DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Materials Degradation In Biomass-Derived Oils

March 22, 2021

Systems Development and Integration

James Keiser

Oak Ridge National Laboratory

Project Overview

- Identify and/or develop materials specifically suited for use in bio-oil production, processing, storage and transporting environments
- The presence of significant quantities of oxygen-bearing compounds may cause bio-oils to degrade metallic and non-metallic materials
- We are using many techniques to characterize degradation of materials:
  - Chemical characterization of bio-oil components
  - Laboratory corrosion studies of metallic and non-metallic materials
  - Field corrosion studies in operating biomass liquefaction and gasification systems
  - Examination of exposed samples and liquefaction system components
  - Fundamental study of surface interactions of bio-oil components and materials
- We expect to be able to recommend metallic and non-metallic materials that will perform sufficiently well that no thermochemical liquefaction technology fails to be commercialized because of material degradation issues

Project Overview - continued

- As emphasized during the 2019 review, it is essential that we communicate to stakeholders the knowledge we gain from these studies

- This is being accomplished through:

  - direct interaction with, and technical support for, organizations producing biomass-derived products

  - presentations and publications at technical conferences

  - publications in technical journals particularly those directed to relevant topics

  - presentations at the ABLC conferences and publication in Biofuels Digest of a slide deck describing our project

2 - Approach

- Project is divided into seven tasks:

  - Study of corrosion and degradation of metallic materials

  - Development of alternate metallic materials and characterization of degraded samples and components

  - Chemical characterization of bio-oils to identify corrodents

  - Study of degradation of non-metallic materials

  -Neutron studies of surface behavior of elastomers in solvents

  - Development of Electrochemical Impedance Spectroscopy technique

  - Application of solid phase processing techniques to improve material performance in two industrial systems

1 – Management – Participants

- Multidisciplinary – have ORNL staff participants from many specialties
  - Corrosion Science and Technology
  - Surface Processing and Mechanics
  - Engine Technologies Research
  - Carbon and Composites
  - Materials Microanalysis
  - Neutron and X-Ray Scattering
  - Applied Catalysis and Emissions Research
- Have collaborators from national laboratories, universities, industries
  - NREL, PNNL, INL, CanmetENERGY, VTT, Iowa State University, University of Maine, Michigan State University, Georgia Tech, Aarhus University, ThermoChem Recovery Int'l, Frontline Bioenergy, Ensyn, Fortum, ICM Inc

Approach – Technical

- Analysis of bio-oils and corrosion products will be essential in determination of degradation mechanism(s)
  - Utilize existing methods and develop new techniques as needed
- Characterization of samples and degraded components from operating systems, field exposures of test materials, and laboratory corrosion tests of candidate structural materials
  - Employ light and advanced electron microscopy, neutron imaging and other material characterization techniques
- Identify or develop alternate materials with sufficient resistance to degradation. Analysis will focus on lowest cost materials that meet goals
- Technical success based on
  - Assessment and determination of degradation mechanism(s)
  - Successful identification of sufficiently low cost degradation resistant materials to enable advancement of bio-oil technologies to the commercialization stage

3 - Impact

- Success in this project will enable project designers to make wise selection of structural materials and will help reduce the frequency of component replacement and/or maintenance required by system operators
- We are striving to make the information we collect available to designers and operators through many mechanisms
  - direct interactions,
  - participation in conferences (both those directed toward bioenergy and general conferences),
  - open literature publications,
  - ABLC conferences,
  - Biofuels Digest,
  - workshops
- Technical support has been provided to some organizations, and requests are being received from other organizations for technical support

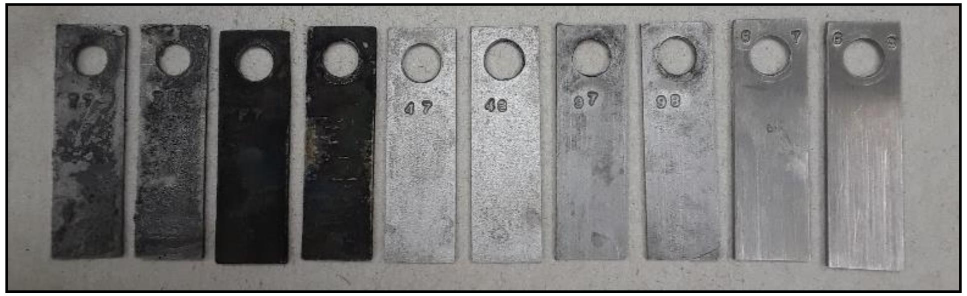
4 – Progress and Outcomes - Low temperature corrosion

- Want to assess effect of long-term exposure in bio-oil at temperatures ≤ 50°C
- Exposed samples of 3 alloys in drums of bio-oil at NREL for ~26,750 hr

  - 2¼ Cr-1Mo badly corroded, 409 SS thinned

- Exposed samples of 5 alloys in drums of bio-oil at ORNL for 12,480 h

  - 2¼ Cr-1Mo, 7 Cr-1 Mo, and 9 Cr-1 Mo had unacceptably high corrosion rates



2¼ Cr-1 Mo 7 Cr-1 Mo 409 SS 9 Cr-1 Mo 316L SS

- Conducting 1000 h studies of other alloys with Cr ≥8.5 but ≤14 wt% to identify alloys with sufficient corrosion resistance for long time, low temperature use

4 – Progress and Outcomes - Low temperature corrosion

- Other low temperature tests are underway or planned
- **Frontline Bioenergy** needs a nonmetallic coating for a storage tank intended for high boiling point fraction of bio-oil. We are exposing candidate coating materials in bio-oil – currently exposed 2,500 h

Blistered, delaminated sample after initial 500h test

Alternate sample coatings before follow-up testing

- Preparing transfer agreement with **Ensyn** for 20 gallons of bio-oil for blending and corrosion studies of metallic and nonmetallic materials
- Collaborating with **Maine Maritime Academy** to make arrangements to expose samples in their Thermal Deoxygenation system

4 – Progress and Outcomes – High temperature corrosion

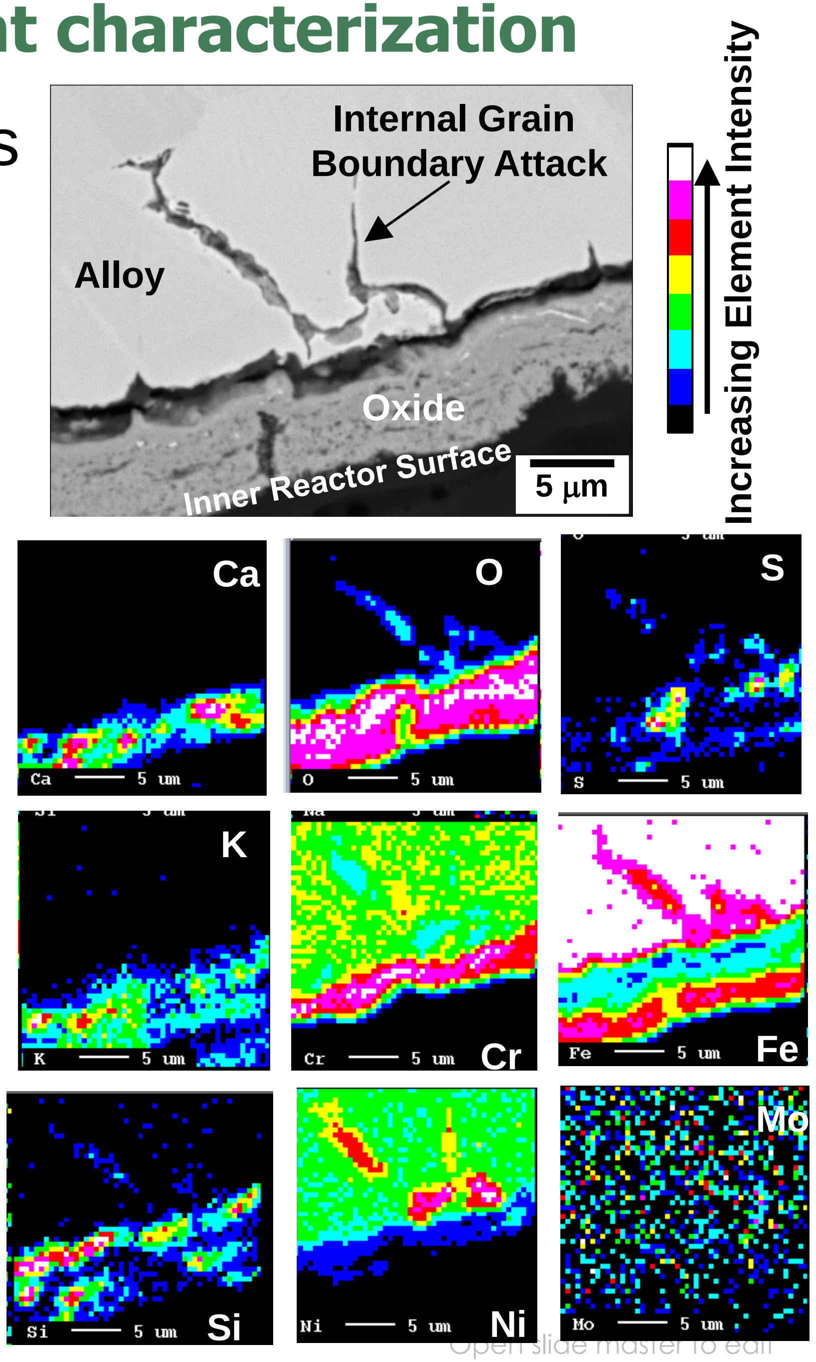
- We are not able to simulate in our laboratory the environment developed during thermochemical production of bio-oil
- We are collaborating with many laboratories and universities to expose samples, spool pieces and components in actual environments
- Spool pieces and cyclones sent to NREL (left) and returned from NREL after long duration operation (right)

4 – Progress and Outcomes – Component characterization

- High temperature corrosion studies are more difficult because simulated conditions can not be produced in the lab; consequently, we have to rely on samples exposed in operating systems and components exposed extended times in those systems
- NREL, Iowa State and VTT have provided samples and components with significant exposure times
- NREL recently sent spool pieces and components with significant exposure times, and these have been sectioned and are currently being examined
- Spool pieces sent to NREL in 2014

4 – Progress and Outcomes – Component characterization

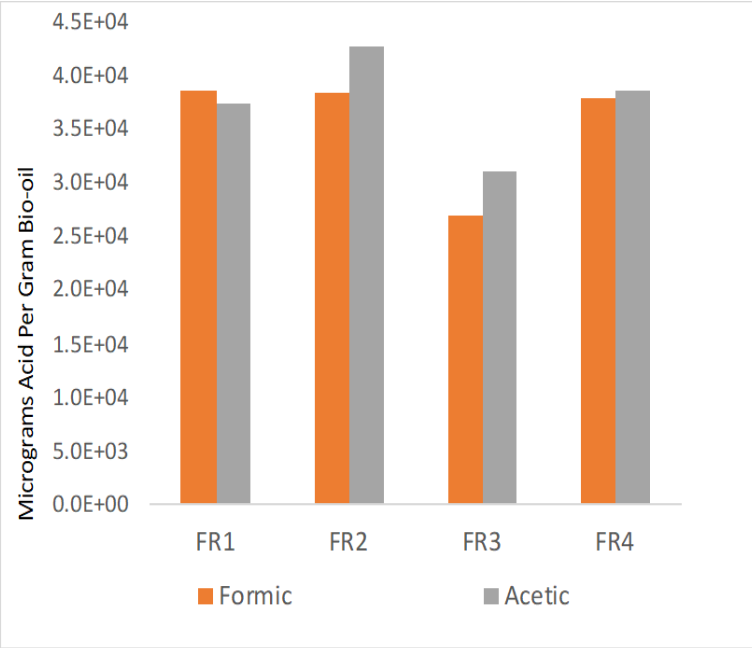
- Components of an Iowa State fluidized bed pyrolysis reactor were examined using advanced microstructural characterization techniques
- The extent of surface scaling and internal attack were significantly greater than seen on a sample exposed in air for the same time and temperature
- High scaling rates were likely influenced by the Ca, K, S, Mg and P present in the reactor
- Internal attack likely related to diffusion of Cr along grain boundaries to the surface to support the rapid scaling
- Studies of additional samples with significant exposure times are needed to further our understanding of the corrosion mechanisms



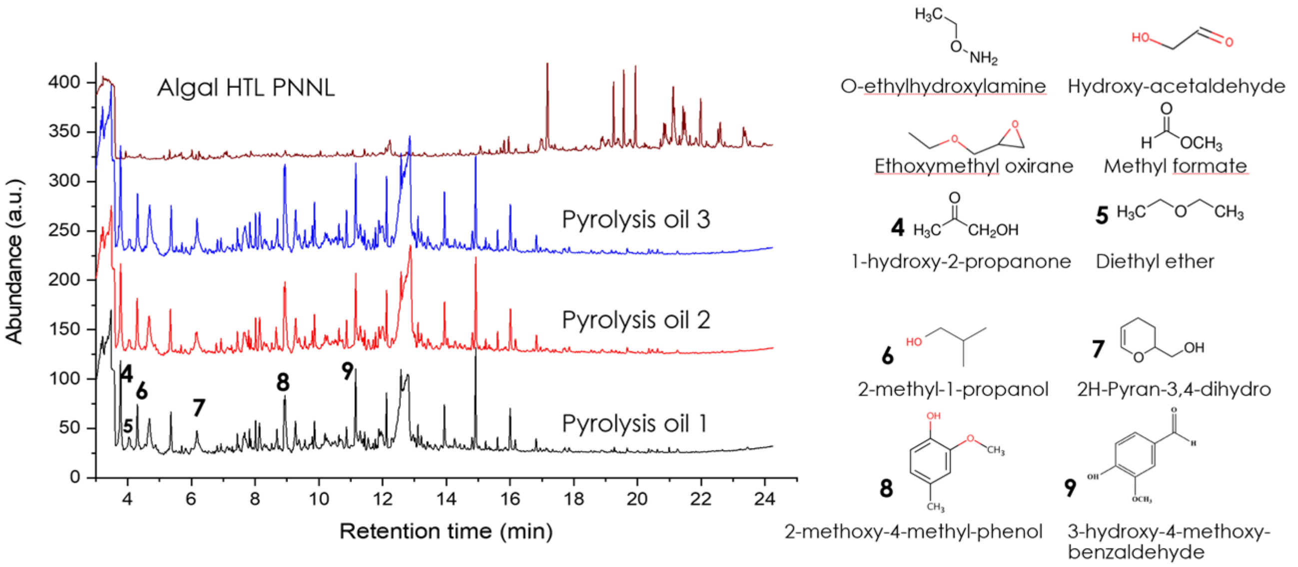
4 – Progress and Outcomes – Chemical characterization

- Major emphasis is to identify major components, and particularly those that will degrade metallic and nonmetallic materials including acids, ketones and chelating compounds

Concentration of formic and acetic acids in fast pyrolysis oils, micrograms acid per gram of bio-oil as determined by capillary electrophoresis

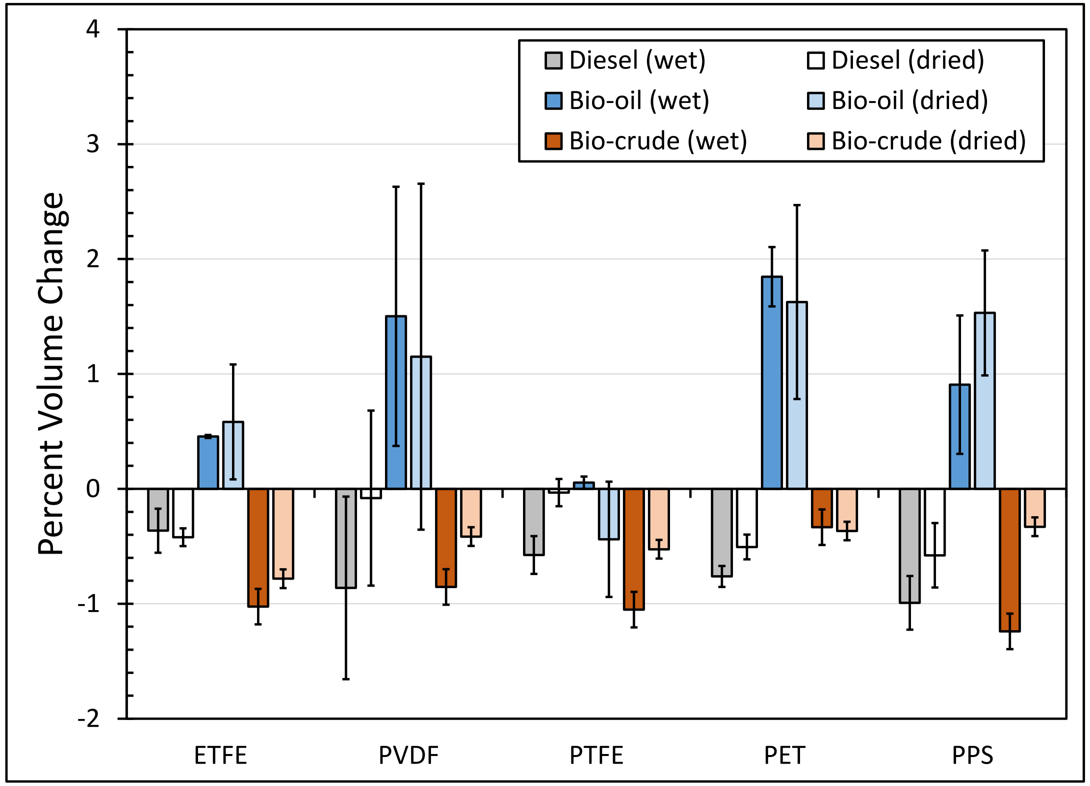


Gas chromatograms of four bio-oils: Algal hydrothermal liquefaction oil (top), B3 pyrolysis post-alloy exposure oils (middle) and Pyrol 803 pyrolysis oil (bottom).



4 – Progress and Outcomes – Nonmetallic corrosion

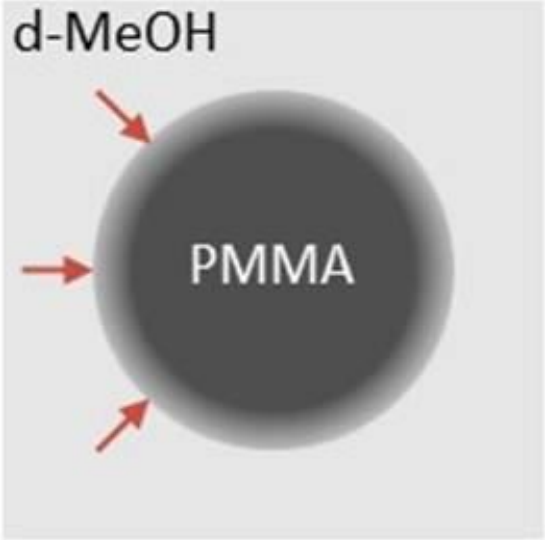
- Studies are directed at understanding the compatibility of elastomers and plastics with biomass and petroleum derived oils
- Recent studies compared the performance of several plastics with diesel fuel, pine-derived fast pyrolysis oil and algae-derived HTL bio-crude
- There are notable differences in the volume change for the materials in the different liquids
- However, the changes are all less than 2% meaning all are suitable for service in these oils



OAK RIDGE National Laboratory

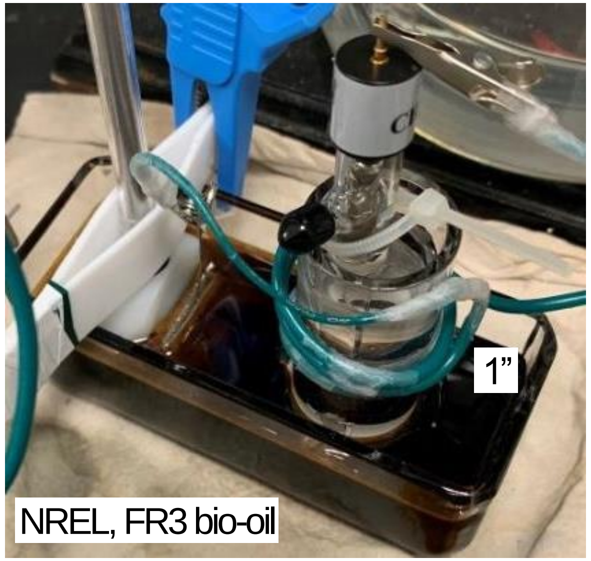
4 – Progress and Outcomes – Neutron studies

- Neutron imaging campaigns were conducted on beam lines at Oak Ridge National Laboratory and the National Institute of Standards and Technology
- These campaigns were designed to image methanol permeation in polymethyl methacrylate (PMMA) in order to determine whether bulk molecular relaxation is the sole mechanism governing permeation
- Initial studies successfully captured the permeation event, but the resolution was impacted by surface irregularities and beam time limitations that prevented an accurate determination of the permeation profile
- Follow up studies are planned using samples prepared so as to avoid some of the edge effects encountered in the initial tests
- This information should provide necessary information to improving polymer compatibility with fluids



4 – Progress and Outcomes – Electrochemical impedance spectroscopy
During FY20, EIS-based corrosion analysis became available using “real” bio-oils

- Early FY20, EIS was attempted for a real bio-oil (Forest residue pyrolysis from NREL)



ORNL custom-design electrochemical cell for bench-top scale EIS measurement

- Minimized the distances between the electrodes to reduce ohmic drop
- Only need a small amount of bio-oil (~120 mL) per measurement

The EIS system is being used to assess the corrosion behavior of a series of commercial and model alloys prepared at ORNL

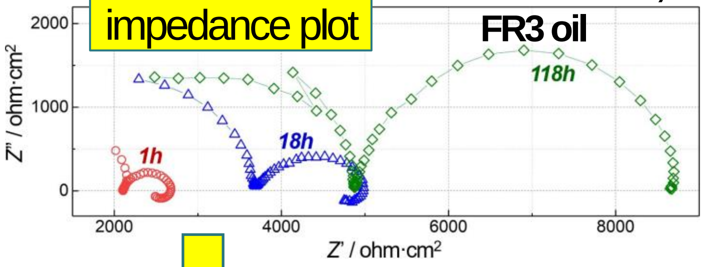
Composition (wt%) of model alloys prepared for corrosion studies

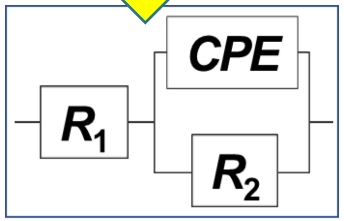
Fe	Cr	Ni	Mn	Si	C	Mo
Bal	8.5	0.5	0.4	0.3	0.03	
Bal	10	0.5	0.4	0.3	0.03	
Bal	11.5	0.5	0.4	0.3	0.03	
Bal	11.5	0.5	0.4	0.3	0.03	1
Bal	11.5	0.5	0.4	0.3	0.03	2
Bal	13	0.5	0.4	0.3	0.03	
Bal	14.5	0.5	0.4	0.3	0.03	

edit

4 – Progress and Outcomes - Electrochemical impedance spectroscopy

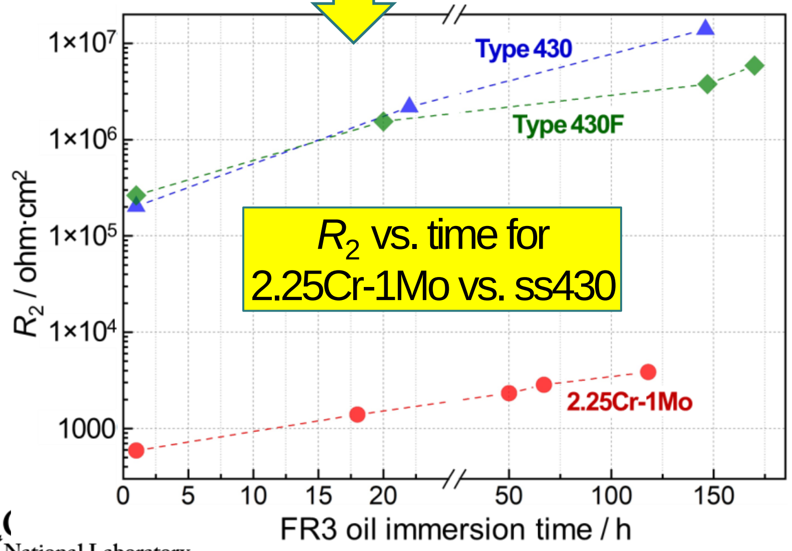
During FY20, EIS-based corrosion analysis became available using 'real' bio-oils



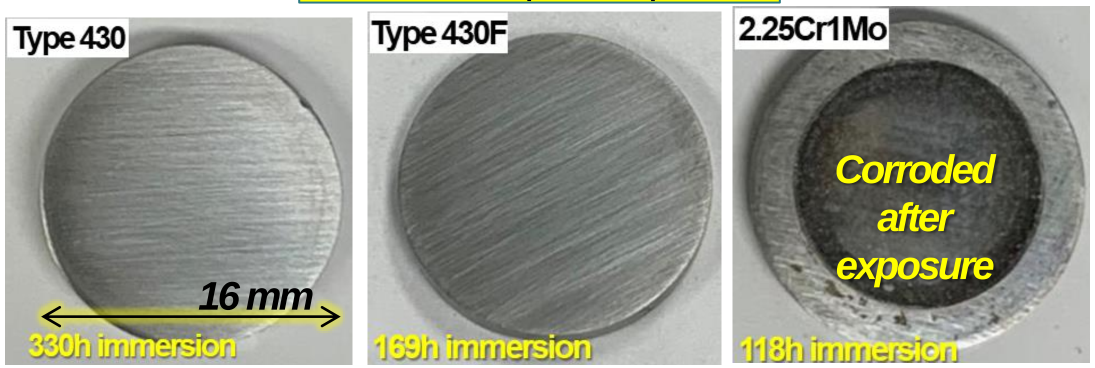


Equivalent circuit fitting to determine R_2

R_2 ~ corrosion resistance



Post FR3 exposure photos



***High R_2 during EIS measurement* → No apparent corrosion**

Recent EIS analysis results

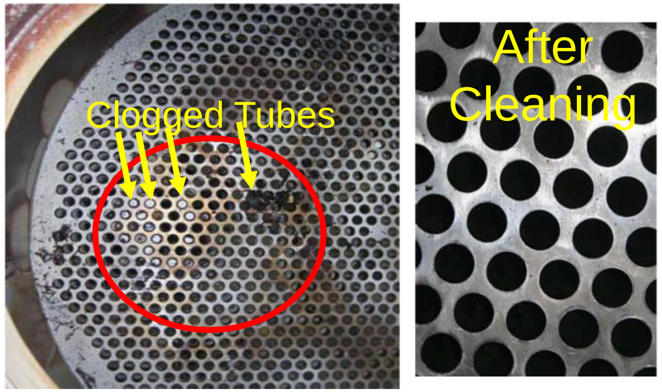
- Corrosion resistance is highly dependent on alloy compositions, **Cr & Cr+Ni+Mo**
- For commercial alloys, ss41x & 42x series (**12~13Cr**) were not resistant in FR3 bio-oil, while **14.5Cr, 16Cr & 12Cr-5Ni-2Mo** were resistant.
- For model alloys, **14.5Cr** was resistant, but **13Cr, 11.5Cr-2Mo** were not resistant.
- Further studies are needed for commercial and model alloys using less acidic bio-oils

4 – Progress and Outcomes – Solid phase processing

- Materials of construction are extremely important for biorefineries due to the corrosive and erosive environments
- PNNL and ORNL are collaborating on a project to determine the suitability of solid phase processing materials in bio-oil production systems
- Corn ethanol producer, **ICM Inc**, initially agreed to participate in the project, and opportunities were identified where alternate materials might provide savings; however, because of reduction in ethanol consumption, ICM had to withdraw from project
- Similar opportunity areas have been identified in **ThermoChem Recovery International**'s (TRI) municipal solid waste (MSW) gasification system which is being used for the Sierra Biofuels facility being constructed by **Fulcrum Bioenergy** in Nevada

4 – Progress and Outcomes – Solid phase processing - PNNL

- Solid Phase Processing (SPP) could potentially alleviate wear and erosion in vital unit operations
- This effort looks at SPP technology such as Friction Stir Processing and Cold Spray Deposition to extend the lifetime of select materials
- Significant industrial engagement (TRI, ICM, Fulcrum) has allowed us to tailor our efforts to maximize industrial relevance
  - Pulse heater tube corrosion
  - Multi-effect evaporator fouling
  - Screw feeder tip fouling
  - Hammer mill fracturing
  - Erosion of refractory lining in high temperature cyclones
- Collaborative experimental work combined with cost modeling quantifies potential savings over the lifetime of the plant
- PNNL is preparing components to be exposed in actual and/or simulated environments
- Modeling and TEA are being conducted on selected components



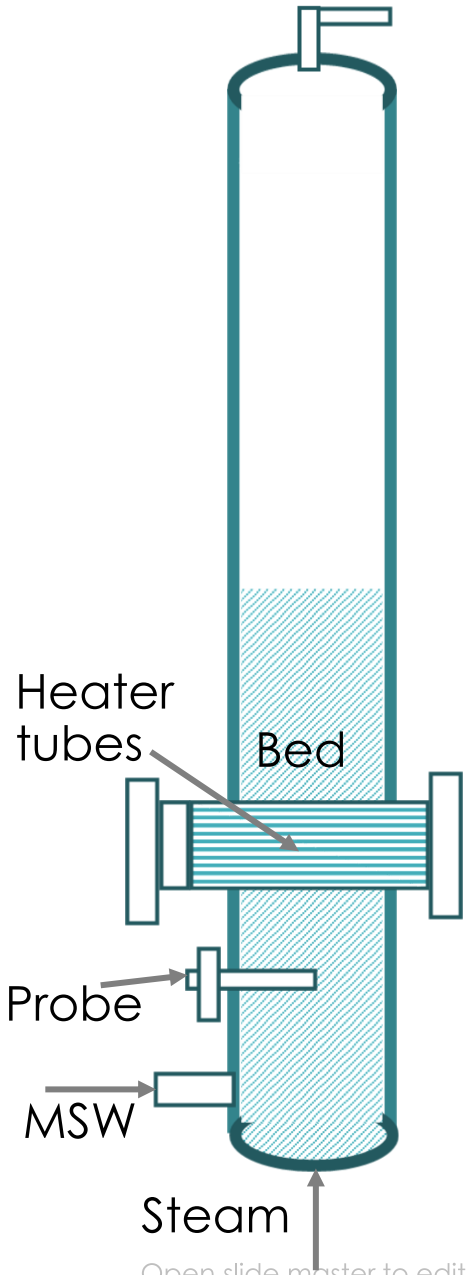
4 – Progress and Outcomes – Solid phase processing - ORNL

- Arrangements are being made with INL to conduct tests on hammer mill materials that are used to prepare corn for further processing in ethanol production

- Initial tests have been conducted in ORNL's tribometer to assess fouling tendency of feed screw surfaces in hot simulated Municipal Solid Waste (MSW)

- We are making arrangements with TRI and Fulcrum Biofuels to expose a corrosion probe to evaluate alternate pulsed heater tube materials – requires FE modeling to address fatigue concern

- We are making arrangements with a company that can conduct high velocity, high temperature tests in a stream of abrasive particles like seen by the high temperature internal cyclones



Summary

- Conducting studies to identify corrodents and corrosion mechanisms through laboratory studies and exposure and analysis of samples and components exposed in operating systems
- Providing direct support to designers and operators of biomass liquefaction and gasification systems
- Communicating results of our studies through direct contacts, presentations at subject matter-related conferences, open literature publications, ABLC conferences and Biofuels Digest
- Goal is to provide sufficient information and guidance so that materials degradation does not prevent commercialization of developing technologies

Quad Chart Overview

Timeline

- Project start date October, 2010
- Project end date October, 2021

	FY20	Active Project
DOE Funding	(10/01/2019 – 9/30/2020)	$1,650,000

Project Partners:
NREL, PNNL, CanmetENERGY, Iowa State University, Michigan State University, University of Maine, Aarhus University, Georgia Tech, Fortum, Ensyn, Thermochem Recovery Int'l, Frontline Bioenergy

Barriers addressed

Ct-M – Current reactors not designed to handle harsh conditions inherent in converting biomass feedstock

ADO-H – Materials compatibility and equipment design and optimization

Project Goal

Identify and/or develop cost-effective materials specifically suited for use in bio-oil production, processing, storage and transporting environments

End of Project Milestone

Identify structural materials that are suitable for any biomass type and processing technique so that materials issues do not prevent commercialization of any biomass liquefaction or gasification technology. This will be accomplished through direct support of designers and operators, technical presentations at conferences and workshops, and technical publications

Funding Mechanism

AOP funding

*Only fill out if applicable.

Additional Slides

Responses to Previous Reviewers' Comments

- More extensive dissemination of results encouraged – team members have expanded number of publications and presentations including the ABLC conferences and Biofuels Digest
- Coatings should be addressed – in task supporting Frontline Bioenergy we have been and are continuing to expose coated samples to bio-oils for extended periods (>2,500 h)
- Need to address corrosion at interfaces – samples exposed at NREL at 10°C and room temperature were partially immersed in bio-oil thus providing information on interface effects
- Need to address kinetics – periodic examinations of samples exposed in bio-oil are providing some kinetic information

Publications

- J. R. Keiser, G. Warrington, J. Jun, D. Sulejmanovic, M. Brady, and M. Kass, *Long-Term Corrosion Studies Of Pine Derived Bio-Oil And Blends With Heavy Fuel Oil*, TAPPI PEERS 2020 proceeding (Nov. 2020).
- Jim Keiser, Mike Brady, Maggie Connatser, Sam Lewis, Gavin Warrington, Jay Jun and Mike Kass**,** *Structural Materials for Thermochemical Processing, Handling and Storage of Bio-Oils***,** poster presentation, tcbiomass 2019
- M. P. Brady, D. N. Leonard, J. R. Keiser, L. Whitmer, *Performance of Structural Materials in Biomass Liquefaction Environments*, TAPPI PEERS 2019 proceeding (Oct. 2019).
- M.P. Brady, D.N. Leonard, J.R. Keiser, E Cakmak, L. Whitmer, *Degradation of Components After Exposure in a Biomass Pyrolysis System*, Corrosion, 75 (9), pp. 1136-1145 (2019)
- R. M. Connatser, M. G. Frith, J. Jun, S. A. Lewis Sr., M. P. Brady, and J. R. Keiser, *Approaches to investigate the role of chelation in the corrosivity of biomass-derived oils*, Biomass and Bioenergy 133, 105446 (2020).
- M. D. Kass, B. L. Armstrong, B. C. Kaul, R. M. Connatser, S. Lewis, J. R. Keiser, J. Jun, G. Warrington, and D. Sulejmanovic, Stability, *Combustion, and Compatibility of High-Viscosity Heavy Fuel Oil Blends with a Fast Pyrolysis Bio-Oil*, Energy & Fuels 34(7), 8403 (2020).
- M. D. Kass, S. A. Lewis, Sr., R. M. Connatser, C. J. Janke, and J. R. Keiser, *Elastomer Compatibility with a Pyrolysis-Derived Bio-Oil (Paper No. 2020-14613)",* NACE CORROSION 2020, physical event cancelled (June 2020).
- J. Jun, M. G. Frith, R. M. Connatser, J. R. Keiser, M. P. Brady, and S. Lewis, Sr., *Corrosion Susceptibility of Cr-Mo Steels and Ferritic Stainless Steels in Biomass Derived Pyrolysis Oil Constituents*, Energy & Fuels 34(5), 6220 (2020).

Presentations

- J. Jun, J. R. Keiser, M. D. Kass, C. Janke, *Compatibility of Polymeric and Metallic Materials in Fossil Fuel, Bio-Oil and Their Blends*, Oral presentation, TAPPI PEERS 2020 (Nov. 2020).
- J. Jun, D. Sulejmanovic, J. R. Keiser, M. P. Brady and M. D. Kass, *EIS-Based Evaluation of Corrosion-Resistant Structural Steels in HAHM Biomass Pyrolysis Oil*, Oral presentation, TCS 2020 meeting (Oct. 2020).
- J. Jun, D. Sulejmanovic, J. R. Keiser, M. P. Brady and M. D. Kass, *Corrosion Behavior of Structural Stainless Steels in LALM Biomass Pyrolysis Oil*, Oral presentation, ACS Fall meeting 2020 (Aug. 2020).
- J. Jun, R. M. Connatser, J. R. Keiser, M. P. Brady, and S. Lewis, *Corrosion of Cr-Mo Alloyed Steels and Stainless Steels in Selected Organic Constituents of Biomass Derived Pyrolysis Oils*, Poster presentation, tcbiomass 2019, Rosemount, IL (Oct. 2019).
- M. D. Kass, C. J. Janke, R. M Connatser, S. A. Lewis, and J. R. Keiser, *Compatibility of Fast-Pyrolysis Bio-oil with Infrastructure Elastomer Materials*, Poster presentation, tcbiomass 2019, Rosemount, IL (Oct. 2019)
- D. Sulejmanovic, J. Jun, G. Warrington, and J. R. Keiser, *Analysis of corrosive compounds and corrosion studies in bio-oils*, Oral presentation, TCS 2020 meeting (Oct. 2020).
- D. Sulejmanovic, J. Jun, and J. R. Keiser, *Corrosion product analysis on the surface of bio-oil-exposed alloys*, Oral presentation, ACS Fall meeting 2020 (Aug. 2020).
- James R. Keiser, Michael P. Brady, Donovan R. Leonard, Ercan Cakmak, Lysle E. Whitmer, and Richard J. French, *High-Temperature Corrosion in Biomass Pyrolysis System Components*, Oral presentation, TCS 2020 meeting (Oct. 2020).
- J. R. Keiser, G. Warrington, J. Jun, D. Sulejmanovic, M. Brady, and M. Kass, *Long-Term Corrosion Studies Of Pine Derived Bio-Oil And Blends With Heavy Fuel Oil,* Oral presentation, TAPPI PEERS 2020 (Nov. 2020).
- J. R. Keiser, M. Brady, J. Jun, M. Kass, J. Qu, D. Sulejmanovic, G. Warrington, R. M. Connatser, and S. Lewis, *Oak Ridge National Laboratory's Support To BETO On Materials Degradation/Corrosion*, Oral presentation, ABLC 2020 (June 2020)
- J. R. Keiser, M. Brady, R. M. Connatser, J. Jun, M. Kass, S. Lewis, and G. Warrington, *Oak Ridge National laboratory Studies To Identify Corrosion Resistant Materials For Bio-Oil Production*, Processing And Storage, Oral presentation, ABLC NEXT 2019 (Nov. 2019)

Roles of Participants

- Mike Brady – characterization of degraded metallic samples, alloy development and coking studies
- Xin He – wear, erosion, fouling of components
- Dan Howe and PNNL coworkers – solid phase processing techniques
- Chris Janke – nonmetallic corrosion
- Jay Jun – low temperature corrosion and electrochemical impedance spectroscopy
- Mike Kass – nonmetallic corrosion and neutron studies
- Jim Keiser – project leader and metallic corrosion and degradation
- Jun Qu – wear, erosion, fouling of components
- Dino Sulejmanovic – chemical characterization of bio-oils

Laboratory Study Of Bio-Oil – Heavy Fuel Oil Blends

Blending Of Bio-Oil With Heavy Fuel Oil Could Provide Several Benefits

- As produced pine-derived fast pyrolysis bio-oil is very acidic and rapidly corrodes carbon steel and other low alloy structural materials

- Heavy fuel oil is very viscous and requires heating in order to pump it

- Heavy fuel oil also contains sulfur which contributes to the production of greenhouse gases

- It was proposed that blending the two fuels would produce a mixture that was less corrosive and less viscous and would produce less greenhouse gases when combusted

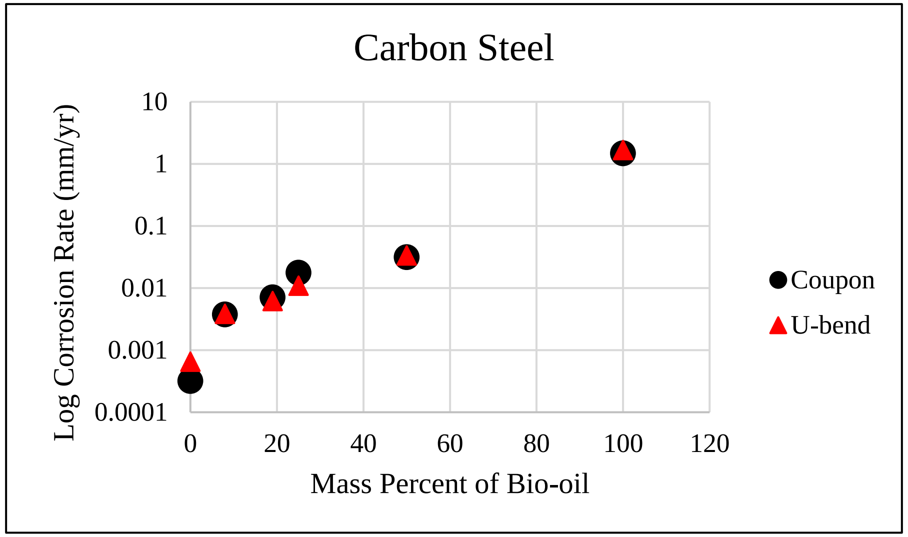
Corrosion Tests Were Conducted With The Pure Components And Four Blends

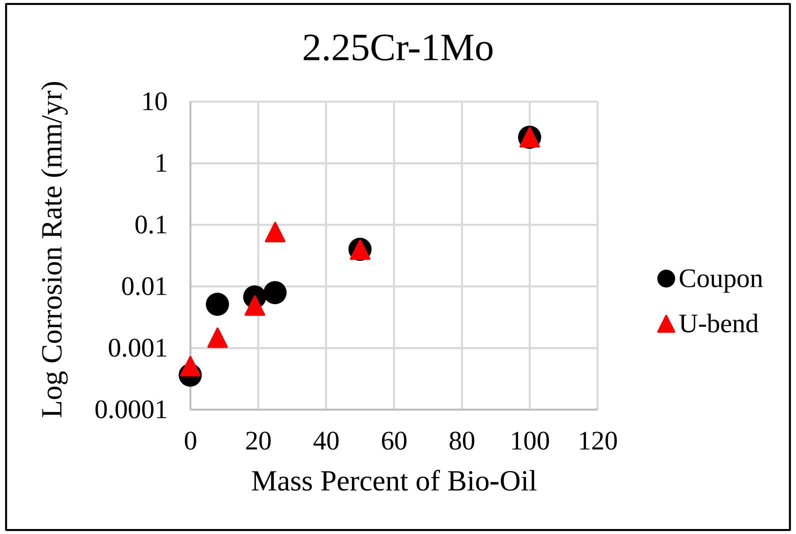
- Samples were exposed 1,000 h at 50°C
- Blends included 8%, 19%, 25% and 50% bio-oil in heavy fuel oil
- The acidity of all samples was determined using the aqueous extraction modification of the Total Acid Number (D-664) technique (AMTAN) and blends showed a significant reduction in acidity

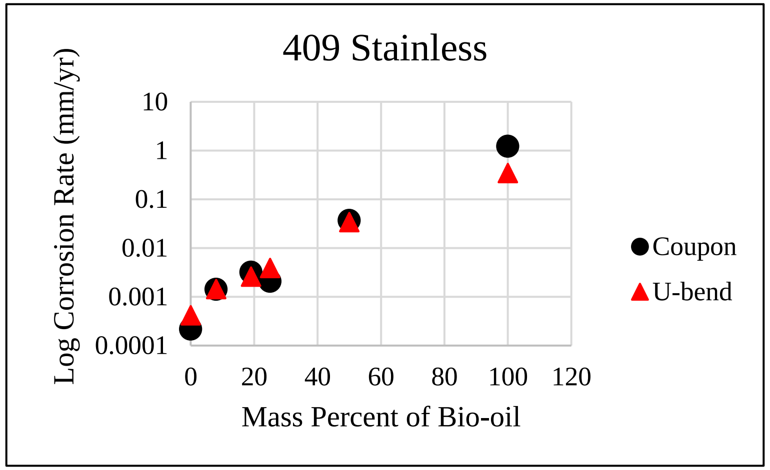
	100% bio-oil	50% bio-oil	25% bio-oil	19% bio-oil	8% bio-oil	100% HFO
AMTAN	112	35	18	13	3	2

- Similar reductions in viscosity were also found

Blending Bio-Oil And HFO Provided Large Improvements In Corrosion Rates Calculated From Weight Changes

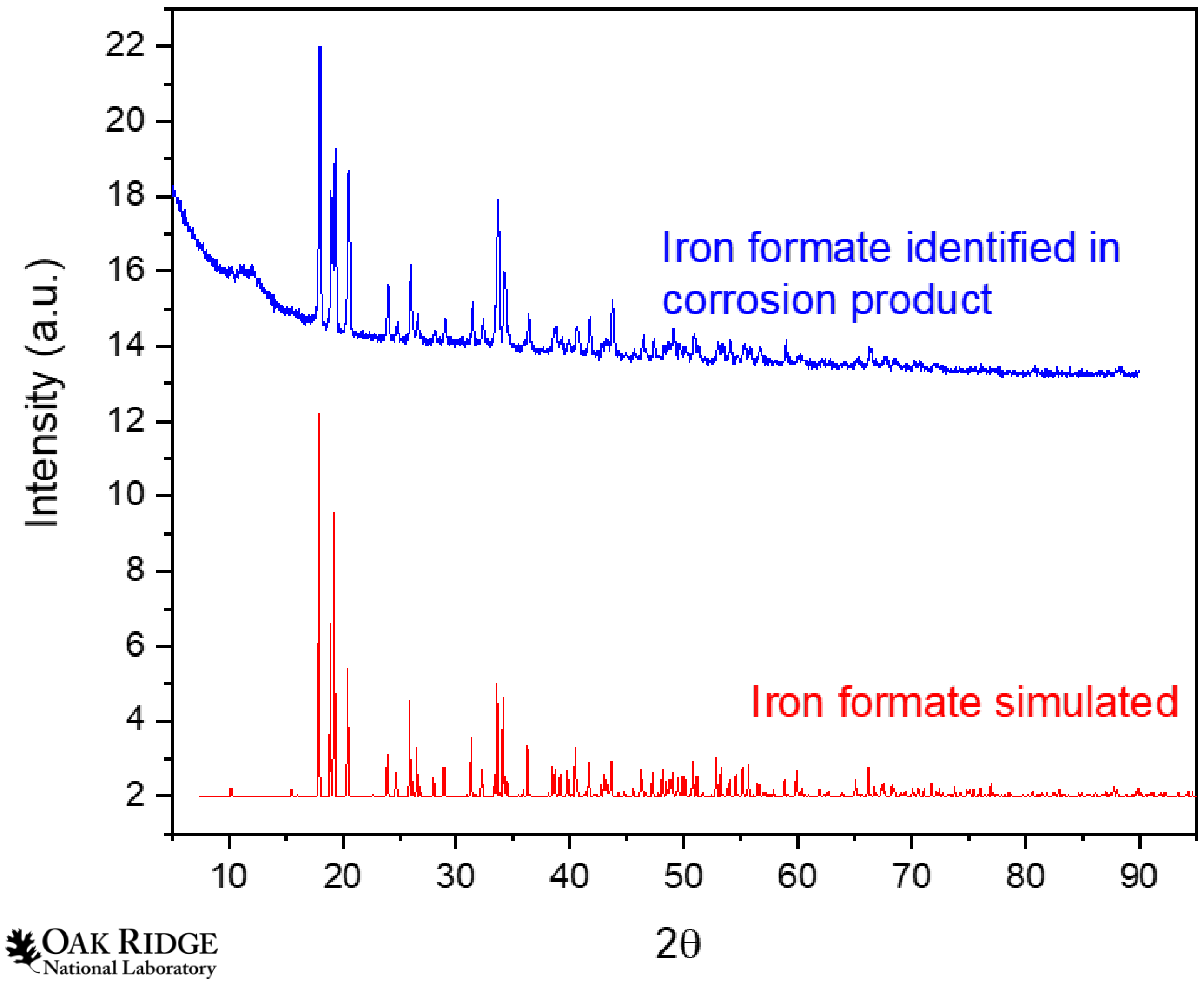




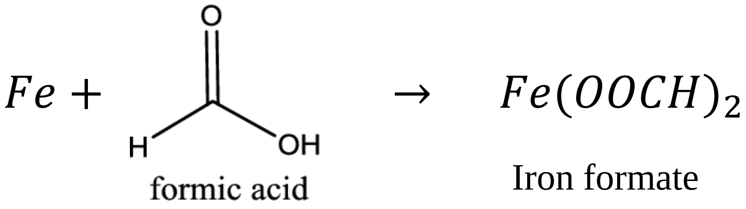


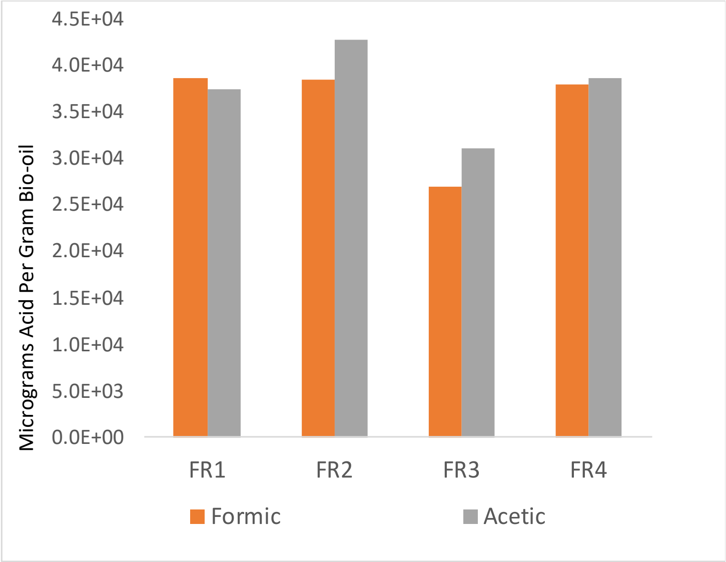
Note corrosion rate axis is a log scale

X-ray Diffraction Shows Formation Of Iron Formate Dihydrate As The Main Corrosion Product



Possible reaction pathway:



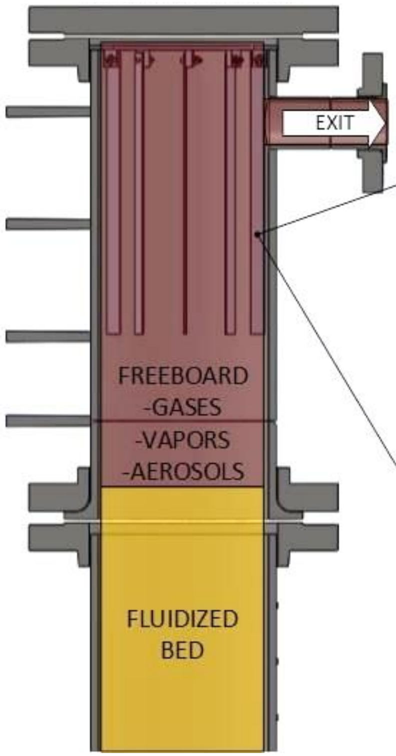


Concentration of formic and acetic acids in selected bio-oils provided by NREL

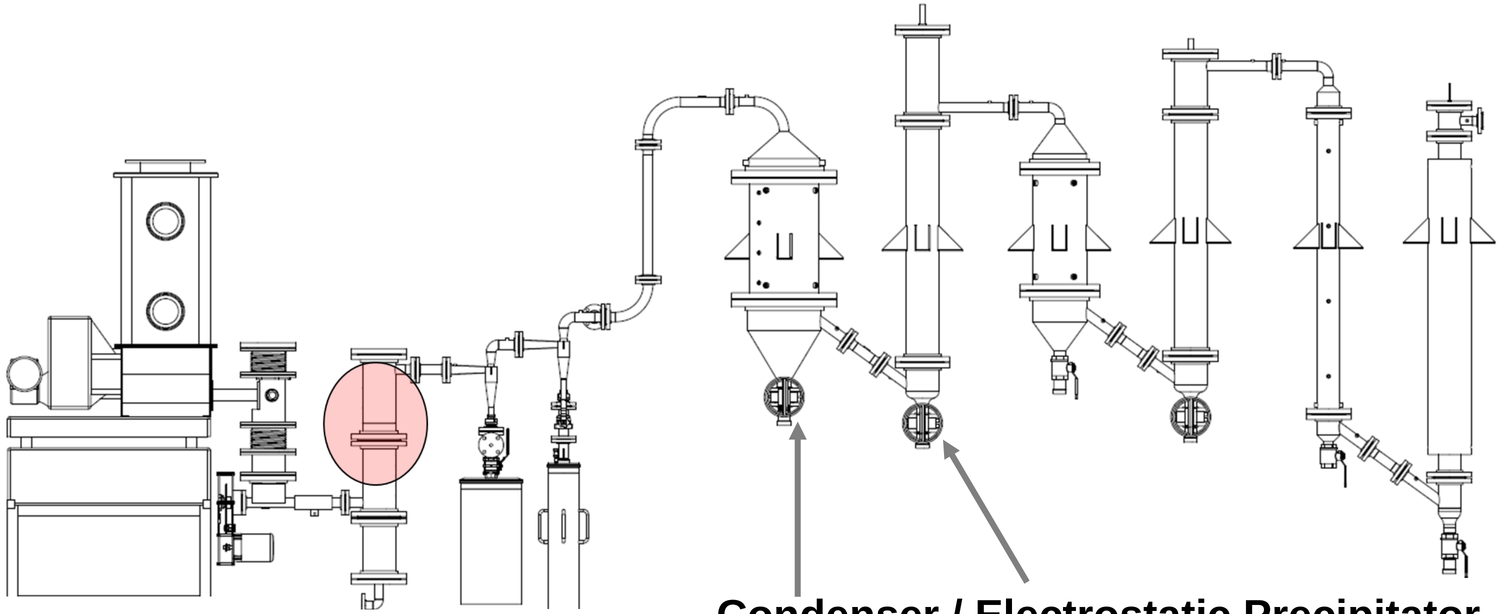
Examination Of Samples Exposed In ISU's Pyrolysis PDU

In-Situ Sample Exposures In The Reactor Freeboard In Iowa State's Pyrolysis Process Development Unit (PPDU) Facility

Reactor



Alloy Test Samples (10" x 1/2" x 1/16")



Feed System **Reactor** **Cyclones** **Condenser / Electrostatic Precipitator**

- **Fast pyrolysis primarily run at ~500°C with Red Oak**
  - -multiple 6 h range runs from 350-550°C
  - -corn stover, pine, mixed softwoods, switchgrass, and corn starch also used

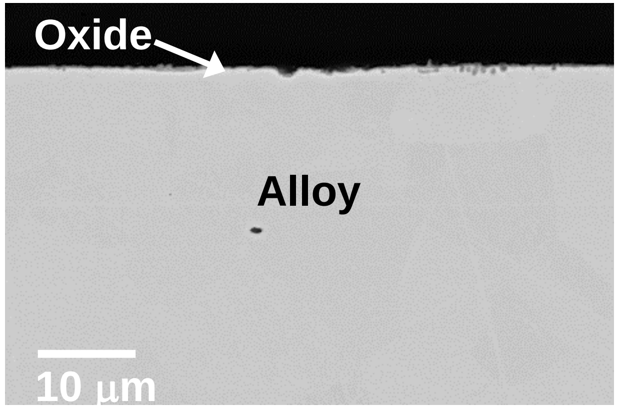
- **Section test samples at bottom (nearest fluidized bed) and top of freeboard**

Fast Pyrolysis Far More Corrosive Than Air Oxidation

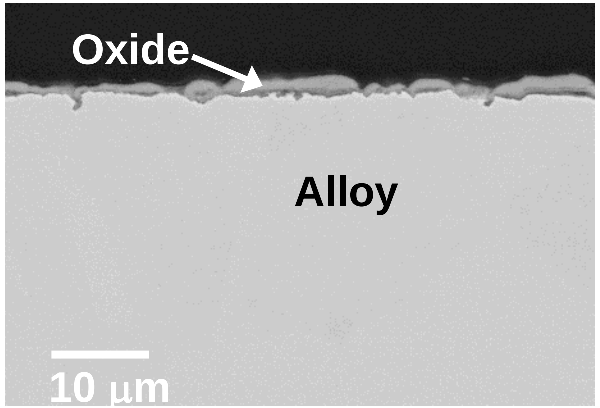
Cross-Section SEM Images of Test Sample Areas of Greatest Attack

Air, 550°C, 500 h

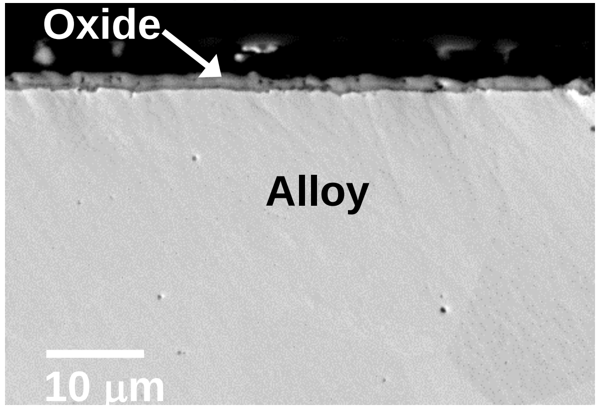
201 (high Mn, low Ni)



316L (base Cr, Mo, Ni)

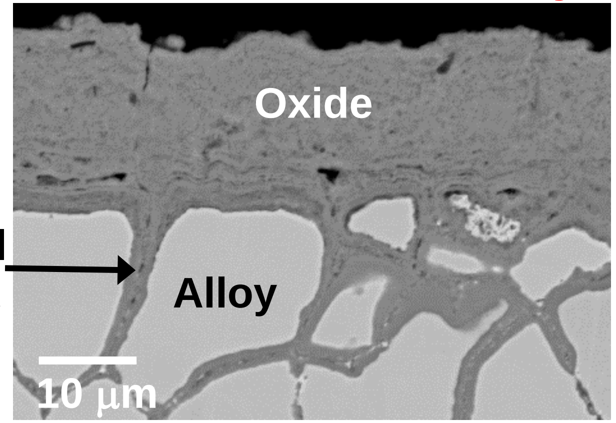


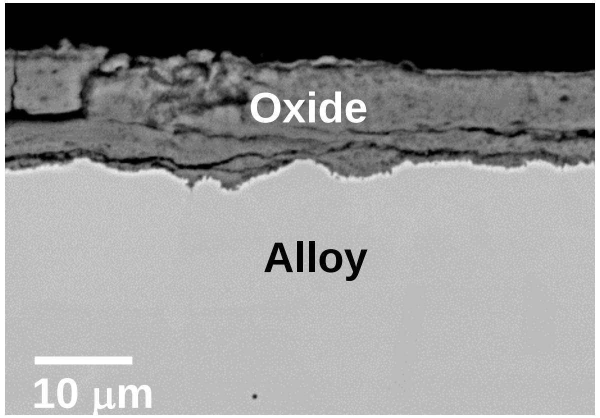
317L (high Cr, Mo, Ni)

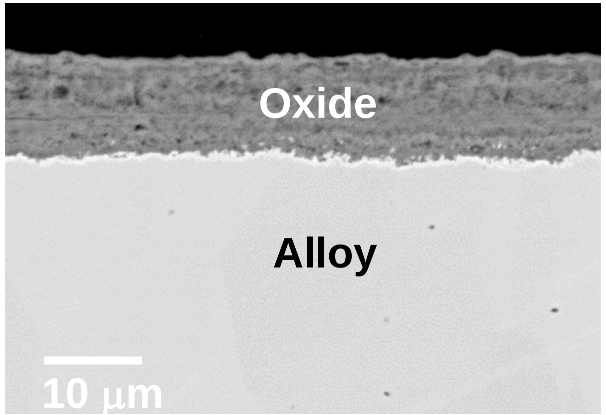


Pyrolysis, 500°C, 360 h, Bottom Location

Internal Attack



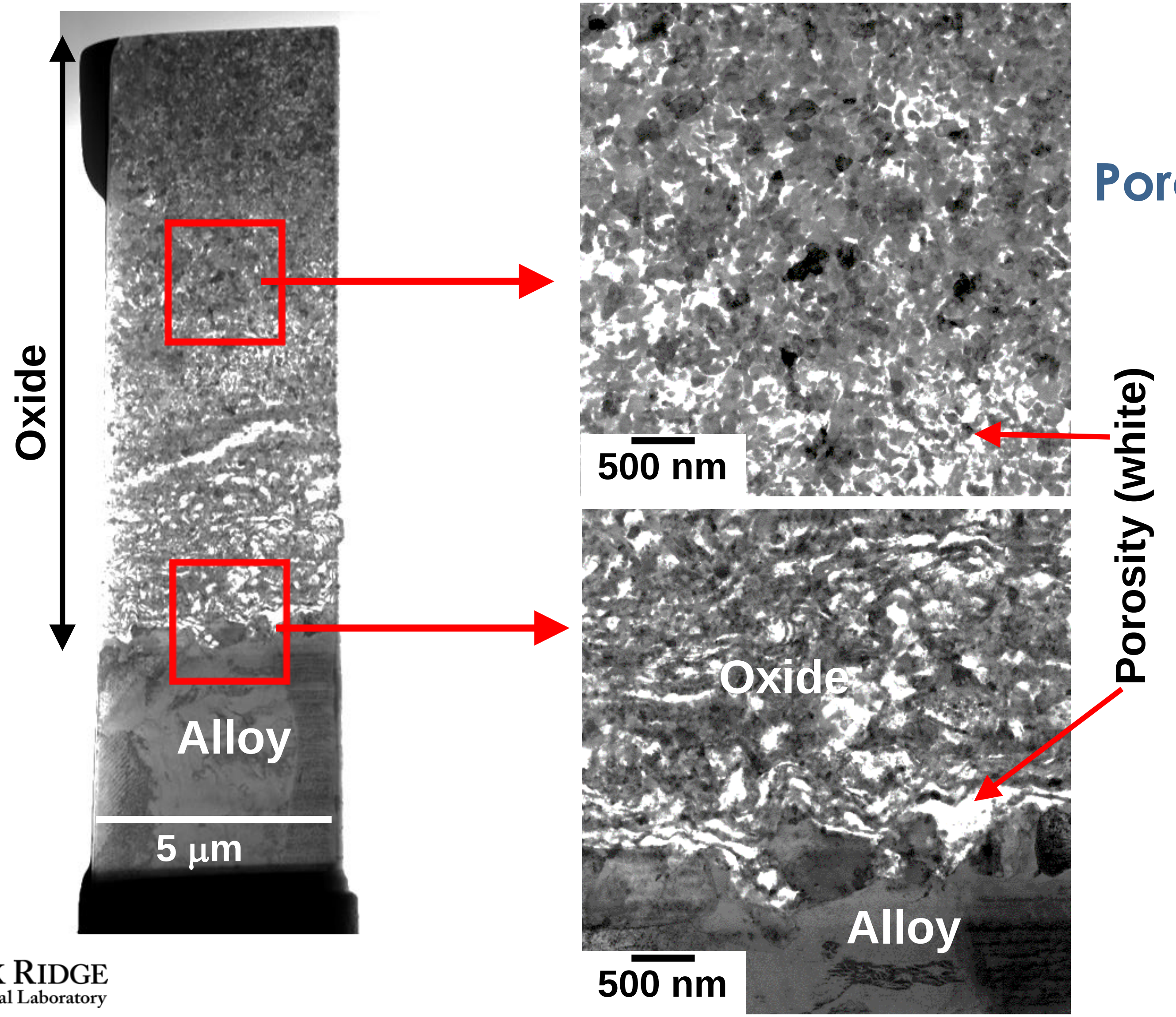




Oxide scales ≤ 1 micron thick in air vs > 10 microns thick in pyrolysis reactor

Porous, Nanocrystalline Oxide Formed on All Alloys

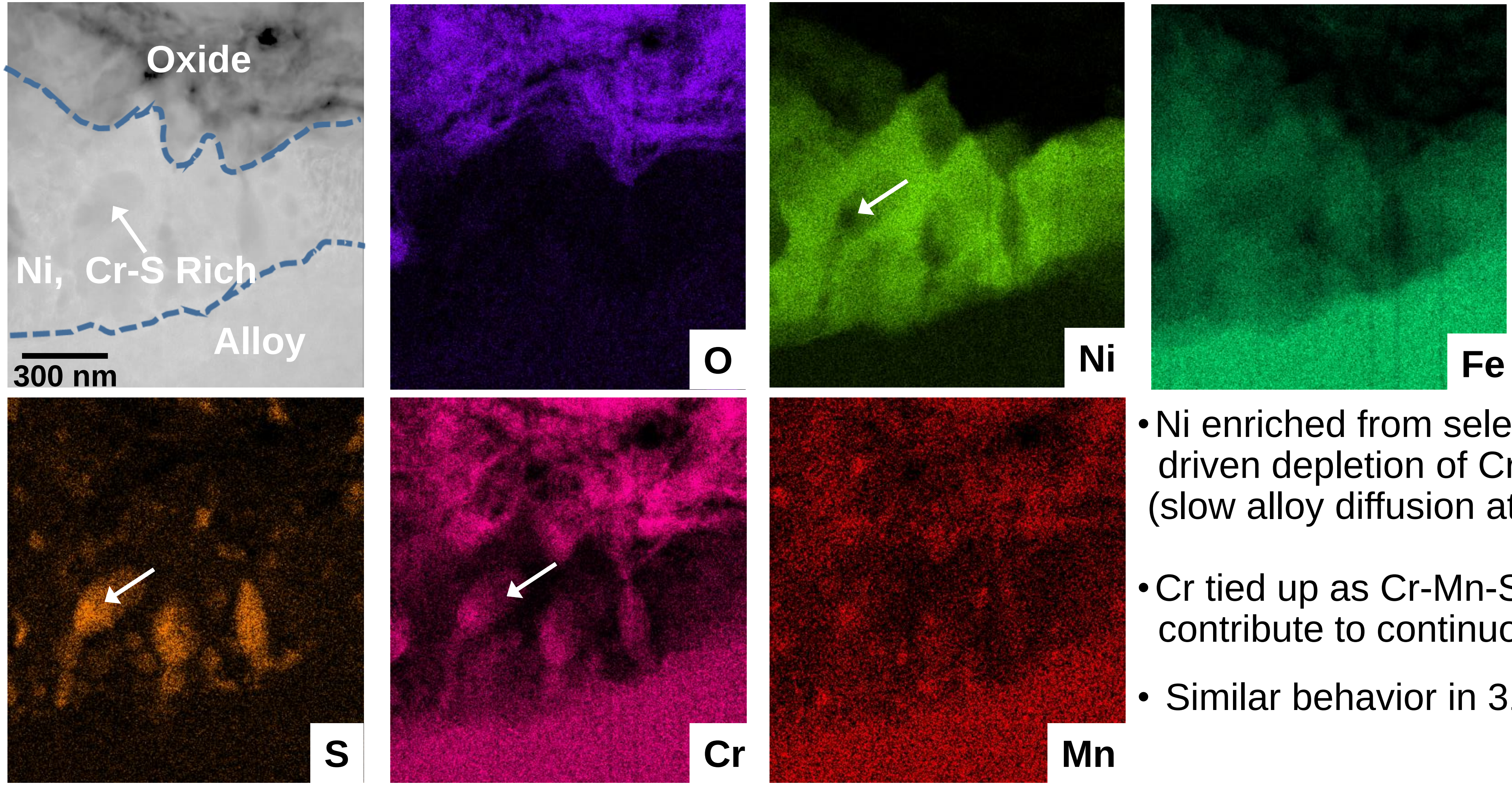
Cross-Section Scanning Transmission Electron Microscopy (STEM) Bright Field (BF) Images of 360 h 316L Bottom Pyrolysis Sample



Porosity Reduces Protectiveness of the Oxide Scale

Cr-Rich Sulfides Formed at the Alloy-Oxide Interface Make it Harder to Establish a Continuous, Protective Cr_2O_3 Scale

Cross-Section STEM HAADF Image and Elemental Maps of 277 h 316L Bottom Pyrolysis Sample



- Ni enriched from selective oxidation driven depletion of Cr, Fe, and Mn (slow alloy diffusion at 500°C)
- Cr tied up as Cr-Mn-S-O not able to contribute to continuous Cr_2O_3
- Similar behavior in 317L and 201

Production Of Hammers For Hammer Mill Simulations

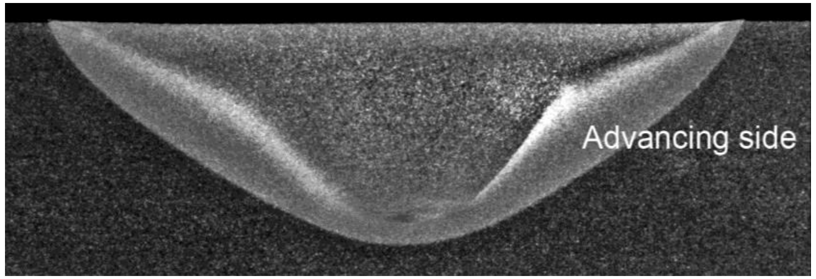
Approach to Production Of Candidate Hammers For Testing In INL Bench-Top Hammer Mill

Solid Phase PROCESSING

- For the 4 candidate materials set for hammer-mill, two alloy suggestions, 3rd would be a friction processed steel, and 4th would be the baseline existing steel hammer.
- Alloy Suggestions:
  - Martensitic SS 15-5 PH: 250-460 Hv, ~333 MPa-sqrt (m), ~9-10$/Kg (mid- grade hardness, v. high fracture toughness, but expensive)
  - AISI 4135 steel, Qnch-Tmp.: 140-693 Hv, ~80-135 MPa-sqrt(m), <1$/Kg (higher hardness, somewhat low fracture toughness, but cheap)
- Other candidates:
  - Aermet 100: 568-594 Hv, 100-150 MPa-sqrt(m), ~8.5-10$/Kg (good combination of mid-high hardness and fracture toughness, but expensive)
  - Iron base Cr-Ni A286: 287-803 Hv, 132-150 MPa-sqrt(m), ~8-8.50$/Kg (high hardness, mid-high toughness, but expensive)

PNNL Experience with FSW of ASTM 387 Gr91 Class 2 Steels from DOE-FE work

- Gr91 is easily FSW welded
- Defect free welds can be made at a wide range of process parameters
- Tool temperatures can be maintained during welding at any point from 780C to 980 C
- Travel speeds are comparable to SMAW but process is single pass

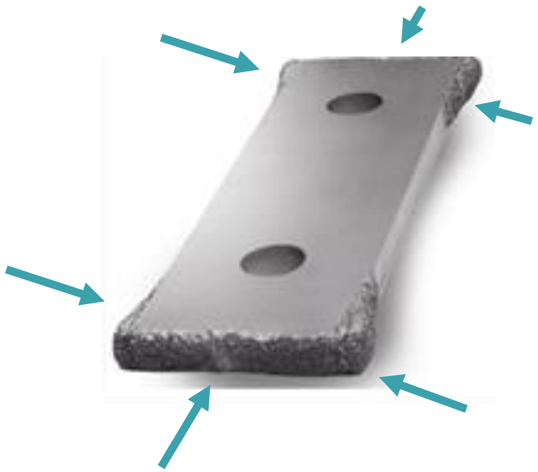


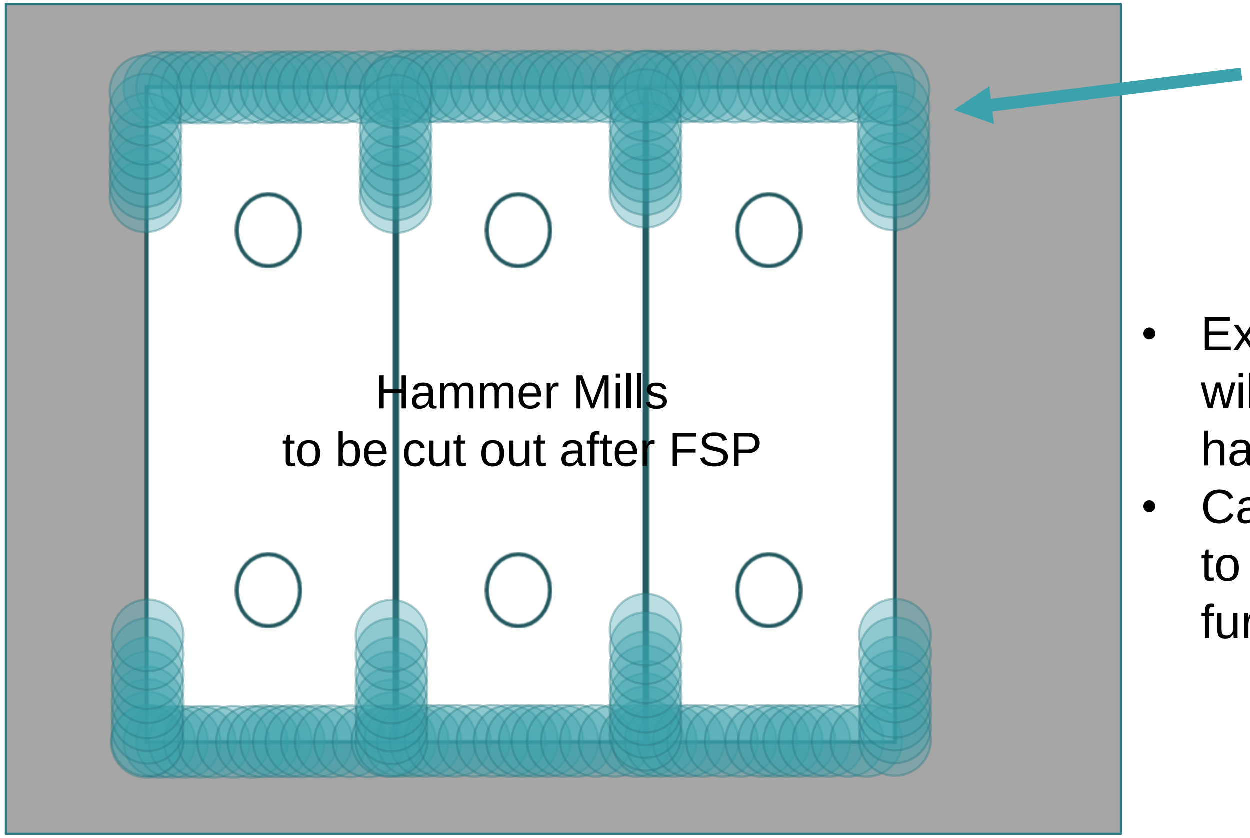
FSP Approach

Solid Phase PROCESSING

- FSP plate in critical contact areas prior to cutting hammer mill shapes out

Damaged edges





- Expect that FSP alone will create higher hardness tough region
- Can also add materials to increase hardness further if needed

Goal: Hardness increase at edges

- Side view of a hypothetical final part to show where hardness is increased

Half of nugget located at striking edge

- This approach would allow us to use previously developed FSP parameters and avoid application of FSP directly to small edges (would need new geometry tools, new parameter development, new experience).

Oak Ridge National Laboratory

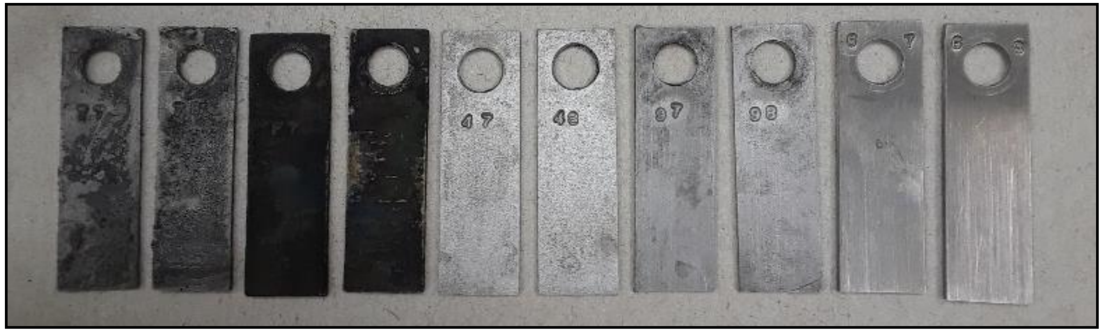
42

Long-Term, Room Temperature Corrosion Studies

Long-Term Exposure Studies Have Been Conducted

- Duplicate samples of 2¼ Cr-1 Mo, 7 Cr-1 Mo, 9 Cr-1 Mo, 409 SS and 316L SS were exposed in drums of four different liquids
- Exposures were conducted at room temperature in drums containing three different pine-derived bio-oils and one drum containing diesel fuel
- Two bio-oil exposures were for 12,480 h while the third bio-oil and the diesel fuel exposure were for 7,650 h
- Results reported are for one of the 12,480 h bio-oil exposures and the diesel fuel exposure for 7,650 h

Significant Corrosion Was Seen On Samples After 12,480 h In Bio-Oil



2¼ Cr-1 Mo 7 Cr-1 Mo 409 SS 9 Cr-1 Mo 316L SS

X-ray diffraction measurements identified phases on surface of corroded samples

	2¼ Cr-1 Mo steel (sample #1)	2¼ Cr-1 Mo steel (sample #2)	7 Cr-1 Mo steel (sample #1)	7 Cr-1 Mo steel (sample #2)
Material detected	Iron formate hydrate, iron	Iron formate hydrate, iron	Iron formate hydrate, iron	Iron

Weight Change Measurements Showed Negligible Loss By Samples Exposed In Diesel But Significant Losses In Bio-Oil

	2¼ Cr-1 Mo		7 Cr-1 Mo		9 Cr-1 Mo		409 stainless		316L stainless	
	mg lost	mm/y	mg lost	mm/y	mg lost	mm/y	mg lost	mm/y	mg lost	mm/y
Diesel	16	<0.01	<1	<0.01	<1	<0.01	<1	<0.01	<1	<0.01
Diesel	3	<0.01	<1	<0.01	<1	<0.01	<1	<0.01	<1	<0.01
FR3 oil	1,476	0.18	2,442	0.30	3,100	0.38	1,329	0.16	3	<0.01
FR3 oil	1,609	0.19	2,612	0.32	2,687	0.33	1,354	0.16	1	<0.01