Introduction to Solvent Reclaiming .... the CCR Way

CCR Technologies Ltd. is a public company with shares traded on the Toronto Stock Exchange and has offices in Calgary, Alberta and Houston, Texas. CCR Technologies was founded in 1987. Our company owns a series of patents and has twenty years experience operating continuous vacuum distillation technology. We apply this technology in two primary lines of business:

- Our mobile reclaiming services business uses four high capacity (400 – 500 gph) mobile units to provide chemical reclaiming services to oil, gas and chemicals companies around the world, with a principal focus on amine and glycol reclaimation.
- Our engineered reclaiming systems business designs and provides operating support for permanent chemical reclaiming units for clients that include refineries, LNG and other offshore gas production plants, and, more recently, pilot CO2-capture projects that utilize amine solvents.

CCR’s patented, vacuum distillation technology is state-of-the-art. The CCR approach is unique as it is the only process capable of removing virtually all the contaminants found in gas treatment chemicals in a single pass through the reclaiming unit without fouling or degrading the solvent. The process assures the high solution purity necessary for optimal plant operation.

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Perspective: In Operations Mode for Our Customers

Pete Graham, CCR’s Vice-President of Operations & Human Resources, has over 30 years management experience in petrochemical processing plants across both North America and Europe. His mantra is to always view things from the customers’ perspective, understanding the responsibilities and concerns they are charged with as operators. Pete says: “CCR developed the mobile processing concept over 20 years ago. While we have evolved with our customers to meet and exceed rising safety, environmental and other operating requirements, one thing has not changed: Our commitment to great quality and our flexible, no-hassle approach to reclaiming valuable solvents. This is what keeps our customers coming back to CCR”.

Pete’s mobile unit team leaders and team members are experienced, skilled, and trained to interact with our clients so that CCR performs above clients’ expectations and exceeds their safety and environmental mandates. Our operators have a broad experience base with different facilities in North America and the Middle East. Pete says: “It’s all about agreeing on a set of expectations, and then delivering a quality project every time.”

For a typical reclaiming project with a CCR mobile unit at a refinery or gas plant, the sequence of events is as follows: An on-site project planning meeting will be held in advance of the CCR mobile processing unit’s arrival. We identify the site where the customer would like the CCR mobile processing unit located, and outline specific plans for process, residue, and utility connections. We agree on the appropriate communication and reporting protocols, as well as analytical testing procedures.

The CCR team will begin their set up at the site as soon as they arrive on the premises. The crew will require approximately 20 hours setting up and completing the tasks agreed upon at the project planning meeting. The customer usually provides a suitable hookup for the treated solution, such as a surge tank, as well as a tank for the contaminants. The first important step of our reclaimation process is to send an initial sample of the solution to our independent laboratory to establish the exact starting levels of contaminants.

The CCR crew then begins processing the contaminated solution and continues for as long as is required to meet the customer’s objectives for contaminant reduction. At regular intervals during the processing stage, CCR will have an independent laboratory test the solution to establish precise contaminant levels. Once we have processed the solution to the customer’s satisfaction, the CCR crew will disconnect, flush, and rig down the mobile unit, which will take about 20 hours over two days, and remove the mobile unit from the site.

The results are a solvent that is as good as new and significant cost savings compared to buying new chemicals.
Product recoveries are as high as 95 - 99%. The key differentiator of the CCR process is the ability to remove all major groups of impurities regardless of the nature or concentration of impurities in the contaminated feed solution.

Reclamation of amines

Refinery, gas plant and CO₂ capture amine systems are highly likely to experience contamination problems at some point in time. If ignored for too long, these problems can become serious issues leading to increased utility consumption, significantly reduced acid gas stripping capacity and even system upsets with off-spec products and unscheduled shutdowns.

But what is an amine contaminant? It is really anything that is not amine or water (and potentially corrosion inhibitor and antifoam). The contaminants compromise the acid gas stripping efficiency of your amine system. Some of the potential amine contaminants include heat stable amine salts, amine degradation products created through heat or oxidation, byproducts caused by chemical reaction with incoming gas components, plus other non-volatile particulates like metals, dirt or scale.

There are several amine management methods available to deal with contaminated amines including complete dump and replace, bleed and feed, or reclamation with ion exchange, membrane or vacuum distillation technologies. With rising amine prices and growing disposal costs, the dump and replace and bleed and feeds methods are becoming increasingly cost-prohibitive. This typically leaves reclamation as the most cost-effective method.

All reclamation technologies – ion exchange resins, electrodialysis membranes and thermal vacuum distillation – can effectively remove moderate amounts of Heat Stable Salt (HSS) contamination. However, only vacuum distillation is able to remove non-HSS, i.e., non-ionized impurities. In addition, if salt levels are high, the ion exchange process produces large amounts of waste water. This is not the case for vacuum distillation.

Only CCR Technologies’ patented vacuum distillation process will remove virtually all amine contaminants regardless of their concentrations, while producing a minimal and highly concentrated waste stream. This is the case whether the amine reclamation is performed with one of our mobile processing units or with one of our permanent installations.

Reclamation of glycols

Glycols are used for hydrate inhibition in subsea flow lines from offshore gas fields, for gas dehydration in gas plants, as well as for airplane de-icing agents and windshield washer fluids. The prices for glycols increased significantly in recent years, making effective reclamation the critical factor for the cost-efficiency of these applications.

Different from amines, the reclamation of glycols involves removing the water in the feed. But just like amines, glycol quality can be affected by decomposition and contamination. Glycol contaminants may be liquids or solids entering with the inlet gas or as corrosion products produced in the process. Deposition can be caused by excessive heat or oxidation and can be accelerated by low pH created by the degradation byproducts.

Salts, entering with entrained water, are not removed with the stripped water, but instead accumulate until they reach saturation limits causing deposition on hot surfaces of the solvent regeneration system. Liquid hydrocarbons can also enter with the inlet gas or condense in the absorber and cause foaming. At times, black solids and sludge that is suspended in the circulating glycol can be visually observed. These sticky and abrasive materials can cause erosion of pumps, valves, and other equipment and fouling of the absorber or stripper trays.

Particulate filters and activated carbon filters can effectively remove certain sized solid particles, various hydrocarbons, some chemical additives plus other impurities. But only CCR’s vacuum distillation process can effectively remove all the impurities, including the many other miscible liquids that cannot be separated through filtration alone. Likewise, glycol systems contaminated by amine carryover, especially if excessive, will require vacuum distillation to adequately maintain glycol performance.

Again, only CCR Technologies’ patented vacuum distillation process will remove virtually all contaminants regardless of their concentrations and produce only a small concentrated waste stream. This is the case whether the glycol reclamation is performed with one of our mobile processing units or with one of our permanent installations.

Case Study: Serving Egypt– Processing Glycols on the Mediterranean

The Idku gas hub in Egypt is a major contributor to the country’s export revenues as well as domestic energy needs. The plant is using Monoethylene Glycol (MEG) for hydrate inhibition in its subsea flow lines in the Mediterranean Sea. Over fifteen months ago, the plant had an urgent need for reclamation of glycol that comes onshore at Idku. CCR responded by shipping two of its mobile units to North Africa, where they continue to be stationed.

This has been the most challenging glycol reclamation CCR had undertaken thus far. The feed contains low percentages of glycol (20 wt% or lower) and lots of salts, sand, hydrocarbons and even Methanol. Because of close collaboration with the client, the CCR Team used a lot of adaptation, optimization and all our accumulated knowledge from 20 years of operating experience to be able to reclaim large amounts of the glycol used by the plant. The effort was well worth it, and our continuous improvement efforts have resulted in an increased quality and volume of the glycol we deliver to the client. The economic benefits of reclaiming vs. the purchase of new glycol are significant for the client. As a result, it is very likely that some of CCR’s mobile units will be processing on the shores of the Mediterranean Sea for another few years until new permanent equipment becomes operational.

We at CCR are proud to make a small but important contribution to the Egyptian economy.
The Reclaimer

Case Study: CCR’s Technology Above the Arctic Circle

After 5 years of development, Statoil’s Hammerfest LNG facility began production of the Snohvit gas field in late 2007. This Arctic field rests at the bottom of the Barents Sea, approximately 145 kilometers off the northern-most coast of Norway, with depths reaching over 300 meters.

In a very inhospitable climate, the vast reserves of the Snohvit field were originally considered unattainable due to the enormous expenses associated with traditional methods of offshore exploration and production. Statoil found their solution by placing the production equipment on the seafloor with an extensive network of pipes to connect the wells to the processing facility on the island of Melkoya off the coast of Hammerfest. It was clear early on in the project that effective hydrate risk management was going to be key for operational success.

Statoil chose CCR Technologies to provide the two MEG reclaimers for their plant. CCR was able to draw on 20 years operating experience reclaiming glycols as well as our application base from three previous off-shore reclaiming units constructed in the Gulf of Mexico utilizing CCR technology to come up with the optimal design for Statoil. The Statoil plant at Hammerfest is the northern-most LNG facility in the world with the largest glycol regeneration and reclamation capacity.

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Frequently Asked Customer Questions

“How much waste is generated, and what do I do with it?”
The volume of residual waste is dependent on actual contaminant levels. However, typical volumes are less than 5% of the volume on a water free basis. Although the waste generated is highly concentrated and can be drummed and disposed of as solid waste, this material is usually discharged to tanks where it can be quenched and subsequently bled to the waste effluent system.

Technology: Carbon Capture and CCR Technologies

Carbon Capture and Storage (CCS) is an approach to mitigate global warming by capturing carbon dioxide (CO₂) from large point sources such as fossil fuel power plants and storing it instead of releasing it into the atmosphere. When capturing CO₂ from a typical air-fired combustion unit after the burning process has taken place, it is referred to as post-combustion capture. Post-combustion systems can be tagged-on to existing facilities, e.g. power plants or industrial facilities that use conventional process heaters and industrial utility boilers. The disadvantage of these systems is that typical flue gas streams have CO₂ concentrations of 20% or less. Although the CO₂ can be separated using membranes or cryogenics, these are costly endeavours, and only absorption using chemical solvents - typically amines - is viable and proven today.

One of the key success factors for economically viable use of amine for CO₂ absorption is a state-of-the art process for amine reclamation with effective removal of contaminants, high recovery rates and efficient energy use. CCR has been removing contaminants from a wide variety of amine solutions, including MEA, DEA, MDEA, SULFINOL, UCARSOL, FLEXSORB, and many others, for over 20 years. The CCR process uses vacuum distillation technology combined with a novel heating scheme to remove virtually all contaminants from the feed solution. Up to 99% of contaminants are removed while generating only a small waste stream. CCR’s technology is ideally suited for CO₂ capture applications.

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**Chemistry: MDEA Reclaiming**

Methyl Diethanolamine (MDEA) was introduced to the industry as one of the first amines used extensively in tail gas treating (TGTU) service. MDEA is one of the solvents of choice due to its ability to slip CO₂ while still meeting stringent H₂S specifications. While generic MDEA is often employed, many suppliers offer formulated solvents to enhance the performance of the amine. MDEA was initially thought not to degrade, but it has recently been shown that it will degrade in TGTU service and efforts are under way to improve reclaiming options for solvent quality control. There are several reclaiming alternatives available in the market and it is important to understand the chemistry involved and how each reclaiming technology affects this chemistry.

*Heat Stable Salts*

Heat Stable Salts (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 MDEA), making the MDEA unavailable for acid gas absorption. These HSS anions increase the corrosive nature of the solvent and they must be controlled to insure unit reliability and longevity. All available amine-reclaiming options are able to remove HSS anions in batch mode or while processing a slipstream of the circulating solution. While removal of HSS often plays a critical role in optimizing MDEA system performance, it is important to remember that HSS anions are not the only contaminant that must be removed. Products formed from the degradation of the MDEA molecule may also need to be removed for optimum gas stripping capacity and unit reliability.

*DEA and MMEA*

In the presence of certain chemical compounds or catalysts the MDEA molecule may degrade or break down to simpler amines. Diethanolamine (DEA) and Monomethylethanolamine (MMEA) are some of the simpler amines that may be formed from MDEA. It is important to monitor the level of DEA and MMEA in the circulating MDEA system due to concerns associated with DEA and MMEA selectivity. Since they are secondary amines, they will react directly with CO₂ and will negatively affect the performance of the MDEA solvent. Ion Exchange and electrodialysis are not able to remove non-ionic compounds, so amines cannot be separated from each other. Vacuum distillation is able to separate amine compounds with different boiling points.

*Bicine*

Bis-(hydroxyethyl) glycine (Bicine) is a degradation product formed in the presence of DEA and unstable chemical intermediates. It is considered corrosive and may be removed by vacuum distillation. It has been shown that ion exchange is not very effective in removing this compound since it is dipolar or a zwitterion (essentially meaning it may behave as an anion or a cation depending on the pH of the solution).

*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 many other possible contaminants in an amine system. The accumulation of all of these contaminants adversely affects the physical properties of the solvent. At constant amine strength, the accumulation of contaminants essentially “backs out” the corresponding percentage of water from the circulating solution. Water content probably has the greatest effect 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 increase amine losses in liquid treating service. While these are only two examples of the effects of a change in physical properties of the circulating solution, numerous other examples exist.

*Customer TGTU Example – Before and After Vacuum Distillation*

This table contains data from a third party laboratory for an actual vacuum distillation reclaiming project completed for a customer on their TGTU specialty MDEA-based solvent. The customer experienced corrosion problems that they were associating with the condition of the solvent for several months prior to reclaiming the solution. However, the main driver in the decision to improve the solvent quality was the fact that the plant had difficulty achieving treated gas specifications with the accumulation of the MDEA fragments during summertime operating conditions.

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The data shows that the removal of the items causing a concern from a corrosion standpoint, the strong acid anions (or HSS) and the Bicine, was very effective. The data also shows that the removal of the MDEA Fragments, which were causing the summertime operation concerns, was also rather effective. Significant further improvements in the removal of these MDEA fragments have been accomplished with newer versions of mobile vacuum distillation reclaiming units that have a second distillation tower. It is important to note that this customer did not monitor MMEA (one of the MDEA Fragments) during this project due to the fact that they see it “weather” out of the system, which is consistent with the industry data.

**Summary**

When evaluating your various reclaiming options, remember that HSS anions are not the only – and maybe not the biggest – issue.

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**Meet the CCR Business Development Team**

With over 600 reclaimation 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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