



CSP Program Summit 2016

# High-Operating-Temperature Heat-Transfer Fluids for Solar Thermal Power Generation (Liquid Metals)

Principal Investigators:

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# Outline

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- Overview
- Problem Statement
- Value Proposition
- Objectives
- Milestones
- Results
- Path to Market

# Overview

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- Project Name: High Operating Temperature Heat Transfer Fluids for Solar Thermal Power Generation
- Funding Opportunity: MURI: High Operating Temperature Fluids (DE-FOA-0000567)
- Principle Investigators: Mark Asta, UC Berkeley  
Peter Hosemann, UC Berkeley  
Y. Sungtaek Ju, UCLA  
Jan Schroers, Yale
- Other Contributors: Alan Bolind, UC Berkeley  
Gopinath Warriar, UCLA
- Project Duration: 5 years (10/2012– 12/2017)
- Project Budget: \$1,104,727 including cost share, for Phase 3

# Problem Statement

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The problem, then, is...

- to develop a **liquid-metal heat-transfer fluid** for CSP that can operate above  $650\text{ }^{\circ}\text{C}$ , while still satisfying traditional CSP requirements, namely,
  - chemical stability,
  - low melting temperature,
  - existing or potential commercial availability,
  - and reasonably slow corrosion of pipes.



# Problem Statement

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*De facto* main problem: CORROSION of pipe materials by liquid-metal alloys

The corrosion takes two forms:

1. **Dissolution** of the pipe-material constituent elements
2. **Excessive oxidation** of the pipe material

Fight #1 (dissolution) with slight #2 (oxidation).

# Value Proposition

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In words...

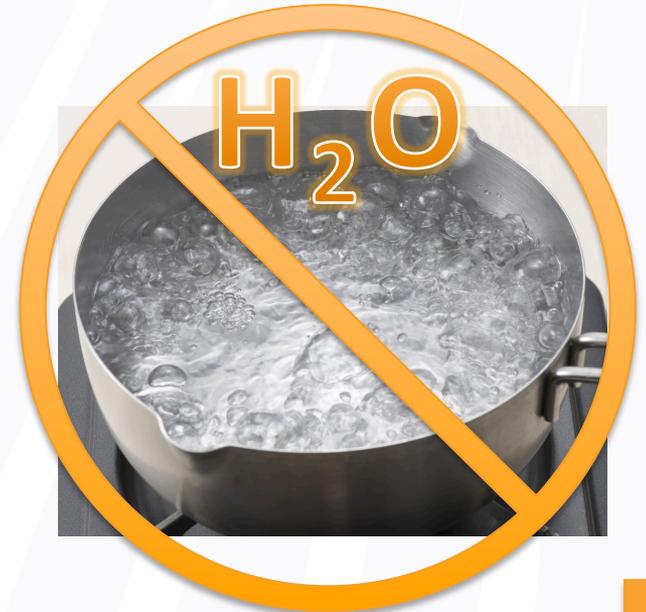
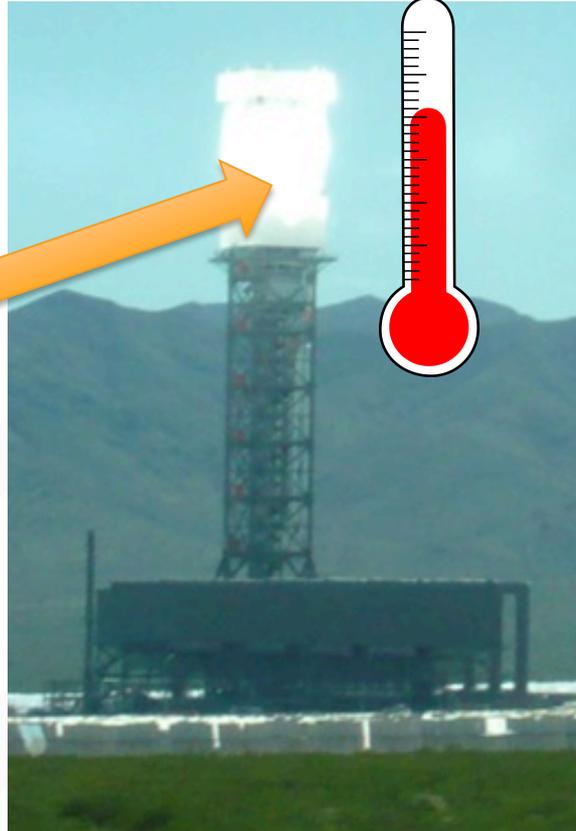
A liquid-metal heat-transfer fluid that solves the stated problem will enable CSP companies to operate their CSP plants at higher temperatures and thereby achieve greater efficiencies and concomitant lower costs.

Unlike high-temperature gases that need high pressures for sufficient density, and unlike molten salts that either fail to melt at low temperatures or decompose at high temperatures, liquid metals stay liquid, without excessive pressure, over the temperature range of interest for CSP operations.

# Value Proposition

In pictures...

800 °C !!  
 $\eta > 50\%$  !!



# Objectives

UCLA Sungtaek Ju

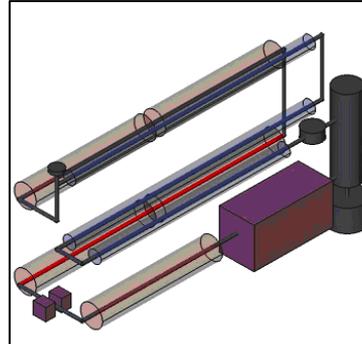
Objectives of each team member

LM: Liquid Metal

PM: Pipe Material

## Flowing, loop experiments

- Corrosion testing in flowing LM
- Operational data for a LM loop

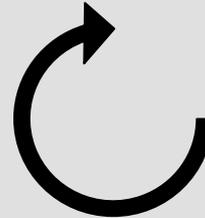


## Static, autoclave experiments

Cal

Peter Hosemann

- Corrosion testing of PM strips in crucibles of LM
- Development of control of oxygen dissolved in LM

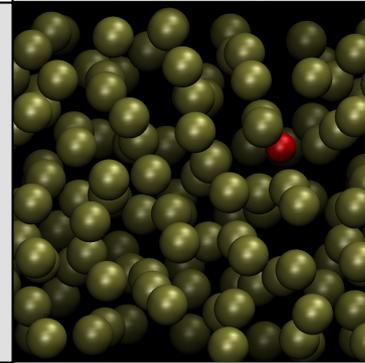


## Modeling

Cal

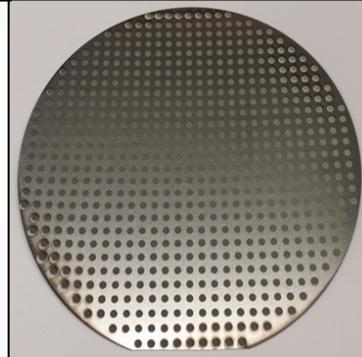
Mark Asta

- Thermodynamic calculations of...
- Properties of LM
  - Protective scales on PM
  - Oxygen dissolved in LM



## Fast-screening experiments

- LM thermophysical properties
- LM/PM corrosion reactions



Jan Schroers

# Milestones

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- Identified > 50 LM alloys with  $T_{\text{melting}} < 300 \text{ }^{\circ}\text{C}$ .
- Established optimal oxygen concentration range; quantified oxide growth and dissolution rates as functions of temperature and oxygen concentration; and identified 1 PM alloy with corrosion < 150  $\mu\text{m}/\text{yr}$
- Calculated free energies of formation of protective oxide and intermetallic scales for LM alloys of LBE + a third additive.
- Quantified LM/PM reaction with additives (e.g., Zn, Sb, Ge), by both fast screening and static corrosion tests.
- Identified the best Pb-Bi alloy composition for LM/PM reaction.
- Conducted tensile testing to show absence of liquid-metal embrittlement.
- Verified the leak-tightness of the flow loop at room temperature.

# Results

## Selection of LM components

1 IA												18 VIIIA																																					
1	H Hydrogen											B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine	He Helium																																
2	Li Lithium	Be Beryllium											Al Aluminum	Si Silicon	P Phosphorus	S Sulphur	Cl Chlorine	Ne Neon																															
3	Na Sodium	Mg Magnesium	3 IIIA	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	Al Aluminum	Si Silicon	P Phosphorus	S Sulphur	Cl Chlorine	Ar Argon																															
4	K Potassium	Ca Calcium	Sc Scandium	Ti Titanium	V Vanadium	Cr Chromium	Mn Manganese	Fe Iron	Co Cobalt	Ni Nickel	Cu Copper	Zn Zinc	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium	Br Bromine	Kr Krypton																															
5	Rb Rubidium	Sr Strontium	Y Yttrium	Zr Zirconium	Nb Niobium	Mo Molybdenum	Tc Technetium	Ru Ruthenium	Rh Rhodium	Pd Palladium	Ag Silver	Cd Cadmium	In Indium	Sn Tin	Sb Antimony	Te Tellurium	I Iodine	Xe Xenon																															
6	Cs Cesium	Ba Barium		Hf Hafnium	Ta Tantalum	W Tungsten	Re Rhenium	Os Osmium	Ir Iridium	Pt Platinum	Au Gold	Hg Mercury	Tl Thallium	Pb Lead	Bi Bismuth	Po Polonium	At Astatine	Rn Radon																															
7	Fr Francium	Ra Radium		Rf Rutherfordium	Db Dubnium	Sg Seaborgium	Bh Bohrium	Hs Hassium	Mt Meitnerium	Ds Darmstadtium	Rg Roentgenium	Uub Ununbium	Uut Ununtrium	Uuq Ununquadium	Uup Ununpentium	Uuh Ununhexium	Uus Ununseptium	Uuo Ununoctium																															
												<table border="1"> <tr> <td>1193 45</td> <td>Ce</td> <td>Pr</td> <td>Nd</td> <td>Pm</td> <td>Sm</td> <td>Eu</td> <td>Gd</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>La Lanthanum</td> <td>Ce Cerium</td> <td>Pr Praseodymium</td> <td>Nd Neodymium</td> <td>Pm Promethium</td> <td>Sm Samarium</td> <td>Eu Europium</td> <td>Gd Gadolinium</td> <td>Tb Terbium</td> <td>Dy Dysprosium</td> <td>Ho Holmium</td> <td>Er Erbium</td> <td>Tm Thulium</td> <td>Yb Ytterbium</td> <td>Lu Lutetium</td> </tr> </table>								1193 45	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La Lanthanum	Ce Cerium	Pr Praseodymium	Nd Neodymium	Pm Promethium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutetium
1193 45	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																			
La Lanthanum	Ce Cerium	Pr Praseodymium	Nd Neodymium	Pm Promethium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutetium																																			

T<sub>m</sub> USD/kg  
Symbol  
Name

- Radioactive
- Prohibitively expensive
- Toxic
- Gaseous
- Meets requirements
- Under consideration for alloying

= rejected after initial screenings

= tested and most acceptable

= rejected after static corrosion testing

= still to be tested, as an additive

# Results

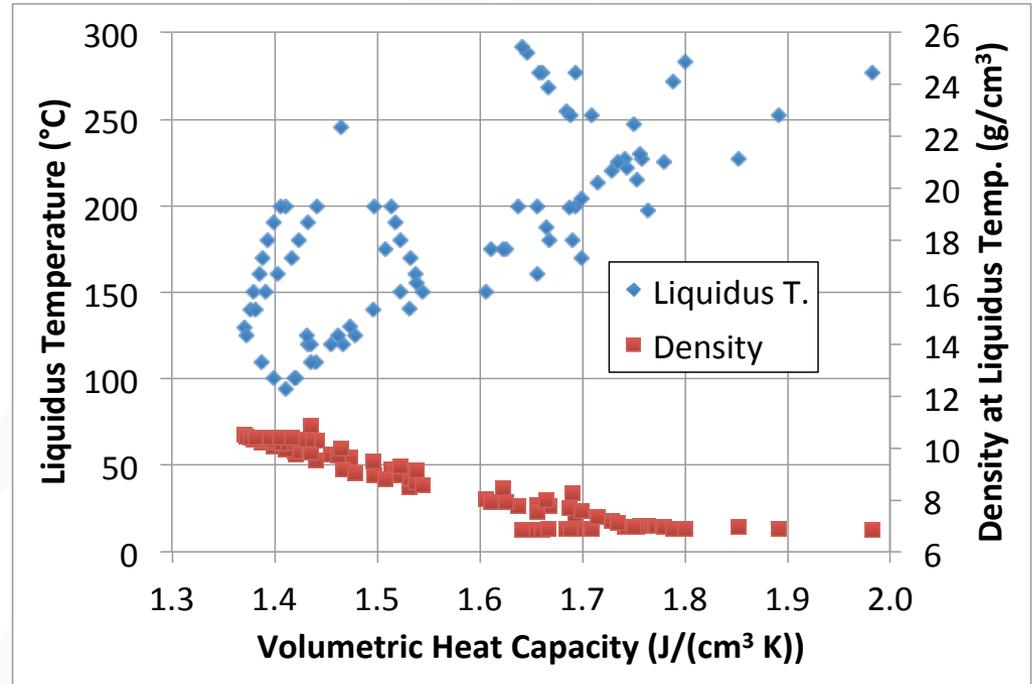
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- Lead-Bismuth Eutectic (LBE) is 45% Pb, 55% Bi, by mass.
- This LBE is our default liquid metal of choice, because...
  - it is not too expensive (Pb is very cheap),
  - it is not excessively chemically reactive or toxic,
  - Pb and Bi are the least corrosive of the elements,
  - and the eutectic composition has the lowest melting temperature (125 °C).

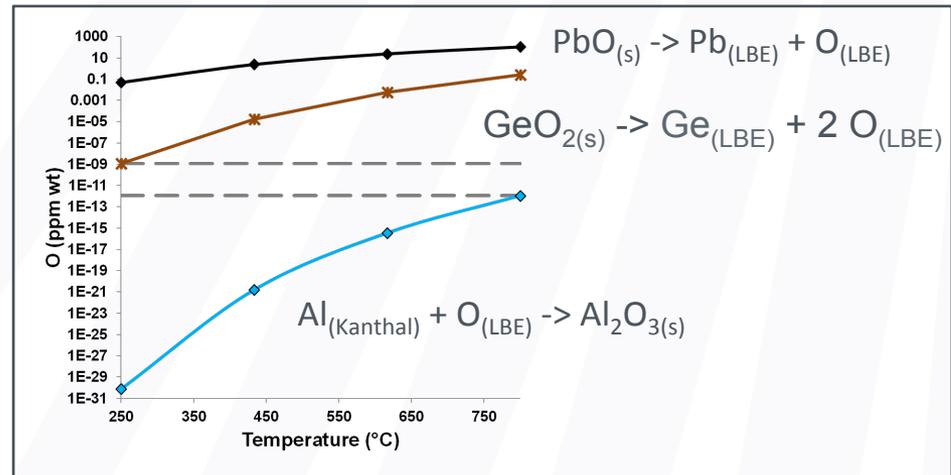
# Results

- Examples of calculations

LM properties

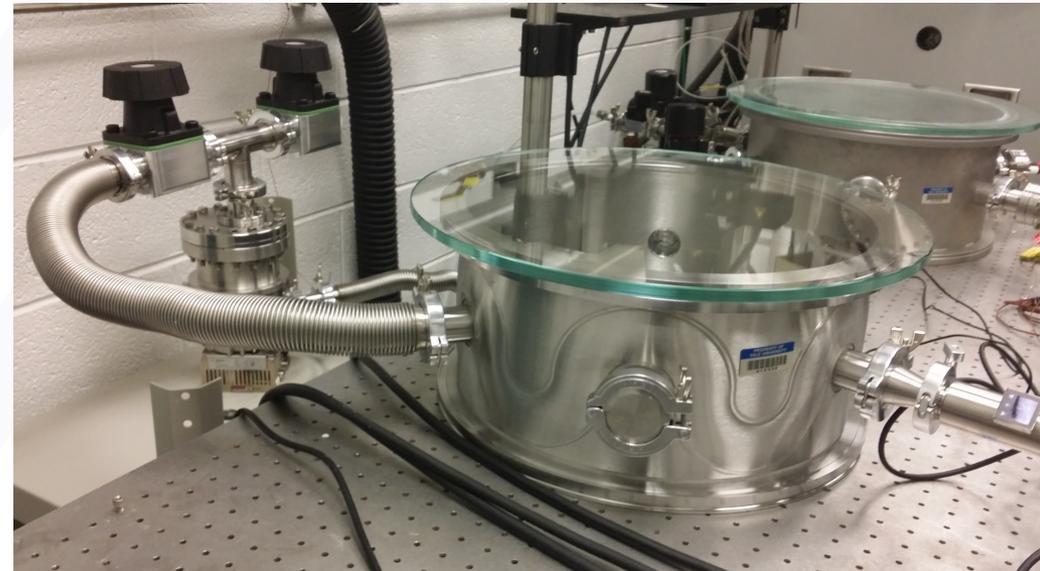
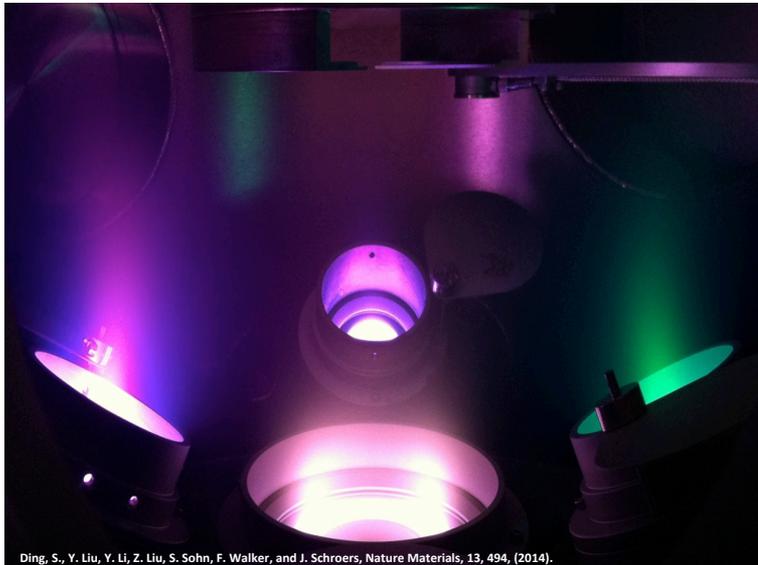
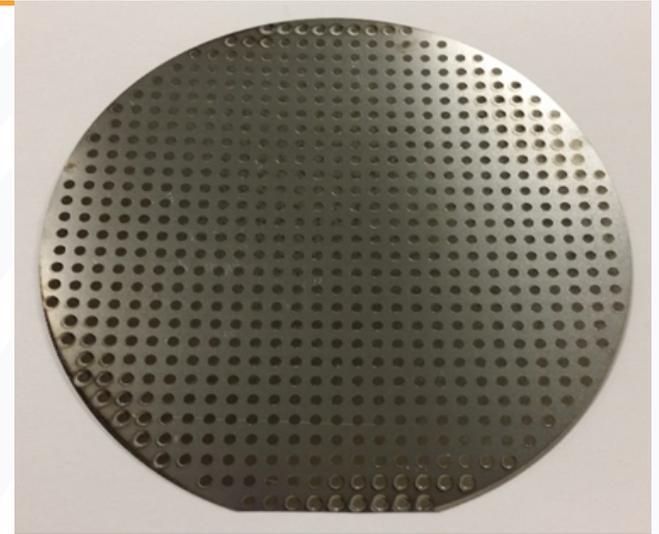


Window for proper oxygen control



# Results

Yale's setup for fast screening:  
drops of LM on a PM disk



Ding, S., Y. Liu, Y. Li, Z. Liu, S. Sohn, F. Walker, and J. Schroers, *Nature Materials*, 13, 494, (2014).

# Results

- Example of fast-screening of LM/PM corrosion reactions

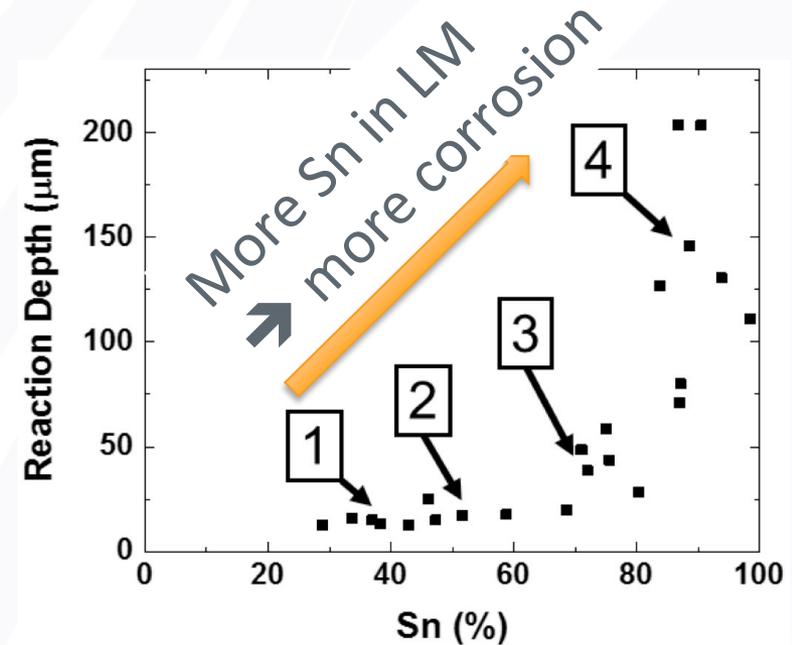
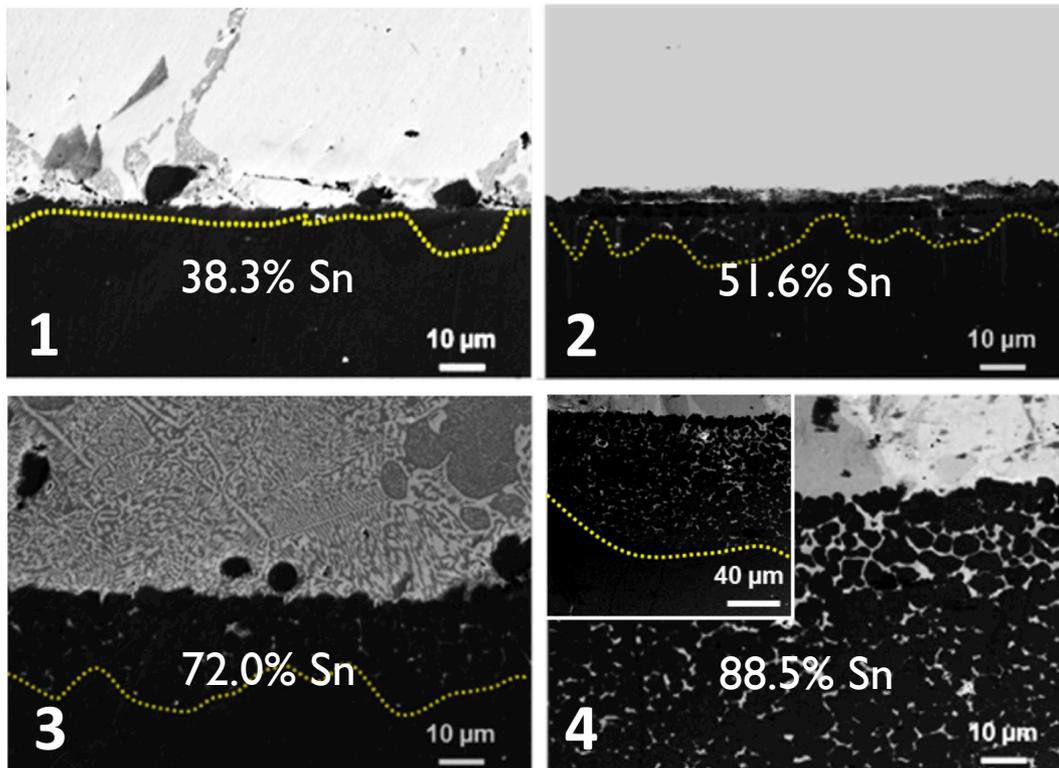
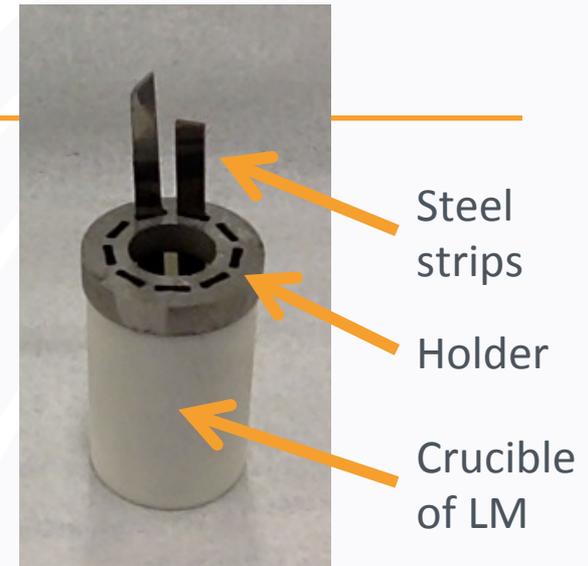


Figure 2.1.2-3: The effect of Sn content on the penetration depth (denoted by the dotted yellow lines) of LM into Kanthal steel PM.

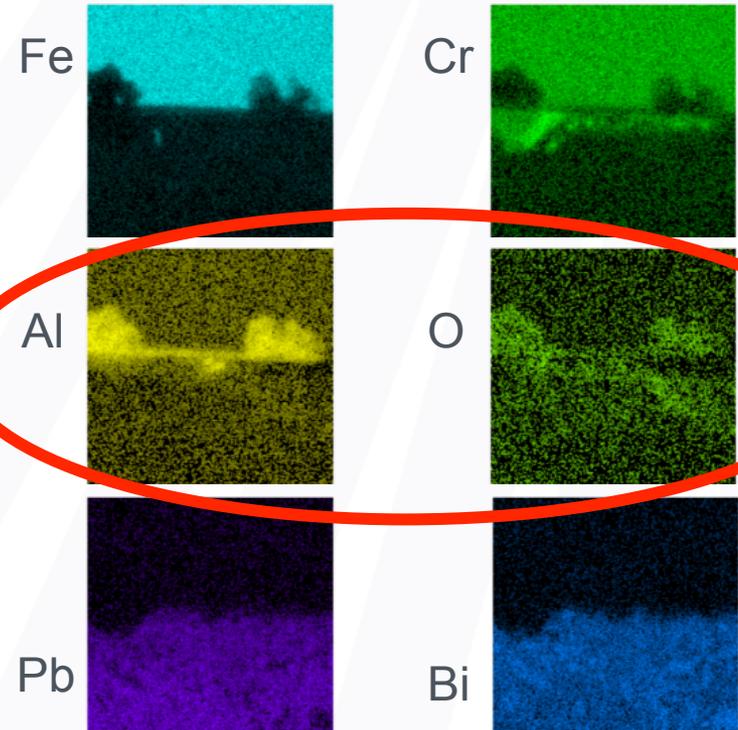
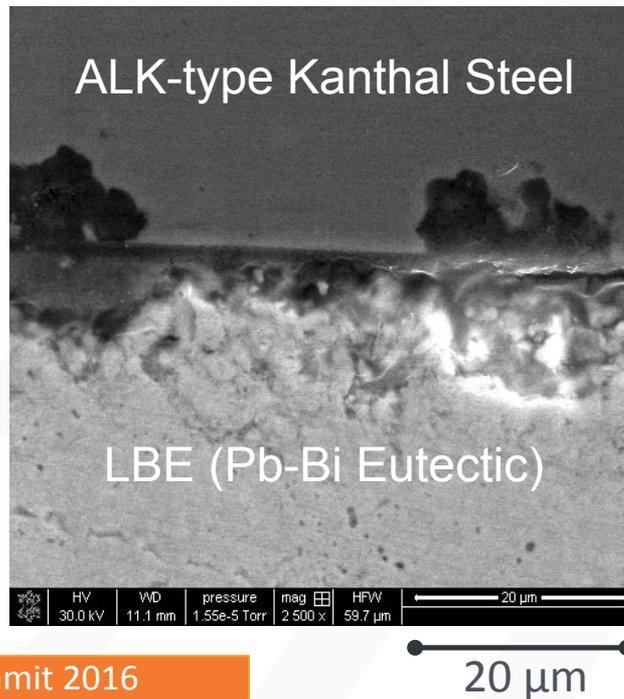


# Results

- Longer-term static corrosion tests
  - Dissolution protection is by aluminum-oxide scales ( $\text{Al}_2\text{O}_3$ ).
  - Therefore, we use Kanthal steels because they have 6% Al, by mass.

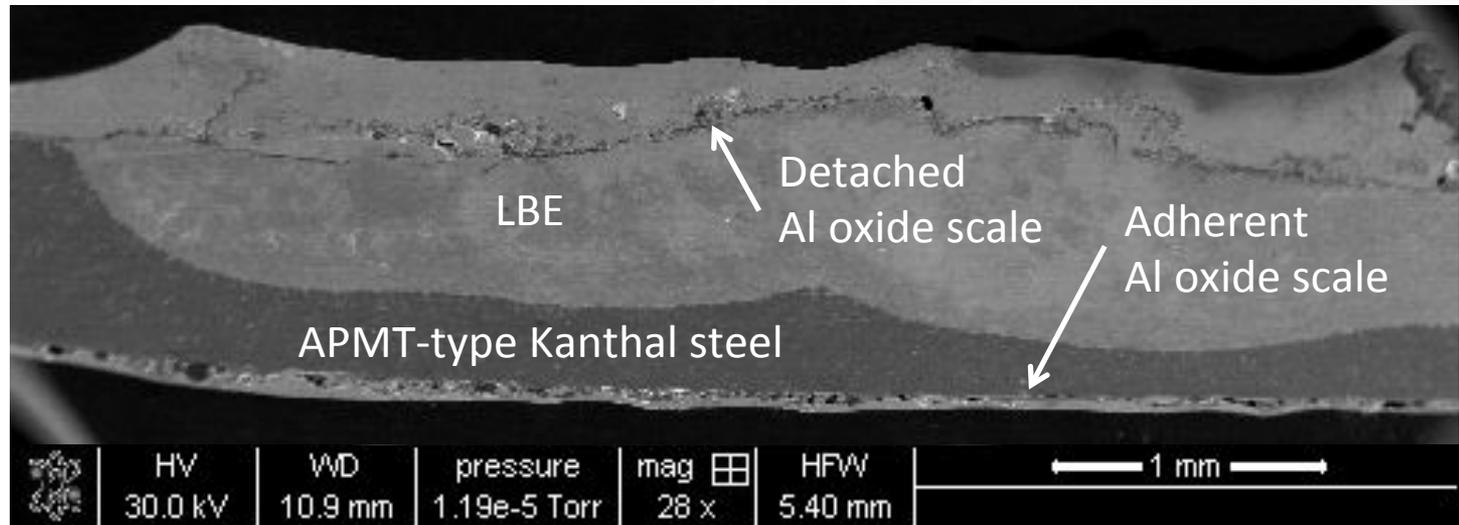


**Good Example**  
1000 hours  
700 °C  
 $10^{-6}$  wt.% dissolved oxygen



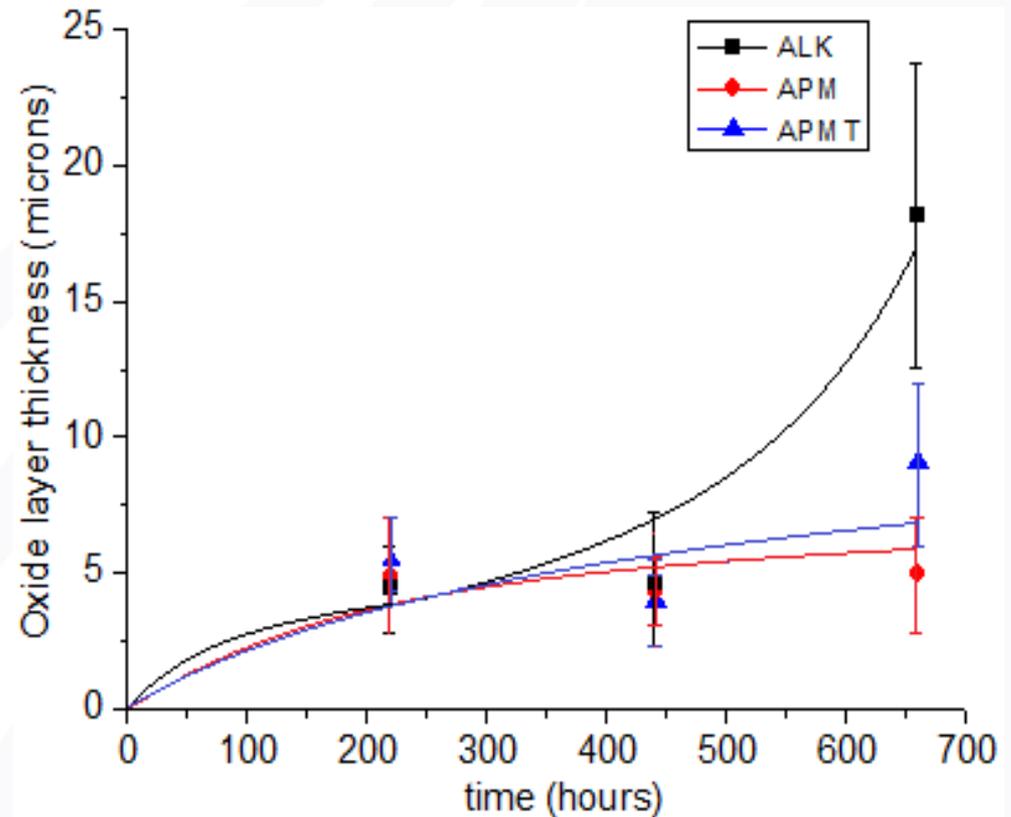
# Results

**Bad Example**  
1000 hours  
800 °C  
 $10^{-6}$  wt.%  
dissolved  
oxygen



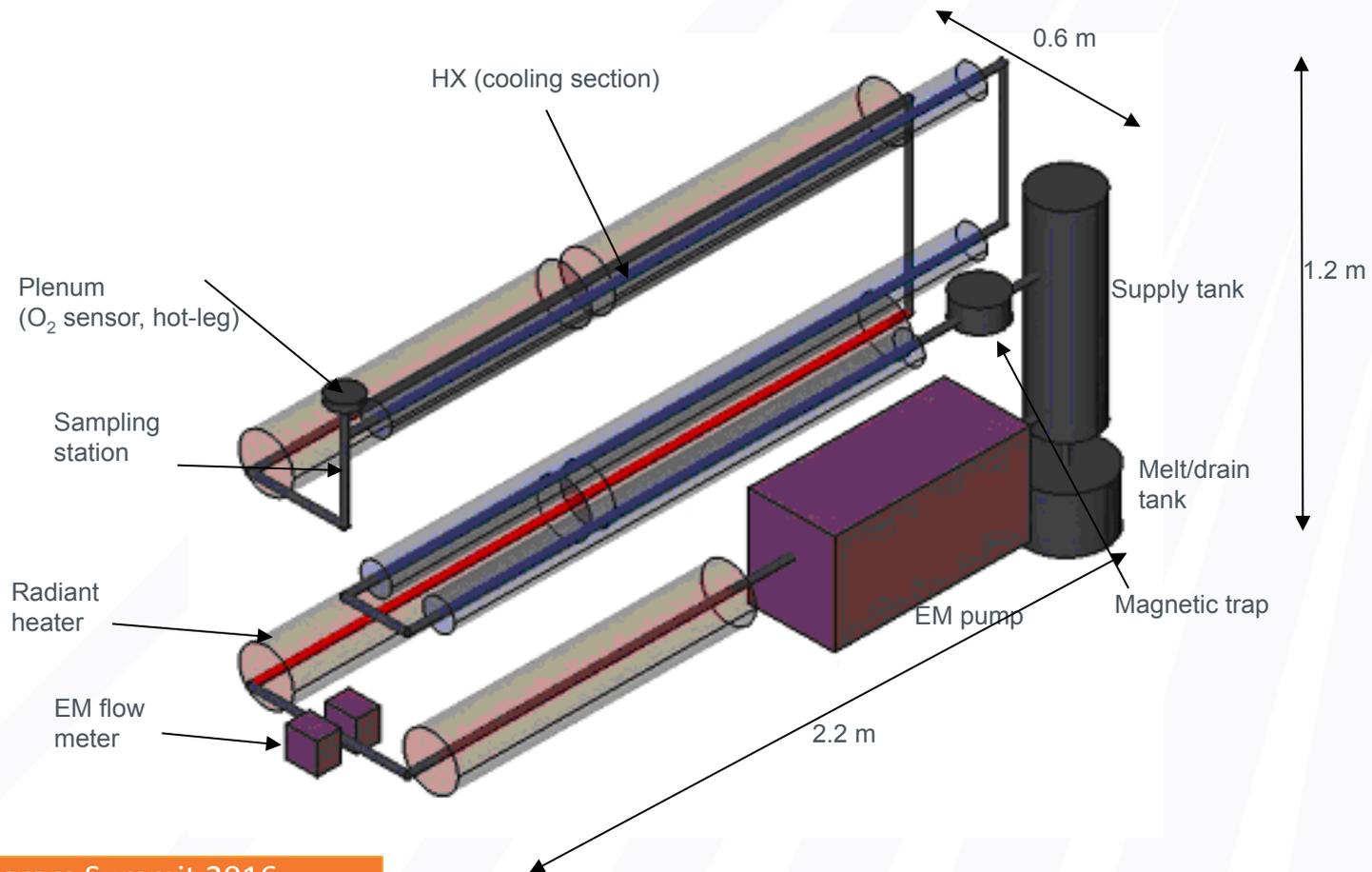
# Results

Oxide growth on Fe-Cr-Al ferritic steels (Kanthal) during exposure to static LBE at 700°C with  $1 \cdot 10^{-6}$  wt. % O for up to 660 h



# Results

- A forced-convection liquid-metal flow loop has been designed, constructed, and leak tested with gas at room temperature.
- Work is continuing to initiate flow experiments using a liquid metal (LBE).



# Path to Market

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- This research project → Experimental evidence of LBE as a high-temperature heat-transfer fluid
- Industrial collaboration → Build a scaled test loop with CSP-like configuration, and test over a more exhaustive range of operating parameters
- Industry → Build a prototype CSP plant with liquid metal as the heat-transfer fluid

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