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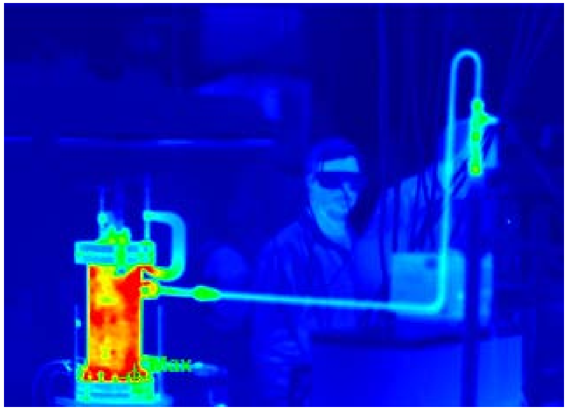

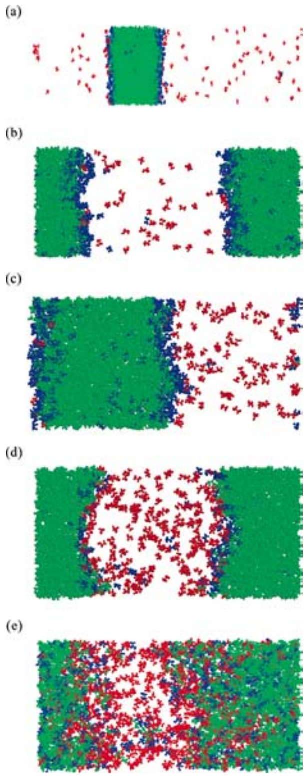

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Working Fluids and Their Effect on Geothermal Turbines

May 19, 2010

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Specialized Materials, Fluids, and Power Plants

Overview

- Timeline
  - start date 9/24/09, end date 9/30/11, 15% complete
- Budget
  - Total project funding $ 945K, DOE share – 100%, awardee share - none,
  - funding received in FY09, $90 K – ORNL; $150 K - SNL
  - funding for FY10, $ 705 K – ORNL
  - Funding was delayed at ORNL (21 % funding on 9/09, 100% on 4/10)
- Goals and Barriers
  - Goal 9 – developing low-cost, high-efficiency energy conversion technologies
  - Barrier N (Energy conversion at low temperature)
- Partners
  - SNL and Barber-Nichols

Relevance/Impact of Research

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Project objective:

Identify new working fluids for binary geothermal plants

Challenges/Innovative aspects:

- Experimental PVT data of new working fluids, especially mixtures, is not available. Measure *PVT* properties of working fluids
- Binary fluids often cannot be described as ideal mixtures. Assess effect of composition & impurities on properties using MD simulations.
- Material degradation data is seldom available for working fluid, including impurities (water). Perform autoclave tests to assess component lifetime.
- New working fluids will be identified based on a systematic study involving property measurements, molecular dynamics modeling of mixture properties, thermodynamic cycle modeling, and material compatibility testing into a laboratory supercritical loop.

Relevance/Impact of Research

Relevance: Accurate *PVT* properties of working fluids are essential for design of energy conversion systems. Vapor-liquid equilibrium phase boundaries and critical lines for the working fluid strongly affect the performance of subcritical and transcritical cycles.

Project impact:

- The composition of mixed fluids will be tuned to maximize plant efficiency for wide a range of well temperatures.
- The increase in the turbine cycle efficiency through the use of new working fluids will allow the successful exploitation of low temperature wells, increasing the options available for geothermal energy use in more sites across the country.

Scientific/Technical Approach

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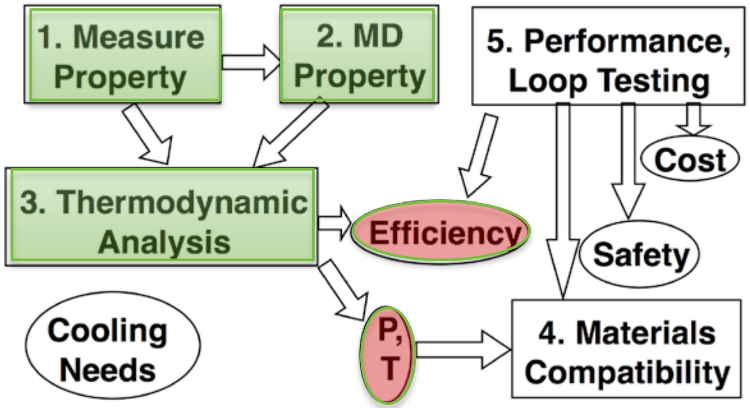


Scientific research method: Measurement of densities and liquid-vapor phase boundaries, will conducted using a unique, high-pressure, vibrating tube flow apparatus and novel methods (ORNL)

Technical feasibility: Vibrating tube densimetry allows the detection of phase boundaries (dew-points and bubble-points) as discontinuities in the vibration frequency response while avoiding the main barriers: (1) assuring complete thermodynamic equilibrium, and (2) accurate determination of the compositions of phases in equilibrium.

Obtain PVT data, including vapor-liquid equilibria and mixture-critical loci, using ORNL vibrating tube densimetry for four different compositions of a non-azeotropic mixture fluid.

Obtain PVT data for the entire composition range of the non-azeotropic mixture fluid using unique ORNL molecular dynamics methods.

Thermodynamic cycle models will be developed for geothermal binary plants.

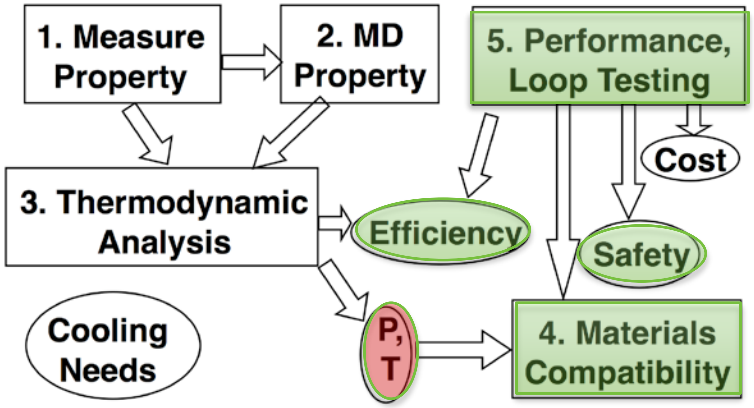
The sensitivity of the plant thermodynamic efficiency to the thermophysical properties of the working fluid will be investigated.

Rank SF_6+CO_2, C_4F_8+CO_2 and other non-azeotropic mixtures of fluids based on thermodynamic efficiency, safety, and cost.

Calculate cycle efficiency for a wide range of compositions.

Identify optimum composition for the non-azeotropic mixture with highest efficiency.

Scientific/Technical Approach



Material degradation issues will be investigated for the chosen non-azeotropic mixture including different impurities (water).

Assessing the potential for 30-year lifetime systems using relatively inexpensive containment materials.

If no safety concerns, one mixture of the working fluid will be tested at a unique pilot-scale Brayton cycle facility at SNL, obtaining experimental data on thermodynamic efficiency.

1) 09/2010 – Choose a typical site and thermal conditions for a feasible binary geothermal power plant. Select a typical working fluid combination and CO_2, CO_2-SF_6.
2) 03/2011 – Perform sensitivity analysis for thermophysical variables on thermodynamic efficiency for target cycle and geological formation.
3) 07/2011 –Complete thermodynamic simulations of a power plant using for a mixture of supercritical CO_2-SF_6.
4) 09/2011 - Obtain the full vapor-liquid equilibrium envelopes and critical points for one set of mixtures.

Accomplishments, Expected Outcomes and Progress

- Progress-to-date:
  - Identification of fluids to be considered in a lab-scale test Brayton loop and for material compatibility autoclave testing based on survey of working fluids: sc-CO_2, SF_6, CH_2F_2, CHF_3, c-C_4F_8, SF_6.
  - Testing and commissioning of experimental apparatus for physical properties measurements
  - Screening tests of S-CO_2, SF_6 and mixtures of CO_2, with He, Propane, and Hexane were issued to SNL staff.
- Planned accomplishments:
  - Measurement of densities in vibrating-tube densimeter
  - Calculation of physical properties of binary mixtures (SF_6+CO_2 and C_4F_8+CO_2) based on molecular dynamics and EOS models.
  - Model implementation of heat transfer coefficients at critical points
  - Thermodynamic cycle with temperature dependent properties of non-azeotropic mixtures
  - Materials testing and loop preparation at SNL

Accomplishments, Expected Outcomes and Progress

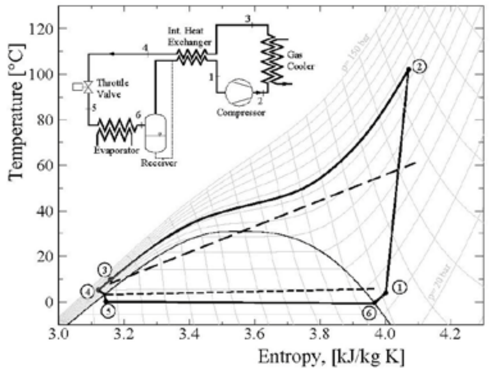
Experimental measurements of Thermodynamic Properties of Working Fluids

Goals:

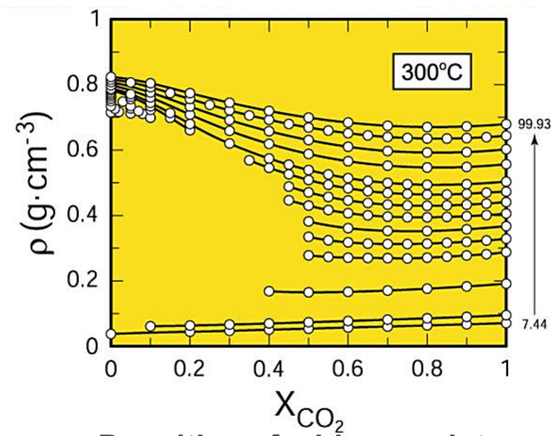
- Obtain densities, vapor-liquid equilibrium (VLE) phase boundaries, and critical lines for a selected non-azeotropic working fluid candidate mixture
- Use experimental results to validate numerical modeling of thermodynamic properties.

Relevance to EGS: VLE and critical loci strongly affect the performance of subcritical and transcritical cycles. The composition of mixed fluids can be tuned to maximize efficiency over a range of source temperatures.

Approach: A unique high-temperature vibrating tube densimeter (VTD) developed at ORNL can provide volumetric and VLE data faster and with better accuracy than other methods.



Example of data: T-S diagram showing a transcritical (pure) CO_2 cycle used for water heating (from Nekså, 2004)

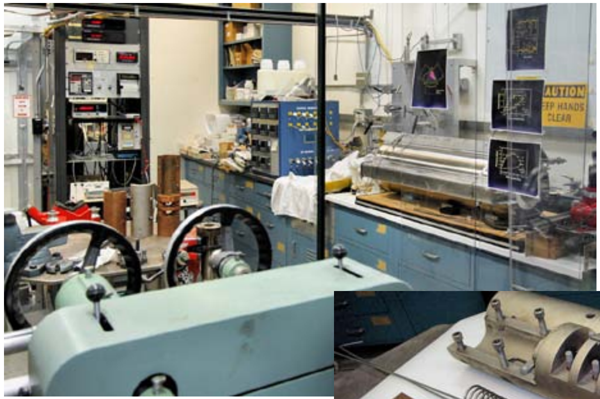


Densities of a binary mixture (H_2O+CO_2) obtained at ORNL by vibrating tube densimetry close to the vapor-liquid equilibrium envelope.

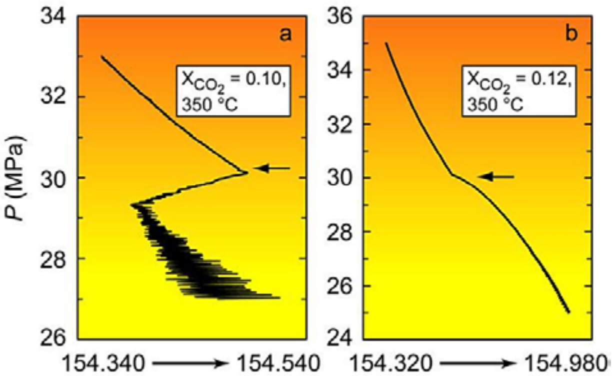
Accomplishments, Expected Outcomes and Progress

Experimental measurements of Thermodynamic Properties of Fluids

- Custom-built flow vibrating tube densimeters (VTD) have been used at ORNL to rapidly and accurately determine densities and phase diagrams of fluid mixtures to 400 ºC and 1,000 bar
- Initial test revealed decreased performance caused by corrosion of the copper isothermal block and electromagnet silver wire coils



ORNL vibrating tube flow densimeter for bulk fluid mixtures operating to 400 ºC and 1000 bar.



The principle of phase boundary detection by VTD (Blencoe *et. al.*, 2001)

- The block was nickel plated and new coils, sealed with moisture-resistant high-temperature glass-ceramic compound will be installed to prevent corrosion at high temperature.

Accomplishments, Expected Outcomes and Progress

Modeling Thermodynamic Properties of Mixture Fluids

Goals:

•Calculate thermodynamic properties of fluid mixtures needed for thermodynamic simulations: enthalpy, entropy, heat capacity, viscosity

•Assess the effect of composition & impurities on properties

Relevance to EGS:

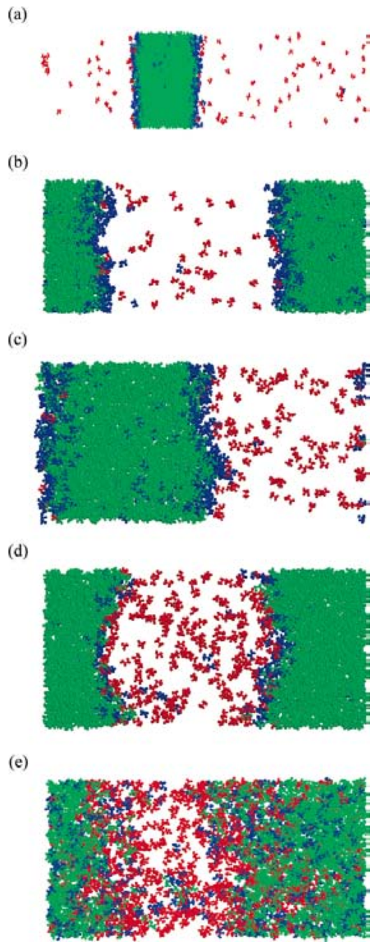
Thermodynamic properties of working fluids through the critical point are essential for design of EGS.

Binary fluids often cannot be described as ideal mixtures. The effect of impurities on phase behavior, such as He introduced for leak detection in CO_2, must be understood.

Approach:

Unique ORNL computational models based on equation of state, molecular dynamics, and statistical methods will be used to develop correlations for fluid compositions.

ORNL models will be validated against experimental results.



Approach to critical point of ethanol through molecular dynamics simulation: liquid is green, vapor is blue, interfacial is red (Steele et al 2007)

Accomplishments, Expected Outcomes and Progress:

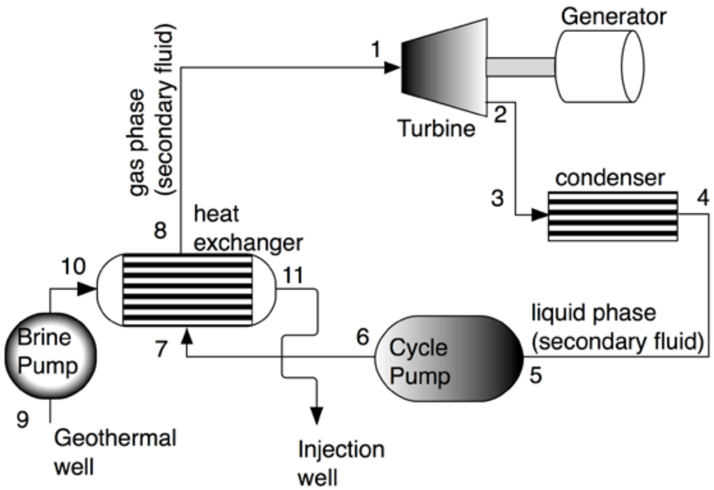
Modeling Thermodynamic Efficiency of Supercritical Cycles

Goals

Obtain P-T for each system component.
Obtain cycle efficiency based on measured/predicted properties of new working fluids.

Relevance to EGS

•Identify optimum mixture composition for maximum cycle efficiency.
•Obtain data on the operating environments experienced by critical components.



$$H^o(T)/RT = -a_1T^{-2} + a_2 lnT/T + a_3 + a_4T/2 + a_5T^2/3 + a_6T^3/4 + a_7T^4/5 + b_1/T$$

$$S^o(T)/R = -a_1T^{-2}/2 - a_2T^{-1} + a_3 lnT + a_4T + a_5T^2/2 + a_6T^3/3 + a_7T^4/4 + b_2$$

Approach

•Employ thermodynamic cycle models for temperature dependent properties of pure mixtures that are availablefor Brayton cycles at ORNL (gas turbine, NASA DB) and SNL (NIST DB)
•Increase the computational efficiency of supercritical cycles by improving the heat exchanger models.
•Consider both air and evaporative cooling for the condenser component.

Testing of New Working Fluids & Materials Compatibility

Goals

•Obtain experimental data from testing a working fluid into a supercritical loop.
•Assess potential for 30-y service lifetime due to working fluid corrosion of containment materials

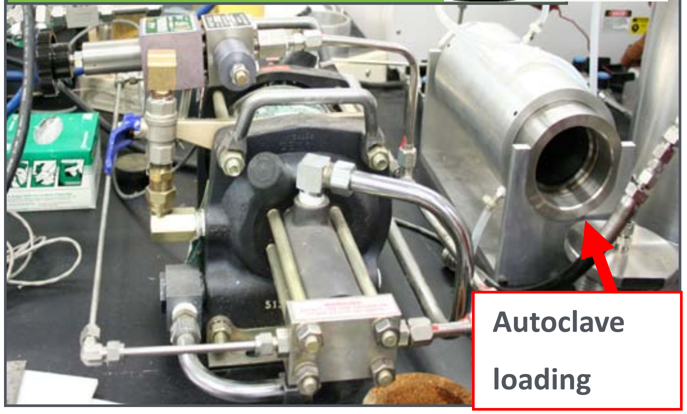
Relevance to EGS

•Experimental data is crucial for concept validation.
•Materials compatibility is important for successful plant design.

Approach

•Conduct several autoclave tests at SNL.
•Test one supercritical fluid at a unique facility, pilot-scale Brayton cycle, at SNL.
•Obtain corrosion modes/rates from bench-scale corrosion tests for mixtures with impurities.
•Surface analysis and metallographic evaluation of materials exposed in autoclave/flow loop.

Autoclave front view



CO_2 20 h Autoclave tests were conducted at SNL

- CO2 pressurized to 1750 psi
- 1h fill time, and depressurization

SF6, and mixtures CO2 + He, Neon, Propane, Hexane are now considered at SNL

Review available information regarding corrosivity of CO_2, SF_6, and mixtures toward inexpensive containment materials (mild steel)

Project Management/Coordination

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- Task leaders were assigned,
- Budget was allocated per each task
- PIs meet monthly to discuss progress and challenges
- Project was delayed to funding at ORNL (21% funding – 09/09; 100% funding received 04/10)
- Budget spent to-date - 13% ORNL
- Scope of work was rewritten for 2 year project
- Project effort evolve according to 2y SOW/Gantt chart

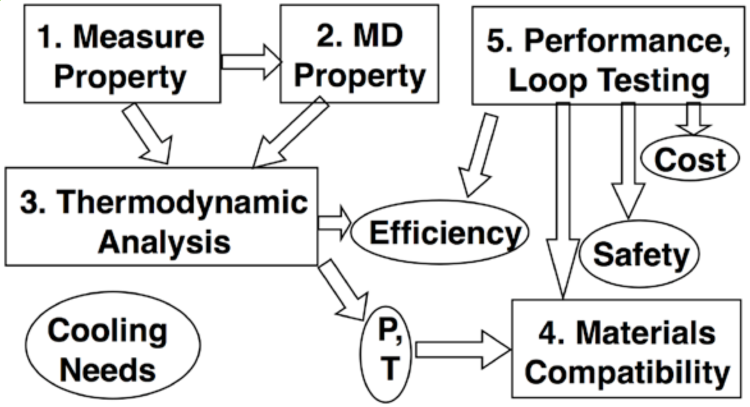
P , I– Preliminary/Detailed investigations,

D – Development, T – testing and validation

Task	1	2	3	4	5	5
Task Leader	MiroslawGruszkiewicz	Joanna McFarlane	Adrian Sabau	Steve Pawel	Lou Qualls	Steve Wright
Year 1	125	115	110	40	25	50
Year 2	125	100	85	40	30	100

Task	1	2	3	4	5	6
Measure thermodynamic properties						
1.1	I	D	T			
1.2		I	D	T		
1.3			I	D	T	T
Modeling mixture properties						
2.1	I	D				
2.2		I	D	D	T	
Thermodynamic analysis						
3.1		I	D	T		
3.2		D	D	T	T	
3.3			I	D	T	T
Materials compatibility						
4.1	I	D	D	T		
4.2		D	D	D	T	T
Supercritical loop testing						
5.1	P	D				
5.2		D	T	T		
5.3			T	T	T	

Future Directions



The cycle efficiency will be calculated for different mixtures of supercritical CO_2-SF_6, assuming perfect mixture properties.

Formulate desired requirements for the thermophysical properties of the working fluid based for maximum efficiency.

Choose one non-azeotropic mixture for detailed investigations based on performance, safety, and cost.

Obtain PVT data for four different compositions of the non-azeotropic mixture fluid.

Obtain PVT data for the entire composition range using molecular dynamics methods.

Calculate cycle efficiency for a wide range of compositions; identify optimum composition.

Material degradation issues will be investigated.

Test one supercritical fluid at a SNL pilot-scale Brayton cycle.

1) 09/2010 – Choose a typical site and thermal conditions for a feasible binary geothermal power plant. Select a typical working fluid combination and CO_2, CO_2-SF_6.

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3) 07/2011 –Complete thermodynamic simulations of a power plant using for a mixture of supercritical CO_2-SF_6.

4) 09/2011 - Obtain the full vapor-liquid equilibrium envelopes and critical points for one mixture.

Summary: new working fluids for binary geothermal plants will be identified

- Experimental PVT data of new non-azeotropic working fluids will be obtained
- Accurate, non-ideal mixture constitutive equations for properties of binary fluids, including impurities will be obtained using MD simulations.
- Lifetimes of components exposed to the working fluid with impurities will be obtained from autoclave tests.
- New working fluids will be identified based on a systematic study:
  - property measurements,
  - molecular dynamics modeling of mixture properties,
  - thermodynamic cycle modeling,
  - material compatibility testing into a laboratory supercritical loop.