AOI [1] Advanced Manufacturing of Ceramic Anchors with Embedded Sensors for Process and Health Monitoring of Coal Boilers

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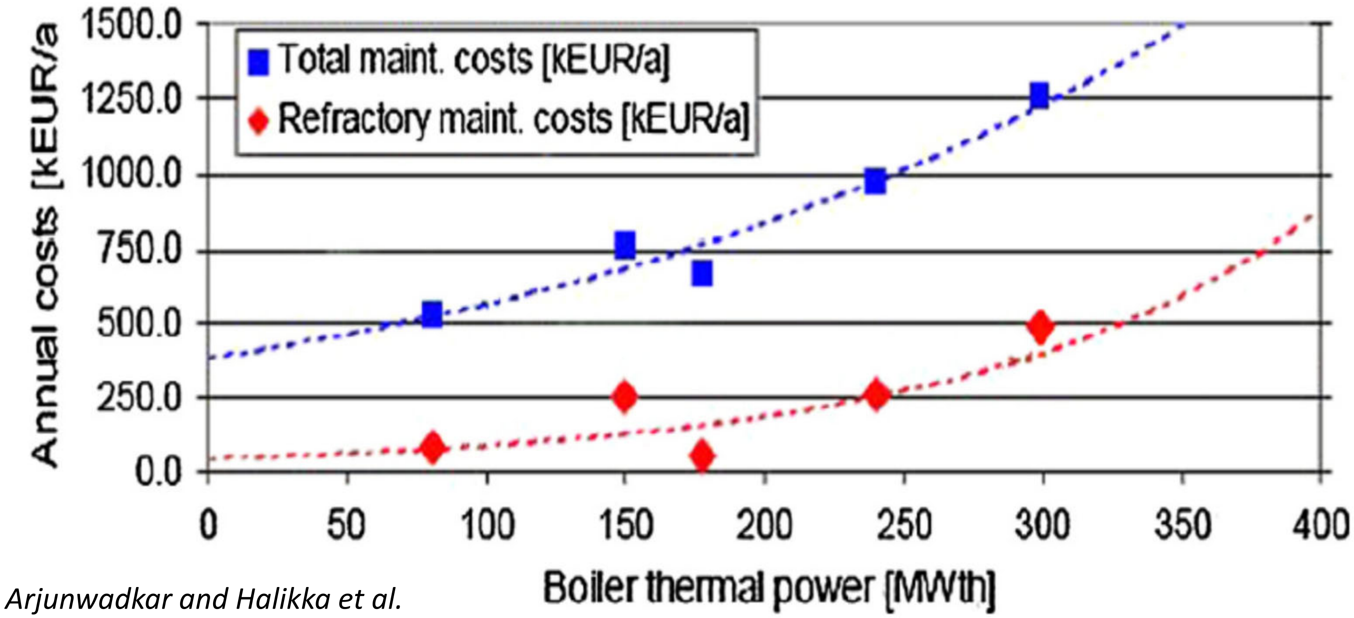
Background:

- Many different coal boiler technologies, but similar harsh environment requirements for the refractory.
    - High temperatures (~850-1500°C)
    - Erosion environment (by particles up to 6 mm OD and velocity of 30 m/s)
    - Corrosive environment (due to molten slag)
- Refractory maintenance is on average 25% of the annual total cost of coal boilers, and can reach as high as 40% of the total.



Arjunwadkar and Halikka et al.

Background:

- Boiler floors and walls are improvement locations due to the critical nature within the primary furnace (volumetric demand perspective).

- Boiler floors (and ash hoppers) stand out as locations that contribute the most to refractory maintenance cost.

- *Real-time* information regarding the following required:
  - Thickness loss, spallation, temperature and degree of thermal shock during operation.
  - Crack propagation and stress/strain development during dry-out of the monolithic liner.

*This information will provide precise operational and refractory monitoring and permit planning for refractory replacement.

Background:

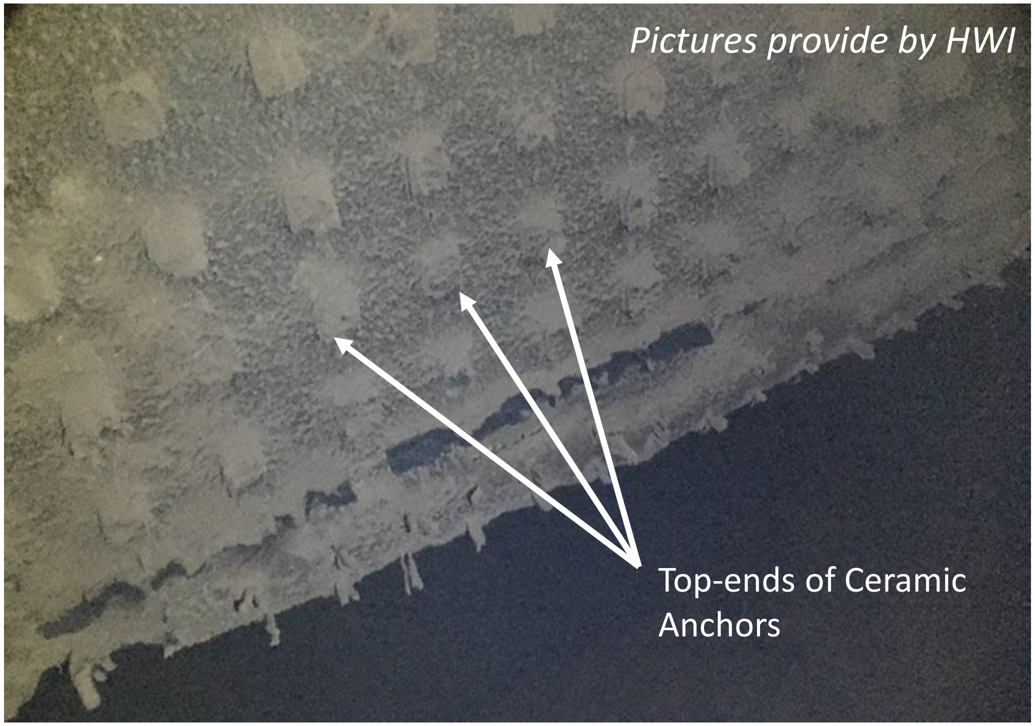


Figure description:

- ➢ Furnace wall after shut-down, where the wall was significantly eroded/corroded during operation.
- ➢ Anchors protruding through the "monolithic" refractory wall.

- "Monolithic" will be used to describe a seamless refractory that is casted/jetted into position (allowed to set, dry and densify during initial furnace operation).
- Ceramic anchors are used to hold the monolithic refractory into position and support its weight in the wall, roof, and floor.
- Properties of the anchor are different than the monolithic refractory (in picture); composition would be the same to produce a seamless connection to the main liner.

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The Technology:

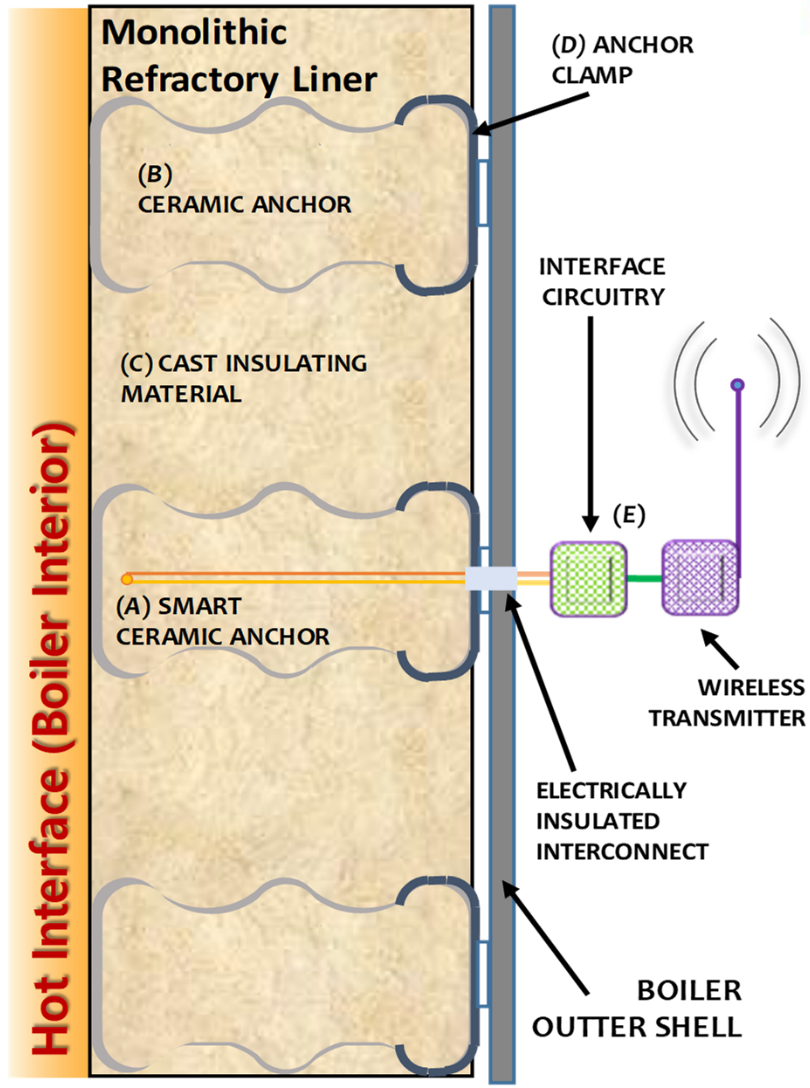
Item A= represents the "smart ceramic anchor", where an example thermistor sensor structure was formed within the brick

Item B= non-smart anchors may also be located within the casted monolithic refractory liner

Item C= Ceramic anchors are typically held into position by an array of anchor clips

Item D= Anchor clips (clamps) are used to allow limited movement during operation, but generally holds the anchor in position.

Item E= signal is acquired by the low-power electronics on the exterior of the boiler shell



Program Objectives:

The specific project objectives are as follows:

Task 2- Materials Development: Define high-temperature, stable conductive ceramics to be embedded within refractory anchors.

Task 3- Robotic Direct-Writing of Sensors: Develop 2D/3D direct-writing printing technology to pattern sensor circuit arrays into anchor refractory.

Task 4- Smart Refractory and Interconnect Development: Demonstrate the smart ceramic anchor with required properties and sensor signal for demonstration *(which includes interconnection strategy for wire/sensor connection).*

Task 5- Electronics/Wireless Development: Develop low power analog electronics and wireless communication hardware to efficiently collect the sensor signal at each processing unit and transmit data to a central hub for data analysis.

Task 6- Industrial Demo: Demonstration of entire smart anchor system within a coal boiler (or similar harsh-environment reactor system).

SUMMARY of TECHNICAL TASKS and MILESTONES

Task 2.0 – Fabrication and Characterization of the Conductive Ceramic Composites (Sabolsky)

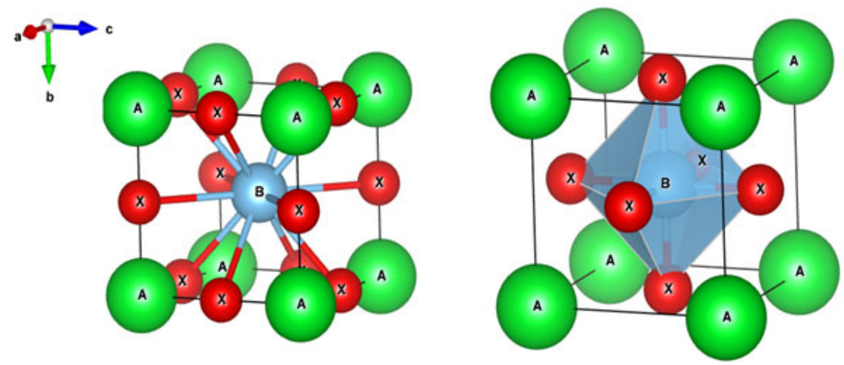
Task 2.0 Objectives:

- Synthesize conductive ceramic materials to be embedded within refractory with proper stability and conduction properties. (up to 1500°C).
- Evaluate electroceramic/refractory composites stability (refractory used in current HWI refractory products).
- Characterize electrical conductivity of the materials in a broad temperature range up to 1500°C to understand their electrical mechanism.
- Characterize chemical, microstructural and thermomechanical stability in various environments and temperatures.
- Prototype sensors fabricated and tested.

Tasks 2 Initial Electroceramic Sensor Material:

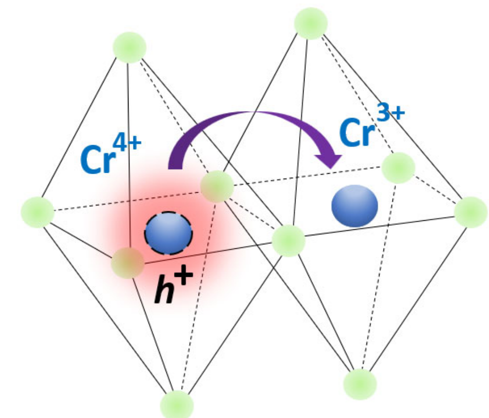
Strontium Doped Lanthanum chromite (LSC)
$La_{1-x}Sr_xCrO_3$

- High melting point (~2500 °C).
- Chemical stability under oxidative and reducing atmospheres.
- Compatibility (thermal expansion coefficients matching) near refractory materials (~10×10^{-6} C^{-1}).
- Electronic conductivity at high temperature(~1 S/cm).



A atom cubic unit cell *B atom cubic unit cell*

Perovskite Structure



Tasks 2 Introduction:

Sol-Gel Pechini Synthesis

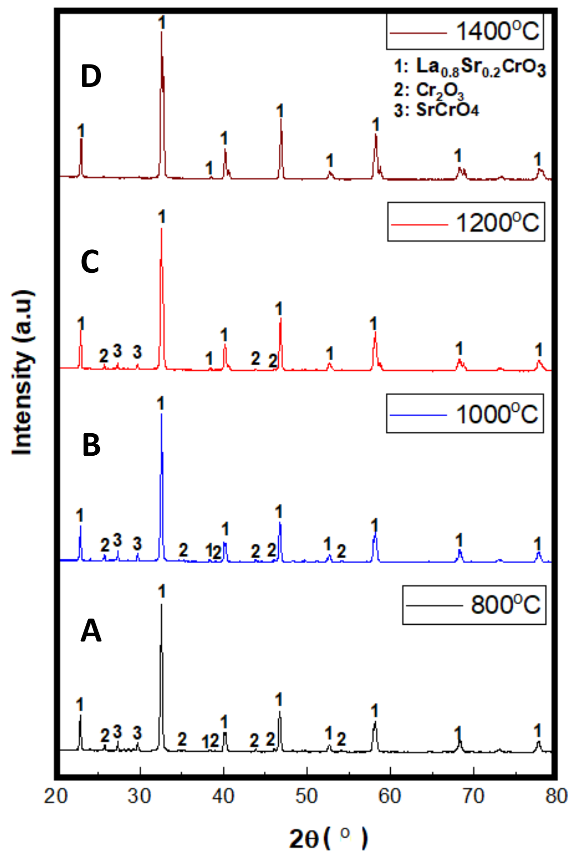
- Wet method based on citric acid reaction with metals from nitrates sources.
- Easy formation of ordered polymer that leads to high homogenous crystalline oxides.
- Crystalline single phase can be obtained at lower calcination temperatures (<1400 °C)
- *Low volume* of product.

Solid-State Synthesis

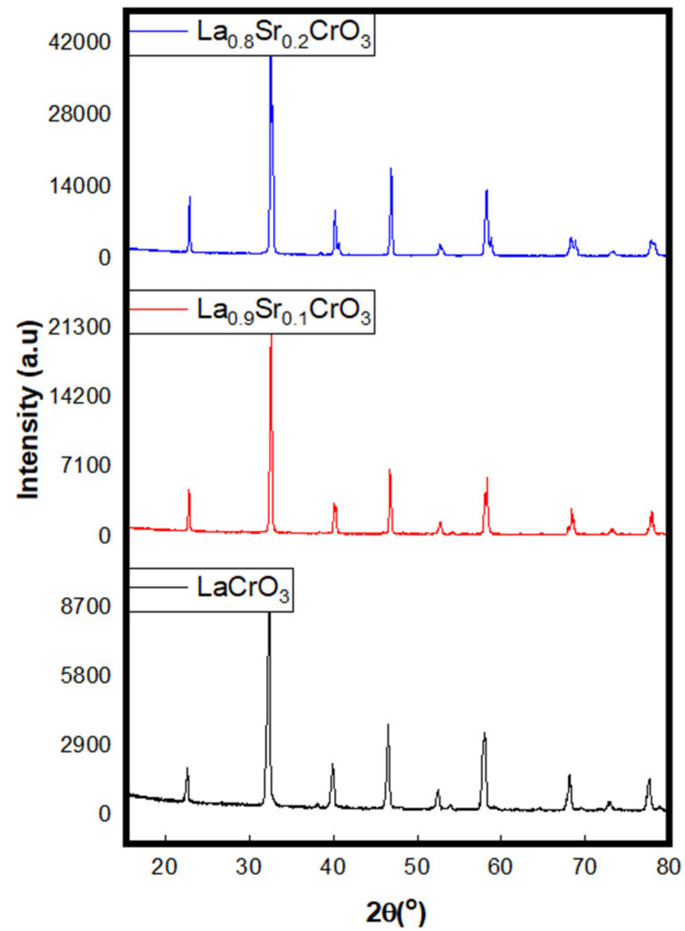
- Based on solid diffusion of metallic oxides or carbonates mixed/milled together in bulk container.
- Lower homogeneity in comparison with Sol-Gel (formation of oxides byproducts)
- Working calcination temperatures >1400 °C.
- *High volume* can be obtained easily.

LSC Pechini Sol-Gel Method Synthesis:

Precursors Calcination (800°-1400°C)



Strontium doping level (x= 0.0; 0.1; 0.2)



- **Single Sr doped Lanthanum Chromite phase is obtained at 1400°C.**
- **Cr2O3 and SrCrO4 phases are present at lower calcination temperature. The method is reproducible to obtain doped lanthanum chromites.**

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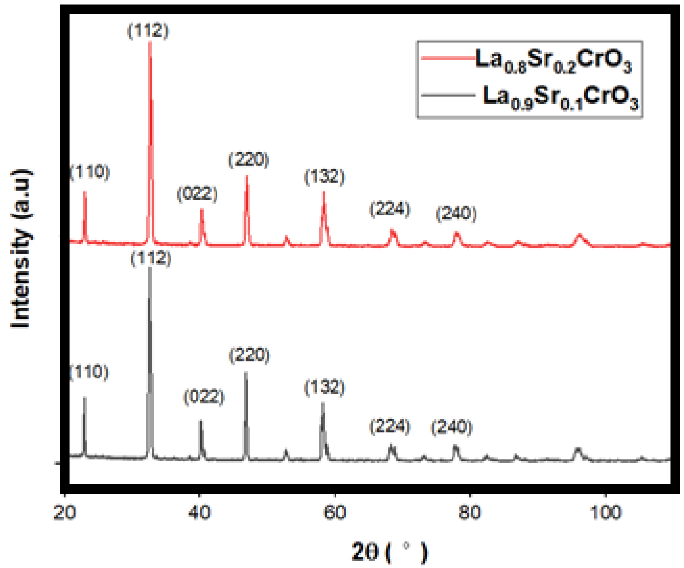
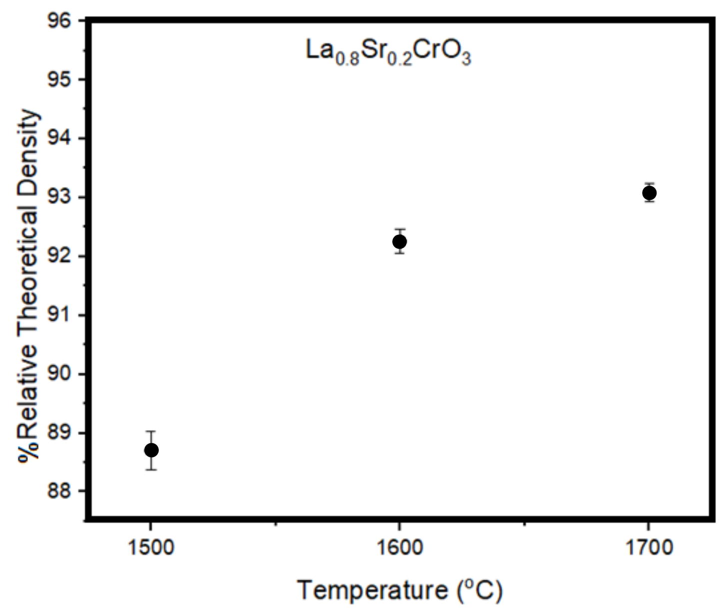
LSC Solid State Synthesis – High Energy Milling:

Strontium doping levels (x= 0.1; 0.2)



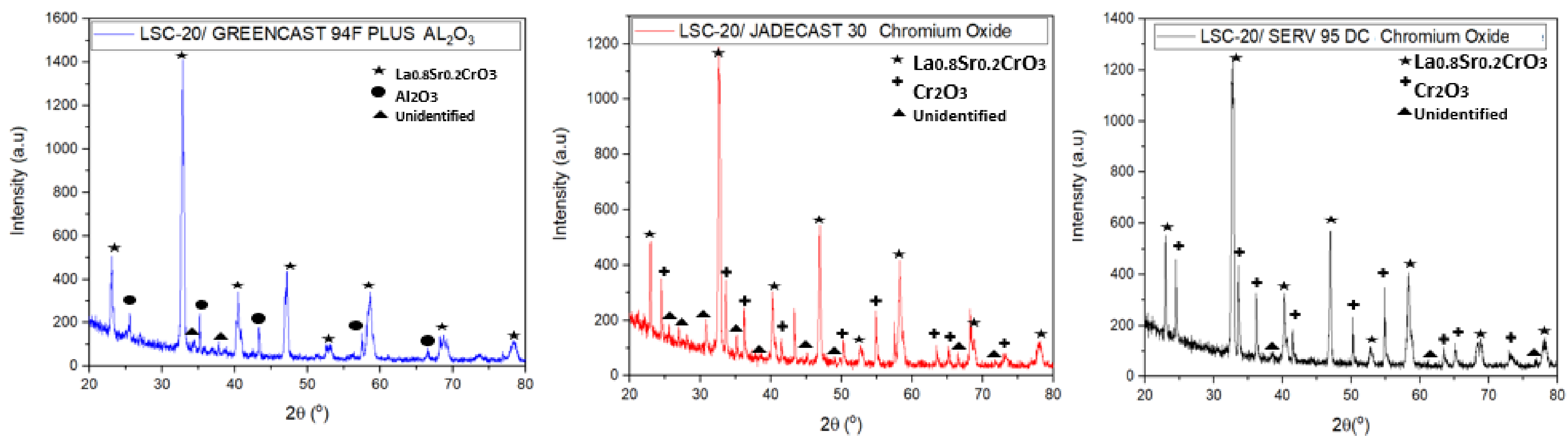
Sintering Temperature (1500°C-1700°C) Bulk density



- LSC powder materials can be obtained in single phase at calcination temperature of 1500°C, the Solid-State Synthesis is reproducible for various strontium doping levels.
- Maximum density achieved was 93% theoretical density at sintering temperature of 1700 °C for 4 hours in open air.

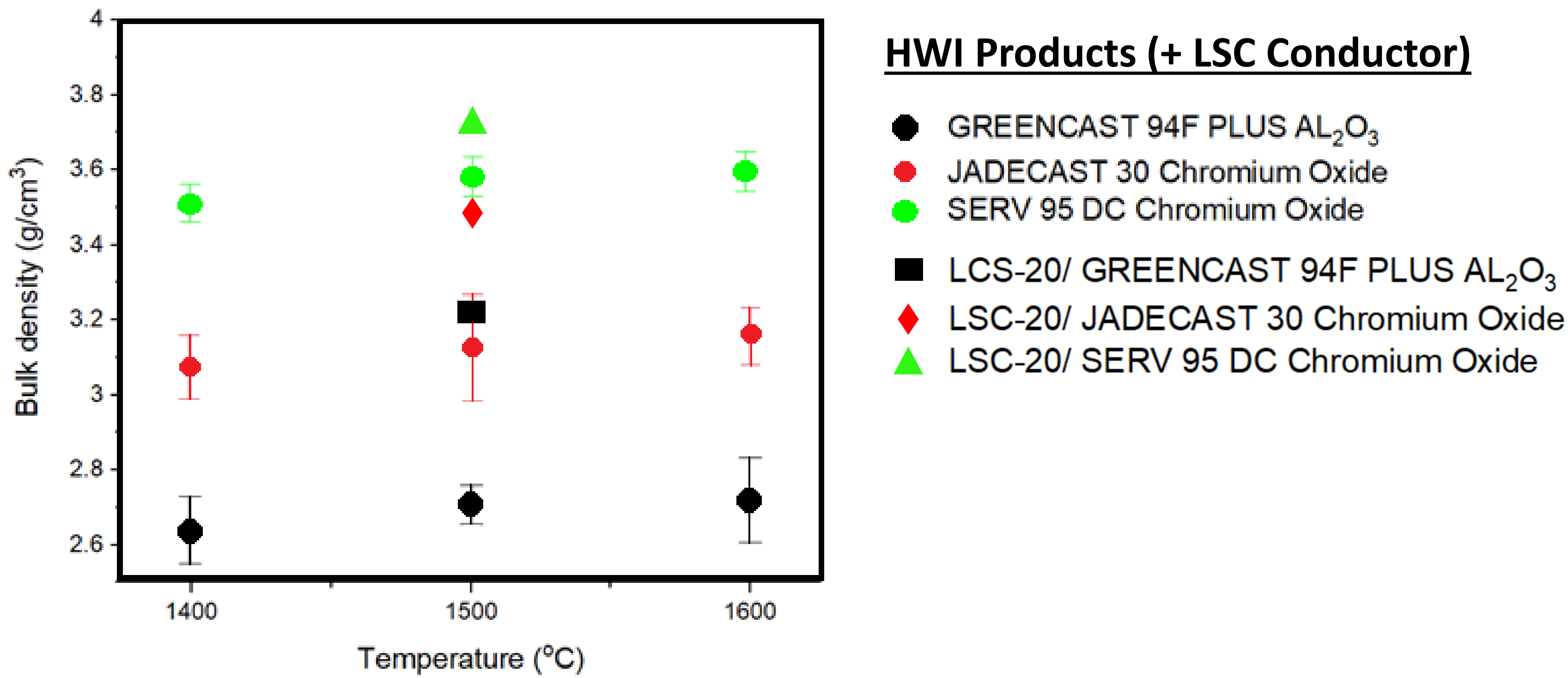
Phase Stability Studies of LSC/Refractory Composites:

PURPOSE: Study chemical/structural stability of LSC materials in composites mixtures with industrial refractory compositions, powders were mixed in a 50/50 volume ratio and fired at 1500°C.



- LCS-20/Refractory phase composites XRD data evidence not significant chemical modification of conductive phase (for three refractory compositions).
- Low intensity unidentified peaks are present in composite mixture, that can be related to reaction products between materials.

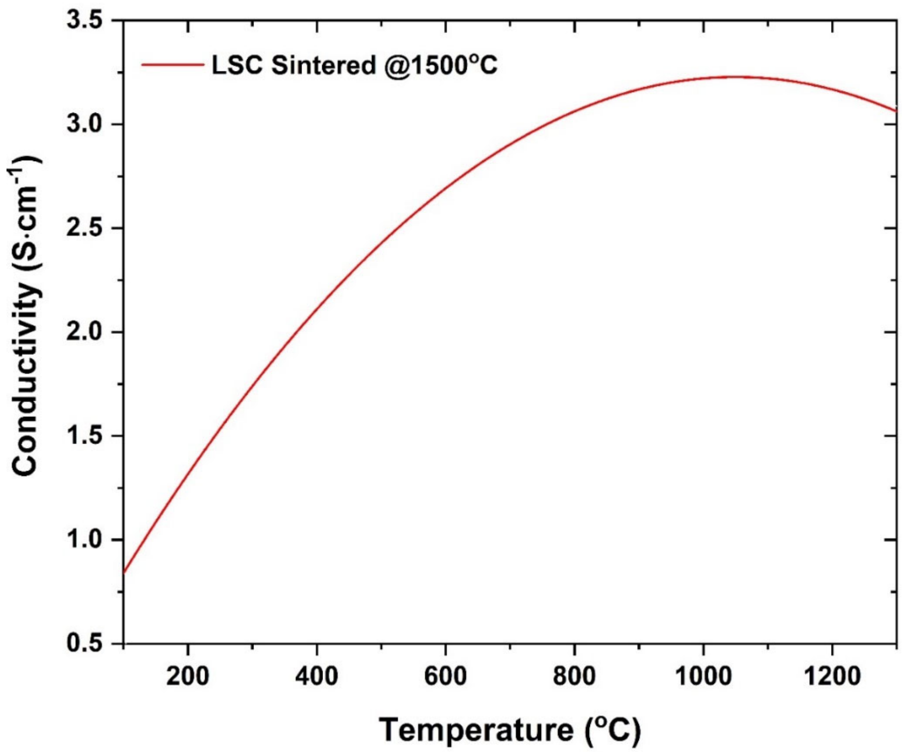
Sintering Studies of LSC/Refractory Composites:



- Single Al_2O_3 refractory powders sintered pellets show low average densities in comparison with theoretical value (3.95 g/cm^3), this can be related to particles size.
- Bulk Densities for LCS-20/ Refractory composites increase, however exhibits low densities in comparison with theoretical values.

LSC-20 Electrical Conductivity Measurements:

- Thick film conductivity (σ) with thickness ~35 μm was tested from 100 – 1400°C.
- σ = **~1 – 3.3 $S \cdot cm^{-1}$** within the temperature range.
- The increase in conductivity up to 1000°C and a slight drop ~1200°C shows degenerate semi conductor behavior of the LSC.



Task 2 Conclusions and Future Work:

- Single-phase LSC were synthesized by solid-state synthesis and Pechini sol-gel methods.
- LSC-20/refractory composites stability characterized by XRD patterns (showed very low secondary phase formation).
- Electrical conductivity for LSC-20 vs temperature measurements indicated proper conductivity to start fabricating embedded sensors.

Future Work:

- Synthesis of alternative doped-LC compositions to increase and control conductivity trend.
- Characterize electrical conductivity behavior studies at different working atmospheres (oxidizing and reducing).
- Thermomechanical studies of different compositions at different working atmosphere.
- Alternative materials and designs will be investigated to prevent the reaction between doped-LC and refractory.

Task 3.0 – Direct-Writing of Refractory and Sensor System (Sierros)

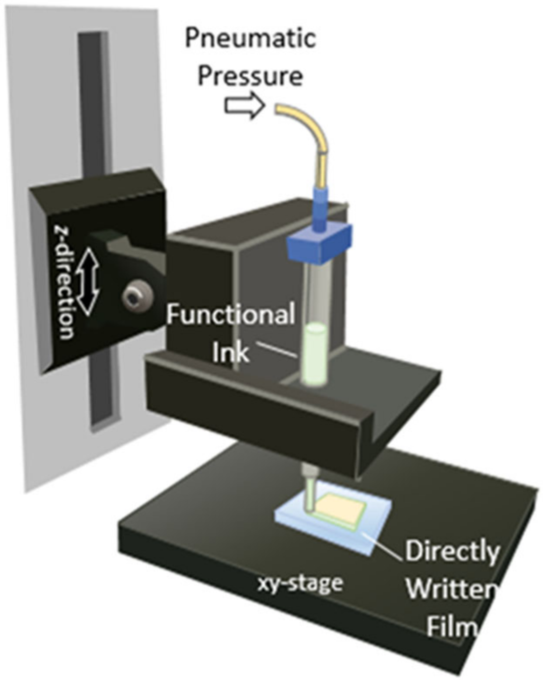
Task 3 Objectives:

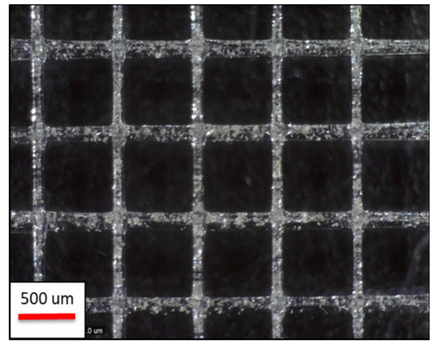
- Ink formulations will be fabricated within a permissible surface tension and viscosity range for direct-writing.

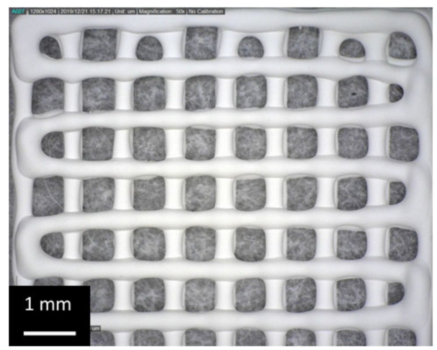
- Direct writing deposition, drying, and thermal post-processing will be defined, which includes methods to control wetting and drying characteristics of the deposited composite solutions (for both refractory and sensor circuit formulations).

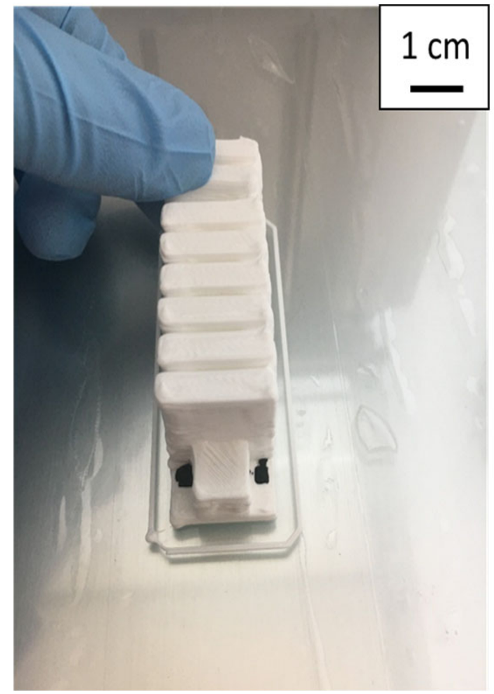
- Ink formulations, direct writing parameters (printing nozzle shape and size, writing speed, extrusion pressure), drying procedures, and post-processing temperatures will be included as variables, and printing fidelity will be characterized by optical, SEM and AFM microscopy

Direct Ink Writing Process Overview:





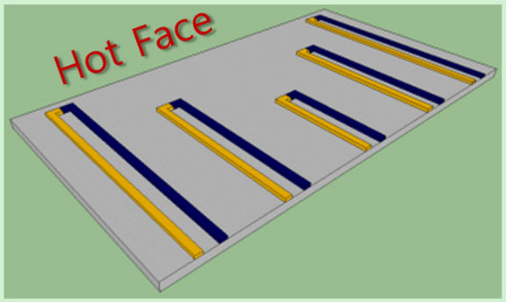




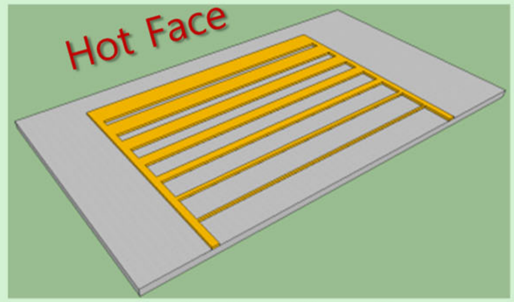
- Nozzle-based extrusion of viscoelastic inks
- Facile multimaterial printing of ceramic, polymeric, and soft materials

- 3D Printing of bone scaffolds, ceramics, and soft robots at WVU

Proposed Smart Refractory Sensor Designs:

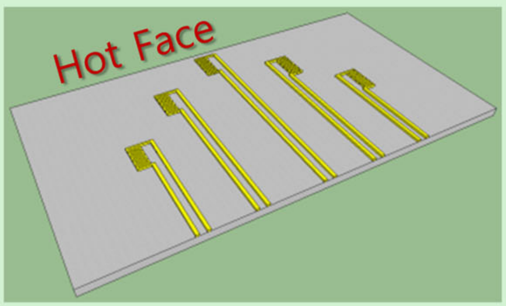


Thermocouple/Thermistor

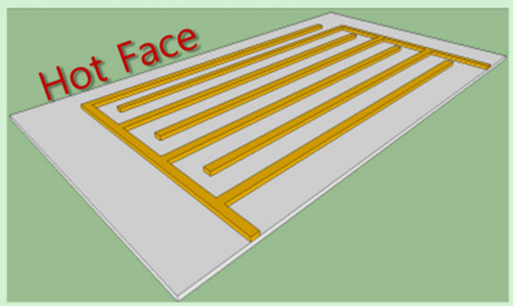


Resistive Circuit

Temperature	Spallation



Strain Sensor (Rosette)



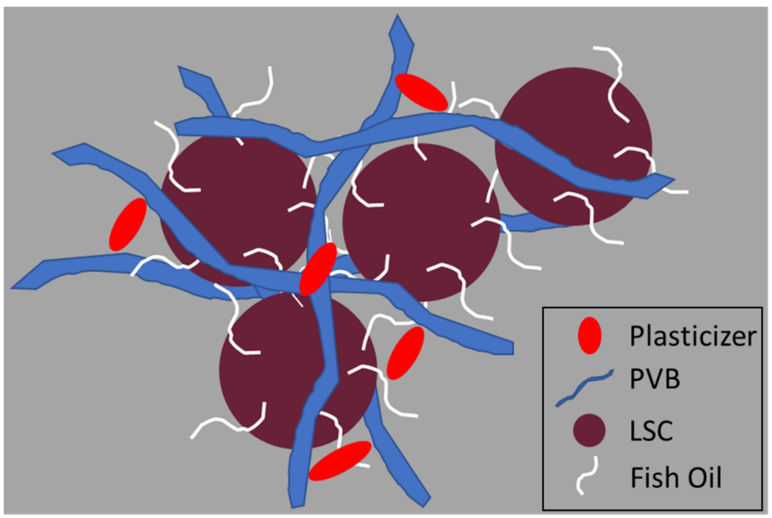
Capacitive Sensor

Stress/Strain

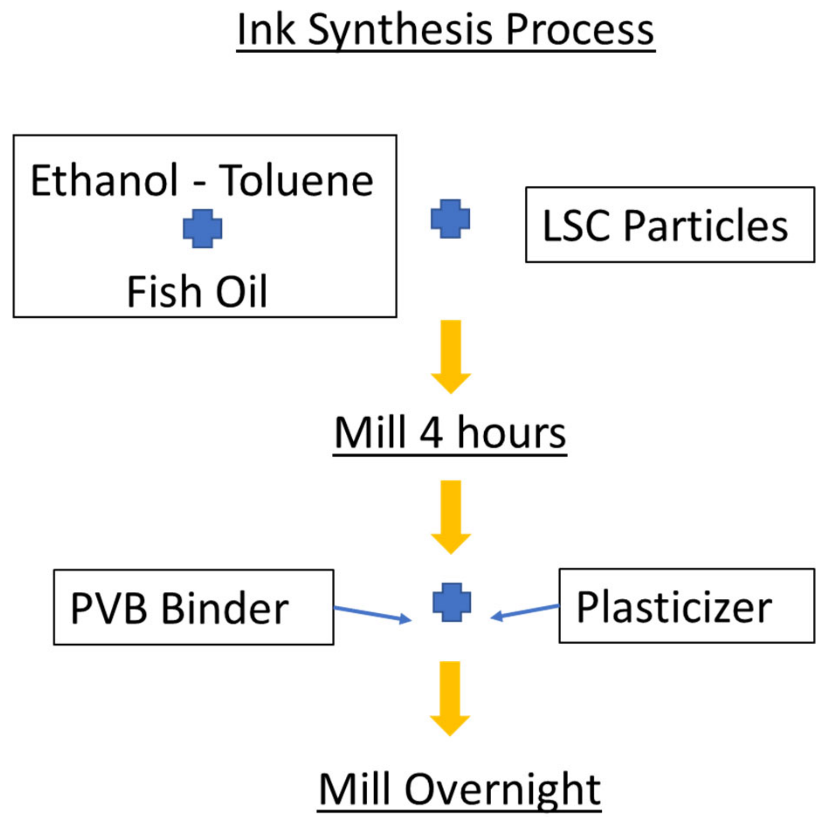
- 2D and multimaterial designs highly compatible with DIW process
- Temperature monitored via LSC thermistor arrays and multimaterial thermocouples

LSC Ink Composition and Synthesis:

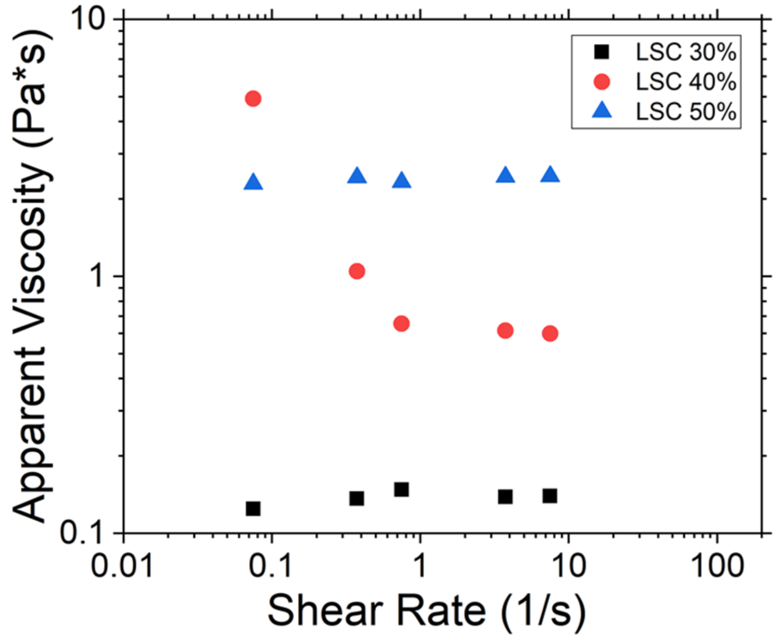
- High particle loading achievable
- Similar polymer and solvent systems as substrate provide strong adhesion



LSC ink schematic. Fish Oil acts as a dispersant, and PVB the matrix material. Ethanol – Toluene cosolvent system (gray) prevents nozzle clogging, while enabling high resolution features.

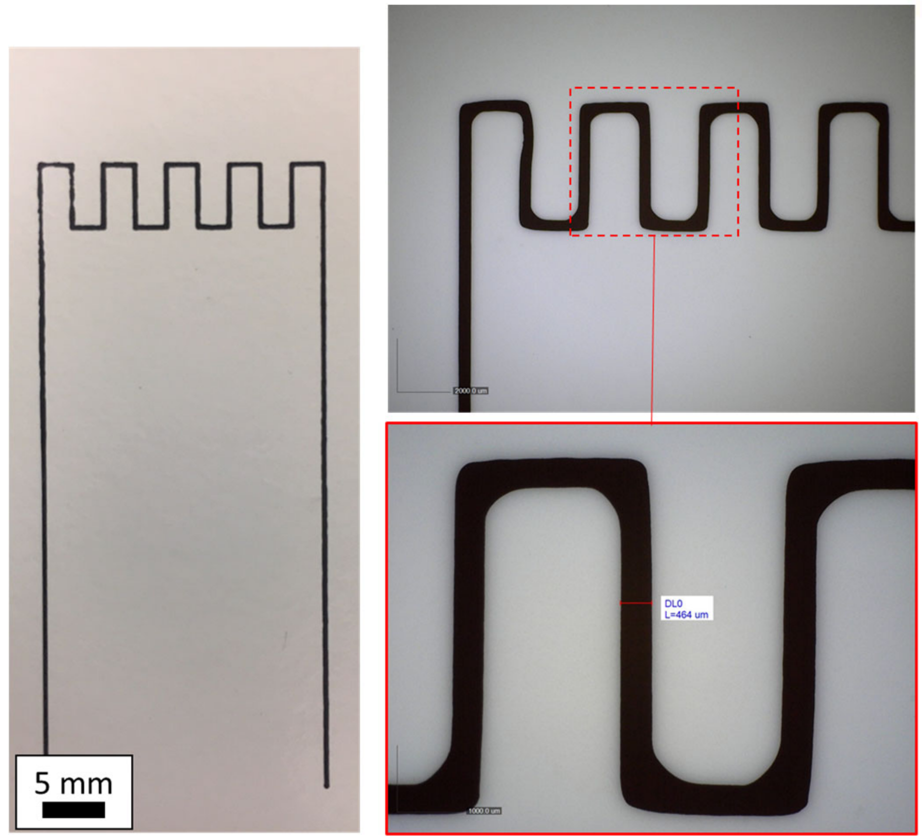


LSC Ink Rheology and Printing:



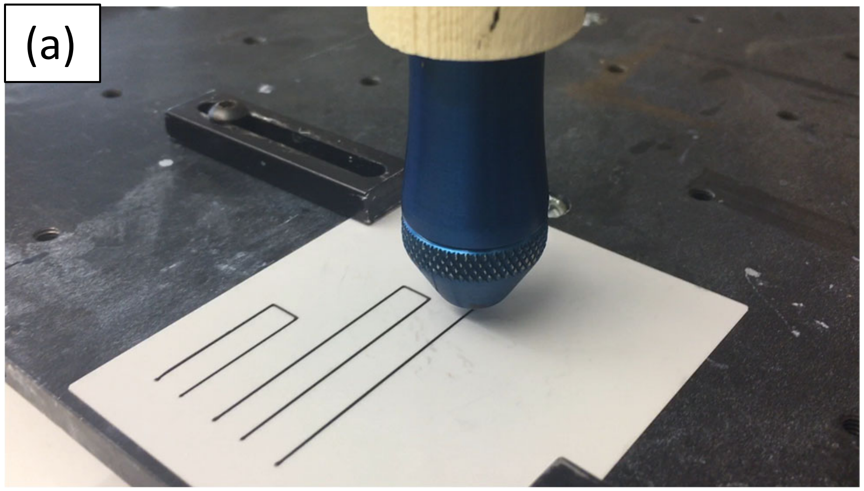
Apparent viscosity vs. shear rate. Percents represent solids loading

- Rheological properties tailorable through particle loading
- Shear thinning inks typically ideal for DIW

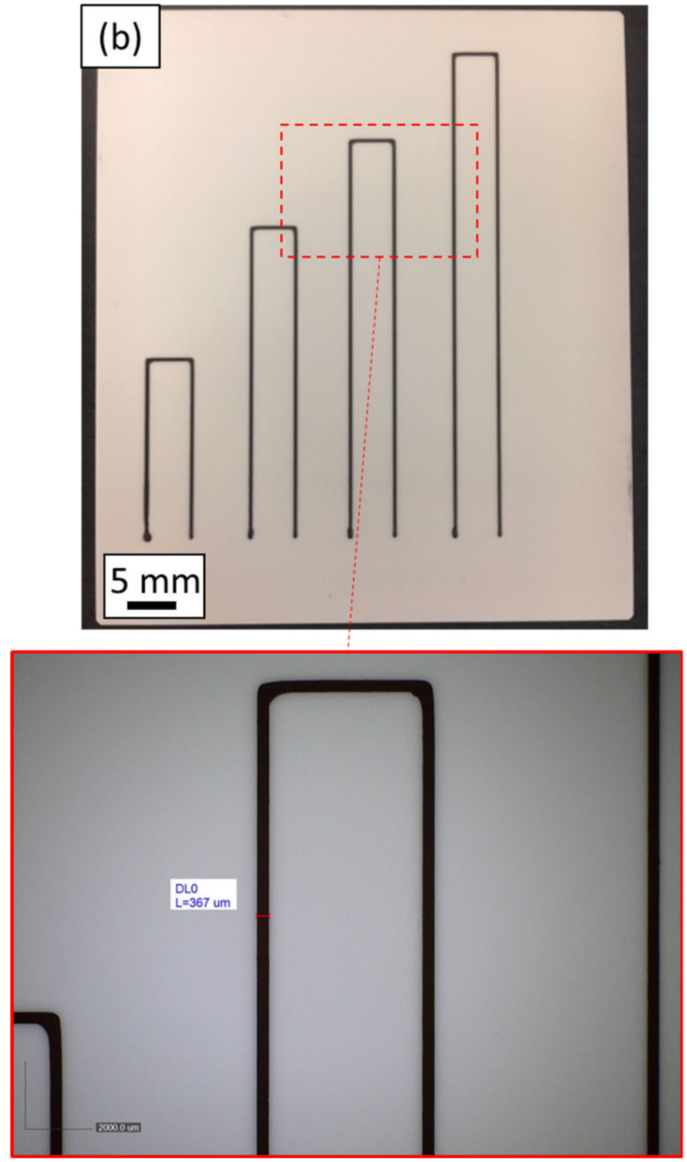


Strain gauge printed using LSC 40% ink from a 100-um nozzle on YSZ tape and alumina. The high wettability allows for strong adhesion, while cosolvent system provides high resolution printing.

Direct Ink Writing of Thermistor Array:



a) Direct ink writing of thermistor array (video). b) Optical image of printed array detailing approximately 400 um features.



- Ink printed in ambient conditions from 100 µm nozzle
- Sensor dimensions may be tailored to achieve desired electrical properties

Task 3 Conclusions:

- 3D printable LSC inks with high solids loadings have been synthesized
- Ink rheology may be tailored through varying the solids loadings to achieve printable inks and high-fidelity features

Future Work:

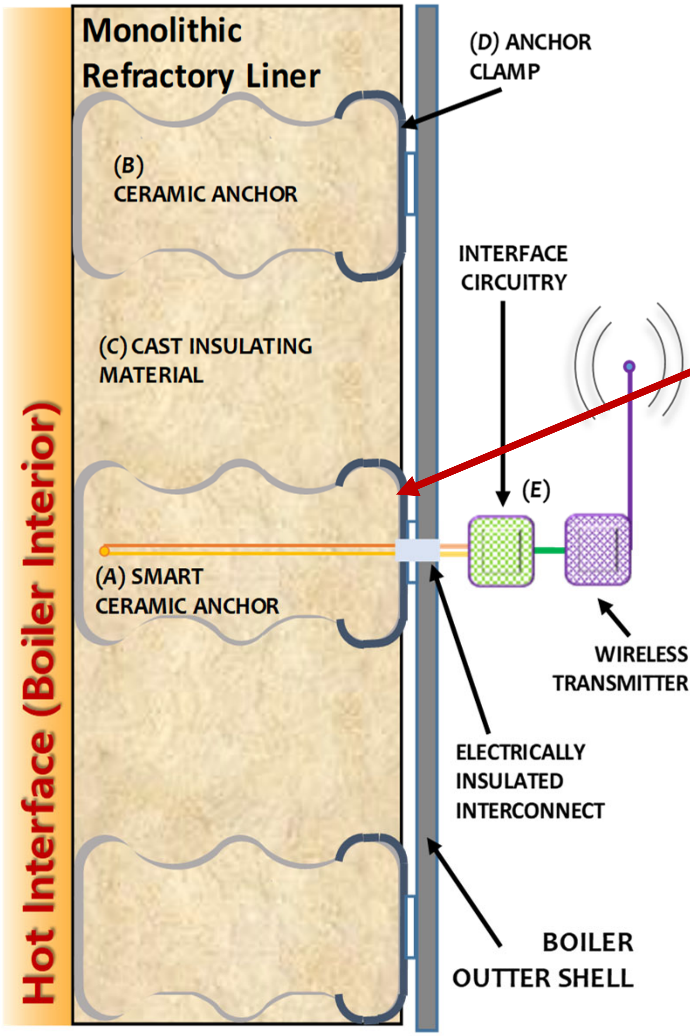
- Continue rheological and printing studies to achieve highest solids loading
- Tailor design parameters to meet electrical requirements
- Scale-up all sensor preforms and printing process
- Print, laminate, and embed thermistor in smart refractory

Task 4.0 – Development of Embedded Interconnection Design and Smart Anchor Testing (Sabolsky)

Task 4 Objectives:

- Ceramic/metal brazes will be evaluated to connect the electroceramic embedded sensor to metal wire to electronics (stable connection required).
- The electrical (and chemical) stability of the connection will be evaluated as a function of time/temperature to insure a stable interconnection to the electronics.
- Prototype ceramic anchors will be fabricated and tested within static slag conditions at 900-1350°C extending over 24-500 hours.
- Anchors will undergo static slag exposure within the refractory testing system already available to test sensor-ed refractory brick.

Task 4 Introduction:



- Ceramic refractory and sensor must be electrically connected through insulation clamp to electronics.
- Ceramic/metal joint is required to connect ceramic sensor to metal wire.
- *Requirements of* connection:
  - Electrically conductive and stable
  - Adequate mechanical strength
  - Thermally and chemically stable

Task 4 Introduction:

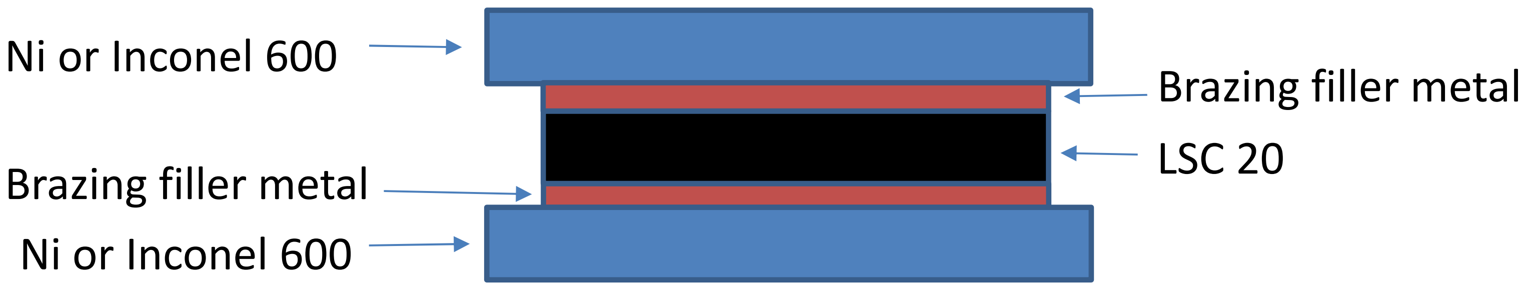
- Lanthanum Chromite doped with 20% Strontium (LSC 20) was brazed to Ni and Inconel 600 (Ni-Cr-Fe)

- Four brazing filler metal pastes purchased from Wall Colmonoy Corporation. Their chemical compositions in weight percentage is shown in the table below.

Element	Nicrobraz 130-S (AWS BNi-3)	Nicrobraz 135-S (AWS BNi-4)	Nicrobraz 30-S (AWS BNi-5)	Nicrobraz 150-S (AWS BNi-9)
Ni	Balance	Balance	Balance	Balance
Cr			19.44	15.52
B	2.97	1.95		3.8
Si	4.53	3.54	10.17	

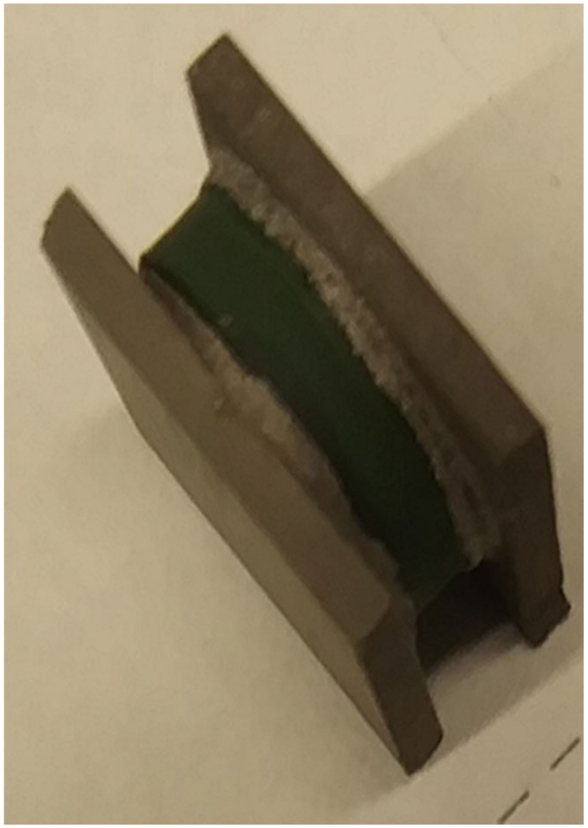
- Future brazing filler metals to be investigated:
  Nicrobraz LM-S (AWS BNi-2)
  Nicrobraz LC-S (AWS BNi-1a)
  *More resistant composition to oxidation, but wetting and melting issues.

Task 4 Symmetrical Brazing Experiments:



1) Square Ni and Inconel 600 samples 12.7 x 12.7 x 1.51 mm.
2) LSC-20 pellets fabricated and sintered to >90% density (and polished, 11 mm OD and 2 mm thick).
3) Braze deposited uniformly at specified thicknesses over metal substrates and symmetrical sample formed.
4) Symmetrical samples fired to 1000-1400°C in argon and various cover gasses.
5) Electrical characterization (4-point conductivity and impedance spectroscopy) completed from 400-1300°C in air and argon.

Task 4 Brazing Experiments:

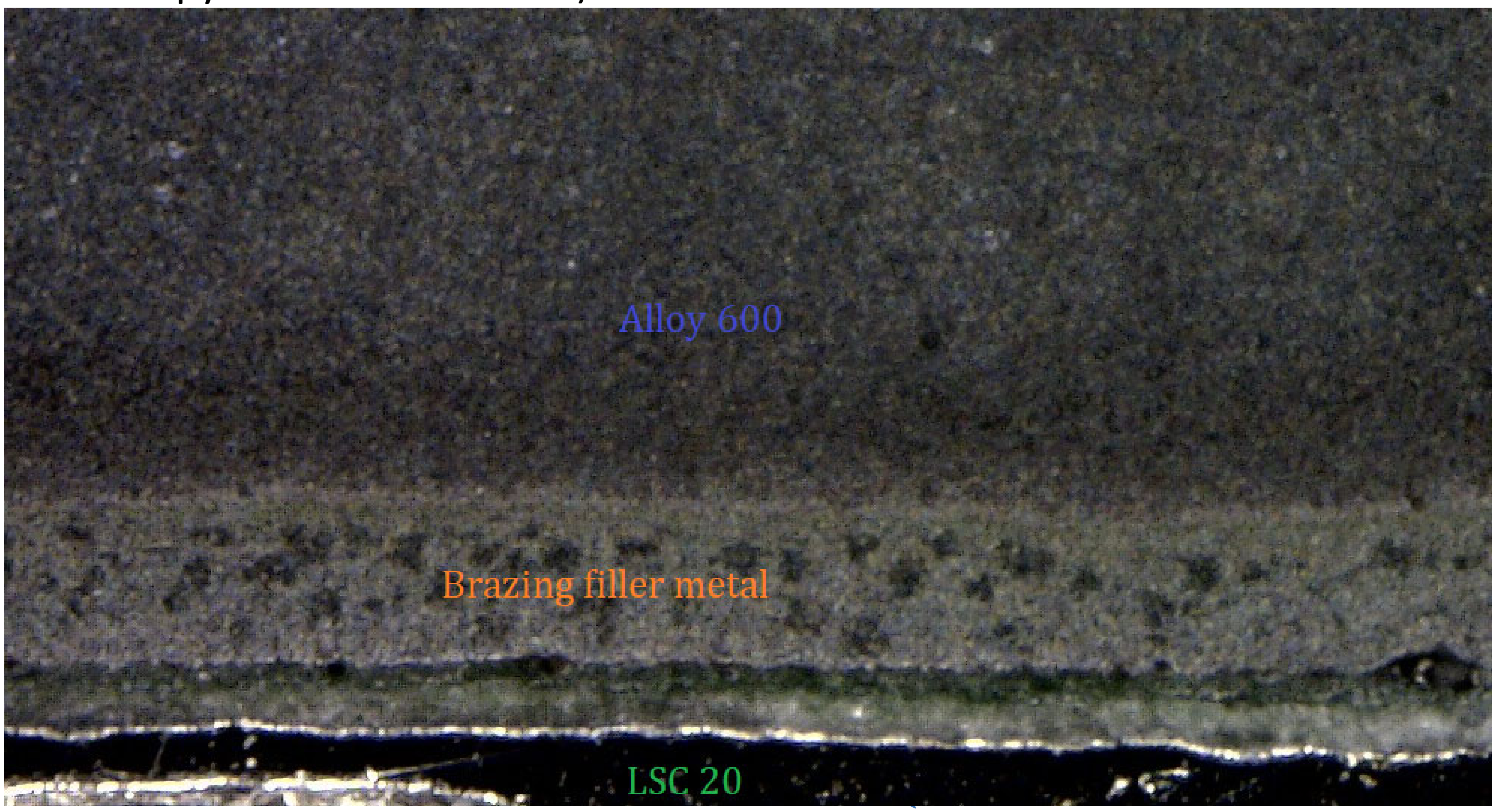


Ni-LSC-Ni joint brazed with Nicrobraz 135-S at 1160 °C for 20 minutes in an Argon gas flow rate of 80 SCCM

Ni-LSC-Ni joint brazed with Nicrobraz 130-S at 1160 °C for 20 minutes in an Argon gas flow rate of 80 SCCM

Task 4- Brazing Experiments:

- Nicrobraz-150 on Inconel 600 at 1200°C for 20 minutes in Argon.
- Braze thickness was ~0.29 mm
- First connections available, but waiting on microstructural analysis (when electron microscopy becomes available).



Optical Microscopy at 600x

Task 4 Conclusions and Future Work:

- Ni-based brazing filler metal pastes were used for brazing Ni and Alloy 600 in Argon at 1160-1200 °C.

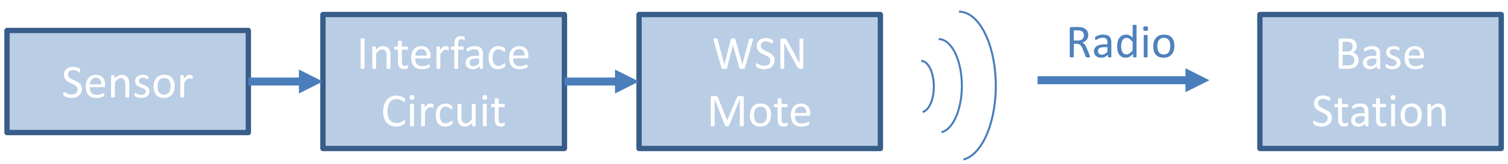
Future Work:

- 4-wire electrical resistance and impedance spectroscopy tests of brazed joints at temperatures from 200-1200 °C will be performed in various atmospheres (purpose to find intrinsic joint resistivity).
- Evaluate variables such as brazing temperature, atmosphere and braze thickness on electrical properties.
- Complete cyclic thermal testing on joints.
- Evaluate alternative metal wire and braze compositions to increase stability and lower interconnect resistance.

Task 5.0 – Electronics and Wireless Communication Interfacing with Smart Ceramic Anchors (Graham)

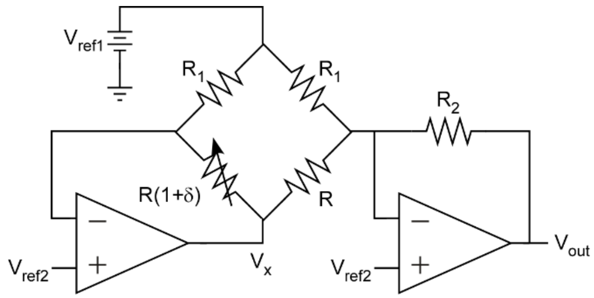
Task 5 Objectives:

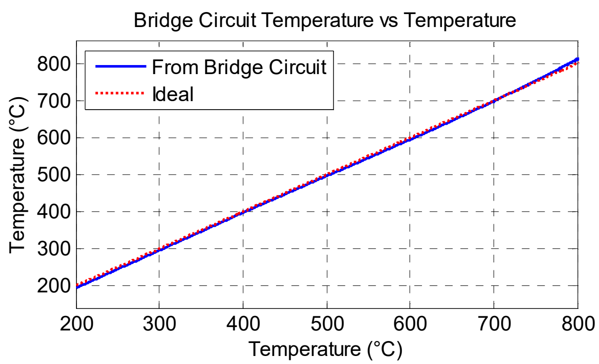
- To develop methods to interface the electrical sensing outputs from the smart refractory with an embedded processor
- To design a wireless sensor network to efficiently collect the data at a processing unit for further data analysis
- To improve the signal processing capability and scalability by introducing a reconfigurable interface

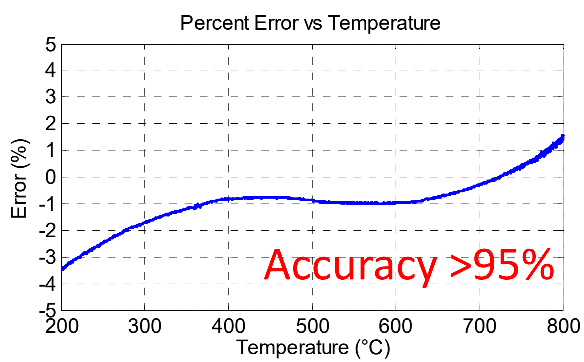


Task 5.0 - Sensor Interfacing

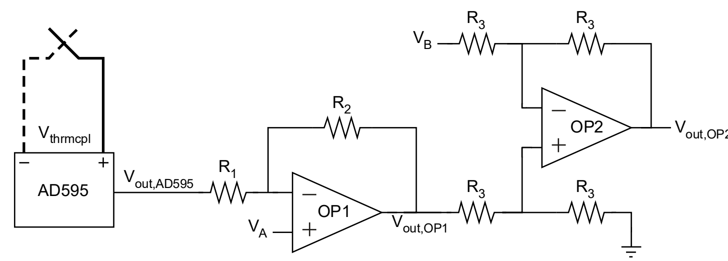
Resistor-Based Sensors

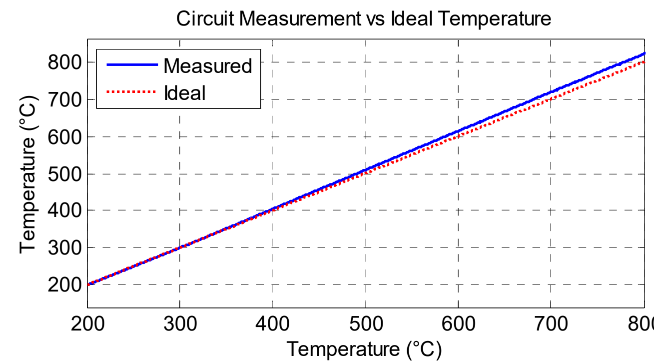


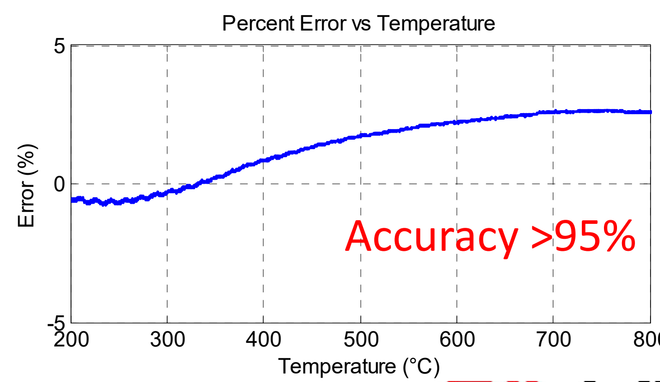




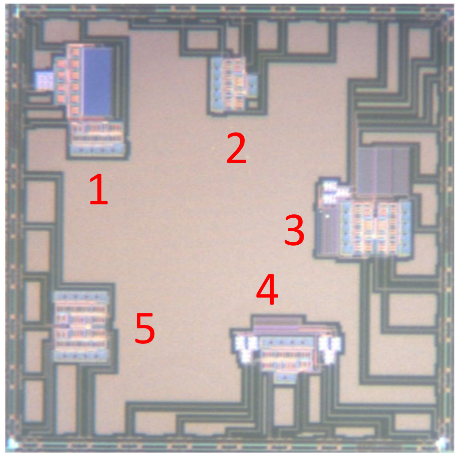
Thermocouple-Based Sensors





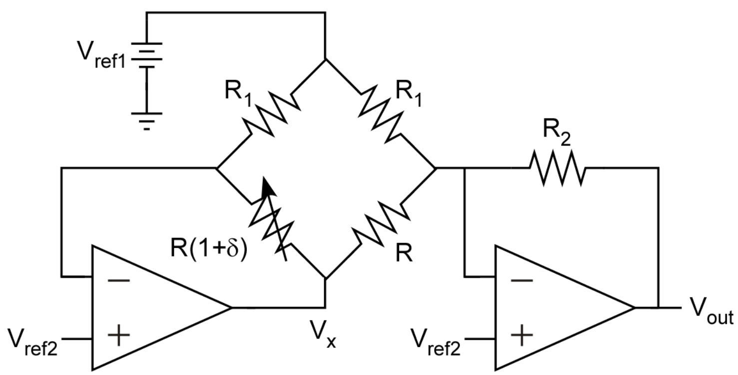


Task 5.0 - Custom Integrated Circuit for Sensor Interfacing

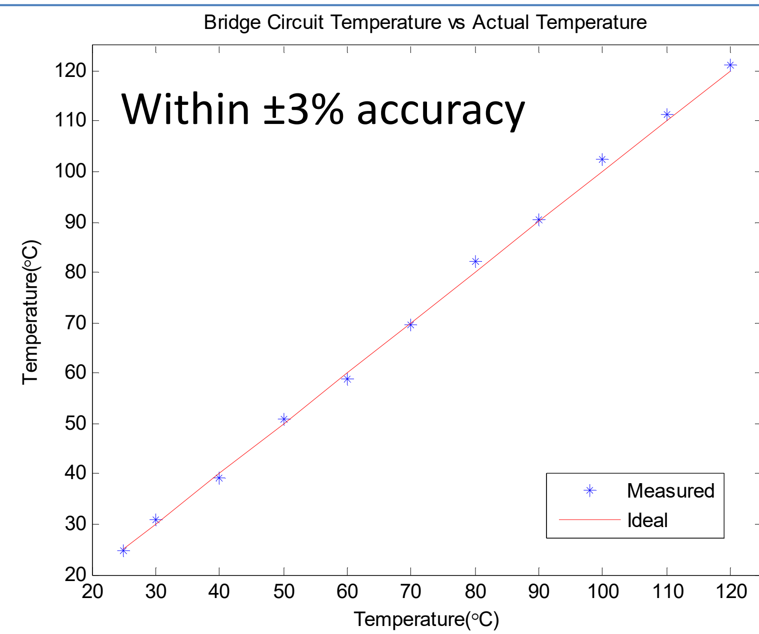


1. Cold-Junction Compensator
2. Thermocouple Amplifier
3. Capacitive Sensor
4. Thermocouple Amplifier V2
5. Wheat-Stone Bridge

Resistance-Based Sensor

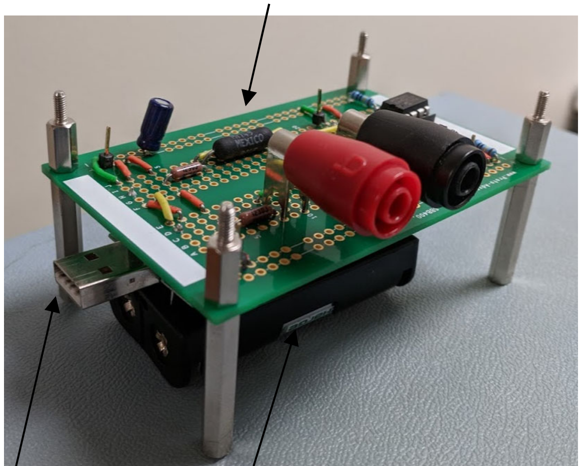


$$V_{out} = V_{ref2} + \frac{R_2}{R_1}\delta\left(V_{ref1} - V_{ref2}\right)$$



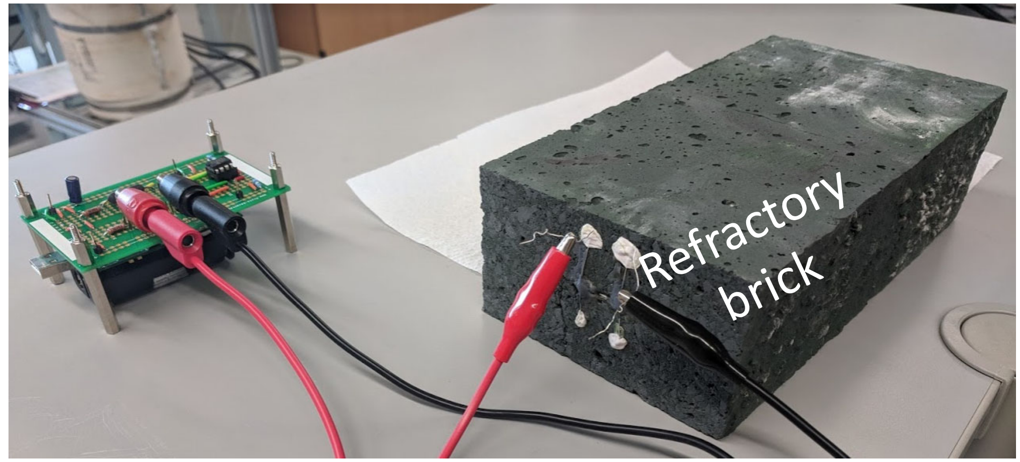
Task 5.0 – Interfacing with the Smart Anchors

Resistive Sensing Circuit

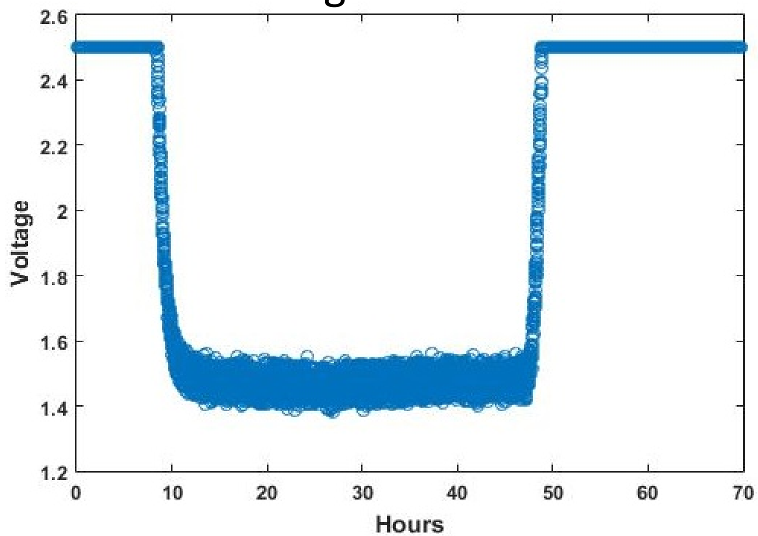


Wireless Mote

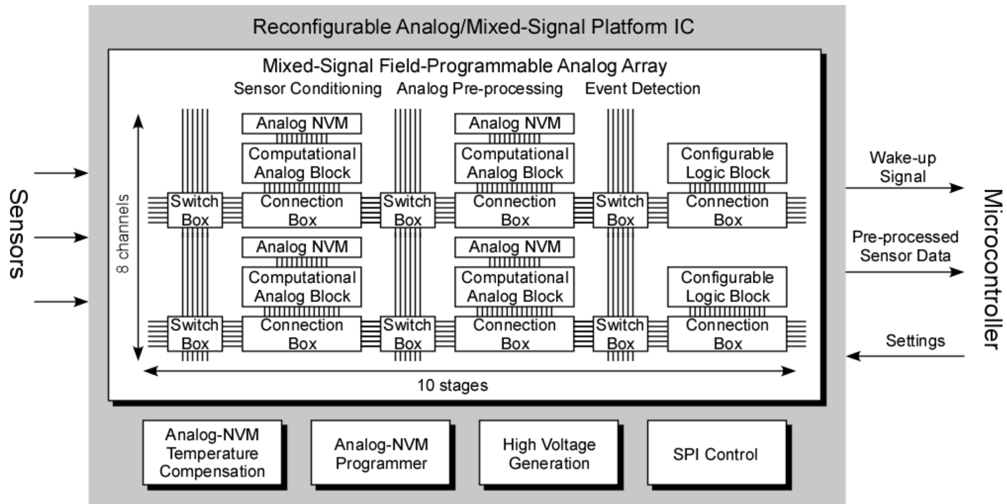
Battery Pack



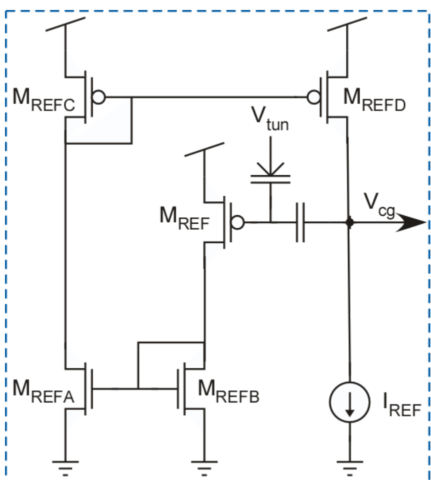
Received Signal at Base Station

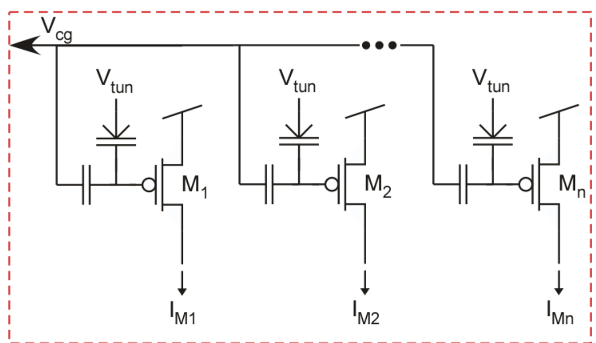


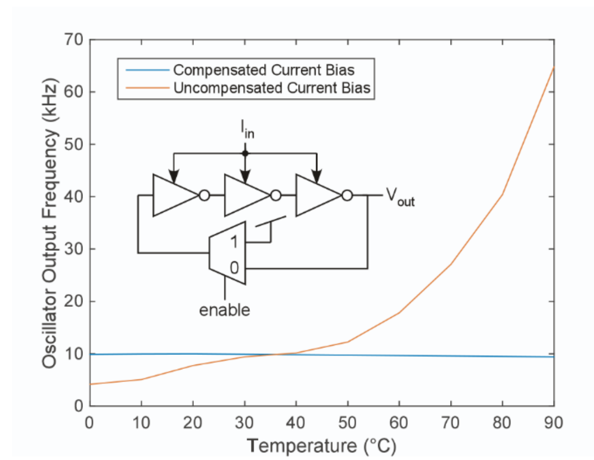
Task 5.0 - Reconfigurable Circuits for Sensor Interfacing



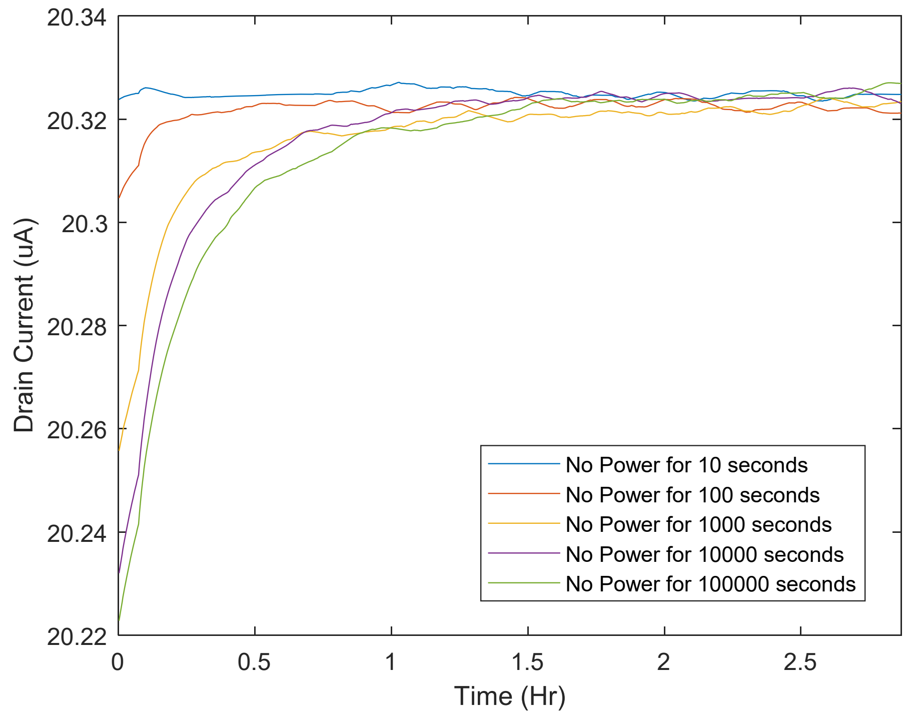
- Maintain flexibility—in-the-field updates to sensor-interfacing circuits
- A variety of sensor interface circuits can be constructed from a single chip
- Internal temperature compensation using floating-gate transistors







Task 5.0 - Reliability Testing for Reconfigurable Interfacing



- The performance of Floating-gate (FG) transistors as non-volatile memory elements in a reconfigurable interface was investigated.
- The startup transients were directly dependent on the duration that the FG transistors were powered off.

Task 5.0 - Conclusions and Future Work

Recently Completed

- Initiated reliability testing for our custom non-volatile memory (NVM)

Future Work

- Continue NVM testing, focusing on retention characteristics
- Evaluate sensor node platforms (e.g. TI Launchpad) within the context of interfacing our custom circuitry and wireless connectivity
- Construct a proof-of-concept sensor network for end-to-end system evaluation

Major Milestones:

Original Proposal (with Proposed Start Date of Oct. 1, 2019)

	Task/ Subtask	Milestone Title & Description	Planned Completion Date	Verification Method
√	2.2	Downselect the materials for thermistor and degradation sensor printing	06/30/2020	Demonstrate continuity and resistance of <5000 ohm at 1300°C in 4-pt conductivity measurement
√	3.1	Defined basic ink/paste formation for 3D printing trials	06/30/2020	Demonstrate direct-writing continuous sensor legs showing conductivities >0.5 S/cm at >500ºC
√	3.4	Demonstrate 3-D printing of sensor preform designs (2 designs)	09/30/2020	Demonstrate continuity and resistance of <5000 ohm at 1000°C for sensor 20 cm long sensor
	4.1	Demonstrate initial braze for sensor interconnection	12/31/2020	Demonstrate ohmic connection with less than 5% change in resistance at 300°C
√	5.1	Demonstrate operational prototype of sensor interfacing electronics	09/30/2020	Correct measurements with 95% accuracy

- Actual start date of contract was January 1, 2020 (3-month delay in contract initiation).
- Another 3-month delay due to COVID lab lockout at WVU.
- Only 4-5 months of research out of 11 month planned from original Oct 1, 2019 start.

HWI