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HIGH TEMPERATURE GAS SENSOR FOR COAL COMBUSTION SYSTEM

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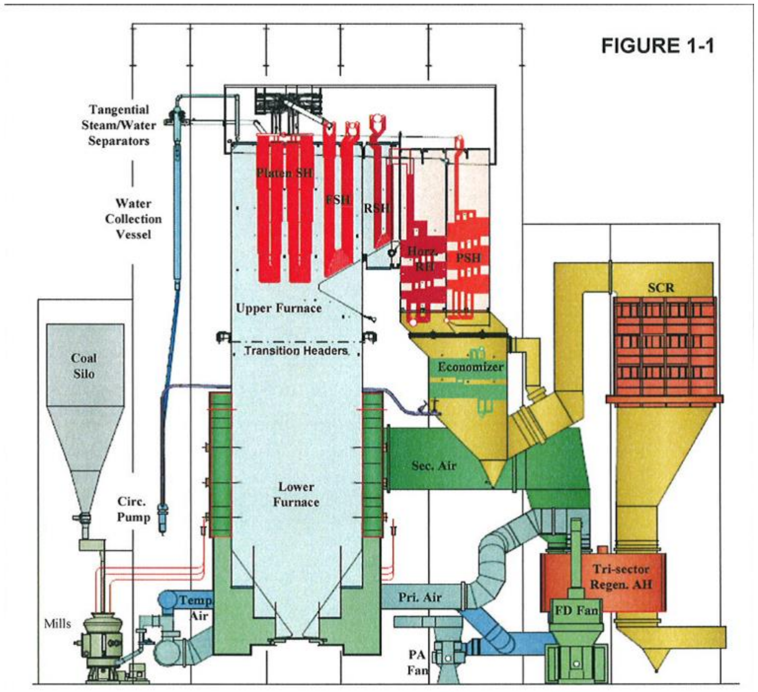
OUTLINE

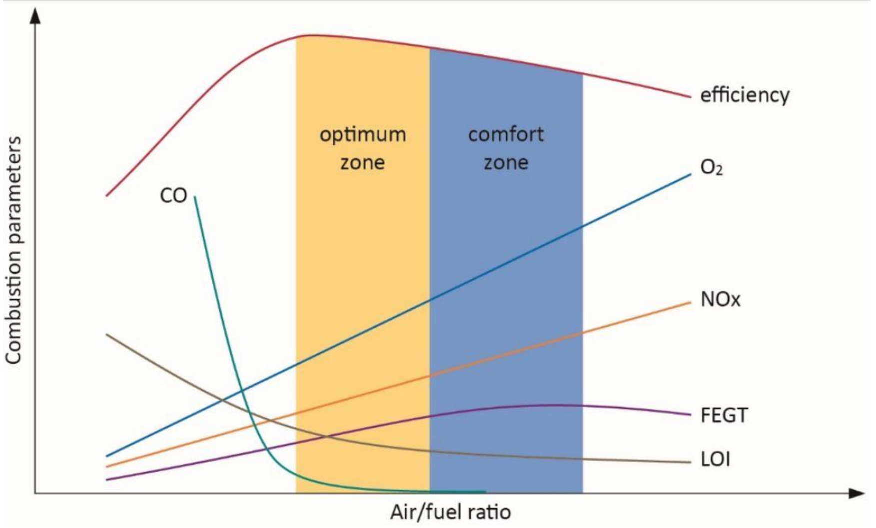
- Background & Scientific Approaches
- Project Objectives
- Project Team
- Planed Tasks & Milestones
- Research & Development Progress
- Summary

Background

Structure of a coal-fired power plant



The variation of key combustion parameters with air/fuel ratio



Efficiency ⟷ Optimization of combustion process ⟷ **Sensor**

Background

Requirements

In situ, online sensors

Accurate

Robust

Low cost

Direct measurement of combustible gases e.g. CO

Miniature and easy for deployment

targeting →

Challenges

High temperature

Corrosive conditions

Various kinds of gases

Poisoning gases and dusts

Local imbalance

High Temperature Gas Sensors

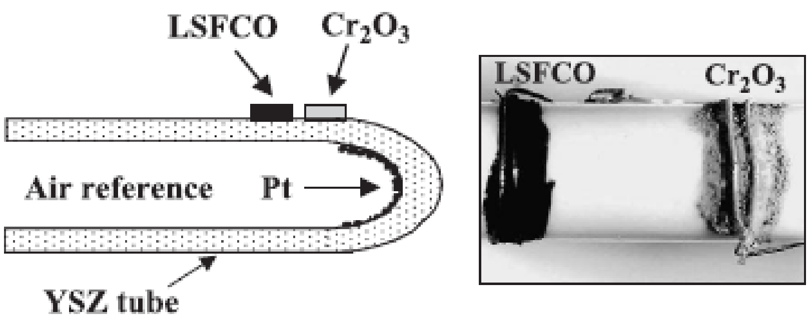
GC/MS, Infrared spectroscopy, Chemiluminescent etc.

SiC-base (Schottky diode) sensors – Silide formation

Physical properties based sensing (mass, dielectric constant, temp, surface stress etc.)

Electro-Chemical Sensors

- Potentiometric
- Amperometric



Nicholas F. Szabo, Prabir K. Dutta: Correlation of sensing behavior of mixed potential sensors with chemical and electrochemical properties of electrodes, Solid State Ionics 171 (2004) 183–190

PROJECT OBJECTIVES

(1) To develop an accurate, robust, high temperature oxygen sensor based on refractory, reliable, catalytically inactive materials capable of monitoring combustion in a coal-fired plant in real time to improve combustion performance;

(2) To investigate the feasibility and sensitivity of a new catalytic/non-catalytic sensor design to detect “oxidizable” target gases at high temperatures where other electrochemical sensors have failed;

(3) To test the basic components of the proposed sensor in a commercial, 700 MW power plant.

Project Team Member – Longview Power

Location	Monongalia County, near Maidsville, WV
Status	Operational
Commission date	2011
Owner(s)	Longview Power
Thermal power station	
Primary fuel	Coal and natural gas
Type	Steam turbine
Power generation	
Nameplate capacity	700 MW

- Officially a "zero discharge" power plant in WV
- Includes a new air pollution control system that results in emissions that are Among the lowest in the nation for coal plants.
- Emits less CO2 than most other coal plants because of its fuel efficiency

PLANNED TASKS & MILESTONES

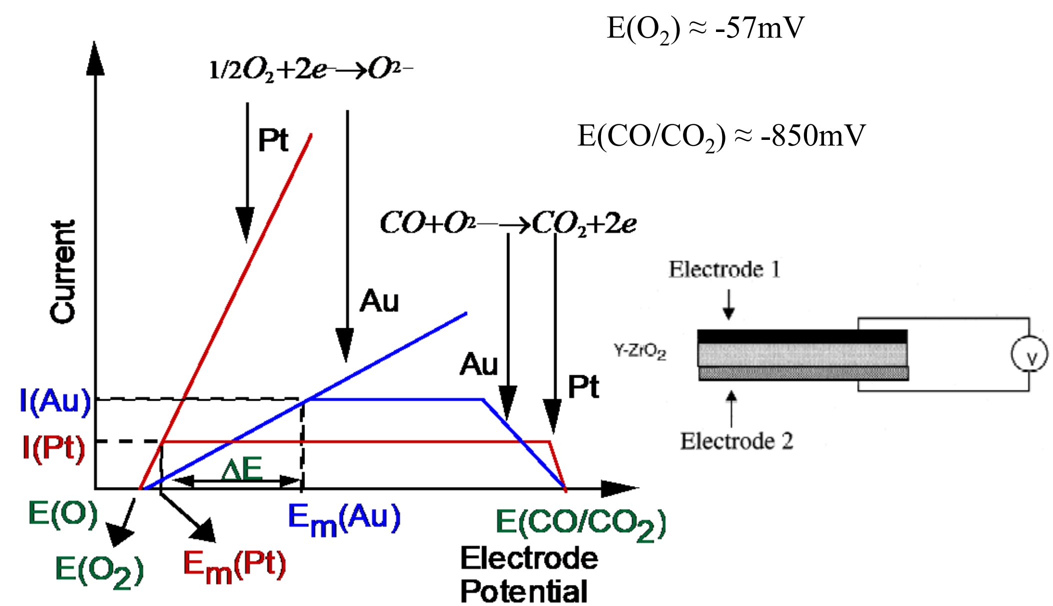
I.D.	Task	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1.0	Project Management	■	■	■	■	■	■	■	■
2.0	Sensor Development	■	■	■		■	■		
3.0	Sensor Packaging		■	■			■		
4.0	Lab-scale Sensor Testing		■	■			■	■	
5.0	Post-mortem Characterization			■	■			■	■
6.0	Electrochemical Mechanisms Investigation	■	■	■	■	■	■		
7.0	Sensor Testing in Utility Boiler							■	■

Task 1.0 Quarterly, annual, and final reports
Task 2.0 High temperature gas sensor with the temperature capability up to 1300^{o}C
Task 3.0 Packaging for the sensor developed by LANL in Task 2
Task 4.0 Library of performance matrix for the sensor in lab-scale power plant simulator
Task 5.0 Microstructures of high temperature gas sensor after lab-scale testing
Task 6.0 Verification of the electrochemical mechanisms of high temperature gas sensing on maximum reading and temperature-proportional signal.
Task 7.0 Library of performance matrix for the sensor in utility boiler & microstructures of high temperature gas sensor after testing

DECISION POINTS:

1. Q1 – Finish PMP
2. Q3 - Sensing ability (lab) <=800ppm CO concentration in a Po_2 range of 0.5-2% @ 1000C
3. Q7 – Sensing ability (lab) <=400ppm CO concentration in a Po_2 range of 1-3% @ 1000C

Current Mixed Potential Sensors



CO electrochemical oxidation kinetics

$$i_{CO} = 2FAD_{CO}\frac{C_{CO}}{d}$$

Oxygen reduction kinetics

$$i_{O_2} = i^o_{O_2}\frac{4F}{RT}(Em - E_{O_2})$$

Heterogeneous catalysis decrease CO available for electrochemical oxidation

Fernando H. Garzon, Rangachary Mukundan, **Eric L. Brosha**: Solid-state mixed potential gas sensors: theory, experiments and challenges, Solid State Ionics 136–137 (2000) 633–638

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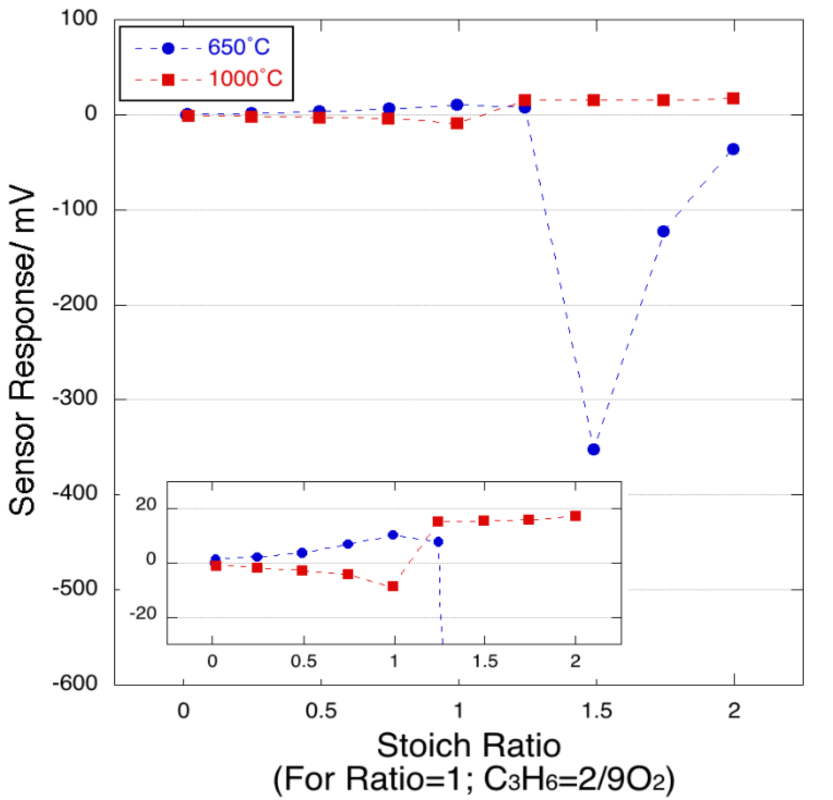
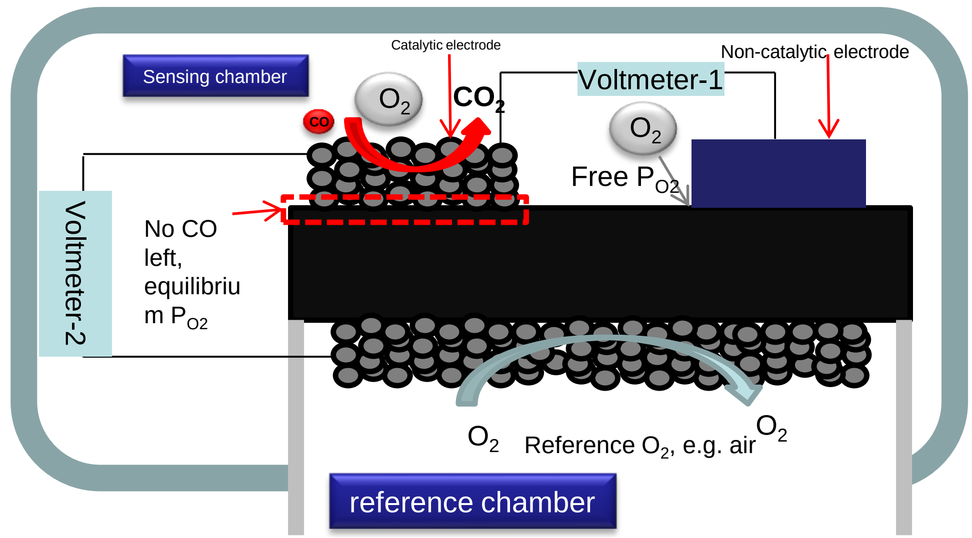
Sensor Development

Tapecast Pt|YSZ|LSCr
Sensor response to C3H6 around stoichiometry





$$\Delta E_1 = \frac{RT}{nF}\ln\left(\frac{P_{O2,Free}}{P_{O2,Eq}}\right) \qquad \Delta E_2 = \frac{RT}{nF}\ln\left(\frac{P_{O2,Eq}}{P_{O2,\,ref}}\right)$$

High Temperature Electrochemical Gas Sensors

NATIONAL ENERGY TECHNOLOGY LABORATORY

Determine reducing gas composition in a background of oxygen

Working principle

$O_2^{'} + 4e^{-} \Leftrightarrow 2O^{=}$	(1)	Oxygen reduction
$CO^{'} + O^{=} \Leftrightarrow CO_2^{'} + 2e^{-}$	(2)	CO electrochemical oxidation
$CO^{'} + \frac{1}{2}O_2 \Leftrightarrow CO_2^{'}$	(3)	CO heterogeneous oxidation

Current Mixed-potential sensors

- Mixed potential sensors
- $T_{op} < 600\ ^{o}C$
- High sensitivity to CO/HCs/NOx
- High durability
- Dense electrodes/Porous electrolyte

Proposed HT sensors

- Oxygen (Free vs Equilibrium)
- T_{op} up to 1500 ^{o}C
- Higher sensitivity as T$\uparrow$ and $P_{O2}\downarrow$
- High durability
- One dense and one porous electrode

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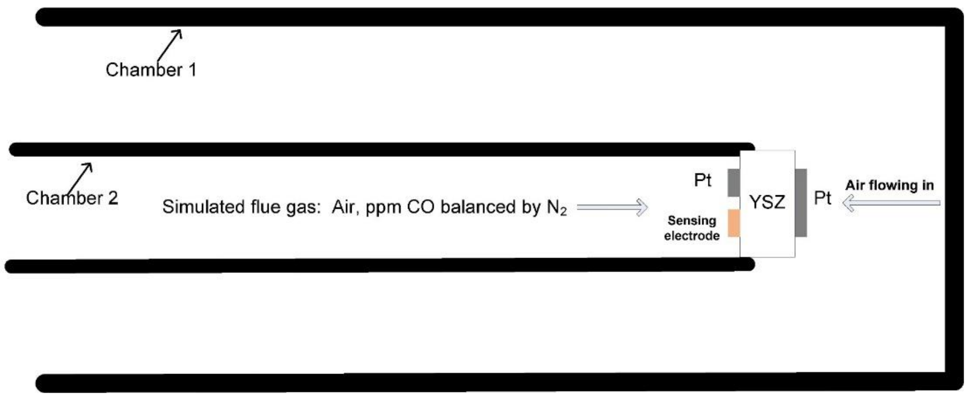
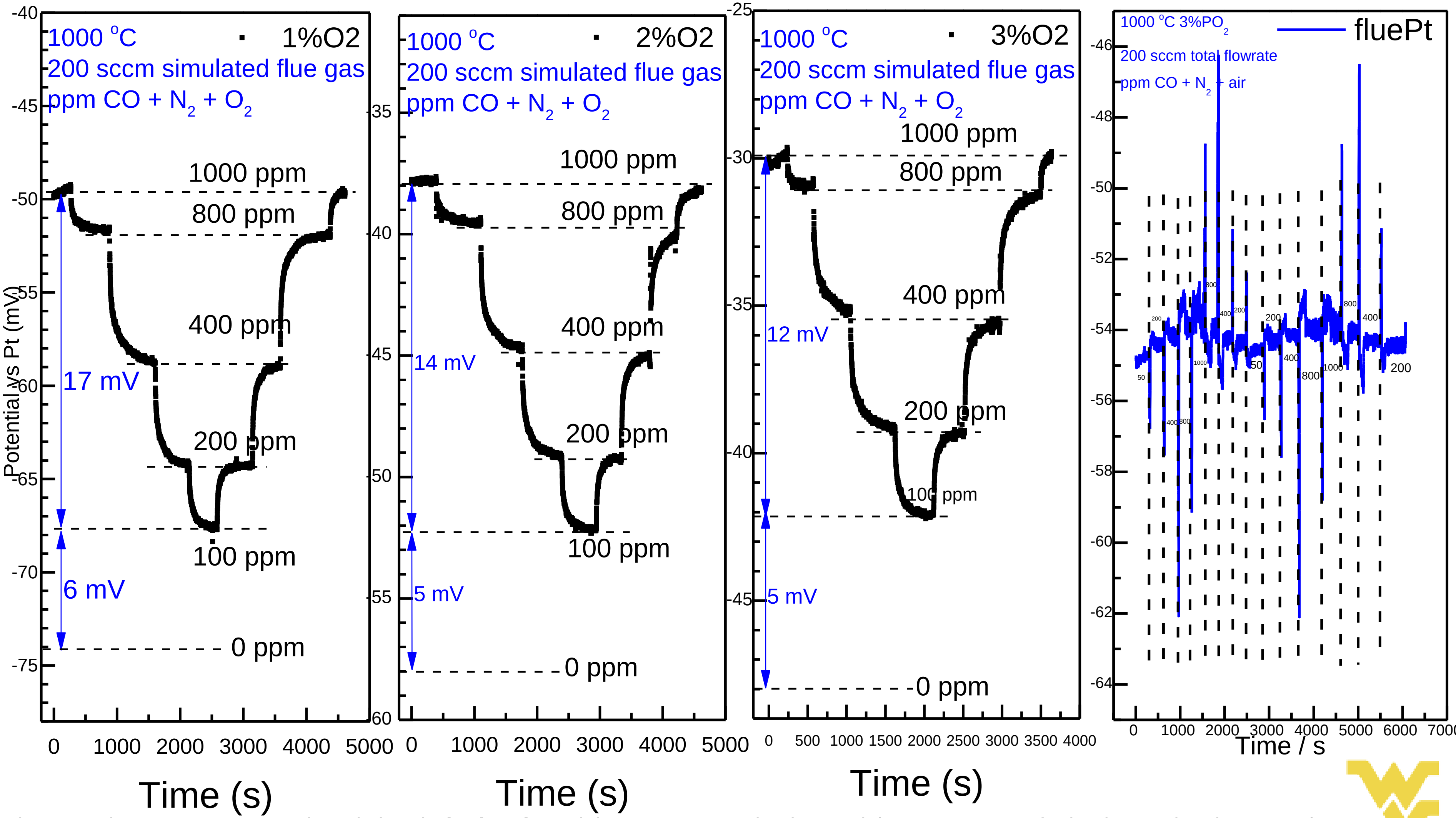
Sensor Development



Schematic illustration of the lab-scale testing for the sensor sample, two-chamber testing

Sensor Testing – Lab-Scale

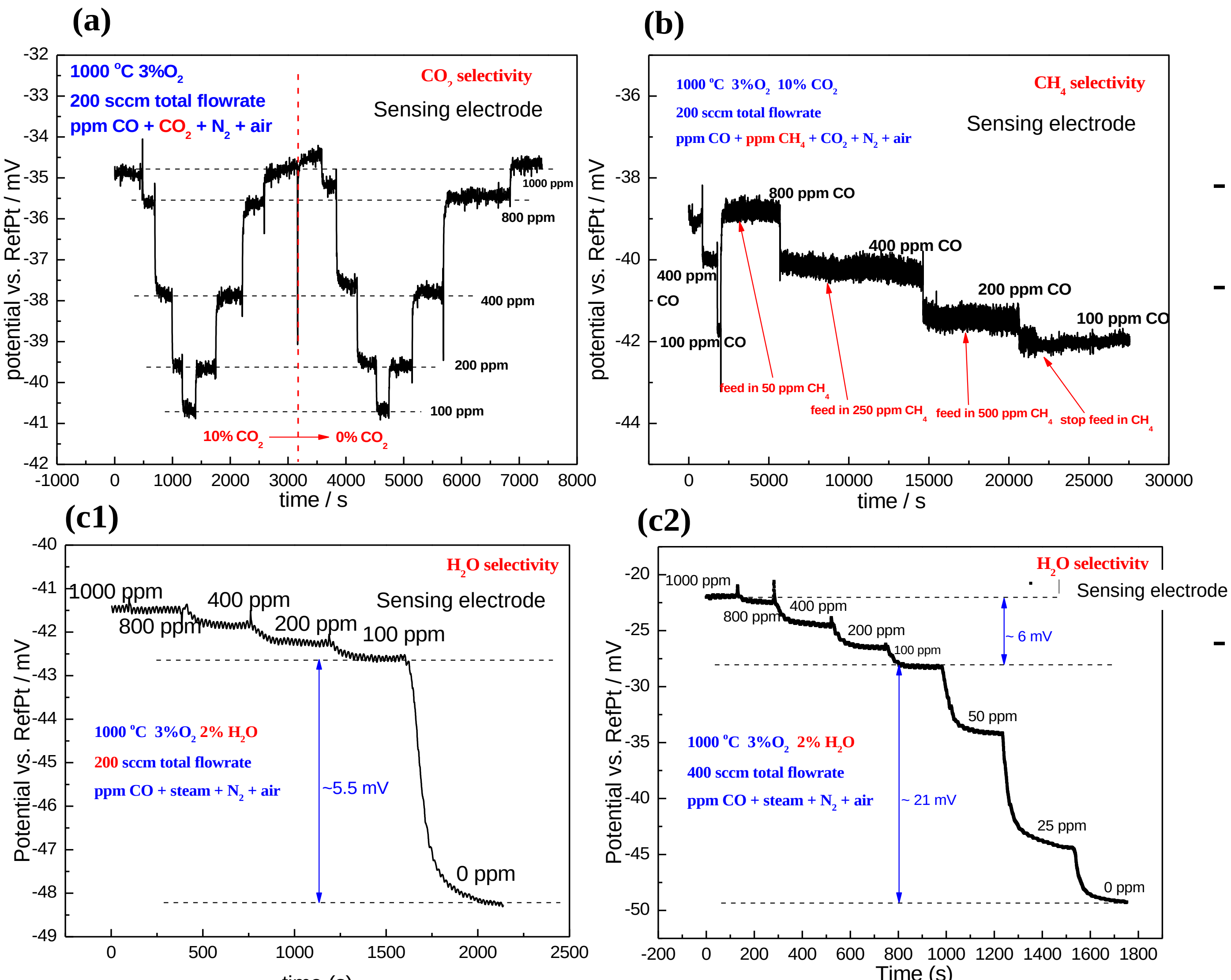
<u>3rd decision point – Demonstrate</u> Sensing ability (lab) <=400ppm CO concentration in a Po_2 range of 1-3% @ 1000C



Yi Wang, Liang Ma, Wenyuan Li, Wei Li and **<u>Xingbo Liu*:</u>** High-temperature mixed potential CO gas sensor for in-situ combustion control, *<u>Journal of Materials Chemistry A (2020) DOI: 10.1039/D0TA06320G</u>*

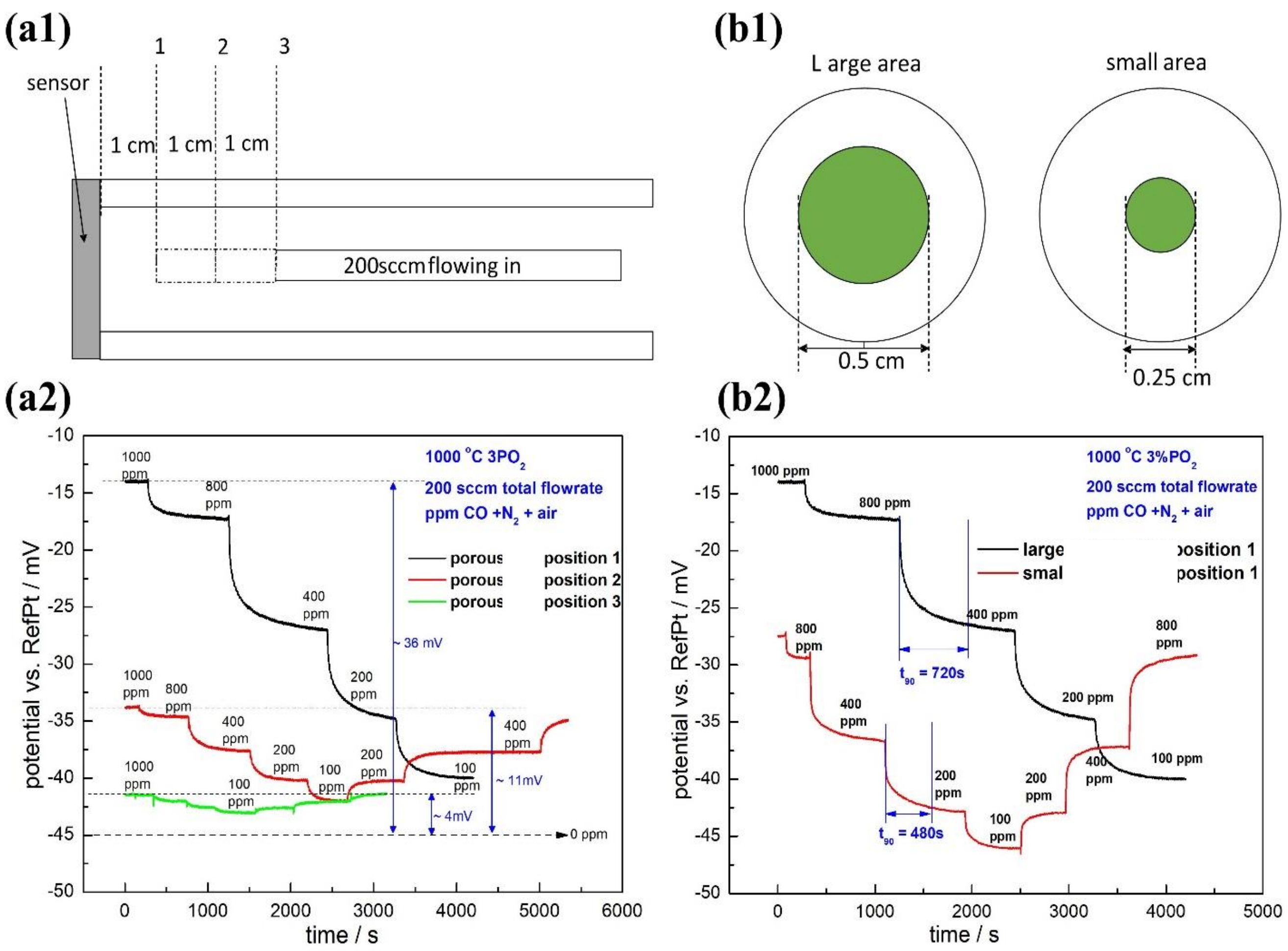
Sensor Testing – Lab-Scale

Selectivity tests for CO_2 CH_4 and steam



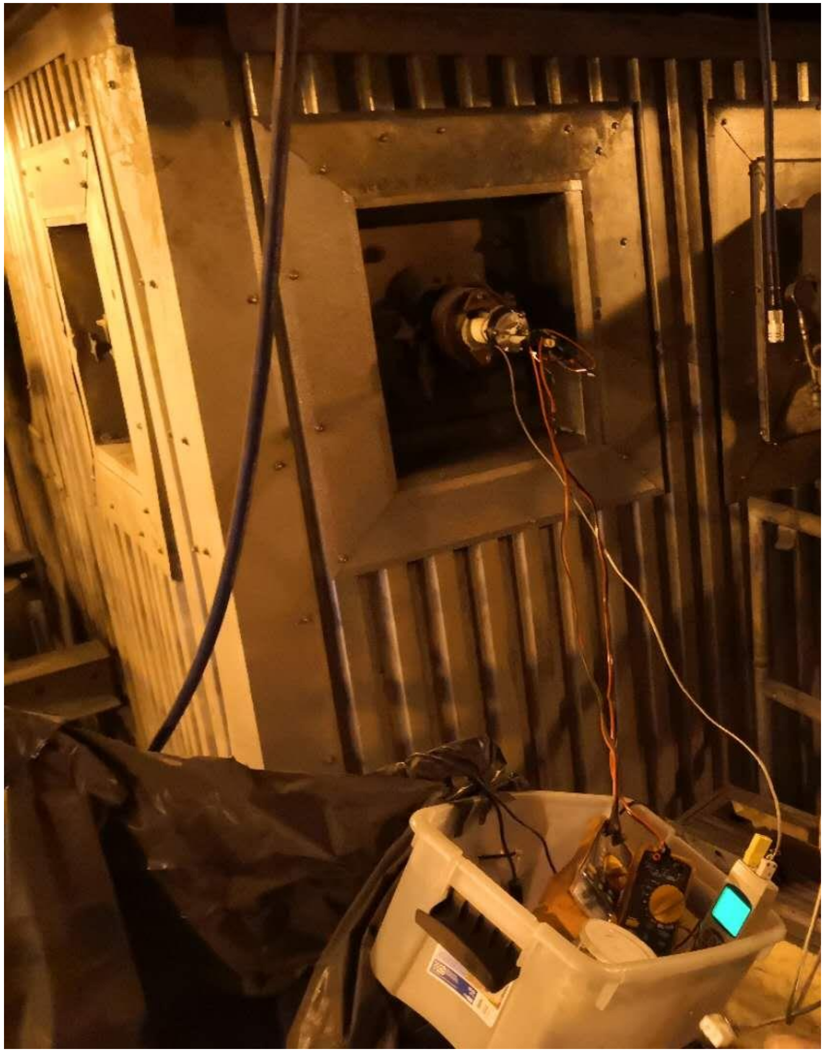
- Insensitive to CO_2
- CH_4 increases the signal oscillation, however doesn't change the medium value in each CO content.
- H_2O increases the sensitivity to CO in the low concentration range

Effect of Gas Transport and Electrode Area

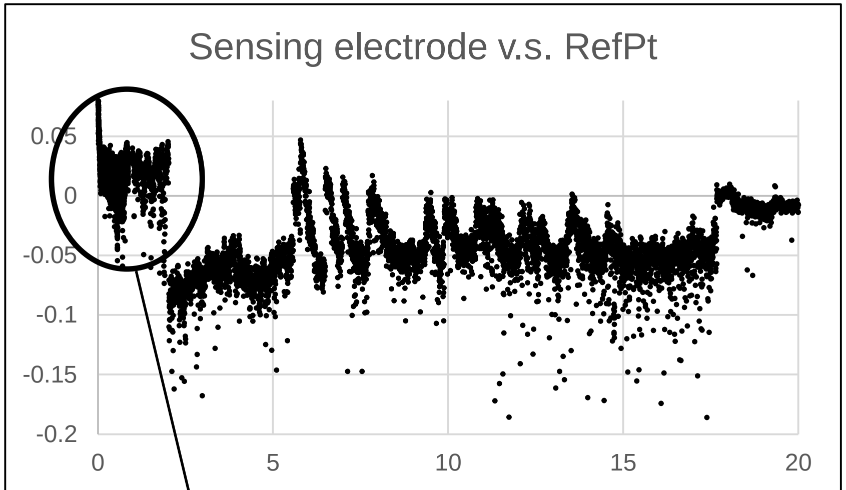


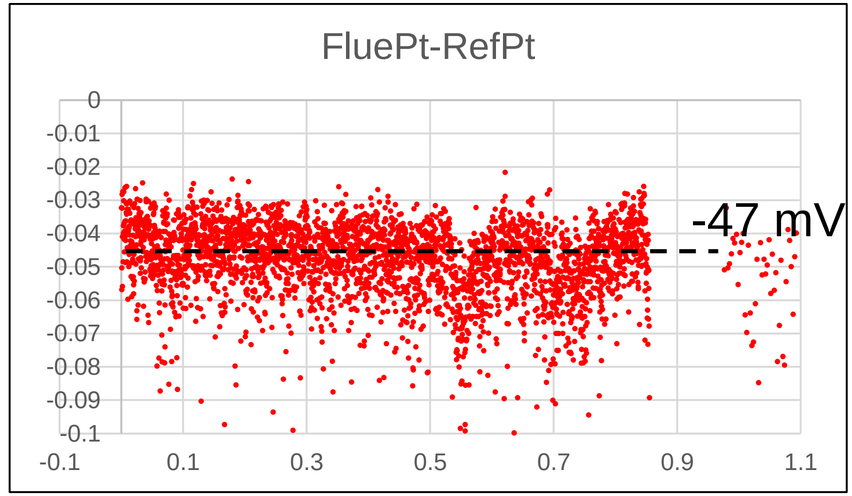
- Increased gas transport increases the sensitivity to CO
- Enlarged electrode area is beneficial to a increased signal. However, it's more related to the distribution of gas relative to the sensor electrode surface.

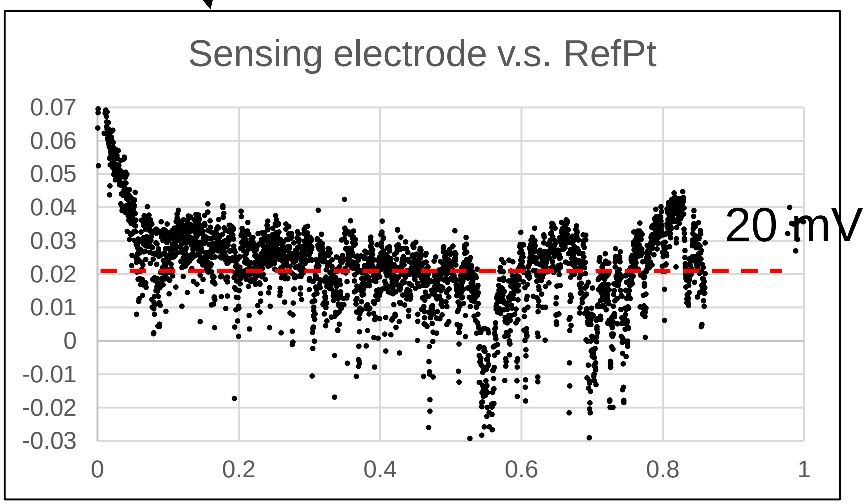
Utility Boiler Sensing Test @ Longview Power



Utility Boiler Sensing Test @ Longview Power







- Temperature: 950-975 ^{o}C
- Although testing 20 hours, only 1st hour data is valid, because of the connection problem
- FluePt-RefPt signal is -47 mV means 2.5%-3.5% O_2
- Sensing sensor-RefPt signal is 20 mV means CO content is 2000 ppm according to polynomial fitting

Utility Boiler Sensing Test @ Longview Power

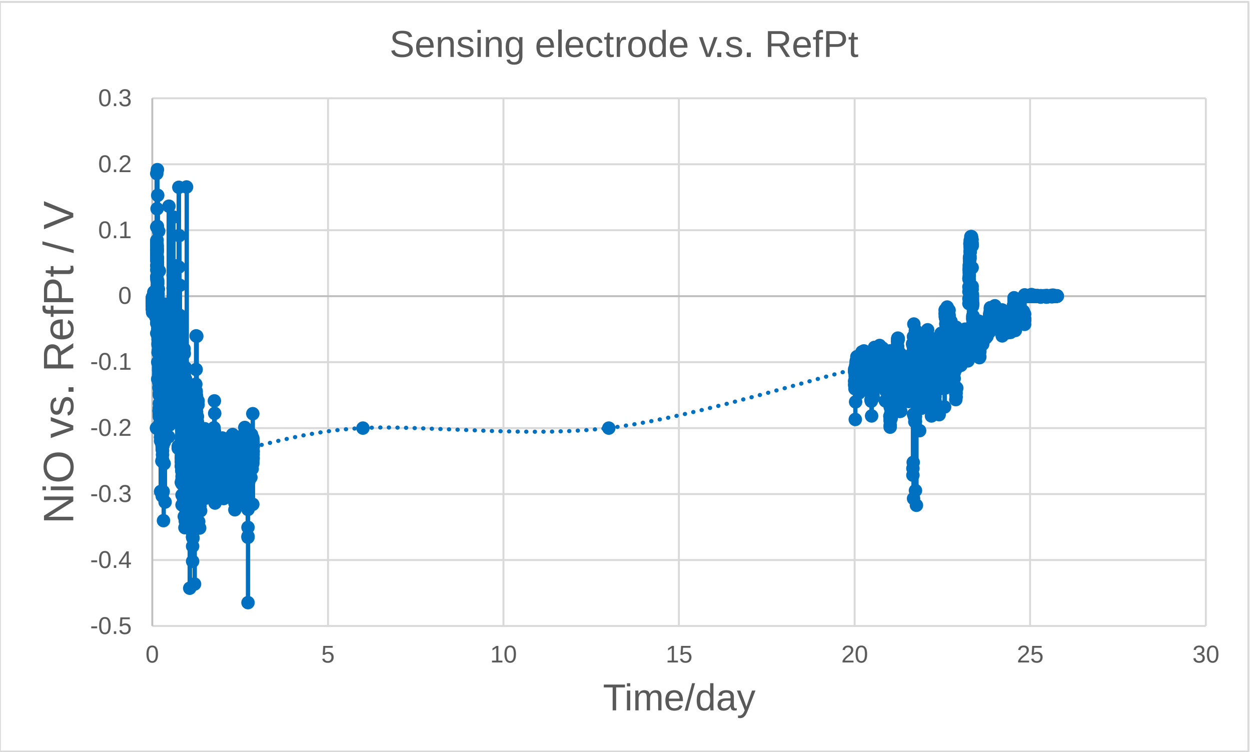
Images of the sensor after 20 h operation in the Longview's utility boiler.

- Dusts and ashes already covered the sensor top after 20-h field test

- The packaging method is good because the sensor is not broken and the sealing is good.

Utility Boiler Sensing Test @ Longview Power

2nd trial for 25 days



- 2-week data was lost because of the accidental shutdown of the power at that floor in Longview

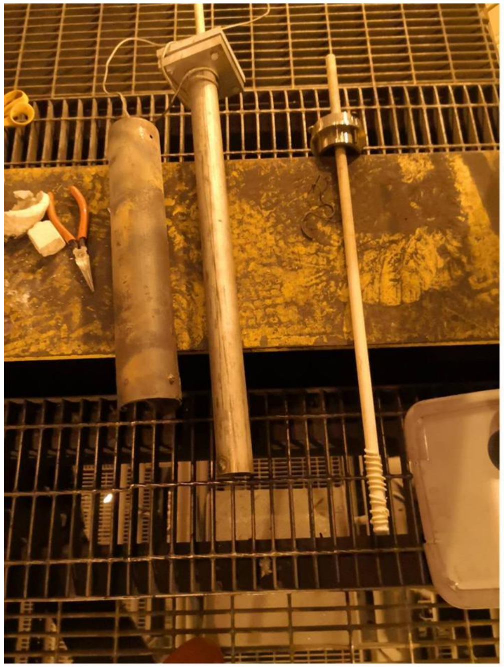
- After 25-Day test, the connection of electrodes were broken. Durability of sensor itself is good

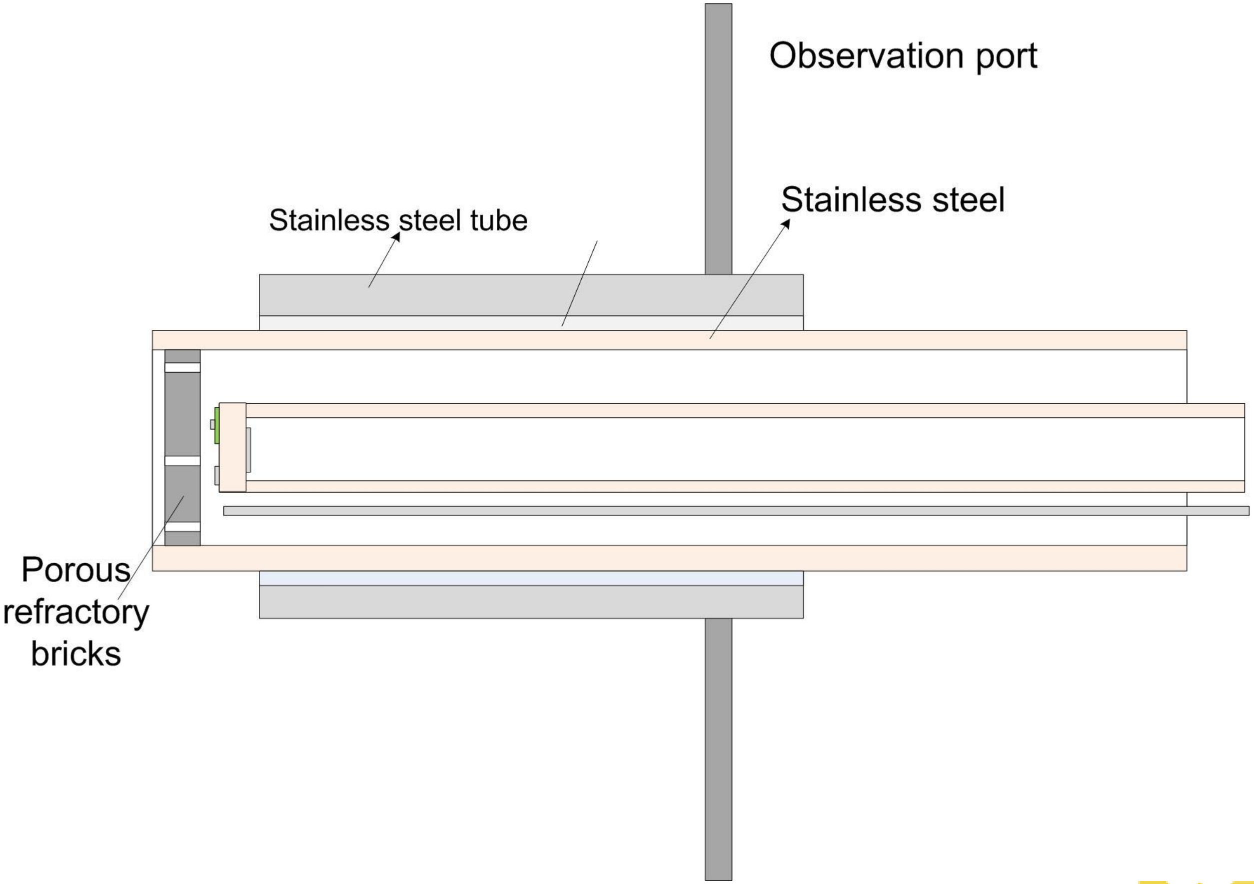
Utility Boiler Sensing Test @ Longview Power

- Dusts and ashes fully covered the sensor top after 25-day field test. That layer was very stiff and hard.
- The dusts are very aggressive because the Pt wires were already corroded.
- The packaging method is good because the sensor pellet is not broken and the sealing is good.

Utility Boiler Sensing Test @ Longview Power

- 3rd trial with a modified packaging.
  - Add porous refractory bricks to prevent the dusts and ashes contaminating the sensor.
  - Inner chamber is made of stainless steel as well, for a better robustness.

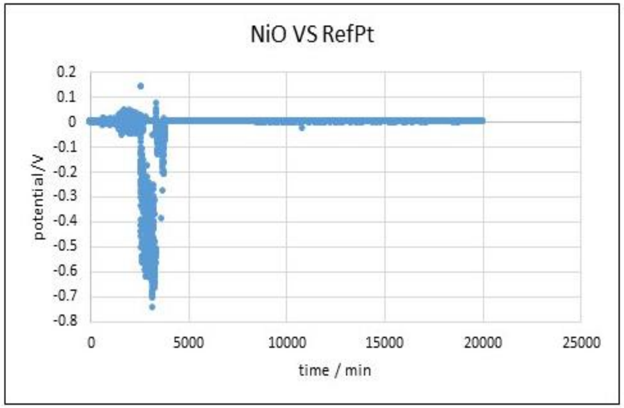




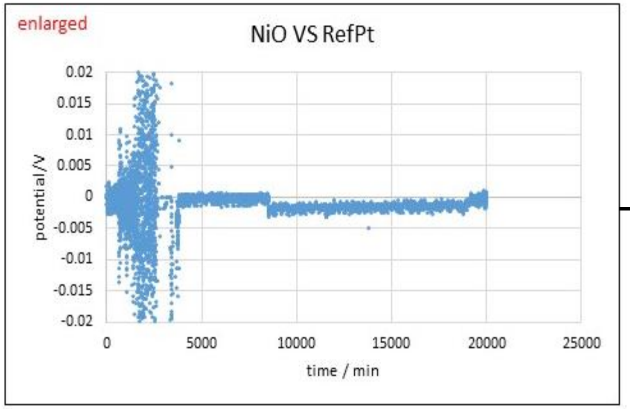
Utility Boiler Sensing Test @ Longview Power

2 weeks
930-950 C

Sensing electrode vs. RefPt



Sensing electrode vs. RefPt



- The huge oscillation is due to the violent atmosphere change in the sensor chamber as the flue ash started to build up on the sensor shield.

- We suspect that the ashes and dusts blocked the porous structure of the porous refractory bricks eventually, preventing the gas exchange between the boiler and the sensor chamber.

SUMMARY & FUTURE WORK

Major Progress To-Date

- Developed/Identified a promising sensing material
- Clearly met the 3rd Go/No-Go Target
- TRL-4
- Successful installation of the sensor test station in Longview boiler and obtained a good preliminary data and proved the durability

Future Work

- Mechanisms Investigations
- Packaging Development for a better performance in field test in Longview boiler

ACKNOWLEDGEMENT

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- NETL Project management team – John Rockey, Briggs White, Sydni Credle, Barbara Carney
- Our partners and team members