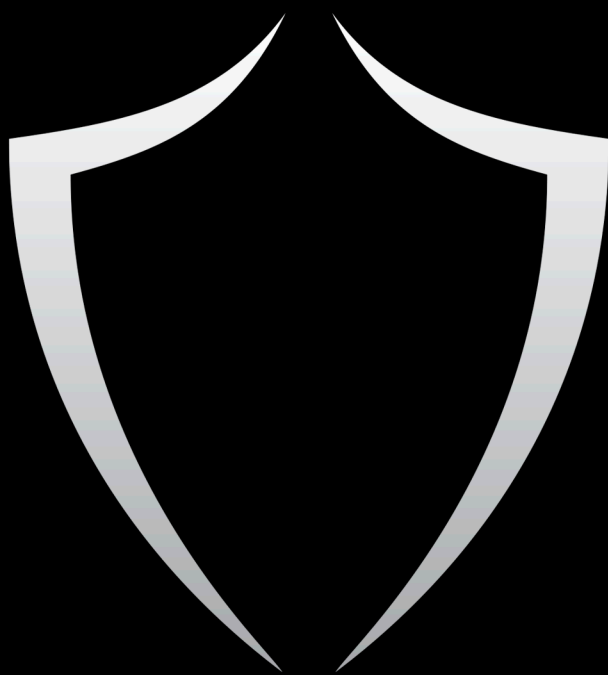


# AMINE CONTAMINATION PROTECTION



**James M. Ondyak, Dorf Ketal Chemicals, USA,** discusses the most effective ways to protect refinery overhead systems from amine contamination.

**C**ontamination of crudes with amines, most notably monoethanolamine (MEA), is an operating risk to refinery overhead systems. MEA gets into the crude oil supply chain through the addition of MEA-triazine, used for scavenging hydrogen sulfide ( $H_2S$ ).

When MEA is in the crude, incomplete removal of MEA in the desalter results in the MEA entering the crude column, increasing the risk of salt formation that can cause fouling and corrosion in the overhead system. Conventional desalting approaches, including acid addition, are unable to reduce the MEA concentration in the desalted crude to low enough levels to protect against this risk. Testing for the presence of MEA in the crude is also not sufficiently protective.

This article offers new cost-effective best practices for dealing with the risk of MEA getting into the system.

## Insufficient protection

This conclusion is derived from newly published data in a Phillips 66 patent,<sup>1</sup> USA patent US 10,114,001, that describes laboratory

methods for measuring MEA and other amines in the crude. The data in the patent demonstrates that microwave extraction, a new laboratory method invented by P66, is superior to acid extraction for measuring the concentration of amines in crude, including MEA.

Table 1, taken directly from this patent, compares microwave heating extraction (MWE) with acid extraction (AE).

Table 2 is the same data as Table 1, presented in a format to show the quantity of MEA left in the crude after acid extraction. Acid extraction left at least 1.5 ppm MEA in crude 1, 3.6 ppm in crude 2, and 5.1 ppm in crude 3. Amine levels in the low ppm (over even sub ppm) range in the desalted crude can result in an amine level exceeding 100 ppm in the overhead water stream of a refinery atmospheric distillation tower.<sup>1</sup> These levels of amines in the overhead can cause significant deposit and corrosion problems.

Comparing acid extraction in the laboratory to a refinery desalter using acid, the former removes more amines and salt. This is because the laboratory extraction has more mixing, up to

**Table 1. Comparing amine detection sensitivity of microwave heating extraction (MWE) vs acid extraction (AE)**

	Crude									
	1		2		3		4		5	
Amine	Method									
	MWE	AE	MWE	AE	MWE	AE	MWE	AE	MWE	AE
MEA	2.1	0.6	4	0.4	6.1	1	*	*	*	*
DEA	*	*	*	*	*	*	*	*	*	*
MDEA	*	*	*	*	*	*	*	*	*	*
DMEA	*	*	*	*	*	*	3	0.1	10.6	1.9

(\* = below 0.1 ppm)

Note: Table taken directly from Phillips 66 patent, US 10,114,001

MEA contamination is one of those upset possibilities. Raman spectroscopy is now available to get the MEA result in the boot water in a few minutes and at low cost. Best practice is to increase the frequency of MEA monitoring in the boot water using this technology.

It is important to recognise that precipitation of MEA as a salt in the tower overhead exchangers will not be measured in the boot water. Monitoring of MEA must be combined with salt point prediction to effectively manage risk.

**Table 2. MEA left in crude by AE**

Crude	MEA by MWE	MEA by AE	MEA left in crude after AE
1	2.1 ppm	0.6 ppm	1.5 ppm
2	4.0 ppm	0.4 ppm	3.6 ppm
3	6.1 ppm	1.0 ppm	5.1 ppm

20 times more water, can be done at a lower pH than is safe in the desalter, may use mineral acids, and has better dehydration due to toluene addition. There is no possible scenario in which a refinery desalter would be expected to deliver as much MEA extraction as the laboratory acid extraction. If the laboratory extraction does not remove sufficient levels of MEA, neither can the desalter, even when using acid. It is now understandable why some refineries with excellent salt removal efficiencies can have salting problems in the overhead system if some of the crude in the blend has been treated with MEA-triazines.

### Effective monitoring of MEA in the system

Once MEA-triazine is in the crude, there are two mechanisms for MEA and other amines to be released: reaction and thermal decomposition. The triazine reacts with H<sub>2</sub>S and releases MEA as a product of the reaction. There is always some unreacted triazine left in the crude. The unreacted triazine and the reaction byproducts of triazine and H<sub>2</sub>S will thermally decompose in the crude furnace, releasing amines as products of decomposition.

The MEA and amines from both mechanisms rise up the crude column and concentrate in the overhead water. Water content of the desalted crude is approximately 1/60<sup>th</sup> to 1/200<sup>th</sup> the volume of the crude, concentrating the MEA that was in the crude into the water at up to a 200-fold concentration of MEA. MEA that was in the crude at sub ppm levels is now in the boot water at much higher levels. Measuring MEA in the boot water offers an important indicator of the presence of MEA in the crude.

Refiners are already routinely monitoring amine and chloride concentrations in the boot water to calculate salt points. What is typically lacking is the necessary frequency to capture MEA contamination upsets and the understanding to properly assess the corrosion risk. It is widely accepted that up to 90% of the overhead corrosion damage occurs during upset conditions that occur about 10% of the time.

### New chemistry options for improving the removal of MEA in the desalter

A new class of chemistry has been discovered that improves MEA removal to levels below that available from using acid in the desalter. It has been discovered that certain aldehydes are synergistic with emulsion breakers to increase rate of emulsion breaking at remarkably low dosages; on the order of 1/10<sup>th</sup> the dosage of emulsion breakers. The aldehydes are added to the desalter in a separate feed along with the emulsion breaker, similar to other adjunct chemistries such as wetting agents and reverse emulsion breakers. Wetting agents and reverse emulsion breakers are surface-active chemicals, as are emulsion breakers. To contrast these adjuncts with the use of aldehydes, this new class of adjunct chemistry is called 'reactive' adjunct, to make the point that this adjunct is reactive, not a surface-active agent.

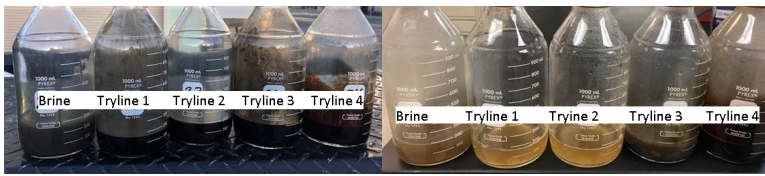
Three mechanisms explain the improvement available to better control MEA contamination: chemical scavenging, reduced desalter pH, and better extraction in the desalter.

The chemical scavenging mechanism of reactive adjunct is the reaction of the aldehydes in the formulation with amines to form imines. This reaction converts some of the harmful MEA to a harmless imine. The amine to imine conversion reaction reduces desalter pH without the risk of a low pH excursion.

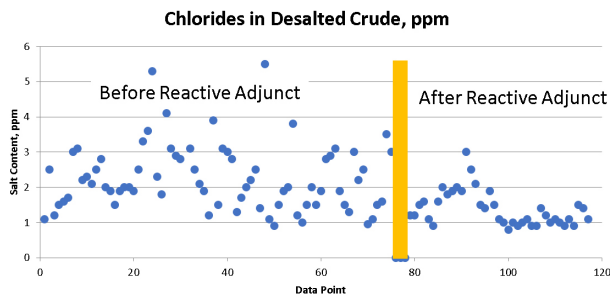
Increased extraction of MEA in the desalter is the result of two mechanisms: better mixing in the desalter improves MEA removal by virtue of the increased extraction efficiency, and the driving force for extraction is improved as the aldehyde-amine reaction reduces the MEA concentration in the brine.

It is a relatively common practice for refiners to back off on the mix valve, reducing mixing in the desalter. The reason for this may be based on the desire to reduce emulsion breaker dosage or, more likely, to reduce the amount of oil in the brine or concerns about water carryover. Less mixing means less energy to drive the MEA from the organic to aqueous phase.

With the new best practice for MEA monitoring in the boot water and adding reactive adjunct, the need for improved MEA extraction is triggered by watching the trend of the MEA concentration in the boot water. In the absence of MEA contamination in the crude, the boot water concentration of MEA is very low. When the monitoring of MEA in the boot water shows an increase that raises concern in salt point



**Figure 1.** Desalter brine and tryline samples. Left without reactive adjunct. Right with reactive adjunct.



**Figure 2.** Salt data over six months of operation.

calculations, the reactive adjunct provides flexibility to increase mixing energy and improve extraction. Increased mixing improves extraction of both MEA and chlorides; reductions in both are beneficial in the salt point calculation.

A rag layer in the desalter is visible evidence that mixing energy is too high for complete resolution of the emulsion in the desalter. Rag is unresolved emulsion caused by more mixing than the emulsion breaker can handle. The unresolved emulsion reduces the ability of the water to drop and the oil to rise, increasing the risk of oil in the brine or excess water in the crude. The unresolved emulsion also reduces MEA extraction.

Reactive adjunct improves rag layer control and reduces oil undercarry in the brine. This allows for increased mixing energy to maximise amine removal in the first stage of the desalter. This reduces the amine loading in the crude going to the second stage of the desalter. Reduced amine loading and superior mixing and dehydration in the second stage further improves the amine extraction.

## Improving asset flexibility

The measures described in this article are focused on improving the ability to deal with MEA contamination. Implementation of reactive adjunct will also improve asset flexibility for dealing with other types of desalter upsets including upsets in metals, water, and solids content in the raw crude. Aldehydes in the reactive adjunct formulation are also effective on metals removal. Faster speed of emulsion breaking means faster dehydration to manage an upset in water content. An upset in solids increases rag formation – reactive adjunct also resolves rag. For refineries concerned about the risk of upsets in the wastewater treatment plant due to oil or solids undercarry, reactive adjunct reduces this risk.

Experience with multiple management of change (MOC) processes in implementing reactive adjunct and references provides potential users with confidence in the safety and cost efficiency of implementing reactive adjunct.

## Case history

A heavy oil refinery in the US had suffered with oil undercarry problems for years. Oil in the brine brought fine solids into the brine that resulted in costly secondary treatment of the brine and slop waste. In over 20 years of refinery operation, the refinery had never been able to consistently produce clear brine and had become accustomed to the added costs of wastewater treatment.

The crude diet contains high levels of filterable solids that contributed to rag formation. A heavy rag was a constant in both stages of the desalter, reducing desalter capacity. The crude mix was known to have periodically contained crudes that had been treated with MEA triazines. Salt removal and dehydration efficiency were compromised by the inability to increase mixing energy because of the rag.

The combination of salt and amines led to a long history of overhead problems that were not solved by upgraded metallurgy and water washing.

The refiner now uses reactive adjunct technology successfully. Typical pictures of desalter samples with and without reactive adjunct are shown in Figure 1. The elimination of rag allowed the refiner to increase mixing energy to improve salt removal, as shown in Figure 2. Overhead monitoring was put into place to establish norms between boot water chemistry, salt temperature calculations, and salt content in the desalted crude. Salt problems have been dramatically reduced as a result.

The refinery was able to reduce water level to improve dehydration without the risk of oil undercarry. Reduced chlorides in the desalted crude reduced demand for overhead neutraliser. When using reactive adjunct, there is no need to adjust pH of the brine from the desalter. This is an advantage over the use of acid where pH adjustment of the brine (when required) can increase the risk of fouling the brine heat exchangers.

## Conclusions

For any refinery operating in the world of opportunity crudes, MEA contamination is a risk to safe and efficient operation that justifies implementation of best practices, as described in this article. New technology, called reactive adjunct, is now available to allow for better amine extraction by offering a combination of: amine to imine chemical conversion, reduced desalter pH, and increased mixing energy. Reactive adjunct is an aldehyde formulation, not an acid. The set-up is safe, low cost, and reduces risk of upsets to the wastewater treatment plant due to oil and solids in the brine. As contrasted with the option to add acid, there is no risk to a low pH excursion in the desalter. The system can be used on a continuous or intermittent basis.

Reactive adjunct is a new weapon against the risk of amine contamination. When the indicators show increased risk of amine contamination, it makes good sense to have reactive adjunct available to reduce operating risk, and improve asset flexibility to process opportunity crudes. [1,2](#)

## Reference

1. Phillips 66 patent, US 10,114,001.