DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Combustion/Materials Durability Relationships for Improved Low-Cost Clean Cookstoves

March 26, 2015

Technology Area: Cookstoves

M.P. Brady and T.J. Theiss, Co-Principal Investigators

Oak Ridge National Laboratory

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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Goal Statement

- 3 billion people worldwide use open fire/inefficient cookstoves
  - -4 million premature deaths/year from indoor cookstove smoke
  - -significant carbon black and other pollutant emissions with environmental consequences

- Low-cost, clean cookstoves are engineering challenge
  - -advanced modeling and design for clean combustion
  - -**combustors experience highly corrosive conditions**

- Virtually no cookstove relevant corrosion and materials selection guidance is available

This project 1) develops corrosion test methods, 2) generates corrosion data for wide range of alloys, 3) identifies alloy/coating paths for > 40% improved corrosion resistance

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Quad Chart Overview

Timeline

- Begin: Oct 1, 2013
- End: Sept 30, 2015
- 75% Percent complete

Budget

	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs ($k)	Total Planned Funding (FY 15-Project End Date ($k)
DOE Funded	0	0	278k	321k
Project Cost Share (Comp.)*	0	0	9k	9k

Barriers

- Barriers addressed
  - Corrosion data under cookstove relevant conditions not available
  - Cookstove relevant corrosion test methods not established
  - Alloy/coating candidates for cookstove combustor must be very low cost to permit widespread adoption

Partners

- Partners
  - **Colorado State University** (CSU) (subcontractor, 25%)
  - **Envirofit International** (cost share partner)
- Coatings for test from Stony Brook U. and NETL
- Input for relevant alloys from Burn Design Lab and BioLite Stove

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Project Overview- Metal Combustor Corrosion

Example Test Stove Combustion Chambers

Corrosion Resistant = Years of Use

Excessive Corrosion = Won't be Used

- Metal alloy combustors lightweight, robust, permit range of designs
- Challenging conditions → High temperature & burning biomass produces mixtures of corrosive H_2O, **salt**, ash, and sulfur species
- **Efficiency and emission benefits of clean cookstoves not realized if they fail after a few months of use**
- **Develop corrosion test methods, data, and mitigation strategies**

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Technical Approach

- Develop and compare in-situ cookstove and lab furnace corrosion test methods
  - Can lab furnace test yield relevant findings? (also compare with previous cookstove field exposures)

- Establish corrosion rates and mechanism(s) for candidate commercial alloys (publish data for access by all)
  - OEMs use findings to guide metal combustor alloy selection
  - OEMs use findings as basis for corrosion lifetime modeling

- Assess future alloy and coating directions for improved corrosion resistance
  - 40% reduced corrosion rate target
  - Cost is key design property criteria (varies with OEM, targeted use/region)

- Develop combustion model for insight into biomass fuel effects
  - Impacts temperature and corrosive species generated
  - Evaluate in light of sustainability indicators and relevant biomass

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Management Approach

- Critical Success Factors
  - -wide public dissemination of alloy corrosion test data for OEMs
  - -ID low-cost alloy/coating strategies to reduce corrosion
- Challenges
  - -Materials must be very low cost to permit widespread adoption
  - -How to simulate cookstove combustor environment in lab
- Teaming Strategy
  - -CSU and Envirofit have extensive field experience (permits us to compare lab corrosion to field-observed corrosion mechanisms)
  - -Envirofit has extensive cookstove commercialization experience (650,000 stoves in 45 countries): previously identified CSU-Envirofit-ORNL Combustor Alloy in Use (2014 patent)

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Barriers Addressed

- Lack of relevant corrosion data for candidate combustor alloys

- Tradeoff between cost, cookstove lifetimes, and improved operations
  - Lower emission/better efficiency designs → higher temperatures & more corrosion
  - Low cost materials corrode and fail → not used
  - High cost materials are not affordable → not used

- Cookstove OEMs typically have insufficient resources to identify or develop suitable cookstove combustor materials
  - Leverage extensive ORNL expertise in high-temperature energy system materials to select or design corrosion-resistant, low-cost alloys/coatings for improved cookstoves

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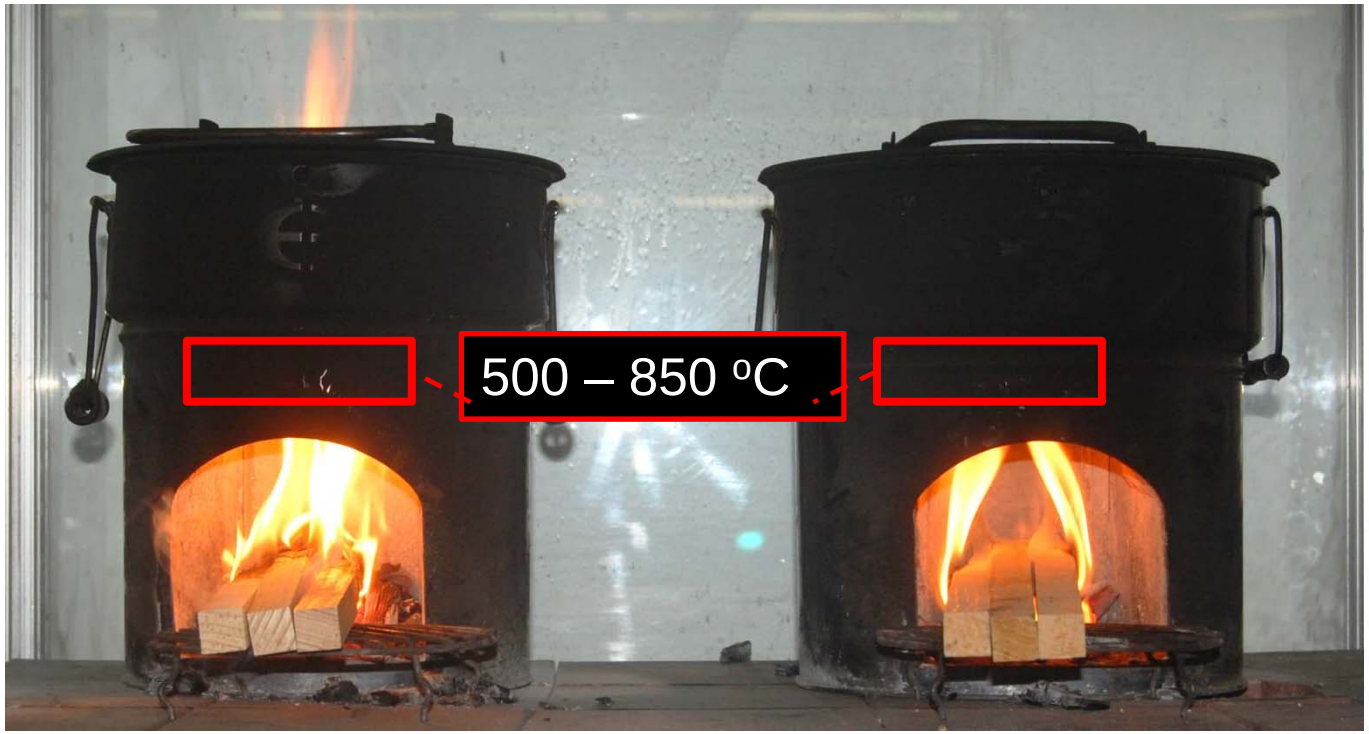
“Rough” Cookstove Lifetime Parameters

- 5 h usage per day → 10,000 h hot lifetime needed for ~5 years use
- 1000 h In-Situ Cookstove test → 10-20% of Desired Lifetime: enough to extrapolate for lifetime estimates of metal combustors (test samples both faces exposed to biomass corrosion, actual combustor 1-face only)
- Corrosion rates in biomass cookstoves VERY biomass fuel dependent



Evaluate multiple candidate alloys at high temperatures with <u>model salted wood</u>

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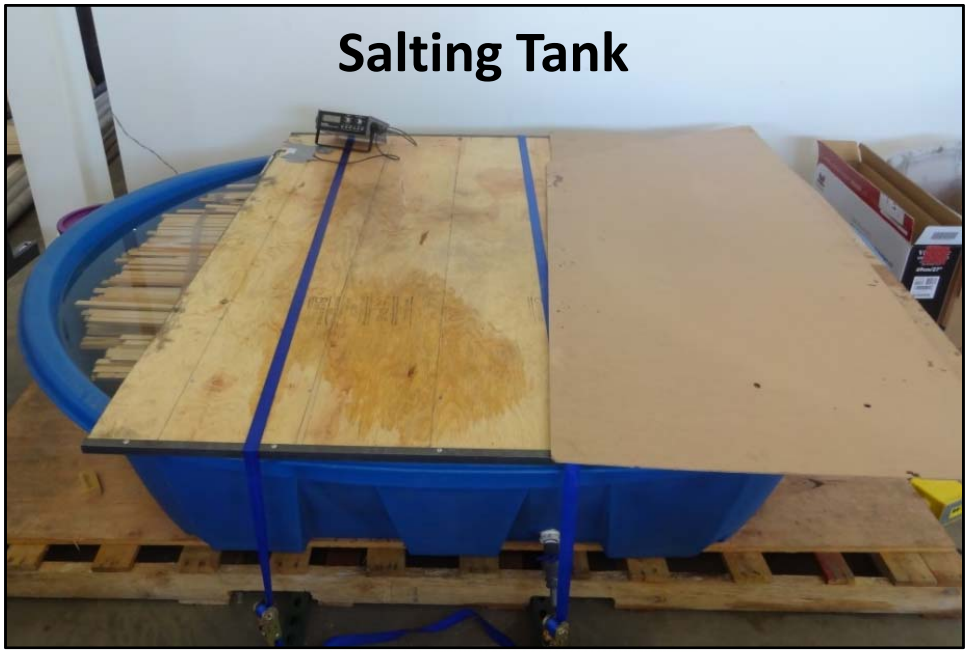
Cookstove Test: Burn Model Salted Wood to Promote Corrosiveness

- Soak Acacia wood trim in salt water
- 1000 μg/g salt level targeted based on analysis of field-encountered corrosive biomass



- Monitoring of approximate salt absorption by conductivity meter
- Salted wood dried for use in stove
- Batches analyzed for salt content to ensure repeatable and relevant results

Instant Ocean® Sea Salt

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Utilizing Two Corrosion Test Methods

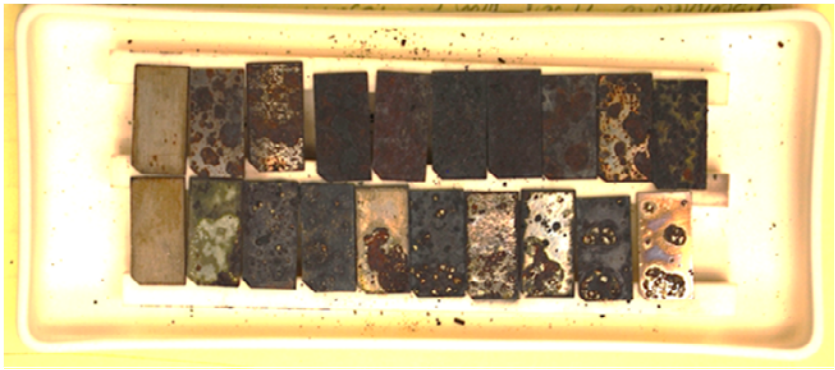
In-Situ Cookstove Test

Top View: Test Samples In Cookstove

- Better method but time intensive/costly
- Model salted wood to simulate corrosive biomass, ~600-650°C average temperature

Lab Furnace Test

Top View: Test Samples



Test Temp: 600 & 800°C,

10 vol.% H_2O, Salt

- Lab furnace test: cheaper/faster, sufficiently realistic?
- 100 h cycles, simulate biomass by add 10 vol. % H_2O, salt sample face every cycle

1000 h total: assess corrosion by sample mass change and sectioning

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Wide Range of Alloys/Coatings in Test
(Cr, Ni, Mo Drive Cost but Help Corrosion)

15 alloys and coatings under test. Alloys $1/lb to $10/lb Coatings cost TBD

- Austenitic Stainless Steels
  - 201: Fe-18Cr-7Mn-5Ni (0.6x cost 316L)
  - 316L: Fe-17Cr-10Ni-2Mo (~$2/lb range)
  - 310S: Fe-25Cr-20Ni (2x cost 316L)
- Ferritic Stainless and Related
  - 446: Fe-25Cr (comparable cost 316L)
  - FeCrAlY: Fe-20Cr-5Al-0.05Y (1.5-3x cost 316L)
- Fe-Cr-X model developmental alloys (X = Al, Si)
- Alumina-Forming Austenitics (AFA): Fe-14Cr-(12-25)Ni-(2.5-4)Al
  - ORNL developed, commercialization initiated, 1.5 – 5x cost 316L
- Coatings (evaluated on FeCrAlY)
  - Pre-oxidized to form Al_2O_3
  - CeO_2 washcoat developed by National Energy Technology Lab
  - Thermal spray ZrO_2 + cermets (with Stony Brook University)
- Claddings/Coatings: Pure Ni (evaluated as solid Ni piece)

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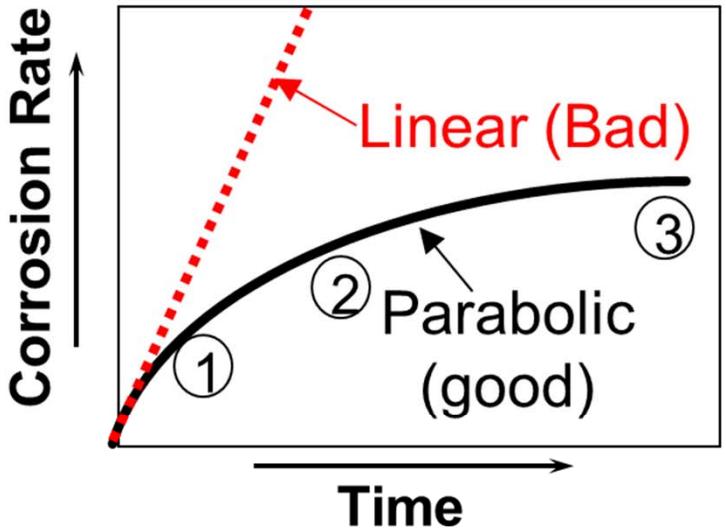
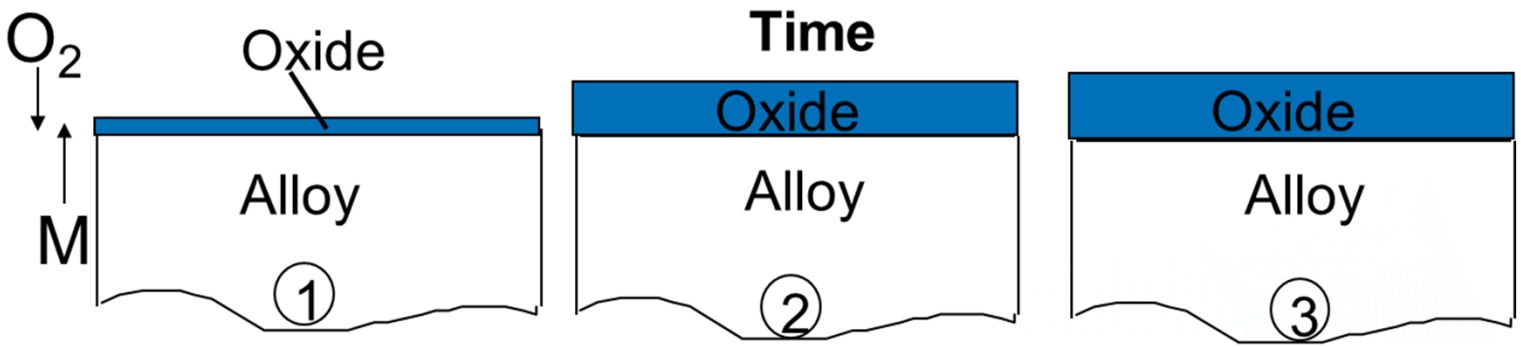
Manage High Temperature Corrosion by Forming Slow-Growing Oxide on Metal Alloy





- Corrosion can completely consume a metal component-can't stop corrosion, just manage it for intended lifetime
- Want diffusion-limited growth of dense, continuous, and adherent oxide layer: typically use Cr_2O_3 or Al_2O_3 above 600°C

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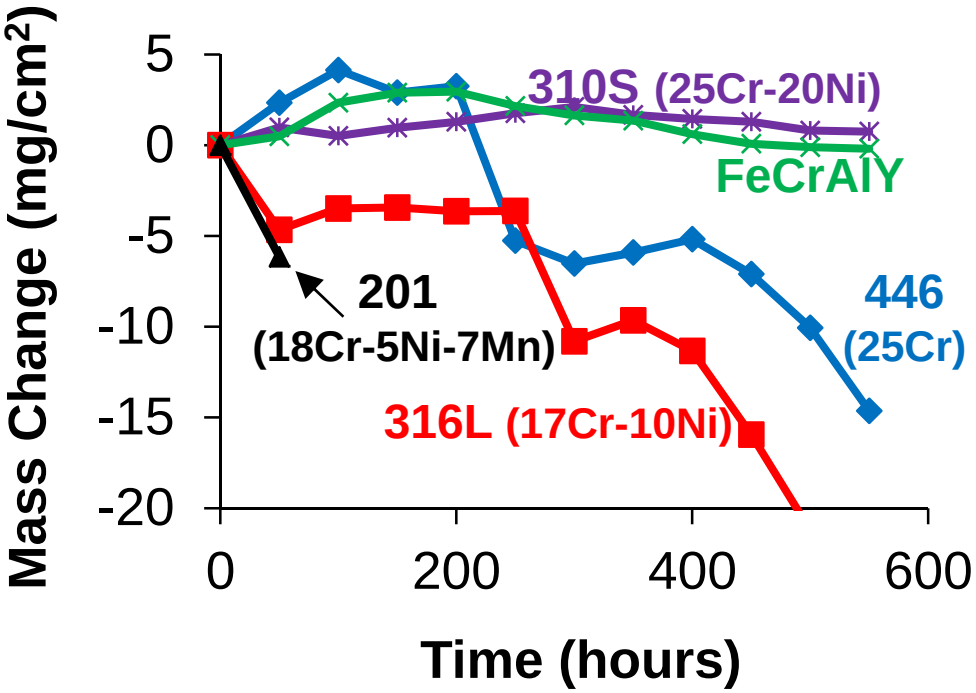
FeCrAlY and 310S Lowest Mass Change of Commercial Alloys From In-Situ Cookstove Testing

In-Situ Cookstove Test 500-850°C range, 600-650°C average



-High mass change = BAD

-Low mass change = MIGHT be good, cross-section to assess

- Significant mass loss (oxide scale flake off) for 201, 316L, and 446
  - -salted wood successfully yielding corrosive conditions
  - -samples running to 1000 h, duplicates pulled for sectioning at 100, 500,1000 h

- FeCrAl ± Y and 310S are benchmark, state-of-the-art alloys for cookstoves

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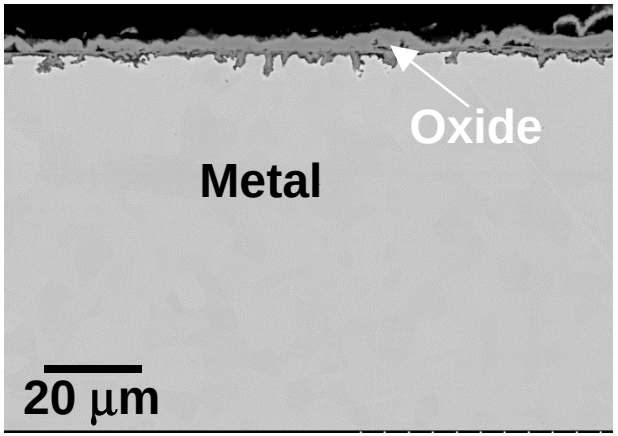
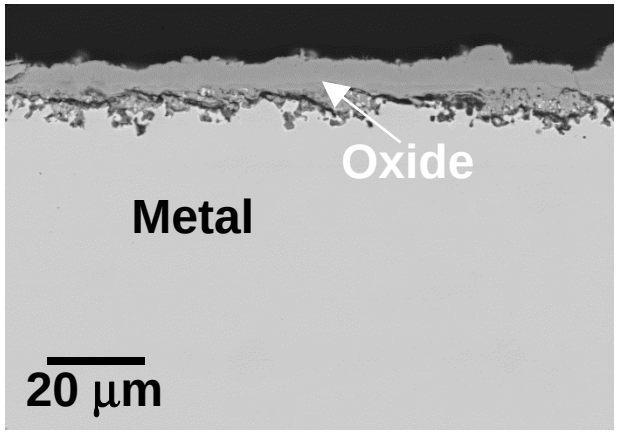
Lab Furnace & In-Situ Cookstove Tests Comparable (similar attack)

Electron Microscopy Cross-Sections of 316L (17Cr-10Ni) Stainless Steel

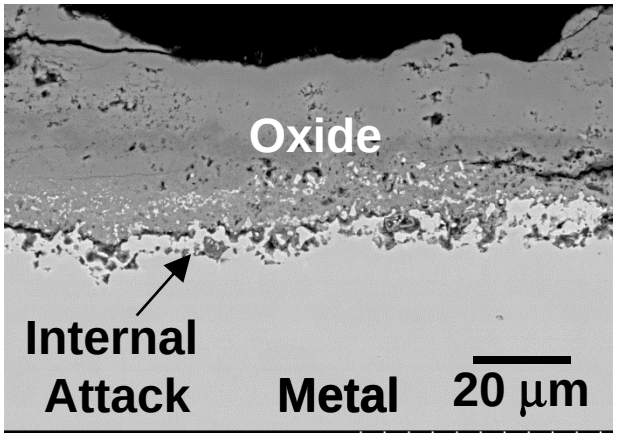
100 h 600°C Furnace Test



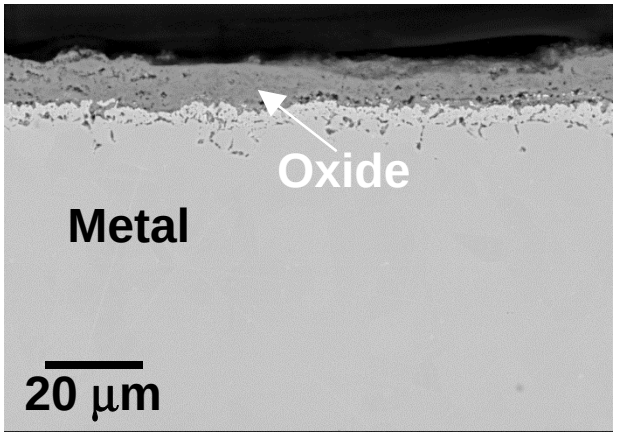
500 h 600°C Furnace Test



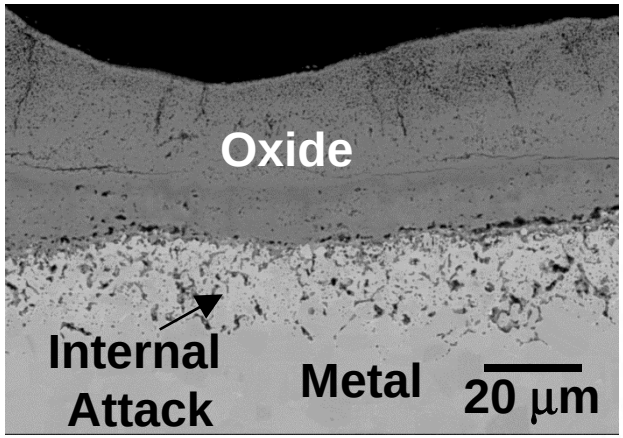
1000 h 600°C Furnace Test



100 h CookstoveTest



500 h CookstoveTest



- Corrosion features similar
- Corrosion rate higher in cookstove test than 600°C furnace test; 800°C test started
- Corrosion rates basis to estimate combustor lifetime

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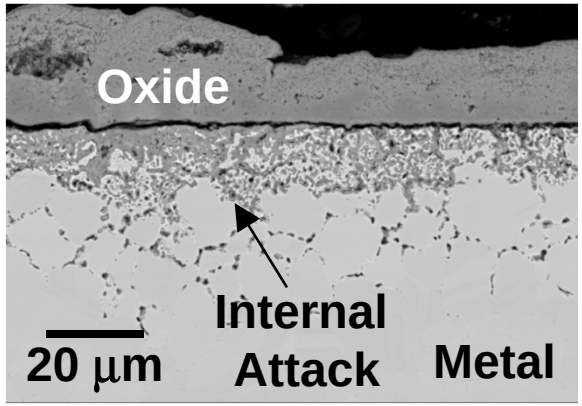
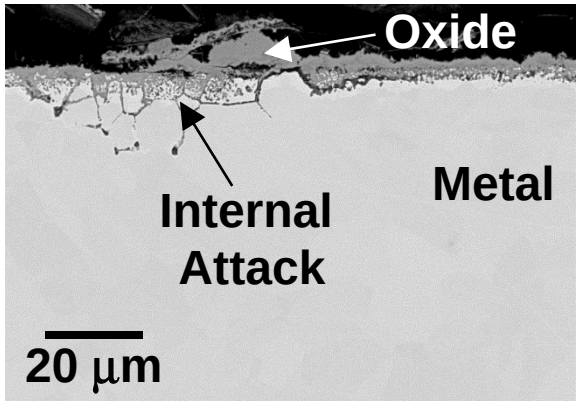
Similar Attack of 310 (20Ni-25Cr) Between CSU Cookstove Tests, ORNL 600°C Furnace, and Field-Tested Combustor Chamber Exposure

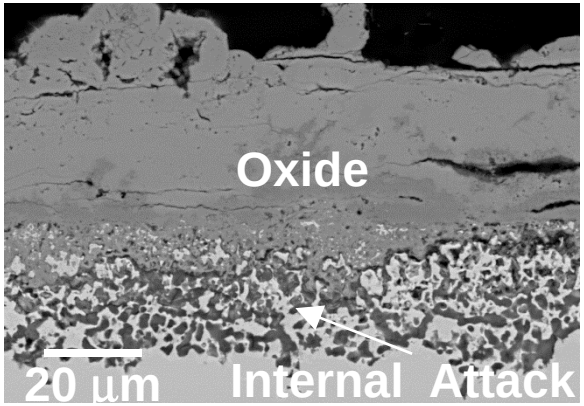
100 h In-Situ Cookstove



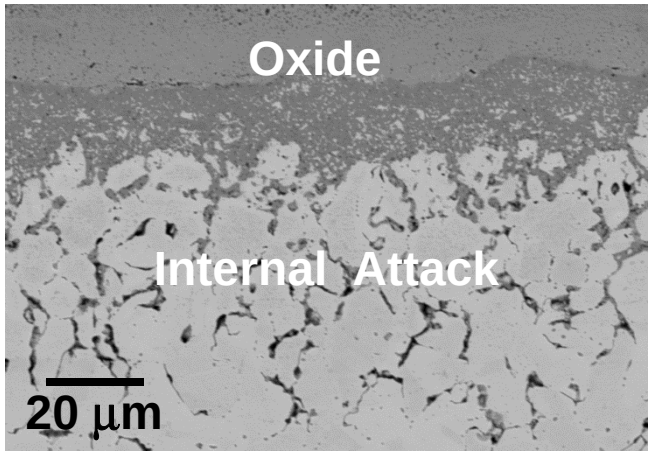
100 h 600°C Lab Furnace



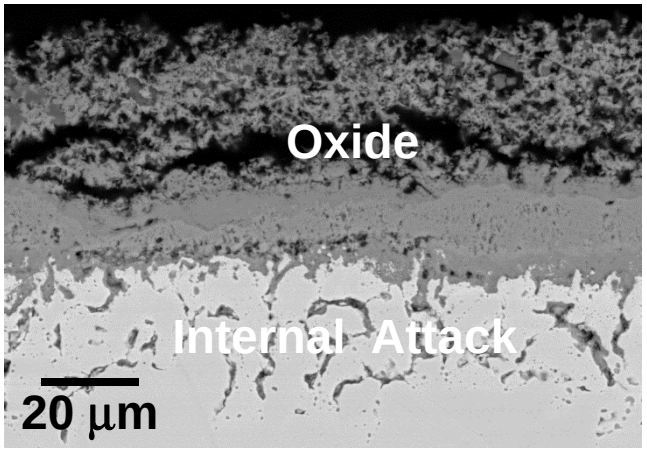
1000 h 600°C Lab Furnace



500 h In-Situ Cookstove

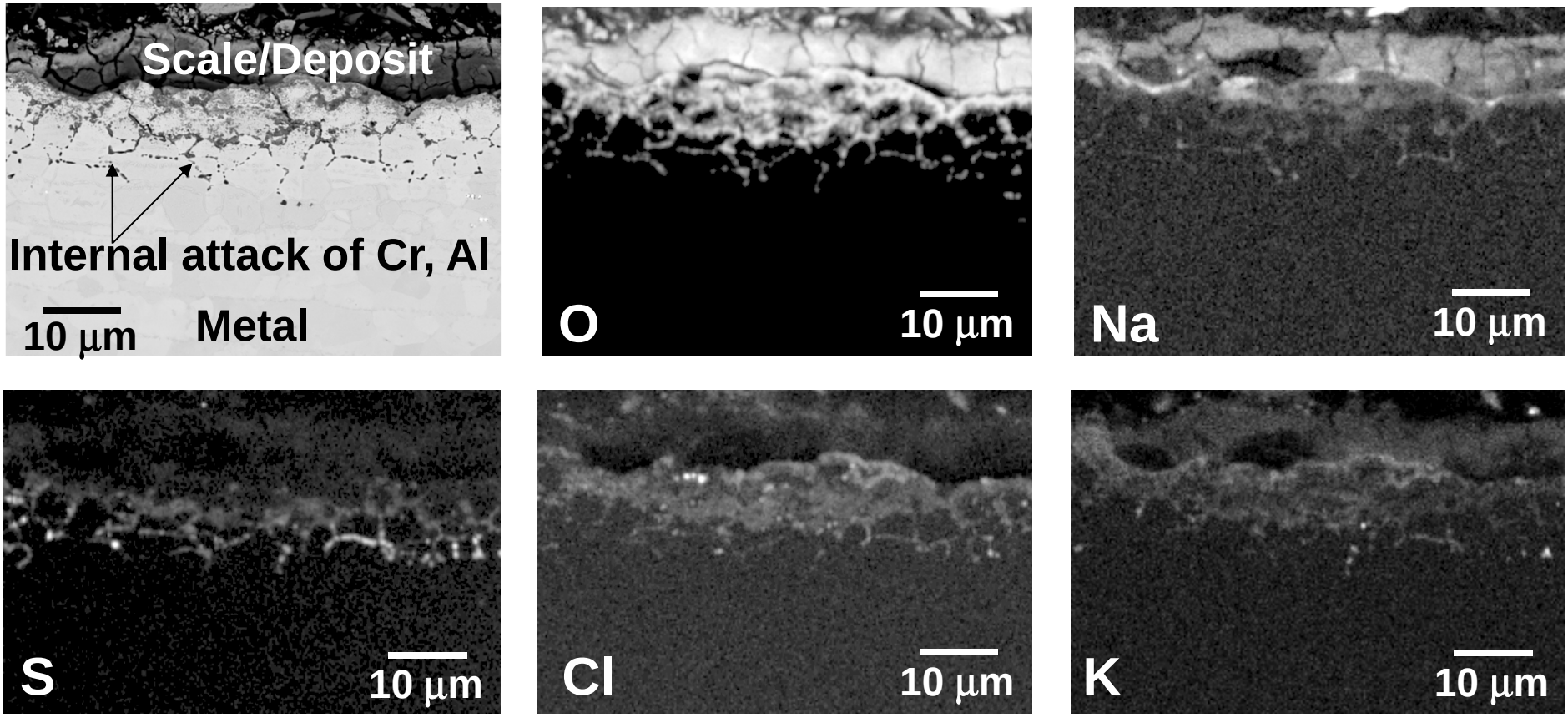


Field-Evaluated Test Chamber



Electron Microscopy/Elemental Mapping to Understand Corrosion Attack Mechanism

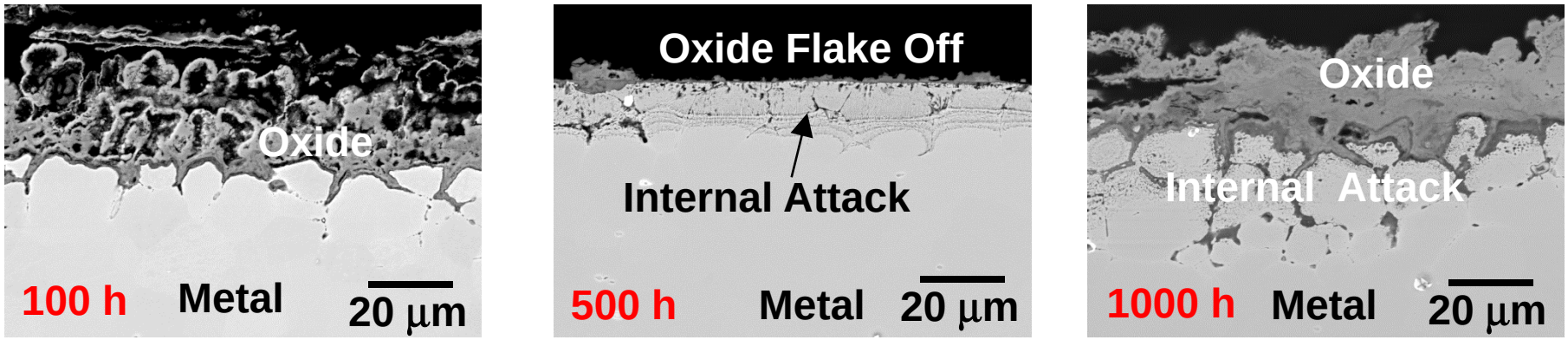
Cross-Section/Elemental Maps Show Multiple Species Attack of FeCrAl Type Metal Combustor After Field Use (prior analysis)



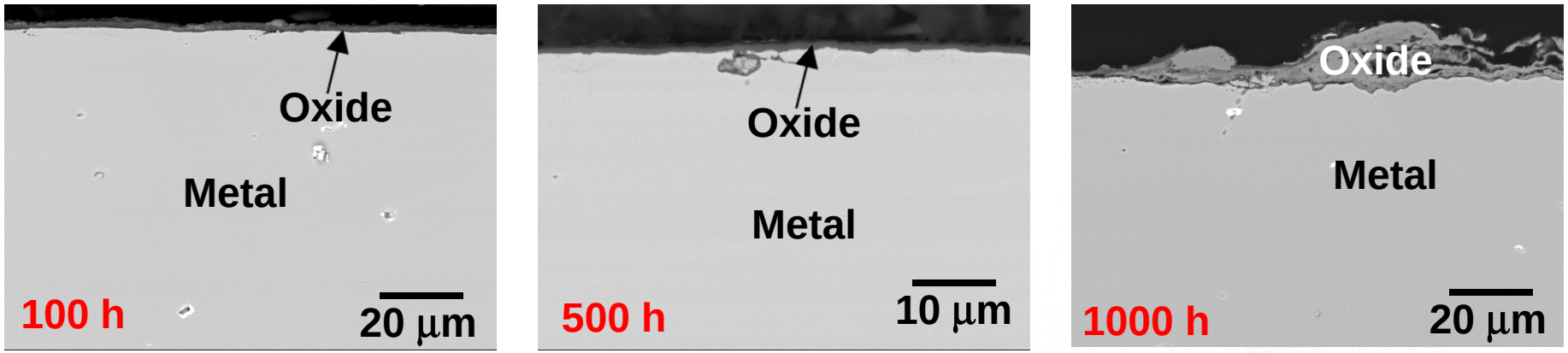
- Findings used to guide material selection or development for reduced corrosion
- Similar characterization in progress on in-situ cookstove and lab furnace samples

Pre-Oxidized FeCrAlY Shows Reduced Corrosion in 600°C Lab Furnace Test

Electron Microscopy Cross-Sections of FeCrAlY Alloy



Electron Microscopy Cross-Sections of Pre-Oxidized FeCrAlY Alloy



- Pre-oxidation forms protective 1-2 micron Al_2O_3 surface layer before salt attack
- Insights for attack mechanism and possible coating strategies
- Limited time/temperature effect before lose protection (commercially viable?)

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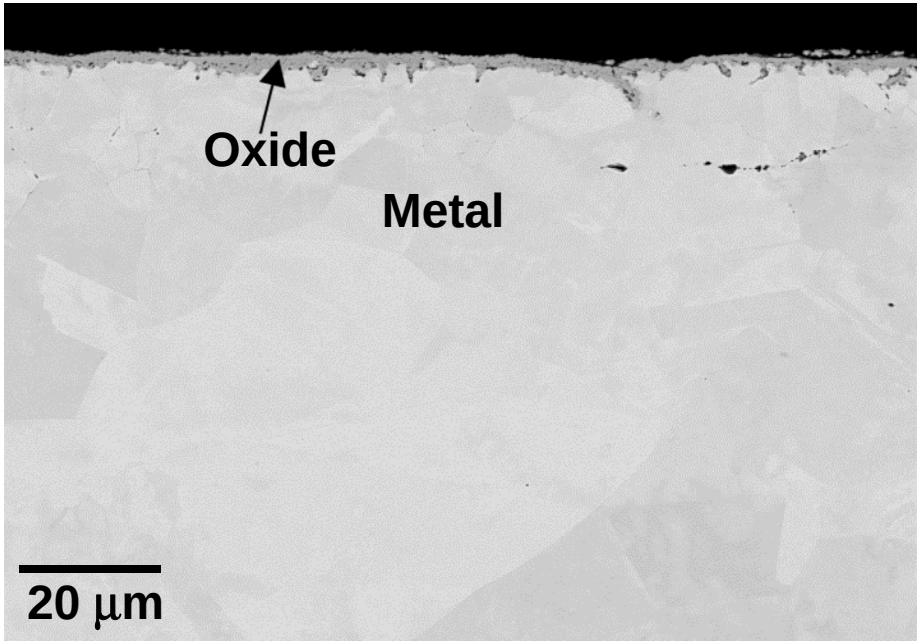
Pure Nickel Shows Outstanding Resistance to Salt in 600°C Lab Furnace Test

Electron Microscopy Cross-Section of 500 h Pure Nickel



Test Sample Surface Pictures

- Ni oxidation may be too fast > 700°C+ (800°C test in progress, ok thus far)
- In-situ cookstove test started: good early results (concern is Ni susceptible to sulfur species attack, S level varies with biomass source)
- Ni costly but may be of interest as clad/coat if continues to show promise

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Ongoing Plans For Corrosion Testing

- Complete 1000 h in-situ cookstove test data with model control salted wood

- Complete 1000 h lab furnace testing at 800°C (600°C already completed)
  - up to ~15 alloys/coatings under study (cross-section and analyze)

- Too early to give definitive feedback on which alloys/coatings doing best (showed only a portion of results to date)
  - hints that pure Ni may resist salt attack well
  - internal attack + flaking oxide for many alloys → both mass change and cross-section analysis to properly assess corrosion

- Anticipate submission of open literature publication(s) on corrosion findings by Sept 2015.

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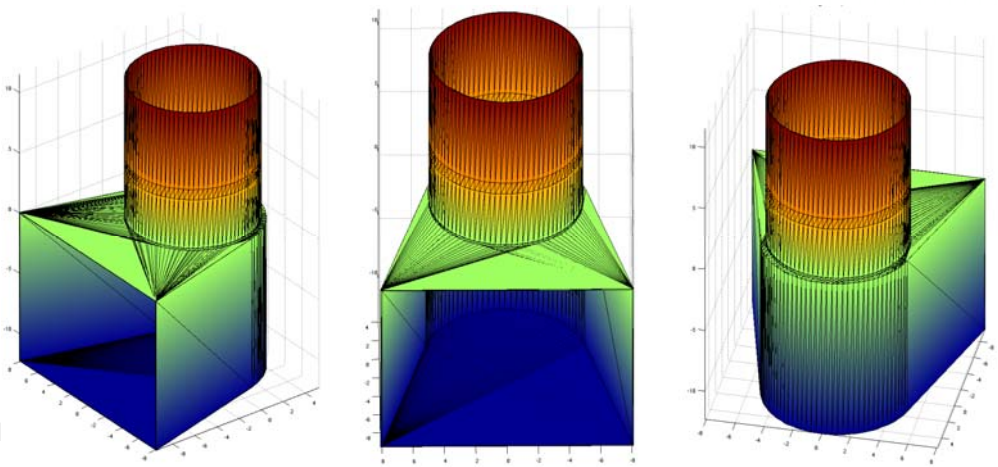
Predictive Computational Model of Biomass Combustion to Support Corrosion Studies

- Objectives
  - Evaluate combustion performance of multiple biomass fuel chemistries
  - Provide insight for cookstove combustion chamber environment
  - Model temperatures and chemistries (key corrosion variables)
- Approach
  - Envirofit G-3300 rocket-type cook stove as model test bed
  - Leverage available experimental and temperature data

Computational Domain of Simplified Combustion Chamber Geometry: Colors represent vertical location, not temperature.



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Implementation in Progress

- Framework: **MFIX** (**M**ultiphase **F**low with **I**nterphase e**X**changes), open-source, DOE-sponsored code initially developed for coal gasification starting in the late 1980s
  - Solves continuity, momentum and energy equations with programmable chemistry coupling on a structured grid (cut-cell Cartesian available)
  - Radiative heat transport treatment can be traditional view-factor approach or discrete ordinate method with participating media
- Chemistry: gas-phase combustion of biomass gasification products, inclusion of solids pyrolysis leveraging on-going Computational Pyrolysis Consortium in late implementations
  - Output: thermochemical profile in stove, particularly in chimney; flame front not resolved
- End product: publicly available simulation setup to assess how biomass fuel impacts temperatures and corrosive species

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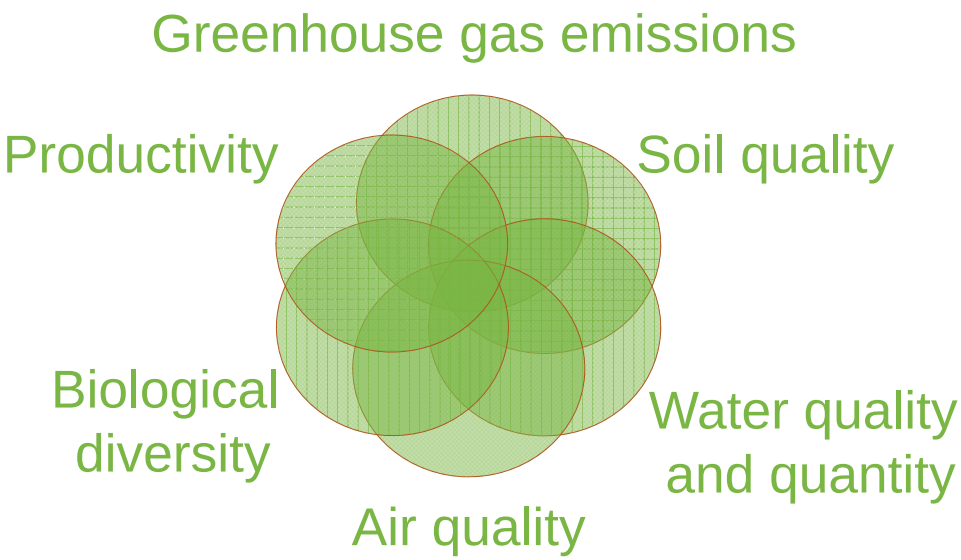
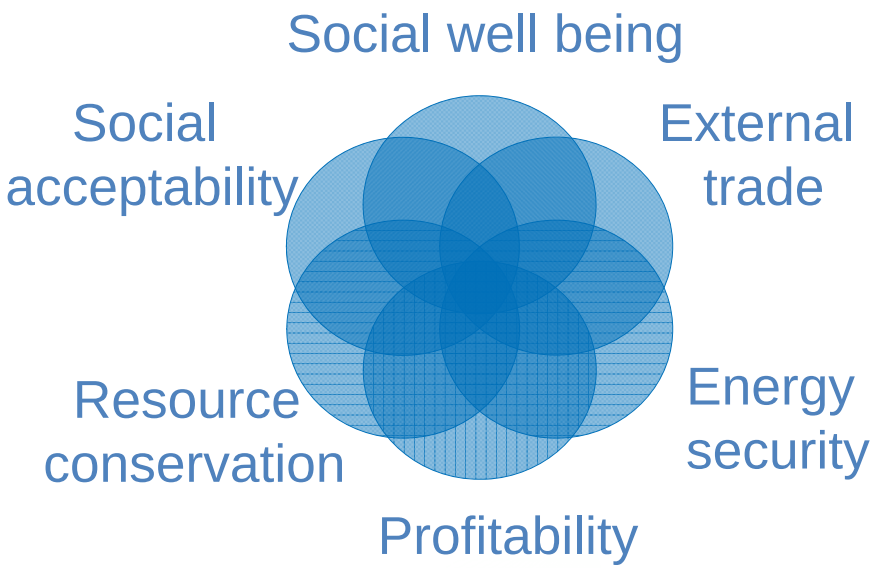
Examining Sustainability Criteria Developed for Bioenergy for Application to Cookstoves



McBride et al. (2011)
Ecological Indicators
11:1277-1289



Dale et al. (2013)
Ecological Indicators
26:87-102.

Small support task: qualitative assessment of potential to extend this approach to improved cookstoves (ICS) and assessment of biomass cookstove fuels

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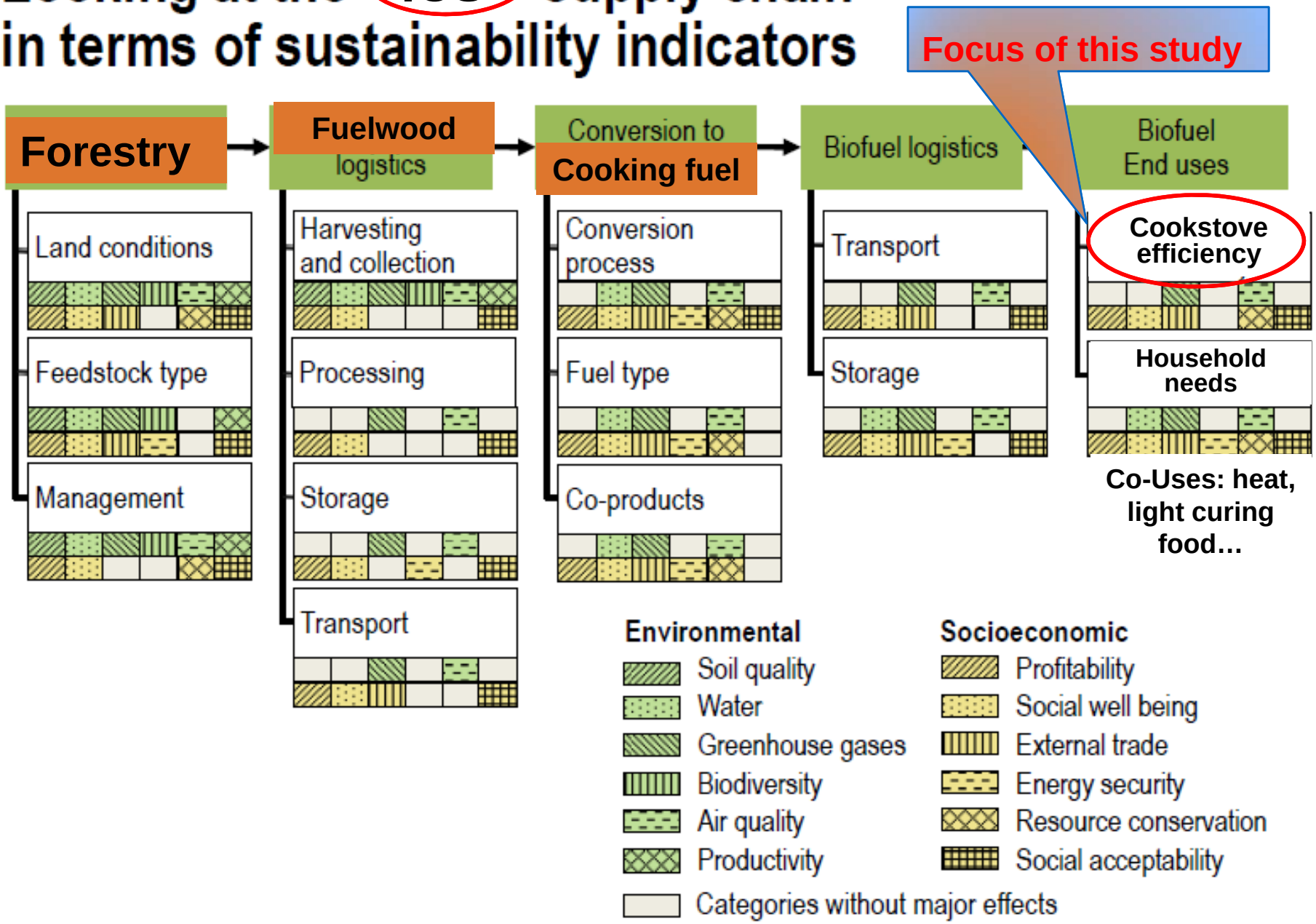
Looking at the ICS supply chain in terms of sustainability indicators



Continued Examples of Criteria and Indicators Applied to Improved Cookstoves

Category	Indicator	Units	Score
Environment	**Indicator**	**Units**	
Greenhouse gases	12. CO_2 equivalent emissions (CO_2 and N_2O)	kgC_{eq}/GJ	
Air quality	15. Tropospheric ozone	ppb	
	16. Carbon monoxide	ppm	
	17. Total particulate matter less than 2.5µm diameter ($PM_{2.5}$)	$\mu g/m^3$	
	18. Total particulate matter less than 10µm diameter (PM_{10})	$\mu g/m^3$	

Positive Impact
Positive or Negative
Negative Impact

Public data from field trials on improved cookstoves considered to complete "red-yellow-green" sustainability appraisal

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Examples of Criteria and Indicators Applied to Improved Cookstoves

Category	Indicator	Units	Score
Social well-being	Employment	Number of full time equivalent (FTE) jobs	
	Household income	Dollars per day	
	Work days lost due to injury	Average number of work days lost per	
Resource conservation	Depletion of non-renewable energy resources	MT (amount of petroleum extracted per year)	
	Fossil Energy Return on Investment (fossil EROI)	MJ (ratio of amount of fossil energy inputs to amount of useful energy outputt	

Positive Impact
Positive or Negative
Negative Impact

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Relevance

Envirofit G-3300 Wood-Burning Cookstove

-Envirofit-CSU-ORNL 2012 FLC Tech. Transfer Award
-2014 CSU-Envirofit-ORNL Patent

- 2007-2011 ORNL Interaction with Envirofit and CSU led to identification and specification of low-cost, corrosion-resistant metal combustor alloy
  - -now utilized across multiple Envirofit cookstove platforms: ~650,000 stoves sold
- Current project will publish corrosion test methods, data, and mitigation approaches to achieve next generation cookstove combustor materials
  - -better corrosion resistance → higher-temps./increased efficiencies/less emission
  - -better corrosion resistance → more corrosive fuels for wider cookstove usage

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Future Work

- Project ends Sept 2015

- Key Milestone is open publication of corrosion findings
  - -1000 h in-situ cookstove test, 1000 h lab test (600°C, 800°C)
  - -15 commercial and developmental alloys/coatings assessed

- Complete supporting combustion model to predict biomass fuel temperature and species. Complete assessment of sustainability indicator approach to clean cookstoves.

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Summary: Multi-Pronged Project Focused on Metal Combustor Corrosion

- ✓ Developing corrosion test methods relevant for improved cookstoves
- ✓ Evaluating commercial, developmental, and model alloys and coatings for corrosion resistance
- ✓ Developing combustion model to aide assessment of biomass fuels for temperature and chemical species effects relevant to corrosion
- ✓ Assessing potential for DOE developed sustainability indicators to be applied to clean cookstoves

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Additional Slides

Acknowledgements

[1]Mike Brady, [2]Kelly Banta, [2]John Mizia, [1]Charles Finney, [1]Keith Kline, [2]A. Lelek, [2]Morgan DeFoort, [3]Nathan Lorenz, [1]Jim Keiser, and [1]Tim Theiss

1. Oak Ridge National Laboratory, Oak Ridge, TN
2. Engines and Energy Conversion Lab, Colorado State University
3. Envirofit International, Inc., Fort Collins, Colorado

Responses to Previous Reviewers' Comments

- Project started FY14, not previously reviewed
- Go/No-Go Decision Points

-FY14: combustion modeling approach modified from lumped-zone steady-state model to a high-dimensional numerical implementation to permit greater focus on the biomass pyrolysis, combustion and radiative heat-transfer models and leverage efforts of the Computational Pyrolysis Consortium for cookstoves

-FY15: Additional developmental alloys and coatings were added to the corrosion test matrix based on assessment of corrosion resistance of the initial alloy and coating test set after 500 h lab testing. Goal is to identify path to > 40% reduction in corrosion rate

Publications, Patents, Presentations, Awards, and Commercialization

- "Corrosion Considerations for Metallic Combustors in Low-Cost, Clean Biomass Cookstoves", presented at ETHOS 2015, January 24-25, 2015, Kirkland, WA USA
- "Combustion Materials Durability Relationships for Improved Low-Cost Clean Cookstoves", presented at DOE BETO Cookstove Program Review, January 23, 2015, Seattle, WA USA
- Journal paper submission(s) planned for Sept 2015
- Past Collaboration with Envirofit-CSU-ORNL (before current DOE project) led to 2012 FLC Tech. Transfer Award and Joint CSU-Envirofit-ORNL Patent (US 8,899,222 B2, Cook stove assembly, Dec. 2, 2014. 650,000 stoves sold by Envirofit.

1000 μg/g Target Wood Salt Level Based on Highly Corrosive Haitian Charcoal

- Measurement - Total halogen content: $\frac{\mu g \text{ halogen}}{g \text{ fuel}}$
- Ideal test fuel same halogen content as known highly corrosive fuel: e.g. Haitian charcoals (many fuels have high halogen levels)
- Target wood salt value: ~ 1000 μg/g

Charcoal Stove Fuel Grate (2 Mos. Use)

Haitian Briquette Charcoal 1390 μg/g Salt

Haitian Mangrove Lump Charcoal 760 μg/g Salt

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Exposure in Cookstoves

- Before burning, coupons are cleaned, measured, weighed, and photographed.
- Every 50 hours, coupons are removed then weighed and photographed to track progress
- 2 stoves, 15 coupons per stove

Coupons in Fixture

Fixture in Stove

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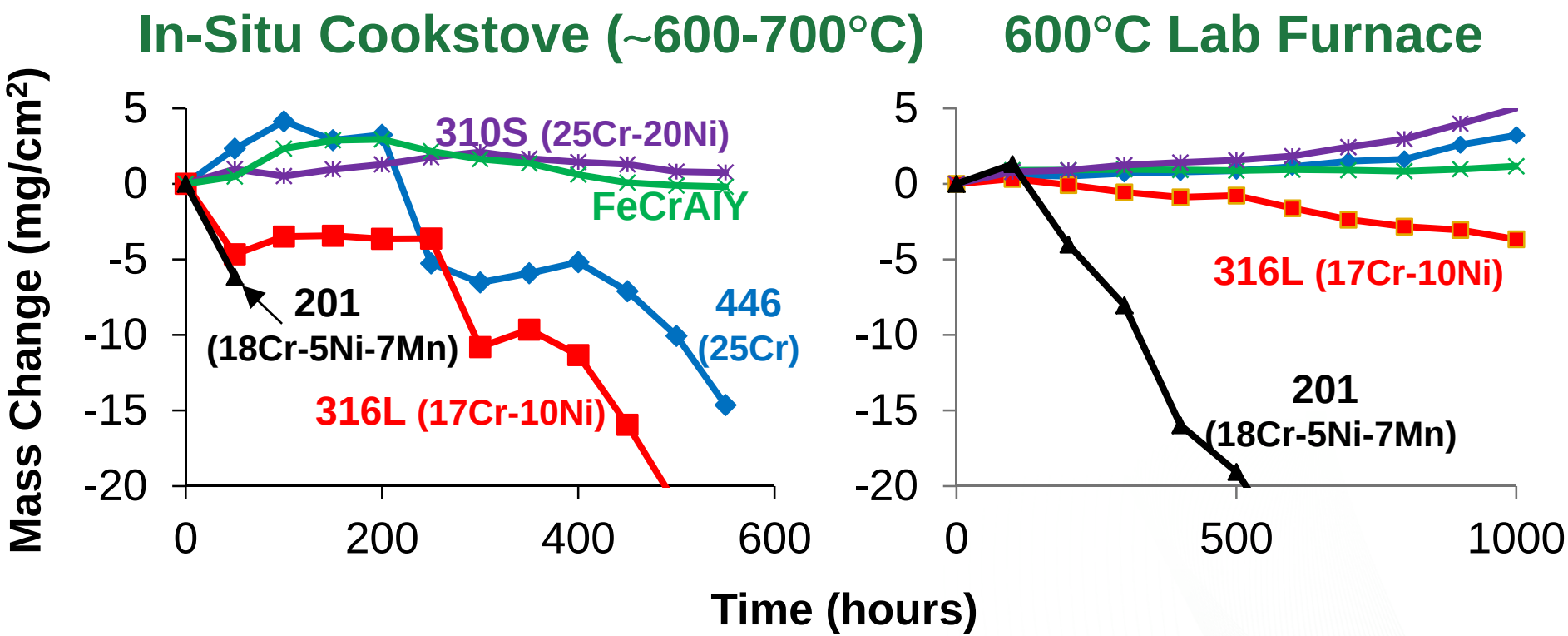
Comparison Between In-Situ Cookstove and 600°C Lab Furnace Mass Change Data



- Significant mass loss (material loss) for 201, 316L, and 446 in cookstove
- 201 very poor at 600°C lab furnace test, 316L borderline
- High mass loss/gain = BAD; low mass loss/gain = MIGHT be good, section to assess

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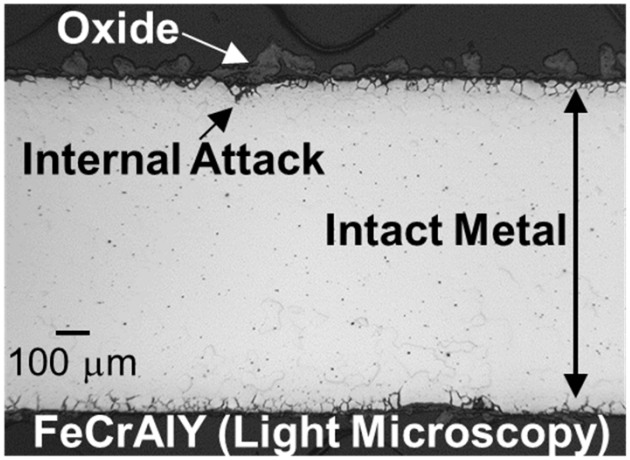
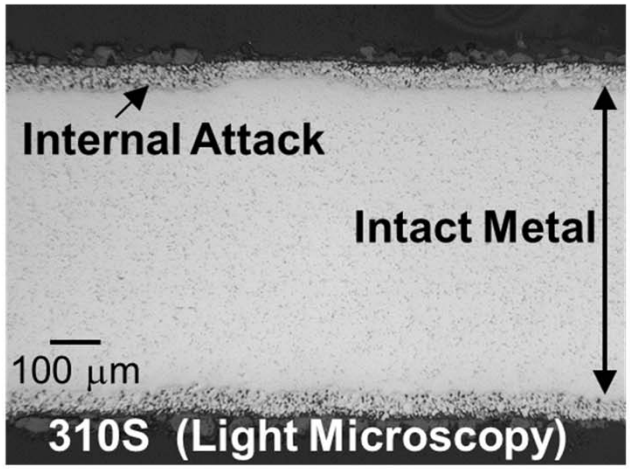
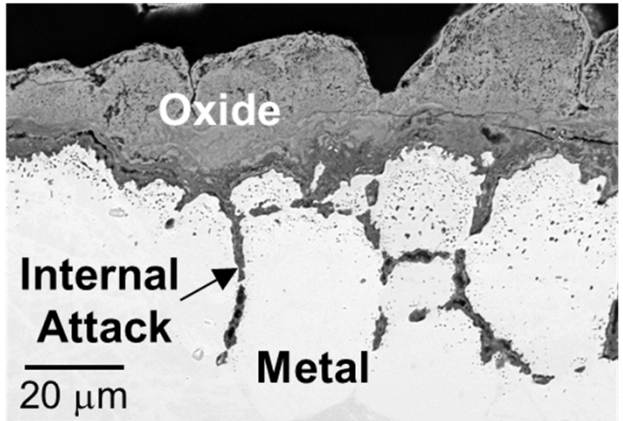
500 h Cookstove Test Alloy Cross-Sections Show Internal Attack in FeCrAlY and 310S



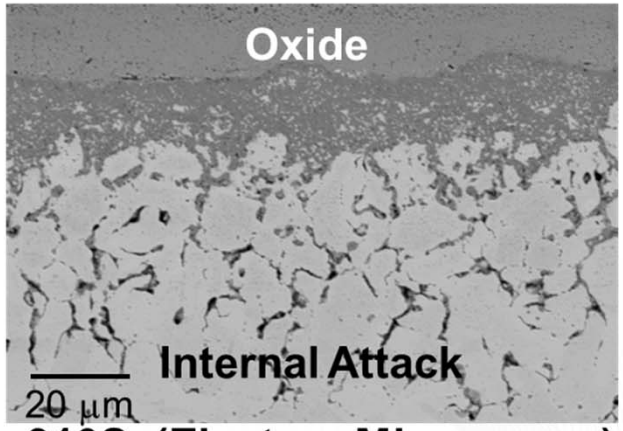
FeCrAlY (Light Microscopy)



310S (Light Microscopy)



FeCrAlY (Electron Microscopy)



310S (Electron Microscopy)

- Internal attack =oxide (sulfide, etc) protruding into metal: tolerable if slow grow
- Corrosion faster for 310S and FeCrAlY than suggested by mass gain data

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