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HTC Solvent Reclaimer System at Searles Valley Minerals Facility in Trona, California

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Abstract

Chemical solvents such as alkanolamines that are used for CO₂ capture from flue gases are vulnerable to quality deterioration which causes a number of operational challenges due to the accumulation of degradation products and other types of impurities within the solvent. To maintain solvent absorption efficiency and avoid operating problems, it is important to continuously remove the accumulated contaminants from the solvent by including a reclaiming process within large commercial CO₂ capture plants. The new HTC solvent reclaimer system, called delta Reclaimer, has been integrated within the 800 ton per day CO₂ amine capture plant at the Searles Valley Minerals Facility (SVM) to remove the undesirable contaminants from a solvent slipstream and return the clean solvent back to solvent circulation in the CO₂ plant. The detailed analysis of the feed stream, product stream and waste stream shows that the delta Reclaimer is capable of removing most of the undesirable impurities and restoring the solvent to its original purity at a high recovery rate and minimum energy consumption. At normal operating conditions the recovery rate of the MEA solvent reaches 98% and the steam consumption is about 1 lb steam (40 psig) per 1 lb of recovered solvent. Very concentrated waste is collected periodically while the reclaimer process is in continuous operation. This technique contributed to a huge reduction of the quantity of waste collected for disposal.

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Keywords: Monethanolamine, CO₂ capture system, Solvent reclamation, Reclaimer, degradation products, heat stable salts, delta Reclaimer

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1. Introduction

Most of the chemical solvents used in natural gas processing, oil refinery, and chemical/petrochemical industries require reclaiming in order to maintain the solvent absorption efficiency and to minimize some operation problems caused by degradation products, heat stable salts and other impurities accumulated in the solvent [1-13]. These operating problems may be reduced solvent absorption capacity, adverse solvent physical properties, increased corrosion rate, increased solvent foaming tendency, plugging, fouling, and increased energy consumption.

Currently, three technologies are widely used to reclaim chemical solvents: thermal distillation/evaporation, ion exchange and electro dialysis. The last two technologies are only able to remove ionic degradation products such as organic heat stable salts. Thermal reclamation can handle and remove both ionic and non-ionic contaminations in addition to removing any other non-volatile or solid impurities. However, the existing thermal reclamation technologies are complicated, expensive, consume high energy, and could cause further thermal degradation to the solvent. The existing reclaimer technologies may also have a low solvent recovery rate and a high solvent loss in the waste stream.

Existing reclaimer kettles for primary amines, such as Monoethanolamine (MEA) and Diglycolamine (DGA) solvents, are usually operated at the stripper pressure to allow easy return of the reclaimer product vapour to the stripper. On the other hand, the existing reclaiming units for secondary and tertiary amines, such as Diethanolamine (DEA), Diisopropanolamine (DIPA), Methyldiethanolamine (MDEA), Triethylene Glycol (TEG), are usually operated under reduced pressure [1]. Secondary and tertiary amines or glycols cannot be reclaimed in a conventional reclaimer unit because these solvents degrade at temperatures corresponding to atmospheric or higher pressure operation. These types of amines are reclaimed on a contract basis on-site using mobile units or off-site because of the use of sophisticated reclaimer designs and requirements for highly experienced operators.

The delta Reclaimer, Δ ReclaimerTM, is a patented technology [2] based on a simple vacuum unit operation, which has the capability to reclaim single and mixed amines or glycol solvents more efficiently at minimum capital and operating costs. The delta Reclaimer is designed to remove all high-boiling degradation products, ionic species, impurities and fine suspended solids from the chemical solvents. It is also designed to operate continuously by feeding the contaminated solvent to the delta Reclaimer as a slipstream or from a storage tank.

To demonstrate the performance of the delta Reclaimer, it was integrated into the largest CO₂ capture plant in operation, which has captured 800 ton per day of CO₂ from coal flue gas for more than 30 years at Trona, California. Figure 1 depicts the integration diagram of the delta Reclaimer within the CO₂ capture plant. The reclaimer feed is withdrawn from the bottom of the stripper by gravity and the vacuum created within the reclaimer. Feeding the solvent to the reclaimer at the stripper temperature minimized the heat duty of the reclaiming process. The cold recovered amine was returned to the plant's surge tank for solvent.

2. Delta Reclaimer Process Description

Figure 2 depicts the delta Reclaimer process unit operation, which consists of an inline mixer unit for mixing the feed solvent with chemical solutions, solvent evaporator unit with sidearm heater to maintain the solvent at specified temperature, condenser unit with liquid/gas separator to recover the solvent, vacuum pump unit to maintain the required operating pressure and solvent condensate pump [2]. At the SVM amine plant installation, the reclaimer feed slipstream is tied into the lean solvent pipe from the bottom of the stripper. The solvent used to capture the CO₂ from the coal flue gas is about 20 wt% monoethanolamine (MEA). Sodium hydroxide, 50% NaOH, and Sodium Carbonate, 28% Na₂CO₃, have been used successfully to liberate the amines from the accumulated heat-stable salts, HSS, in the feed solvent. The amount of chemical injection in the inline mixer depends on the HSS concentration and the feed rate. The main utilities used to operate the reclaimer are a small slipstream of saturated steam at 40 psig, cooling water at average temperature of 77 °F, process water, and instrument air.

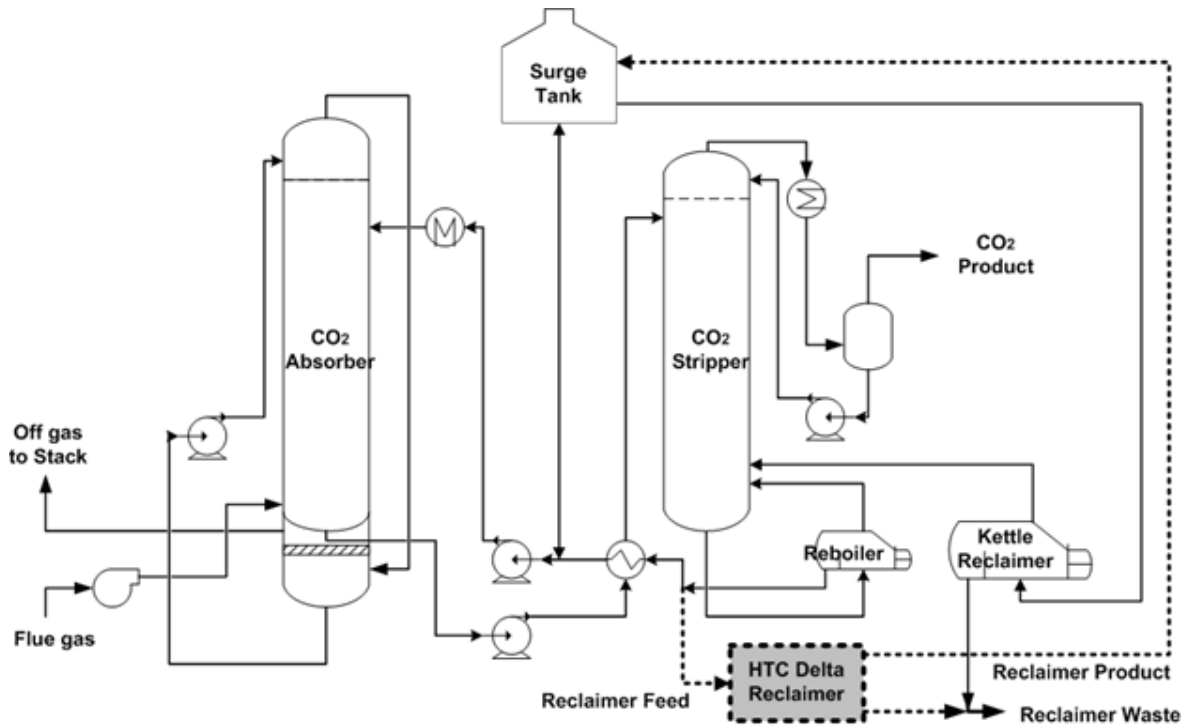


Figure 1. Delta Reclaimer Integration at the SVM CO₂ Capture Plant

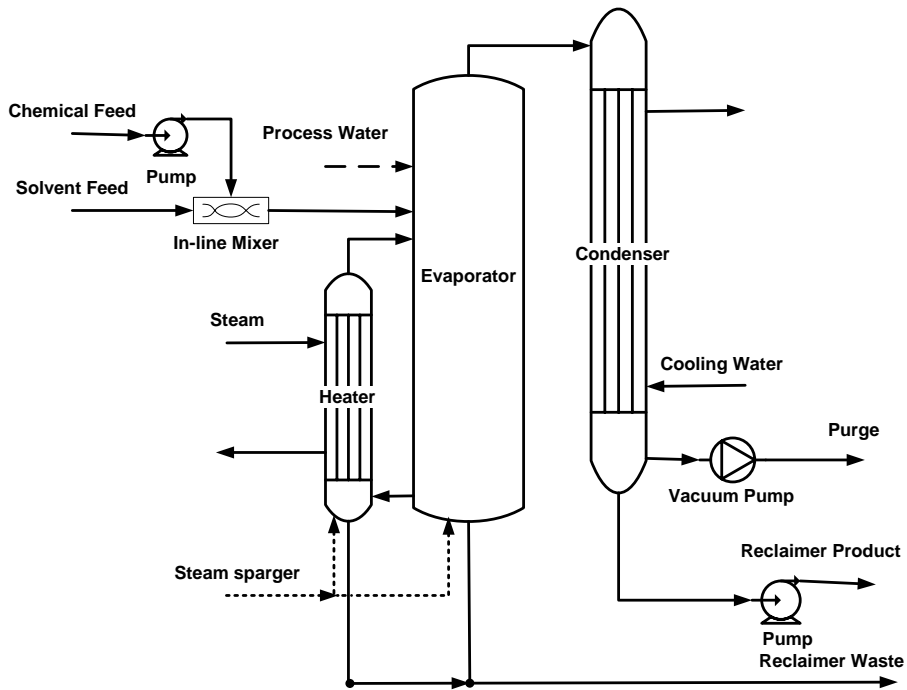


Figure 2. Delta Reclaimer Process Flow Diagram

In the evaporator of the delta Reclaimer, the concentration of the salts and the high-boiling organic compounds (degradation products) increases as reclaimed solvent is evaporated, condensed and then returned to the CO₂ plant for reuse. When the wastes reach a high concentration and darken the accumulated fluid, part of the accumulated waste is withdrawn from the bottom of the evaporator, while the reclaimer remains in continuous operation. Any non-condensable gases, of which there are very few, are removed by the vacuum pump and sent to a safe location.

3. Laboratory Analysis

The sample analysis type and method are selected based on the degradation products and the required performance parameters. MEA solvent can degrade in three ways: thermal, oxidative, and carbamate degradations. The first type, thermal degradation, can be minimized or prevented by ensuring that the solvent within the process stays below its decomposition temperature at atmospheric pressure, which is higher than 147°C [3]. The second type, oxidative degradation, from the reaction of MEA with flue gas contaminants such as O₂ or SO₂ to form organic heat stable salts and their amides, which cannot be thermally regenerated within the CO₂ capture process. Also, it has been reported that the MEA reaction with O₂ will lead to the formation of formic acid, formamides, ammonia, and high molecular weight polymers [5]. The third type of solvent degradation is carbamate degradation. The main reaction between MEA and CO₂ is the formation of carbamate. This is normally thermally reversed at the stripper temperature. However, a small amount of CO₂ is involved as a catalyst in some catalysis degradation reactions, which leads to the formation of degradation products, such as N-(2-hydroxyethyl)-ethylenediamine [6, 7].

During the reclaimer runs, three samples were collected each shift for field lab analysis. These samples were for lean amine feed, product amine, and process fluid. The reclaimer waste is usually taken whenever the reclaimer waste is removed from the process for disposal. The routine field-testing conducted each shift are the MEA concentration, HSS, CO₂ loading, pH, specific gravity, refractive index and sample color. These are used to monitor the reclaimer operation. From time to time or as required, some samples have been sent to the University of Texas Laboratory, Austin, Texas, for detailed analysis. The detailed data analysis include the concentration of MEA and amine degradation products which was measured using cation chromatography on a Dionex ICS2100 with an IonPac GC 17 guard column and an IonPac CS 17 analytical column with quantification limit of 100 ppm in diluted samples. Anion chromatography (Dionex ICS-3000) was used to measure the concentration of carboxylic acids “HSS anions” and other anions with a quantification limit around 1 ppm in diluted samples. The amino acid N-hydroxyethyl-glycine (HEGly) was quantified on a Dionex ICS-3000 with an AminoPac PA10 column. The system used a AAA-Certified Gold Working electrode for gold-oxide catalyzed oxidation of the amino acids. Detection was achieved through Pulsed Electrochemical Detection (ECD) in the electrochemical detector compartment with a quantification limit of approximately 20 ppm for HEGly.

For complete determination of HSS anions and others, the samples have been treated with NaOH. The NaOH hydrolyses any amides into their constituent base amines and carboxylic acids. The total amount of carboxylic acids (free heat-stable salts and amides combined) and amino acids can be measured using anion IC and AA-HPLC. Reclaimer waste samples were heated in a water bath at 50 °C for 30 minutes before dilution to decrease viscosity and re-dissolve any precipitates into solution.

4. Results and Discussion

Table 1 represents the steady state performance and samples analysis data of the Delta Reclaimer operation at the SVM site. At normal operation, Run-1, the average contaminants concentration in the lean MEA (feed to the reclaimer) is 1.5 wt%. Run-2 and Run-3 data represent the results of two test campaigns to reclaim MEA from a 17 wt% MEA solvent that was contaminated with 3 to 5 wt% Sodium Chlorides (NaCl), 1 to 2 wt% Sodium Sulfate (Na₂SO₄) and lesser concentrations of other inorganic salts. These aberrant scenarios could happen if brine or seawater were to leak into the solvent via one of the cooling heat exchangers or the solvent headers that linked to the solvent sump.

The main operating parameters of this test campaign are as follows:

1. Saturated low pressure steam at 40 psig
2. Reclaimer operating at an absolute pressure of 190 mmHg (Torr)
3. Reclaimer operating temperature 180 to 105 °F
4. Cooling water at 75 °F
5. Chemical injection 28 wt% Soda ash or 50 wt% Caustic soda

As can be seen in Table 1, the solvent recovery in Run-1 reaches 98%, when the total contaminants is about 1.5 wt%. This recovery rate dropped to 91% when the solvent was highly contaminated at about 8.5 wt% contaminants. Based on this it can be concluded that the delta Reclaimer can handle very excessively contaminated solvent with sodium salts and other contaminants and still maintain reasonable recovery rates.

The average solvent concentration in the product is very close to the feed concentration, about 17 Wt% MEA. Also, physical properties such as specific gravity and refractive index revealed that the product quality is very close to clean MEA solution. As can be seen in Table 1, Run1 1, the measured average feed specific gravity was 1.04 while the product was 1.01, which confirms the removal of impurities from the solvent.

The color of the sample is a visual indication for the solvent purity as well. The fresh MEA solvent, whether in pure form or a solution dissolved in water, is colorless. The yellowish – brownish color of the solvent that is usually found in CO₂ capture plants is due to the CO₂ loading, formation of degradation/corrosion products, and the presence of inhibitors/additives. Darker color of the solvent usually indicates higher solvent contamination. Photo 1 represents the three samples, reclaimer feed, reclaimer product, and the process fluid (sample taken from the reclaimer vessel periodically during operation). It should be mentioned that the process fluid will show two layers after an extended period of operation. The upper layer is liquid with dark brown color while the lower layer is a thick dense layer with yellowish creamy color. This two-layer sample is an indication to start removing the accumulated waste from the bottom of the reclaimer.



Photo 1 The Colours of the Samples from right to left; Reclaimer Feed, Reclaimer Product, and Process Fluid.

The bottom of the reclaimer vessel is designed in such a way to provide settling space for the accumulated sludge and the high-boiling degradation products/HSS. Since the accumulated sludge is a viscous liquid at the reclaimer operating temperature and can easily crystallize at lower temperature, a 2 inch dumping pipe is used to facilitate draining/quantifying the sludge on a continuous basis once the process fluid sample indicates the presence of the two layers; dark-brown color layer and the creamy-yellowish color layer. Photo 2 is a photo of the concentrated waste (sludge form) that was collected on a continuous basis while the reclaiming process is in operation. This technique, continuous concentration of the sludge with batch wise dumping, is the key for minimizing the volume of waste for disposal



Photo 2. The Collected Concentrated Waste for Disposal on a Continuous Basis

Table 1 HTC Delta Reclaimer Summary of Results

Process Data	Run No. 1			Run No. 2			Run No. 3		
	Feed	Product	Waste	Feed	Product	Waste	Feed	Product	Waste
Reclaimer Operating Pressure, mmHg	17.51	17	54-65	16.75	17.04	41.87	17.25	16.87	-
Reclaimer Operating Temperature, °F	185 ±5			185 ±5				200 ±5	
Chemical Injection for neutralization	28 wt% Na ₂ CO ₃			28 wt% Na ₂ CO ₃			Orang-Yellow	Colourless	Dark Brown
Average total impurities, wt%	1.50			5.80			10.51	10.94	
Total Solvent Recovery, %	98%			95%			91%		
lb saturated steam (40 psig)/ lb product	0.97			1.1			0.95		
Process Streams									
MEA Concentration, wt%	17.51	17	54-65	16.75	17.04	41.87	17.25	16.87	-
Colour	Orang-Yellow	Colourless	Dark Brown	Orang-Yellow	Colourless	Dark Brown	Orang-Yellow	Colourless	Dark Brown
CO ₂ loading, mol/mol	0.085	0.128	-	0.100	0.120	-	0.070	0.055	-
Specific gravity	1.0393	1.013	-	1.0485	1.0145	-	1.0705	1.023	-
Refractive Index at 20 °C	1.3636	1.352	-	1.3673	1.3493	-	1.3701	1.3492	-
pH with CO ₂	10.4	10.65	-	10.42	10.57	-	10.51	10.94	-
pH without CO ₂	10.91	11.39	-	10.91	11.25	-	-	11.17	-
Heat stable salts (HSS), wt% as MEA	1.24	0.15	-	1.18	0.23	-	1.105	0.1	-
T. Formate, ppm	846	13	4,104	915	0	4,695	644	30	-
T. Acetate, ppm	793	9	5,143	917	35	6,012	673	9	-
T. Glycolate, ppm	289	78	1,251	424	11	2,232	477	141	-
T. Oxalate, ppm	372	78	2,633	356	185	670	284	94	-
Sulfate, ppm	8,656	25	1,643	10,575	76	113,106	11,183	23	-
Chloride, ppm	6,452	16	38,306	10,263	23	56,145	17,193	21	-
Nitrite, ppm	68	0	16	61	0	6	56	0	-
N-(hydroxyethyl)-glycine, ppm	3,874	0	24,103	4,771	16	34,613	4,291	0	-
N-(N-hydroxyethyl)ethylethylenediamine)-ethylethylenediamine, ppm	15	0	85	7	-	103	-	-	-
Heavy metals	5	0.3	13.6	7	0.1	66.4	4.8	0.1	-

Also pH measurement was used to demonstrate product quality. Table 1 illustrates average pH values measured during the test campaigns. For Run-1, the average pH value of the lean amine feed is 10.40 while its average is 10.91 after CO₂ has been stripped from the sample. This shows that some alkalinity was increased by freeing MEA from HSS after the neutralizing process. For the reclaimers product stream, the average pH before and after CO₂ stripping is 10.65 and 11.39 receptivity. This pH confirms that the solvent is highly restored as most of the impurities and degradation products are removed.

The accumulation of the organic and inorganic HSS reduce the solvent capacity available for CO₂ absorption leading to reduced CO₂ production capacity. The delta reclaimers is capable of removing 85 – 95% HSS from the feed solvent as shown in Figure 3,

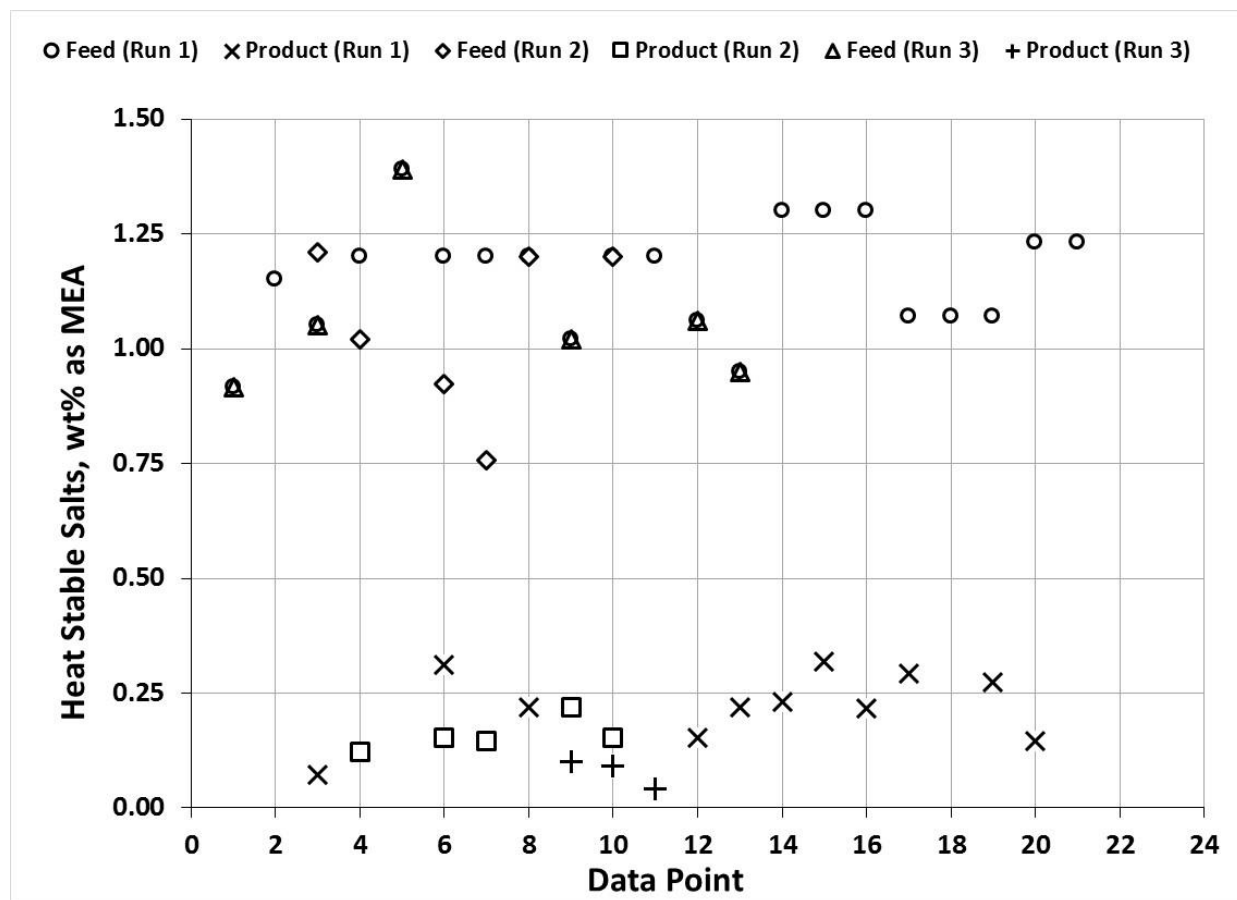


Figure 3 Heat stable salts for feed and product samples for the three runs

More detailed analysis was carried out by the University of Texas laboratory at Austin to determine specific degradation products, heat stable salts, anions, and heavy metals. Cation Chromatograph was used to determine N-(N-hydroxyethyl-ethylamine)-ethylenediamine or MEA trimer while HPLC was used to determine N-(hydroxyethyl)-glycine or HEGly. Anion Ion Chromatograph “IC” was used to determine the heat stable salts anions such as Formate, Acetate, Glycolate, Propionate, Butyrate, Sulfate, Oxalate, Nitrite and Chloride. The samples have been treated with NaOH to reverse amide formation and return it back to the anion of heat stable salts and then the samples were again analysed for the same anions of heat stable salts and letter “T” is add before the specie name to show total amount of that specie. This can be also used as an indirect way to quantify how much amides have been

formed or removed from the system. For heavy metals in all samples, ICP-OES was used to quantify Fe, Ni, Cr, and Mn.

As can be seen in Table 1, the individual impurities concentration in the feed to the reclaimer were high while the product samples were significantly lower than the feed. For some species their concentration in the product was zero, which means they were eliminated from the product completely. Most impurities were removed from the reclaimer product at 95-100% efficiency while Oxalate and Glycolate were removed with around 60-70% efficiency. Propionate and butyrate have not been detected in any samples. Nitrite has been found in the feed but it was not detected in any product samples.

For further illustration, Figure 4 gives the impurities concentration for Run-2 that most of contaminants were removed and concentrated in the waste. Analysis of heavy metals in the product samples revealed that Fe was reduced by 95-97% in the product compared to the feed. Other heavy metals of Ni, Cr, and Mn were found at very low concentrations in all samples.

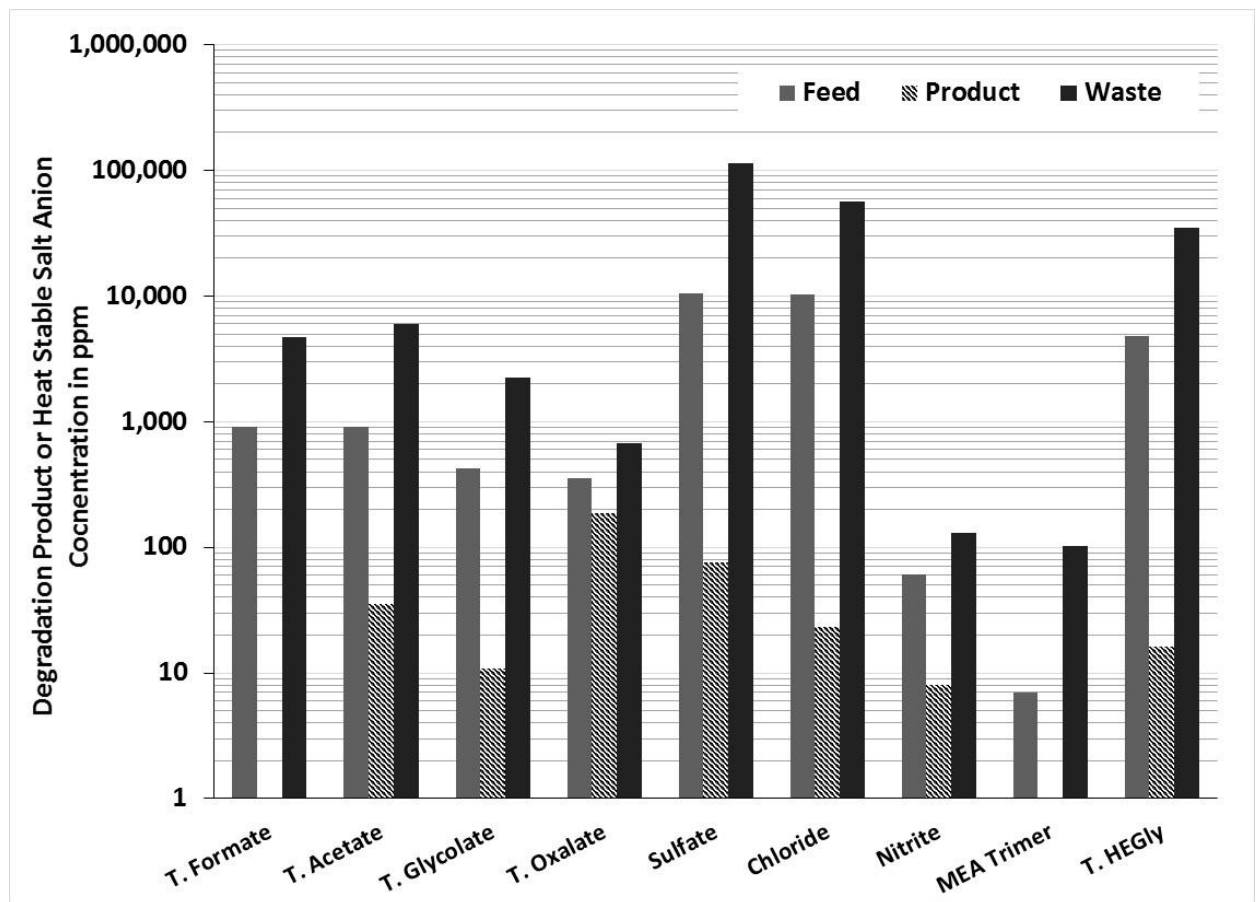


Figure 4 Some Major impurities found in the reclaimer feed and product for Run-2

5. Conclusion

1. The Delta Reclaimer is able to reclaim contaminated solvent even under excessive contaminated condition and restore the solvent to almost its original purity: colorless and 17 wt% MEA.
2. The recovery rate can reach 98% when treating solvents with 1.5 wt% contaminants while this recovery rate could be dropped to 91% if the solvent is highly contaminated, about 8.5 wt% contaminants.
3. The average consumption of low pressure, saturated steam at 40 psig, is 1.0 lb steam per lb of recovered amine (product).
4. Concentrated waste was collected periodically while the reclaimer process was in continuous operation or at the end of reclamation cycle. Concentrating the waste is the approach that contributed to the huge reduction of the quantity of the waste collected for disposal.

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