The Reclaimer

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Volume 3

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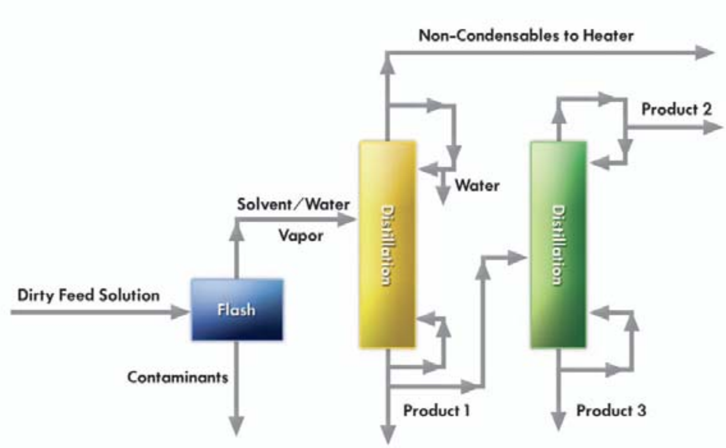
Are You Maximizing Your Solvent Performance?

CCR Technologies is an environmental services company that provides specialized on-site chemical reclamation services. Our proprietary mobile units are designed to meet the unique needs of refineries, gas plants and petrochemical plants that use alkanolamine and/or glycol chemical absorption processes. Our purification units comes to your site where it custom cleans your solvent by removing impurities and regenerating a high quality solution for reuse. The benefits of the CCR process include:

- Improved process capacity
- Elimination of foaming upsets
- Minimized corrosion
- Increased equipment lifetimes
- Reduced maintenance costs
- Reduced circulation rates
- Reduced energy costs
- Elimination of high disposal and replacement costs
- Significantly reduced environmental costs



The patented CCR Process

CCR has provided innovative reclamation services since 1987. Our proprietary technologies are unique to the industry, using vacuum distillation to purify virtually any gas treating solvent. Our specialized, mobile purification units are adapted for simple system tie-in and perform all remediation on-site. Contamination problems can be solved either on-line or in batch mode, thus greatly reducing transportation and waste disposal costs. Our technology provides an environmentally safe and cost effective solution to your contamination problems. With clean chemical solution, your production capabilities are enhanced and processing costs are reduced.

Technology: Glycol Injection and Regeneration for Hydrate Control in Subsea Flowlines

The formation of hydrates in natural gas may be inhibited by the injection of glycols or methanol. Glycols have low volatility and are easily separated from liquid hydrocarbons and from the water they absorb. They allow continuous hydrate control in plant and pipelines that have suitable regeneration and reclamation equipment. Monoethylene, diethylene and triethylene glycols have all been used for injection for hydrate inhibition purposes. The most popular is monoethylene glycol (MEG) because of its lower cost and somewhat superior operating characteristics.

In subsea developments there is the potential to produce formation water, with no opportunity to remove this produced water prior to injecting the hydrate inhibitor. The hydrate inhibitor mixes with the formation water and its associated salts. In a conventional glycol regenerator these salts are not removed. Over time, they will build up to the point where they will deposit on process equipment and cause accelerated corrosion in topside equipment and subsea pipelines.

Conventional regeneration of glycols at elevated pressures involves reboiling at an appropriate temperature with a heating medium that will concentrate the glycol to its original level for reuse as a hydrate inhibitor. However, the higher temperatures required to do this regeneration can cause thermal degradation of the glycols that can reduce its effectiveness. In

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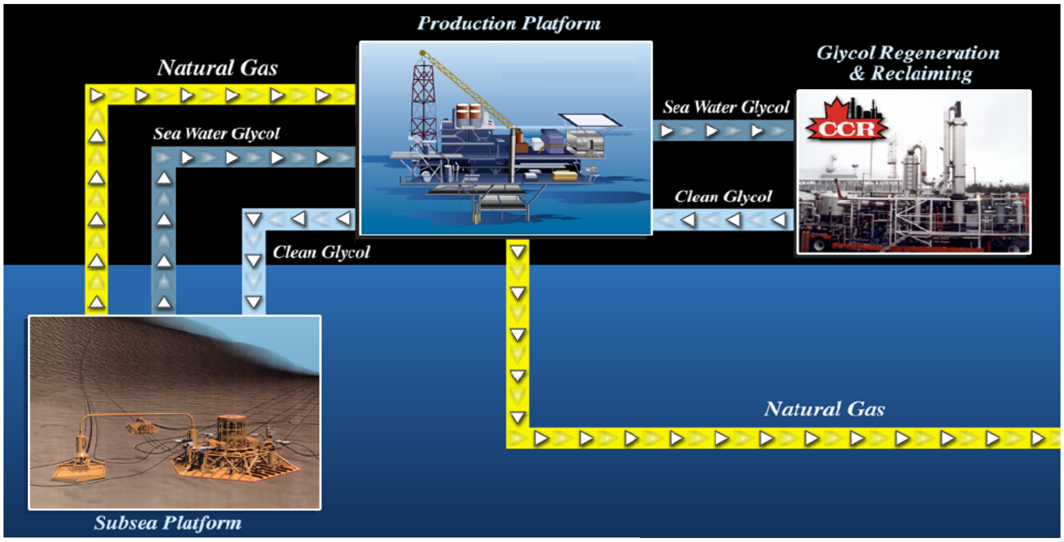

(Continued., Glycol Injection)

addition, as the water is removed the salts remain in the glycol, eventually increasing to unmanageable levels.

Reclamation by means of vacuum distillation has been used to attempt to reduce reboiler temperatures, but thermal degradation and solids deposition still occur. Although the bulk fluid temperature is kept low enough to avoid thermal degradation, static type reclaimers develop elevated film temperatures with long residence times. Not only does thermal degradation lower the solvent effectiveness leading to revenue losses, but the amount of waste generated increases thereby increasing waste disposal costs. Over time, solids deposits can occur along the external surface and the reboiler tubes, negatively affecting heat transfer efficiencies. The reboiler tubes will need to be removed and cleaned. In most instances, reboiler fouling leads to localized corrosion due to hot spots developing on the tube bundle, which can lead to damage and premature replacement. By avoiding solids deposition, costly down time and maintenance can be avoided.

To avoid these problems associated with ordinary reclaimer design, CCR's process utilizes a proprietary vacuum distillation process with a novel heater design. With the patented CCR design, elevated film temperature and long residence times do not occur. In addition, this technique generates a very small waste volume. Typically, the waste stream consist of just the contaminants left behind when the glycol is vaporized, with just enough glycol left to maintain the fluidity of the material for disposal handling. Salts from formation water, pipeline corrosion products and other well treatment chemicals will be removed as part of this waste stream.

Reclaimer for KMG Red Hawk in the Gulf of Mexico. The first floating cell-spar design

Frequently Asked Customer Questions

Why reclaim our amine solution?

Contamination is the major cause of operating problems in amine systems. Foaming, corrosion and degradation can severely impair the amine's ability to absorb acid gases, and may cause mechanical failures. Contaminants can have significant effects on the reliability and cost of the amine unit operation, including off-spec treated gas, upsets to other processing units, amine losses, equipment maintenance problems, more frequent filter changes and increased regenerator heat input.

In order to optimize the amine until it is necessary to have clean, functioning amine.

Operators of clean amine solutions experience the following:

- Treated gas consistently on-spec
- High quality acid gas to SRU with no upsets caused to the sulfur plant
- Low amine losses
- Low corrosion
- High reliability - mechanical and processing
- No unscheduled downtime
- Operating goals met at minimum cost

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One of CCR's processing trailers in action

(Continued., Frequently Asked Questions)

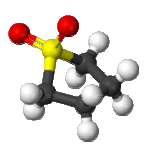
What indicators tell me that reclamation needs to be considered?

Laboratory analysis of amine solutions can highlight a wide variety of contamination and degradation problems that can be rectified by reclaiming. Simple visual inspection of the amine may reveal discoloration or the presence of particulates or hydrocarbons. There are also numerous operational indicators that may point to a need to reclaim:

- Foaming
- Fouling
- Corrosion
- Loss of Absorption Capacity
- High Amine Losses
- High Energy Input
- Frequent Filter Changes
- Environmental Non-Compliance
- Off-Spec Gas
- Unstable Operations

Case Study: Reclaiming Sulfolane

The technology employed on CCR Technologies' mobile processing units is the distinctive attribute which allows us to offer our customers the capability and on-site flexibility to effectively reclaim a broad variety of process solvents found in most refineries and gas plants. However, the technology itself is only half the story. Our mobile unit supervisors and operators know how to maximize the utility of our processing equipment and distillation columns so that customer expectations are met or exceeded. In turn, the results produce products of both the highest purity and the highest yields. There is no better example than Sulfolane (tetrahydrothiophene 1,1-dioxide) to exemplify the importance of high purity and yields. This expensive solvent serves a critical function in the overall efficiency of BTX plants, and CCR Technologies is in the unique position to offer our customers what they want – i.e., the ability to effectively reclaim Sulfolane.



$CH_2CH_2CH_2CH_2SO_2$

Sulfolane's role as an efficient BTX extraction solvent is well-documented for both liquid/liquid solvent extraction (LLE) and extractive distillation (ED). Sulfolane's very low solvent-to-feed ratio from most any reformate feedstock makes this solvent a highly valuable commodity in a refinery's supply chain for the production of high-purity aromatics. But at some point, the Sulfolane will break down into acetic byproducts. The loss of solvent efficiency will directly impact the value of the BTX streams. For example, reduced purity of a BTX product could cause it to be off-graded and affect financial performance of the BTX unit. A number of measures have been developed to remove these byproducts, allowing the Sulfolane to be reused and increase the lifetime of a given supply. Some methods that have been developed to regenerate spent Sulfolane include vacuum and steam distillation, back extraction, adsorption, and anion-cation exchange resin columns.

Modern Aromatics Complex with BTX-Sulfolane Unit

If your spent Sulfolane is contaminated with more than just ionic salts, CCR's proprietary vacuum distillation is the technology-of-choice which will allow effective removal of all Sulfolane solvent contaminants, including particulates and hydrocarbons which will compromise the efficiency of your aromatics complex. And remember – CCR processing of Sulfolane can be performed on-site via a slip stream so that operations can continue without interruption and so reclaiming results are immediate. Sometimes, it is just not possible to wait for the next turnaround of your Sulfolane unit. If the Sulfolane contamination becomes extensive, the unit may even shut down before the turnaround.

Historically, CCR has achieved Sulfolane recovery yields over 95% with minimal waste for disposal. CCR recently completed a Sulfolane reclamation at a large Gulf Coast refinery. The sulfolane was contaminated with acid salts, hydrocarbons and residues. The quality of the Sulfolane solvent significantly diminished unit responsiveness. Contaminants in the Sulfolane created a need for equipment repair during the turnaround. CCR was called in to perform an on-site, batch processing of the Sulfolane. The results were as follows:

Contaminant	Start	Conclusion
Acid Loading	0.183%	Below detectable limits
Hydrocarbons	3.5%	Below detectable limits
Residues	0.5%	0.02%

Sulfolane is also one of the components used in the Sulfinol® Gas Treatment Process. This process, licensed by Shell, purifies acidic or sour gas streams by removing sulfur compounds and carbon dioxide to provide gas to meet commercial specifications. Sulfolane is blended with water and amines to provide blends for use in the Sulfinol Processes. CCR is also able to effectively reclaim Sulfinol-D and Sulfinol-M.

Perspective: How CCR Works with Clients for Engineered Systems

CCR's engineered reclaiming systems business designs and provides operating support for permanent chemical reclaiming units for clients that include refineries, LNG plants, offshore gas production plants and, more recently, pilot CO_2 capture projects that utilize amine solvents. Recently, there has been strong client interest for what we like to call *CCR's Proprietary Package*. Such a package includes:

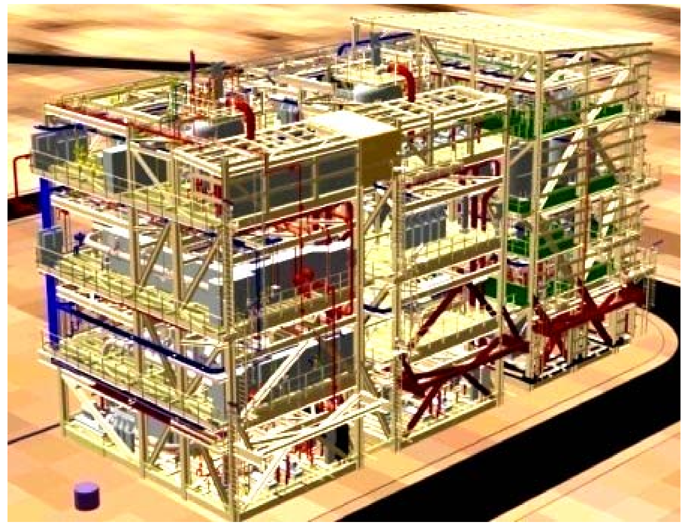
- The FEED study including all proprietary engineering (process engineering package). This is typically done in collaboration with a strong third-party engineering partner of the client's choice
- Proprietary procurement management or support for selected pieces of equipment
- Supervision and support of detailed engineering as required
- A full CCR technology license.

In such an arrangement, detailed engineering is done by a strong third-party engineering firm of the client's choice. CCR will provide all the support required to ensure successful execution of the project. Fabrication will also be done by strong third-party fabricators of the client's choice. Overall project management and procurement management can be provided by CCR, by the lead engineering firm or another third-party of the client's choice.

Of course, other arrangements are possible ranging from complete turnkey solutions to the provision of technology licenses.

In addition, depending on the client's needs, CCR Technologies can also provide:

- Supervision of installation
- Testing of the unit
- Commissioning support
- Operator training (incl. training materials in local language)
- Development of computer-based simulation packages
- Ongoing operating support for optimization and trouble shooting (including emergency backup support with CCR mobile units).



Above: 3D model of a large reclaimer for an LNG

CCR Technologies is the only company that designs reclaimers and also operates them. During our more than 20 years of experience operating reclaimers in over 600 projects for more than 80 clients worldwide, we have accumulated a wealth of experience for reclaimer design and operations that make a big difference for our clients.

Technology: Using Biotechnology to Remove Hydrogen Sulfide from Gas Streams

The Shell-Paques biological gas desulphurization process is the most environmentally friendly mid-range hydrogen sulfide (H_2S) removal solution for gas streams. CCR Technologies has a license to market the Paques technology from Shell and has significant process know-how in its application.

The Shell-Paques process integrates gas purification with sulphur recovery in one process unit. H_2S removal efficiencies above 99.8% can be reliably achieved, and treated gas can contain less than 4 ppm of H_2S. The technology has been developed by Shell Global Solutions International BV and Paques BV.

The technology avoids many of the typical challenges associated with redox chemistry through the completely non-fouling or hydrophilic nature of the created bio-sulphur. The process is ideally suited to sensitive locations where flaring or incineration is undesirable. Its application ranges from 0.1 to 50 tons per day of sulphur per train. There are potential capital and operating cost advantages over regular redox processes for most new and facility-retrofit applications.

There are several process applications, including:

- Natural gas (direct treatment) within the pressure range of 0.1 to 90 bar
- Amine regenerator acid gas, refinery of chemical plant gases
- Synthesis gas
- Fuel gas
- Low-pressure and associated gas
- Oxygen containing waste gases that cannot be successfully treated with other solvents.

Above: The thiobacillus are naturally occurring. The yellow and red zones at a hot spring in Yellowstone National Park are large populations of thermal-tolerant thiobacilli oxidizing reduced sulfur and iron in the water.

In this process, a gas stream containing H_2S contacts a aqueous soda solution containing sulphur bacteria (thiobacillus) in an absorber. The soda absorbs the H_2S and is then transferred to a regenerator consisting of an aerated atmospheric tank where hydrogen sulfide is biologically converted to elemental sulphur. Sulphur may be recovered as a moist filter cake or as pure liquid sulphur.

Chemistry: MEA Reclaiming

Monoethanolamine (MEA) was introduced to the industry as one of the first amines used extensively in gas treating service. MEA is very popular in refinery gas/liquid treating service and has many advantages that some of the newer amines introduced into the industry have not been able to match. MEA removes both H_2S and CO_2 and is very reactive towards COS, all of which are of concern in refinery combined treating systems. Another advantage of MEA is the fact that due to its low boiling point, slipstream thermal reclaiming may be employed.

This has proven to be beneficial in refinery service where HSS accumulation and MEA degradation have been issues. Due to more stringent disposal considerations for reclaimer bottoms and efforts to minimize amine consumption, there has been focus on improving reclaiming options. There are currently several alternatives to conventional thermal reclaimers used by refiners, and it is important to understand fully the chemistry involved in these systems, and how each merchant reclaiming technology affects these chemical compounds.

Heat Stable Salts

Heat Stable Salts (HSS) have received a lot of attention in the industry. HSS are acid anions with a stronger acid strength than the acid gases that are removed from the process gas. These anions bind to the usable amine (in this case MEA) making the MEA unavailable for acid gas absorption. The industry has agreed that these HSS anions also raise the corrosive nature of the solvent, so they must be controlled to assure unit reliability. All available amine-reclaiming options are able to remove HSS anions in batch mode or while processing a slipstream of the circulating solution. While the industry has focused heavily on this issue lately, it is important to remember that HSS anions are not the only contaminants that must be removed from solution.

Formamides

N-formyl amines (formamides) are generally found in gas treating solutions that are based on primary (MEA and DGA®) and secondary (DEA) amines. Under certain conditions primary and secondary amines react with the formic acid in solution (via dehydration) to form n-formyl amines. For the rest of the discussion we will focus only on n-formyl MEA (also called MEA-F).

The data from process solutions containing formate as a Heat Stable Salt (HSS) anion shows that there is an equilibrium relationship that exists between the amount of formate HSS in solution and the amount of MEA-F in solution. See the equation below.

Formic Acid + MEA <=> MEA-F + Water

Since the above equation represents equilibrium, it is then possible to also hydrolyze MEA-F back to MEA and formic acid. The heat and water content both present in the stripper of the amine unit will generate a new equilibrium if the balance of the equation is disturbed by removing one of the above components. If a slipstream of the circulating solution is processed while the unit is on line, it is then possible to remove a portion the MEA-F from solution *indirectly* by removing the formate anion and disturbing the above equilibrium. This removal mechanism takes place regardless of which reclaiming technology - ion exchange, electrodialysis, or vacuum distillation - is used. However, vacuum distillation is the only process able to directly remove both the formate anion and the MEA-F.

If the MEA solution is reclaimed in batch mode (tank to tank) rather than processing a slipstream of solution while on line, it necessary to understand what happens to the MEA-F in solution. If ion exchange or electrodialysis is employed to remove the formate anion (since these processes only remove ions), the MEA-F remains in solution. The remaining MEA-F will then “liberate” a formate anion to re-establish equilibrium when the treated solution is returned to the circulating solution. However, using vacuum distillation to process in a batch mode, the formate and the MEA-F will be removed since the process achieves complete removal on a per pass basis.

HEED

Hydroxyethylethylenediamine (HEED) is a well-known degradation product of MEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of HEED. While much of the literature has focused on MEA in CO_2 service only, HEED has been found in combined refinery systems treating H_2S and CO_2. While it may not be the main degradation product in refinery amine systems, it must be monitored and removed from the system due to its corrosive nature. Vacuum distillation is the only merchant reclaiming technology that is able to remove HEED.

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HEEU

Hydroxyethylethyleneurea (HEEU) is a degradation product of MEA that is not that well known since most of the literature has focused on degradation in CO_2 service. HEEU is formed via the same reaction pathway as HEED when COS is present in the gas. COS is generally present in combined refinery treating systems where FCC, Coker and other cracking/conversion units are employed in the plant configuration. HEEU has been found to be one of the main degradation products in refinery amine systems. Vacuum distillation is the only merchant reclaiming technology that is able to remove HEED.

Polymeric Material

Under certain high temperature conditions in the presence of HSS, it has generally been agreed upon that MEA forms high boiling point polymeric material. It is also possible that HEED may continue to degrade in the presence of CO_2 to form longer substituted ethlyenediamines, which may also then be characterized as a polymeric material. Vacuum distillation is the only merchant reclaiming technology that is able to remove these polymeric materials.

The Importance of Total Solvent Quality Control

While HSS anions (and to some extent strong base cations such as sodium or potassium) have received much industry attention due to their adverse affects on amine solvent quality, it is important to understand there are likely to be many other contaminants in an amine system. Degradation products reduce the activity of solution, but since they often titrate as amine, their presence may go undetected leaving a refiner to think the amine solution is stronger than it really is, creating an amine deficiency. As more amine is added to compensate for reduced solution activity, the physical properties of the solvent are affected by reducing the water content of the circulating solution. Water content probably has the greatest affect on the physical properties of the solvent, such as viscosity. A higher viscosity will lower mass transfer rates and decrease acid gas removal efficiency. A higher viscosity may also increase amine losses in liquid treating service. While these are only two effects of a change in physical properties of the circulating solution, others must be considered when plants are not running optimally.

When evaluating merchant reclaiming options, remember that heat stable salts are not the only issue, and may not even be the biggest issue.

Meet the CCR Business Development Team

With over 600 reclamation projects for over 80 customers, CCR Technologies has demonstrated its unique ability to offer custom-tailored solutions to reclaiming challenges anywhere in the world – on-land or off-shore.

If you have any needs, questions or comments regarding CCR's mobile reclaiming services or our engineered reclaiming systems, please contact any of our business development managers.

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