrocarbon Processing*, June 1994.
3. ZAMORANO L and STEWART EJ, Application of Amine Systems for Gas Sweetening: Decision Making and Design, *Argentina Oil and Gas Expo '99*, October 1999.
4. SARGENT AL, ROONEY PC, STEWART EJ, VAN LANDINGHAM JV and SEAGRAVES JP, New Deep CO<sub>2</sub> Removal Solvent Useful for Natural Gas, Coal Seam Gas, and Refinery Applications, *Laurence Reid Gas Conditioning Conference*, February 2000.
5. Trademark of Shell Oil Co.
6. ROONEY PC and DUPART MS, Why Metals Solubility May Not Be A Good Indicator Of Corrosion In Alkanolamine Systems, *Corrosion* 99, March 1999.
7. ROONEY PC, DUPART MS and BACON TR, The Role of Oxygen in the Degradation of MEA, DGA, DEA and MDEA, *Laurence Reid Gas Conditioning Conference*, March 1998.
8. ROONEY PC and DUPART MS, Corrosion in Alkanolamine Plants: Causes and Minimization, *Corrosion* 2000, March 2000.
9. NOGUERA AA, DUPART MS and BACON TR, Increasing Gas Processing Capacity and Meeting Tighter Specifications With an Energy Efficient MDEA Based Solvent, *GPA Venezuela Chapter XIII Convention*, 1998.



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