Stress-Assisted Corrosion (SAC) in Boiler Tubes

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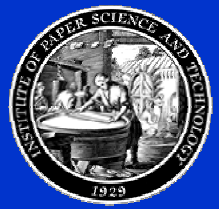
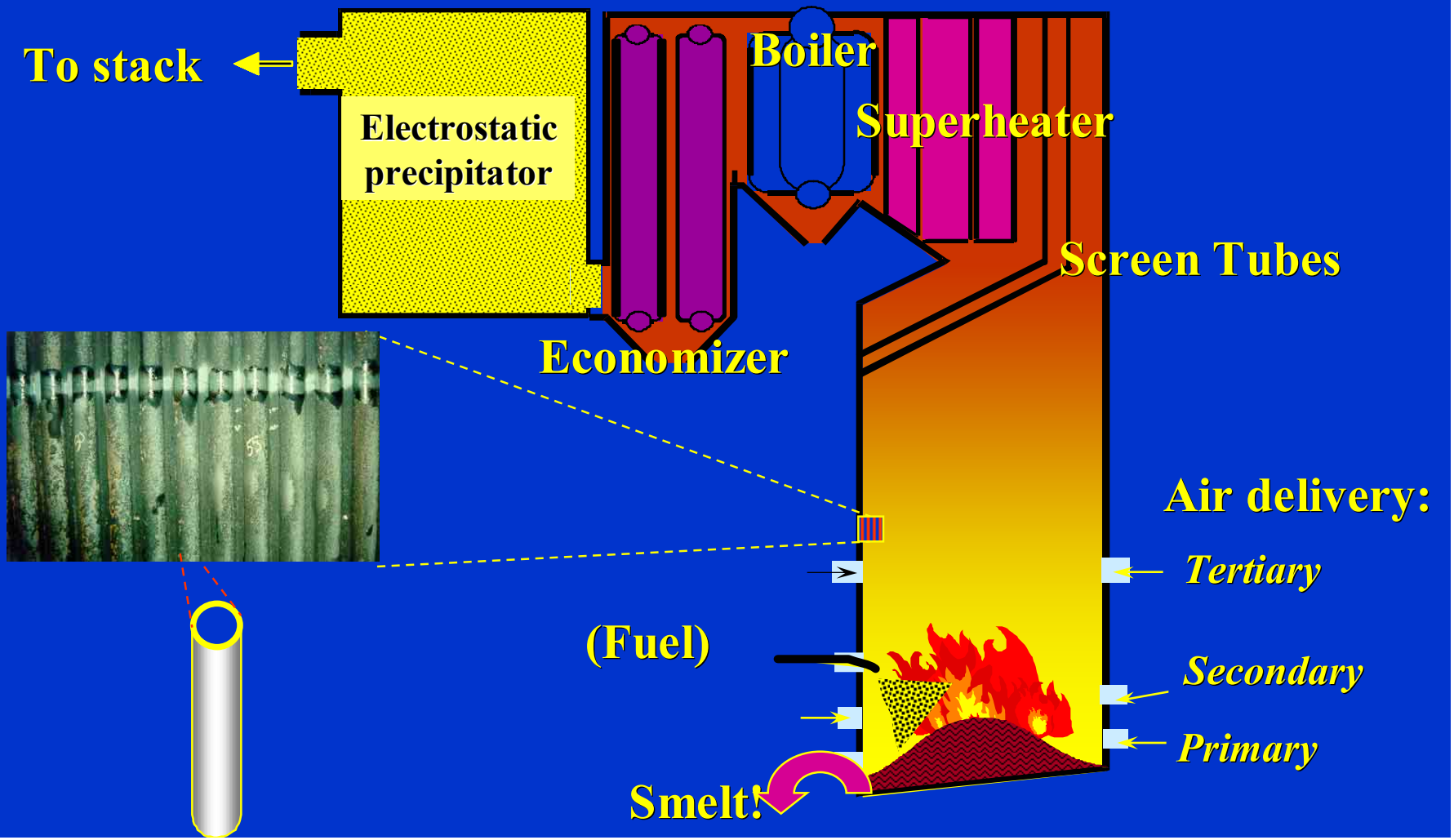


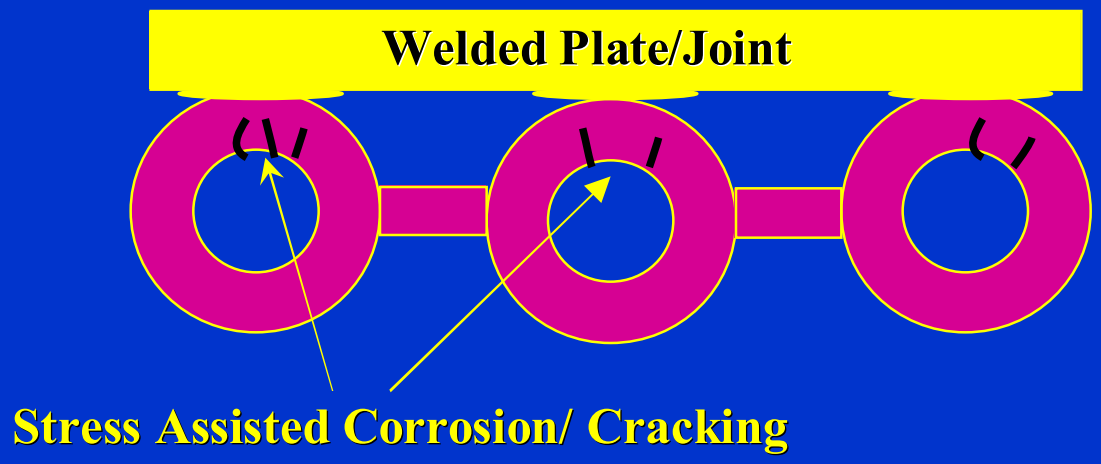
DOE Project #DE-FC07-01ID1443

Project Background

Industrial Boilers



Stress Assisted Corrosion in Waterwall Tubes

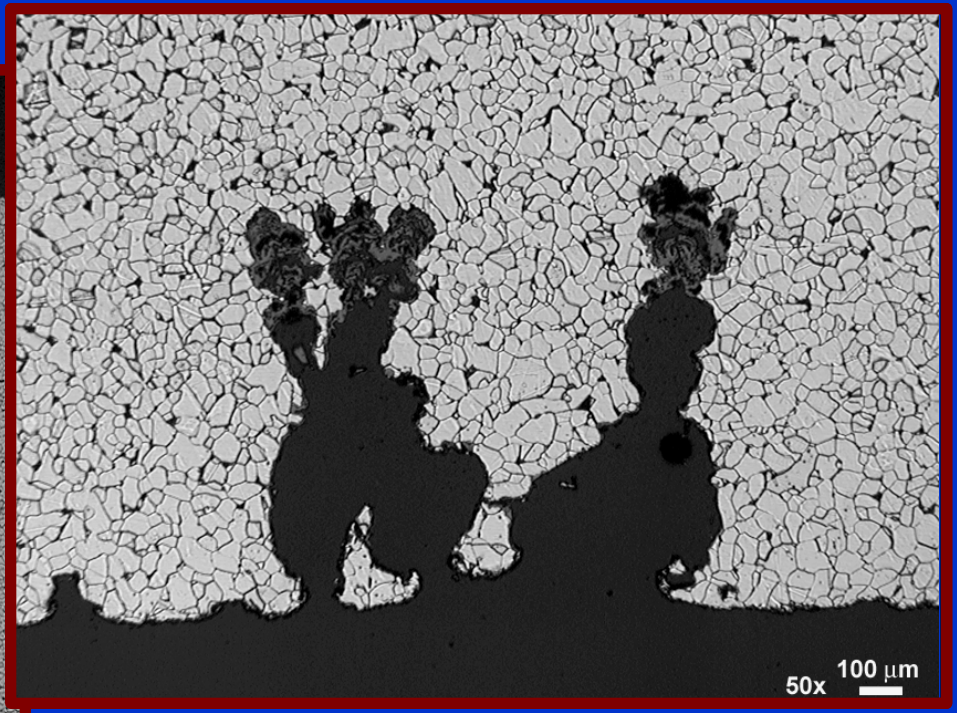


Boilers can experience SAC from waterside in

- Floor
- Waterwalls
- Screens
- Roof
- Economizers
- Floor-to Sidewall Seals
- Smelt Box Attachments
- Port Attachments

Waterside Cracks in Waterwall Tube Near Attachment Weld

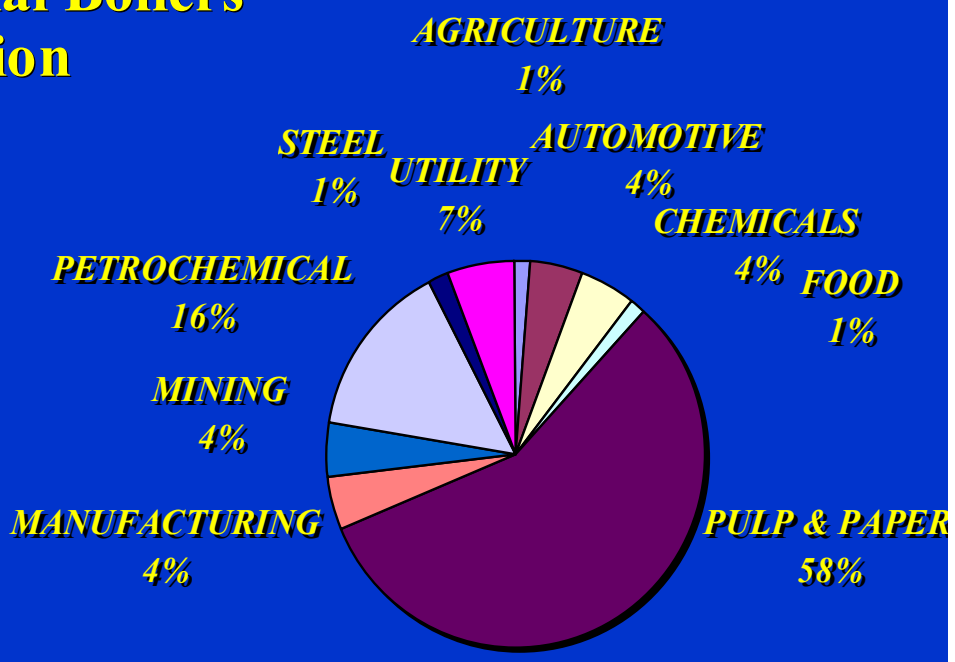
SAC in Recovery Boiler Tubes



Industrial Boilers and SAC

SAC is Experienced in Various Industrial Boilers

- **Water Leak in Some Industrial Boilers can Potentially Cause Explosion**
  - **Numerous Accidents Reported**
    - *Some were Fatal*
- **Project Benefits**
  - *~25 Trillion BTUs by 2020*
  - *Cost Savings of ~ $133 Millon/Year*
  - *Safety*



Survey Data from Hercules-BetzDearborn

Project Objective

- To Clarify Mechanisms Involved in Stress Assisted Corrosion (SAC) of Boiler Tubes
- Determine Key Parameters in its Mitigation and Control
  - Microstructure
  - Water Chemistry
  - Stress
    - Residual Stresses Due to Welding
    - Operational Stresses

Project Team

- **Oak Ridge National Laboratory -** ***Dr. Steve J. Pawel***
- **Georgia Institute of Technology -** ***Dr. Preet M. Singh***
- **Others**
  - **Lawrence Livermore National Laboratory - Dr. Mike Quarry**
- **Industrial Partners**

Dr. W.B.A. Sharp– MeadWestvaco
Mr. Steve Lukezich – MeadWestvaco
Mr. Paul B. Desch - ONDEO- Nalco
Dr. Peter Gorog - Weyerhaeuser Company
Mark Labell – Ahlstrom
Mr. John Hainsworth – B&W
Dr. Ray Vasudevan - International Paper
Mr. Mike Cooper – Longview Inspections

- **Other Project Advisors**

Dr. Barry Dooley – EPRI
Dr. Jim Keiser - ORNL
Mr. Mel Esmacher - GE Specialty Materials
Mr. Karl Morency – Georgia Pacific

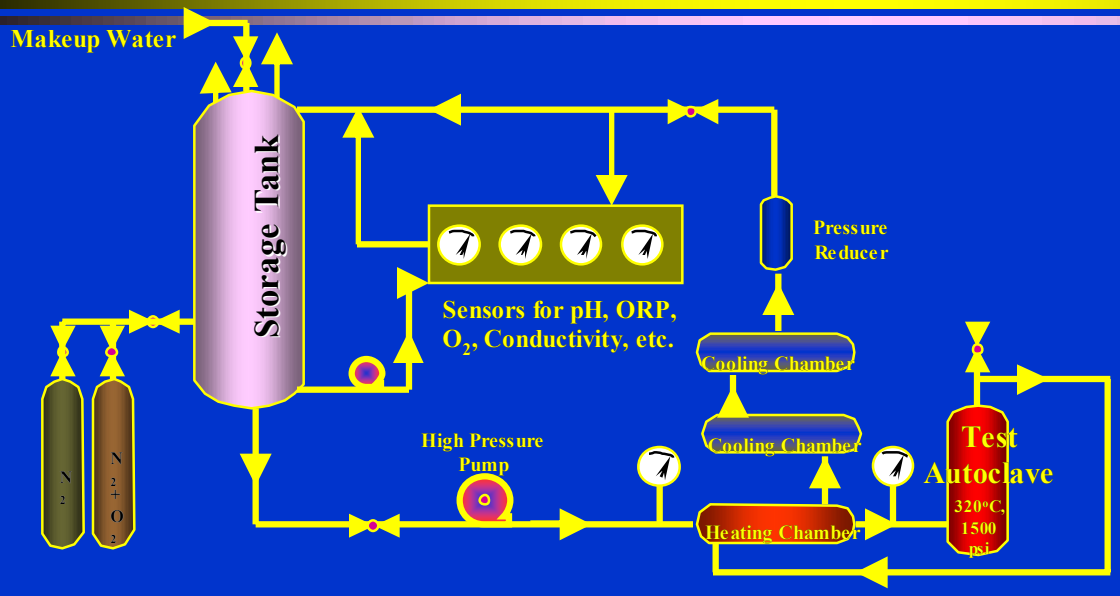
Main Project Tasks

- **Task 1:** ***Laboratory Simulation of SAC***
  - ***IPST-GTech***
- **Task 2:** ***Material Characterization***
  - ***[ORNL and IPST-GTech]***
- **Task 3:** ***Evaluation of Stress Effects***
  - ***[ORNL]***
- **Task 4:** ***Evaluation of Environmental Effects***
  - ***[IPST-GTech and ORNL]***
- **Task 5:** ***Communication to US Industry***
  - ***[IPST-GTech and ORNL]***

Laboratory Simulation of SAC
Task 1

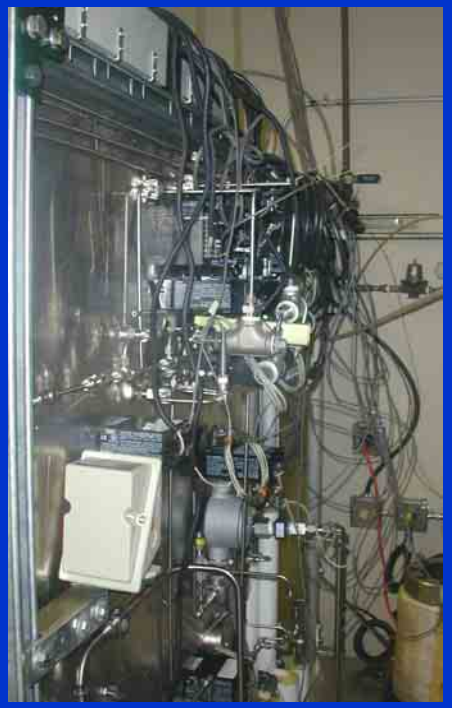
- **Develop Facilities to Simulate Boiler Tube Environment in Laboratory**
- **Capable of Controlling Water-Chemistry Variables**
  - **Dissolved Oxygen**
  - **pH**
  - **Cl^-, SO_4^{-2}, and Other Ions**
    - **Conductivity**

Test Autoclave with Recirculation Loop



- Test Capabilities
  - Temperature up to 350°C, Pressure up to 3500 psi
  - Electrochemical Tests
    - AC Impedance
  - Stressed Samples for SAC
  - Special Fixture for Constant Extension Rate Tests

Autoclave with Recirculation Loop



- 100 Liter Makeup Tank
- Heat Exchangers to Conserve Heat and Achieve Steady State Easily
- High Pressure Pump for Recirculation
- Continuous Water Chemistry Monitoring

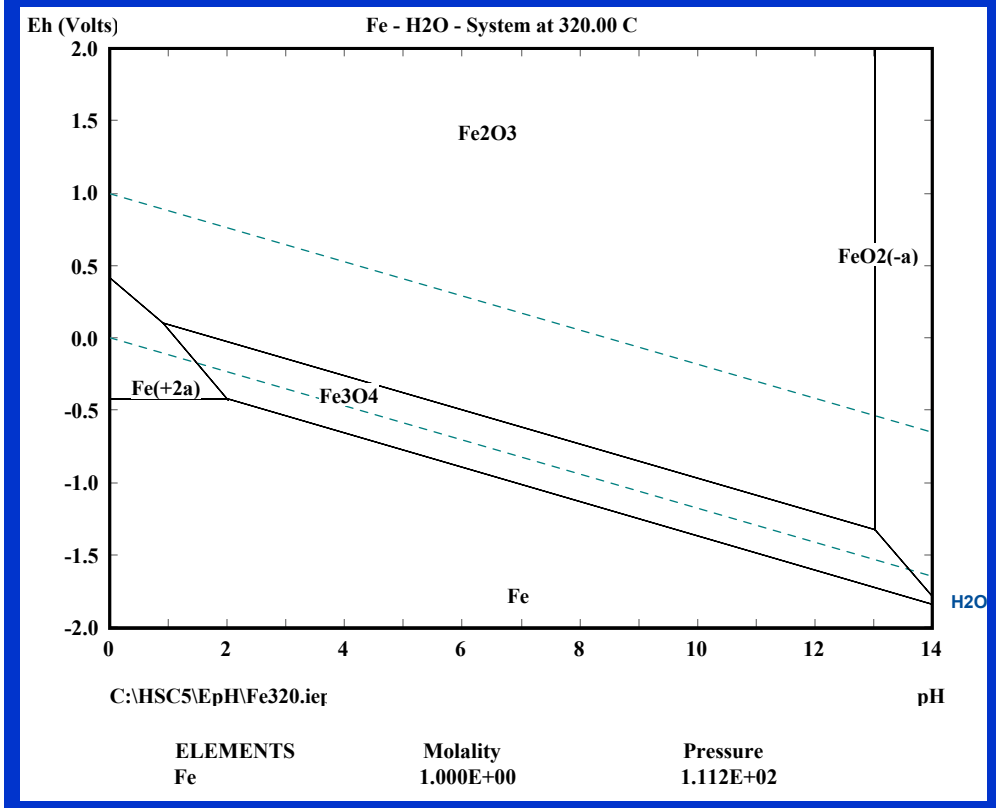
Evaluation of Environmental Effects

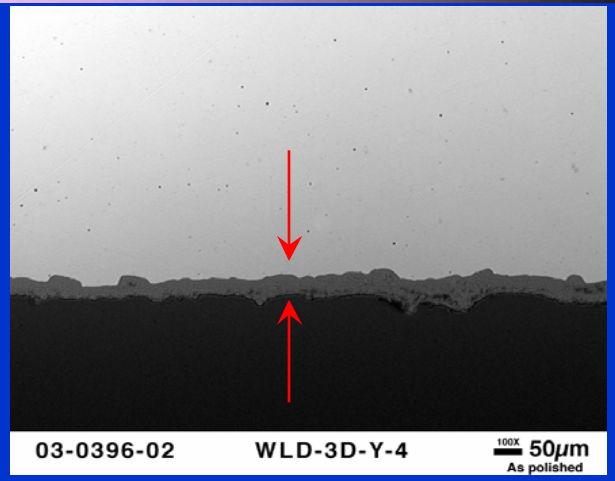
Task 4

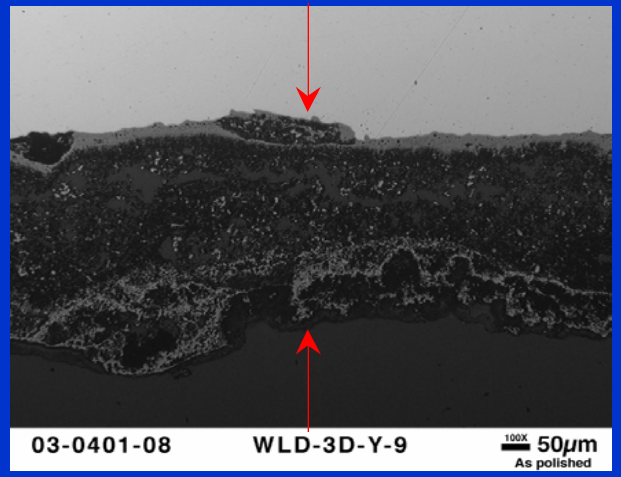
Effect of Environment on Magnetite Growth and Properties

Boiler Environment and Magnetite Film on Tube Surface

$$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2$$

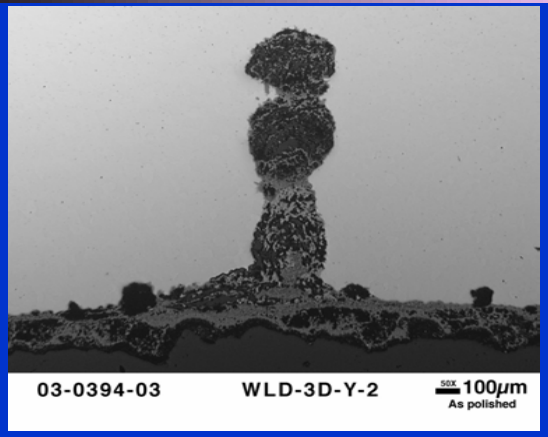


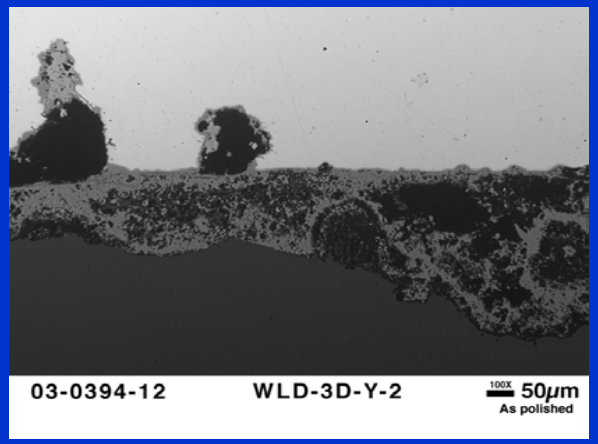


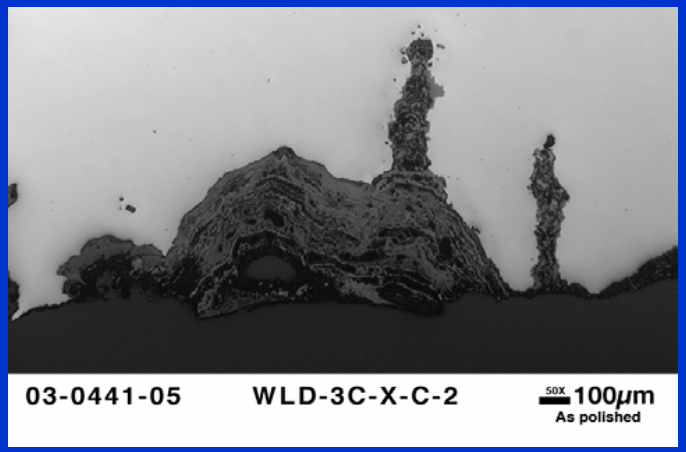


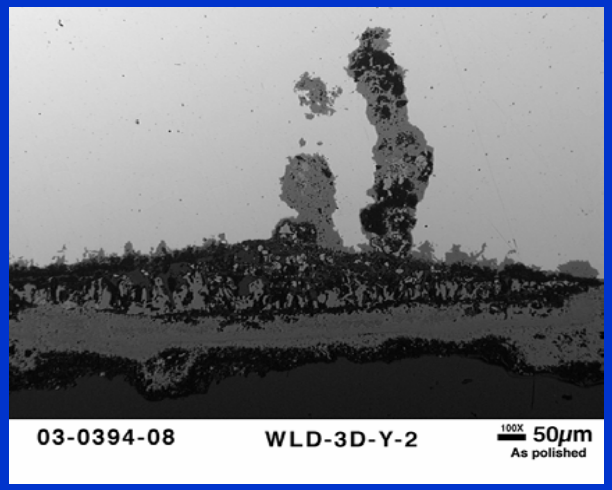
Above ~ 230°C, Magnetite Film Forms on Carbon Steel in Slightly Alkaline Oxygen-free Water

Stress Assisted Corrosion and Oxide Scale Morphology







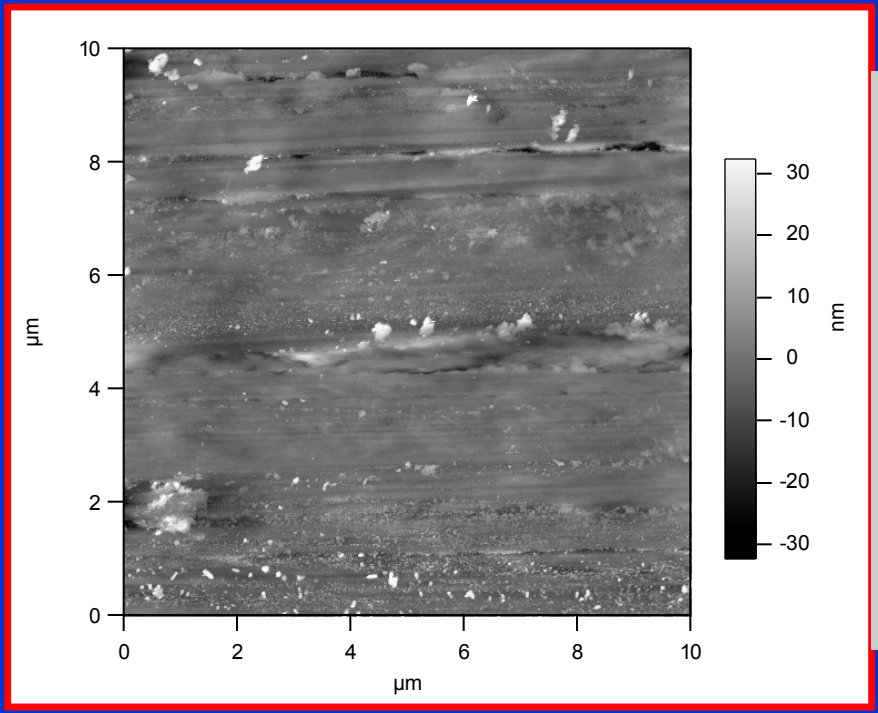


Magnetite Film Growth and Morphology Under Boiler Conditions

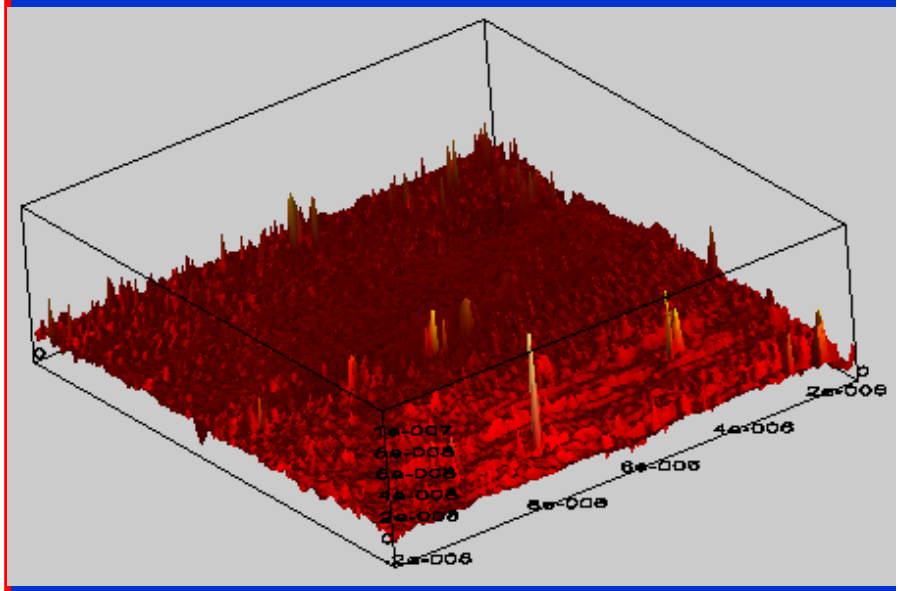
- SA 210 Carbon Steel Tube Samples
  - Electrically Isolated Samples
  - Samples Attached to Large Cathodes with Different Areas
- Pure Water *(Double-Deionized)*
  - With and Without N_2 Purge or O_2 Scavenger
- 250°C to 320°C
- X-Ray Diffraction of Sample Surface and Metallography to Characterize Film
- Atomic Force Microscopy (AFM) for Film Morphology and Properties

Atomic Force Microscopy

Unexposed SA-210 Carbon Steel Surface

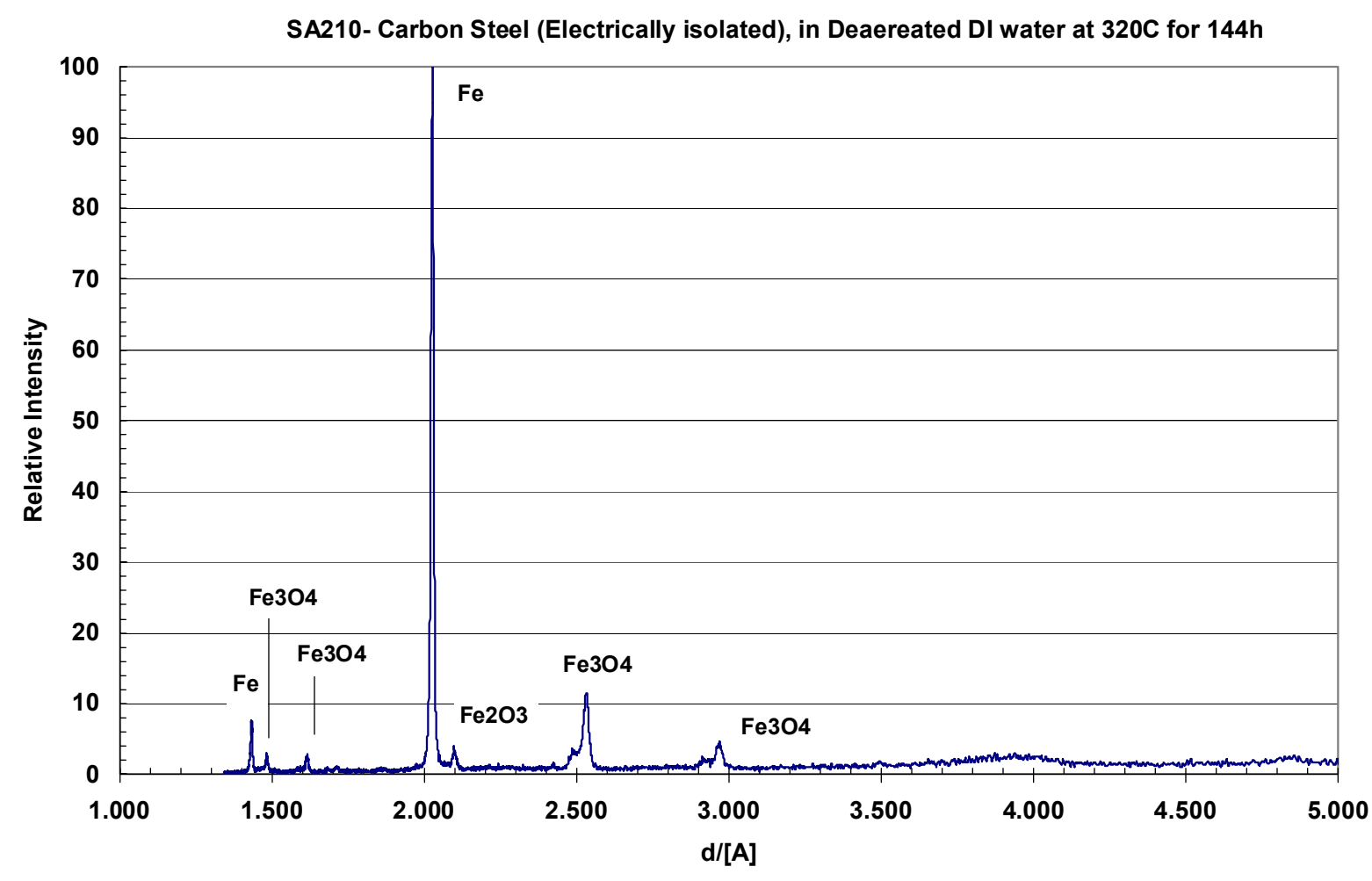


Topography Scan

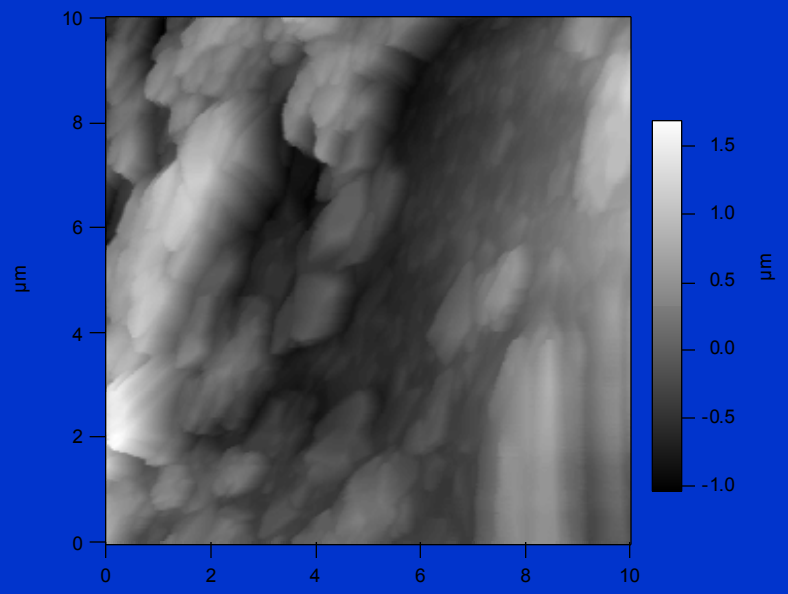


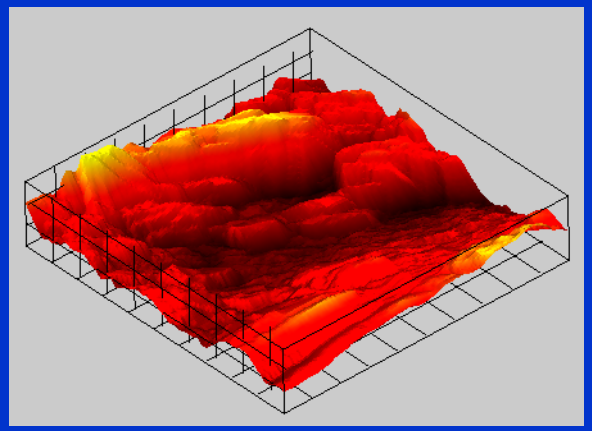
Max. Roughness = 10 nm

Electrically Isolated SA-210 Carbon Steel Exposed to Deaerated DI Water at 320°C for 114 hours



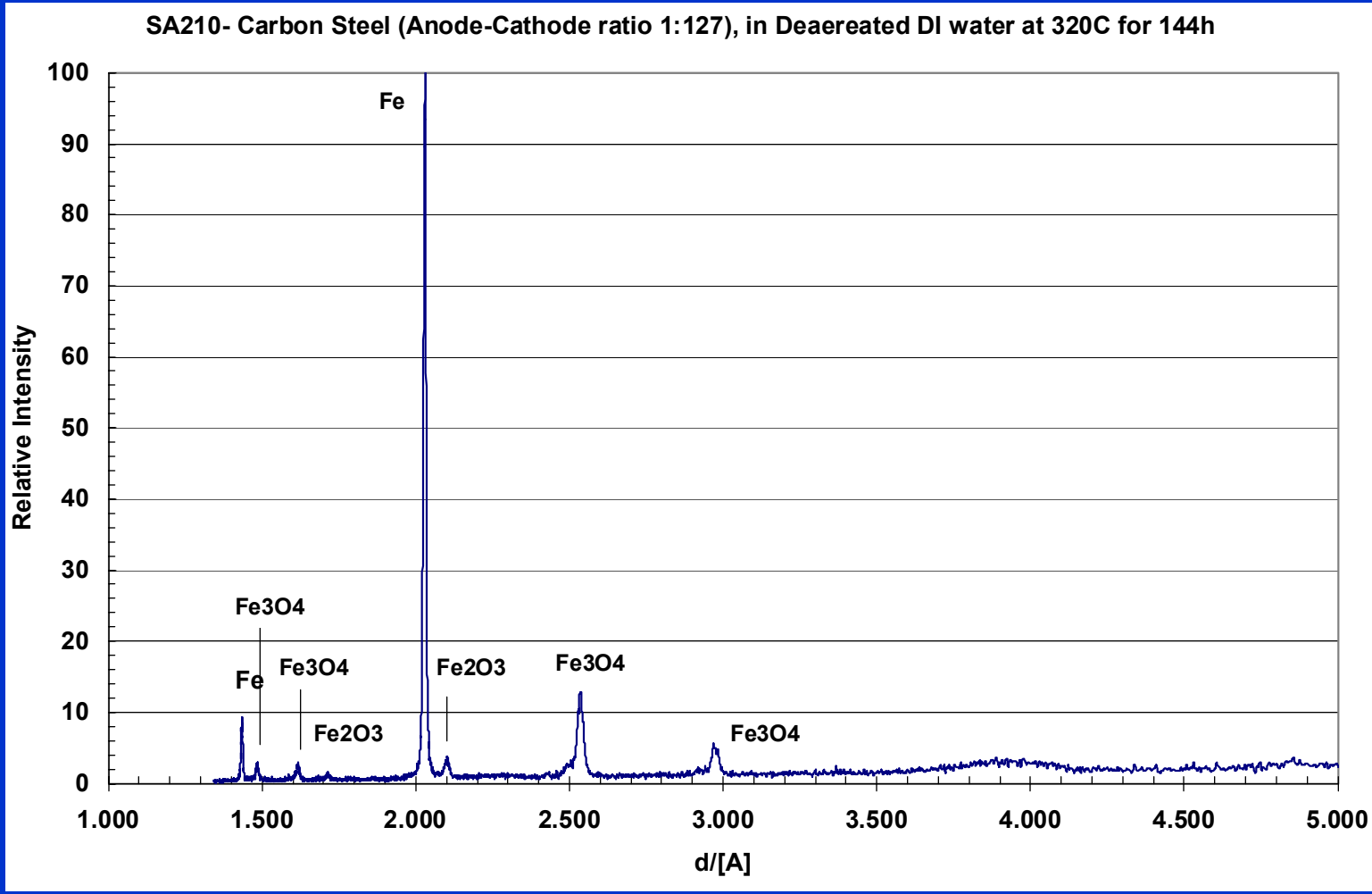
Electrically Isolated SA-210 Carbon Steel Exposed to Deaerated DI Water at 320°C for 114 hours



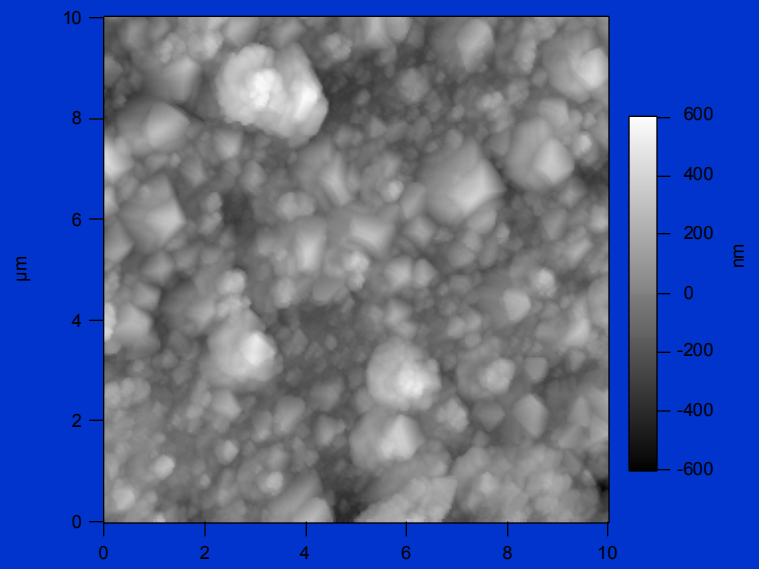


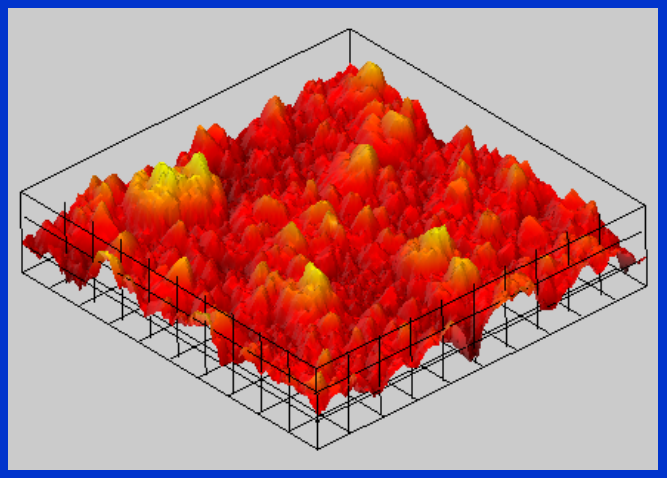
- Electrically Isolated C-Steel in Boiler Environment Forms Dense and Protective Magnetite Film on Surface

SA-210 Carbon Steel in Contact with Large Cathode *(Anode Cathode Area Ratio 1:127)* Exposed to Deaerated DI Water at 320°C for 114 hours



SA-210 Carbon Steel in Contact with Large Cathode *(Anode Cathode Area Ratio 1:127)* Exposed to Deaerated DI Water at 320°C for 114 hours





- Contact with Large Cathodic Area *(Magnetite Film or Noble Metal)* Produces Fine-Grained Porous Film with Tetrahedral Crystals on Surface
- Film Growth Rates are Higher for Porous Oxide Film

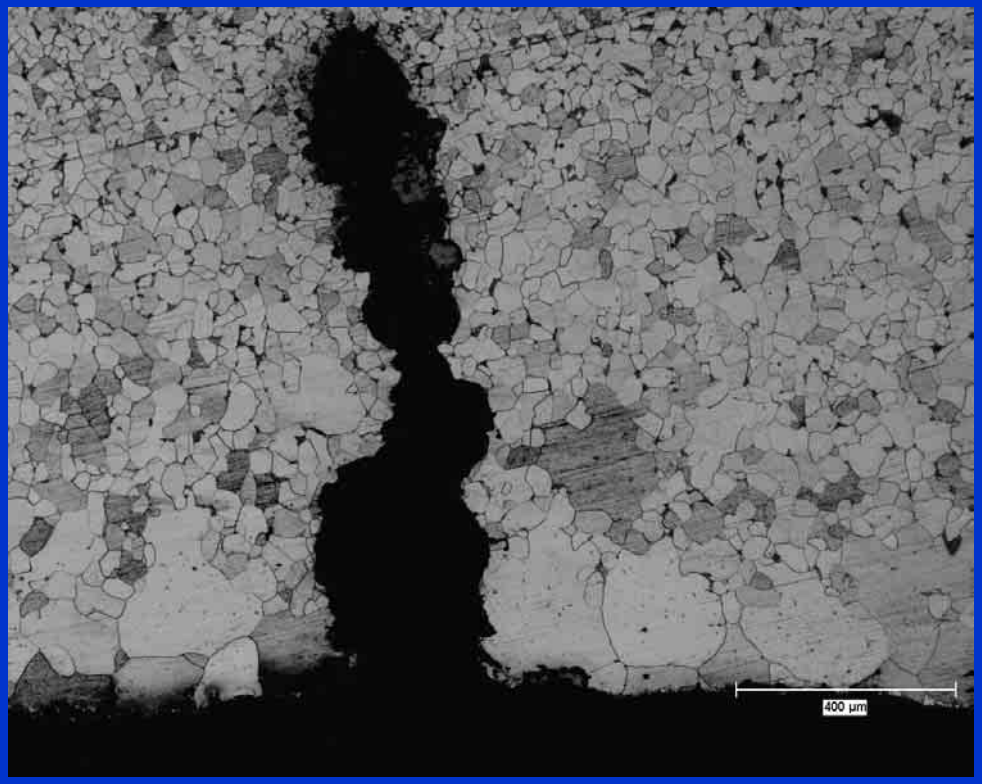
Proposed SAC Initiation Mechanism – *Based on Film Growth Results*

- **Initially Thin Dense Magnetite Film is Formed on C-Steel Tube Surfaces**
  - **New Tubes or Acid Cleaned Tubes**
- **If Thin Protective Magnetite Film is Locally Disrupted *(Stress Effects)***
  - **Remaining Intact Magnetite on the Tube Will Act as Cathodic Surface**
  - **New Oxide Growth in the Damaged Areas may Form Porous Oxide Film**
- **Further Damage Accumulation by Disruption or Fracture of Porous Film Due to Stress Concentration at Notches Developed**
  - **SAC Initiation and Growth!!**
- **Further Tests Going on to Test This Mechanism**

Material Characterization

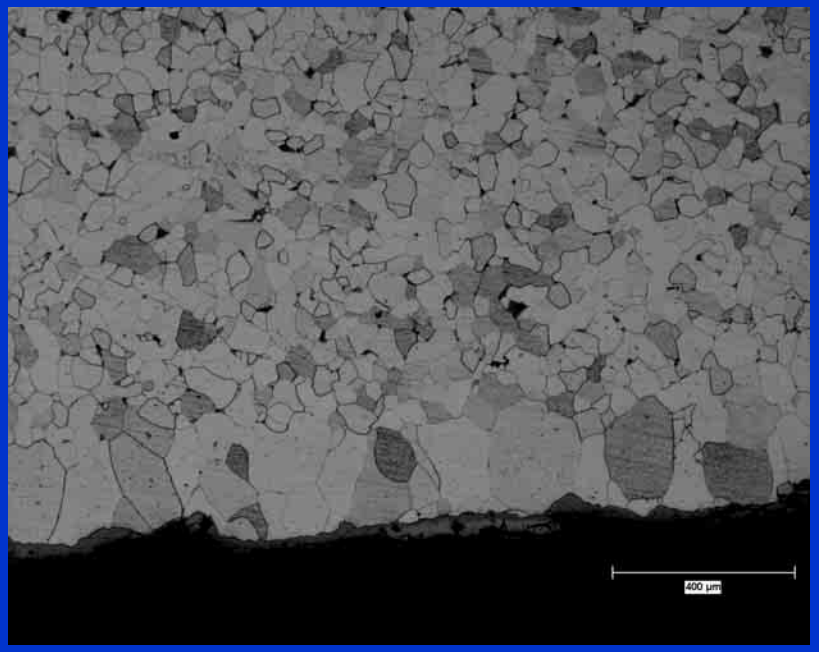
Task 2

- **Tubes from Over Ten Boilers Analyzed at GTech and ORNL**
- **Role of Microstructure on SAC Initiation and Propagation-Rate**

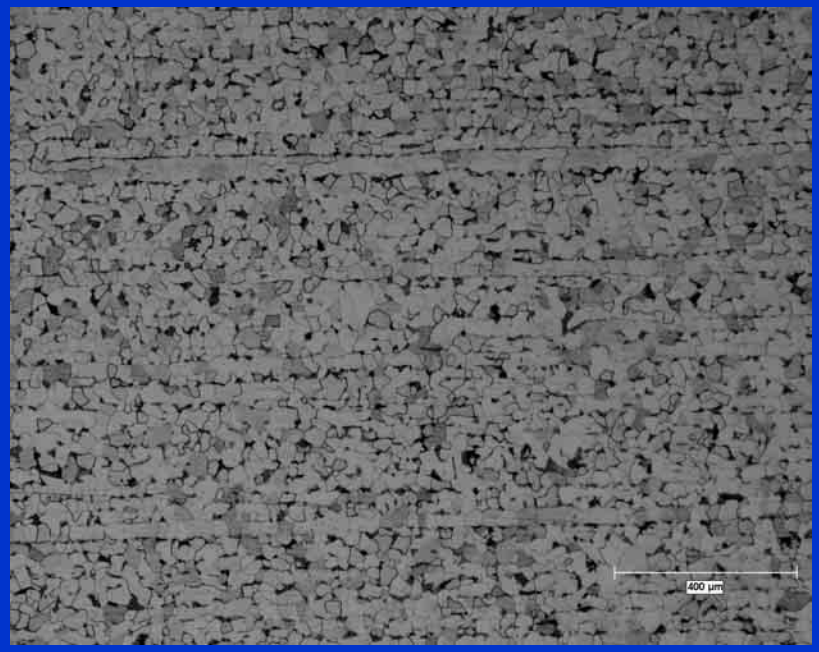


Microstructure of Carbon Steel Tubes With SAC

Not Necessary for SAC but may facilitate easier Initiation

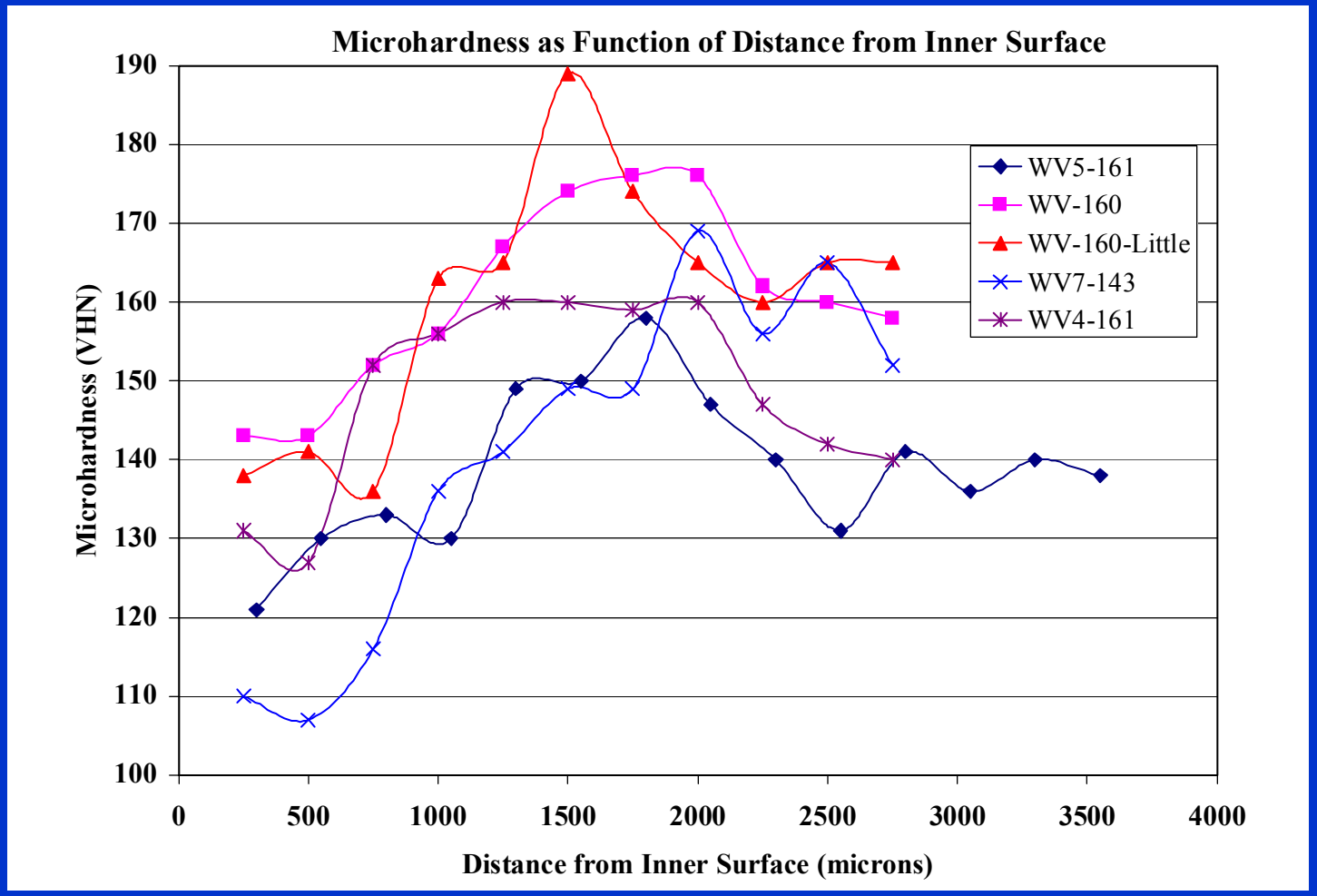


Inner Tube Surface



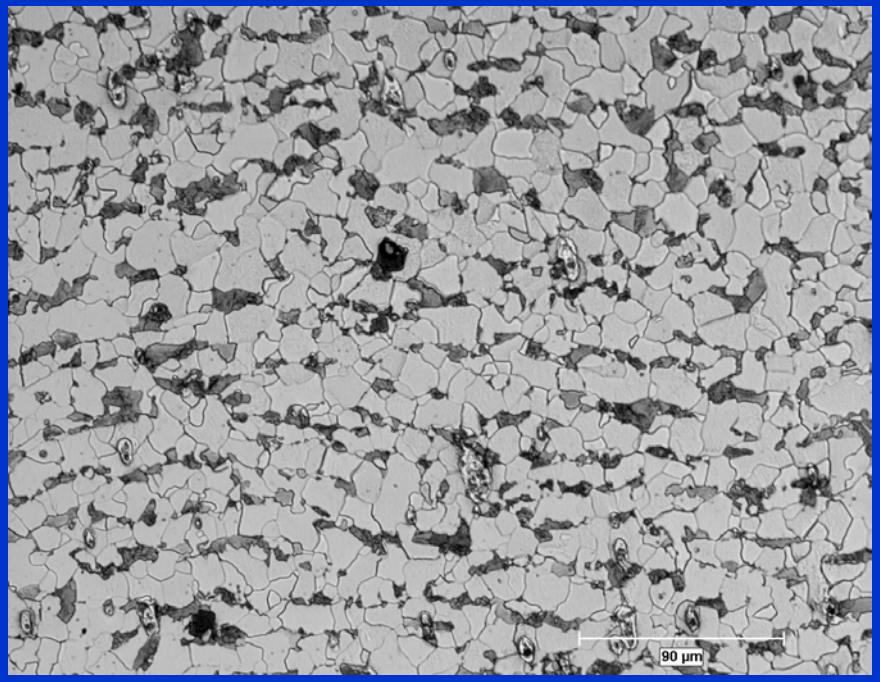
Middle of Tube

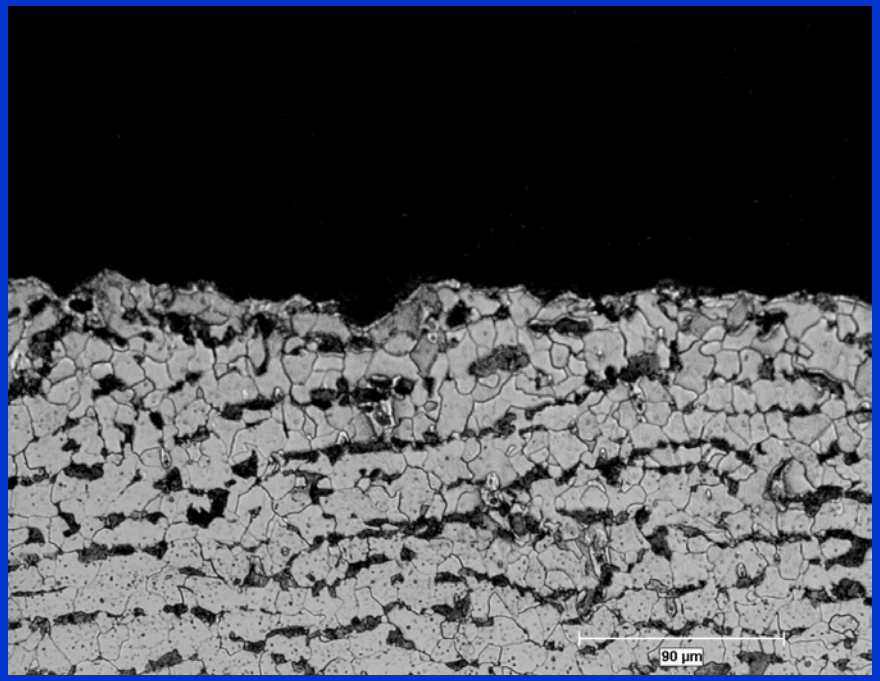
Microhardness and Microstructure



Microstructure of Composite Tubes Removed from Front Wall *(near smelt spouts)* of Recovery Boilers

No SAC in these Tubes



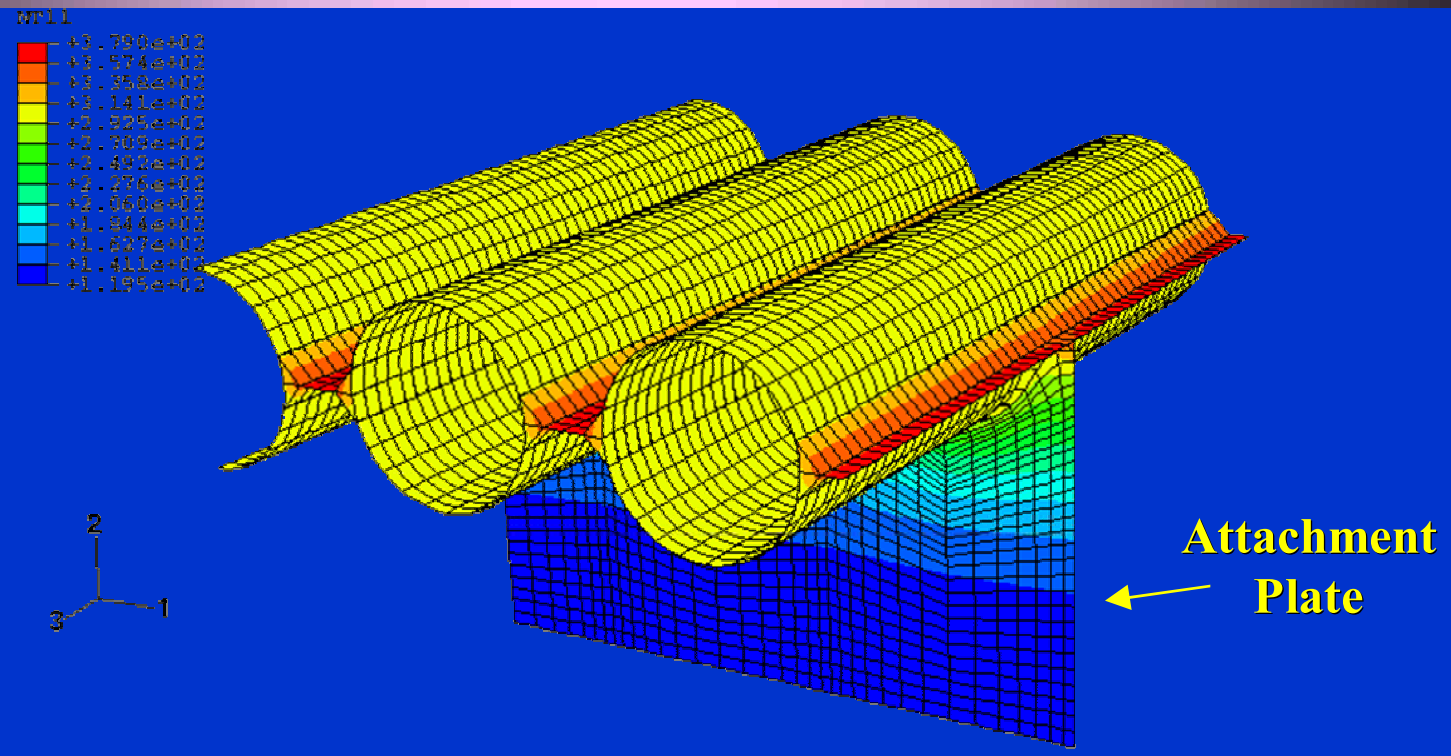


Evaluation of Stress Effects

Task 3

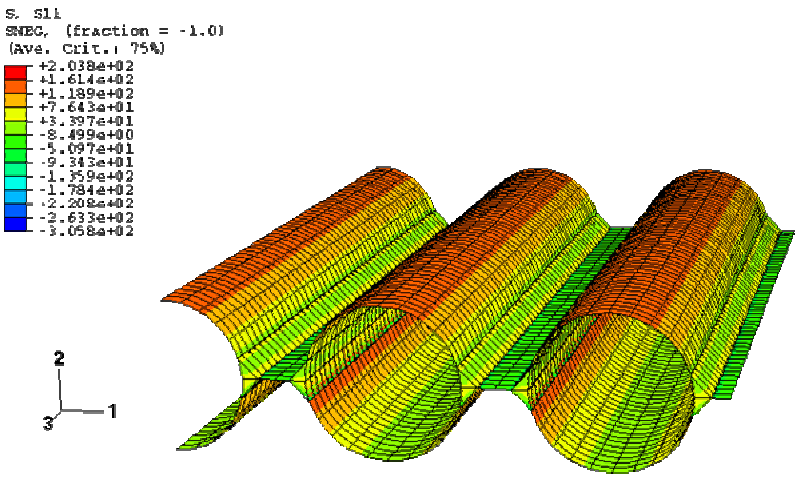
- **Finite Element Modeling - Effect of Attachment Plate on Recovery Boiler Wall Panel Stresses –** ***Gorti Sarma - ORNL***
- **Stress Measurements on Boiler Tubes**
- **SSRT Tests in Simulation Autoclave**

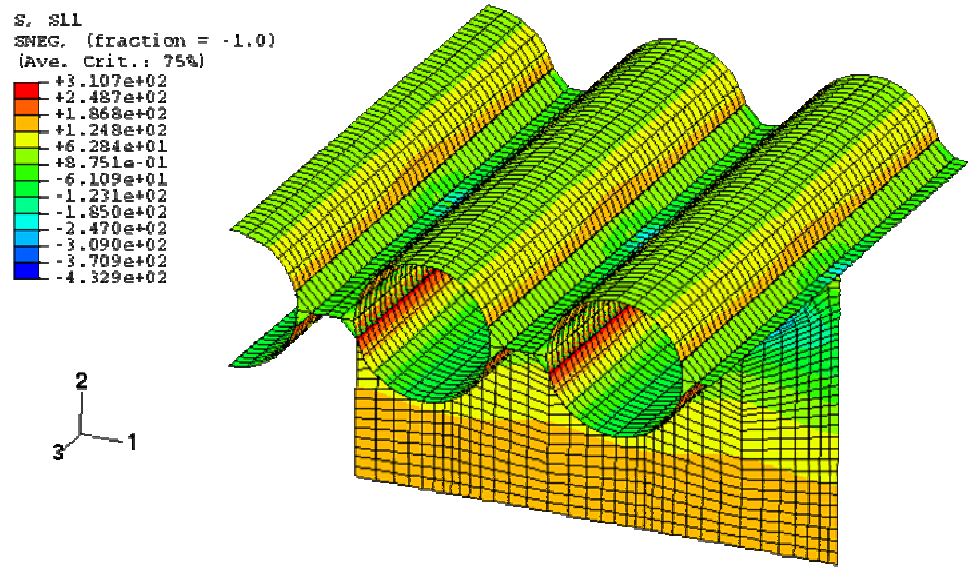
Temperature Distribution in the Panel



- Uniform heat flux of 0.3 W/mm^2 was applied on the fireside of the panel
- Tube inside surface was assumed to be in contact with water at 305°C
- Cold side of panel was assumed to be exposed to air at 100°C

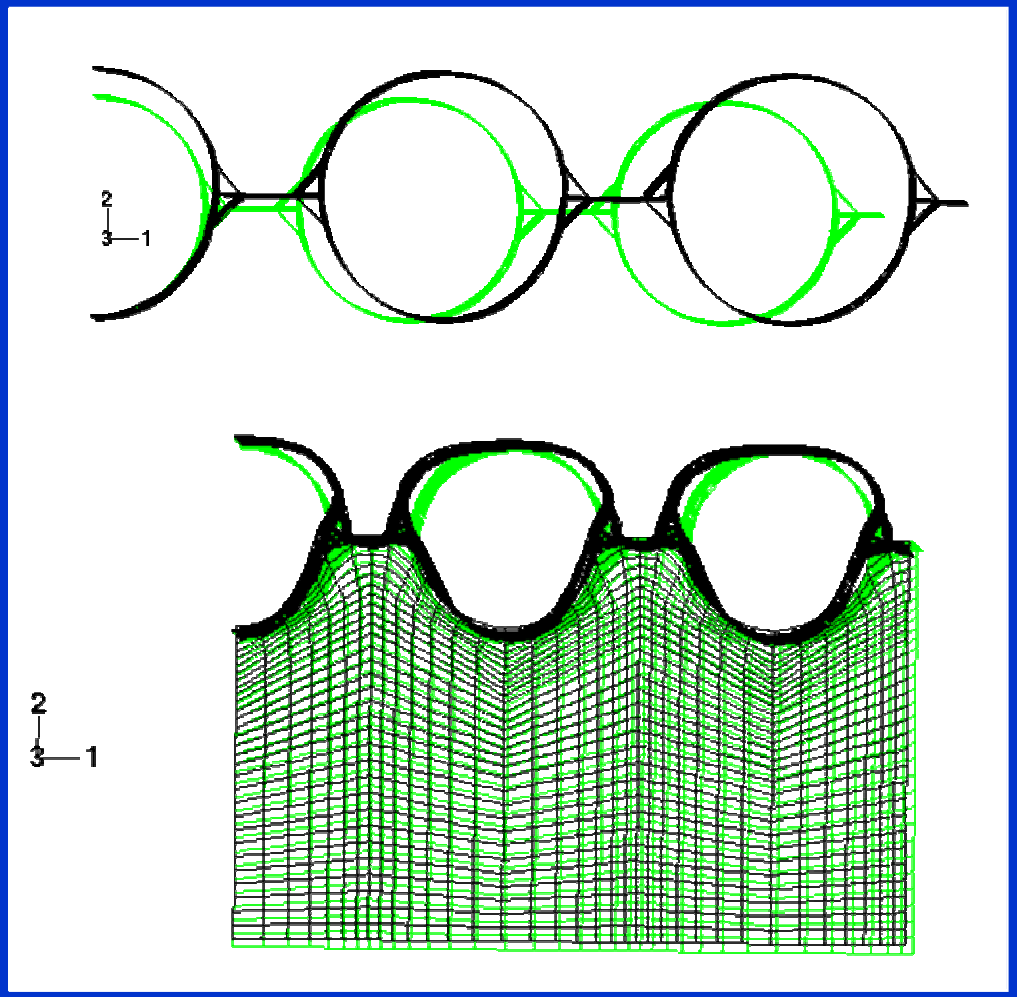
Stress Distribution Due to Temperature Differences





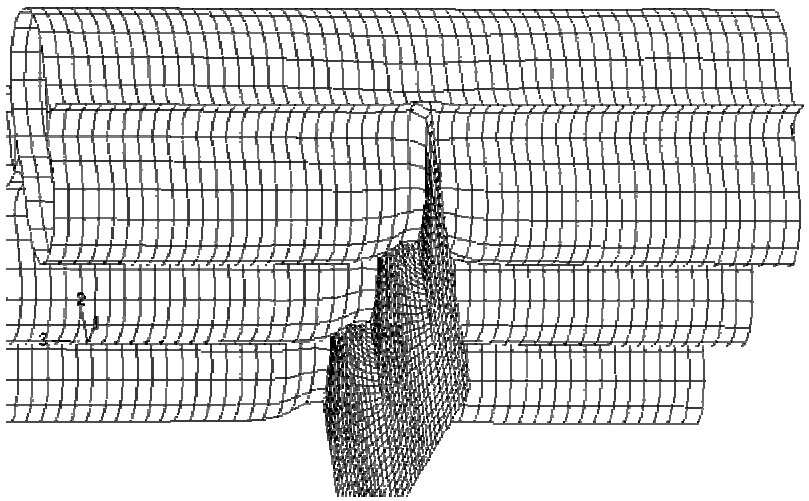
- Load due to pressurized water on inside surface of tube was 8.62 MPa
- Residual stress values calculated from 2-D welding analyses
- Stresses due to welding of attachment plate to the wall panel were not included in this initial analyses

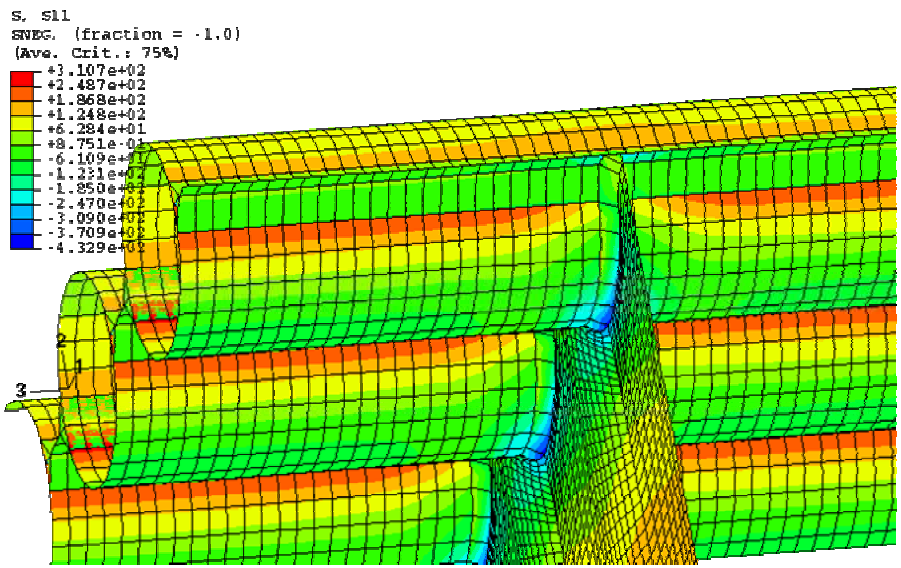
Constraint on the Expansion of Panel Due to Attachment plate



- Highly magnified view of the deformed mesh shows effect of attachment plate
- Constraint from attachment plate influences the stresses in the tube

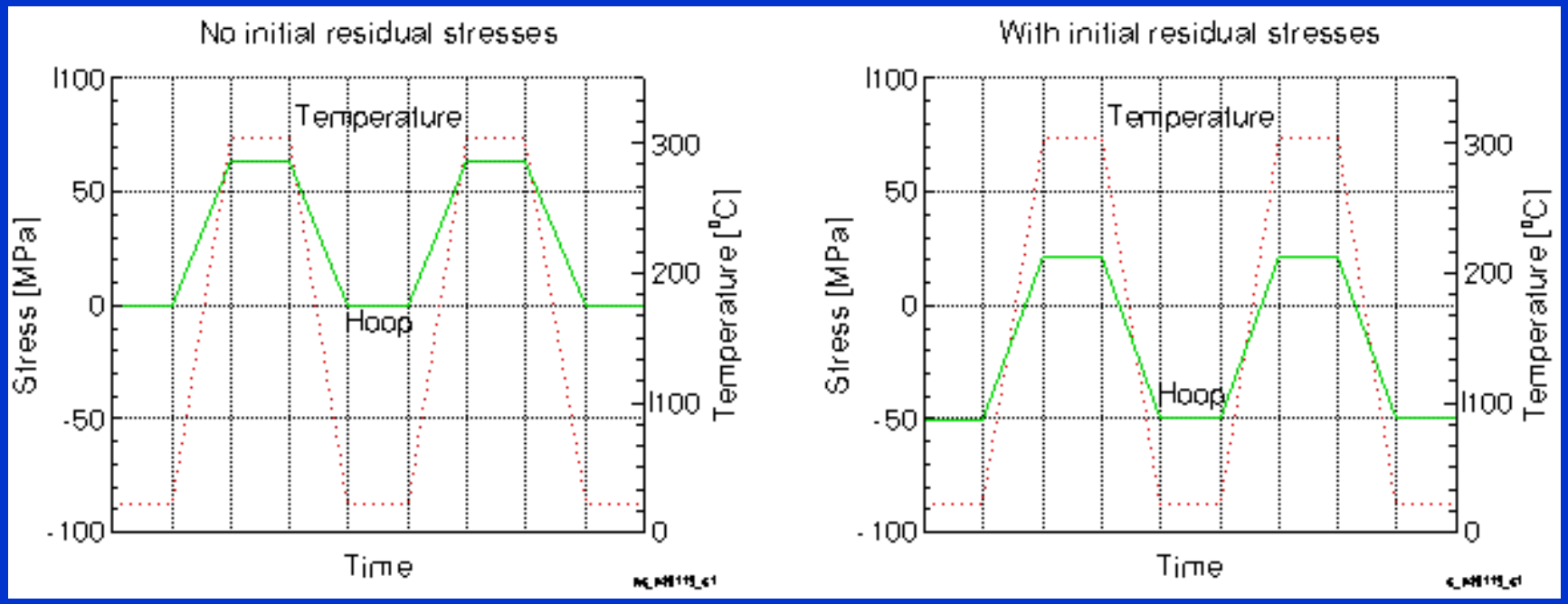
Attachment Plate Constraint on Deformation of Wall Tube Panel Due to Operational Hoop Stresses





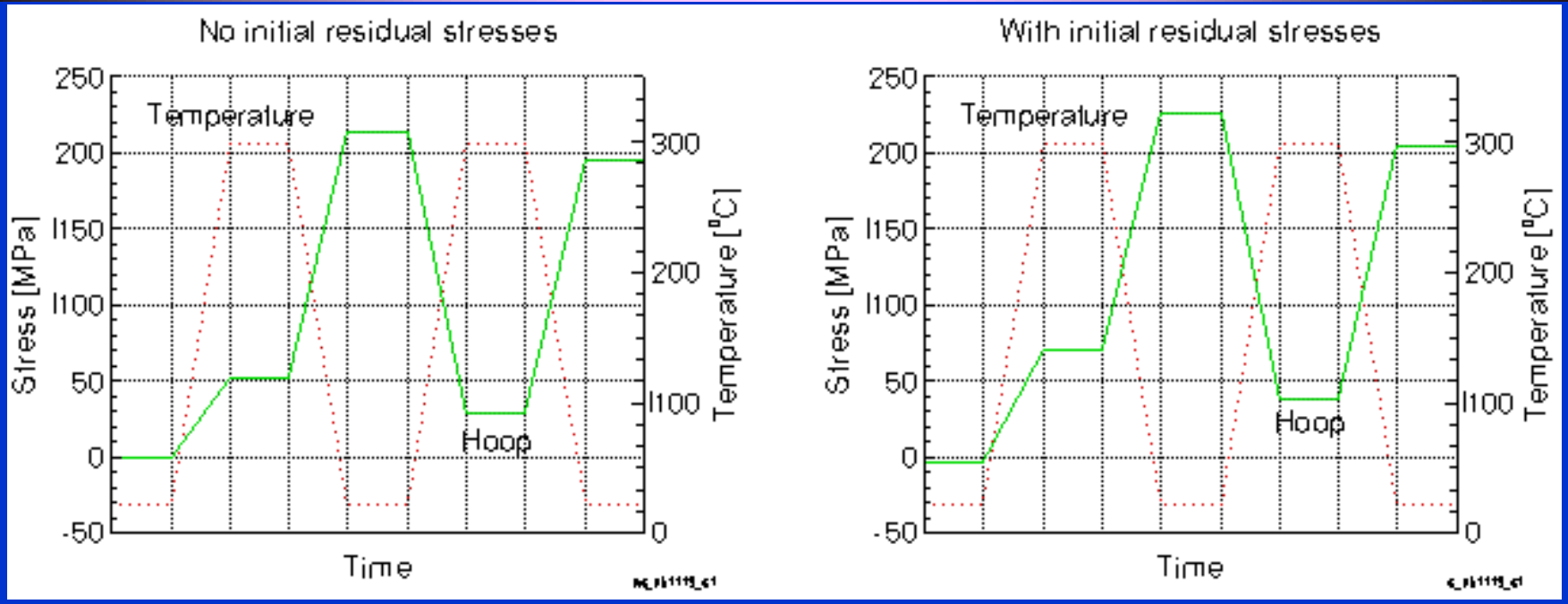
- **Attachment plate causes changes in stress state in the vicinity of the weld, with fairly sharp gradients**
  - **Stresses change significantly on either side over a length of 3 elements, which is about 18.3 mm (0.72 in.)**

Hoop Stresses at Inside Surface Under Operating Cycles for Panel Tubes without Attachment Plate



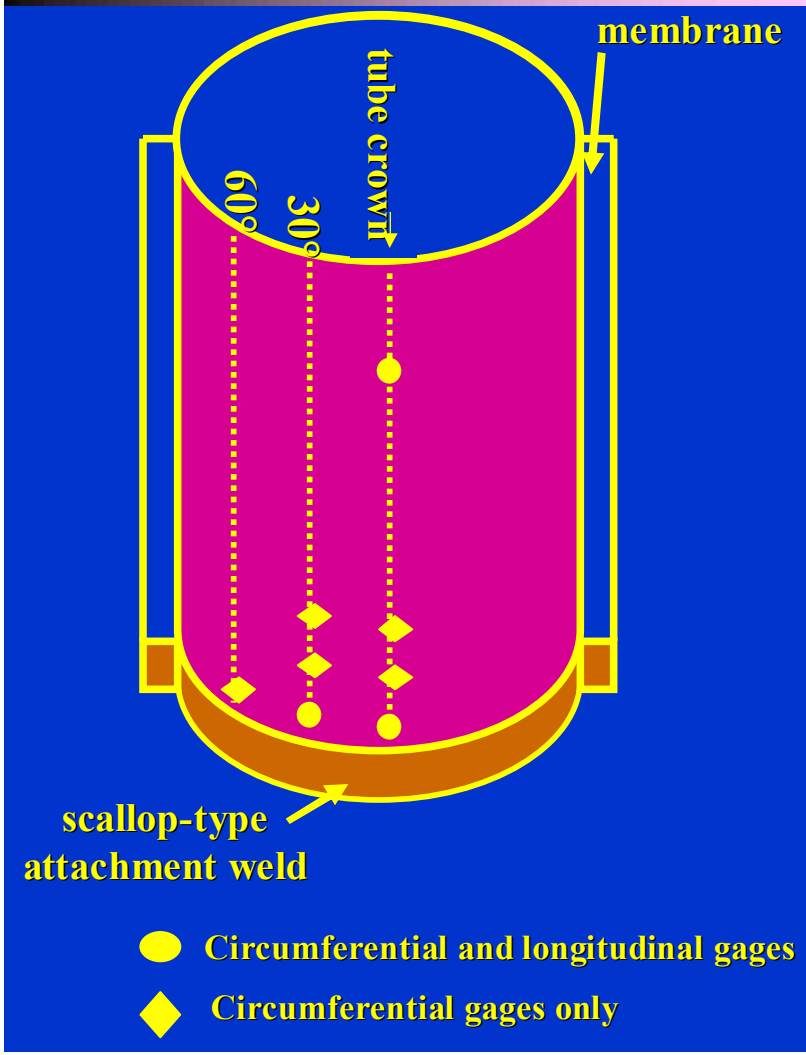
- **Hoop stress at the inside surface of tube crown on the cold side becomes slightly tensile during operation, but returns to initial value upon shutdown**

Hoop Stresses at Inside Surface Under Operating Cycles for Panel Tubes with Attachment Plate



- Hoop stress at the inside surface of tube at the weld becomes slightly tensile at operating temperature, and even more tensile after shutdown
- Hoop stress remains tensile during subsequent operating cycles

Stress Measurements on Boiler Tubes



- Identify a Boiler with Known SAC Problem Areas
- Make installation during outage (prior to restart)
- - $50K budgeted for gages, equipment
- Collect data every 15-30 seconds for 6^{+} months
- Use data to support finite element model
- Attempt post-test evaluation of the instrumented areas

  - radiography, ultrasonics, borescope

Future Tasks for FY 05

- Role of Water Chemistry on Magnetite Film Formation and its Properties
  - X-Ray Diffraction, SEM and AFM Analysis of Films to Characterize Composition, Morphology, and Mechanical Properties
- Role of Microstructure on SAC Initiation and Propagation – *Tests on As Received and Heat Treated Steels*
- More Failure Analysis of Tubes Removed from Boilers
- Continue FEM Modeling to Calculate Inner Tube Surface Strains At Attachment Welds
- SSRT Tests to Evaluate Role of Stress on SAC Initiation and Propagation
- Strain Gages on Boiler Tubes with Attachment to Measure Strains Experienced During Startup and Shutdown as well as During Operation

Georgia Institute of Technology

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Energy Savings

Impact by the year 2020					
ENERGY SAVINGS	Electricity	Gas	Oil	Coal	Total Energy Savings
Vision Industry	[billion kWh]	[billion ft3]	[million barrels]	[million tons]	[trillion BTU's]
Petrochemical	0.13	4.0	0.05	0.04	6.25
Chemical	0.08	2.3	0.025	0.01	5.5
Other Manf.	0.07	2.2	0.025	0.01	5.0
Metal	0.05	1.8	0.02	0.01	2.5
Glass	0.07	2.0	0.02	0.01	3.0
Paper	0.02	0.05	0.002	.003	0.75
Total Savings	0.42	12.4	0.14	0.083	23

Energy Impact *(in Dollars)*

Impact by the Year 2020	
Energy Cost Savings *Vision Industry*	**Energy Savings [Million $/Year]**
Petrochemical	48
Chemical	28
Other Manufacturing	25
Metal	12
Glass	15
Paper	5
Total	**133**

Project Status Summary

Task ID	Milestone	Planned Completion	Actual Completion	Comments
1.0	Lab simulation of SAC			
1.1	Establish autoclave operation	April 2003	Completed	Autoclave and heaters are working satisfactorily
1.2	Develop tensile test rig	August 2003	Completed	
1.3	Simulate SAC in lab tests	Sept. 2004	On-Going	
1.4	Oxide growth experiments	Sept 2004	On-Going	
2.0	Material characterization			
2.1	Examine tubes with SAC	Sept. 2003	Completed (On-Going)	Various tubes were received and were examined at ORNL and IPST
2.2	Document inspection reports	Dec. 2003	NA	
2.3	Inspections to assess SAC rate	Sept. 2004	On-Going	
3.0	Evaluation of stress effects			
3.1	Document failure reports	April 2004		Some data was received and is being reviewed. Required information is missing in most cases
3.2	Deploy field strain gages	Dec. 2004	On-Going	
3.3	Model internal stress/strains		On-Going	
4.0	Environmental effects			
4.1	Assess key chemistry data	Mar. 2005	On-Going	
4.2	Deploy on-line monitoring	April 2005		
4.3	Document effect of cleaning	Sept. 2005		
5.0	Communication to US industry			Presentations were made at TAPPI and NACE meetings and appropriate Committees attended by US industry reps.
5.1	Technical review meetings	Every six months		Second meeting will be held in June 2003