

Work Life Balance – Revisiting the Relationship between Desalting Efficiency and Overhead Corrosion Control

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ABSTRACT

It has been well documented that improved desalting efficiency reduces the risk of corrosion and vice versa. The work life balance of the refinery corrosion engineer is frequently challenged by concerns that the risk of overhead corrosion is increasing as refineries process more challenging crudes and run lengths increase.

One component of this problem is the risk of ammonia and amine salt formation. As the concentration of ammonia and amines increase, the probability of salt formation increases. Computer modelling is employed to calculate this risk and to assure the selection of a neutralizing amine used to control overhead pH does not also contribute to the risk of salt formation.

Traditionally however, the natural level of ammonia and amines that are present in the system, meaning those not due to addition of the neutralizer, has been a “given” in the risk calculation. They are typically monitored, but not controlled. The material balance of amines/ammonia is complicated, the level of these contaminants cannot be easily correlated with desalting efficiency.

This paper introduces a new way of using the desalting process to help control overhead corrosion. A new adjunct chemistry, fed in combination with the emulsion breaker is shown in case histories to be able to increase the removal of salt, ammonia, and amines in the desalter, reducing their levels in the overhead. The nitrogen compounds are removed in the desalter and leave the system in the brine. The end result is the corrosion engineer has a new tool to reduce the risk of salt formation. This will improve crude flexibility, refinery profit margin, **and** work life balance.

Key words: corrosion, overhead corrosion, desalting, amine removal, ammonia, tramp amines

INTRODUCTION

In recent years, changes in crude supply have created new crude quality related challenges. More crudes are treated for H₂S with scavengers that increase amine content in the crude.

High nitrogen in heavy and high TAN crudes leads to increased sour water production. Processing more of these crudes increases the load on sour water strippers, often resulting in more ammonia in the stripped sour water, which is often used as desalter wash water.

To deal with these increased challenges, there have been a number of articles describing best practices for minimizing risk of corrosion of crude unit overhead exchangers.¹⁻⁴ Beginning with good desalting and caustic injection, these articles typically offer information on mechanical, monitoring, and simulation options for identifying and minimizing corrosion risk.⁵ However, even when best practices are in place, high corrosion rates and resulting operating problems can still occur.

The best practice definition of “good desalting chemical treatment” generally means finding a supplier with a good emulsion breaker (EB) chemistry selected for the refinery crude slate and a strong local site team. There is the expectation that as the refinery crude slate changes, the EB chosen will have enough flexibility to deal with the changes. Occasionally, a need develops for the use of “adjunct” chemistry, i.e., feed of a second product to supplement the EB.

A new class of adjunct chemistry, called “reactive adjunct,” offers the potential to dramatically increase the inherent flexibility of the desalter to respond to changing contaminants in the crude. This chemistry directly benefits the corrosion engineer in terms of their ability to manage risk of corrosion and better adapt to a more dynamic crude environment. This paper describes the chemistry, case histories, mechanism of operation, and strategies for use.

REACTIVE ADJUNCT CHEMISTRY

The emulsion breaker (EB) is the heart of the desalter chemistry program. EB is normally added to the wash water to accelerate the oil/water separation in the desalter. Adjunct chemistry refers to the use of a secondary chemistry to supplement the primary EB. Traditionally the classes of adjunct chemistries are 1) solids wetting, 2) reverse emulsion breaker, and 3) acid. Now there is a new fourth class of adjunct chemistry, one that is “reactive.”

A solids wetting agent is a surface active molecule that works to water-wet oil covered solids to help remove the oil from the solids and ease the transfer of the solid from the oil to the water phase. A reverse emulsion breaker is added to the wash water to help reduce in the amount of oil content in the brine. An acid reduces the pH of the desalter to optimize conditions at the oil-water interface for improved emulsion resolution.

Desalter water acidification has also been the standard alternative to improve amine removal from the system. Many refiners avoid this option due to safety and control concerns. There are also potential issues with acid partitioning in the crude and fouling from salt formation.⁶

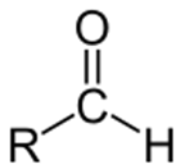
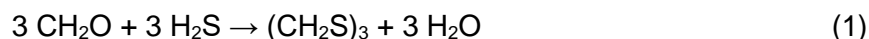


Figure 1: Aldehyde

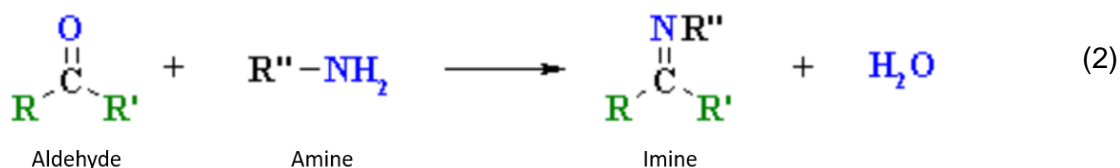
The reactive category is meant to describe chemistry that chemically reacts with contaminants in the crude in a way that is distinctly different from an acid-base reaction. Aldehydes are one class of chemistry in the reactive category, see Figure 1. They are non-acidic, nitrogen free compounds containing a reactive C=O carbonyl bond. The polar nature of the carbonyl bond makes it highly water soluble; it does not partition into the oil phase.

The carbonyl bond is well known to have significant reactivity. It is well known to refiners that aldehydes are commonly used to scavenge H₂S. For example, the reaction between the simplest aldehyde, formaldehyde and H₂S is shown in equation 1.



Refiners who are currently specifying use of nitrogen free scavengers may already have aldehydes and their H₂S by-products in their crude slate.

Aldehydes are also known to react with amines as shown in equation 2. This reaction has been shown to readily occur, even at room temperature and without the removal of water.⁷



Imines formed in this reaction are water soluble. These two examples introduce the rationale for studying the beneficial aspects of aldehydes in desalting.

LABORATORY STUDIES OF REACTIVE ADJUNCT CHEMISTRY

It was earlier mentioned that best practices for “good desalting” involves addition of EB selected for the specific crude slate of the refinery. The portable electric desalter (PED) is the laboratory instrument commonly used for testing the effectiveness of an EB on a specific crude slate. In this test, a water in oil emulsion is prepared under shear and exposed to heat and electric field as in the field desalter. Experience has shown a high correlation between field results and PED testing. Figure 2 shows data isolating the incremental impact of reactive adjunct chemistry on a Merey/WCS crude blend with API of 19. Compared to performance of the EB only, two ppm of reactive adjunct reduces the time required to get to 90% dehydration from eighteen to five minutes. Figure 3 shows the PED tubes from these tests to show the visible evidence of increased dehydration and reduction of oil in the water with use of reactive adjunct.

Figure 4 and Figure 5 give additional examples of the improvement in water clarity and dehydration efficiencies from use of reactive adjunct in PED testing.

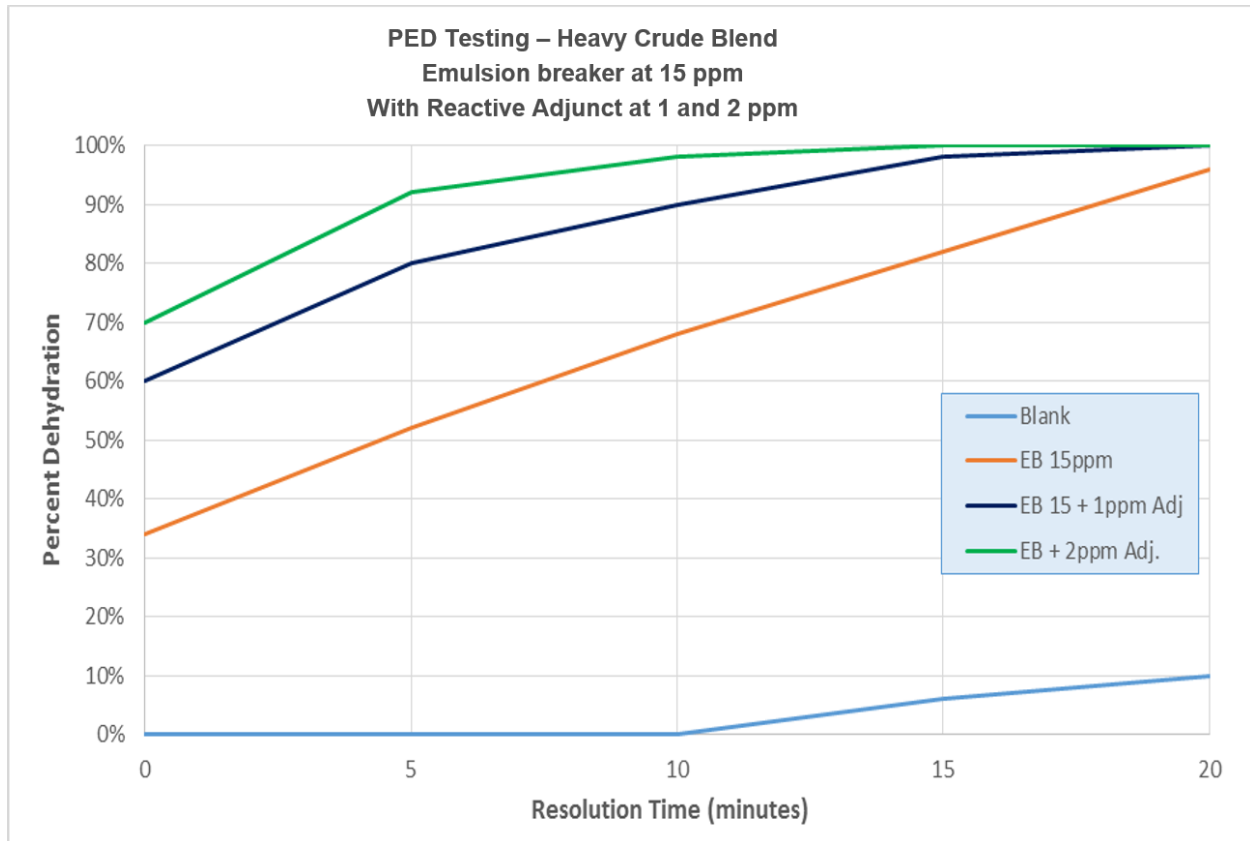


Figure 2: Impact of reactive adjunct on improving resolution time and % dehydration (19 API blend.)

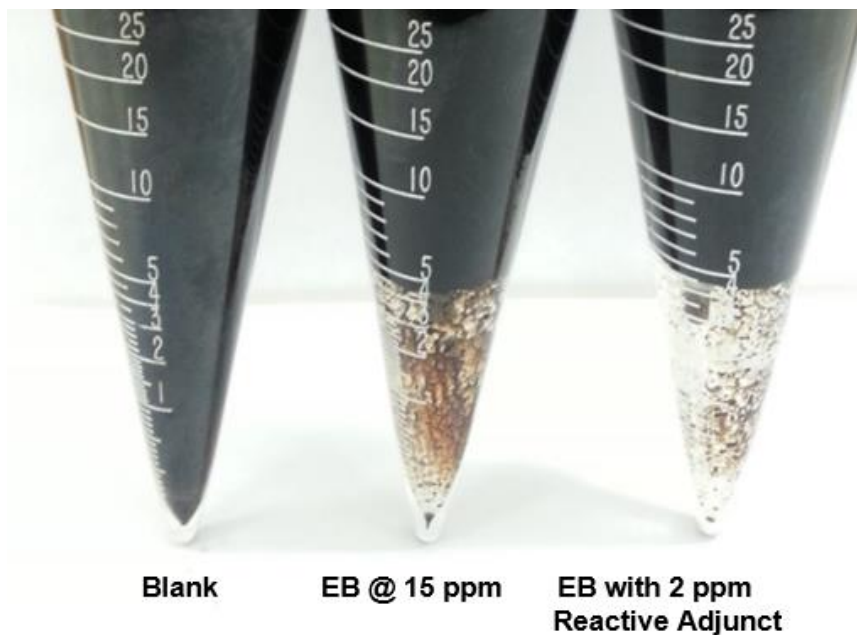


Figure 3: PED tubes showing brine quality impact of reactive adjunct from test results in Figure 2.

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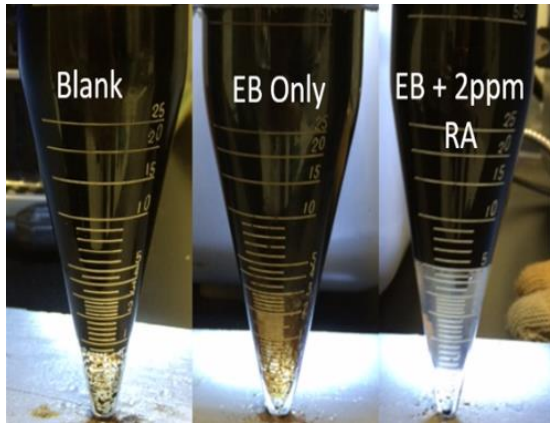


Figure 4: So. American Crude, 24^o API.

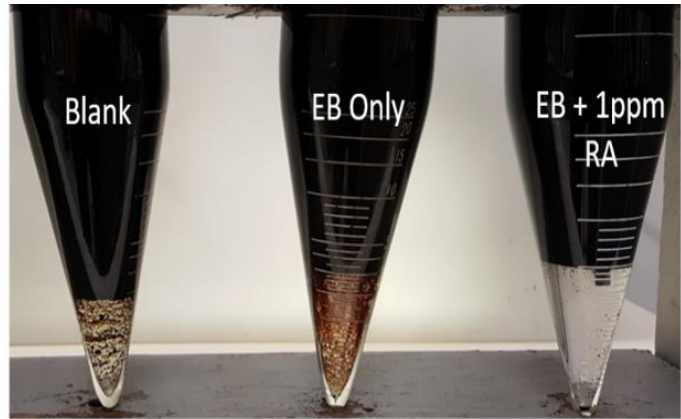


Figure 5: LTO opportunity Crude Blend, 32^o API.

PERSPECTIVE OF CORROSION ENGINEER

The corrosion engineer is often challenged with increased probability of overhead corrosion problems. Root cause analysis typically finds that concentrations of chlorides, amines, and ammonia are increasing in the crude overhead system and there are often spikes in these concentrations. Invariably, this analysis leads the corrosion engineer to work with their desalting partner to better understand what is changing and how to reverse these trends. Review of desalter operation pH typically indicates operation in the range of pH 8. Desalting efficiency is negatively correlated with increasing pH; this affects all contaminants in the crude, including amines. Figure 6 shows the estimated relationship between ammonia partitioning in the crude versus pH. Reduced desalting efficiency is part of the cause of the increase of amines in the desalted crude.

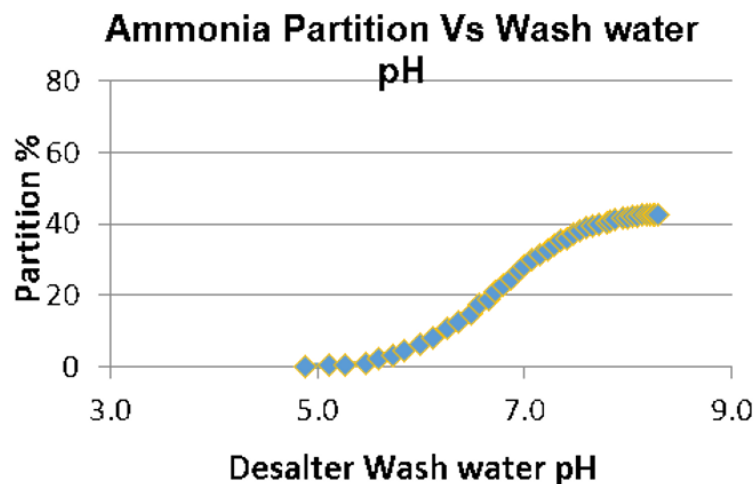


Figure 6: Impact of Wash Water pH on Ammonia Partitioning

Given the well-known reactivity of the carbonyl group with H₂S, amines, and ammonia, and the PED results showing improved emulsion breaking, field tests were organized to address the following questions:

1. Could the improvement in water resolution time lead to reduced water in the desalted crude?
2. Does improved water clarity lead to reduced chlorides in the desalted crude?
3. Will aldehydes react with amines in the crude and wash water to generate imines?

How might this impact:

- a. Desalter pH
- b. Ammonia/amine partitioning into the crude.
- c. Rate of movement of nitrogen containing compounds into the brine.
- d. Overall improvement of desalting for reducing concentration of overhead contaminants.
- e. Ability of the desalter to deal with changes in crude slates.

FIELD DATA – CASE HISTORY I

An Asian refinery processing opportunity crudes had all the elements of a difficult desalting challenge, including:

- Short desalter residence times (charge at 112% of design capacity)
- Opportunity crudes such as Maya, Roncador, Castilla, and Marlim in the normal crude blend.
- High pH wash water (8.7-9.6 range)
- High mix valve dP (to meet stringent salt outlet target)
- Severe feedstock solids (requiring frequent mud washing)
- High slop processing rate (2% of crude slate)
- API of 24-29, viscosity of 15-25 Cst @ 40°C

Despite efforts to optimize the program, the refinery was experiencing 150 to 250 ppm oil and grease in the brine with upsets to greater levels. This high oil content brine hampered waste treatment operation due to the increased slop generated. Tests to resolve the problem with EB selection, by increasing dosage or by adding a reverse emulsion breaker and solids wetting agent did not improve the desalting performance. The refiner did not want the expense and safety issues associated with an acid program, so instead opted to trial reactive adjunct chemistry.

Figure 7 shows the improved salt removal demonstrated during the reactive adjunct trial, which allowed for a 10 to 15 percent reduction in caustic injection into the desalted crude. This was indicative of a lower corrosion potential in the crude tower overhead system resulting from the improved chloride removal in the desalter.

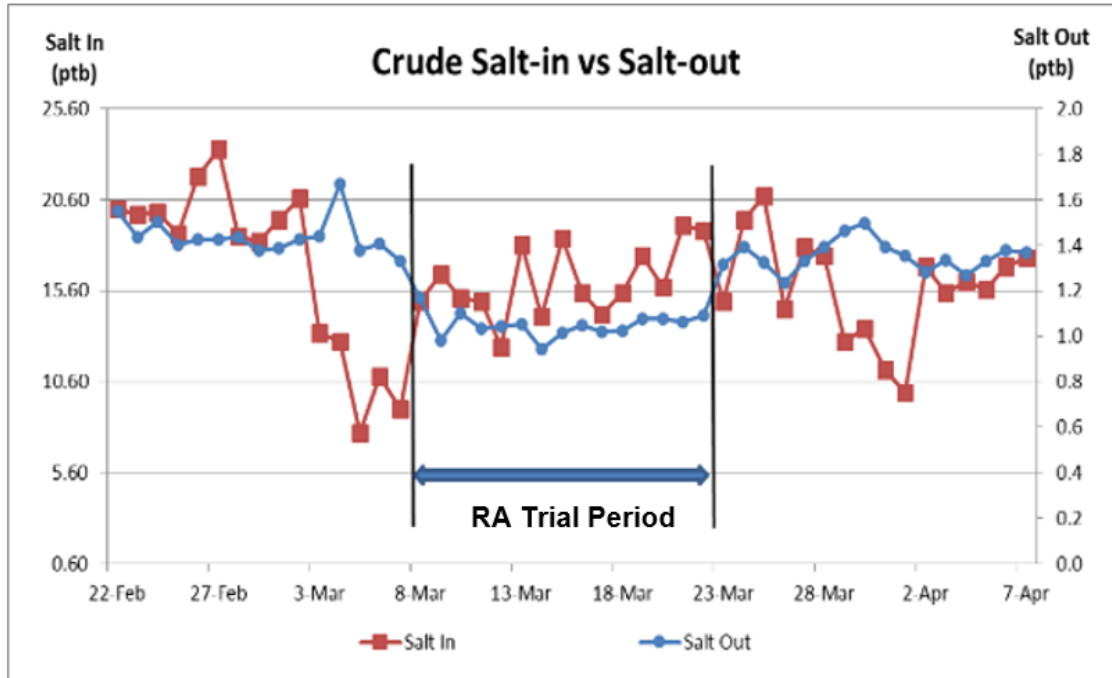


Figure 7: Salt removal improvement with use of Reactive Adjunct (RA.)

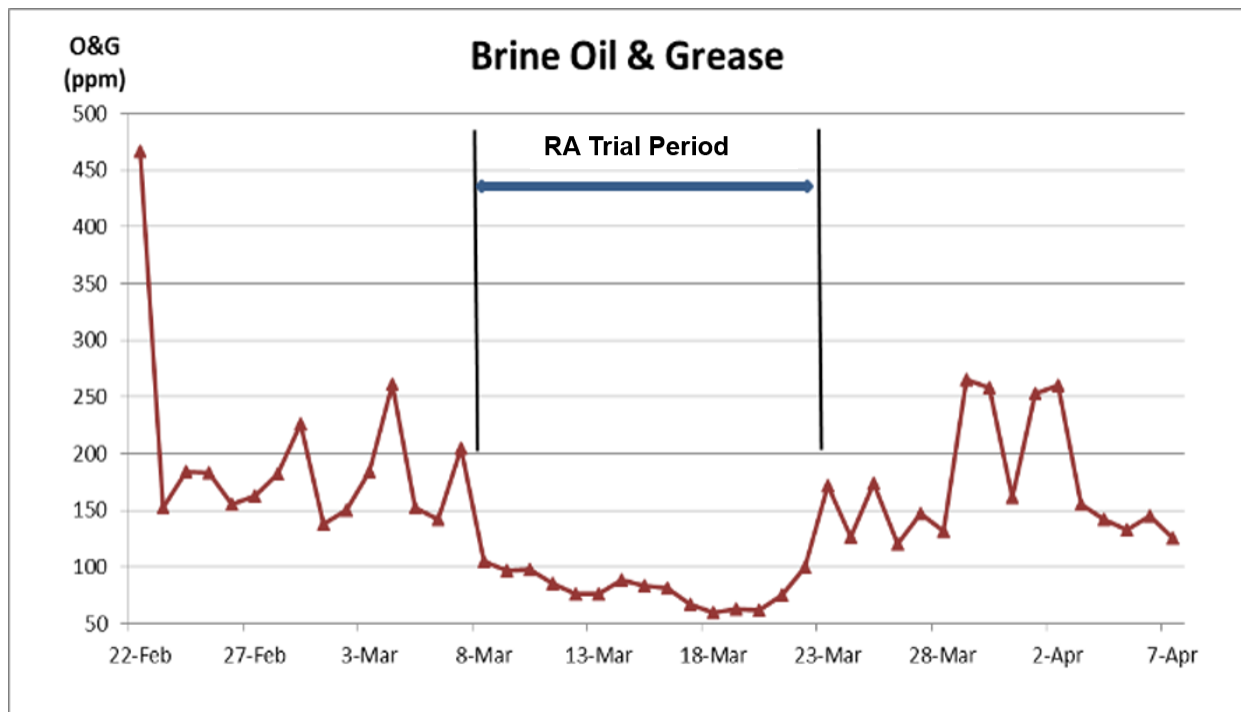


Figure 8: Reactive adjunct (RA) reduced oil in brine by 55% and improved consistency

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Figure 9 shows the dosage of the reactive adjunct chemistry ranged from 2.5 to 3.4 ppm (based on the crude rate) set against the brine pH. The improvement in oil and grease and solids removal was approximately the same at these two dosages, indicating a potential to further reduce dosage while maintaining the desalting improvements. When the dosage was reduced from 3.4 ppm to 2.5 ppm the brine pH trended higher.

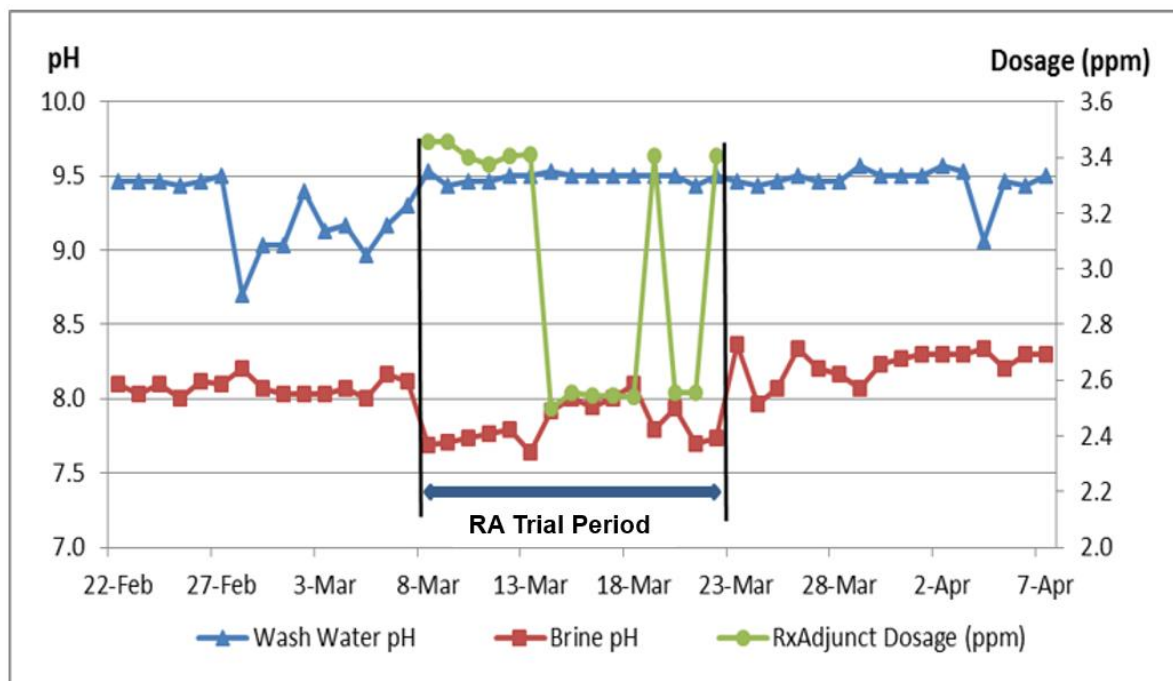


Figure 9: Impact of Reactive Adjunct on brine pH.

This trial demonstrated the desalting improvements and downstream benefits of using the reactive adjunct chemistry at a low dosage range.

FIELD DATA – CASE HISTORY II

A refinery in North America was experiencing severe crude tower salting problems when processing a crude contaminated with tramp amines. The crude slate was typically a 22 to 24 API range blend of various opportunity crude and heavy oil feedstocks. The low gravity and high solids of the crude slate would frequently overwhelm the WWTP with oily brine from the single-stage desalter. These feedstocks arrived by barge and were often heavily treated with amine-based H₂S scavengers. The high tramp amine content also compounded the emulsion and oil under-carry issues of the desalter, further increasing the chloride loading in the overhead.

The generic strategy of adding an acid to the desalter wash water to partition amines into the brine was not practical due to the very low pH control point needed for an acid program (generally less than 3.5) and the WWTP's pH limitations on the incoming waste water. The refiner opted to trial the aldehyde based, non-acid, reactive adjunct chemistry, in part because the pH control point of the program would be around 6.0. The key benefit the customer sought

was the removal of the tramp amines from their system and the resulting improvement in their crude unit reliability.

Table 1 shows the reduction in salt points achieved by feeding 30 ppm (based on the crude rate) of the reactive adjunct to the existing desalting program. Notice how the pH of the brine was reduced from 8.4 to 6.0. Also note the disappearance of the amine (MEA) and ammonia from both the crude tower overhead and the desalter wash water (which consisted mainly of crude tower overhead water). With the reduction of ammonia and amines in the crude tower overhead, the resulting drop in the salting points were indicative of the lower corrosion potential in the crude tower overhead system.

Table 1
Comparison of operating parameters during amine removal trial.

Crude Tower Overhead	Baseline Data	During Chemical Trial	Desalter Parameter	Baseline Data	During Chemical Trial
Ammonia	70 ppm	9 ppm	Wash Water MEA	75 ppm	10 ppm
MEA	75 ppm	29 ppm	Wash Water Ammonia	150 ppm	7 ppm
Chlorides	52 ppm	14 ppm	Brine pH	8.4	6.0
Ammonia salt point		Reduced by 23°F (13°C)	Solids Removal	29%	53%
MEA salt point		Reduced by 15°F (8°C)	Salt Removal	91%	95%
			Ca/Mg/Na/K Removal	63%	75%

CONCLUSIONS

The mechanism indicated by chemistry fundamentals has been reinforced by field and lab results. The carbonyl group is highly reactive with amines to form imines. The conversion reduces desalter pH. Unlike amines, the imines do not partition into the crude in the desalter. They are water soluble and are removed from the desalter with the brine. There are three mechanisms reducing amine carryover into the desalted crude, 1) reduced concentration of amines, 2) reduced pH that directly reduces the amine partitioning effect, and 3) improved desalting efficiency.

The combination of these mechanisms reduces the concentration of amines in the desalted crude and in the crude tower overhead. Lower desalter pH reduces the volume of rag layer, improving salt and solids removal, and reducing oil carry under into the brine.

In Case History II, there is strong evidence of pH reduction, conversion of amines to imines (reduced amine and ammonia concentrations,) and improved solids and salt removal (Table 1). These observations are consistent with fundamental chemistry mechanisms.

The dosage of reactive adjunct in Case History II is nine to twelve times higher than Case History I. In Case History I, there is evidence of the same mechanisms demonstrated in Case History II, but at a reduced effect in proportion to the dosage. Referring back to Figure 9, when the dosage of reactive adjunct was increased (green line,) the pH dropped (red line) and vice versa. This indicates the same mechanisms are at play, albeit at lower intensity because of lower dosage.

RECOMMENDATIONS

There are three strategies available for deploying this new chemistry: 1) Desalter efficiency strategy, 2) Amine removal strategy, and 3) Crude-flex strategy.

The desalter efficiency strategy uses low dosages of the chemistry (1 to 4 ppm based on crude charge) to improve desalter efficiency. It is designed to deliver improved desalter performance beyond that which can be obtained by the primary EB alone, but does not use a high enough chemical dosage for significant amine removal. In this approach, the reactive adjunct chemistry improves the rate of emulsion resolution, improving the dehydration of the oil and the salt and solids removal efficiencies. With a tighter oil/water interface, the brine quality is dramatically improved, resulting in a reduction in slop oil generation and its associated reprocessing costs.

The amine removal strategy uses higher dosages of the reactive adjunct chemistry (10 to 30 ppm based on crude charge) and is designed to reduce the levels of tramp amines coming in with the crude and desalter wash water. By removing these amines in the desalter, there is an associated reduction in the potential for amine chloride salt deposition in the crude tower overhead, as indicated by the lower amine salt point temperatures.

For those refiners with no current operating problems but with the need/desire to be more flexible to accept opportunity crudes, the “crude-flex” strategy is a viable option. This is a preparedness strategy, available at minimal cost to the refiner that is also beneficial to the refiner experiencing an occasional upset in desalter operation.

In this strategy, the reactive adjunct is fed continuously at low levels assuring feed system integrity and operating consistency. When the opportunity crude arrives (or upset condition occurs) the reactive adjunct dosage is increased in accordance with the increased desalting challenge. PED studies can be conducted to predict dosage requirements if time allows. But because of the wide latitude in dosage flexibility, this advance notice for dosage estimation is not required. Think of this option as similar to a stand-by acid option without all the headaches and risks of acid. This option provides the flexibility to handle a wide variety of challenges as shown in Case Histories I and II.

The crude-flex strategy has no incremental operating cost when opportunity crudes are not in use. The reactive adjunct is used to reduce EB dosage, and reduced consumption of the EB pays for the cost of the reactive adjunct. As a side benefit, this strategy also allows for more flexibility to respond to upsets in the sour water stripper or slop formation.

The reduction in overhead corrosion risk gained through use of reactive adjunct chemistry helps corrosion engineers to improve their “work-life balance”.

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