Design and Application of An Ingenious Laboratory Experimental Technique For The Determination Of Accelerated Iron and Silver Corrosion In A Wide Range Of Petroleum Products

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ABSTRACT

Petroleum products are susceptible to deterioration when they are exposed to moisture in the environment. This results in corrosion on interior surfaces, damage in pipelines and form deposits in engines. The method used for the determination of the corrosiveness of gasoline and distillate fuels in preparation for transport through a pipeline was developed by National Association of Corrosion Engineers (NACE) named NACE TM0172 that takes 4 hours to perform with 300mL of sample. Due to high popularity of the test method, there has been a growing interest from the key stake holders for a quicker method with faster turnaround, smaller sample size and better repeatability and reliability. Additionally, Silver corrosion is an important factor in automobile applications, and the test method for studying this process could also benefit from a quicker turnaround in the process as well.

In collaboration with key refineries around the country, and with numerous trial and error experimental setups, a quicker, easier, and more efficient method has finally been developed-the new ASTM test method, ASTM D7548 for Determination of Accelerated Iron Corrosion in Petroleum Products (AICT). The new test method only requires a 50-mL sample and less than a 1/4 of time to complete testing compared to the NACE TM0172 and ASTM D665. This accelerated method will be significantly efficient at pipeline transfer stations, where a quick QC turnaround time is key to determine the corrosiveness of products. Its revolutionary characteristics address some engineering concerns expressed by industry leaders regarding the accelerated corrosion test methods of the past. This study will discuss the development of this test technique, and the authors will also present results that show comparative data between the NACE test and ASTM D7548. Work that has begun on the Silver corrosion test will also be discussed.

OBJECTIVES

The main purpose of the Iron Corrosion Tests for Petroleum Products is to to eliminate or minimize damage due to corrosion. Oil pipelines are usually buried and the oil is moved through the pipelines by pump stations along the pipelines. Water is usually a main factor for the corrosion; Corrosion can have the following causes:

- Heavy clay soils can pull the coating away from the pipe as they expand and contract with changes in moisture content
- Bacteria can promote external corrosion by depolarizing the pipe through the consumption of hydrogen gas formed at the pipe surface by the cathodic protection currents
- Water containing NaCl (salt), H_2S, and/or CO_2 initiates the deterioration by dissociating iron into the environment, which reduces the strength of the pipeline.

Figure: Examples of corrosion in pipelines in the environment

ASTM test method D7548 developed by Imran Hussami of Frontier El Dorado Refining is an accelerated, user friendly version of NACE TM0172.

The new accelerated test method has the following benefits:

- Improves efficiency by certifying fuel shipments
- Reduces risks if making direct fuel blends into pipeline

NACE METHOD VS. ASTM D7548

NACE TM0172

- 300mL Sample Required
- 4 Hour Test Time
- 6 Sample Capacity
- 12 Test Results per Shift

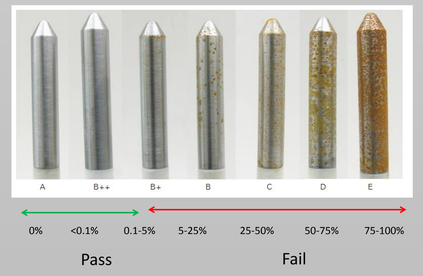
ASTM D7548

- 50mL Sample Required
- 1 Hour Test Time
- 4 Sample Capacity
- 32 Test Results per Shift

Table 1: Example of Rods Tested for one Diesel Fuel Sample

Accelerated				Standard			
Trial 1		Trial 2		Trial 1		Trial 2	
Rater 1	Rater 2	Rater 1	Rater 2	Rater 1	Rater 2	Rater 1	Rater 2
D	D	D	D	E	E	E	E

Both NACE TM0172 and ASTM D7548 use the same specimen grading scale pictured to the right. This allows for results and data to be easily compared between both experiments.

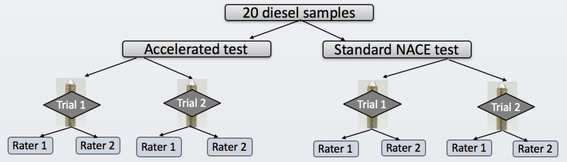


COMPARATIVE ANALYSIS

Experiments have been completed by BP, Frontier El Dorado Refining Company, and Flint Hills Resources to determine if the Accelerated Test ASTM D7548 is a valid replacement for the original NACE TM0172.

BP Laboratory Experiment

The BP Experiment was set up in the following manner and the purpose of the experiment was to look at bias between the tests (Accelerated and NACE), variability / precision, and indistinguishability.



From the results of the BP Experiment shown above, the following conclusions can be made:

- **Bias:** There is no bias between methods – paired t-test (p = 0.8345)
- **Precision / Variability:** Both tests have same precision – 75% agreement within each test
- **Indistinguishable:** The tests are not indistinguishable – 53% agreement between tests
- **Rater Agreement:** Excellent agreement between readers – 93.75% or 75 out of 80 test rods

Table 2: Comparing Accelerated and Standard Test Methods using 1-7 Rank - Diesel Samples

Diesel Samples	Accelerated ASTM				Standard NACE			
	Trial 1		Trial 2		Trial 1		Trial 2	
	Rater 1	Rater 2	Rater 1	Rater 2	Rater 1	Rater 2	Rater 1	Rater 2
1 22733-140	B	B	B	B	B	B	B	B
2 22733-140	B	B	B	B	D	D	B	B
3 22733-144	C	C	C	C	C	C	C	C
4 TK 3505	C	C	C	C	C	C	C	C
5 ULSD#1	D	D	C	C	C	C	C	C
6 ULSD#2	B	B	B	B	B+	B+	B++	B++
7 May	A	A	A	A	A	A	A	A
8 2256-34	B+	B+	B+	B+	B+	B+	B+	B+
9 Rochelle ULSD #2	B+	B+	B+	B+	B	B	B	B
10 ULSD#2 composite Sept	D	D	B	B	B	B	B	C
11 ULSD#2 composite Aug	C	C	C	C	D	D	D	D
12 ULSD #2 composite Nov	D	D	D	D	E	E	E	E
13 ULSD #2 composite Oct	B	B	B	B	D	C	D	D
14 22716-5	A	A	A	A	A	A	A	A
15 Rochelle #2 w/ L	B++	A	A	A	A	A	B++	B++
16 Rochelle #2 w/ I Opt 1	A	A	B++	B++	A	A	A	A
17 Rochelle #2 w/ I Opt 3	B++	B++	B++	B++	A	A	A	A
18 Louisville June	A	A	A	A	A	A	A	A
19 22733-30	B	B	C	C	B	B	B	B
20 I Diesel Sample	C	D	D	D	B	B	D	E

ASTM Ruggedness Study

ASTM Ruggedness Studies are used to pinpoint variables associated with performance of the test method before running a full Interlaboratory Study (ILS) to determine the precision statement section of the standard test method. For this test, samples of Gasoline, Jet Fuel, and Ultra-Low Sulfur Diesel (ULSD) were used.

- 95mL of each sample with an initial corrosion rating of E was supplied
- 5mL of corrosion inhibitor of required volumes were supplied to get the sample to the target rating

Ruggedness Study
Determination of Accelerated Iron Corrosion In Petroleum Products-ASTM D7548-09

Sample	CR	CR	CR	CR	CR	CR
Gasoline						
GA	B+	1	B	20	C	40
GB+	B+	3	B	20	D	60
GB+	B+	5	C	40	C	35
GB	B*	3	C	25	B*	2
GB	C	40	C	40	D	60
GE	E	98	E	100	B*	4
Jet Fuel						
JA	B++ <0.1		A	0	D	50
JB+	B++ <0.1		A	0	C	40
JB+	A	0	B++ <0.1		B*	2
JB+	B++	4	A	0	D	55
JB+	B++	3	B+ <5		B*	2
JE	D	70	E	75	B*	2
ULSD						
UA	B*	4	A	0	B+	4
UB+	B	10	B* <5		B	8
UB+	B	20	B	10	B	15
UB	C	33	D	50	C	30
UB	C	35	B	10	C	40
UE	E	90	E	75	C	28

The results of the test performed during the ASTM Ruggedness Study shown above are within the acceptable level of one corrosion rating of each other. Wider differences are due to under or over performance of the corrosion inhibitor which will have to be more accurately monitored during the ILS.

Conclusions

The Accelerated Iron Corrosion Test Method, ASTM D7548, successfully captures the corrosion level of the samples involved at the time of test. Due to no bias and same precision, ASTM D7548 is a valid replacement of the original NACE TM0172 Test Method.

REFERENCES

- **NACE Standard TM0172-2001** "Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines" (Houston, TX: NACE International).
- **ASTM D7548-2009** "Standard Test Method for Determination of Accelerated Iron Corrosion in Petroleum Products" (West Conshohocken, PA: ASTM International).
- **BP Global Fuels Technology** "Assessing the Equivalence of the ASTM D7548-09 Accelerated Iron Corrosion Test and the Standard NACE TM-0172 Test Using Diesel Fuels" ASTM June 2013 Meeting. PowerPoint Presentation.
- **Original Work – Imran Hussami** "Comparative Tests – 1h AICT vs. 4h NACE" Done at Frontier El Dorado Refining Company and Flint Hills Resources, 2008.

ACKNOWLEDGEMENTS

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