### White Paper

Impact of Opportunity Crudes on Fouling in Preheat, distillation, and furnace systems

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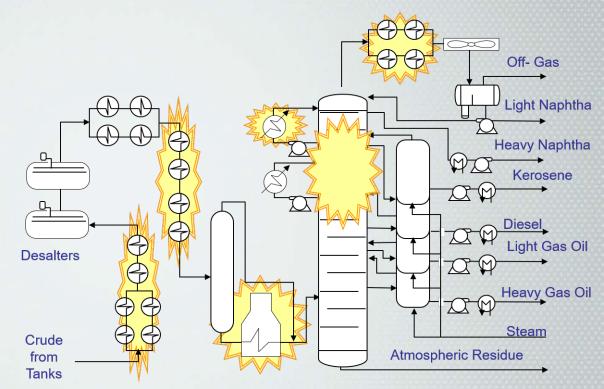
# **Fouling in CDU**

Relative to crudes that are not price advantaged, opportunity crudes contain higher level of contaminants that increase processing costs. Fouling occurs as a result of the inability to get the contaminants efficiently out of the refinery.

The areas highlighted in yellow are the primary locations of fouling in the CDU. Heat, vaporization, reactions, and physical settling of contaminants cause the fouling.

The desalter is the most important contaminant removal process in the refinery. Opportunity crudes not only increase contaminant loading on the desalter, they reduce desalting efficiency.

The combination of more contaminant loading and reduced desalter efficiency may cause a step change increase in the rate of fouling. The cost of this fouling reduces the benefit of processing opportunity crudes.

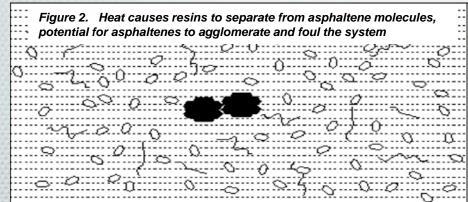


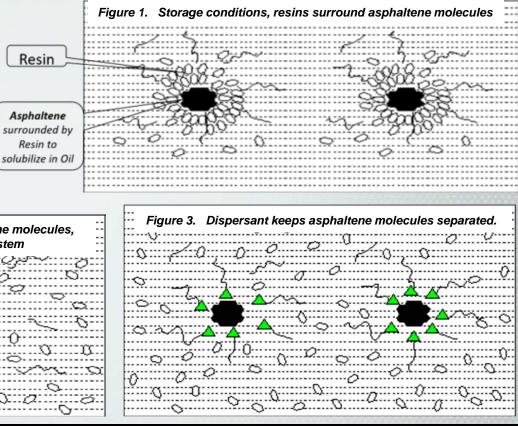


## **Asphaltene Fouling in Pre-Heat System**

Figure 1 shows, that at storage temperatures, the asphaltenes are surrounded by naturally occurring resins. Figure 2 shows that conditions occurring in the pre-heat system before the desalters disperses the resins in the oil, allowing the asphaltenes to agglomerate and foul the pre-heat. One tactic to manage this fouling problem is to add an asphaltene dispersant, figure 3. The idea is to surround the asphaltene molecule with thermally stable synthetic resins to reduce the rate of fouling.

Vaporization of water in the crude upstream of the desalter can cause precipitation of salts. The salts will deposit on the hot heat transfer surfaces and can react with organics in the crude to form tenacious deposits. Corrosion products and other filterable solids in crude can also deposit in the cold pre-heat section.





## **Opportunity Crudes Contaminants impact fouling potential**

- Contamination from H2S scavengers, amines and unreacted triazines
  - These contaminates are water soluble, but difficult to remove in desalter. Can cause salting in overhead and reduce distillation efficiency to manage salting problems.
- Phosphate esters, either added to crude or added with high temperature corrosion inhibitors
  - Cannot be removed in desalter, can cause crude column fouling
- Organic chlorides

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- Can be present in crude, cannot be removed in desalter, can increase potential for salting in overhead
- Higher filterable solids content
  - Fine particles are especially difficult to remove in desalter, can create rag layer impeding transfer of oil and water at the interface causing oil under-carry or water carryover.
  - Efforts to reduce rag can be less mixing energy and less salt removal.
  - Solids Prone to physical settling as they concentrate due to distillation.
  - Higher metals content can catalyze coking reactions
  - Potential for crude incompatibility (see OCMS seminar 3)
  - Heavier crudes reduce specific gravity difference and driving force for oil water separation

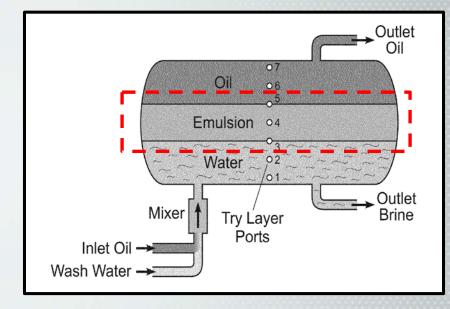


# What is a Rag Layer

- Rag is a stable emulsion of oil, water, and solids.
- Stable is a relative term, the more stable the emulsion the longer it takes to resolve.
- One can think of rag layer in material balance terms, if the rate of formation of rag layer emulsion is greater than the resolution of rag, the rag layer increases in size.
- The specific gravity of the stable emulsion is higher than oil but lower than water, it sits at the oil/water interface.
  - Ray layer inhibits mass transfer at the interface.

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- Mass transfer of oil from water phase to oil phase is reduced, increasing oil under-carry.
- Mass transfer of water from oil phase to water phase is reduce, increasing water carryover.





# What Causes Rag Layer?

- Rate of emulsion breaking is too slow and incomplete
- Rate of emulsion breaking is a function of:

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- Difference between specific gravity of oil and water
- Mixing energy. The greater the mixing energy, the better the contact between water and oil for removal of water soluble contaminants. However, increased mixing energy creates a more stable emulsion.
- Presence of contaminants that are antagonistic to emulsion breaking: ammonia, amines, precipitated asphaltenes, solids
- Precipitated asphaltenes will stick to fine solids, creating material of a specific gravity between that of oil and water.
- Small particles most problematic, < 1 micron diameter. Very slow to settle.</li>
- Rag layer problems are an obvious industry dilemma. In 2014-2017, over 30 patent applications on rag layer control were filed, most involved physical removal from desalter and external treatment. External treatment reported to be relatively easy, this is indirect indicator there is potential to reduce rag in desalter.
- Without physical removal of rag, speed of emulsion breaking chemistry is important variable for reducing rag layer.
  - There is more variation in speed of emulsion breaking chemistry than is generally recognized, many refiners place a low priority on investigating emulsion breaker chemistries.



## Why does speed of emulsion breaking chemistry vary?

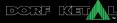
#### Emulsion breakers are not alike

- All suppliers have multiple formulations to optimize the EB to the crude slate.
- Suppliers compete on EB capability, advisable to check selection as crude slate changes.
- When a single component program is not giving desired results, suppliers offer adjuncts.
- Suppliers offer adjunct chemistries to supplement EB for faster emulsion breaking
  - Various acids to take advantage of pH dependency of rate of emulsion breaking and to remove certain metals.
  - Solids wetting to address issues with oil covered solids
  - Reverse emulsion breaker to coagulate oil in brine, making it easier to rise in desalter
  - Reactive adjunct. Increases speed of emulsion breaking which improves rag layer control and results in higher desalter efficiency
  - Amine removal agent. Non-acid additive that reduces corrosion risk in crude column overhead by breaking amine cycle.



## **Fouling in Hot Preheat and Furnace**

- Just as in cold pre-heat, vaporization of water in the desalted crude can cause precipitation of salts. The salts will deposit on the hot heat transfer surfaces and can react with organics in the crude to form tenacious deposits
- Corrosion products and other filterable solids in crude can also cause fouling
- Metal catalyzed fouling is the reaction of metals with asphaltene constituents to form coke
- Soluble and suspended asphaltenic material can lose solubility and foul heat transfer surfaces



## **Use of Anti-Foulants for Pre-heat System**

- Anti-foulants can reduce rate of fouling
- May contain:
  - Dispersants to keep asphaltenes from settling out in equipment
  - Metal deactivators to reduce the rate of metal catalyzed coke reactions
  - Anti-oxidants to suppress oxidation reactions
  - Scale inhibitors
  - Corrosion inhibitors
- One size does not fit all, actives customized to fouling mechanisms in the specific system
- Important for anti-foulant to have thermal stability and caustic tolerance



## **Caustic Addition and Downstream Fouling Issues**

- Thermally unstable chloride salts of Mg and Ca in the desalted crude release hydrogen chloride gas in the crude column
- The acid gas condenses in the overhead causing corrosion.
- Caustic is added to desalted crude to improve thermal stability of Mg and Ca salts, reducing HCl generation
- Caustic feed to protect against overhead corrosion adds sodium to system that can cause downstream furnace fouling, sodium is a catalyst for coke formation
- Improved desalting reduces caustic demand and potential downstream impact of sodium



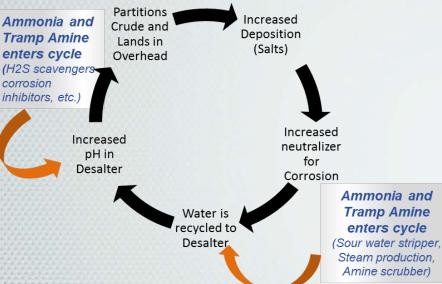
## **Furnace fouling downstream of CDU**

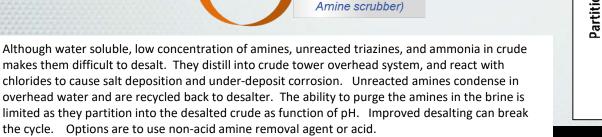
- The distillation process concentrates metals in the system, the rate of metal catalyzed coking increases as the metals increase in concentration.
- Studies at Tulsa Joint Industry Project reported that empirical measurements showed fouling rates are a function of soluble (Na, Ca, Mg) and insoluble (Fe, Al, Si) metals.
- Coking furnace manufacturers recommend Na limits in feed to furnace
  - Limits vary, as low as 10 ppm Na in coker feed
  - 20 ppm limit in coker feed often used as rule of thumb
- High efficiency desalting is necessary to keep Na below 10 ppm in coker feed

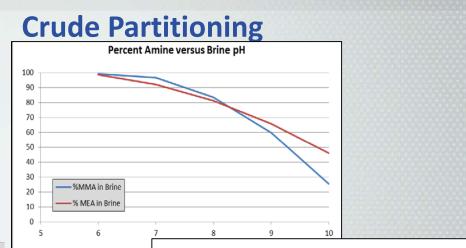


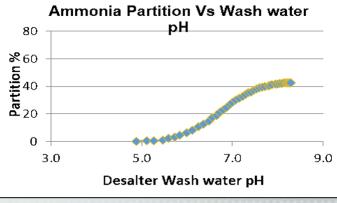
# **Fouling from Tramp Amines**

## **Amine and Ammonia Cycle**



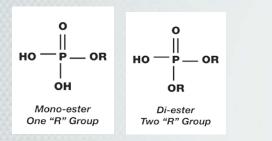




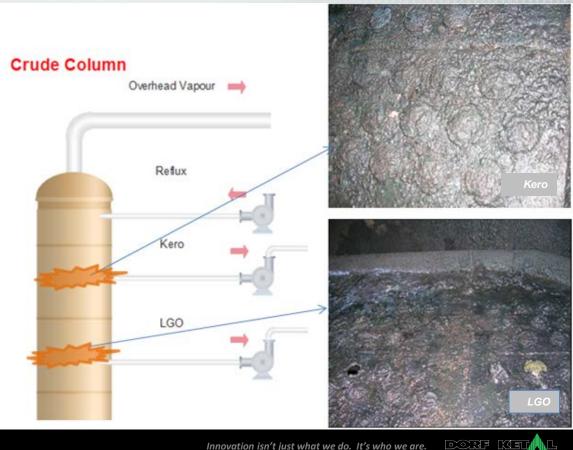


## **Crude Column Fouling from Phosphate Esters**

**OCMS Seminar 1 discussed fouling from** thermally unstable partial phosphate esters. Partial esters are as acidic as phosphoric acid.



- OH bond is thermally unstable, decomposes at temperatures in CDU
- **Products of decomposition are volatile** phosphorus compounds that accumulate in the Crude column as shown
- Two sources of phosphate esters corrosion • inhibitor for high TAN corrosion and upstream corrosion inhibitor



## Example of deposit analysis from crude column

High ash content indicates significant presence of inorganic content

Phosphorus is 67% of the ash

Low pH of the water extracted deposit shows acidic nature of the sample, identified as phosphoric acid

**Opportunity crude contained high TAN,** refinery was using phosphate ester corrosion inhibitor

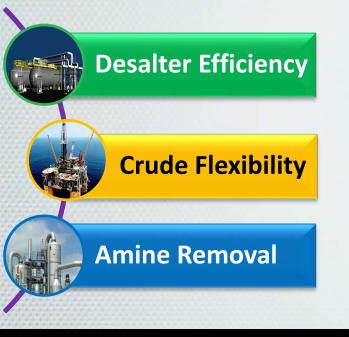
Phosphorus deposits the result of thermal decomposition of the corrosion inhibitor, settling out in column trays

Kero Tray Deposit Sample analysis results				LGO Tray Deposit Sample analysis results			
Sr. No.	Test carried out		Deposit Sample	Sr. No.	Test carried out		Deposit Sample
1	Appearance		Black solid	1	Appearance		Black solid
2	LOD @120°C (%)		36.22	2	LOD @120 <sup>0</sup> C (%)		36.65
3	Ash@800 <sup>0</sup> C (%wt)		47.02	3	Ash@800 <sup>0</sup> C (%wt)		57.02
4	DCM insoluble (%wt)		96.49	4	DCM insoluble (%wt)		95.59
5	Water insoluble (%wt)		95.86	5	Water insoluble (%wt)		94.15
6	PH of water s	soluble portion (pH	2.79	6	PH of water soluble portion (pH of		2.64
7	Cations (By IC of water	Fe	66	. 7	Cations (By IC of water	Fe	54
	soluble part) [ppm]	Ca	Nil		soluble part) [ppm]	Ca	Nil
	Anions (By IC of water soluble part) [%]	PO <sub>4</sub> <sup>3-</sup>	6-7%		Anions (By IC of water soluble p art) [%]	PO4 <sup>3-</sup>	б-8%
8	Metal analysis of Ash (%wt)	Fe	37.66%	8	Metal analysis of Ash (%wt)	Fe %	24.03%
		Ca	848 ppm	]	ASI (70WL)	Ca	2777 ppm
		Р	66.62%			Р	85.47%



DORF KET

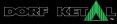
Innovation isn't just what we do. It's who we are.™ Two new patented desalter chemistries are now available to supplement emulsion breaker –
1) Reactive Adjunct for desalter efficiency and
2) Amine Removal Agent for improved amine control.



Increases the speed of emulsion breaking which improves rag layer control and results in higher desalter efficiency without capital investment

Improves the ability of the refiner to make faster purchasing decisions and respond more effectively to occasional upsets in desalter operation

Non acid additive that reduces corrosion risk in Crude Column Overhead by breaking the amine cycle without safety risks of acid





Innovation isn't just what we do. It's who we are.™ TANSCIENT<sup>™</sup> minimizes risk of corrosion and phosphorous fouling when acid content from high TAN crudes requires corrosion inhibitors

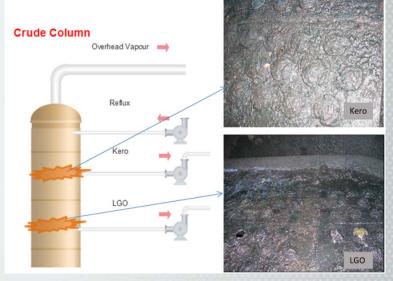
**TANSCIENT<sup>™</sup>** is a patented breakthrough in corrosion science that increases safety and reliability of refining high TAN crudes.

#### Superior phosphorous efficiency

- Increases your control of corrosion protection
- Reduces risk in addressing variations in naphthenic acid composition.

#### Superior thermal stability and oil solubility

- More effective passivation and ongoing protection with up to 80% less phosphorus than competitor HTCI products
- Minimizes risk of phosphorus fouling and catalyst impairment.





## Conclusions

- Opportunity crudes increase fouling risk
- Best in class desalter operation is critical for desalting opportunity crudes and for managing tramp amines
- Innovation is happening at rapid pace, significant efforts in new intellectual property for rag layer control
- If using high temperature corrosion inhibitors, thermal stability is critical for fouling control
- Important to stay current on new technologies
- There are new advances in desalting chemistry technology to improve speed of emulsion breaking to reduce rag layer

