FINAL CRADA REPORT: Prevention of Iron-Sulfide Deposition in Petroleum Processing


Project Status: LTR Funds are expended – CRADA is extended with cash-in industry contribution.

Company: Originally, Equilon Enterprises, LLC
Now, Shell Global Solutions, Inc.

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Abstract:

The purpose of this CRADA extension which effectively ended in 2003 was to quantify the effect of iron-sulfide formation on the fouling propensity of crude oil. The specific objectives are focused on fouling of the Crude Distillation Unit (CDU-1) at the Shell Refinery in Mobile, Alabama. The technical approach consists of analyzing the plant data, chemical analysis of crude oil to detect key precursors, performing refinery tests using the Argonne Field Fouling Unit, and verifying the effectiveness of a physical device of tube insert and enhanced tubes to change threshold conditions and thereby reducing fouling.
Technical Progress

The technical approach consisted of the major tasks:

1. Analysis of the plant data;
2. Field fouling experiments at the Shell Mobile, Alabama Refinery;
3. Laboratory experiments, including chemical analysis of process fluid and fouling deposits, at the Shell Westhollow Research Center;
4. Analysis of the experimental data and determination of root-cause of fouling and threshold fouling conditions; and
5. Characterization of crude oil fouling.

**Analysis of plant data:** The Refinery provided plant data collected over one year ending in 2003 and the analysis showed that several heat exchangers were operating above threshold fouling conditions. The Argonne field-fouling unit confirmed the plant data.

**Field fouling experiments:** The Argonne field-fouling unit was shipped from the Shell Wood River, Illinois Refinery to the Mobile, Alabama Refinery. The fouling unit was installed and series of tests were conducted. The focus was to determine threshold-fouling conditions for metal induced fouling. The results confirmed the plant data that several heat exchangers were found to be operating above threshold fouling conditions. Also, the rate of fouling for the enhanced tube was negligibly small, which provided further evidence that higher wall shear would reduce fouling significantly.

**Chemical analysis of crude oil and deposits:** This was a major task to determine the root cause of crude oil fouling. The chemical analysis identified iron sulfide as a possible fouling precursor.

**Characterization of crude oil fouling:** Argonne’s high-temperature, high-pressure autoclave-based fouling unit was transferred to the Shell Westhollow Research Center. This fouling unit will be used to determine the effects of crude oil blending and chemical impurities on fouling for the Mobile Refinery as well as other Shell refineries. As a result, this technology transfer will have greater impact on mitigation of petroleum fouling than the originally envisioned in the small CRADA.

**Major Highlights/Accomplishments:**

- Shell Global Solutions recognized the value of this project and continued the CRADA on a “cash-in” basis.
- Threshold-fouling conditions were validated with the Argonne’s field fouling unit in an operating refinery.
- The Argonne’s threshold fouling model was used to analyze fouling trend of the preheat train system and determine threshold velocities for individual heat exchangers.
- The threshold model also showed that the spirally indented enhanced tube specified by Argonne should significantly reduce the rate of fouling. The field data confirmed this prediction.
- The project now focuses on fouling mitigation using physical and chemical techniques.
The effort pointed the way to future work on petroleum fouling which should focus on Monitoring-Based Mitigation, where the three elements of the Argonne’s research development are integrated. The three elements are:

- 1) sensing techniques, experiments and analytical, for real-time monitoring of fouling trend;
- 2) on-line diagnostic techniques, such as root-cause analysis and threshold fouling condition, and
- 3) proactive response to fouling conditions.

In collaboration with Shell, two papers were presented at professional meetings in 2004:
