Creative MDEA Reclamation Avoids Downtime

Richard Pearson, Athlon Solutions, USA, shows how an ammonia plant reclaimed 30 000 US gal. of MDEA without a costly and unscheduled turnaround.

There is a lot at stake. If not corrected, contaminated methyl-di-ethanol-amine (MDEA) will impact a plant's production, product quality, asset integrity and bottom line by millions of dollars.

MDEA is a tertiary amine used in ammonia plants to remove carbon dioxide (CO_2) from the synthesis gas stream. The colourless, ammonia-odour liquid is an industrial process treatment staple not only in the ammonia and fertilizer manufacturing world, but also in the chemical, refining and petrochemical industries.

When MDEA is contaminated, plant operations are often forced to shut down or expedite a scheduled turnaround to reclaim or replace the MDEA and correct the underlying issue. If not, excessive acid gases in the process

gas stream and lean MDEA can cause corrosion and impact production. The contaminants can also form deposits causing mechanical obstructions in the absorber and stripper trays restricting amine system circulation rates.

During ammonia production, CO_2 generated in the reformer must be removed from the process gas stream. System contamination can reduce efficiency in absorption and stripping processes. Poor absorption of CO_2 stresses the methanator catalyst and reduces production rates. Poor stripping of the CO_2 causes corrosion in the reboilers on the stripper towers.

Athlon Solutions' experience with a major global ammonia-UAN manufacturer in the US presents the challenges, solutions and benefits that have become a successful blueprint for the industrial water and process company in similar engagements. The result – increased production reliability and equipment preservation.

MDEA contamination

A leading ammonia manufacturer's Midwest plant had a major issue.

The plant has a long history of manufacturing quality anhydrous ammonia and UAN fertilizers. In fact, it is an important part of the Midwest's extensive plant and terminal system serving the US agriculture industry. So, when there is a hiccup in operations and the supply chain, it is noticed. A solution needs to be fast – not only for the company's operations, but also for the welfare of the supply chain.

Routine quarterly analysis performed by Athlon Solutions' lab showed unusually high levels of chloride (approximately 600 ppm) and sulfate (approximately 1250 ppm) ions in the MDEA circulating in the plant's absorber/stripper system. Athlon Solutions advised the local plant team that a problem existed after the detailed analysis disclosed a previously undetected issue. The MDEA was contaminated.

Chloride levels in the MDEA had increased dramatically and signs of damaging corrosion and deposition were beginning to show on the plant's assets.

The plant's operations team had already thought of options to correct it. The leading one required an unplanned shutdown to replace the existing volume (30 000 US gal. or approximately 114 000 litres) of MDEA with a new solution.

Doing this would cost the company millions of dollars factoring in the recovery of the contaminated MDEA and the manufacturing downtime.

The plant was also not authorised to handle the highly regulated piperazine, which is a crucial chemistry blended into the MDEA solution. Shipping and storage costs would be incurred to manage the blending of piperazine into the clean concentrate.

The addition of piperazine is essential. MDEA reacts rapidly with some gases, such as H_2S, to aid in scrubbing the acid gas. Due to no direct reaction with carbamates, MDEA reacts very slowly with CO_2.

To increase MDEA's CO_2 reaction and removal rate, small concentrations of piperazine (a cyclic, secondary diamine) are added. This combination is known as activated MDEA (a-MDEA). It has been the preferred choice of plants for more than 25 years.

Corrosion is always a concern

The concern for corrosion was high. Elevated corrosion rates (typical for many amine plants) and stress-corrosion cracking of stainless steel are usually attributed to high chloride levels. This also creates serious safety concerns.

High corrosion leads to costly repairs, potential environmental implications and production loss.

Corrosion is prevalent in amine systems. The result of a survey taken by the National Association of Corrosion Engineers (NACE) indicates that 60% of 24 amine systems surveyed experience stress-corrosion cracking in the amine absorbers. A similar survey by The Japanese Petroleum Institute (JPI) reported 72% occurrence of stress corrosion cracking at amine gas treating facilities. Carbon steel corrosion is often attributed to the amine contaminants that cannot be stripped and thereby accumulate in the amine solution.

The issues were stacking up for the ammonia plant. There was a sense of urgency for a solution, especially since the plant's primary water and process treatment vendor was not able to help and the scheduled turnaround was nearly a year out.

Benefits of MDEA/piperazine

MDEA reacts slowly with CO_2 on its own. When piperazine is added, it becomes a-MDEA. The CO_2 reaction and removal rate increases. This process was patented more than 25 years ago. The patent has expired. Now, a-MDEA is the choice of many new ammonia and fertilizer plants and older ones that have invested equipment to use a-MDEA.

The benefits of include the following:

- Higher capacity for reaction with CO_2 than other absorbents such as MEA/DEA.
- Low heat of absorption allows cooler absorber temperatures. This favours CO_2 absorption.
- Low heat of absorption means low heat of desorption requiring lower energy for regeneration, desorption of CO_2.
- More concentrated solutions with low corrosion further increase capacity for CO_2 removal.

Benefits to the owner/operator to overcome the higher cost relative to MEA/DEA include reduced capital investment, lower operating costs and improved removal of CO_2 as a result of the following:

- Lower equipment size because of its greater capacity for CO_2 removal.
- Less energy for regeneration (i.e. reboiler steam requirements).
- Less corrosive in use even at higher use concentrations than MEA/DEA.

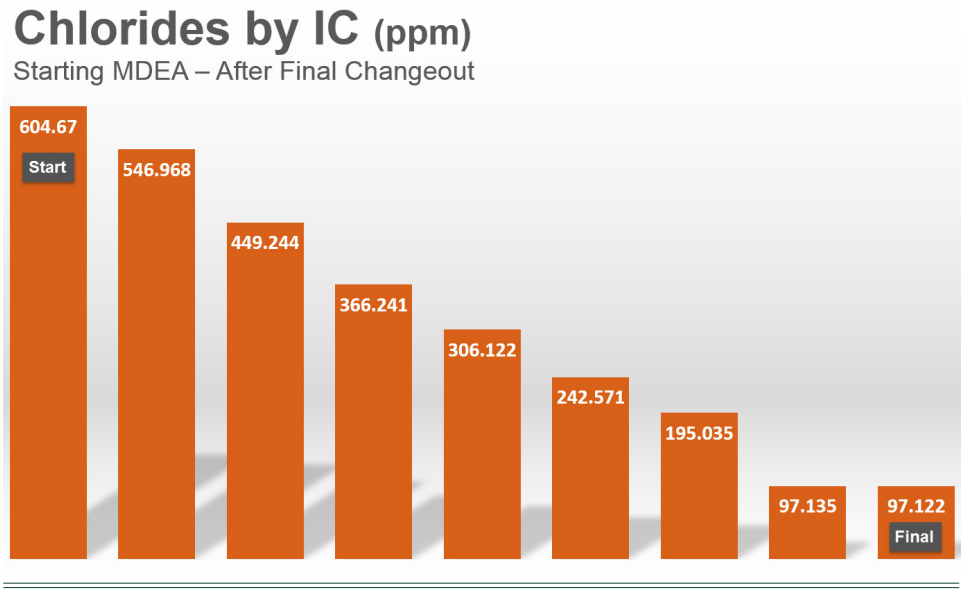

Figure 1. Reduced chloride levels after changeouts.

Table 1. MDEA analysis of the key areas of concern after the final batch changeout

Element	Starting MDEA	After final changeout
Chlorides by IC	605 ppm	97 ppm
Sodium by ICP	915 ppm	222 ppm
Sulfate by IC	1233 ppm	152 ppm
Glycolate by IC	29 ppm	45 ppm
Acetate by IC	3239 ppm	985 ppm
Formate by IC	1953 ppm	744 ppm
Propionate by IC	61 ppm	27 ppm
Oxalate by IC	99 ppm	16 ppm

To clean or replace?

The first step was to analyse the data. This allowed the team to determine the scope of the problem and establish if the cause was mechanical, operational or chemical.

As noted earlier, the plant's operations team had already been notified by Athlon Solutions that the chloride and sulfate ion levels were high in the MDEA. However, an underlying cause was escaping detection. The plant team could verify that a cooling water system leak (a potential cause) was not the source and the contaminant levels did not seem to be increasing. After much investigation, it was determined that snow melt had entered the MDEA system through the sumps. The packed and hardened snow had accumulated large deposits of de-icing salt and other contaminants.

The analysis of the contaminated MDEA using inductively coupled plasma (ICP) spectroscopy, ion chromatography (IC), titration and foam testing confirmed the high chloride and sulfate levels, but it also showed several other areas of concern, including issues with sodium. Finally, elevated organic acid levels were indicating oxygen ingress into the system (also from the sumps).

The elevated chlorides were the biggest concern. They were going to drive corrosion and stress-corrosion cracking of stainless steel. This would result in costly repairs and downtime if not corrected.

The big question facing the plant and the treatment team was whether 30 000 US gal. of MDEA should be cleaned or replaced. Either way, it was a daunting task. Although, keeping the plant operational was the most attractive option as the production losses would amount to several million dollars.

After reviewing the data and discussing the options with the plant's leadership, the best option was to reclaim the MDEA. Doing so would keep the plant running, avoid the purchase of new MDEA and all the costs associated with an unscheduled turnaround.

Athlon Solutions and plant operations decided to reclaim the MDEA through a series of batch changeouts (approximately 5000 US gal. each). Having the analysis of the contaminated MDEA would allow the team to track the recovery between batches and determine how many batch changeouts would be needed.

As for blending the piperazine into the MDEA, that could be handled by Athlon Solutions and its partners. Athlon Solutions would supply its MDEA product, Prosorb, which is premixed with piperazine. It could be shipped in concentrated amounts to its reclamation partner to custom blend the returned a-MDEA to meet the specifications required in the customer's online amine system.

Commitment to production reliability and equipment preservation

After 10 months and nine changeout batches, the plant's MDEA and acid gas removal levels returned to optimum operational standards.

There was no unplanned turnaround and no loss of production for the plant. The investment in the changeout volume and the supporting services was much less than the millions of dollars the plant would have lost with downtime.

An unscheduled turnaround was avoided due to an experienced operations and treatment team identifying a problem during routine analysis. They worked together to understand options and the associated impacts. Moreover, it was an example of all parties understanding that without an experienced water and process treatment program and team to implement, maintain and optimise it, a plant's production and equipment are at great risk.

Effective water and process treating is imperative to successful ammonia and fertilizer plant operations. WF