

Adjusting Gas Treatment Strategies to Resolve Methanol Issues

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Abstract

It is not uncommon today for producers to introduce methanol into their hydrocarbon systems, either as a means of hydrate inhibition, as an additive blended with H₂S scavengers, or for other purposes. While much of the methanol is recovered in liquid knockout drums, a portion of it remains in the natural gas or natural gas liquids where it eventually makes its way to downstream processing units.

The presence of methanol can have negative consequences for gas processors, such as penalties by pipeline operators for excessive methanol in NGL feeds, problems meeting propane quality specifications in fractionation units, or regulatory issues from methanol emissions.

If a reduction of the methanol content in hydrocarbon streams is desired, it can be done with an aqueous wash stream such as is found in an amine sweetening unit. Methanol will be readily removed by the aqueous amine at first but will steadily accumulate in the amine sweetening unit until some equilibrium is reached, after which the methanol escapes in both the sweetened gas and the acid gas.

Several options are available to the operator when confronted with methanol in amine units, and the correct solution depends on the needs of downstream processes. The methanol can be removed almost entirely through a purge of the regenerator reflux stream. These and other strategies are evaluated with a process simulator, the results of which are compared to vapor-liquid equilibrium and operational data.

In practice, a purge of the liquid reflux to the regenerator is an excellent means of providing an outlet for the methanol. Purge rates and disposal options are evaluated along with the possibility of recovering the methanol as a product for reuse.

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Introduction

In recent years, more and more attention has been paid to methanol use in the oil and gas industry. It is a component that is quite common, used for a variety of purposes, and one that has been in use for decades. However, its use, or overuse, is beginning to cause issues for midstream processors as they struggle to meet new natural gas liquids (NGL) product specifications.

Historically, little attention has been paid to the presence of methanol in upstream and midstream facilities. Methanol enters a plant with inlet gas or is injected directly within the process, concentrating in the recovered NGL product with trace amounts present in the residue gas, depending on the process. The methanol then follows propane through fractionation, presenting a challenge for downstream customers as propane demand shifts away from fuel and into petrochemical markets.

To that end, NGL shippers - who had not historically been concerned about methanol - have begun imposing stringent methanol limits and levying penalties on producers for barrels found to be out of compliance. Some typical pipeline specifications for methanol are listed in Table 1.

Table 1: A list of NGL pipelines and their respective specifications on methanol content.

Operator	Pipeline	Methanol Specification
Phillips 66	Powder River	<200 ppmw
	Borger-Skellytown	<50 ppmw
	Skelly-Belview	<50 ppmw
Williams/ONEOK	Overland Pass	<i>no mention of oxygenates</i>
Energy Transfer	Lone Star	Commercially Free of Oxygenates
	West Texas Gate Way	Commercially Free of Oxygenates
	Justice	Commercially Free of Oxygenates
	Freedom	Commercially Free of Oxygenates
Enterprise	Mid-America	<200 ppmw
	Seminole	<200 ppmw
	Chaparral	<200 ppmw
	Chisholm	<10 ppmw
DCP Midstream	Southern Hills	No Detectable Oxygenates

Sources of Methanol

While methanol is a very common component found in the oil and gas industry, it is not a natural occurring component of petroleum. Its presence is entirely due to intentional addition into natural gas and liquid streams.

Methanol can enter a midstream facility in various fluid phases and from various sources. Understanding what these sources are can be instrumental in forming a complete plan to prevent it from ending up in the finished products.

The primary use for methanol in this industry is hydrate inhibition, a topic that has been well studied. [1] Hydrates are solid crystalline structures that form from a combination of water and hydrocarbons. The formation of hydrates has negative effects on operations, such as plugging of piping, valves, and other safety issues. Once formed, it is often necessary to shut down operations to allow equipment to warm up, a situation that could cost the producer considerable time and money. Inhibiting the formation of these solids is therefore quite important.

Hydrate formation is primarily influenced by temperature, thus, methanol injection is most often used in the winter time, creating a peak “Methanol Season” that most operators define as the period between October and February. Since methanol is also a common carrier solvent, it is not only present during the Methanol Season. It peaks during winter operations and subsides through the summer, but may always be present.

In general, industry has become complacent with regards to methanol injection, deferring to the most conservative mode of operation to reduce exposure to downtime and call-outs. The average cost of methanol in 2015 is on the order of \$1.50 per gallon, though the total cost must also factor items such as handling, disposal, and potential off-specification penalties on the order of \$1.00 per barrel. Recognizing that the use of methanol has become excessive, operators had begun curtailing usage even prior to the enforcement of NGL specifications. For example, timing injection coincidental with plunger operations as opposed to simply keeping injection on while the well is not producing could curtail excess methanol usage.

Tools are available to accurately predict hydrate inhibition with methanol, such as ProMax® [2], and thus the optimal amount of methanol to use can be calculated. Such optimizations have been done with success. [3] Simulating the system could help reduce the use of methanol considerably, helping producers avoid penalties and the additional cost of the excess methanol. With the correct amount of methanol known, producers could still be conservative in their use of the inhibitor without using orders of magnitude more methanol than required.

The Path of Methanol through a Midstream Facility

Understanding the route that methanol takes through a gas plant can be helpful in developing strategies for its removal. When it arrives at the inlet knock-outs, it can typically be found in all three-phases of the plant feed.

While some of the inlet methanol is removed at the front end of an NGL plant, enough can carry through in the hydrocarbon phases to violate pipeline NGL specifications. A good model is required to accurately predict the distribution of methanol within a recovery process, accounting for polar and non-polar properties of methanol. For this study, ProMax's Peng-Robinson Polar equation of state is used to demonstrate the distribution of methanol between the vapor, hydrocarbon liquid, and aqueous liquid phases at the plant inlet. For systems containing amine solvents, the Electrolytic ELR package is used in combination with the Peng-Robinson Polar package. The results from this package are compared to data from GPA Research Report-149 [4] in Table 2 below:

Table 2: GPA RR 149: Comparison of Vapor-Liquid-Liquid Equilibrium Composition with ProMax 4.0.

T	P		Feed	Vapor		Organic Liquid		Aqueous Liquid	
			Feed	Data	ProMax	Data	ProMax	Data	ProMax
<i>F</i>	<i>psia</i>		<i>mol frac.</i>						
53.8	1000	C1	0.135	0.942	0.947			2.34E-03	2.55E-03
		H2S	0.0139	0.0573	0.0519			6.84E-03	7.72E-03
		MeOH	0.135	5.01E-04	5.59E-04			0.156	0.156
		H2O	0.717	3.13E-04	2.43E-04			0.834	0.833
51.8	1000	C1	0.196	0.899	0.913			2.03E-03	2.48E-03
		CO2	0.0218	0.100	0.0861			3.75E-03	4.43E-03
		MeOH	0.124	4.39E-04	4.79E-04			0.157	0.157
		H2O	0.659	4.61E-04	2.30E-04			0.837	0.836
51.8	1004	C1	0.180	0.971	0.952	0.283	0.354	0.003	0.003
		C3	0.0156	0.0253	0.0265	0.103	0.096	6.60E-05	7.15E-05
		n-C5	0.0706	0.0030	0.0203	0.612	0.548	5.00E-06	4.95E-05
		MeOH	0.116	5.26E-04	4.74E-04	1.62E-03	1.67E-03	0.157	0.157
		H2O	0.618	3.22E-04	2.15E-04	2.66E-04	1.06E-04	0.840	0.840
51.8	1004	C1	0.154	0.968	0.965	0.244	0.252	0.003	0.003
		C3	0.0222	0.0283	0.0321	0.126	0.122	6.40E-05	9.00E-05
		MCyC6	0.094	0.002	0.002	0.628	0.623	1.30E-05	6.48E-05
		MeOH	0.115	5.53E-04	4.54E-04	1.52E-03	2.05E-03	0.157	0.157
		H2O	0.614	3.14E-04	2.18E-04	2.07E-04	2.50E-04	0.840	0.840
51.8	1004	C1	0.140	0.956	0.952	0.157	0.187	2.36E-03	2.57E-03
		C3	0.0258	4.16E-02	4.54E-02	0.129	0.123	1.06E-04	1.27E-04
		Toluene	0.115	1.70E-03	1.53E-03	0.707	0.683	2.01E-04	2.01E-04
		MeOH	0.115	7.47E-04	4.58E-04	6.06E-03	6.43E-03	0.157	0.157
		H2O	0.605	3.37E-04	2.17E-04	1.35E-03	9.93E-04	0.840	0.840

As can be seen from these data, the methanol present in the inlet vapor is significant enough that, when concentrated in the NGL stream, it can create off-specification products. Liquid hydrocarbons entering the plant can also contain significant quantities of methanol, as much as 3 to 7 percent by volume. [5]. Liquids collected at the front end knock-outs are typically stabilized, and the overhead vapors are routed back to the NGL recovery plant for processing, carrying methanol with them. So both the inlet vapors and inlet liquids can be a source of methanol feeding into the gas plant.

Once the methanol enters an NGL recovery process, it generally follows the NGL through the process, as can be seen in Anadarko’s Chipeta Plant Train 2. Methanol is condensed in the demethanizer and exits with the NGL product, leaving only trace amounts remaining in the overhead residue gas. Models show this to be true regardless of whether the process is operating in ethane recovery or rejection mode. The methanol concentration in the NGL product will be greater while operating in rejection mode as the total volume of NGL will be less due to the reduction of ethane in the liquid product. This can be evidenced by the simulated results in Table 3.

Table 3: Predicted methanol in NGLs for a GSP Expander plant operating in ethane rejection/recovery modes.

	Rejection Mode (data)	Recovery Mode (simulated)
Ethane Recovery	15%	80%
MeOH in Feed	10 ppmw	10 ppmw
MeOH in NGL	145 ppmw	204 ppmw

As the methanol will concentrate in the NGL product, even small amounts in the inlet vapor can push that product off specification. A block flow diagram showing the path of methanol through Chipeta’s Train 2 can be seen in Figure 1, showing the concentration of methanol into the product NGLs.

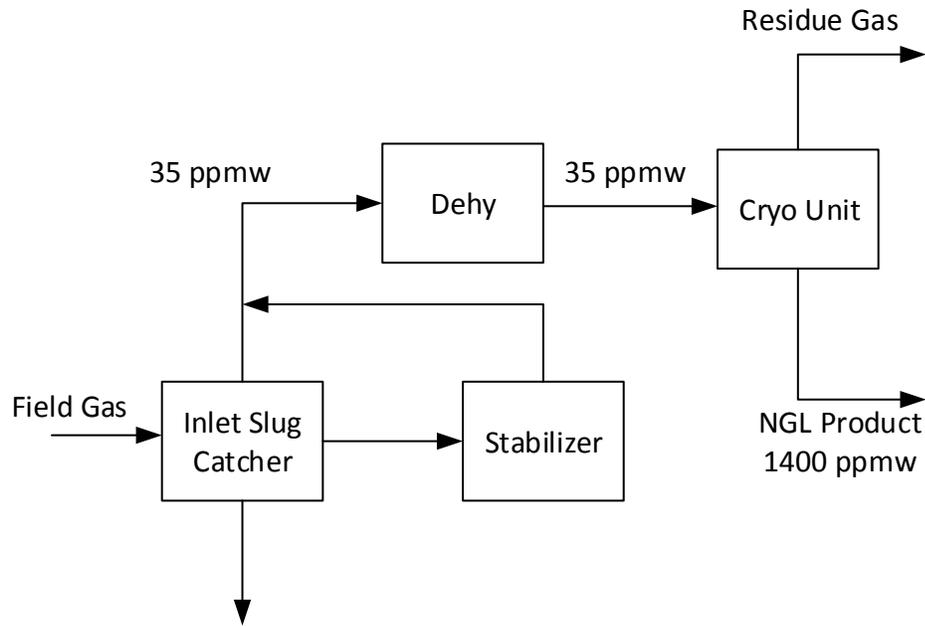


Figure 1: Block diagram for Chipeta Train 2 showing methanol concentration in NGL product as based on measured values.

Once in the NGL product, the methanol travels to a fractionation train where it primarily follows the propane, leaving trace amounts in ethane and butane, depending on the split. Evidence of this behavior can be seen for a representative analysis of fractionated products during the Methanol Season in Table 4, as well as in the Gas Processor’s Association Research Report 219 [6].

Table 4: Distribution of methanol in representative analysis of fractionated products during the Methanol Season

	Propane Product (wt%)	Butane Product (wt%)	Gasoline Product (wt%)
Nitrogen	0.00	0.00	0.01
Methane	0.00	0.06	0.02
CO ₂	0.00	0.00	0.00
Ethane	3.10	0.03	0.03
Propane	95.10	0.10	0.18
i-Butane	1.61	1.97	0.06
n-Butane	0.19	85.82	1.10
i-Pentane	0.00	9.67	16.19
n-Pentane	0.00	2.35	11.29
Hexanes	0.00	0.00	20.19
Heptanes+	0.00	0.00	50.93
Methanol	1194 ppm	10 ppm	50 ppm

In the entire flow of methanol from the well head to finished product, it is at the fractionation step where methanol finally becomes a true problem as the finished products, such as propane, must be

essentially free of methanol if it is not being used as domestic fuel. The costs of removing methanol from those finished products are pushed all the way back the pipeline to the producers.

Keeping Methanol out of the Products

Knowing that methanol is present in the feed and can concentrate to levels high enough to push products of specification, it is important for operators to develop strategies to keep methanol out of their finished products. In almost all cases, these strategies center on a wash of some type, either by treating of the inlet gas or NGL product. While molecular sieve has the capacity to remove methanol, it is displaced by water and subject to breakthrough and carryover into the downstream process and is therefore not effective on feeds with an appreciable water content. Methanol removal from NGL with molecular sieve can also be problematic as regeneration with natural gas introduces other equally detrimental contaminants; namely methane and carbon dioxide.

In some cases, using the amine sweetening unit as a methanol removal unit has been successful. This option does not require any additional equipment if the amine plant is already present, and the amine solvent already has the capability of removing methanol from the sour gas or sour liquid. This is the strategy put in place at Anadarko's Chipeta facility. Chipeta's Train 3 has a traditional vapor treatment system upstream of the cryogenic unit, while Train 2 has amine treatment of the NGL products. Diagrams of these configurations, as well as measured methanol concentrations, can be found in figures Figure 2 and Figure 3.

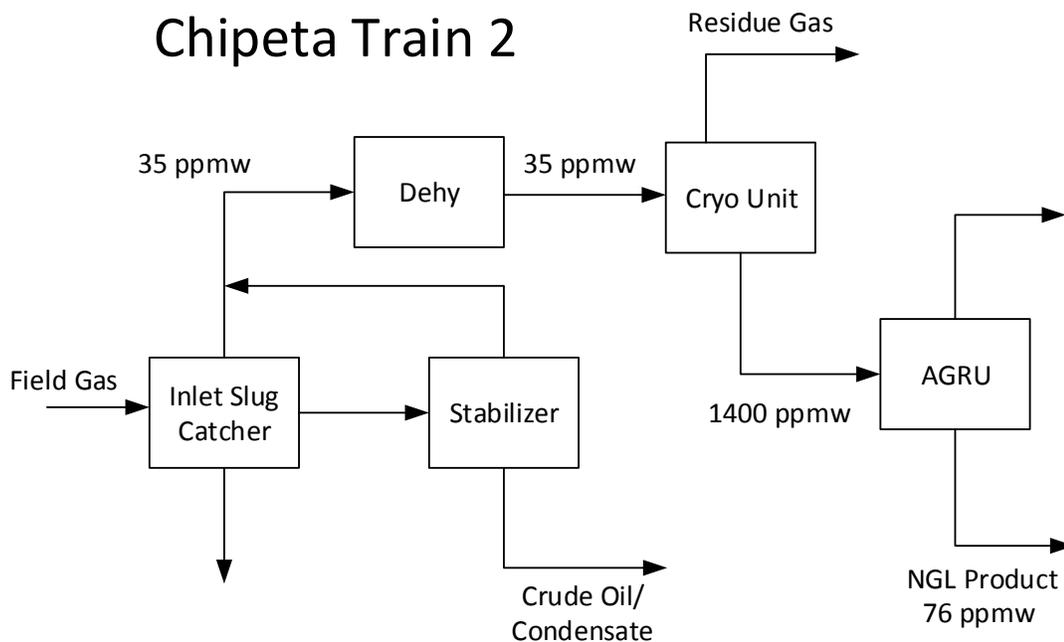


Figure 2: Block diagram for Chipeta Train 2 showing methanol concentration in NGL product and its removal based on measured values.

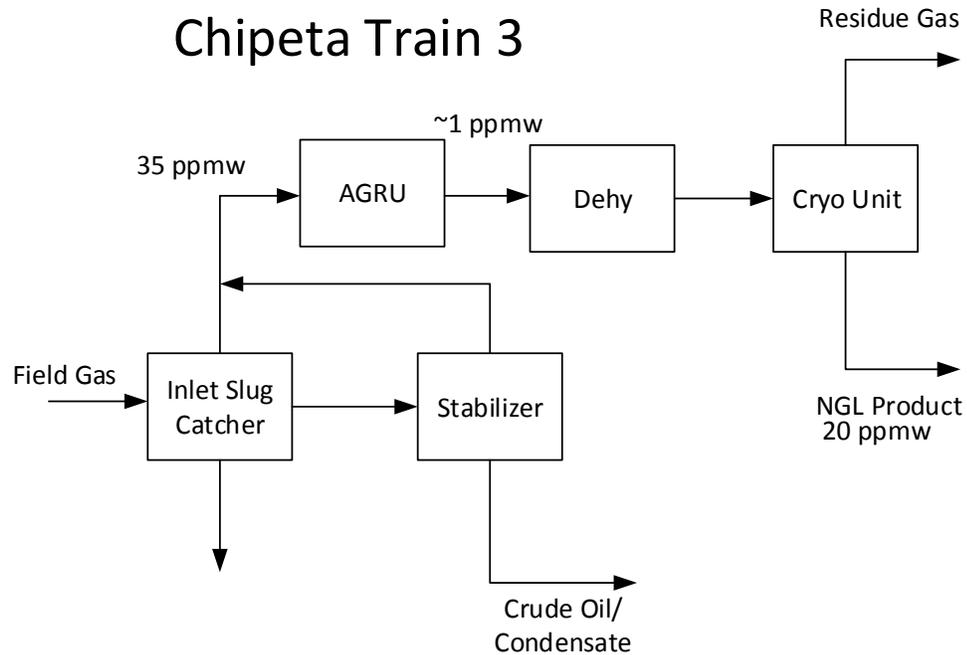


Figure 3: Block diagram for Chipeta Train 3 showing methanol concentration in NGL product and its removal based on measured values.

If evaluating the option between treating the NGLs for methanol removal or treating the gas, the most economical choice is to treat the NGLs. The NGL itself is a significantly smaller stream as compared to the gas, and it will have a higher concentration of methanol. This allows the operator to treat the NGL with significantly lower circulation rates of amine, resulting in significant savings in terms of operation. Chipeta’s Train 3 treats the gas *before* processing and uses 550 sgpm of circulation. Meanwhile Train 2 treats with 60 sgpm of circulation *after* processing. As can be seen in Table 5, methanol removal from the NGLs can be 10 times cheaper than treating the gas.

Table 5: Reboiler Cost of Treating for Methanol assuming \$2.00/MMBTU fuel

	NGL Production	Amine Circulation	Reboiler Duty	Reboiler Cost	Cost to Treat
Train 2 (liquid treater)	7,000 bbl/d	60	2.5 MMBTU/h	\$120/d	\$0.0017/bbl
Train 3 (gas treater)	6,600 bbl/d	550	25 MMBTU/h	\$1,200/d	\$0.18/bbl

With some cost involved, treating with amine solutions can be an effective means of removing methanol in the vapor or liquid phase, as was done at the Chipeta facility. However, some operational changes to the amine unit may be required. If the amine unit is operated “normally”, methanol can accumulate in the amine solvent to the point that the system loses its ability to remove methanol to sufficiently low quantities in the treated product. As methanol has a polar character and high affinity for water, it will be removed at first by the aqueous amine in the contactor and then stripped out in the amine still. However, most of the methanol leaving the still overhead will be condensed in the reflux circuit and returned to the system. This can cause an accumulation of methanol within the amine solvent loop, as seen in Figure 4.

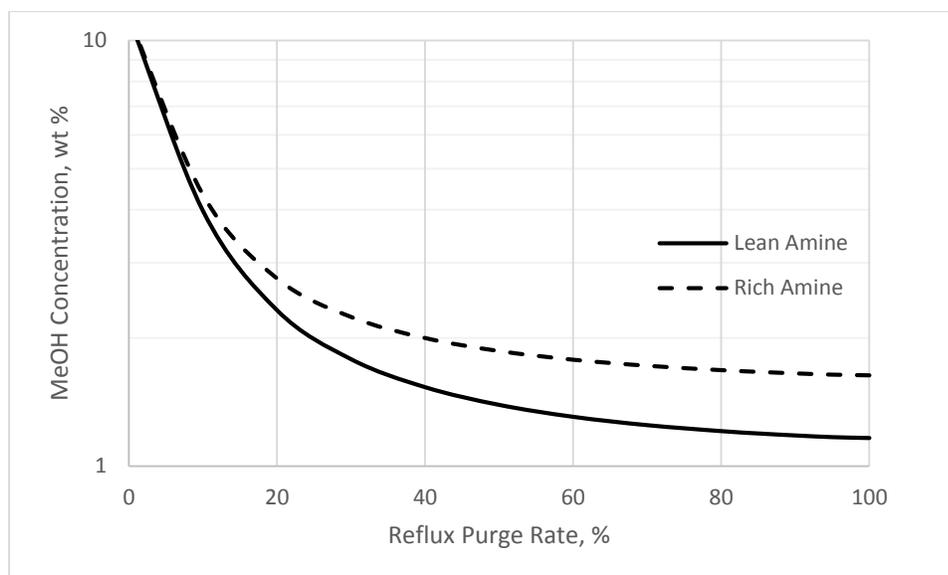


Figure 4: Predicted buildup of methanol in amine loop for Chipeta Train 2 at various purge rates.

Higher concentrations of methanol remaining in the lean amine will subsequently reduce the amine solution's ability to deeply remove methanol from the treated vapor or liquid. The effect of methanol remaining in the lean amine can be understood using GPA RR184 [7], found in Table 6.

Table 6: GPA RR184: Vapor-Liquid Equilibrium Studies on Water-Methanol-MDEA-C1-C3-CO₂ systems

T	P	MeOH in Amine Solution	MeOH in Vapor	
		Data	Data	ProMax
F	psia	%	ppm	ppm
80	1000	1.197	63	64
80	1500	1.196	52	52
120	1000	1.194	224	172
120	1500	1.194	169	132
120	1000	1.15	208	176
150	52.5	1.16	4640	4998

Besides reduced treating capability, this methanol build-up can also cause multiple operational issues for the amine unit itself, including excessive foaming and solvent loss [8], depression of the reboiler temperature, and general dilution of the amine solvent if the methanol is allowed to build to significant concentrations. However, changes can be made to operations to mitigate these issues.

To retain the amines capacity to recover methanol, as well as to avoid operational issues, some or all of the regenerator overhead reflux can be purged and replaced with fresh water. It is at this location in the facility where methanol is at its highest concentration, and the amine portion of the liquid is at its lowest. The effect of this purge on both the methanol removal efficiency of the unit as well as the increased cost of make-up water can be seen in Figure 5 and Figure 7. The make-up is typically inserted at the surge tank or still bottoms as opposed to still reflux. Without liquid

entering onto the wash trays of the amine regenerator, an increase in solvent losses can be expected, increasing the cost of operations.

Besides solvent losses, the increase in required make-up water itself can be a significant cost. While some facilities have access to relatively low cost demineralized water, others, such as operators in the Rockies, pay as much as 40¢ per gallon. This additional cost can be seen in Figure 6 and Figure 8.

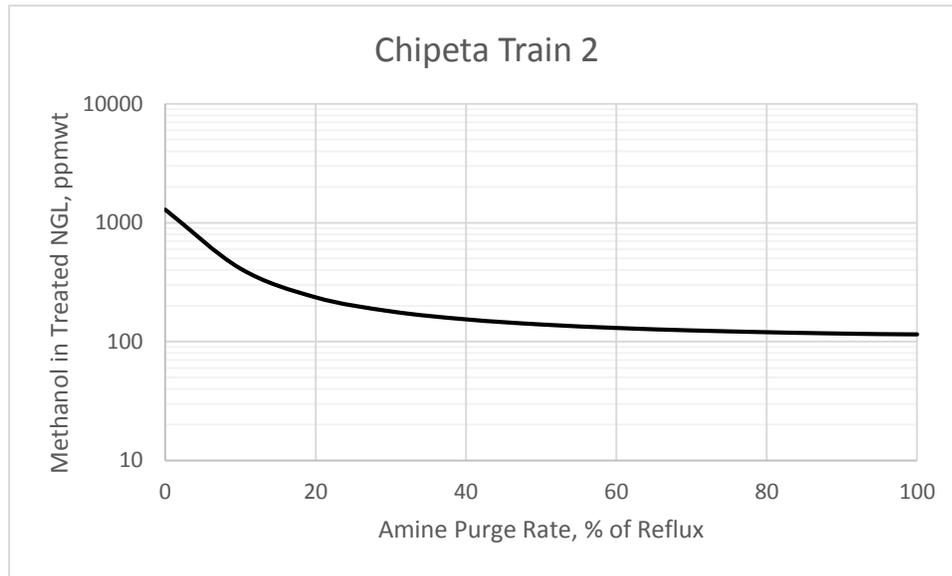


Figure 5: Effect of Purge Rate on AGRU’s ability to remove methanol in Chipeta Train 2 (NGL treater). Feed NGL contains 1400ppmw methanol.

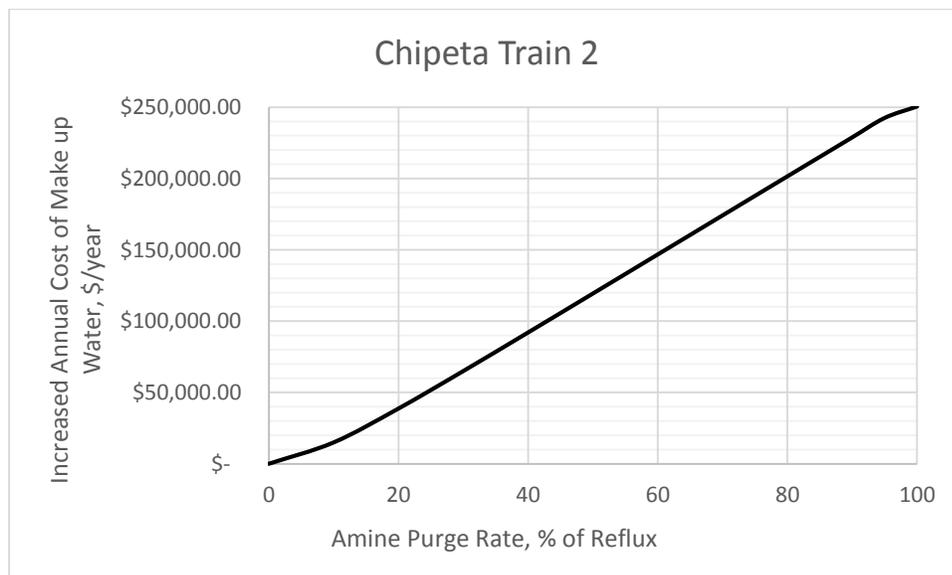


Figure 6: Increased cost of make-up water at various purge rates for Chipeta Train 2 (NGL treater). Cost assuming \$0.40/gallon of water and compared to the same system with no reflux purge.

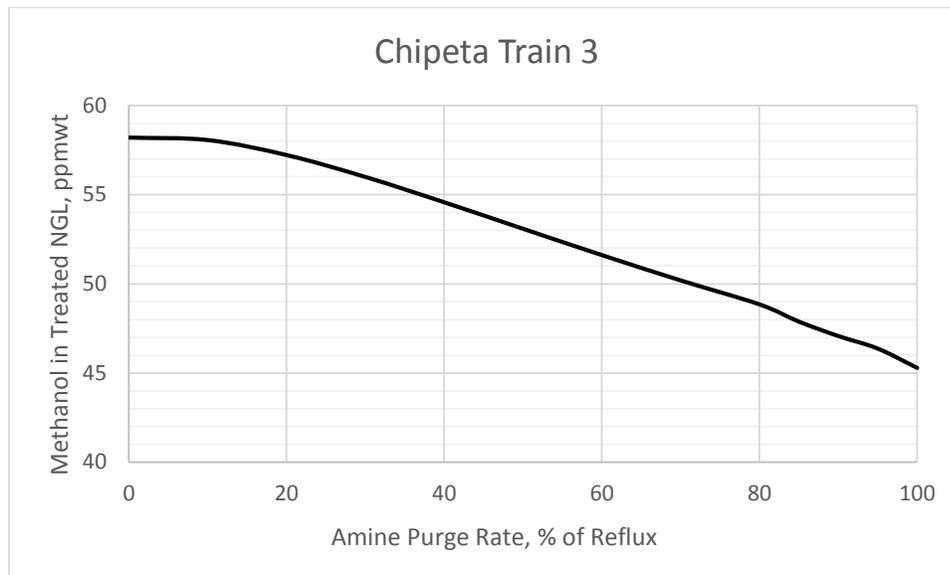


Figure 7: Effect of Purge Rate on AGRU’s ability to remove methanol for Chipeta Train 3 (gas treater). Feed gas contains 10ppmw methanol.

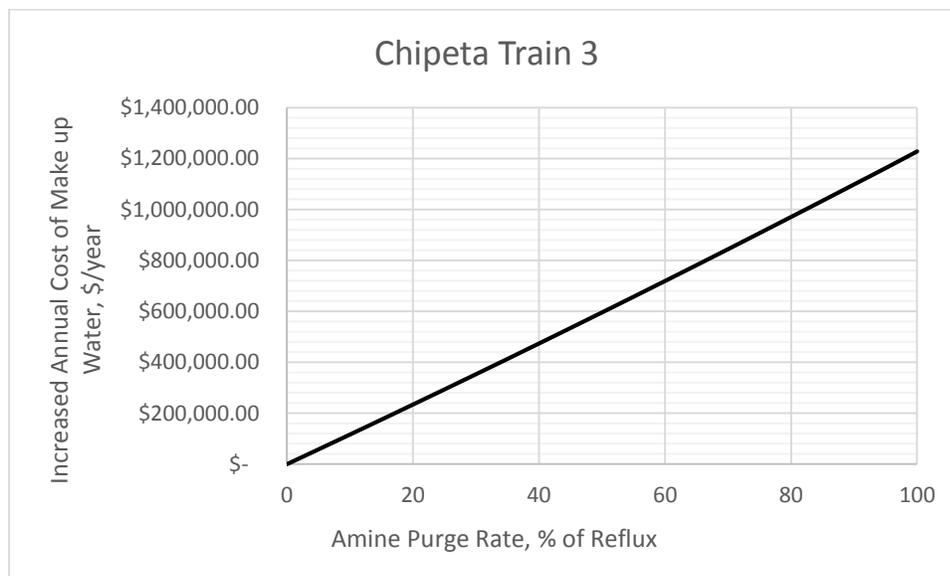


Figure 8: Increased cost of make-up water at various purge rates for Chipeta Train 3 (gas treater).. Cost assuming \$0.40/gallon of water and compared to the same system with no reflux purge.

For Anadarko’s Chipeta facility, the choice was made for a full reflux purge (100%) for Train 2. This system has a relatively low circulation rate, and therefore a very low rate of reflux. Operationally, it was easier to simply set-up a complete purge as opposed to trying to return 0.5-1 sgm back to the top of the column. Train 3, however, has a significantly greater circulation rate and a significantly greater reflux rate. Operations began with approximately 50% reflux purge, and, assisted by simulation, began to back the purge down to balance effective methanol removal with operating costs. For this train, the purge rate settled in the 10-15% range. Doing so gave approximately 1-2 ppm methanol in the treated gas overhead. Once through the gas plant, this

methanol concentrated in the NGL to less than 50 ppm, well below the 200 ppm pipeline specification.

At Chipeta, no sulfur recovery unit (SRU) was in use. However, if an SRU is present, a full on water wash may make more sense. Methanol contains carbon in its molecular structure, and its destruction in the SRU burner can result in COS and CS₂ formation. Non-combusted methanol can also cause issues similar to those of hydrocarbons across catalyst beds.

An amine system or a water wash can be used to remove methanol, but it does not mean that the products will be completely on specification. This is certainly the case when treating NGLs. Treating the product NGLs has the advantage of treating a smaller stream with more highly concentrated methanol. However, there is a negative effect in that the hydrocarbons leave the wash saturated with water. NGL specifications typically include limits on free water such as “No free water at 34F”. This is the case with the Enterprise Mid-America, Seminole and Chaparral Pipelines.

One common way of getting the NGL back on free water specification is to chill the NGL and remove the water in a coalescer. In multi-train facilities, NGL treatment may only be performed on one or some of the trains, while other trains have methanol removal upstream of the cryogenic unit. If dry NGL is available to comingle with the wet, then full water removal down to 34F may not be required. The wet NGL may only need to be cooled to 40-50F, depending on expected hydrate formation temperatures and available wet/dry volumes, so that the blended product is on specification. If a facility has only one train, or if all trains receive treatment of the NGL product, then deeper removal of water may be required.

Refrigeration down to lower temperatures, followed by liquid-liquid separation, can provide adequate water removal. After the wash, ethylene glycol is injected to inhibit hydrate formation and the commingled liquid is refrigerated to 25-30°F. The immiscible phase (ethylene glycol, water and methanol) is removed from the hydrocarbon phase at a liquid-liquid coalescer with a 99.5% capture efficiency. NGL is injected into the pipeline and the immiscible phase is routed to a regenerator where Ethylene Glycol is re-concentrated to 80 wt% and returned to the system. While methanol could be recovered from the still effluent, it is typically routed to an incinerator for containment.

An alternative to refrigeration is dehydration via mole sieve beds. While these beds can and do perform well in removing water from the NGL, care must be taken in the selection of gas used in the regeneration cycle. If the regeneration gas contains CO₂, for example, the CO₂ can build up on the bed during the regeneration cycle, only to be removed by the NGL during the water absorption cycle. The net result is an NGL that is now on specification for free water, but is no longer on specification for CO₂.

Once Methanol is Removed

In most cases, when methanol is removed from the gas plant, it is in an aqueous solution. The next step in the methanol removal process is to address the options for disposal of methanol/water mixtures.

In some instances, methanol rates may be small enough to warrant simple off-site disposal of the contaminated water. While this may be the simplest method, as methanol quantities increase, other options become more attractive.

In large facilities with either water wash systems or large purges from amine units, methanol regeneration columns may be present. There are multiple advantages to methanol regeneration columns. In some cases, their presence and use can help mitigate the overall cost of methanol injection as the methanol recovered from the hydrocarbons can be recycled for field use. *Note that use in a cryogenic process is not recommended as operating temperatures requires a level of purity not necessarily possible with anything less than an industrial grade methanol plant.* Concentrating the methanol could also convert it from a waste stream to a product stream, allowing its sale to nearby methanol users.

The methanol regenerator has an additional advantage that you reclaim the water required to wash out the methanol. This water can then be sent back to the amine system or water wash loop, thus reducing the cost of the amine unit reflux purge.

Conclusions

As many midstream operators have learned in recent years, methanol is a contaminant that cannot simply be overlooked. Even with a three-phase knockout in the front of the plant, methanol is certainly still entering with the hydrocarbons. Depending on the requirements of the operator accepting the gas plant products, very small amounts of methanol in the plant feed can trigger costly penalties.

These penalties can be avoided in a variety of ways. Producers can take greater care in the amount of methanol they are injecting, reducing both their costs as well as the problem that methanol poses to processors. The processors themselves can either alter operations of sweetening plants or can elect specialized treatment processes for methanol removal.

In most cases, a combination of these approaches will provide the most efficient removal of methanol.

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