Fertiliser Industry
ANNUAL REVIEW
2001

A New Deep CO_2 Removal Solvent for Ammonia Industry

Mike DuPart, Randy Kuroda and Andy Sargent
INEOS LLC, GAS/SPEC Technology Group, Freeport, Texas, U.S.A.

Reprinted from *Fertiliser Industry Annual Review* , 2001 issue

INEOS Oxide

INEOS LLC
Head Office
2925 Briarpark Drive, Suite 870, Houston, TX 77042
713.243.6200 main 866.865.4767 customer service
www.gasspec.com

A New Deep CO2 Removal Solvent for Ammonia Industry

MIKE DUPART, RANDY KURODA and ANDY SARGENT
INEOS LLC, GAS/SPEC Technology Group, Freeport, Texas, U.S.A.

ABSTRACT

A new deep CO_2 removal solvent has been deveoped and field-tested for ammonia production applications which reduces many of the limitations of previous products utilizing methyldiethanolamine (MDEA) blends. Results are presented from plant data, showing improved solvent stability, capacity, and energy requirements for the solvent versus previously available products.

INTRODUCTION

It has long been known that one of the most demanding applications in gas treating is the removal of CO_2 when there is little or no H_2S present in the gas stream. In an amine system a small amount of H_2S can assist in forming a passivating layer in the unit. In the 1950's and 60's the amine of choice was monoethanolamine (MEA). The use of 15-20 wt. percent MEA was common as a deep-CO_2 removal solvent. In applications where higher capacity was required such as CO_2 removal in ammonia production or refinery hydrogen syngas treating, often 25-30 wt. percent MEA was inhibited with heavy metal corrosion inhibitors such as arsenic, antimony or vanadium. Outlet gas CO_2 concentrations of 100ppmv and lower could be achieved, even at low pressure. But even with its popularity, it was well known at the time that MEA systems designed for CO_2 removal often encountered corrosion problems.[1]

The main disadvantage of MEA is that it requires a high reboiler heat duty. For example, a 15 wt. percent MEA solution operating with a lean loading of 0.1 mol/mol CO_2 and a rich loading of 0.35 mol/mol CO_2 typically requires a reboiler heat duty of at least 85,000 BTU / lb-mole of CO_2.[2] Inhibited MEA, while having a lower energy of 60,000 BTU/lb-mol CO_2,[2] also incurs the disadvantage of disposal costs and environmental and health concerns of the heavy metal inhibitors. In the mid and late 1980's, MDEA-based products gained popularity in ammonia production and other deep-CO_2 removal applications due mainly to lower energy requirements compared to MEA. In addition, formulations containing up to 50 wt. percent amine could be used while not requiring heavy metal corrosion inhibitors. Reboiler heat duties for 50 wt. percent solution operating with a lean loading of 0.01-0.02 mol/mol CO_2 and a rich loading of 0.45 mol/mol CO_2 typically required 50,000 to 57,000 BTU / lb-mole of CO_2 in a standard amine plant design.[3] Disadvantages of the earliest of these solvents were high solvent additive degradation and occasional corrosion concerns.

By 1993 most ammonia plants had converted their MEA systems to an MDEA based product. Two variations emerged as the market leaders. On one side were the formulated MDEA products such as GAS/SPEC* CS-Plus[4] which had lower energy requirements (50,000 to 54,000 BTU / lb-mol of CO_2), improved solvent degradation characteristics, and higher capacity while being able to meet outlet gas CO_2 concentrations of 50 ppmv and lower. The other group was the MDEA / piperazine blends which had low degradation characteristics and also took advantage of low energy designs by incorporating significant modifications to the standard amine unit configuration.[5] The tradeoff of the two types of products was, formulated products could have issues of product degradation and corrosion if recommended operating guidelines were not maintained but the MDEA / piperazine blends are claculated to have about 15-30 percent less capacity,[6] due to piperazine carbamate solubility limitations.

Over the last few years, there have been increasing demands on plant personnel to increase production far beyond name-plate capacity to improve margins throughout the ammonia industry. To accomplish this, without new capital, requires pushing the CO_2 loadings higher in a fixed volume of amine solvent. The result is that the temperature bulge in the absorber moves up to about the middle of the tower due to the exothermic CO_2 reaction with the solvent promoter. In GAS/SPEC CS-Plus Solvent, rich loadings above the recommended 0.45 mol/mol CO_2 in combination with the increased absorber temperature results in increased solvent promoter degradation and CO_2 flashing problems. Lean amine loadings often are 2-3 times the recommended level of 0.015 mol/mol CO_2 in the stripper due to exceeding the regeneration capacity of the plant, also resulting in increased solvent promoter degradation. The solvent will perform at these severe conditions, but the long-term quality of the solvent can be compromised, resulting in eventual replacement or reclaiming. It should be noted that these plants often utilize improved metallurgy such as 316 stainless steel to allow for operation with excessive loadings.

GAS/SPEC CS-2000 DEVELOPMENT

To assist customers requiring ever-increasing capacity requirements without expensive equipment change-outs or modifications, a new solvent, (GAS/SPEC CS-2000), was developed that provides a combination of deep CO_2 removal with lower energy, higher capacity and long term stability compared to solvents that are currently available.

To improve the degradation characteristics, especially in severe applications, an extensive research program was undertaken. To evaluate the solvents, accelerated CO_2 degradation tests were utilized to compare the various solvents. The new CS-2000 product has noticeably decreased the degradation versus other formulated MDEA products (Table 1). Note that the MDEA portion of each solvent has very little degradation; it is the promoter that has the most significant degradation due to high CO_2 loadings in combination with high process temperatures.

Table 1 - Comparison of Accelerated Degradation of other MDEA Formulations compared to GAS/SPEC CS-2000.

Formulation	Start wt.%	Finish wt.%
1st Formulation	50	27.8[a]
2nd Formulation	50	42.7[a]
GAS-SPEC CS-2000	50	49+[b]

a) Conditions 400 psig CO_2, 248˚F for 7 days.
b) Conditions 260˚F, 0.05 mol/mol CO_2 for 28 days.

Table 2 - Comparison of Carbon Steel Corrosivity of other MDEA Formulations Compared to GAS/SPEC CS-2000.

Formulation	Carbon Steel Liquid Corrosivity[a]
1st Formulation	58 mpy[b]
2nd Formulation	5[b,c]
GAS-SPEC CS-2000	<1[c]

a) mpy is mils per year.
b) Conditions 400 psig CO_2, 248˚F for 7 days.
c) Conditions 260˚F, 0.05 mol/mol CO_2 for 28 days.

Next, the test solutions were evaluated for corrosivity using carbon steel weight loss coupons. This test verifies the improvement in solvent stability and the benefit of reduced

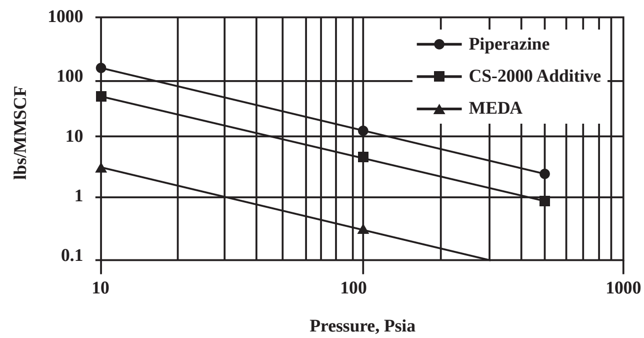

Fig. 1 - Comparison of Solvent Vaporization Losses for Piperazine and MDEA Compared to GAS/SPEC CS-2000 Additive.

solution corrosivity (Table 2). The relative improvement from the first generation solvents to the second-generation material was good, but GAS/SPEC CS-2000 solvent further improved stability and solvent corrosivity.

The degradation study was one aspect of verification of additive losses and thus solvent stability with the new solvent. The other is preferential loss of additive due to differences in vapor pressure from MDEA. When compared to piperazine in a typical MDEA-piperazine formulation, GAS/SPEC CS-2000 additive has lower vaporization losses[7] (Fig. 1). This important factor can affect not only the long term chemical makeup costs of the plant but also the amount of operator attention required to keep the plant treating in specification.

Finally, the GAS/SPEC CS-2000 solvent was found to have excellent kinetics and CO_2 capacity for the CO_2 removal/regeneration cycle while also having a very low potential for CO_2 side reactions. As is seen in Table 3, it has the same capability of achieving less than 50 ppmv outlet CO_2 specification as the other formulated products.

Table 3 - Comparison of Deep CO2 Removal Capabilities of other MDEA Formulations Compared to GAS/SPEC CS-2000.

Formulation	Outlet CO_2 capability
1st Formulation	~100ppmv
2nd Formulation	<50
GAS-SPEC CS-2000	<50

GAS/SPEC CS-2000 Applications

The first use of GAS/SPEC CS-2000 for removal of CO_2 occurred in 1998. Most of the early applications for the product were in natural gas treating applications. There were several refinery hydrogen unit conversions also, but most of these were “running conversions” from another MDEA based product. Conversions were handled this way at many plants so there would be no forced shutdown. While these conversions all occurred smoothly and have presented no subsequent problems, by doing the conversion in this manner the full benefits of the use of GAS/SPEC CS-2000 will not be realized for many months or even years, depending on the relative loss rate of amine the particular unit exhibits.

In gas treating applications there can be a wide range of inlet temperatures, pressures, CO_2 inlet contents, required specifications, and installed equipment. Because of these variations GAS/SPEC CS-2000 developed into a family of products with slight variations in composition. The data provided covers the range of these series of products. But usually for efficiency, the ammonia plants require the products which can attain very low CO_2 levels while maximizing solution CO_2 carrying capacity.

Two of the plant conversions have been full changeouts in units with CO_2 removal in synthesis gas service. The first was a hydrogen unit and the second an ammonia plant.

The hydrogen unit was converted to GAS/SPEC CS-2000 in August, 1999. The plant had originally been designed for MEA use but had operated on a formulated MDEA product for a number of years. The plant operated very efficiently but would experience packing fouling with iron carbonate. The solution would also build metals content if not closely maintained. After conversion to GAS/SPEC CS-2000 the plant was able to maintain the same outlet CO_2 content even while operating with significantly higher gas flows. Through a debottenecking project the unit was now needing to treat up to 67 percent more inlet gas to a level 10 percent above nameplate capacity.

Table 4 - Metal Analysis in GAS/SPEC CS-2000 after more than a year of operation.

Metal	ppm Level
Chrome	4
Iron	5
Nickel	1

The unit was inspected after one full year of operation with GAS/SPEC CS-2000. No corrosion was evident in the unit. The fouling of the tower packing had also completely disappeared. Fig. 2 is a close-up of the tower packing.

The solution in the unit is routinely analyzed for metals content. Though metals content is not always a good indicator of corrosion[8], the behavior of the metals in solution was significantly different for GAS/SPEC CS-2000 than with the previous formulation. With GAS/SPEC CS-2000 the metals initially jumped to a range of 50 ppm on iron content with elevated levels of chrome and nickel also present. But these levels did not rise. In fact the initial purple tint the solution had, later became clear. Table 4 shows the analysis for a sample taken in January of 2001 indicating the levels have even dropped.

The first full conversion of an ammonia plant to GAS/SPEC

Fig. 2 - Tower Packing after a full year of Service with GAS/SPEC CS-2000.

CS-2000 was completed in February, 2001. This plant had previously operated on inhibited amine and then formulated MDEA for several years. Like other ammonia plants this site was continually looking for ways to maximize production. After the conversion the unit operated at full capacity with a lower methanator temperature rise than had ever been experienced previously. It was estimated that the outlet CO_2 had dropped from 300 ppm to 100 ppm. The plant uses a standard amine unit design as shown in Fig. 3.[9]

With GAS/SPEC CS-2000 this ammonia plant was able to achieve energy use in the range of 48,100 BTU/lbmole CO_2. The energy use of GAS/SPEC CS-2000 was compared for plants across a broad range of treating conditions. Though there are many variables which impact the results, correlation of energy requirements versus inlet CO_2 level emerged. Fig. 4 shows the data taken from the actual plants.

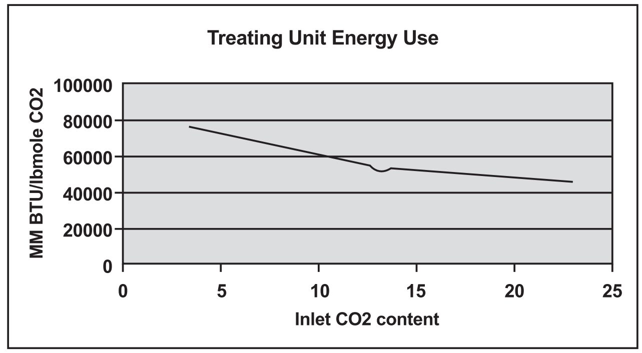

Fig. 4 - Correlation of inlet CO2 to Energy Use in Various Standard Design Amine Systems.

GAS/SPEC Ownership Change

As part of a Federal Trade Commision 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.[10]

At the time, INEOS plc was the UK's second largest chemical company, with group revenues of US$ 3 billion and 6,000 employees, operating 35 facilities. The GAS/SPEC business was a good fit for INEOS because of its division focused on ethylene oxide (EO) and derivatives. Within its EO division, INEOS operates Europe's largest single EO/Glycol unit at the production site in Antwerp, Belgium.

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

CONCLUSIONS

The advancement of deep CO_2 removal solvents for ammonia production applications requires a continued focus on solution CO_2 capacity, energy reduction, long-term low corrosion properties and solvent stability as a result of either degradation or vaporization losses. GAS/SPEC CS-2000

Fig. 3 - Ammonia Plant with Standard Amine System Design.

solvent development addresses all these issues in advancing the capability of an MDEA based product. The primary advantage to the solvent stems from the low potential for side reaction between the additive and CO_2, reducing losses and lowering the long-term solvent corrosion potential. The treating cycle and solution capacity for CO_2 loading remains high for efficient plant design.

REFERENCES

1. Gas Conditioning Fact Book, Published 1957, 1962. The Dow Chemical Company, Midland, Michigan.

2. LeBlanc, J.R; Moore, D.O.; Schneider III, R.V., "Retrofits Can Reduce Energy Consumption in Ammonia Manufacture for Significant Savings", *Oil & Gas J*, 1982, September issue.

3. a) DuPart, M.S.; McCarty, R.L.; Nelson, K.M.; Scott, J. "A Case History: Replacement of an Inhibited MEA System with the more Cost Effective GAS/SPEC* CS-1M Solvent in an Ammonia Plant CO_2 Removal System", presentation at The Gulf Coast Ammonia Producers Meeting, April 7, 1986. b) Dibble, J.H.; Combs, G.A.; Walkowiak, R.W.; Parnell, D.C. "Ucarsol® Solvent CR 401 Saves Energy in Ammonia Plant CO_2 Removal Systems", Presented at the 1986 Ammonia Symposium, AICHE: Boston, MA, August 24-27. c) LeBlanc, J.R. "Retrofit Ammonia Plants to Save Energy and Up Capacity", *Hydrocarbon Processing*, 1986 (August) p39.

4. Niswander, R.H.; Edwards, D.J.; DuPart, M.S. and Tse, J.P. "A More Energy Efficient Product for Carbon Dioxide Separation", *Separation Science and Technology*, 1993, 28(1-3), pp565-78.

5. For example, see: U.S. Patent No. 4,336,233 (1982).

6. For example, see: Hugo, R.S. "Revamp of Hot Potassium Carbonate CO_2 Removal Units to BASF's aMDEA® Process", Proceedings of The AMMONIA ASIA '98 Conference, Singapore: June 23-24, 1998. On p. 5, Hugo reports that the CO_2 loading capacity of lean aMDEA is about 4 lb-mol/m^3. This compares to about 6 lb-mol/m^3 loading capacity of GAS/SPEC CS-Plus when each solvent is loaded to a rich loading of about 0.5mol/mol CO_2.

7. Properties of Aqueous Solutions of GAS/SPEC CS-2000 Specialty Amine, Published March, 1999, The Dow Chemical Company.

8. Rooney, P.C.; DuPart, M.S., "Why Metals Solubility may not be a good Indicator of Corrosion in Alkanolamine Systems", NACE Corrosion '99, Paper No. 263.

9. Oostwouder, Shelby; "The Advantages of GAS/SPEC CS-2000 for the Ammonia Producer", *Fertilizer Focus*, May 2001, pp82-84.

10. Decision and Order document issued by the Federal Trade Commission of the United States of America, Docket No. C-3999, File No. 991 0301 *In the Matter of The Dow Chemical Company and Union Carbide Corporation.*

THE AUTHORS

Mike DuPart *is a Senior Gas-conditioning Specialist in the GAS/SPEC Technology Group of INEOS LLC, Freeport, Texas. He has a wide range of experience in gas processing, from corrosion inhibitor research to process optimization of amine plants. He holds four U.S. patents and has co-authored numerous papers on gas processing. He received a BS degree in Metallurgical Engineering from The University of Texas, El Paso.*

Randy Kuroda *is a Senior Gas-treating Engineer for the GAS/SPEC Technology Group, located in Berkley, California. He primarily services INEOS' refinery and natural gas treating customers in the field. He holds a BS degree in Chemical Engineering from the University of California at Berkley.*

Andy Sargent *is a Technical Service Engineer with INEOS GAS/SPEC Technology Group in Freeport, Texas. For the past 5 years he has been involved in formulated-MDEA technical support in natural and refinery gas and liquid amine processing. His experience includes amine plant computer modeling, design, troubleshooting, and optimization. He earned a BS in Chemical Engineering from Texas Tech University in Lubbock.*