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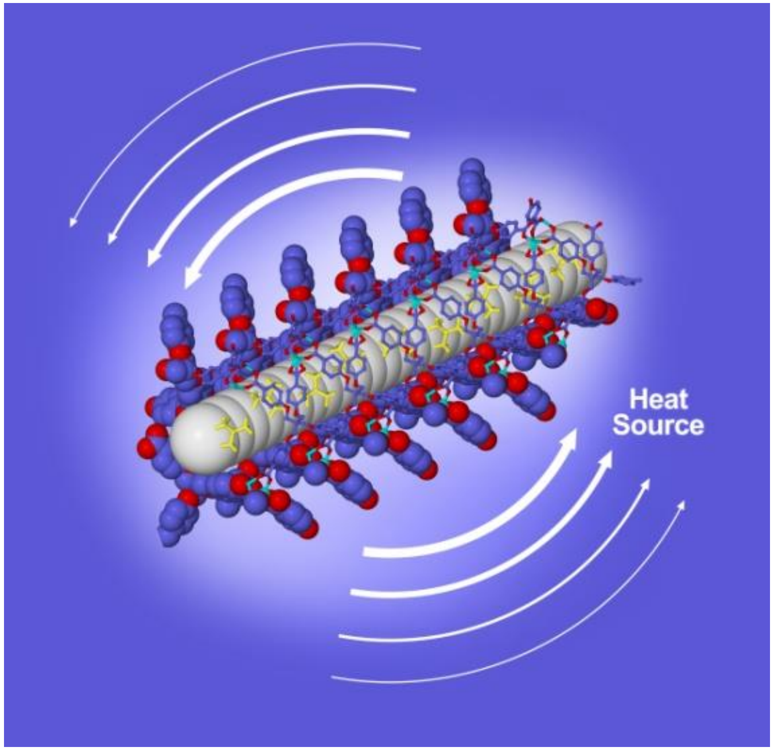

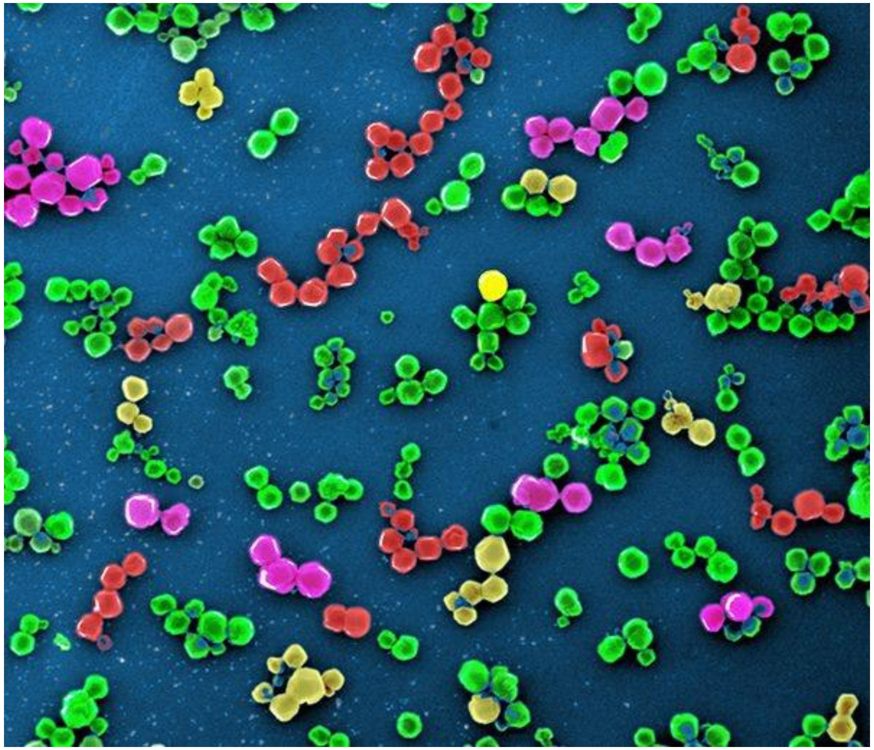

Finalist in PNNL Science as Art Contest

Metal Organic Heat Carriers for Enhanced Geothermal Systems

May 13, 2015

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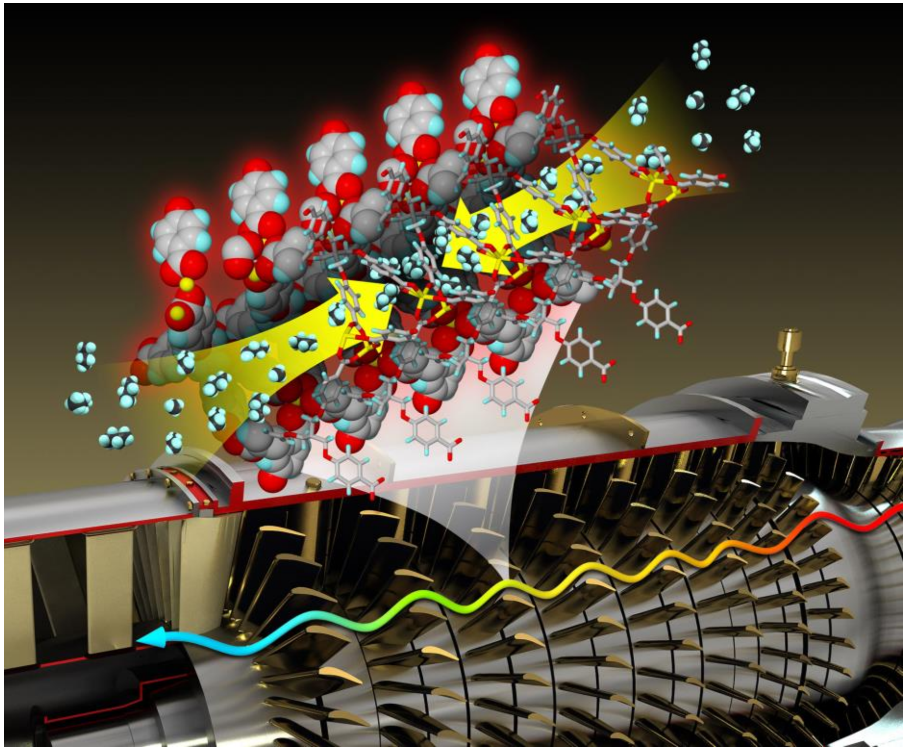
Pacific Northwest National Laboratory

Specialized Materials and Fluids and Power Plants

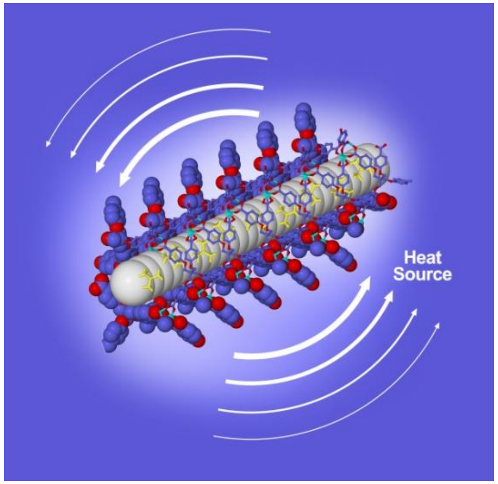
Relevance/Impact of Research

- Nanofluids offer unique potential to improve efficiency of many VLC power generation and heat pump systems without major modifications to equipment or operating conditions
  - Increase thermal conductivity
  - Improve heat transfer coefficient
  - Higher critical heat flux
- Prior work focused on water and chemically passive metal, oxide, or carbon-based nanoparticles
  - Mismatch in particle density versus working fluid
  - Mass/volume displacement of working fluid
  - Need for surfactant stabilizers
- MOHC nanophase materials interact at the molecular level with working fluids
  - Boost heat carrying capacity per kg
  - Equal or potentially exceed molar density of the liquid or vapor phase states of the pure working fluid
  - Near-neutral buoyancy
  - Can be designed to interact with one or more components of a mixture
  - Diminish or eliminate temperature glide with impure working fluids

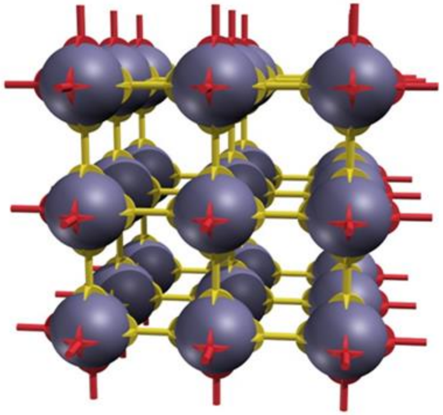


What are Metal Organic Heat Carriers?

- Nanoporous organic or metal-organic solids that interact at the molecular level with a working fluid
  - Tunable binding energy with common working fluids and refrigerants
  - Very high uptake capacity (over 100 wt% for some fluids)
  - High structural and thermal stability >350°C
- Synthesis under mild conditions and templating techniques available to produce nanophase forms
- Many combinations of metal ions and organic linkers
- Self assembly into channels or continuous 3D pore networks



Modulated nucleation

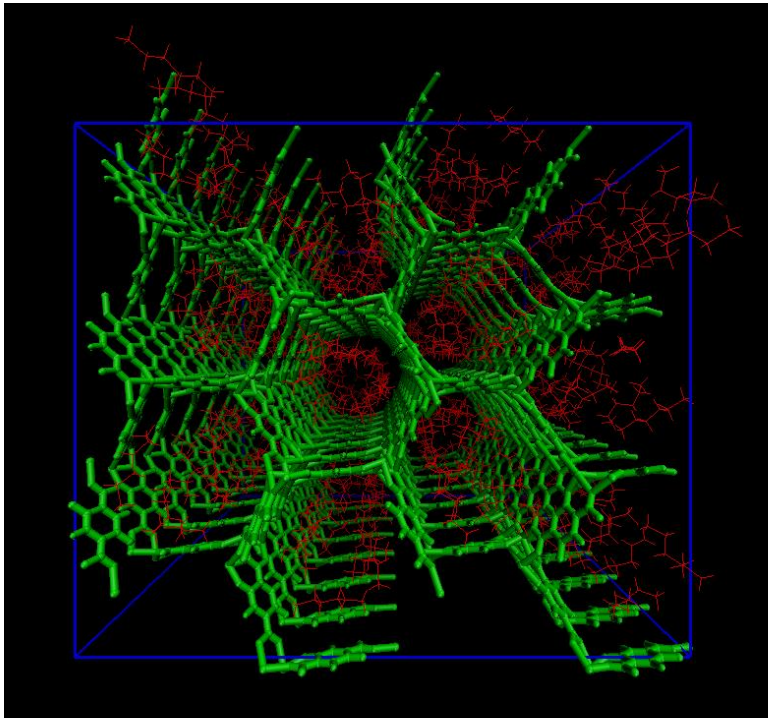


Nanophase-MOHC

Key Scientific Challenges/Questions

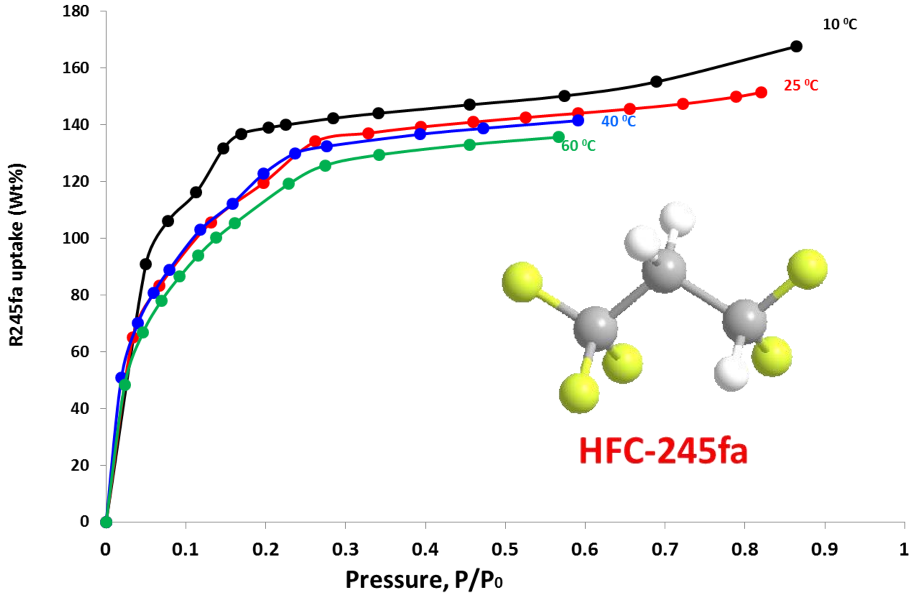
- Can materials be synthesized with the needed uptake capacity and adsorption properties?
- How do working fluid molecules interact with the framework?
- Can stable dispersions of MOHC nanoparticles be made in non-aqueous working fluids?
- How do the MOHC nanofluids perform in a VLCE cycle?
- Do the nanoparticles agglomerate, deposit, or interfere with key system components including heat exchanger, pumps, and turbine generator?
- Does addition of nanoparticles impact physical and/or thermodynamic properties of the working fluid? If so, how?

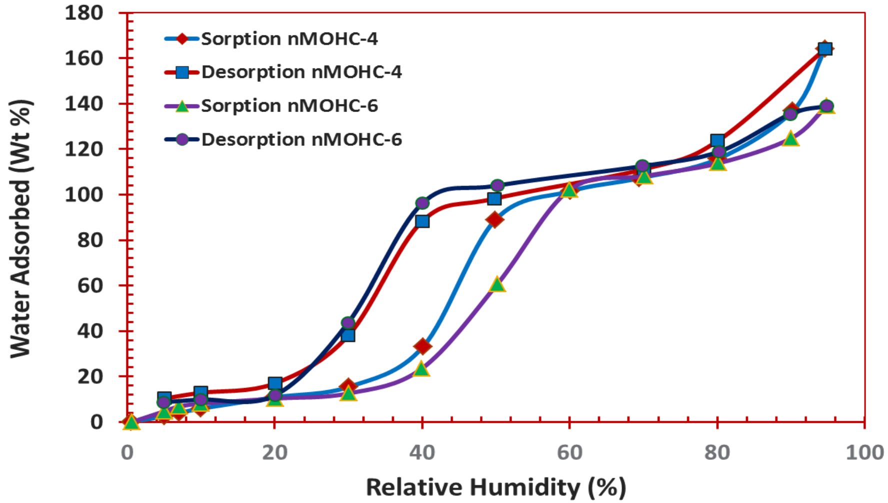
Hexane in Ni-DHTA



Sorption Properties of MOHCs

- Fluorocarbon uptakes were determined for several MOFs (first reported measurements) and with a number of working fluids and show very high capacities
- Nano MOHC-4 exhibited very high water uptake of 163 wt% of water per gram slightly higher than the bulk MOHC-4 clearly indicating the excellent purity and improved performance of synthesized nano MOHC.
- However, nMOHC-6 exhibited only about 131 wt% possibly due to the effect of the modulator rather than the impurity





Technoeconomic Analysis

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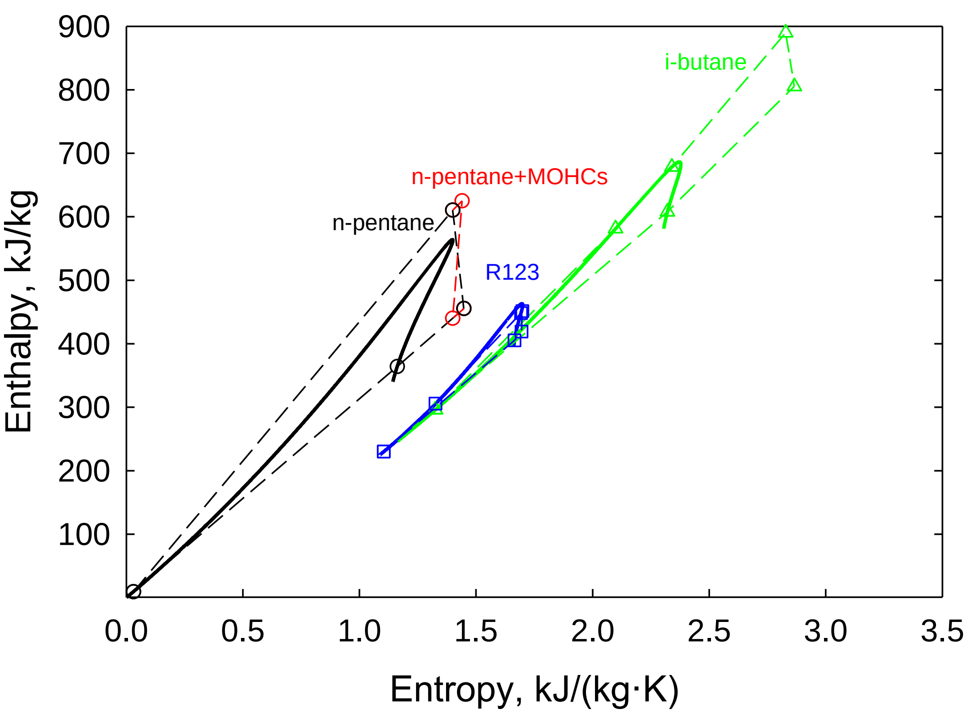
McGrail, B. P., P. K. Thallapally, J. Blanchard, S. K. Nune, J. J. Jenks, and L. X. Dang (2013), Metal-organic heat carrier nanofluids, *Nano Energy*, *2*(5), 845-855.



Performance Summary

Parameters	MOHC	i-C_4H_{10}	R123	Pentane
c_p^p	1.1			
φ	0.007			
Δm_f		0.8	1.6	1.2
ΔH_a		500	250	550
T_o^f		45	30	40
T_e^v		193	175	250
Δh_{sh}		209	16	601
Δh_v		386	167	-
		1.0%	15.5%	4.6%
WF Cost ($/kW)		12.36	128.23	12.86
WF UP ($/kg)		2.24	19.80	2.24
MOHC Cost ($/kg)		300	300	300
NF UP ($/kg)		3.28	20.71	3.28
NF Cost ($/kW)		18.05	134.13	18.79
Power Rate ($/kWh)		0.093	0.093	0.093
Payback Period (d)		**539**	**37**	**117**

$$\Delta h_x^{nf} = [1+\varphi(\Delta m_f - 1)]\ [\underset{\text{sensible heat}}{\Delta h_s^f} + \underset{\text{heat of vaporization}}{\Delta h_v} + \underset{\text{vapor superheat}}{\Delta h_{sh}^v}] + \varphi[\underbrace{\bar{c}_p^{\,p}(T_e^v - T_o^f)}_{\text{sensible heat of nanoparticles}} + \underbrace{\Delta m_f \Delta \bar{H}_a}_{\text{heat of desorption}}]$$

MOHC Dispersions in Water, Methanol and Refrigerants

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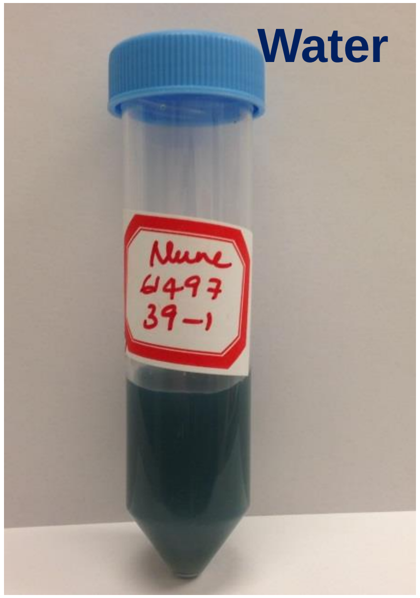
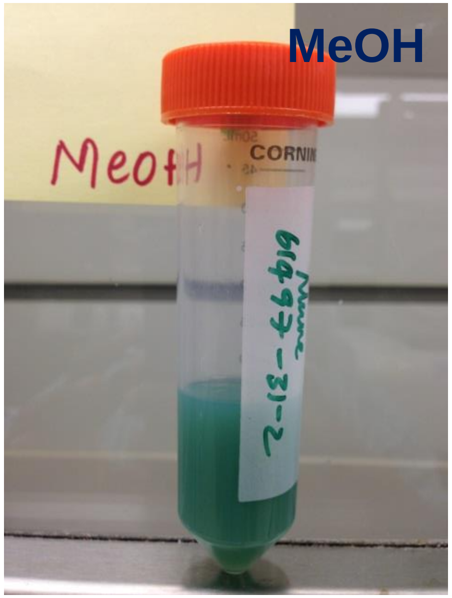
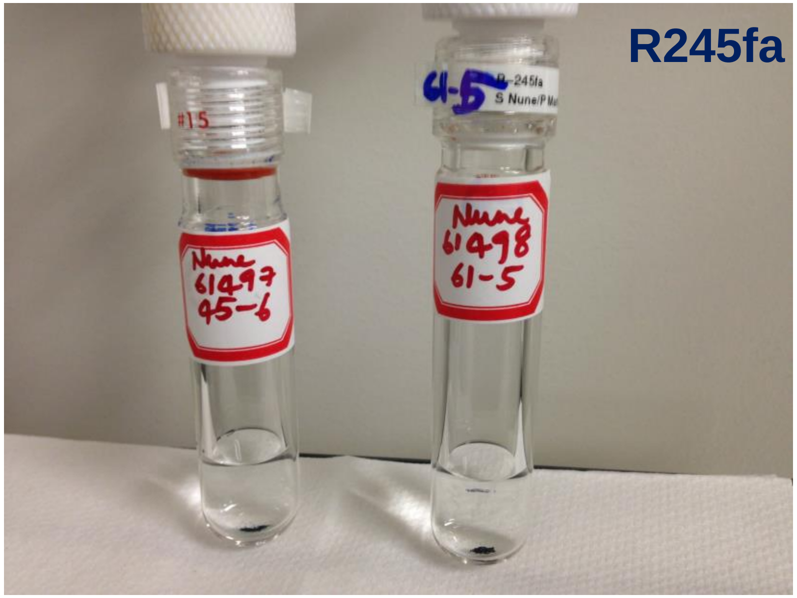


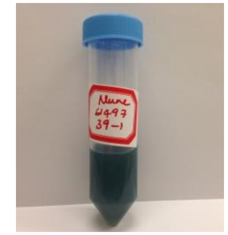




- Stable water and methanol suspensions were easily obtained
  - Hydrophilic surfaces likely assisted dispersion
  - Low density combined with high water uptake minimizes density mismatch with fluid and provides inherent stability
- Dispersions in pure refrigerant (R245fa) could not be formed even with repeated sonication

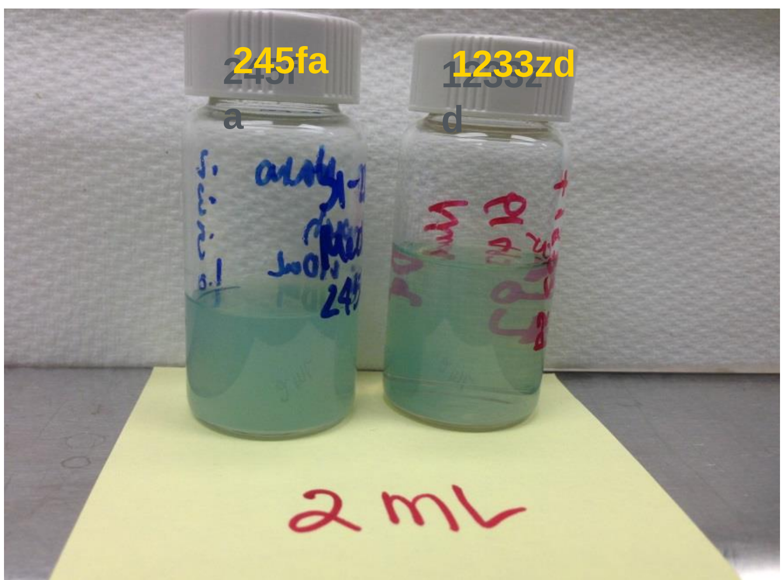
Dispersion of nano MOFs in Refrigerants

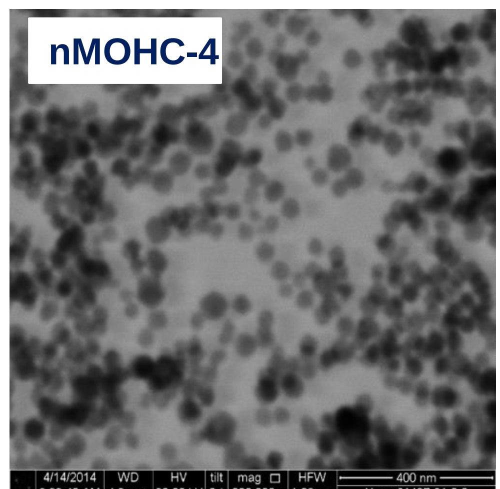
- Key to getting stable dispersions in HFC and HFO refrigerants was initial dispersal in soluble matrix fluid
  - Methanol, tetrahydrofuran, acetronitrile, pentane, etc.
- Will select base fluid for cycle testing once impacts have been assessed

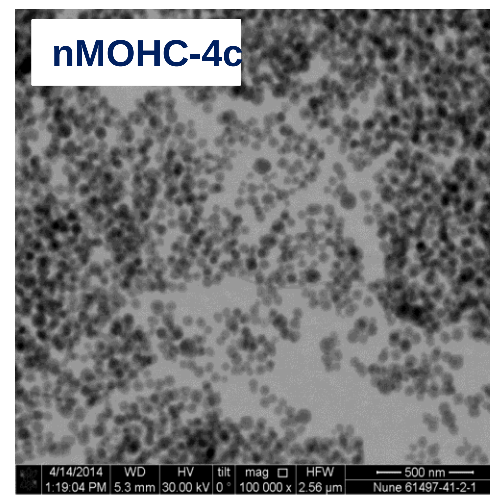


In Water

In Methanol

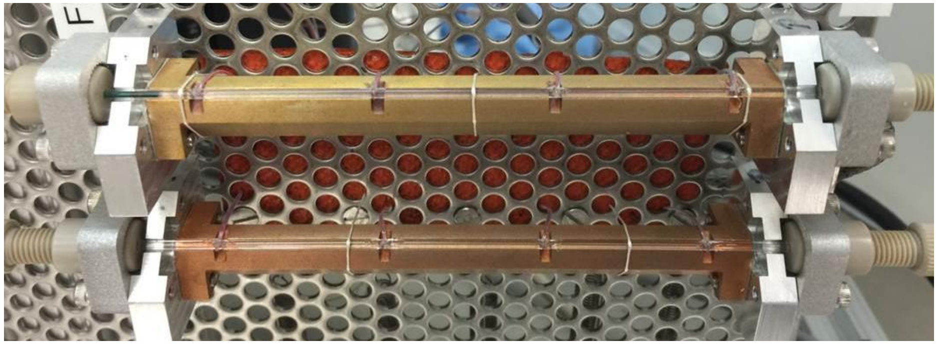






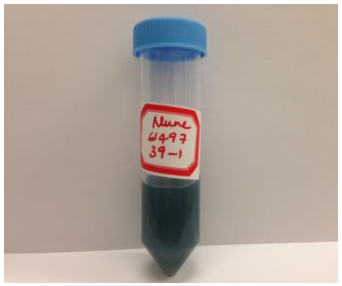
Capillary Tube Test System

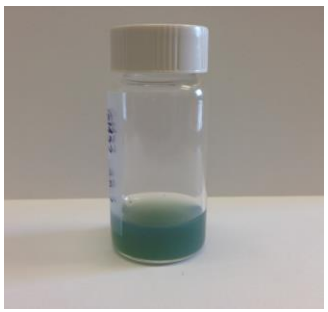
- Enables testing with mL quantities of nanofluids
- Visualization of vapor-liquid transition
- Broad range of Re numbers accessible (10 to 500)
- 300W cartridge heater and heat block provides uniform heat input
- Fine gauge contact thermocouples provide for discrete temperature distributions along capillary
- Dual capillary system provides for fluid preheat just below vaporization temperature and superheat in second capillary



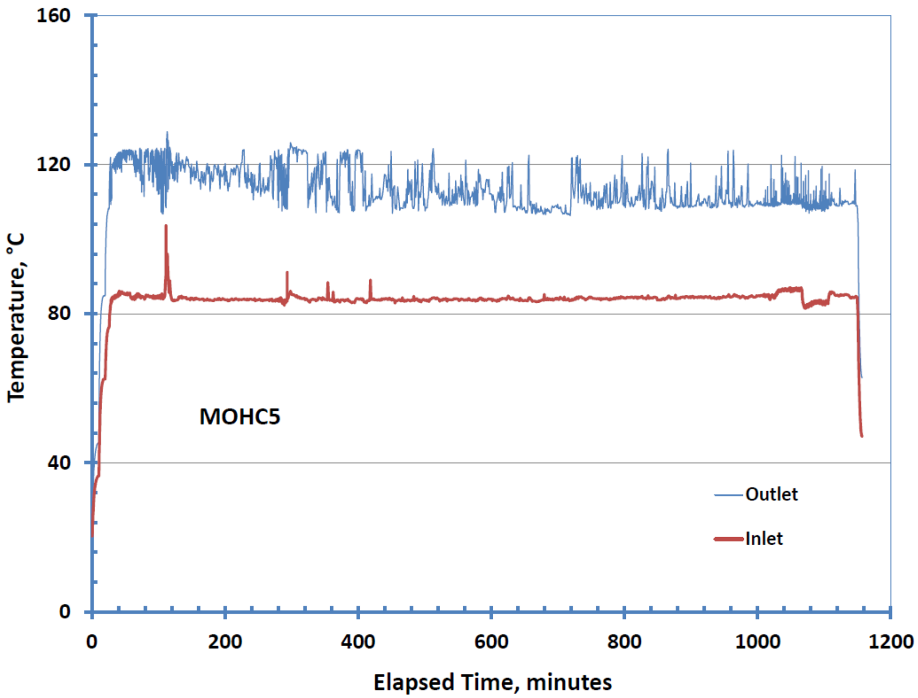
Nanofluid Vaporization

Before





After



- Capillary loop test was used to assess the vaporization behavior of our nano-particle suspensions
- Nanosized MOHC in water were run at 0.465 mL/min giving Reynold's number of 50 in the capillary
- Some limited plating of nanosized MOHCs was observed on the capillary tube walls.

Nanofluids Superheat Microscale Facility

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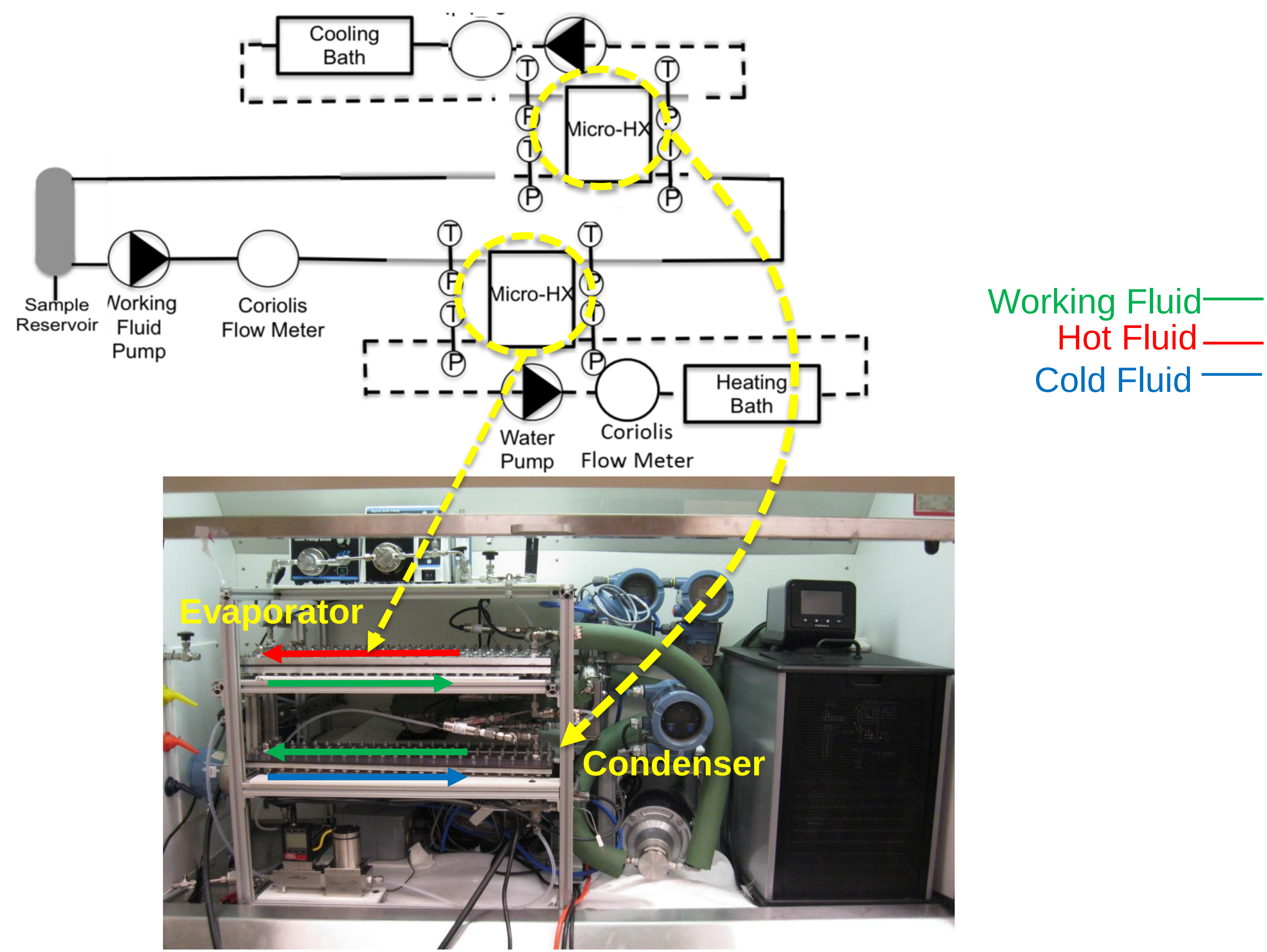
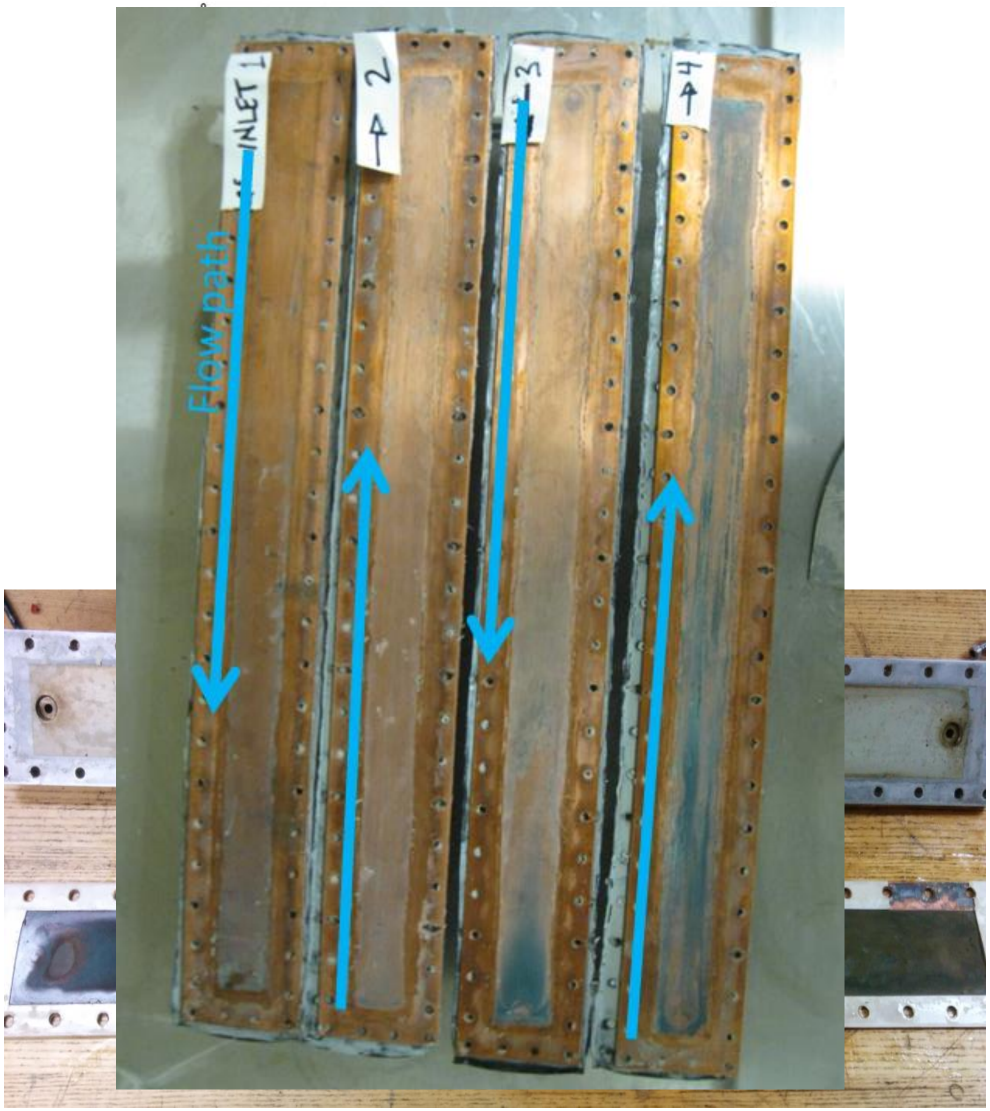
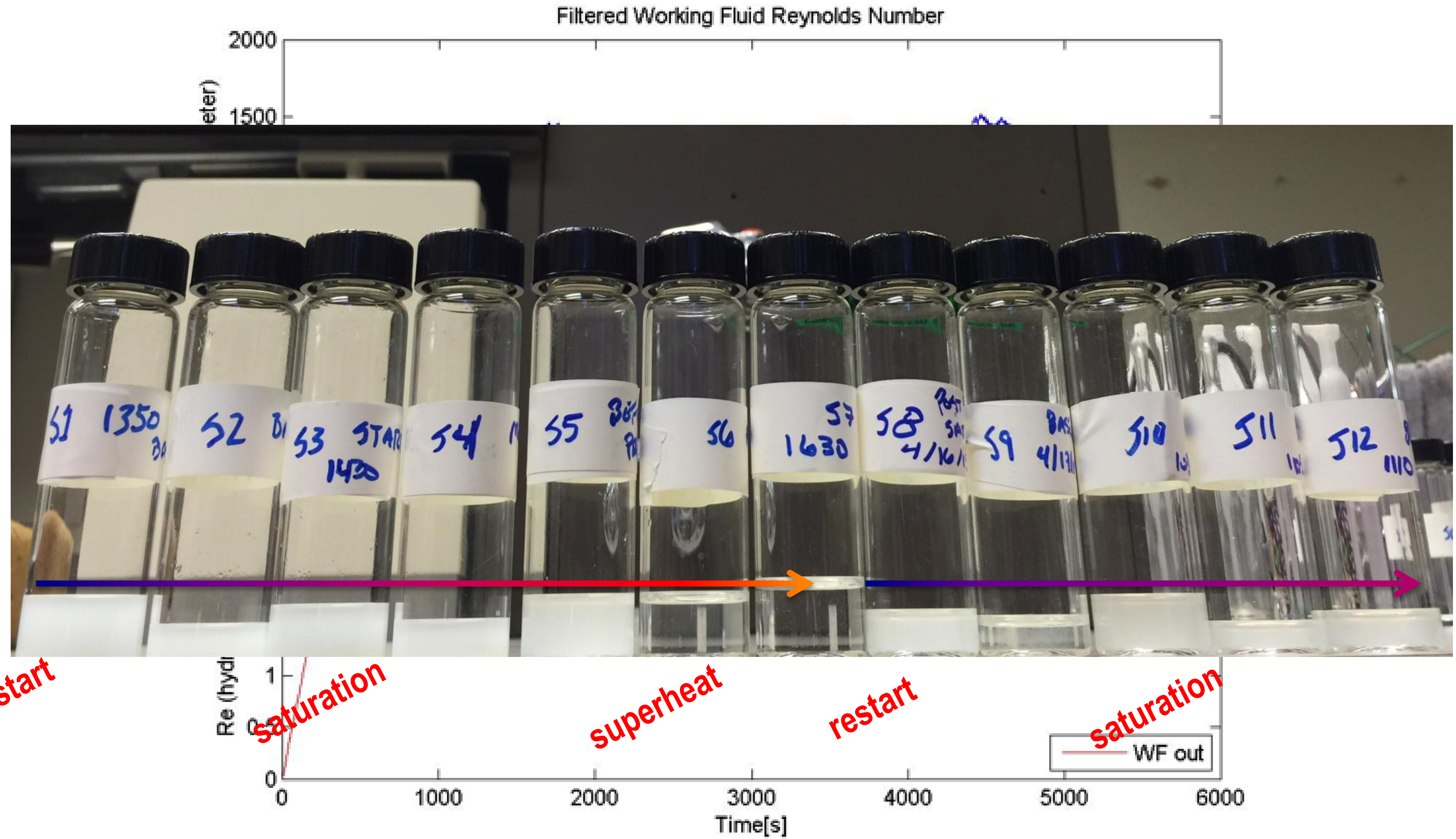


Aqueous Nanofluid Testing

- Laminar flow in Microscale HX
- Particle dropout occurred resulting in partial blockage and pressure increases in HX
- Reduced particle concentration (0.1 wt%) extended test duration but particle dropout still occurred
- Switching to MeOH nanofluid did not solve issue
- Concluded that more advection & possibly turbulent flow was required necessitating a larger tube style HX



Turbulent Flow Re-suspension



Future Directions

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- Existing ORC systems have vapor flows with Re~10^6; Current test facility with tube architecture can only achieve Re~10^4
- Test system is being upgraded with additional pumping power and heat input to achieve higher Re consistent with fully turbulent flow that may allow nanoparticles to completely transition into vapor phase
- Testing in progress with R245fa and other working fluids to determine plateout sensitivity to chemistry of base working fluid

Milestone or Go/No-Go	Status & Expected Completion Date
Issue a journal article on synthesis and characterization of MOHC nanofluids in refrigerants[1]	Complete
Microscale system shows at least 5% improvement in cycle efficiency for non-aqueous nanofluid.	Pending resolution of particle plate out issue

Mandatory Summary Slide

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- Unexpected problems developed in nanoparticle plate out in upgraded systems not observed in previous tests
- FY15 focus will shift to understanding and developing solutions to this issue before proceeding further with system tests (including microturbine)
- Technical and economic promise of MOHC technology remains provided effective solution to plate out issue is demonstrated

Nanofluid Vaporization of MOHC4 in R245fa-MeOH

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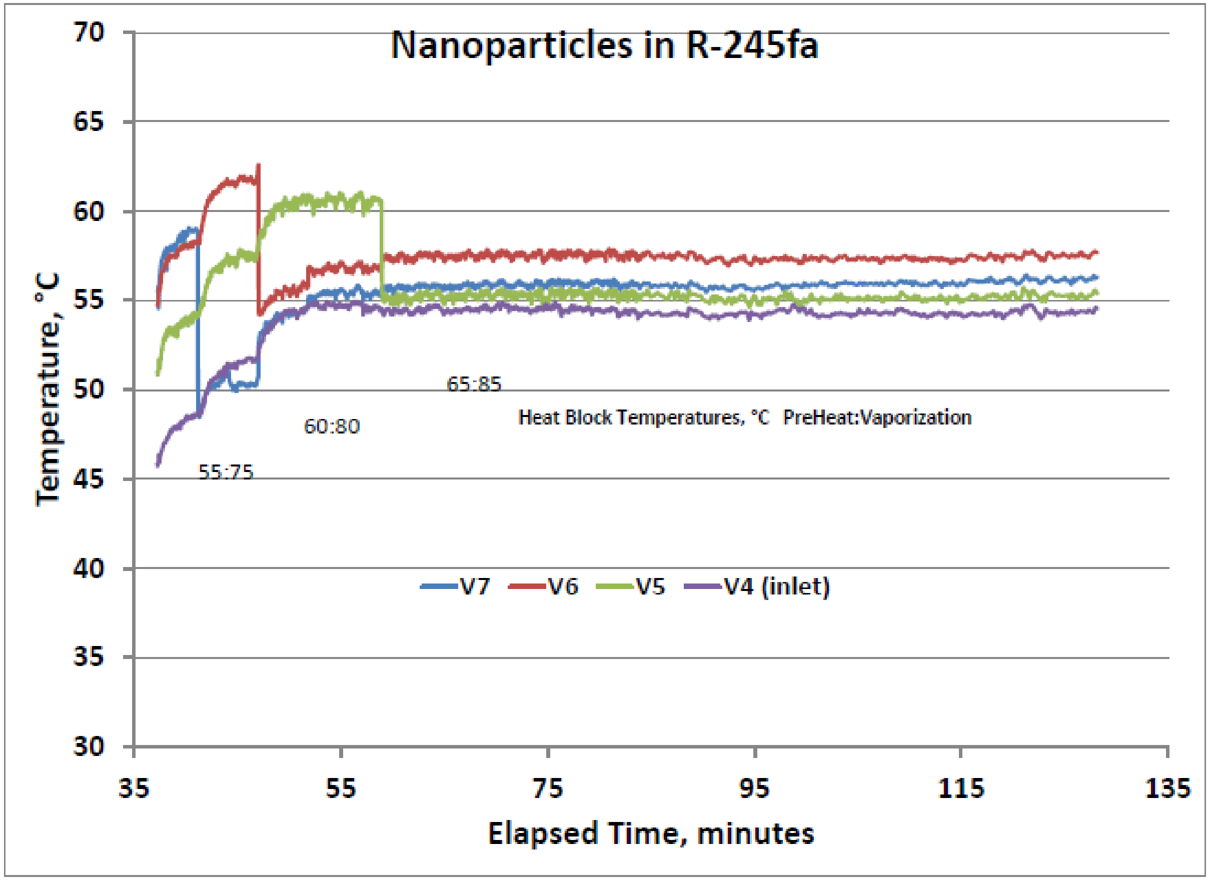

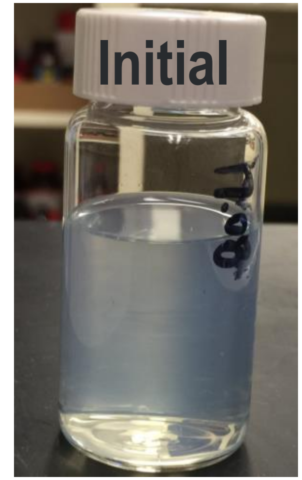

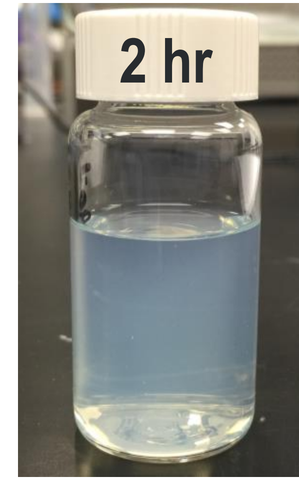

- Nanosized MOHC were run at 1.2 mL/min giving Reynold's number of 158 in the capillary
- After two hours of cycling, we did not observe plating on capillary tube walls