# Impact of Continuous Removal of Heat Stable Salts on Amine Plant Operation

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Amine plant operational problems, such as excessive foaming, corrosion and capacity reduction, are often attributed to the accumulation of amine heat stable salts. Recoflo® short-bed ion exchange technology has been applied to the development of a system to selectively remove these salts.

The first installation of this system, known as AmiPur, was started in October 1998 at Crown Central Petroleum's Co., Pasadena refinery amine plant. The purpose of the installation was to achieve and maintain a low level of heat stable salts on a continuous basis. The compact skid-mounted AmiPur unit is processing a 0.4 gpm slip stream of lean MDEA and removes about 1 kg per hour of heat stable salts. After the first four months of operation, the level of heat stable salts was reduced from 2.4 to 1.5 wt. % as MDEA. The refinery's goal is to keep the corrosion rate below 10 mpy by reducing the amine heat stable salt concentration to below 1 wt. % as MDEA. Plant observations, as well as the history of AmiPur operation are discussed in this paper.

## Introduction

The amine treating unit is of great importance in gas processing and refinery operation. Historically regarded as a secondary piece of equipment, the amine plant now attracts increasing attention due to high pressure for environmental compliance and quality of $H_2S$ and $CO_2$ removal.

Recently announced governmental regulations for gasoline quality require that refineries meet a corporate average gasoline sulfur standard of 120 ppm and a cap of 300 ppm by 2004. By 2006 the average sulfur content in gasoline will be no more than 30 ppm sulfur, with the cap reduced to 80 ppm. Whatever route a refinery chooses to control sulfur levels in gasoline, an increased load on the amine unit can be anticipated. Gas treating facilities will be pressed to ensure a more efficient and cost-effective operation.

Two major problems represent a significant threat to an amine gas treating plant: corrosion and instability of operation, resulting in unscheduled upsets and outages.

High corrosion rates, typical for a number of amine plants, as well as stress-corrosion cracking of stainless steel, usually attributed to chloride, create serious safety concerns. High corrosion leads to high repair costs, potential environmental implications, as well as lost production. The results of a survey conducted by the National Association of Corrosion Engineers (NACE) indicate, that 60% of total 24 amine plants surveyed experience stress-corrosion cracking in the amine absorbers [1]. A similar survey by the Japanese Petroleum Institute reported a 72% occurrence of cracking at amine gas treating facilities [1]. Carbon steel corrosion is often attributed to the amine contaminants which can not be stripped and thereby accumulate in the amine solution. However, preventive measures to reduce corrosion produce good results and improve amine unit reliability at a reasonable cost.

Inefficient and unstable amine unit operation is often a result of the accumulation of impurities in the amine circuit. These contaminants include metals from the unit equipment, specific ions that interfere with the absorption, amine degradation products and amine by-products in the form of heat stable salts. These heat stable amine salts in the solution reduce the amount of amine available for gas treatment, thereby reducing the unit's productivity. Heat stable salts (HSS) also cause corrosion problems and lead to a higher foaming tendency of the solution. Foaming in the absorber columns, higher amine losses, absorber tower pluggage, heat exchanger fouling, shortened amine filter life, and overall unit instability, which then cascades on to the refiner's sulfur plant are the common problems associated with HSS accumulation. Removal of the HSS from the circulating amine will help to improve the performance of the amine unit, decrease maintenance and filter replacement costs, and improve the plant's environmental compliance.

MEA thermal reclaimers were historically a part of amine plant equipment package, doing a good job of reducing the HSS level in amine solution. With the rapidly increasing use of modern, more selective and efficient amine formulations with higher boiling points it became impossible to keep reclaiming equipment on-site; and the industry immediately noticed an accumulation of impurities. The impact of contaminant accumulation is especially dramatic when a plant reduces amine losses. For the last several years amine plants have been making conscious attempts to control impurities, especially HSS. A number of measures have been proposed [2,3]. The most straightforward and least economical is amine purging, which is prohibitively expensive given the current situation of increasing competition and the struggle to reduce operating cost at refineries and gas plants.

Periodic amine clean-ups, either on-site or off-site, have proven to be a much better way of removing the impurities and are used by a number of amine plants. Ion exchange, vacuum distillation and electrodialysis have been applied to clean up amine solutions. However, periodic reclaiming, while providing a solution for HSS accumulation, does not cure 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-site reclaimer ensures that the contamination level is low, the corrosion rate is low and the performance of the amine system is at its maximum at all times. It also ensures that amine unit operation is reliable and provides the designed gas treating efficiency. Furthermore, if an upset occurs upstream of the amine unit (which is sometimes the case with tail gas amine units), the equipment is on-site to address the problem immediately.

## Eco-Tec's Recoflo Technology
### Recoflo concept

An approach suggested by Eco-Tec implements a novel ion-exchange technique called Reciprocating Flow Ion Exchange (Recoflo™) [4,5].

Recoflo, which has been extensively used since 1973 for the recovery of metals from metal finishing wastes [6,7], 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 keeping the resin inside the column under compression [8]. These features include:

- fine particle size resins;
- countercurrent regeneration;
- short column heights ( 3 to 24 inch);
- low resin loading;
- fast flows and short cycles.

Fully packed Recoflo resin beds were originally commercialized for chemical recovery and purification because of their unique ability to treat and produce very concentrated solutions.

Some of the applications that have been extensively exploited include:

- recovery of metal salts such as chromium, copper, nickel, cobalt and zinc from electroplating rinsewaters;
- removal of non-process elements from concentrated electroplating electrolytes;
- purification of metal pickling, etching and anodizing acids;
- recovery of sulfuric acid from metal refinery electrolyte bleeds.

The benefits of small size and low chemical consumption for water demineralization are also obvious. A Recoflo ion exchange demineralizer 6" in height does the same job as a 8 - 16 feet conventional column. In addition to a dramatic reduction in size, Recoflo demineralizers utilizes only about one half the regenerant chemicals of the conventional co-current ion exchange system and produce higher purity water [9].

## AmiPur - HeatStableSaltRemoval

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 capacity. A typical AmiPur unit is presented at Figure 1.

**Figure 1 Skid-mounted AmiPur unit, 60"x 60"x 86"**

**HSS removal capacity: 100 - 150 lb/day**

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

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.

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. 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.). 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.

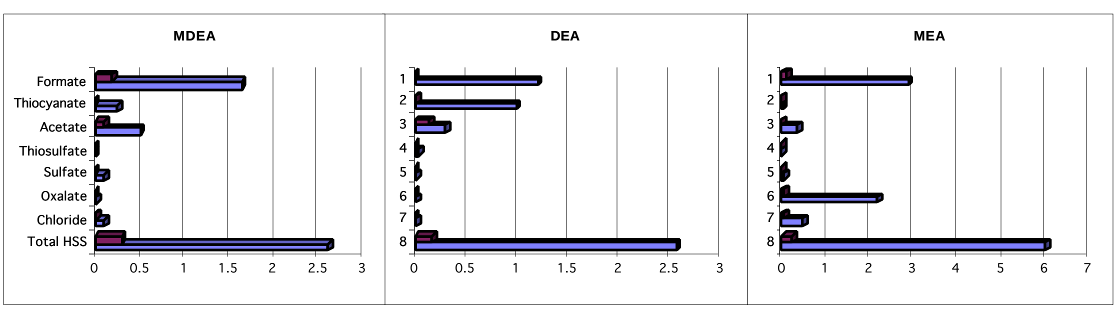



**Figure 2 Anion removal by AmiPur, Eco-Tec laboratory data**

# Case History: Crown Central Petroleum Corporation
# The Refinery's Amine System and the History of Amine Treating

Figures 3. - 6. (Appendix) show a generalized flow sheet for the refinery's primary amine system. The 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 filters, a slip stream amine reclaimer, and several associated pumps.

The main fuel gas absorber is a packed column with 2 beds of random packing and demister type separation at the top gas outlet. The lean amine feeds the top bed of packing through a distributor and flows down the column, contacting the sour fuel gas and removing the $H_2S$. The sour fuel gas enters the bottom of the column above the tower's rich amine liquid level. The tower's pressure drop is measured over the inlet gas line to outlet gas line, and this $\Delta P$ is used to monitor tower pluggage and foaming. A spare, standby absorber was installed to allow the refinery to wash the absorber while maintaining the refinery fuel gas system in compliance with federal environmental standards.

The liquid-liquid amine contactor is a trayed tower with 15 trays. This tower also serves as an amine surge tank, since about 80% of the amine unit's total inventory is kept in this tower. The tower is designed to remove about 1,000 ppm $H_2S$ from 21,000 BPD C3/C4 mix.

Figure 7. (Appendix) shows a generalized flow sheet of the Tail Gas Unit, with its amine system. MDEA is used at the present time in both of the amine systems.

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 tail gas treating amine system faces different challenge. Since the sulfur plant produces $SO_2$ as an intermediate product in the chemical reaction that converts the $H_2S$ to sulfur, any tail gas unit upset where this unconverted $SO_2$ contacts the amine, leads to HSS formation. This HSS then reduces the amine quality in the tail gas system, and may lead to some corrosion and absorber foaming, as well as affects the amine's ability to remove $H_2S$ at the low pressures of the tail gas unit. Once the amine solution degrades to form the HSS, the choices are to "bleed and feed" fresh amine by purging the back amine to the main system (assuming that you have the same amine in both treaters) or reclaim the solution. The "bleed and feed" method requires several iterations to reduce the HSS, so fresh amine make up rates will be high. This method will also increase HSS levels in the main amine system and increase operating levels in the front amine towers.

As HSS build, the amine filters plugged more frequently. Iron in the solution started to climb. Heat exchanger surfaces became fouled forcing the operator to increase the energy input to the unit's regenerator reboiler. Tower internals became fouled, increasing velocities and pressure drop to the point of increasing the overall amine losses. The amine solution itself started to "foam" more easily due to the increase of impurities in the solution, and any rapid changes in absorber feed rates caused amine carryover, amine losses, tower instability, potentially poor $H_2S$ treat, environmental non-compliance and sulfur plant upsets. Figures 8. and 9. (Appendix) demonstrate absorber instability and foaming experiences. Note the rapid increase in absorber pressure drop during the foaming incident.

### AmiPur Operation

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. Figure 10. shows the AmiPur installed at the Pasadena refinery.

The HSS in solution were at approximately 2.4 wt.% (as MDEA) when the AmiPur unit was started up, and within 30 days the HSS went down to less than 2 wt.%. Material that had been accumulated from the amine unit prior to installation and stored in a tank was then introduced back into the process. The HSS level in the solution increased back to 2.4 wt.% , as the 3.5 wt.% HSS material from the tank was brought in. The rented tank was then released; and the AmiPur unit brought the HSS level in solution back down to 2 wt.%.

By March 1999, after a unit shutdown for maintenance and a replacement of the amine regenerator tower, the HSS level was down to 1.75 wt.%. A significant decrease in the corrosion rate was observed. The ultimate goal of the refinery is to the keep 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. Figure 11. is the curve of the heat stable salt decline. Iron levels in solution also dropped significantly (Figure 12.). Corrosion probe readings, which have been as high as 160 mpy before, are now averaging less than 10 mpy.

**Figure 10**
**AmiPur installation at Crown Central Petroleum, Pasadena refinery**

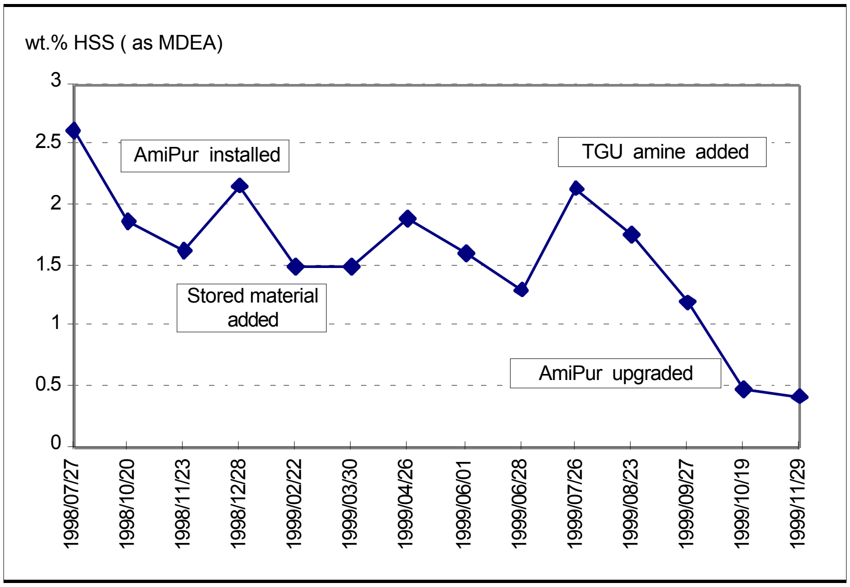



**Figure 11**
**HSS level at the main amine unit at CCPC Pasadena refinery**

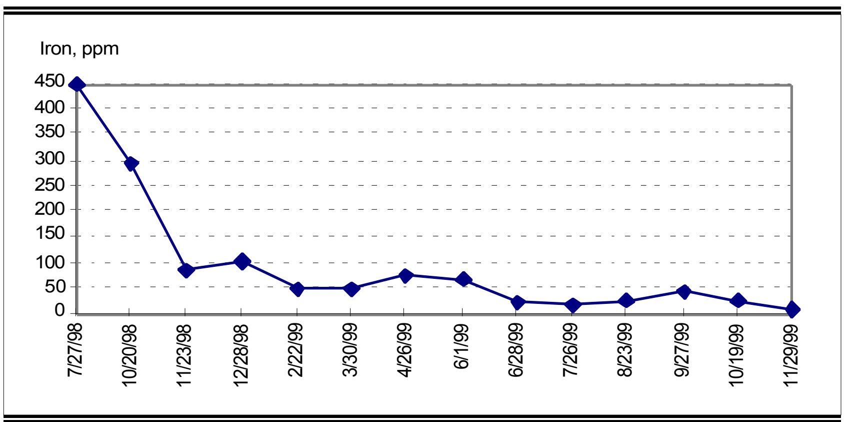
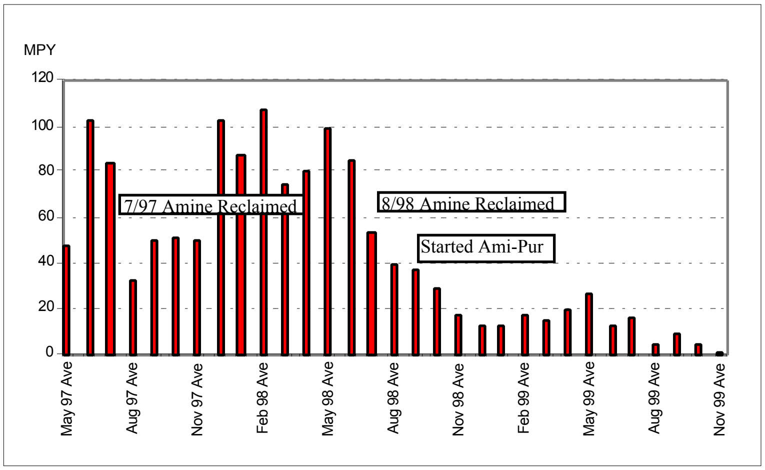



**Figure 12**
**Iron level at the main amine unit at CCPC Pasadena refinery**

The tail gas amine unit was also connected to the AmiPur unit in the summer of 1999 after an upset at the sulfur plant.

At first the refinery tried "bleed and feed" approach used before to control contamination level at tail gas unit by introducing almost 8 wt.% MDEA stream from TGU to mail amine system. Then it was decided to temporarily connect AmiPur to the TGU amine loop. With AmiPur was possible to return HSS levels in the tail unit back to normal within 5 days. Some studies indicate, that when HSS (thiosulfate especially) are left in the amine solution after a severe upset, significant increase in MDEA degradation rate can be observed [10]. The flexibility the AmiPur unit allows the removal of the HSS from tail gas amine systems on a campaign type approach and ensures better amine quality for optimal $H_2S$ selectivity.

The corrosivity of CCPC's main amine solution has been monitored since 1997 using an electrical resistance probe which is installed in the bottom of the main amine regenerator in the piping that connects the regenerator column to the thermosyphon reboiler. 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 Figures 13 and 14. The regenerator tower, built in 1978, was replaced in early 1999 due to t the shell's 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; and it was not unusual to get zero reading since the HSS level dropped below 1 wt.% as MDEA.



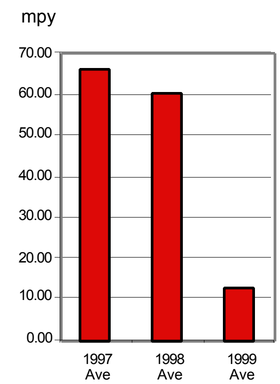




**Figure 14**
**Yearly average corrosion probe readings – 1997-1999**

**Figure 13**
**Monthly average corrosion probe readings -**
**Crown Central Petroleum Corp., May 1997 - November 1999 Yearly average corrosion**

### Benefits of Continuous HSS Removal

For an amine plant it is important to realize what benefits will be generated by installing an AmiPur; and what dollar values can be assigned to them.

It is usually difficult to justify an installation of equipment which will provide such benefits as "better, more reliable performance", "improved compliance with environmental / sulfur regulations" or even "reduction of amine losses due to absorber pluggage".

However, 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. These costs alone are usually sufficient to justify an AmiPur installation.

Table 1. provides an example for the Crown Central Petroleum case which may help in evaluating these benefits.

**Table 1**
**Benefits of AmiPur Installation at CCPC Pasadena Refinery**

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

| Item | Description | Benefit | Annual savings |
|---|---|---|---|
| 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 |

## Summary

A new ion exchange system, which is capable of removing anionic impurities from amine gas treating solutions - AmiPur - was developed and successfully proven. AmiPur is unique in that it utilizes an extremely small ion exchange column in a skid mounted, fully automatic, pre-assembled and pre-tested package. The small space requirement, high efficiency, low operating and capital costs make this system very attractive to the industry.

Installation of a continuously operating HSS reclaimer allows amine plants to ensure consistent reliable gas treating, improve performance of the unit, decrease maintenance cost and helps to ensure the plant's environmental compliance.

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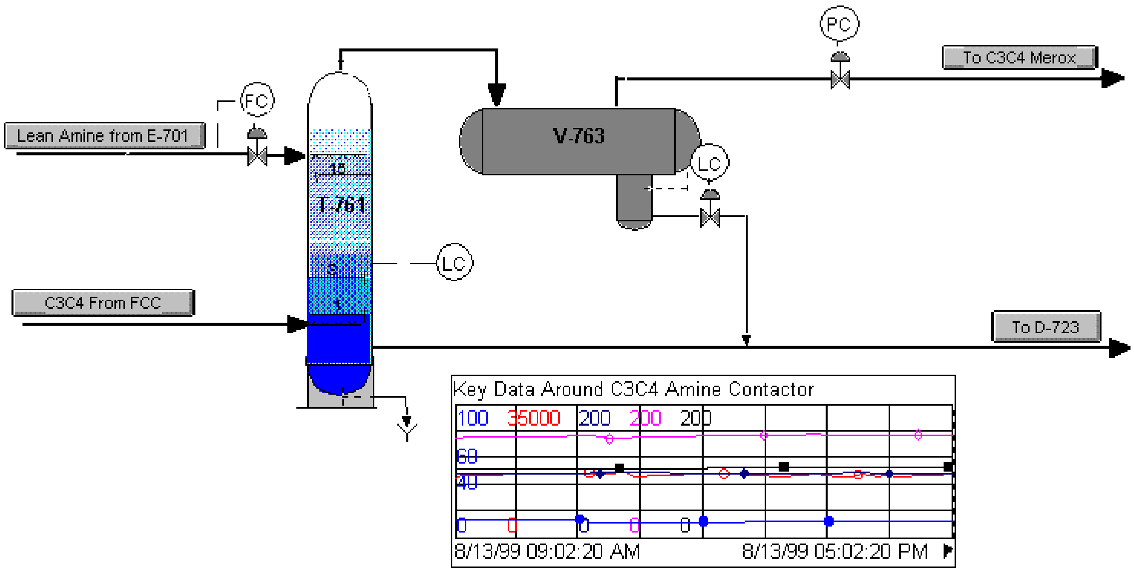


**Figure 3**
**Generalized flow sheet of SRU C3/C4 Amine Treaters**

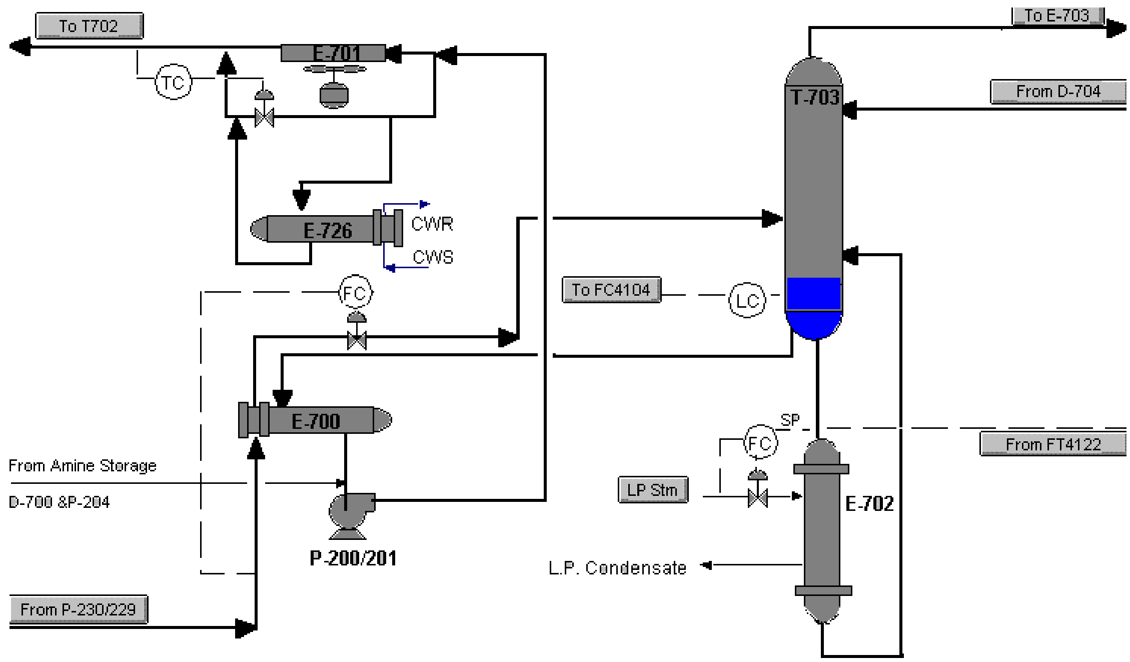


**Figure 4**
**Generalized flow sheet of SRU Amine Regeneration**

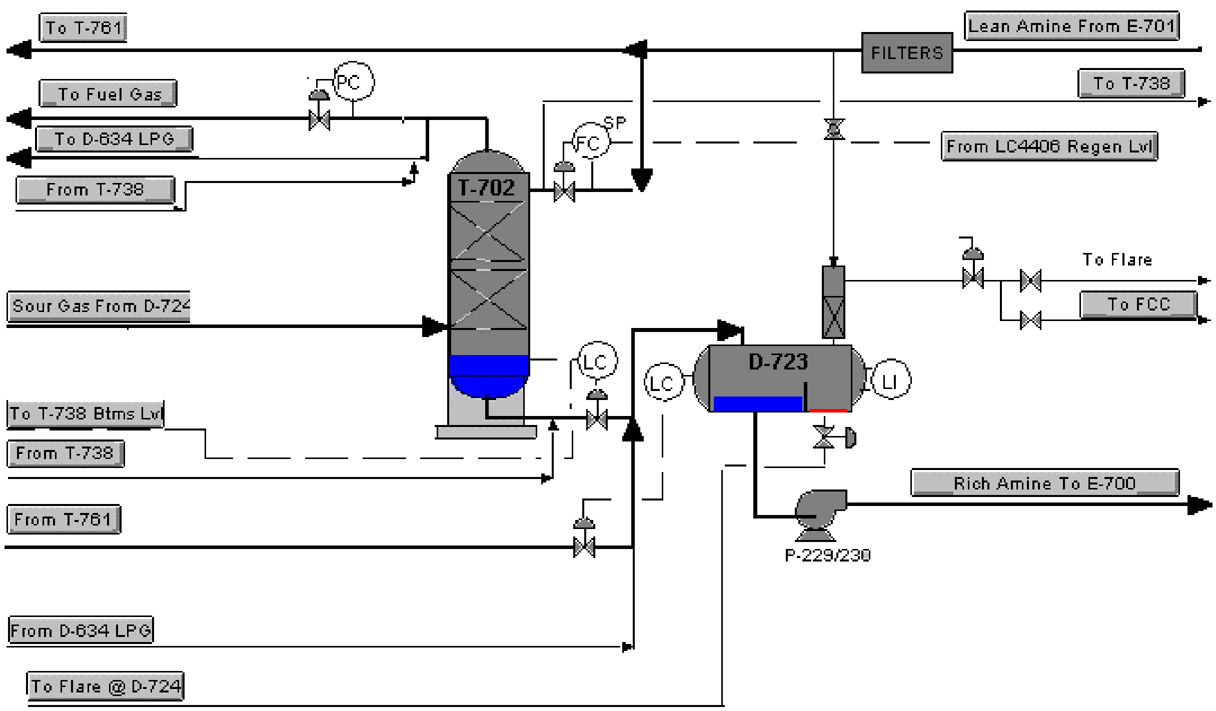


**Figure 5**
**SRU Sour Gas Treating, Crown Central Petroleum Corp.**

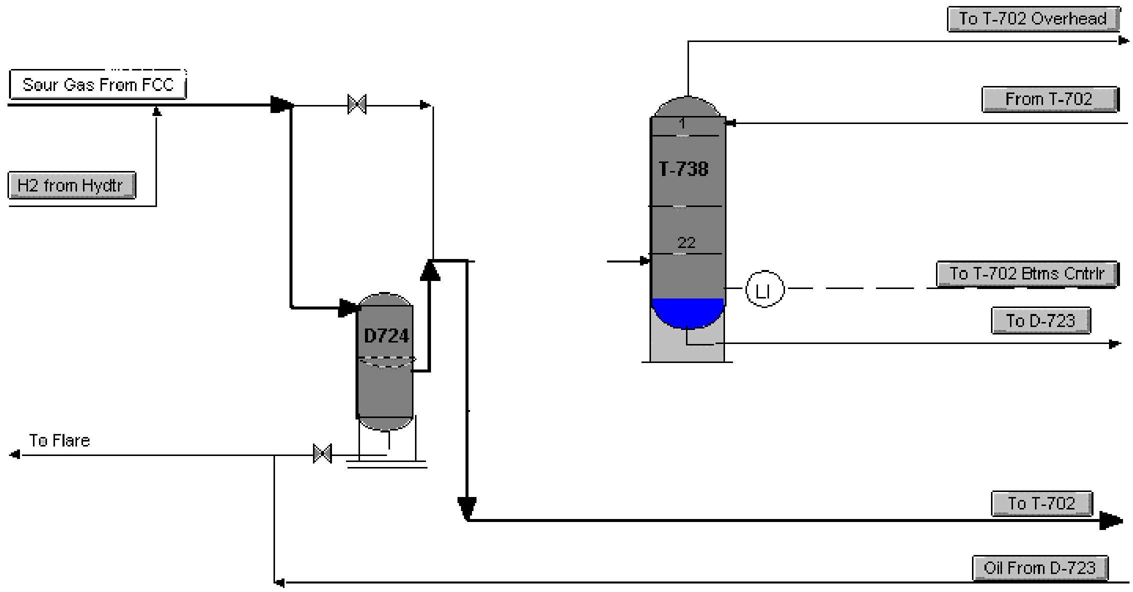


**Figure 6**
**Generalized flow of Feed Separator / AUX Contactor**

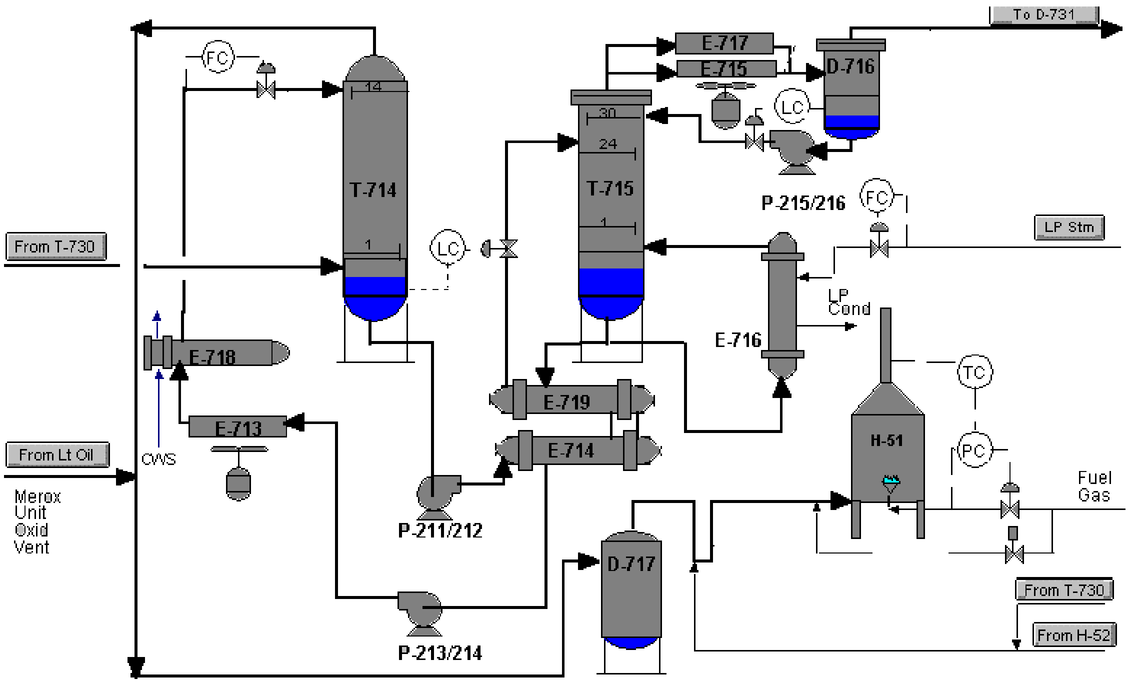


**Figure 7**
**Generalized flow sheet of SRU Scot Absorber and Regeneration Unit, Crown Central Petroleum**

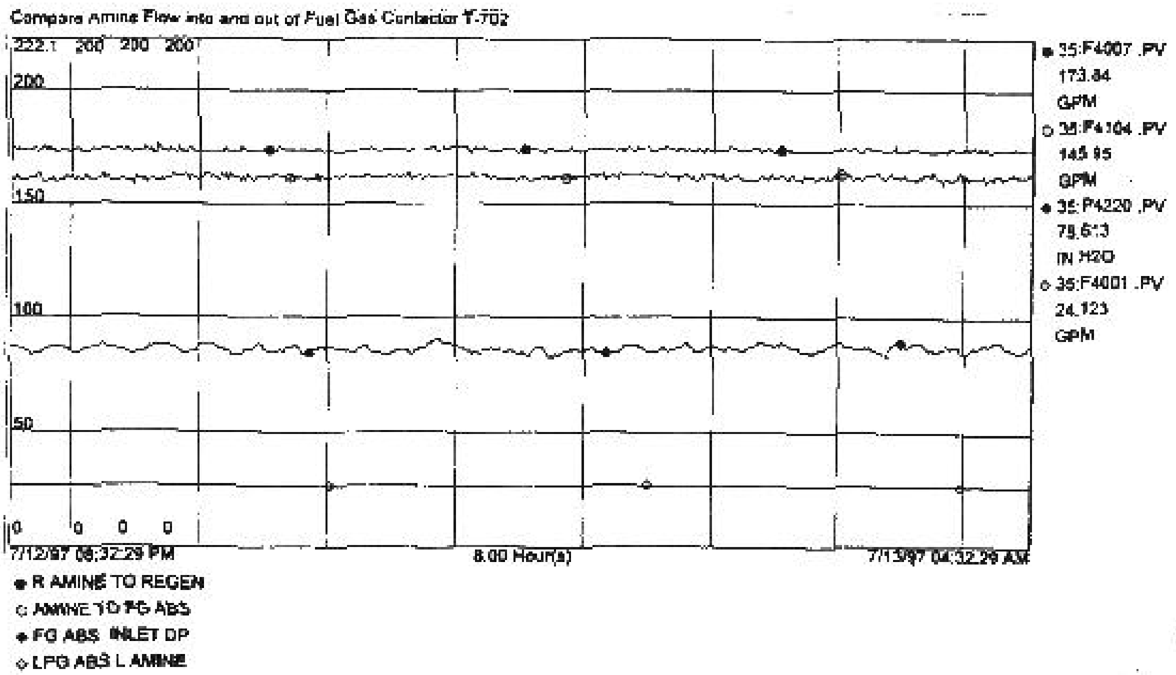


**Figure 8**
**Amine flow, Crown Central Petroleum Pasadena Refinery, 7/12/97**

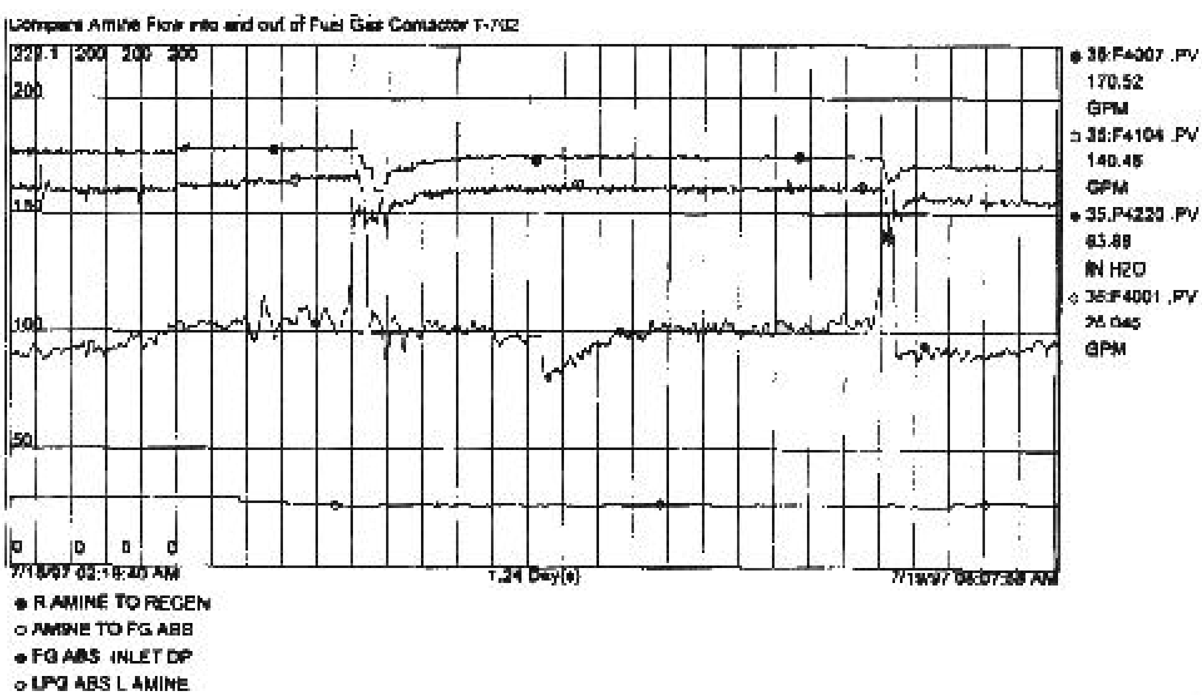


**Figure 9**
**Amine flow, Crown Central Petroleum Pasadena Refinery, 7/18/97**