

THE EFFECTIVE REMOVAL OF FeCO₃ DEPOSITS FROM CRITICAL PROCESS HEAT EXCHANGERS USED IN AMMONIA PRODUCTION USING A PROPRIETARY ULTRASONIC CHEMICAL CLEANING METHOD

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ABSTRACT

This paper examines the problem of ferrous carbonate fouling and removal in lean - rich Diethanol amine exchangers at the CO₂ extraction plants associated with ammonia manufacturing. A method to clean the exchangers using a solution of a proprietary acid mixture applied by ultrasonic chemical cleaning is described. We discuss an effective and safe ultrasonic cleaning method deployed in 5 separate cleaning projects.

INTRODUCTION

The use of ultrasonic technology for cleaning refinery process components has been taking place for over a decade. The use of this in a large scale application for cleaning heat exchangers however, is relatively recent, taking place over the past 4 years. The mechanisms of this technology and its application to shell and tube type heat exchangers are described in (B.Kieser et al., 2011).

This paper describes our work in cleaning badly fouled heat exchangers in one of the largest fertilizer producing plants in the Southern United States. The process functions on a Kellogg plant design and produces ammonia, granular urea, and UAN solutions. In our client discovery phase we learned that there are 20 critically challenged heat exchangers (hx) from their Lean-Rich amine processing unit. They pull one unit of 4 hx offline each year for cleaning and inspection. Using EDS, XRD and chemical analysis of the tube side fouling, the main constituents are noted in figures 1 and 2.

Table 1. Deposit composition

Component	Wt%
FeCO ₃	96
CaMg(CO ₃) ₂	3
Alumino silicates	<1

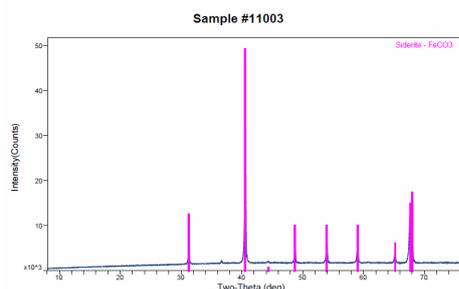


Figure 1. XRD pattern of the deposit

The main fouling component FeCO₃ (*siderite*) had been the main problem of concern for over the past 25 years. Turn-around crews employed everything from the latest high pressure water cleaning ‘rotating tips’ at 40, 000 PSI, to the harshest of chemical including HCl baths to break out the siderite from the tubes. From recent accounts using these methods our client reported that each method provided minimal cleaning results with major expense involved with the amount of ‘rotating tips’ destroyed, chemical stress fracturing of tubes, significant water used in the cleaning process and the over-all time required to clean just 4 units of the one train of 106C Hx Units.



Figure 2. Samples of crystalline deposit (FeCO₃) removed from a tube side from Lean-Rich amine exchanger.

By 2006 this client decided to cap the amount of time they would allow for this process train to be out of operation. Thirty(30) days became the allowable amount of time, giving cleaning crews 7 day per unit for cleaning with the remaining 2 days for the mechanical, to position the final units back into operation. During these outages, many of the units were returning far less than clean, as they needed more time on the wash-pad.

In 2008 the client commissioned an internal study to determine the factors resulting in premature failure of some of the hx units in selected pre-heat trains of 105C, 106C and 109C process type exchangers.

Both IRIS and Eddy current inspection methods used to measure tube wall erosion and integrity revealed that prolonged exposure to the abrasive, high-pressure water cleaning method s had contributed to the early demise of these assets. Hx assets traced to the use of HCL pre-treats proved to be the candidates for early retirement due to wall-sheer failure as discovered through Eddy Current testing.

With brand new, replacement exchangers in place for some trains the challenge would be to maintain the level of through-put now attained using these newly commissioned heat exchanger units. A new, less destructive cleaning

method was not only necessary, it needed to clean Hx units in less time as the price of natural gas was at an all-time low— so downtime needed to be drastically reduced to maximize the uptime for ammonia production

The refinery agreed to consider a cleaning proposal based on a proven, ultrasonic cleaning method. Historical data revealed heavy deposits of FeCO₃ within the ID of the tubes in at least 3 of the 4 Hx units. There wasn't anything noted about the level of difficulty in cleaning the shell-side of these bundles.

METHOD

Utilizing a proprietary combination of ultrasonic technology and aqueous cleaning fluids within specially engineered vessels, this “ultrasonic bath” removes both hydrocarbon and selective inorganic contaminants from the surface of a work piece in a rapid, safe and environmentally friendly alternative to traditional cleaning methods. A more complete description of the method may be found in (B.Kieser et al., 2011).



Figure 3. C105A Before cleaning

It was determined that to effectively remove the siderite from the interior diameter of the tubes, a new companion chemistry to work alongside the ultrasonics, would need to be added. Based on further analysis and solubility testing, the selection of a proprietary organic acid (Paratene® M390) was chosen because of its strength, reasonably good reaction rate and its compatibility with the ultrasonic equipment.

Table 2. Technical Data for Proprietary Organic Acid Paratene® M390

Property	M390
Activity (wt%)	40
Activity (molar)	4.95
Specific Gravity	1.19
Molecular Weight (g/mol)	96.1
g FeCO ₃ dissolved per litre of Concentrate	287

To determine the reaction rates in Paratene®M390 a large deposition sample was placed in 100ml of 8% acid. A 0.5ml sample was taken at intervals of time and was then analyzed by ICP.

Figure 4. shows little or no reaction initially as the solution is heating up, but a rapid dissolution of the solids is seen once a range from 40 and 50°C is reached. Heat is generated as a by-product of the ultrasonic action. The temperature is regulated by The solution stabilizes at about 4% iron. The ultrasonic activity or cavitation process provides both a mechanical surfaces cleaning along with the

optimal temperature range that promotes the rapid dissolution of these solids. This acceleration or multiplier effect of the reaction rate offered by the engineered ultrasonic process is a key component toward reducing the overall cleaning time for these heat exchangers. While the use of ultrasonics combined with aqueous based chemistries could technically be deemed as ‘ultrasonically aided chemical cleaning, it wasn’t until this project where Paratene®M390 was collaborated with a specified ultrasonic cleaning protocol, that coined the phrase *ultrasonic chemical cleaning* became mainstream within the industrial cleaning community.

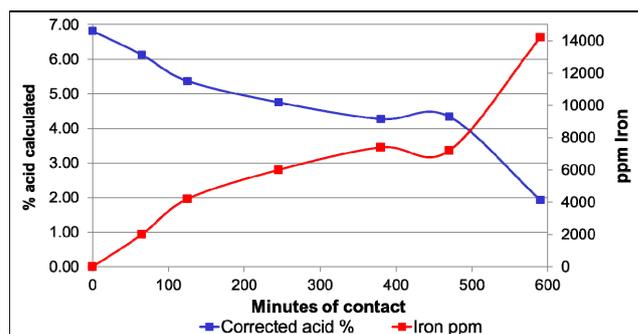


Figure 4. Reaction Rate of Paratene® M390 on deposit over time

In between specifically timed periods in the ultrasonic bath, the heat exchanger tubes were water lanced briefly to remove the now loosened and unreacted material from the interior of the tubes. Titrations for iron and chlorides within the bath chemistry also followed a specific schedule that monitored for an over saturation of iron or a corrosive build-up of chlorides. Chemistry change out when spent, versus “topping-up” ensured better, more effective cleaning rates.

RESULTS

Four exchangers were cleaned for this project. The first exchanger came very clean after a total of 10 hours in the ultrasonic bath and 6 hours of rinse time. The experience gained with this first unit allowed us to alter the cleaning protocol for the subsequent 3 Hx units, dropping the total ultrasonic bath time from 10 to 8 hours per exchanger. In all, the four exchangers were cleaned in 5 days. Visual inspections of the units by the refinery inspection group deemed the units in “like new condition”. Upon receiving the units back to the refinery, the processing group were likewise impressed with the results and the cleaning timeline.

Historically, they allowed 30 days to clean these same 4 units. The difficulty experienced with traditional cleaning methods alone, often meant that at least 2 or more Hx units were going back into operation in a partly fouled state.

Using the ultrasonic chemical cleaning method allowed the refinery to have these units back into operation 21 days sooner than previously experienced.

While the shell side of the Hx units were not initially noted by the refinery client to be of a particular concern, the post-clean observation was that they'd not been seen in this

condition since new. Later, heat transfer performance data provided by the refinery proved this observation to be a significant cost-efficiency benefitⁱ

Of greater benefit was the increased flow-thru-rate. The ammonia production from this operational Hx train was measured one month after the cleaning interval. While initial flow-thru-rates were very impressive, even after leveling off the refinery had an average increase of 23% more production volume of ammonia over the same period the previous year.ⁱⁱ



Figure 6. C105A BEFORE



Figure 7. C105A AFTER

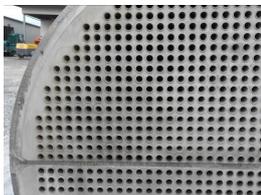


Figure 8. C105A BEFORE



Figure 9. C105A AFTER



Figure 10. C105A BEFORE



Figure 11. C105A AFTER

DISCUSSION POINTS

There were a significant number of lessons learned that came out of this cleaning project:

1. The technique is significantly safer than high pressure water blasting, presenting no significant hazards to the operators
2. Significantly faster per unit turnaround was observed: less than 24 hours per unit is possible, in contrast to conventional high pressure washing, which can take more than a week per unit.
3. Far less waste water generated (typ. <2000 l per bundle) contrasted with high pressure water blasting
4. Chemistry was spent far quicker than expected. Additional chemistry was required to complete the project.
5. Better determination for the amount of expected fouling in these Hx units, will allow for better estimating the amount of chemistry required.
6. As the composition of the scale on the shell-side differed from the *siderite* in the tubes, cleaning of the shell side was complete in half the time of the tube side.
7. The cleaning process did not have to dissolve all of the tube contamination in to solution to be effective. By

shrinking and loosening the adherence of the fouling from the inner walls, the interval water lancing easily removed these large cylindrical chunks of siderite.

8. Titrations of the acid were sometimes inaccurate due to interference by high concentrations of iron. Improved job monitoring of the chemistry is needed to ensure optimal cleaning conditions.

CONCLUSIONS

The project was a success in terms of exceeding the refinery's two basic objectives which were: a) reduce the overall downtime time for this critical processing unit, and b) provide a better clean to improve the performance of these assets.

1. The Paratene®M390 worked well on all samples of the resident fouling. The reactions occurred stoichiometrically and did not have apparent limitations due to saturation.
2. The Paratene®M390 when collaborated with a specified ultrasonic protocol, proved to be an effective *ultrasonic chemical cleaning* method
3. This refinery client has expanded the use of this technology over 5 separate projects to date and continues to introduce the method to its other Plants throughout the US and Canada.

REFERENCES

B. Kieser, S. Smith, R. Phillion, T. McCartney, *The application of industrial scale ultrasonic cleaning to heat exchangers*, Heat Exchanger Fouling Conference IX, Crete (2011)

- i. Heat transfer performance and cost of energy data supplied by the refinery client from historical performance data and post-cleaning data captured from December 2010 to March 2011
- ii. Average increase in Ammonia production provided by the refinery client, February 2011