Construction and Evolvement of a State of the Art Laboratory Technique for Corrosion Measurement: Comparative Study of a Variety of Samples Using NACE/ASTM D665 in Relation to a New Benchtop Accelerated Corrosion Test Method

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ABSTRACT

The muddled composition of some petroleum products contain elements that cause corrosion on interior surfaces, leading to the degeneration of pipelines and formation of detrimental deposits inside engines. The method used for analyzing the corrosive properties of gasoline and distillate fuels in preparation for transport through a pipeline was originally developed by the National Association of Corrosion Engineers. The NACE TM0172 test method requires four hours to produce results and demands a 300mL sample of the product in question. While this test method's success has served the industry well for many years, key stakeholders began expressing a profound interest for an improvement exhibiting a faster turnaround and smaller sample size requirement to promote better repeatability and reliability. Working closely with key refineries around the country and executing numerous extensive laboratory trial and error experiments has all lead to a faster, easier, and more reliable test method. The new ASTM test method, ASTM D7548 for Determination of Accelerated Iron Corrosion in Petroleum Products is the evolution in state of the art laboratory corrosion measurement procedures. Its revolutionary characteristics touches upon some engineering concerns expressed by industry leaders regarding the accelerated corrosion test methods of the past. The new method only requires a 50mL sample and less than a fourth of time to complete testing in comparison to the NACE TM0172 and ASTM D665 accelerated corrosion test methods. This less demanding laboratory setup will save the industry significant time when testing to determine the corrosive qualities of various petroleum products. When applied to pipeline transfer station operations- where a quick QC turnaround time is absolutely critical- the ASTM D7548 test method becomes an adequate substitute for assurance. This poster will discuss the comparative data originating from preliminary instrument testing.

OBJECTIVES

The main purpose of the Iron Corrosion Tests for Petroleum Products is to to eliminate or minimize damage due to corrosion. Water is usually a main factor for the corrosion; Corrosion caused by water can result in the following:

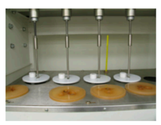
- Damaged Pipelines
- Deposits in Engines
- Damaged Storage Tanks and Facilities

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:

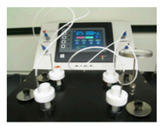
- Improves efficiency by certifying fuel shipments
- Reduces risks if making direct fuel blends into pipeline

NACE METHOD VS. ASTM D7548



NACE TM0172

- 300mL Sample Required
- 4 Hour Test Time
- 6 Sample Capacity
- 12 Test Results per Shift
- Test bullets are polished so that surface is smooth



ASTM D7548

- 50mL Sample Required
- 1 Hour Test Time
- 4 Sample Capacity
- 32 Test Results per Shift
- Test bullets are polished in circular grooves

Rods are then rated based on percentage of the surface that is corroded.
Greater than 5% corrosion is considered failing

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

ASTM procedures polishes rods with circular grooves
Circular grooves on steel rods provide extra surface area for corrosion to seed & grow
Standard NACE polishes bullets so that surface is smooth
Smaller scale in terms of fuel & water
Narrower container, possibility for greater mixing at bullet surface

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

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.

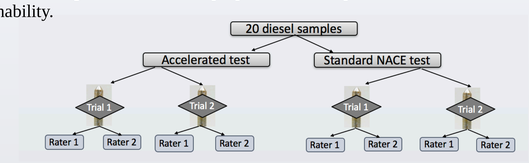


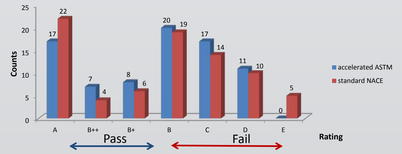
Table 2: Comparing Accelerated and Standard Test Methods using 1-7 Rank - Diesel Samples

	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	ULSDR1	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

Table 3: Comparing the Accelerated and Standard Test Average Ranks with Diesel Samples

	Diesel Sample	Accelerated Average Rank	Standard Average Rank	Absolute Difference	Difference
1	22733-140 Chicago tk28	4	4	0	0
2	22733-140 Chicago tk52	4	5	1	-1
3	22733-144 Corrigan	5	5	0	0
4	TK 3505 MO CETN CK	5	5	0	0
5	River Rouge ulsd#1 11-21-12 Tk 56	5.5	5	0.5	0.5
6	River Rouge ulsd#2 11-21-12 Tk 57	4	2.5	1.5	1.5
7	Buckeye Ford May	1	1	0	0
8	2256-34 Carb Diesel	3	3	0	0
9	Rochelle ULSD #2	3	4	1	-1
10	83-Fin Prod ULSD#2 composite Sept	5	4.25	0.75	0.75
11	ULSD#2 composite Aug	5	6	1	-1
12	ULSD #2 composite Nov	6	7	1	-1
13	ULSD #2 composite Oct	4	5.75	1.75	-1.75
14	22716-5 Corrigan rec'd 6-12-13	1	1	0	0
15	Rochelle #2 w/Lubrizol OS305538 @ 3270 ppm	1.25	1.5	0.25	-0.25
16	Rochelle #2 w/ Innospec Opt 1 @ 3506 ppm	1.5	1	0.5	0.5
17	Rochelle #2 w/ Innospec Opt 3 @ 3713 ppm	2	1	1	1
18	Buckeye Louisville June	1	1	0	0
19	22733-30 Carb Diesel	4.5	4	0.5	0.5
20	Innospec Diesel Sample	5.75	5.25	0.5	0.5
			average	0.5625	-0.0375
			std dev		0.7917
			95% confidence interval		-0.3845 to 0.03094

Rating Counts for Each Test Method



By using 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

18 / 20 (90%) Samples Agreed Pass / Fail

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

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

The results of the test performed during the ASTM Ruggedness Study shown 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.

Corrosion ratings: A=0%; B++=<0.1%; B=5-25%; C=25-50%; D=50-75%;E=75-100%

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.

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