CHEMICAL CLEANING OF CRUDE OIL FOULING DEPOSITS; APPLYING THE COKE SPECTRUM

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ABSTRACT

Fouling of heat exchangers and other refinery equipment by crude oil deposits is a chronic operating problem. Mitigation of crude oil fouling has historically been driven by mechanical cleaning applications. In general, many such deposits are narrowly defined as coke fouling, for which the prescribed cleaning has traditionally been high-pressure water blasting (HPWB). The results for this type of cleaning process are mixed at best. Heat exchangers are being returned to service in less-than-ideal operating conditions, driving the need for more efficient cleaning regimens.

A detailed characterization of 62 field-based crude oil fouling deposits from hydrocarbon process units was presented by the authors at the 2019 conference. This paper demonstrated that such deposits are exceptionally complex, resulting in the introduction of the Coke Spectrum. Here, these deposits are revisited, and chemical cleaning methods are applied.

Chemical cleaning encompasses a variety of applications, which may be used to assist in the complex problem of mitigating crude oil fouling. Circulation, ultrasonic immersion, and clean-in-place techniques were reviewed on laboratory-sized samples to determine what chemical cleaning agents may be most effective on the various categories of foulant which make up the Coke Spectrum. Combination techniques which employ both chemical and mechanical applications simultaneously or in sequence are considered in depth.

The correlation between chemical composition and the effectiveness of the cleaning method is explored with special considerations being made for the scaling of the cleaning process for industrial applications.

INTRODUCTION

Fouling processes can severely impact the overall performance of process units and instrumentation, resulting in losses to heat transfer efficiency and volume throughput; increases in emissions and maintenance requirements; delays in production and many costs from additional fuel gas consumption to the labor for pulling and cleaning the fouled equipment. The formation of undesirable coke products in the refining process is a particularly challenging fouling problem that many refining operations face. Techniques to mitigate coke fouling may include the implementation of temperature limits to avoid the pyrolysis of hydrocarbons in the distillation process, additives may be slip-streamed into the process feed, increases in fuel gas consumption, careful selection of materials or the application of coatings, and periodic in-place cleanings. These techniques can be very costly and may impact production; moreover, they may result in a redesign of the process equipment through capitol projects, added maintenance, and in the end, may not be entirely effective.

As described in the precursor paper by the authors on the subject of coke fouling [1], not all such deposits are identical. The composition of the coke foulant is highly dependent on the feedstock for the process, the process conditions, and the process itself. Though coke fouling is far more likely to be found towards the final stages of the crude pre-heat train, coke can occur in any processes where heavy hydrocarbons are being heated, as hot spots in the process can result in thermal cracking and pyrolysis. Lower carbon chain, low sulfur crude oils, often referred to as light, sweet crude, are less prone to coke fouling; however, processes such as those in the Fluid Catalytic Cracking (FCC) unit, can result in the formation of undesirable coke deposits.

Coke deposits are traditionally one of the most difficult foulants to treat in the refining process [2]. This is due to numerous factors such as, the low hydrogen-to-carbon ratio in true coke deposits, the tight packing arrangement of atoms in the structural lattice, and the incorporation of other fouling products which can tightly adhere to equipment surfaces. As a result, the cleaning of coke fouled equipment has been a major challenge of the industry.

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Traditional cleaning methodology for heat exchangers prone to coke fouling sees the exchanger removed from service during a turnaround or maintenance outage for hydroblasting regularly, with numerous chemical or steam-out cycles done in-place in the interim. Depending on the fouling and metallurgy of the bundle, these may be pulled several times a year, or once every 5 years. These cleaning methods are time consuming and for equipment, such as shell and tube heat exchangers, the two sides of the item may be treated separately and even the use of ultra-high-water pressures may not be effective. As a result, the equipment is often returned to service in less-than-optimal conditions. The remaining foulant may then act as a nucleation point for future fouling and run-times for the equipment become shorter and shorter as the equipment ages.

Ultrasonic chemical cleaning offers an alternative to the traditional methods as it combines both chemical and mechanical cleaning to remove difficult foulant through the incorporation of acoustic energy. The immersion technique sees the simultaneous cleaning of the entire piece with access to all interstitial spaces which may be difficult to reach with other cleaning methods [3]. Ultrasonic scale prevention (USP) is a technology which is still in its infancy [4]; however, there exists some promise that this may offer a true clean-in-place (CIP) ultrasonic technique in the future, combining two mitigation tools to extend the run-time in equipment which cannot effectively be removed from service for general maintenance work. At present, it is possible to create a Closed Ultrasonic System (Closed U/S) in an immersion vessel by sealing off a heat exchanger inside its shell after the fluid has been de-gassed. Benefits to performing ultrasonic cleaning under closed conditions could be the introduction of different chemistries, and capitalization on the effects of vaporous cavitation.

This paper revisits the sixty-two coke foulant samples previously characterized by the authors and evaluates different cleaning methodologies and chemistries to determine whether there is a one-size fits all approach to coke foulant removal or whether each process must be addressed on a case-by-case basis [1].

METHODS

Chemical Selection: The selection criteria for the chemistry used is based on the paper regarding the development of ultrasonic chemistries for industrial applications [5]. It was determined that the same chemistries would be used for all methods to minimize the variables; thus, chemistries compatible with both circulation and ultrasonic techniques were selected.

Two chemical blends were tested to determine their effectiveness towards the samples. The first was an aqueous degreasing agent containing surface active agents (surfactants) and some additives designed to disperse coke particulate and asphaltenes.

The pH of the blends were adjusted to 13.0 using potassium hydroxide. Hydroxide ions are used here to convert organic acids, such as naphthenic and aromatic acids, to their base forms. These organic acids serve to stabilize asphaltenes and resins found in crude oil through hydrogen bonding and π-stacking. Conversion to their base forms have been shown to assist in the dispersion of heavy hydrocarbons in solution. Potassium hydroxide was selected over sodium hydroxide due to its greater effectiveness towards sulfurous compounds common is asphaltic deposits. The temperature of the solution was maintained between 60-65°C (140-150°F) in order to stay under the cloud point of the solution, resulting in maximum effectiveness for the chemical solution.

The second solution is a solvent-based degreasing agent with effective heavy hydrocarbon cutting ability. This is mixed with an asphaltene dispersant and water and brought to a pH of 13.0 with potassium hydroxide to create a stabilized oil-in-water emulsion. The temperature of the solution was maintained between 60-65°C (140-150°F) in order to stay under the flash point of the primary solvent in the mixture, and reduce the number of variables in the experimentation.

Although not discussed in depth in this paper, the effects of corrosion of the chemical solutions on the materials of construction for heat exchangers and other equipment which may be cleaned has been considered and tested. This work is discussed in depth in the paper by Shank et. al [5] on the development of ultrasonic chemical cleaning agents, as well as papers on previous corrosion studies done by the authors [6,7,8].

Circulation: Circulation is a common technique used to clean equipment in place. For heat exchangers, a circulation pump is attached to the inlet and outlet of the exchanger. The hot process side of the exchanger and the cold process side of the exchanger are cleaned separately, though several units may be cleaned in sequence, or cascaded. The velocity of the fluid being circulated may be adjusted to create turbulent flow and increase the shear stresses to dislodge any adherent fouling deposits. Flow reversal is also a common method to break up deposits.

In order to mimic the circulation process in a laboratory setting, each sample was added to a 250 mL glass beaker filled with 200 mL of either the aqueous or the solvent-based degreaser heated to 65°C (150°F) on a hot plate with magnetic stirring capacity. The magnetic stirring was set to a rate of approximately 1000 rpm in order to mimic turbulent flow.

Samples were weighed prior to adding to the pre-heated solution, and the solution was allowed to work on the samples for 6 hours while stirring. A watch glass was placed on top of the beaker to reduce evaporation and prevent spills due to bumping or overheating. Observations regarding the dispersion of any solids in the sample were noted. The solutions were allowed to sit for approximately one hour and further observations regarding the separation of any oils and precipitation of any solids were made. Samples were then decanted through a sieve, gravity filtered, dried and weighed. Pictures were taken of the samples before and after treatment in each solution.

Ultrasonic Immersion: Ultrasonic immersion cleaning is a technique that has been around since the 1950s; however, the large-scale application to industrial processes was introduced to the market in 2009. This technology is a combination of chemical and mechanical cleaning, and an in-depth description of the technique is given in Kieser et al. (2011) [3].

The laboratory ultrasonic tank is a much smaller vessel but was designed to use the same 25 kHz frequency as the large-scale tanks, and outputs approximately 4.7 W/L of acoustic energy into the fluid at any given spot within the vessel, similar to the 4.5 – 6.5 W/L observed in the vessels implemented in the field. Although the temperature in the laboratory vessel is not finely controlled, the temperature output averages around 60°C (140°F) when the lid to the tank is removed.

Only the aqueous chemical blend was tested using this application method as the ultrasonic immersion technique is performed under open conditions. Although, it is possible to utilize the solvent-based degreaser in the open system under ultrasonic conditions, it is not recommended due to the potential generation of a flammable atmosphere above the vessel. The temperatures used are just below the flash point of the primary solvent, and although the laboratory environment is controllable, this is not the case for field applications; thus, only the aqueous blend was tested.

Polyethylene tri-corner beakers were used in the ultrasonic tank to reduce attenuation in the container. Although glass conducts the sound energy better, the frequency of the ultrasonic wave function at 25 kHz matches the resonant frequency of pyrex and kimax borosilicate glass, shattering it within a few hours of application. The polyethylene beakers were filled with 200 mL the aqueous degreaser and heated to a temperature between 60-65°C (140-150°F) and de-gassed by the application of sonic energy. The level of the fluid inside the vessel was brought just to the same level in the sample beakers in order to assist in the delivery of the acoustic waves to the sample material.

Samples were weighed prior to adding to the pre-heated solution, and the solution was allowed to work on the samples for 6 hours in the ultrasonic vessel. A watch glass was placed on top of the beaker to reduce evaporation. Observations regarding the dispersion of any solids in the sample were noted. The solutions were allowed to sit for approximately one hour and further observations regarding the separation of any oils and precipitation of any solids were made. Samples were then decanted through a sieve, gravity filtered, dried and weighed. Pictures were taken of the samples before and after treatment in each solution.

Closed Ultrasonic System: Ultrasonic Scale Prevention (USP) technology applies the acoustic energy directly to the tubesheet of an exchanger while it remains in-place in the unit [4]. This is done by affixing several ultrasonic transducers directly to the tubesheet of the exchanger and tuning the acoustic output to the resonant frequency of the metal in order to propagate the signal throughout the equipment. The constant vibration of the metal is thought to mitigate the nucleation of fouling material on the surface of the equipment while it is running. Thus, it is primarily a technique to prevent scale formation. The sonic energy which is applied to the equipment is fairly low and is applied to the metal and not the fluid. However, application of chemical cleaning solutions to a unit with the USP technology affixed could eventually serve as an ultrasonic Clean-in-Place (CIP) technique with an increase to frequency and power output of the transducers. As such, it is important to note here that the USP technology is not able to produce these frequencies or power outputs at this stage; thus, rather than referring to this as Clean-In-Place (CIP), the authors have chosen to refer to this as a “Closed Ultrasonic System (Closed U/S)”, as the frequency and powers used in this study mimic those involved in Ultrasonic Immersion technology more closely.

In order to mimic the potential application of a Closed U/S, 200 mL of either the solvent-based or aqueous solution was added to polyethylene bottles. The lids were left off as the solutions were brought up to a temperature between 60-65°C (140-150°F) and de-gassed by the application of the sonic energy. The level of the fluid inside the vessel was brought just to the same level in the sample bottles in order to assist in the delivery of the acoustic waves to the fluid.

Samples were weighed prior to adding to the pre-heated solution. Once the sample was added to the solution, the lids to the bottles were replaced in order to create a Closed U/S. The solution was allowed to work on the samples for 6 hours in the ultrasonic vessel. Observations regarding the dispersion of any solids in the sample were noted. The solutions were allowed to sit for approximately one hour and further observations regarding the separation of any oils and precipitation of any solids were made. Samples were then decanted through a sieve, gravity filtered, dried and weighed. Pictures were taken of the samples before and after treatment in each solution.

RESULTS

For information regarding the characterization of the coke fouling samples the reader is encouraged to refer to the precursor paper by the authors presented at the 2019 Heat Exchanger Fouling and Cleaning Conference [1]. The category that each sample belongs to within the coke spectrum is given in the second column in Table 1, located in the Appendix. For the sixty-two samples collected, coke deposits were found in a wide selection of refinery equipment, ranging from the crude pre-heat train, vacuum distillations units, hydrocracker, coker units, reformers, and even column packing. Thus, the process fluid was also from a wide range of operating conditions including feedstock, temperatures, and pressures. Units were in service anywhere from 6 months to 10 years, and in some cases the foulant was layered from years of poor cleaning conditions. Aging of the samples were also taken into account, and drifting of the coke line due to was observed in the FTIR spectrum.

The data collected from the cleaning of the sixty-two coke foulant samples through the circulation, ultrasonic immersion and closed U/S application methods are presented in Table 1 in the Appendix and show the percentage of the sample dissolved and any major visual observations regarding the dispersion, dissolution or break down of the sample in either the aqueous or the solvent-based solution. The method(s) which dissolved the most foulant are bolded in the wt% dissolved column of the table; whereas, those who were observed to visually perform well are bolded in the observation column.

DISCUSSION

Sixty-two deposits from refinery processes labelled by the client as coke fouling were evaluated by three different cleaning application methods: circulation, ultrasonic immersion and closed U/S. Two different chemical blends, an aqueous degreaser and a solvent-based degreaser, were tested in the circulation and closed ultrasonic methods, and only the aqueous degreaser was tested in the ultrasonic immersion method.

The results of the cleaning process were compared to the categorization of the different samples with regards to the coke foulant spectrum developed by the authors in the precursor paper for these same samples. However, just as the coke spectrum is complex, so to appears to be the methods for removing coke foulant from equipment. The following graphs show how each category appears to respond to the different cleaning applications and chemistries. It is important to note here that the percentages in the graphs are percent sample dispersion/break down and not % dissolved. The amount of sample that can effectively be removed or rinsed away from a piece of equipment is more important than the amount of sample dissolved by the chemistry involved.

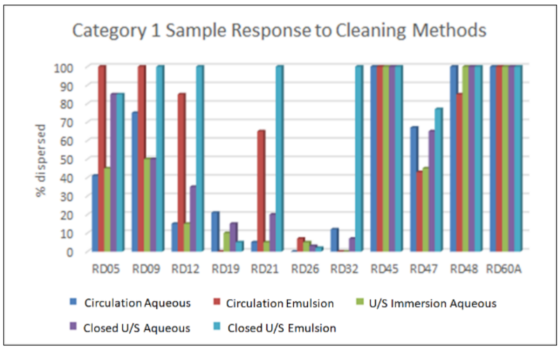

Fig. 1. A graphical representation of the response of samples with characteristics predominantly from Category 1 of the Coke Spectrum (Primarily Asphaltic) to the different cleaning methods and chemistries used in this study.

Nine of the eleven Category 1 samples appear to respond quite well to the solvent-based emulsion chemistry using the closed U/S technique. While seven of these respond well to circulation with the solvent-based emulsion chemistry. Two of the eleven samples did not respond well to any of the techniques used. Three of the eleven samples responded well to all of the techniques used.

One particularly interesting response is seen for sample RD32, which appears to only respond to the Closed U/S emulsion. Perhaps the low vapor pressure of the solvent has a synergistic effect when combined with ultrasonic cavitation. Further investigation is warranted.

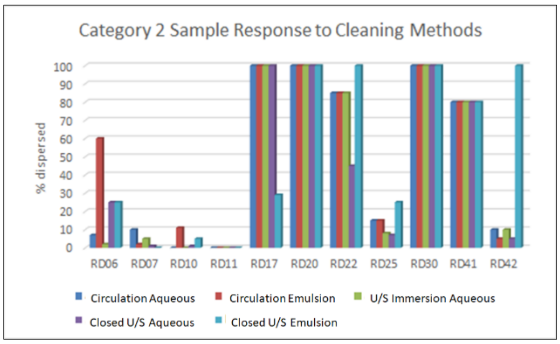

Fig. 2. A graphical representation of the response of samples with characteristics predominantly from Category 2 of the Coke Spectrum (Primarily

Sulfurous) to the different cleaning methods and chemistries used in this study.

Three of the eleven Category 2 samples appear to respond quite well to all of the techniques used. Five of these respond well to the closed U/S emulsion, with one doing so preferentially above all other samples. One sample responded best to the emulsion circulation technique and four of the samples did not respond particularly well to any of the techniques or chemistries used.

Interestingly, sample RD17 responded well to nearly every technique with the exception of the closed U/S emulsion.

It is possible that some of these discrepancies in how the samples respond to the different techniques is due to heterogeneity in the samples, which is difficult to circumvent in some instances. Though most of the samples appear visibly uniform when they are first introduced to the cleaning solutions, visual inspection upon the removal of the oily residue can reveal heterogenicity in the sample. This is depicted in the image for sample RD07 in figure 3.

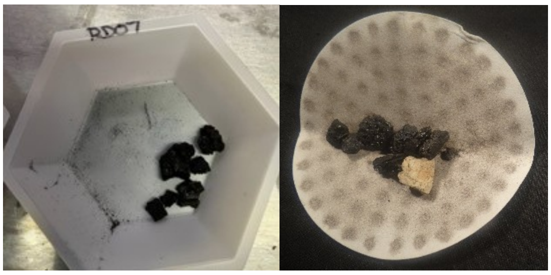

Fig. 3. Sample RD07 before (left) and after (right) Ultrasonic immersion based cleaning in the aqueous chemistry shows sample heterogeneity which was not observed prior to the cleaning process.

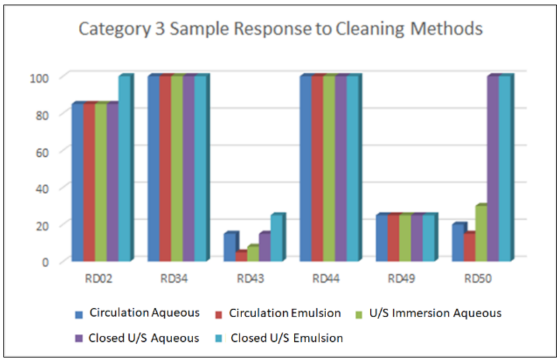

Fig. 4. A graphical representation of the response of samples with characteristics predominantly from Category 3 of the Coke Spectrum (Primarily Silicate) to the different cleaning methods and chemistries used in this study.

Only six samples fall within Category 3 (Primary Silicate); however, several of the mixed samples contain significant silicate components. Of the six Category 3 samples, three of these respond well to all of the techniques and chemistries used, while two of these do not respond particularly well to any of the techniques. RD50 is an interesting sample in that it appears to respond well to the closed U/S technique, but is less responsive to the circulation and ultrasonic immersion techniques.

Category 4 comprises approximately a third of all of the samples. This category contains true coke samples as we have all come to think of them, where the hydrogen to carbon ratio is relatively low and the structure is fairly amorphous. About half of these do not appear to respond significantly to any of the cleaning techniques, and two of the samples respond well to all of the techniques.

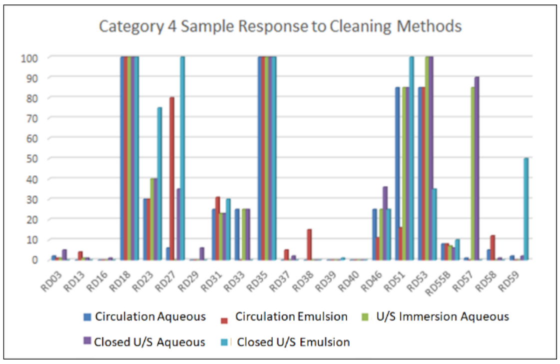

Fig. 5. A graphical representation of the response of samples with characteristics predominantly from Category 4 of the Coke Spectrum (Primarily Amorphous Carbon) to the different cleaning methods and chemistries used in this study.

The other samples appear to have mixed responses, take sample RD23 for example. RD23 responds to all of the techniques to some degree but preferentially to the closed U/S. RD27 appears to respond preferentially to the solvent-based emulsion chemistry; whereas, RD57 appears to respond only to ultrasonic techniques in the aqueous solution, with little response to the aqueous chemistry under circulating conditions. This response in RD57 is particularly important since the fouling is stuck onto metal equipment (Rashig rings in this case).

Further investigation is warranted towards this piecemeal response in the Category 4 samples.

Several of the samples that were tested in the previous paper demonstrated characteristics of more than one of the categories in the Coke Spectrum. These mixed samples were also tested to determine their response to the cleaning methods employed in this paper. Of the six mixed samples tested, two of these responded well to all of the cleaning methods and chemistries. RD08 responded preferentially to the methods employing the aqueous chemistry, and RD04 did not respond well to any of the methods. RD24 has multiple fouling problems and requires that the degreasing step be followed by an acid wash step to remove the calcium carbonate scale that remains once the hydrocarbon fouling has been removed.

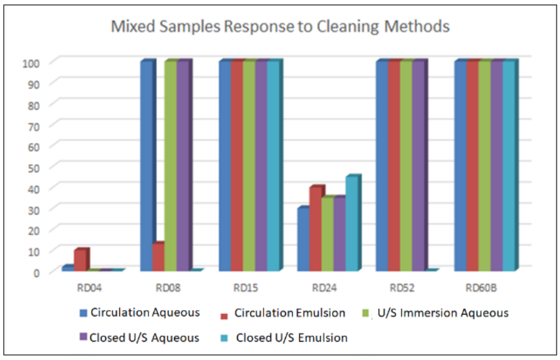

Fig. 6. A graphical representation of the response of samples with characteristics from several of the categories in the Coke Spectrum to the different cleaning methods and chemistries used in this study.

Interesting, RD52 responded well to all of the techniques with the exception of the closed U/S emulsion. This is several instances throughout the testing where the closed U/S emulsion produces distinct results as compared to the other techniques used, which warrants further investigation.

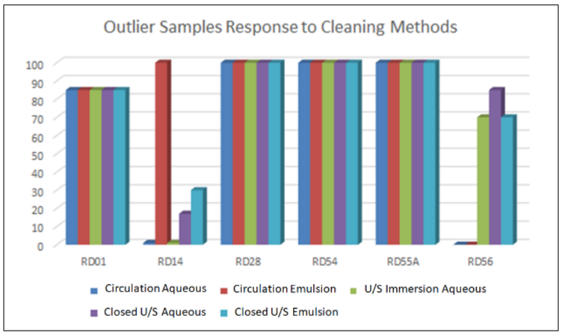

Fig. 7. A graphical representation of the response of samples with characteristics that fall primarily outside of those of the Coke Spectrum to the different cleaning methods and chemistries used in this study.

Just as there were several samples that were comprised of several of the categories of the coke spectrum, there were also several samples that primarily had characteristics that fell outside of the categories defined in the coke spectrum, these are referred to as outlier samples and are shown in figure 7. Six of the sixty-two samples were determined to be outliers, in that more than 50% of the sample exhibited characteristics outside of those categorized by the coke spectrum. Four of these six samples responded well to all of the methods and chemistries assessed in this paper. RD14 responded preferentially to the emulsion circulation method, and RD56 responded preferentially to the methods involving ultrasonic cavitation.

The samples here are mostly sperate from the equipment which has been fouled, with the exception of RD56, RD57 and RD59. These three samples were all from tower packing, and the Rashig rings that were part of the unstructured packing in the towers were included with the foulant. In both the Ultrasonic immersion and closed U/S techniques, the adherence between the foulant and the metal packing was disrupted. This is one of the areas where ultrasonic technology is so powerful, and this phenomenon may play a role in some of the samples that appear to be less responsive, and should not be wholly overlooked.

Finally, it is important to note that many of the samples where ultrasonic immersion produced fair to excellent results could be bolstered by combining this technique with high pressure water blasting (HPWB). Ultrasonic immersion is often paired with HPWB, and allows for shorter HPWB times, lower pressure pumps and lower volume nozzles. Many of the samples appeared to be flaky, crumbly or broken up after ultrasonic immersion, which would result in samples that are easily followed up with HPWB techniques.

In practice, obtaining samples for testing and chemical recommendation is not always practicable. Due to the versatility of the immersion cleaning method, it is recommended that plants strongly consider the use of ultrasonic immersion for the cleaning of heat exchangers and other parts where coke fouling is suspected. The combination of ultrasonic immersion based chemical cleaning and high-pressure water blasting has been shown in the industry to dramatically reduce the overall time that a unit is down for cleaning when combined with appropriate chemistry and a knowledgeable technical team. Thus, in many cases ultrasonic immersion cleaning can be an economically viable option.

CONCLUSION

The fouling in crude oil processes can be complex, and as a result the methods to clean the equipment from these process streams is not always straightforward or intuitive. In particular, coke fouling in heat exchangers from crude oil services can pose a significant challenge even when the characteristics of the crude foulant has been defined and the fouling mechanism for the process is understood.

Several application methods for chemical and mechanical cleaning of heat exchangers from refinery processes exist, including chemical circulation, high pressure water blasting, steam-out technologies, and ultrasonic immersion. New techniques are constantly under consideration, including closed ultrasonic and clean-in-place methods.

Of the methods assessed in this paper, the method which produced the most positive results were those incorporating ultrasonic cavitation energy. When combined with HPWB, the ultrasonic immersion technique gains significant advantages as the residual foulant after the combined chemical and mechanical clean becomes relatively easy to remove.

NOMENCLATURE

HPWB	High Pressure Water Blasting
FCC	Fluid Catalytic Cracking
USP	Ultrasonic Scale Prevention
CIP	Clean-in-Place
U/S	Ultrasonic

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APPENDIX

Table 1: Cleaning Results for all Cleaning methods and Chemistries tested against the Coke Spectrum Samples

		Circulation				Ultrasonic Immersion		Closed U/S			
		Aqueous Degreaser		**Solvent-Based Degreaser**		**Aqueous Degreaser**		**Aqueous Degreaser**		**Solvent-Based Degreaser**	
Sample	**Category**	**Wt% dissolved**	**Visual Observations**	**Wt% dissolved**	**Visual Observations**	**Wt% dissolved**	**Visual Observations**	**Wt% dissolved**	**Visual Observations**	**Wt% dissolved**	**Visual Observations**
RD01	Outlier	20.45	Oil dispersed, solids on bottom	**44.75**	**Oil separates, flakey solid remains**	29.48	Oil dispersed, solids on bottom	24.58	Oil dispersed, solids on bottom	22.59	Oil dispersed, solids on bottom
RD02	3	30.75	**Small chunk of soft solid remains, oil and solids dispersed in solution**	18.21	**Small chunk of soft solid remains, oil and solids dispersed in solution**	24.36	**Small chunk of soft solid remains, oil and solids dispersed in solution**	37.87	**Small chunk of soft solid remains, oil and solids dispersed in solution**	**59.87**	**Oil and solids dispersed in solution, very small soft chunk remains**
RD03	4	1.59	No change	0.99	No change	0.75	No change	5.45	No change	0.00	No change
RD04	Mixed	2.14	No change	9.71	No change	Gain	No change	0.00	No change	Gain	No change
RD05	1	41.25	No visible change, Weight only	**81.89**	**Much of sample dissolved, oil separates**	45.51	No visible change, Weight only	60.57	**Sample dispersed in solution, no true solids remain, only waxy materials**	31.08	**Sample dispersed in solution, no true solids remain, only waxy materials**
RD06	2	6.57	No change	**60.58**	Oil separates, chunks of sticky sample remain	2.35	No change	24.54	Oil separates, chunks of sticky sample remain	Gain	Oil separates, chunks of sticky sample remain
RD07	2	10.24	No change	2.39	No change	5.22	Sample visibly not uniform. No change	1.21	No change	0.00	No change
RD08	Mixed	5.78	**Sample is now powder. Solids dispersed in solution**	12.99	No visible change, Weight only	0.00	**Sample is now powder. Solids dispersed in solution**	2.67	**Sample is now powder. Solids dispersed in solution**	0.00	No change
RD09	1	65.12	Sample dispersed in solution, remaining solids appear waxy	**100**	**Dissolved**	40.64	Sample dispersed in solution, remaining solids appear waxy	54.87	Sample dispersed in solution, remaining solids appear waxy	**100**	**Dissolved**
RD10	2	0.00	No change	11.21	No visible change, Weight only	0.00	No change	1.38	No change	4.83	No change
RD11	2	0.00	No change	0.00	No change	Gain	No change	0.00	No change	Gain	No change
RD12	1	14.57	No visible change, Weight only	**83.01**	**Small Chunk remains, appears waxy**	16.75	No visible change, Weight only	34.57	No visible change, Weight only	**100**	**Dissolved**
RD13	4	0.00	No change	4.14	No change	0.26	No change	1.10	No change	0.00	No change
RD14	Outlier	1.12	No change	**100**	**Dissolved**	0.02	No change	16.47	No visible change, Weight only	29.50	No visible change, Weight only
RD15	Mixed	29.87	Sample dispersed in solution, solids settle to bottom	48.08	Sample dispersed in solution, oil separates, solids drop out	36.03	Sample dispersed in solution, solids settle to bottom	39.88	Sample dispersed in solution, solids settle to bottom	**66.21**	**Sample dispersed in solution, solids drop out**
RD16	4	0.00	No change	0.00	No change	0.00	No change	1.28	No change	0.00	No change
RD17	2	45.17	**Sample dispersed in solution, fine solids remain**	**58.92**	**Sample dispersed in solution, fine powder remains**	55.34	**Sample dispersed in solution, fine solids remain**	**60.76**	**Sample dispersed in solution, fine solids remain**	28.99	No visible change, Weight only
RD18	4	11.47	**Fine solids dispersed in solution**	**72.87**	**Sample dispersed in solution, fine powder remains**	Gain	**Sample dispersed in solution, fine powder remains**	7.45	**Sample dispersed in solution, fine powder remains**	47.55	**Sample dispersed in solution, fine powder remains**
RD19	1	**21.45**	No visible change, Weight only	2.62	No change	9.87	Some of sample has broken away, little change	16.97	Some of sample has broken away, little change	0.00	Some of sample has broken away, little change
RD20	2	**53.18**	**Sample dispersed in solution. Only powdery material remains**	**58.76**	**Sample dispersed in solution. Only powdery material remains**	44.91	**Sample dispersed in solution. Only powdery material remains**	**58.91**	**Sample dispersed in solution. Only powdery material remains**	**56.06**	**Sample dispersed in solution. Only powdery material remains**
RD21	1	5.84	Large chunks of the glassy material remain	65.34	Oil separates and sits on top, waxy chunk remains	3.37	Large chunks of the glassy material remain	19.49	Large chunks of the sample remain	**94.96**	**Most of sample has dissolved, fine powder remains**
RD22	2	5.24	Much of sample dispersed in solution, some solid chunks remain	**33.14**	Much of sample dispersed in solution, some solid chunks remain	0.00	Much of sample dispersed in solution, some solid chunks remain	4.67	Some of sample has broken away, little change	0.23	**Some of material has broken away, small soft chunks remain**
RD23	4	15.47	Some of material has broken away, large chunks remain	27.16	Some of material has broken away, large chunks remain	**33.53**	Some of material has broken away, large chunks remain	**31.27**	Some of material has broken away, large chunks remain	**30.08**	**Some of material has broken away, small soft chunks remain**
RD24	Mixed	26.34	Sample is discoloured and flakey, acid treatment would remove additional foulant	**40.62**	Sample colour change, powdery chunks remain, acid treatment would remove additional foulant	32.09	Sample turned white and flakey, acid treatment would remove additional foulant	33.19	Sample turned white and flakey, acid treatment would remove additional foulant	**44.88**	Sample colour change, small powdery chunks remain, acid treatment would remove additional foulant
RD25	2	14.26	No change	14.14	No visible change, Weight only	7.78	No change	6.76	No change	6.04	**Some of material has broken away, fine particulate remains**

RD26	1	Gain	Sample has softened, large chunk remains	7.20	No change	4.63	Sample has softened, large chunk remains	2.54	Sample has softened, large chunk remains	1.93	Sample has softened, large chunk remains
RD27	4	6.54	No change	79.00	Oil separates, small chunk of sticky sample remain	0.00	No change	34.69	No change	**92.91**	**Most of sample has dissolved, fine powder remains**
RD28	Outlier	18.77	**Sample dispersed in solution, fine solids remain**	25.95	**Sample dispersed in solution, fine solids remain**	16.95	**Sample dispersed in solution, fine solids remain**	**48.71**	**Sample dispersed in solution, fine solids remain**	35.76	Sample dispersed in solution, small solid chunks remain
RD29	4	Gain	No change	0.00	No change	0.00	No change	5.44	No change	Gain	No change
RD30	2	75.88	**Sample dispersed in solution, fine solids remain**	87.25	Sample dispersed in solution, solids drop out	77.79	**Sample dispersed in solution, fine solids drop out**	**91.87**	**Dissolved**	87.37	**Most of sample has dissolved, fine powder remains**
RD31	4	24.58	No visible change, Weight only	**31.26**	No visible change, Weight only	22.44	No visible change, Weight only	22.62	No visible change, Weight only	6.19	Some of material has broken away, chunks remain
RD32	1	12.45	No visible change, Weight only	0.00	Sample now appears waxy	0.00	No change	7.57	No change	**90.24**	**Most of sample has dissolved, fine powder remains**
RD33	4	1.21	Some of material has broken away, remains are flakey	0.00	No change	0.00	Some of material has broken away, remains are flakey	Gain	Some of material has broken away, remains are flakey	0.00	No change
RD34	3	42.15	**Sample dispersed in solution, fine solids remain**	**70.88**	**Sample dispersed in solution, fine solids remain**	54.54	**Sample dispersed in solution, fine solids remain**	65.89	**Sample dispersed in solution, fine solids remain**	42.77	**Sample dispersed in solution, fine solids remain**
RD35	4	1.27	Oil dispersed in solution, solids broke apart and dropped out	**29.81**	**Sample dispersed in solution, fine solids remain**	0.00	Oil dispersed in solution, solids broke apart and dropped out	0.00	Oil dispersed in solution, solids broke apart and dropped out	0.00	Oil dispersed in solution, solids broke apart and dropped out
RD36	Outlier	11.71	No visible change, Weight only	4.26	No change	12.17	No visible change, Weight only	14.54	No visible change, Weight only	9.94	Chunks of rubbery material remain
RD37	4	0.00	No change	5.15	No change	0.00	No change	1.29	No change	10.75	No visible change, Weight only
RD38	4	2.12	No change	0.00	Sample visibly softened	0.00	No change	0.00	No change	Gain	No change
RD39	4	0.00	No change	0.00	No change	0.00	No change	Gain	No change	0.21	No change
RD40	4	0.00	No change	8.97	No change	1.00	No change	0.00	No change	5.39	No change
RD41	2	42.58	Oil dispersed in solution, remaining solids are waxy	**61.16**	Oil dispersed in solution, remaining solids are waxy	11.56	Oil dispersed in solution, remaining solids are waxy	**65.52**	Oil dispersed in solution, remaining solids are waxy	42.93	Oil dispersed in solution, remaining solids are waxy
RD42	2	1.47	Some of material has broken away, large chunk held by wax	4.05	No change	0.00	Some of material has broken away, large chunk held by wax	8.91	No change	**23.55**	**Oil dispersed in solution, remaining solids are small and waxy**
RD43	3	12.47	Some material has broken away, little change	5.27	No change	6.75	Some material has broken away, little change	13.24	Some material has broken away, little change	24.50	No change
RD44	3	**96.48**	**Dissolved**	**100**	**Dissolved**	**97.77**	**Dissolved**	**100**	**Dissolved**	**100**	**Dissolved**
RD45	1	49.95	**Fine solids dispersed in solution**	68.45	Small oily chunks remain	35.83	**Fine solids dispersed in solution**	**100**	**Dissolved**	**93.45**	**Most of sample has dissolved, small chunks remain**
RD46	4	12.46	Some material has broken away, remains are dry and flakey	10.46	Some material has broken away, remains are flakey and oily	**18.38**	Some material has broken away, remains are dry and flakey	14.77	Some material has broken away, remains are dry and flakey	11.89	Some material has broken away, remains are dry and flakey
RD47	1	66.69	Some material has broken away, large chunks remain	42.65	Large waxy chunk remains	45.33	Some material has broken away, large chunks remain	64.58	**Sample dispersed in solution, small waxy chunks remain**	**76.45**	**Sample dispersed in solution, small waxy chunks remain**
RD48	1	43.57	Oil dispersed in solution, solids broke apart and dropped out	63.02	Oil dispersed in solution doesn't want to separate, small tarry chunks remain	28.39	Oil dispersed in solution, solids broke apart and dropped out	45.25	Oil dispersed in solution, solids broke apart and dropped out	**83.30**	**Sample dispersed in solution, fine waxy particulate remains**
RD49	3	14.76	Some material has broken away, remains are dry and flakey	14.22	Some material has broken away, remains are dry and flakey	4.51	Some material has broken away, remains are dry and flakey	12.22	Some material has broken away, remains are dry and flakey	**17.14**	Some material has broken away, remains are dry and flakey
RD50	3	18.58	Some material has broken away, little change	12.13	No change	26.35	Some material has broken away, little change	41.52	Oil dispersed in solution, solids broke apart and dropped out	**81.30**	**Sample dispersed in solution, fine solids remain**
RD51	4	8.71	Sample dispersed in solution, decanted material visibly broken down	16.16	No change	9.50	Sample dispersed in solution, decanted material visibly broken down	9.97	Sample dispersed in solution, decanted material visibly broken down	**74.68**	**Sample dispersed in solution, fine solids remain**
RD52	Mixed	34.57	**Sample dispersed in solution**	**72.05**	**Sample dispersed in solution, fine solids drop out**	35.43	**Sample dispersed in solution**	46.12	Sample dispersed in solution	Gain	No change
RD53	4	32.49	**Sample dispersed in solution, small chunks drop out**	**71.05**	**Sample dispersed in solution, small chunks drop out**	Gain	**Sample dispersed in solution, fine solids drop out**	49.87	**Sample dispersed in solution, fine solids drop out**	32.98	Sample dispersed in solution samples appears to have melted then reformed into a dense, waxy chunk
RD54	Outlier	**93.12**	**Dissolved**	**95.91**	**Dissolved**	**95.15**	**Dissolved**	**100**	**Dissolved**	**100**	**Dissolved**
RD55A	Outlier	33.16	**Sample dispersed in solution**	20.65	Oil dispersed in solution, Tar-sand like solids remain	34.17	**Sample dispersed in solution**	41.23	**Sample dispersed in solution**	**86.86**	**Oil dispersed in solution, sand-like solids remain**
RD55B	4	8.14	No change	7.69	No change	6.77	No change	6.27	No change	8.61	Small sticky chunks remain, consistency different from starting sample

RD56	Outlier	0.00	Little material removed	0.03	Little material removed	1.02	**Material removed from Raschig rings**	1.27	**Material removed from Raschig rings, some polishing of metal**	0.43	**Material removed from Raschig rings**
RD57	4	1.24	No change	0.00	No change	0.00	**Raschig rings visibly polished and material removed**	0.21	**Raschig rings visibly polished and material removed**	0.00	No change
RD58	4	5.12	No change	11.94	No change	0.00	No change	0.69	No change	0.00	No change
RD59	4	1.41	Some material broken away from larger chunk	0.00	No change	0.00	Some material broken away from larger chunk	1.87	Some material broken away from larger chunk	0.53	**Sample chunk visibly broken down, sample adhesion to self disrupted**
RD60A	1	10.47	Sample appears waxy	**59.38**	**Sample dispersed in solution**	0.10	Sample appears waxy	12.54	Sample appears waxy	39.30	**Sample dispersed in solution**
RD60B	Mixed	12.78	**Sample dispersed in solution**	**28.38**	**Sample dispersed in solution**	16.36	**Sample dispersed in solution**	**25.87**	**Sample dispersed in solution**	0.00	**Sample chunks visibly broken down, oil dispersed in solution**