

Removal of Heat Stable Salts – A Solution to Amine Plant Operational Problems

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Introduction

Amine scrubbing solutions are used to remove hydrogen sulfide and carbon dioxide from gas streams in many natural gas conditioning plants and oil refineries.

Two major problems represent a significant threat to an amine gas treating plant: corrosion and instability of operation, resulting in unscheduled upsets and outages. In this process, contaminant byproducts called Heat Stable Salts (HSS) are formed and gradually build up to beyond tolerable limits in the amine circulation loop. Amine plant operational problems, such as excessive foaming, corrosion and capacity reduction, are often attributed to the accumulation of amine heat stable salts. These heat stable salts lead to costly maintenance problems such as corrossions, frequent filter replacement, foaming in the absorber column, absorber tower plugging, heat exchanger fouling and a reduction in the amount of amine available for gas treatment, thereby reducing the unit's productivity.

In order to prevent the HSS from building up beyond critical limits, amine plant operators have been making conscious attempts to control impurities, especially HSS. A number of measures have been proposed [1, 2]. The most straightforward approach is periodic amine purging, which is messy, prohibitively expensive and causes environmental problems. Other periodic amine clean-ups, either on-site or off-site, are also practiced to some extent by certain plants which have to employ large equipment for vacuum distillation, conventional ion exchange or electro-dialysis. However, this approach of periodic reclaiming is cumbersome and expensive and does not overcome the operational and corrosion problems caused by the anions.

Continuous amine reclaiming is being increasingly recognized as the most effective solution for HSS-related problems. The benefits of continuous HSS removal go beyond limiting the level of impurities in the amine loop. A continuous on-line reclaimer helps to ensure a stable and uniform gas conditioning operation where contaminant levels in the amines are prevented from building up, thus minimizing the rate of corrosion. It also ensures that amine unit operation is reliable and provides the designed gas treating efficiency.

Eco-Tec's Recoflo™ Technology Recoflo Concept

Using advanced ion exchange technology, the AmiPur, a unique and cost effective on line amine purification system was developed and introduced to the Petroleum Industry in 1998. This system employs Eco-Tec's Reciprocating Flow (Recoflo™) Ion Exchange technology [3,4].

Recoflo, which has been extensively used since 1973 for the recovery of metals from metal finishing wastes [5,6], is characterized by several features which differentiate it from conventional ion-exchange systems. Since 1987, the performance of these systems has been further improved by maintaining the resin inside the column under compression [7].

These features include:

- Fine particle size resins;
- Countercurrent regeneration;
- Short column heights (3 to 36 inch);
- Low resin loading;
- Fast flows and short cycles;

These on line Eco-Tec Amine Purification (AmiPur) systems are now successfully operating in many Petroleum Refineries in North America.

AmiPur – Heat Stable Salt Removal System

In 1998 Eco-Tec developed a system for the removal of anionic impurities from alkanolamine water solutions, which was named AmiPur – the name easily recognized and accepted by amine gas treatment plants worldwide.



Eco-Tec offers several models of AmiPur, with different HSS removal capacities. A typical AmiPur unit is presented at Figure 1.

Figure 1. Skid-mounted AmiPur unit.
 Skid size: 160 x 160 x 250 cm
 HSS removal capacity: 25 – 70 kg/day

There are basically two steps in the AmiPur operating cycle: HSS loading and caustic regeneration. This cycle is automatically repeated every 20 minutes.

During the HSS loading portion of the cycle, lean amine solution is pumped through a cartridge filter and into the resin column. The ion exchange resin removes the heat stable salts and the purified amine solution is directed to the flash tank or returned into the amine batch.

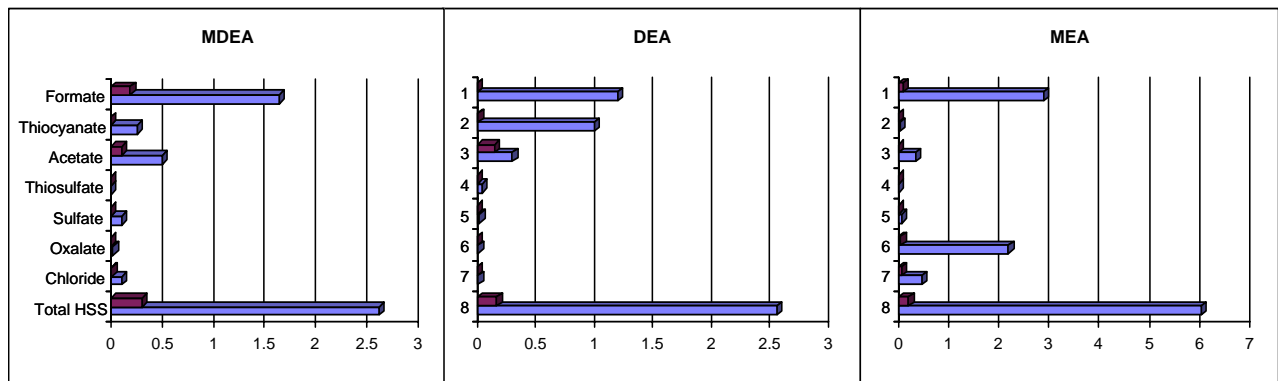


Figure 2 Anion removal by AmiPur, Eco-Tec laboratory data

Dilute caustic soda is used to regenerate the resin column. The unit draws concentrated caustic from tanks or drums and dilutes it to the proper strength automatically, then this solution is then pumped through the column and remove the HSS.

After several minutes of regeneration, the system rinses the excessive caustic from the resin and a new cycle starts.

An initial AmiPur system was installed at the Crown Central Petroleum Corporation (CCPC). The analysis of AmiPur “in” and “out” streams demonstrated that in addition to the removal of acetate, formate, thiocyanate and other anions, AmiPur also reduced iron level. This, together with significant formate removal capacity, resulted in a dramatic decrease in corrosion rates and filter pluggage at the Pasadena refinery.

Since that time AmiPur has been successfully tested on all the major types of amines (Figure 2). Significant decreases are observed on all types of HSS level after the installation of an AmiPur. Existing installations are operating on MDEA and DEA solutions, both at main amine and tail gas units, and have resulted in significant operating benefits for the amine plants.

Case History: Crown Central Petroleum Corporation

This refinery has both primary and tail gas amine treating systems. MDEA is used at the present time in both amine systems.

The primary amine unit contains a gas liquid contactor or fuel gas absorber, a spare fuel gas absorber, a liquid-liquid C3/C4 amine treater, one amine regenerator, a flash drum, heat exchangers, amine filter, a slipstream amine reclaimer, and several associated pumps. For the main fuel gas absorber, the tower's pressure drop is measured over the inlet gas line to outlet gas line, and this ΔP is used to monitor tower pluggage and foaming.

The liquid-liquid amine contactor is a trayed tower with 15 trays. It is designed to remove about 1,000 PPM H_2S from 21,000 BPD C3/C4 mix.

The tail gas unit's amine system is very similar to the main amine system, with no flash drum and only a single amine absorber.

The MDEA amine solution absorbs the H_2S from the gas and liquid feeding the refiner's absorbers, and these absorbers send the rich amine to be regenerated in a relatively simple processing scheme. The amine unit contacts the refinery off gas products from the various unit operations, and while removing H_2S , the contact in the absorbers allows the amine to react with other species in the gas and liquid streams, causing the amine to chemically degrade. These unwanted reactions are known to occur with oxygen, CO, SO_2 cyanides, organic acids such as formates and acetates, inorganic acids such as HCl and H_2SO_4 , all of which can and will be present in the off gas products from the refinery.

As HSS build, the amine filters plugged more frequently. A decrease in the amine filter life is usually the first sign of increased corrosivity, as this increase in the corrosivity starts in the hot lean amine system that feeds the amine filters. If the amine filters do not adequately remove these products of corrosion, filter life may not be affected, but the amine solution color will be dark. Dark amine solution feeding a packed absorber tower will certainly lead to tower pluggage and foaming. This foaming then leads to increased amine losses, and the increased amine make up can temporarily reduce the HSS to slow the corrosion and Improve the amine quality. As the HSS again start to build, the cycle starts again.

There can be no discussion more frustrating than an Amine plant discussion. Low level contaminants in the amine contactors degrade the MDEA and form the HSS, and accumulation of the salts begins to affect amine unit performance. The only way to break this frustrating cycle is to remove these salts from the solution continuously and not allow the accumulation.

At Crown Central Petroleum's Pasadena, Texas refinery, an AmiPur reclaiming unit was installed in 1998 to effectively remove HSS from MDEA solution. The unit was purchased in August 1998 and started up in October. The HSS in solution were approximately 2.4% when the AmiPur unit was started, and within 30 days the HSS was down to less than 2%. Material that had been accumulated from the unit, and stored in a tank was then introduced into the amine unit. The HSS level in the solution increased back to 2.4%, as we brought in 3.5% HSS material from the tank. The rented tank was then released, and the AmiPur unit brought the solution back down to 2%. By March 1999, after a unit shutdown for maintenance, and replacement of the amine regenerator tower, the HSS level was down to 1.75%. A significant decrease in the corrosion rate was observed. The ultimate goal of the refinery is to keep the corrosion rate as close to zero as possible. To achieve this goal it was decided to decrease the HSS concentration further. The AmiPur was designed to maintain HSS at about 1.5 wt.%, so the unit was upgraded to provide extra capacity. This work was completed in October 1999. Since then the HSS level was decreased to 0.4 wt.% as MDEA. HSS level decline is shown in Figure 3 [8,9].

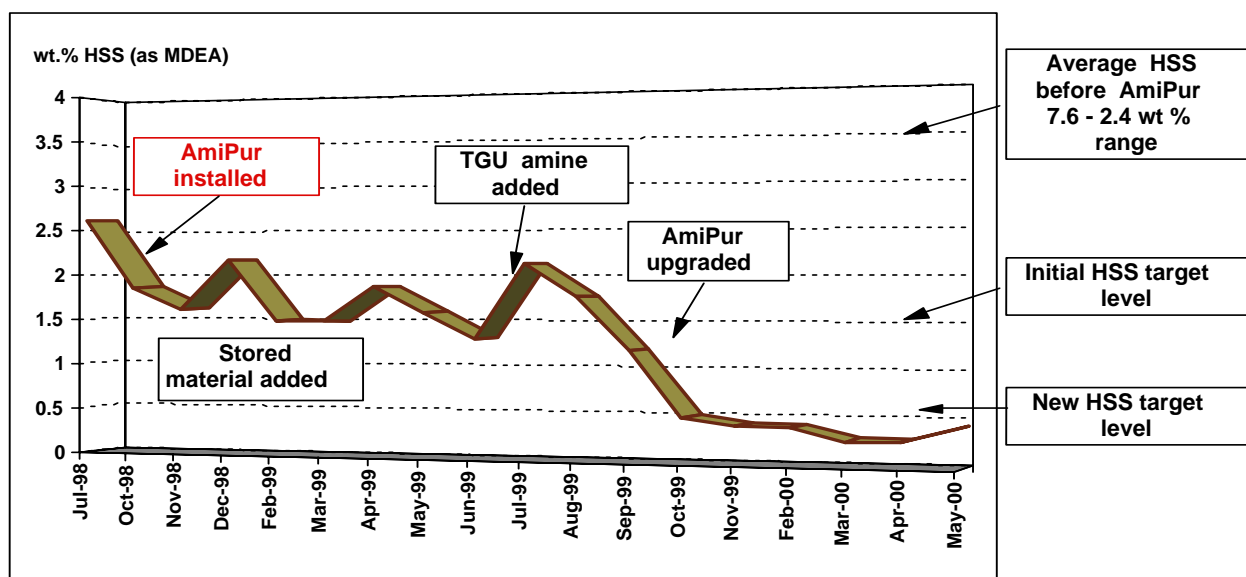


Figure 3.
HSS level at the main amine unit at CCPC Pasadena refinery

The corrosivity of CCPC's main amine solution has been monitored since 1997 using an electrical resistance probe, which is installed at the bottom of the main amine regenerator. This probe reading has compared favorably to monthly ultrasonic thickness measurements taken by the refinery's Inspection Department on the regenerator tower's shell and the amine piping. Summary graphs of these corrosion probe readings shown in Figure 4 [8,9]. The regenerator tower, built in 1978, was replaced in early 1999 due to the shell metal thickness. Since the AmiPur installation it has been possible to keep the corrosion rate at 10 mpy. The average rate for 1999 was 12 mpy. It is not unusual to get zero reading since the HSS level dropped below 1 wt.% as MDEA.

The tail gas amine unit has also been connected to the AmiPur unit to allow removing the HSS from this amine unit, eliminating the need for "bleed and feed" and reducing the amine consumption associated with this operation. The flexibility that the AmiPur unit provides allows the removal of the HSS from either of the amine systems on a campaign type approach. The present plan is to maintain both amine systems at HSS levels below 2%.

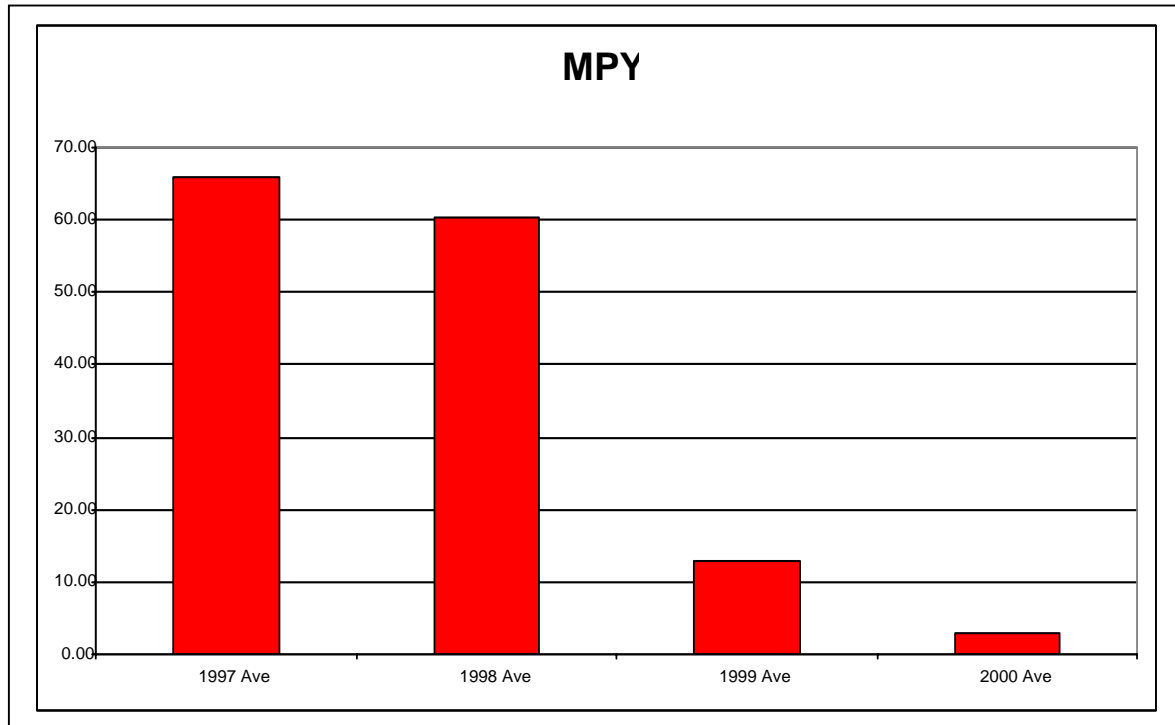


Figure 4.
Yearly average corrosion probe readings, mills per year; 1997-2000

Summary and Conclusions

Amine unit operation is an important part of the refinery’s environmental compliance. Amine degradation causes the formation of heat stable amine salts (HSS) that can lead to corrosion. The amine unit performance begins to deteriorate as the HSS increase, and the H₂S absorber becomes less stable. Iron in solution increases, amine filter life starts to fall, and equipment corrosion and fouling can lead to an unscheduled outage.

One of the most important results of an AmiPur installation is the STABLE and RELIABLE operation of the amine plant, which in turn has a dramatic environmental impact. The continuous removal of HSS has immediate and easily quantifiable results: reduction of filtration costs; elimination of periodic chemical cleaning of the absorber tower; improved gas treating capacity of the unit (due to increased amount of amine available for gas treating); elimination or reduced use of antifoamers, neutralizers and corrosion inhibitors; elimination of the cost associated with previously used methods of HSS removal. AmiPur, installed at Crown Central Petroleum, demonstrated the benefits of continuous removal of HSS for the refinery operation, Table 1 [8,9]. The project demonstrated a payback in the range of four(4) months, exceeding original projections for a six month payback.

Table 1.
Benefits of AmiPur Installation at CCPC Pasadena Refinery

HSS incursion rate: 1 wt. % per month (as MDEA)
Amine inventory: 15,000 Us gal

Item	Description	Benefit	Annual savings (USD)
HSS concentration	decreased from avg. 3.5 to 0.4 wt.% as MDEA	reliable operation	
Amine foaming tendency	Height/break parameters changed from 450/23 to 50/4	less foaming - operating benefits	
Power for reboiler	lower fouling of heatexchangers	lower energy consumption	
Chemical cleaning of the absorber tower	decreased from 3 times per year to zero	eliminated cost	\$16,500
Corrosion	decreased from avg. 60 mpy to avg. 12 mpy	great long-term maintenance savings	
Filter replacement	replacement frequency decreased several times	labor and material savings	\$23,000
Amine inventory	amount of free amine increased by 3.1 wt.% (as HSS level decreased from avg. 3.5 to avg. 0.4 wt.%)	More amine is available to treat acid gas; cost savings and operating benefits	
Other costs		Elimination of previously used practice of HSS control	\$35,000
Reduced amine loss	lower and more consistent absorber feed rates (less fouling and foaming)	cost savings	\$120,000
Additives	antifoamer use eliminated	cost savings	\$300

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