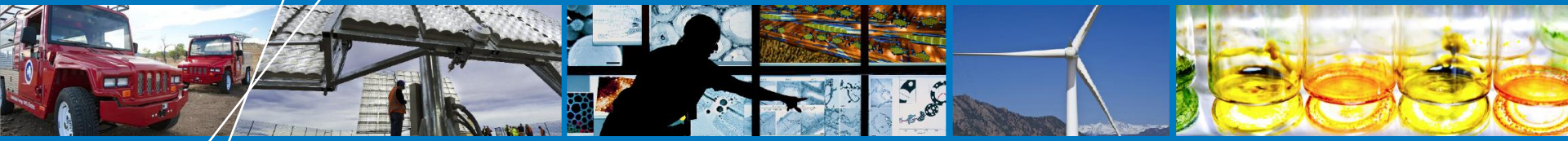
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Refueling Infrastructure-Status of Biofuels and Investigations



NIST Workshop on Alternative Fuels and Materials: Biocorrosion

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July 22, 2013

Agenda

- **Stations Background**
- **Refueling Equipment**
  - Manufacturers
  - Below ground equipment
  - Above ground equipment
- **UL**
  - NREL UL Test Results
- **STP Corrosion Scoping Study**
- **ORNL Ethanol Corrosion Results**

Gas Stations Statistics

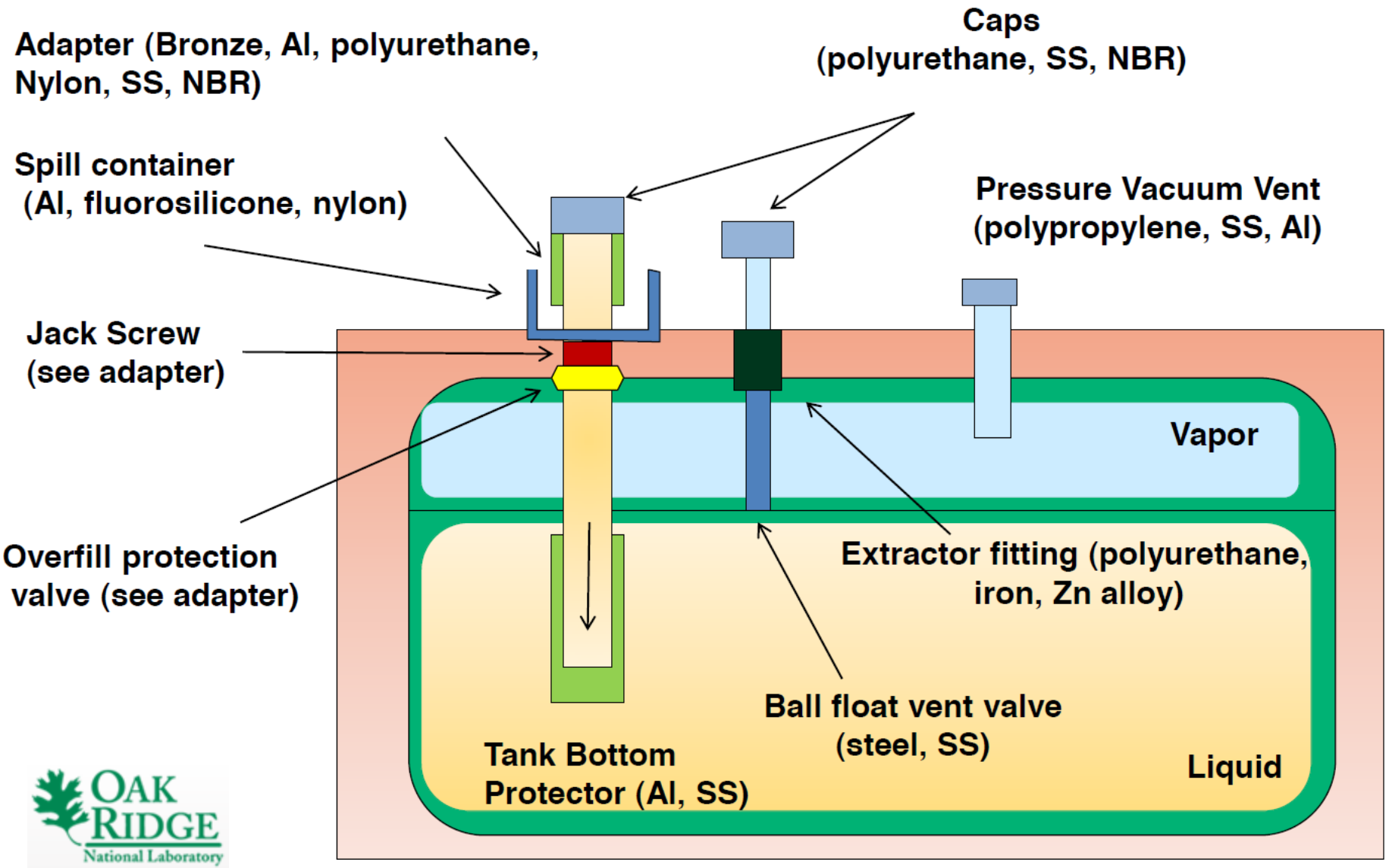
- **156,065 retail refueling stations**
- **80% of gasoline sold by gas stations with convenience stores**
- **Half of convenience stores sell branded fuel (oil company or refiner branded)**
  - A Conoco station is not owned by the oil major; it is an independently owned station selling fuel supplied by Conoco
- **Oil companies own less than 0.4%**
- **Nearly 60% of stations are one-store operations**
- **Average pre-tax earnings are $45,000 per store**

Refueling Equipment Manufacturers

- Most of the refueling equipment at retail stations is manufactured in the U.S.
- These companies export products all over the world to many countries who do not use biofuels
- Manufacturers have labs and most have tested their equipment with biofuels
- Manufacturers have upgraded elastomer materials in equipment due to changes in fuels market
- DOE Labs work with manufacturers to determine methods to deploy biofuels into existing equipment

Codes and Standards for Infrastructure

Below Ground Equipment



OAK RIDGE National Laboratory

Status of Tanks

- **EPA Office of Underground Storage Tanks (OUST) Guidance - Compatibility Of UST Systems With Biofuel Blends**
  - EPA was not aware of any incompatibilities of storing ethanol blends below E10 or B6-B20 in existing underground storage tanks
  - Guidance was developed to cover blends above E10 and B20
  - Allows tank owners to meet 40 CFR Part 280
  - Compliance was achieved by letter from each manufacturer stating compatibility
    - A letter from the equipment manufacturer with an affirmative statement of compatibility
    - Use of components certified by a nationally recognized independent testing laboratory

Tank Compatibility

- **Steel Tank Institute has letters from 24 steel tank manufacturers stating compatibility with all ethanol (up to E100) and biodiesel blend (up to B100)**
- **Fiberglass Tank Compatibility:**
  - Owens Corning—single wall up to E10; double wall E10 (1965-7/1/1990) and E100 (7/2/1990-12/1994); no statement on biodiesel
  - Containment Solutions—all tanks all blends E0-E100; B0-B100
  - Xerxes—Tanks prior to 1981 not compatible with any blend; single wall E10 (2/81-7/2005) E100 (7/2005-present); double wall E10 (prior-4/1990) E100 (4/1990-present); all tanks all years for B0-B100
- **Statements of compatibility from associated equipment manufacturers: Ameron, Bravo, Brugg Pipesystems, Morrison Bros., National Environmental Fiberglass, NOV Fiber Glass Systems, Nupi Americas, Omegaflex, Plasteel, Vaporless Manufacturing, and Western Fiberglass**

- **Steel Tank Institute Letters Stating Compatibility: http://www.steeltank.com/Publications/E85BioDieselandAlternativeFuels/ManufacturerStatementsofCompatibility/tabid/468/Default.aspx**

- **Petroleum Equipment Institute Letters Stating Compatibility: http://www.pei.org/PublicationsResources/ComplianceFunding/USTComponentCompatibilityLibrary/tabid/882/Default.aspx**

ULSD Corrosion

- **Clean Diesel Fuel Alliance funded a hypothesis study to identify issues seen in diesel tanks**
  - Corrosion issue appears to have started occurring after the move to ULSD
  - The study suggests ethanol contamination in ULSD may be causing the corrosion
- **Per DOE request, NREL tested diesel samples (refiner and retail stations) we already had onsite; none contained ethanol (we can detect to 0.1%)**
- **NREL/DOE reviewed the study with API and Battelle Staff**
  - Concern about using ethanol to clean tank sampling equipment
  - Only six sites evaluated where biofuels use is less extensive (CA, NC, NY); no control site
  - One of the samples did not have ethanol content in either water or fuel sample
  - Made many suggestions for follow on study including sampling tanks in midwest, demonstrating that cleaning sampling with equipment ethanol did not cause the previous results, Test ULSD across the supply chain for ethanol content

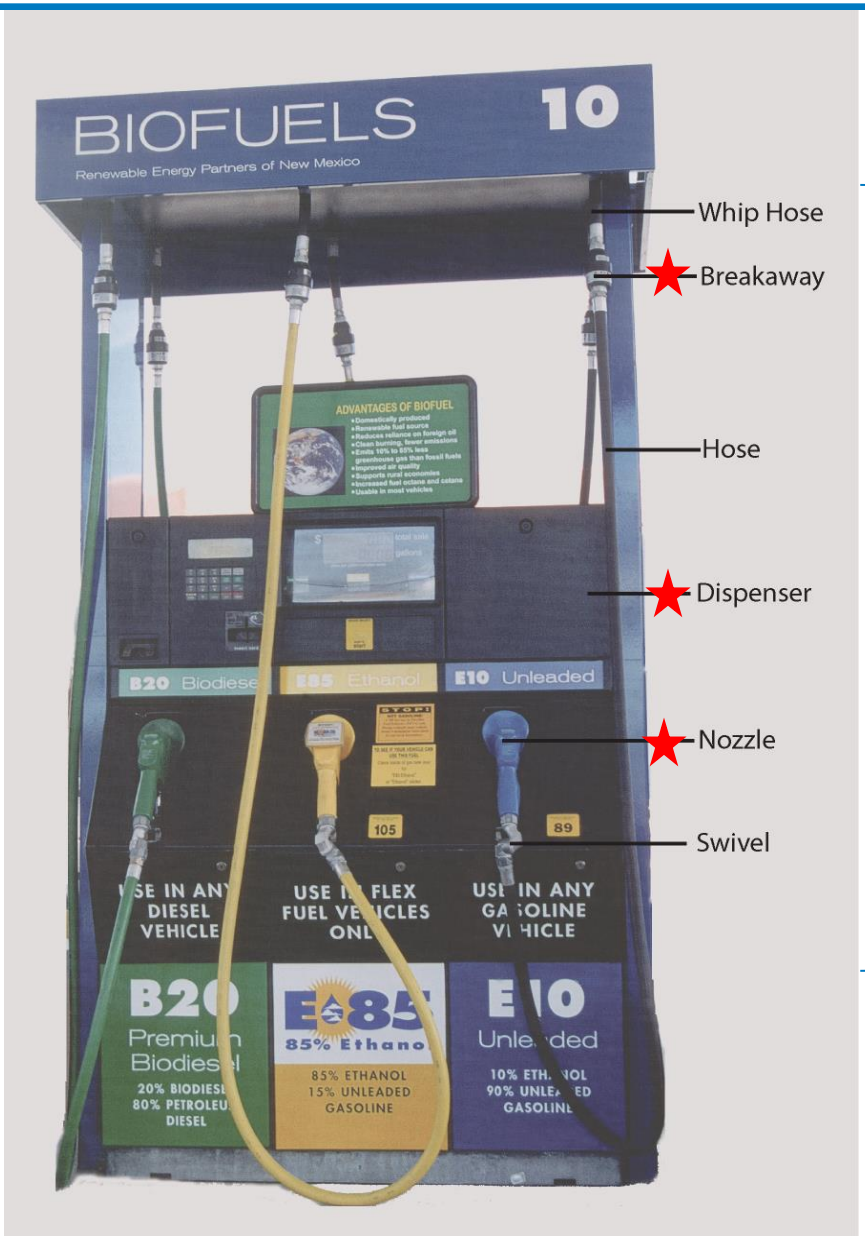
Flammability Issues

- Ethanol is more flammable than gasoline
- DOE and EPA do not recommend the storage of E98 at stations

Fuel Gas	Lower Explosive or Flammable Limit (LEL/LFL) (% in air)	Upper Explosive or Flammable Limit (UEL/UFL) (% in air)
Gasoline	1.4	7.6
Ethanol	3.3	19

Above Ground Equipment

- **Dispensers**
  - Average life 15 years
  - Cost $15k-$20k
- **General**
  - E85 products have nickel plated metal
  - E25 dispenser uses specific elastomers
- **Handing Hardware**
  - Average life 3 years
  - Inexpensive
- **OSHA requires third-party listing for specific fuels** ★



UL Testing Protocols

	E10 and B5	Greater than E10 and B5
UL Testing Protocol	• UL Standard 87 • In existence for more than 100 years; amended in 1980's for E10 • Minimal fluid exposure for some equipment for 70 hours at room temp • Performance testing unique for each equipment type • Manufacturers want to keep this standard as it applies to many countries in the world	• UL Subject 87A (ethanol) & 87B (biodiesel) • Developed with significant industry input (biofuels and refueling equipment manufacturers) • 15 week fuel exposure at 60°C • Performance testing unique for each equipment type • Will replace UL Standard 87 (sunset date unknown)

UL is the only third-party lab testing and listing refueling equipment in the U.S.

Ethanol and Biodiesel Test Fluids

ETHANOL

- Reference Fuel C (50% toluene, 50% isooctane)
- Desired % ethanol with aggressive elements
- UL tests with E25 (for E0-E25) and E85 (for E0-E25)

Aggressive solution component	Grams per liter of ethanol
Deionized water	8.103
Sodium chloride	0.004
Sulfuric acid	0.021
Glacial acetic acid	0.61

BIODIESEL

- Reference Fuel F (diesel, fuel grade no.2)
- Desired % Biodiesel (ASTM D6751) with aggressive elements of 0.25 grams of decononic acid and 1,000 grams of deionized water
- UL tests with B25 (for B6-B25) and B100 (for B100 only); there is no test fluid or listing for B21-B99

NREL UL Test Results

ETHANOL (2010)

- Funded by DOE
- Aggressive 17% ethanol test fluid
- Mixed results
- Resulted in development of retrofit kits for dispensers and a recommendation to replace hanging hardware with E25 or E85 equipment

Equipment	Pass New	Pass Used	Pass Overall
Breakaways	2 of 5	1 of 4	3 of 9
Flow limiters	1 of 1		1 of 1
Hoses	8 of 9	4 of 6	12 of 15
Dispensers	0 of 2	0 of 4	0 of 6
Nozzles	3 of 6	1 of 4	4 of 10
Shear Valve	3 of 3		3 of 3
Submersible Turbine Pump	1 of 1		1 of 1
Swivels	3 of 4	3 of 5	6 of 9

Biodiesel (2012)

- Funded by NBB
- Aggressive 25% biodiesel test fluid
- Better results partly due to upgrades manufacturers made for ethanol and ULSD
- Resulted in UL listed B20 equipment

Equipment	Pass
Reconnectable Breakaways	4 of 6
Non-reconnectable Breakaways	3 of 3
Hoses	4 of 4
Nozzles	6 of 10
Shear Valve	4 of 4
Swivels	8 of 10
Dispensers	1 of 1

STP Corrosion – EPA OUST Photos

E10 STP, unknown grade (Florida) – Feb. 2011

91 octane STP (California) – August 2010

Premium/E10 STP (Tennessee) – March 2010

Same sump!

Premium/E10 STP (Tennessee) – August 2010

STP Corrosion Scoping Study

- **EPA's Kerr Center analyzed the samples for ethanol, acetic acid, benzene, and total BTEX in vapors and sump water**

- **Study Statistics on presented data (EPA has not published a full data set):**
  - 20 inspectors from 9 states provided photos
  - 70 vapor samples were collected from 15 sumps in TN; 13 sumps in FL; 2 sumps in CA; collected in 2010 and 2011
    - 33 regular gasoline
    - 29 premium gasoline
    - 7 E85
    - 1 diesel
  - 13 sump vapor samples exhibited a concentration of ethanol greater than 10,000 mg/l
    - Of this; 60% occurred in premium
- **8 sump water samples were provided**
  - 6 samples exhibited low ethanol and acetate concentrations
  - 1 sample exhibited high acetate and low ethanol (STP exhibited corrosion)
  - 1 sample had high ethanol and low acetate (STP exhibited little corrosion)
- **A concentration of ethanol in vapors of 10,000 mg/L generally correlated to corrosion on the STP**

STP Corrosion Scoping Study

- **NREL interviewed county UST inspectors and state UST office staff in California, Florida, Illinois, Iowa, Kansas, New York, Tennessee, Washington, and Wisconsin**
  - No states keep STP corrosion statistics
  - **No inspectors or states reported a leak or early replacement of a STP as a result of the corrosion**
- **NREL held meetings with lead engineers at both manufacturers**
  - Manufacturers are aware of the issue and have investigated it; no warranty claims made on this issue
- **NREL contacted a major oil company with multiple refineries and asked about higher incidence of STP corrosion with premium**
  - There may be residual acids or caustic left behind from the alkylation process which uses concentrated sulfuric or hydrofluoric acids, later neutralized with caustic (NaOH) which should then be washed out with water. This step is expensive and some producers might either skimp on the washing or inadequately wash, thereby leaving some small amount of acid or caustic behind.

STP Corrosion Potential Solutions

- **Use corrosion resistant STP components**
  - Manufacturers state that using all stainless steel housing would be cost prohibitive
- **Improve STP sump ventilation**
  - Sumps are not designed to ventilate—sumps are intended to be air/water tight and contain any leaks
  - It is unlikely that EPA's Office of Transportation and Air Quality (OTAQ) will agree to venting vapors from sumps
  - Tennessee found that piping running through a 4" chase connecting the STP sump to the dispenser sump unintentionally allows adequate ventilation to prevent corrosion
  - Once updated, EPA OUST revised Underground Storage Tank may include monthly inspection of STP sump—in theory this would ventilate sumps at least once per month
- **Corrosion resistant coating**
  - A few inspectors mentioned some type of product applied once per year

POET Fuel Quality versus NACE Corrosion Rating

POET - Innospec Retail Fuel Corrosion Survey

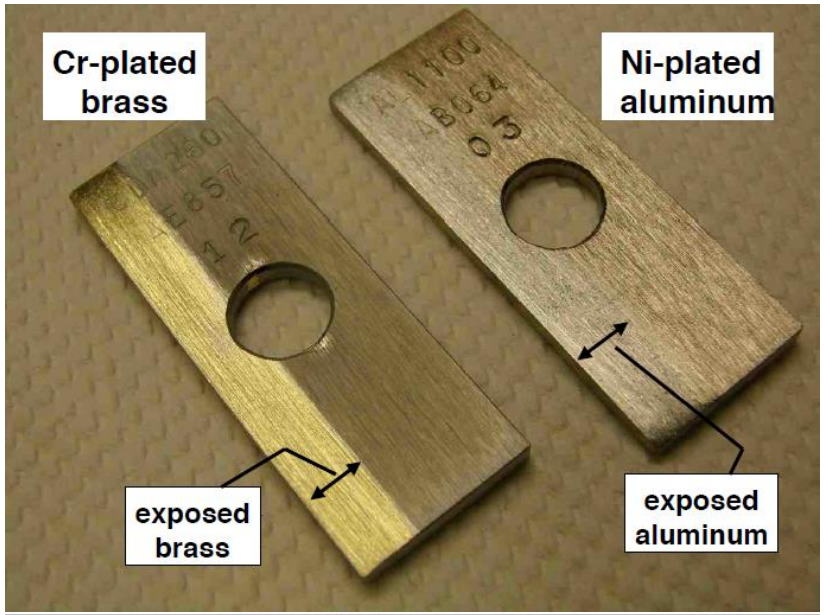
			As-is NACE Corrosion Rating									
Retail Site #	State	Sample Month, Year	Unleaded		Super Unleaded		Premium		E30		E85	
			Rating	% Corr.	Rating	% Corr.	Rating	% Corr.	Rating	% Corr.	Rating	% Corr.
100	SD	January, 2011	A	0	A	0	A	0	A	0	A	0
101	MN	January, 2011	A	0	A	0	A	0	A	0	A	0
102	MO	January, 2011	A	0	A	0	A	0			A	0
103	IA	January, 2011	B	25	A	0	B	15	A	0	A	0
104	MI	January, 2011	A	0	A	0	A	0	A	0	A	0
105	IN	January, 2011	A	0	A	0	A	0	A	0	B++	<0.1
106	OH	January, 2011	A	0	A	0	A	0			A	0
107	MN	February, 2011	A	0	A	0	C	45			B	10
108	SD	February, 2011	A	0	A	0			A	0	A	0
109	IA	February, 2011	A	0	A	0	B++	<0.1	A	0	A	0
110	MO	February, 2011	B++	<0.1	A	0	A	0	A	0	A	0
111	IN	February, 2011	A	0	B++	<0.1	A	0			A	0
112	OH	February, 2011	A	0	A	0	A	0			A	0
113	MN	March, 2011	A	0	A	0	B++	<0.1	A	0	A	0
114	SD	March, 2011	A	0	B++	<0.1	A	0	B++	<0.1	A	0
115	IA	March, 2011	B+	<5	A	0	C	30	B++	<0.1	A	0
116	MN	March, 2011	B++	<0.1	A	0	A	0	B++	<0.1	A	0
117	IN	March, 2011	A	0	A	0	B++	<0.1			A	0
118	OH	March, 2011	A	0	A	0	A	0			B++	<0.1
119	SD	April, 2011	B++	<0.1	A	0	A	0	A	0	A	0
120	SD	April, 2011	B++	<0.1	A	0	B++	<0.1	A	0	A	0
121	IA	April, 2011	A	0	B++	<0.1	B++	<0.1			A	0
122	IA	April, 2011	A	0	B++	<0.1	A	0	A	0	A	0
123	IN	April, 2011	A	0	A	0	A	0			A	0
124	IA	May, 2011	A	0	A	0	B++	<0.1			A	0
125	SD	May, 2011	A	0	A	0	B+	<5	A	0	A	0
126	IA	May, 2011	B+	<5	A	0	A	0	A	0	A	0
127	SD	May, 2011	A	0	A	0	A	0	A	0	A	0

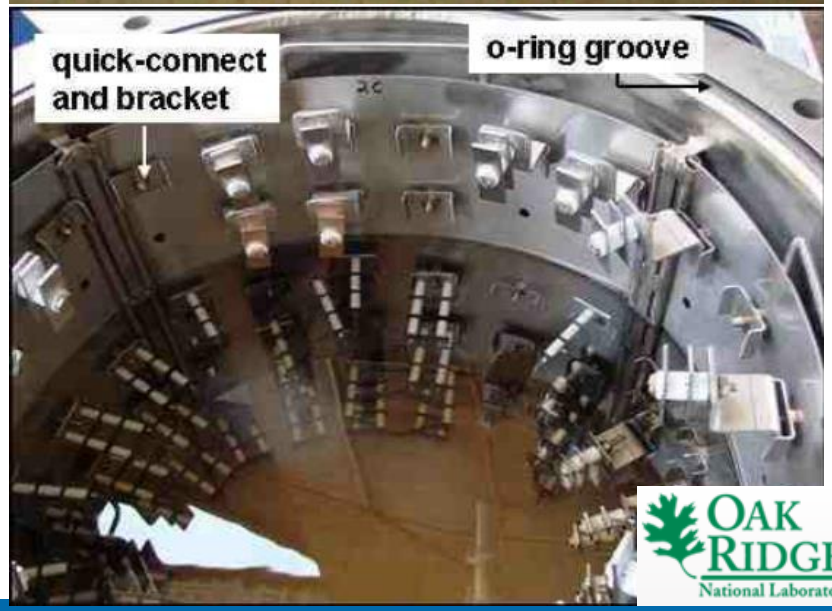
Color Key	Rating	A	B++	B+	B		C	
	% Corrosion	0	<0.1	<5	5	25	26	49

D		E	
50	75	76	100

ORNL Metals Ethanol Corrosion Tests

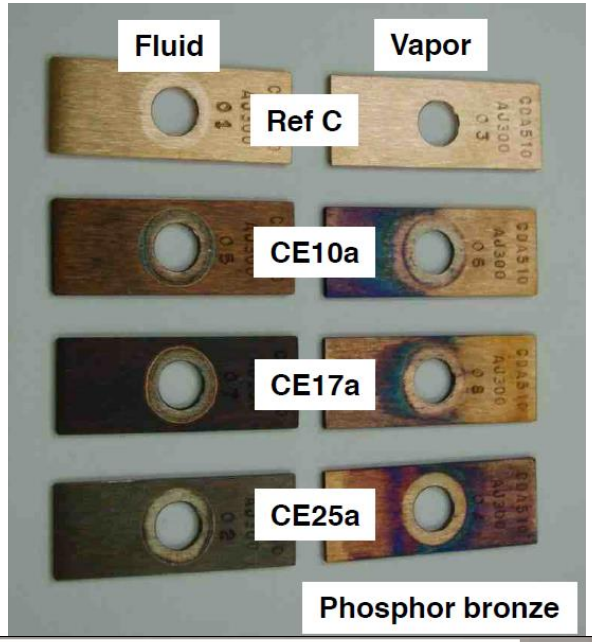
- **Single Material Coupons**
  - 304 stainless steel
  - 1020 carbon steel
  - 1100 aluminum
  - Cartridge brass
  - Phosphor bronze
  - Nickel 201
- **Plated Coupons (exposed fully plated and with plating partially removed to generate galvanic couple)**
  - Terne-plated (Pb) steel
  - Galvanized (Zn) steel
  - Cr-plated brass
  - Cr-plated steel
  - Ni-plated aluminum
  - Ni-plated steel
- **Analytical Techniques**
  - Appearance
  - Mass loss
  - X-ray Photoelectron Spectroscopy (XPS)Sample main point





ORNL Metals Ethanol Corrosion Test Results

- **Vapor Exposure**
  - Coupons exhibited slight discoloration but no measurable corrosion
- **Fluid Exposure**
  - No measurable or accelerated corrosion resulted for either the completed plated or the partially-plated specimen
  - Aggressive ethanol content resulted in modest corrosion and film formation on Cu-based alloys; highest corrosion rate (~30 µm/y) for brass in CE10a, but original machining marks are still visible on surface
  - Zn surfaces experienced discoloration due to film formation also modest weight change



ORNL Metals Ethanol Corrosion Test Results 2

- Brass, bronze, zinc, and lead were most affected by the test fluids
- No apparent trends with ethanol concentration
- Corrosion rates are considered modest and not likely to impact overall component performance

	Fuel C	CE10a	CE17a	CE25a
Brass	0.4	29	deposit	8
Bronze	0.2	6	4	13
Zn (galv)	0.2	1	deposit	deposit
Pb (terne)	1	0.9	0.2	0.5

µm/y

http://info.ornl.gov/sites/publications/files/Pub27766.pdf
http://info.ornl.gov/sites/publications/files/Pub35074.pdf

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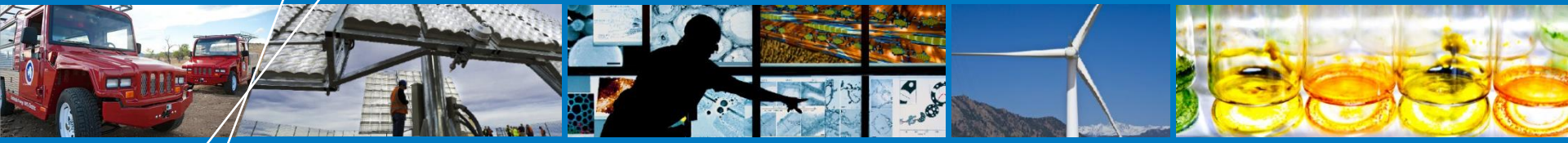

Thank you

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