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Modeling Hydrogen Transport and Precipitation of Hydrides in Zircalloy using Thermo-Chemistry Solver in BISON

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April 30, 2014

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Outline

- Project highlights
- Introduction to thermodynamics and THERMOCHIMICA
- New implementation of THERMOCHIMICA and reaction-diffusion equation for Zr hydride precipitation in BISON
- Examples

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Highlights

- **This project contributes to the NEAMS vision by:**
  - Developing an efficient thermochemical code, THERMOCHIMICA, for coupling to depletion, transport and material models
  - Utilizing thermochemical models to simulate chemical evolution in nuclear fuel and reactor components
  - Providing information to various material and process models
- **The tasks for FY13 were:**
  - Advancement of THERMOCHIMICA utilizing fuel models/databases
  - Integration of THERMOCHIMICA with BISON
  - Expansion of a thermochemical database for fuel-fission products
- **The main accomplishments in FY13 were:**
  - Initial integration of THERMOCHIMICA with BISON
  - Demonstration of prediction of oxygen potential across oxide fuel radius at high burnup
  - Initial demonstration of hydriding of clad using transport coupled with THERMOCHIMICA

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Highlights (cont.)

- **FY14 Tasks**
  - Refine/improve coupling of THERMOCHIMICA with Moose/Bison
  - Couple THERMOCHIMICA with Marmot
  - Expand THERMOCHIMICA capability for handling complex thermochemical models
  - Simulate fuel-fission product behavior including transport

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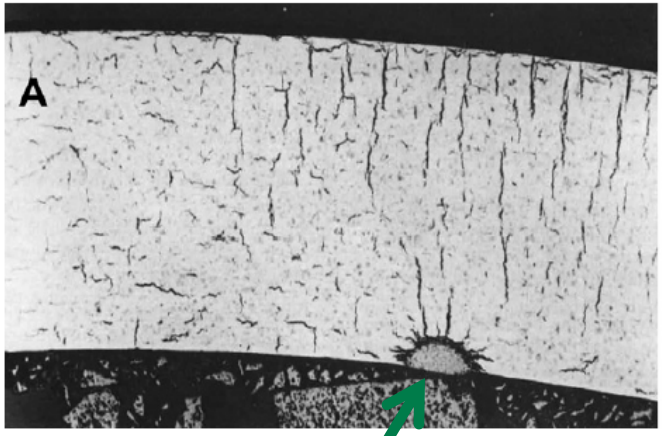
Thermochemistry Applications in Nuclear Fuel

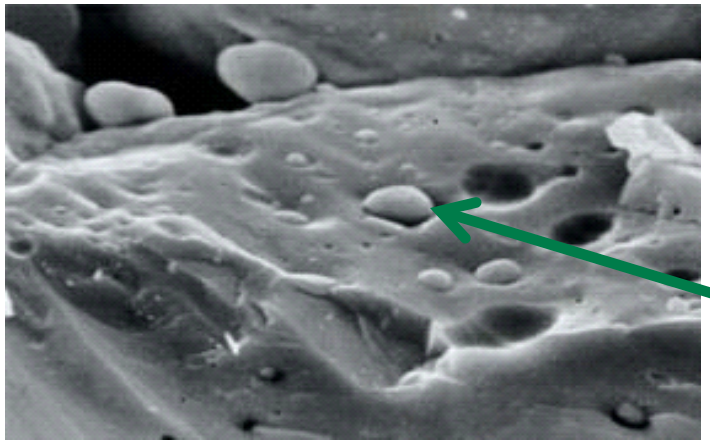
- **Example applications include:**
  - Zirconium hydriding,
  - Irradiated fuel chemistry in-reactor,
  - Irradiated fuel chemistry out-reactor,
  - Fission gas retention,
  - Iodine-induced stress corrosion cracking (I-SCC interaction (PCI)
  - CRUD formation.

LWR Clad Image



Sunburst formation (hydride blister) in fuel clad.

SEM in high burnup structure UO_2 fuel



Noble metal HCP "white phase".

Above: Figure kindly provided by T. Wiss and V.V. Rondinella (ITU)
Top right: Markowitz, WAPD-TM-351, Bettis Atomic Power Lab., 1963.

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Thermodynamic Modeling

Define components, species, phases, conditions

↓

Define solution models, activities

↓

Develop thermodynamic model and database

↓

Define initial species, pressures, temperatures

↓

Calculate chemical equilibrium

- Thermodynamic databases
- Thermodynamic software
- Process model
  - e.g. BISON
- THERMOCHIMICA

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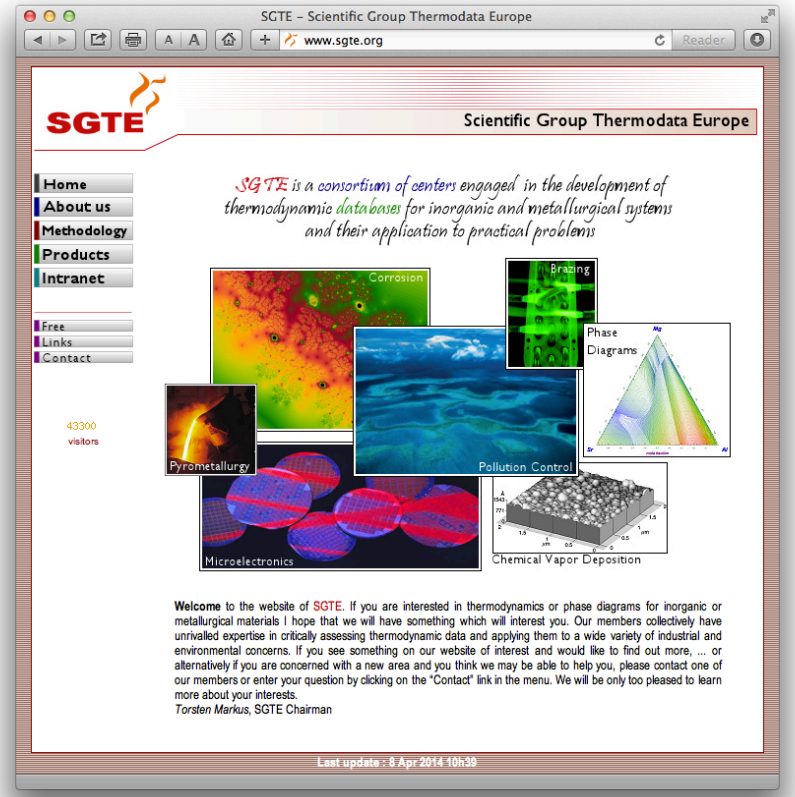
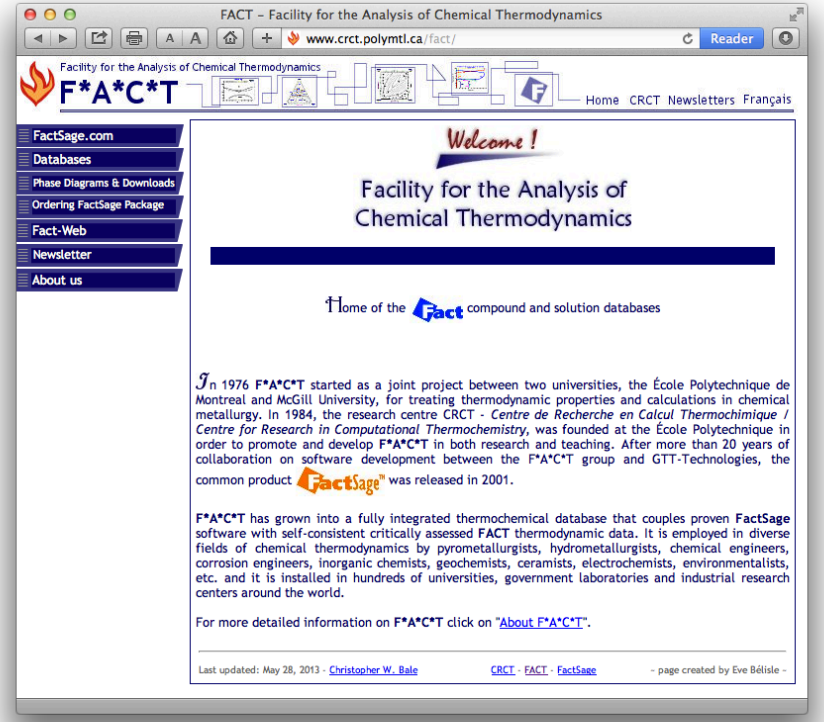
Thermodynamic Databases

- **SGTE (Scientific Group Thermodata Europe)**



- **FACT (Facility on Analysis of Chemical Thermodynamic)**



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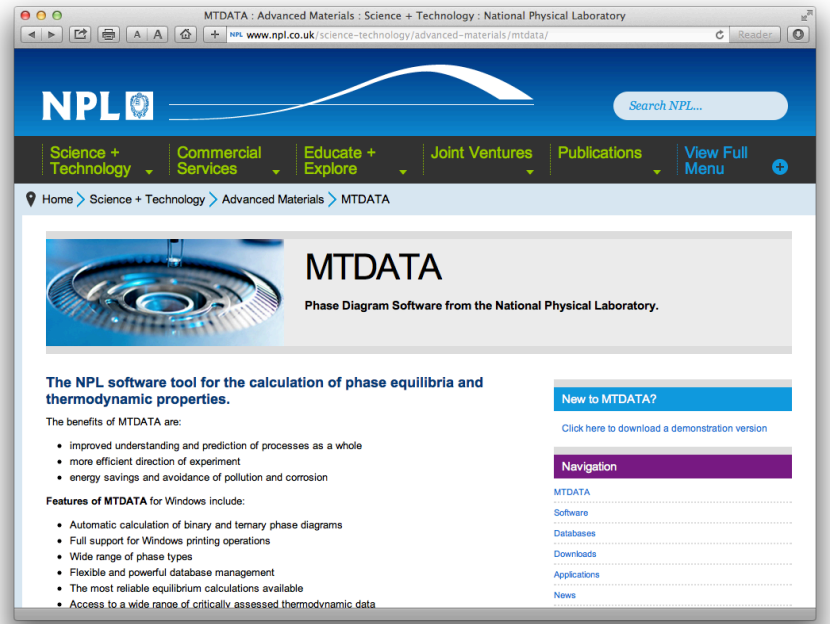
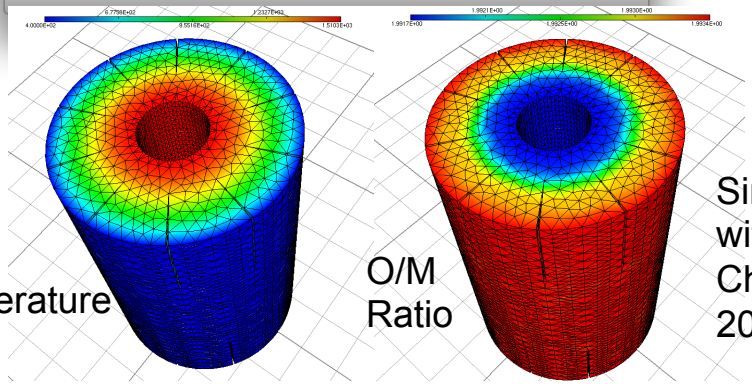
Thermodynamics Software with APIs

■ FACTSAGE & ChemApp

■ MTDATA NPL

- Windows only





Temperature

O/M Ratio

Simulations with ChemApp in 2009

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History of THERMOCHIMICA

- THERMOCHIMICA is an open-source thermochemistry library.
- History: Initiated during M.H.A. Piro thesis at RMC, continued during Post-Doc at ORNL, currently maintained by Piro, his students and S. Simunovic.
- The main source code is maintained on a repository managed by Piro. A copy in the Moose/Bison repository contains additional APIs .
- The solver has similar capabilities as commercial codes.
- Several algorithms have been advanced/developed to speed up the computations and make the solver more robust.

M.H.A. Piro, "Computation of Thermodynamic Equilibria Pertinent to Nuclear Materials in Multi-Physics Codes," PhD Thesis, Royal Military College of Canada (2011).
M.H.A. Piro, S. Simunovic, T.M. Besmann, B.J. Lewis and W.T. Thompson, Comp. Mater. Sci., 67 (2013) 266-272.

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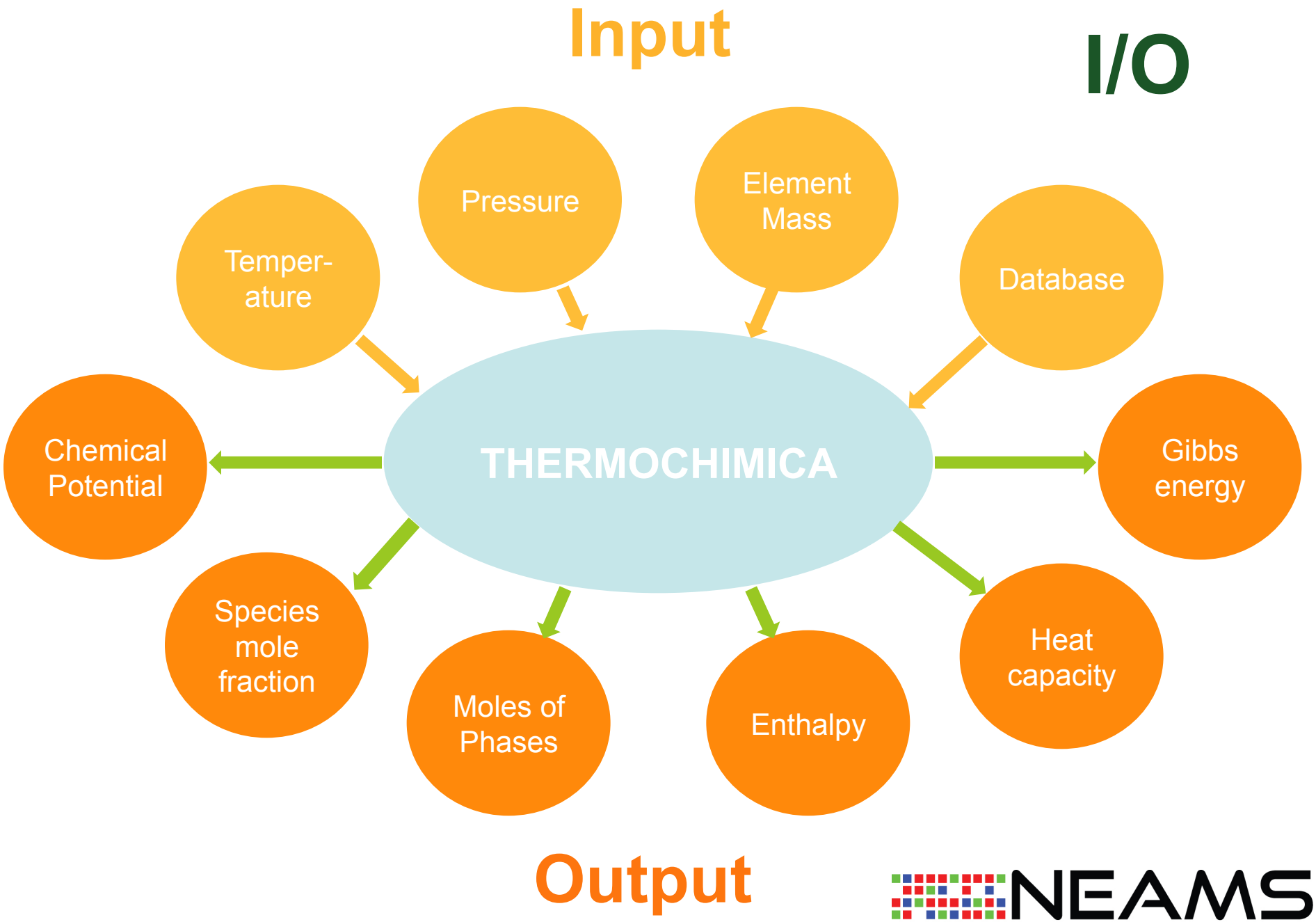
Thermochimica: Input / Output

- **Input:**
  - Temperature,
  - Hydrostatic pressure,
  - Mass of each chemical element, and
  - Thermodynamic data-file.

- **Output:**
  - Which phases are stable and their quantities (e.g., does it rust? does it melt?),
  - What is the composition of each phase (e.g., how much Cs/I is in gas and how much is solid?),
  - Chemical potentials of every component in the system (useful for mass diffusion), and
  - Heat capacity, enthalpy, entropy and Gibbs energy of system (useful for Phase Field simulations).

I/O



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Gibbs Energy Minimization in a Nutshell

- At thermodynamic equilibrium, the Gibbs energy of a closed system at constant temperature and pressure is at minimum.
  - Satisfying conservation of mass, the first and second laws of thermodynamics, and Gibbs phase rule.
- The numerical procedure determines a unique combination of co-existing phases with a unique composition of constituents that yields a minimum in the integral Gibbs energy function.
- Different types of thermodynamic models are capable of describing different physical-chemical behavior.
- **Time dependency is not considered.** This is generally a good assumption when temperature is high and time scale is long.

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Numerical Methods

- From a mathematical point of view, this is a numerical optimization problem of a non-convex function with linear and non-linear equality and inequality constraints. Also, the active set of constraints change throughout the iteration process.

- The overall objective is to minimize the integral Gibbs energy of the system subject to the mass balance constraints and Gibbs' Phase Rule.

- Numerical methods employed by THERMOCHIMICA are described in the literature (1-4).

1. M.H.A. Piro and S. Simunovic, CALPHAD, 39 (2012) 104-110.
2. M.H.A. Piro, S. Simunovic, T.M. Besmann, B.J. Lewis and W.T. Thompson, Comp. Mater. Sci., 67 (2013) 266-272.
3. M.H.A. Piro, T.M. Besmann, S. Simunovic, B.J. Lewis and W.T. Thompson, J. Nucl. Mater., 414 (2011) 399-407.
4. M.H.A. Piro and B. Sundman, to be published.

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Numerical Methods – Local Minimization

- Minimize the integral Gibbs energy of the system (i.e., 1st and 2nd law of thermodynamics):

$$G = \sum_{\lambda=1}^{\Lambda} n_\lambda \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \mu_{i(\lambda)} + \sum_{i=1}^{\Omega} n_\omega \mu_\omega$$

- Subject to the following linear equality constraints (i.e., conservation of mass):

$$b_j = \sum_{\lambda=1}^{\Lambda} n_\lambda \sum_{i=1}^{N_\lambda} x_{i(\lambda)} a_{i,j} + \sum_{i=1}^{\Omega} n_\omega a_{\omega,j} \qquad \sum_{i=1}^{N_\lambda} x_{i(\lambda)} = 1$$

- and inequality constraints (i.e., non-negative mass and Gibbs' Phase Rule):

$$x_{i(\lambda)} > 0 \qquad n > 0 \qquad \Lambda + \Omega \leq E$$

M.H.A. Piro, S. Simunovic, T.M. Besmann, B.J. Lewis and W.T. Thompson, Comp. Mater. Sci., 67 (2013) 266-272.

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Numerical Methods – Global Minimization

- At thermodynamic equilibrium, the following linear equality constraints must be satisfied for all stables phases:

$$\mu_{i(\lambda)} - \sum_{j=1}^{E} a_{i,j}\Gamma_j = 0 \qquad \mu_{\omega} - \sum_{j=1}^{E} a_{\omega,j}\Gamma_j = 0$$

- and the following non-linear inequality constraints must hold true for all other phases in the system (i.e., the system is not metastable. Equivalently, a global minimum has been reached and not a local minima):

$$\min_{x} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^{E} a_{i,j}\Gamma_j \right) > 0 \qquad \mu_{\omega} - \sum_{j=1}^{E} a_{\omega,j}\Gamma_j > 0$$

- A modified branch and bound approach has been adopted for the non-linear inequality constraints. This is tested when a local minima has been reached.

M.H.A. Piro and B. Sundman, to be published.

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Current Status / Future Plans of THERMOCHIMICA

- **Current capabilities:**
  - Ideal solution phases and pure condensed phases,
  - Substitutional Kohler-Toop model with regular polynomials,
  - Substitutional Redlich-Kister-Muggiano model with Legendre polynomials,
  - Compound energy formalism with Legendre polynomials (up to 5 sublattices).
  - Parse ChemSage data-file on input. Data-files can contain a maximum of 48 chemical elements, 1500 chemical species and 24 solution phases.

- **Limitations and future work:**
  - Only ideal gases can be considered (not real gases),
  - Aqueous phases cannot be considered (needed for CRUD/corrosion),
  - FactSage (commercial software) is required to generate a database,
  - More work is needed in software quality assurance,
  - More work is needed in enhancing computational performance, and
  - Expand user group.

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Hydride Precipitation in Zircalloy: Motivation for Modeling

- As Zirconium is corroding, it is absorbing a fraction of the H released by the oxidation reaction
- H precipitates as hydrides when the solubility limit is exceeded
- Zr-base system phases: hcp, low-temperature α phase, and bcc high-temperature β phase have different H solubility and mobility
- Crack grows by increments that are proportional to the size of hydride region. Sub-critical crack growth mechanism (DHC).
- The large local volume mismatch associated with hydride formation makes it difficult to measure a true equilibrium value of TSS.

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Hydrogen Transport and Hydride Formation Equation in Bison

- **Heat Diffusion *(T)***

$$\rho C_p \frac{\partial T}{\partial t} - \nabla \cdot k \nabla T - q = 0$$

- **Hydrogen Transport *(H)***

$$J = -D\left(\nabla H_{SS} + \frac{Q^* H_{SS}}{RT^2}\nabla T\right) \qquad \frac{\partial H_{ss}}{\partial t} - \nabla \cdot J - Q = 0$$

- **Hydride Precipitation *(ZrH_x)***
  - Use material model to calculate thermo-chemical equilibrium using THERMOCHIMICA
  - Calculate source/sink, **Q**, for hydrogen in transport equation based on the material model data
  - First order model

$$Q = \frac{H_{ZrH_x}^{(t+\Delta t)} - H_{ZrH_x}^{(t)}}{\Delta t}$$

- **…**
- **Other physics (a.k.a. kernels) and material models can be now easily added**
  - **Make sure thermo-chemical equilibrium is calculated once per integration point because it is expensive**

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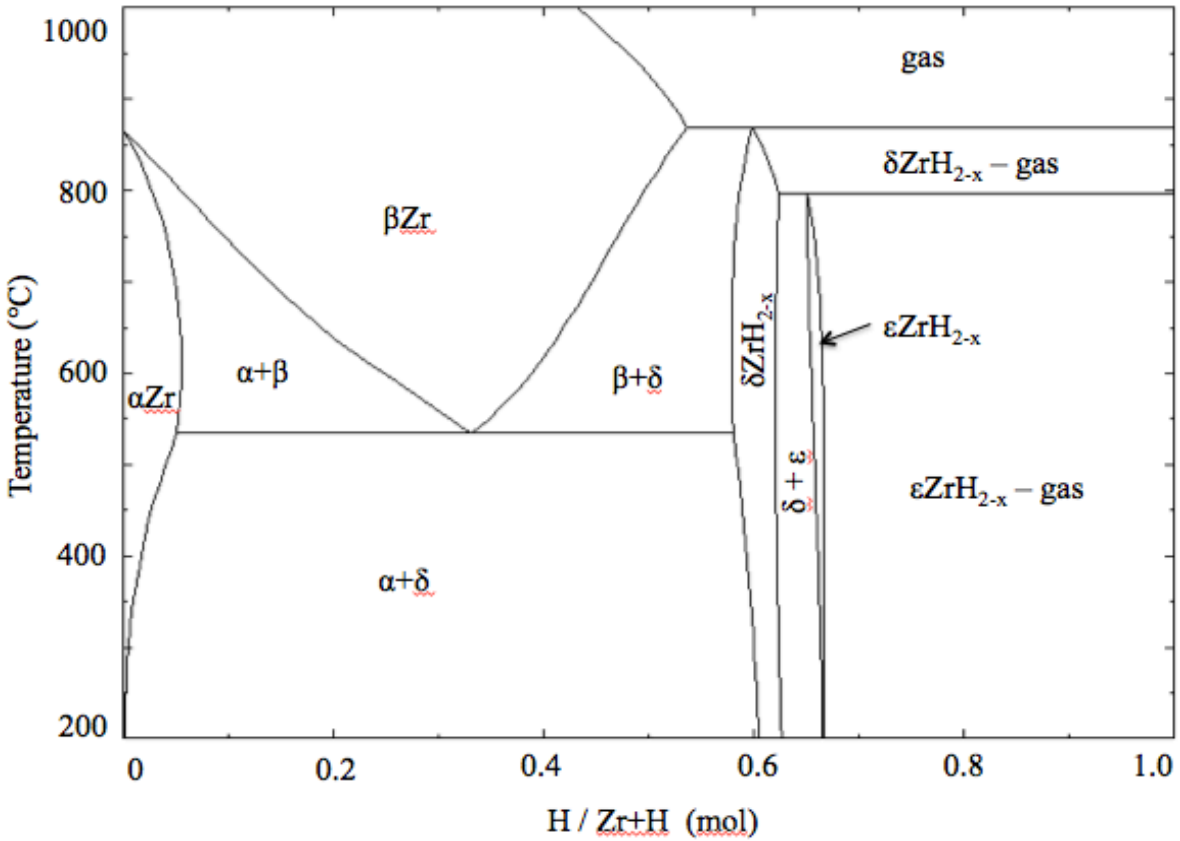
Thermodynamic Model for Zr-H System (FactSage File)



- THERMOCHIMICA Calculations were in a close agreement with the commercial thermochemical equilibrium solver FactSage

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Implementation of Material Model for Zr Hydride Formation

```
void MaterialHZrH::computeQpProperties(){
…
FORTRAN_CALL(Thermochimica::ssinitiatezrhd)();    // read model data file, read only once
…
HinZrHppm = _hhydride_old[_qp]; // H in ZrH, immobile, ppm
Hppm = _transported[_qp]; // H in solid solution, mobile, ppm
HTotalppm = Hppm + HinZrHppm;
…
FORTRAN_CALL(Thermochimica::settemperaturepressure)(&Temperature, &Pressure); // set T, p
iElement=40; FORTRAN_CALL(Thermochimica::setelementmass)(&iElement, &dBMol); // Zr
iElement=1;  FORTRAN_CALL(Thermochimica::setelementmass)(&iElement, &dAMol); // H
…
FORTRAN_CALL(Thermochimica::thermochimica)(); // calculate thermochemical equilibrium
…
iH=2;        // get second element in the model, H
char s1[] = "ZRH2_DELTA,ZRH2_EPSILON";            // Hydride phases to search for in eq. solution
FORTRAN_CALL(Thermochimica::ssfindsolnspecies)(s1, iPhNameL, iH, dMolSum); // mol of H in s1
dZrHRatio = dMolSum / dAMol;              // fraction of hydrides in total moles of H
…
_hhydride[_qp] = HTotalppm * dZrHRatio;       // H in hydrides in ppm, new value
…
_dhhydride[_qp] = _hhydride[_qp] -  _hhydride_old[_qp]; // difference in hydrides for source rate
}
```

Partial source code.

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Source/Sink for Zr Hydride Formation

```
template<> InputParameters validParams<HZrHSource>()
{
  InputParameters params = validParams<Kernel>();
  params.addParam<Real>("scaling", 1.0, "The scaling factor for the source.");
  return params;
}

HZrHSource::HZrHSource(const std::string & name, InputParameters parameters) :
    Kernel(name, parameters),
    _scaling(getParam<Real>("scaling")),
    _dhhydride(getMaterialProperty<Real>("dhhydride"))
{}

Real HZrHSource::computeQpResidual()
{
  Real value;
  value = _dhhydride[_qp] / _dt;
  value *= _scaling;
  return _test[_i][_qp]*value;
}
```

Entire source code!

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Examples

- One element problem
- Multiple-elements

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Example Model Parameters

Thermal Model

- ρ = 6551 kg/m^3
- k = 16 W/m-K
- c = 330 J/kg-K
- T=573K (distributed 573K - 673K for larger problems)

Hydrogen Diffusion Coefficient

- Kearns, J of Nuclear Materials, 43, 1972
- D_0 = 7.9e-7 m^2/sec
- Q = -4.49e+4 J/mol

$$D = D_0 e^{-Q/RT}$$

Hydrogen Heat of Transport

- Sawatzky, J of Nuclear Materials, 2, 1960
- Q* = 2.51e+4 J/mol

Thermo-Chemical Equilibrium Model

- FactSage

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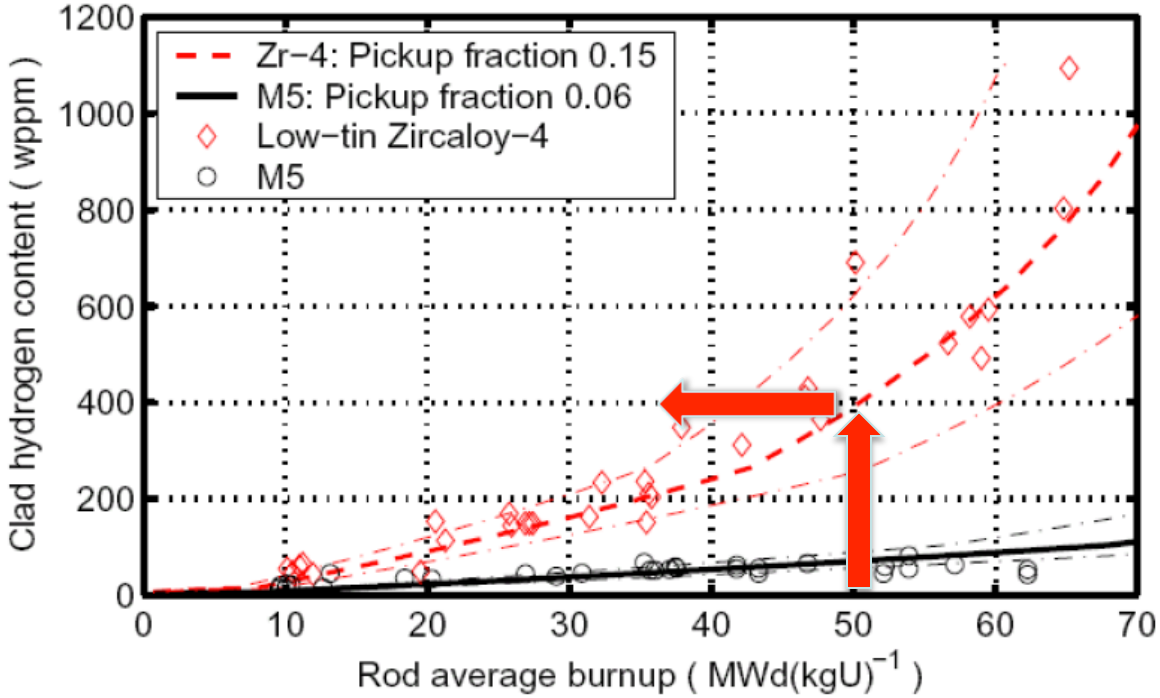
Problem Data



- **H content based on 50 MWd(kgU)$^{-1}$, 400 wppm**

P.Bouffioux (EDF R&D) –B.Cheng (EPRI)

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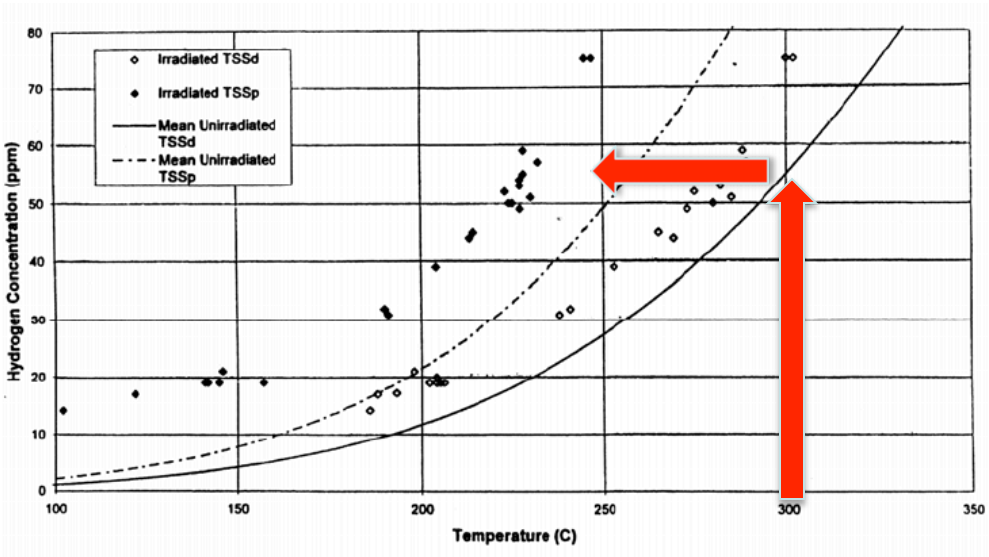
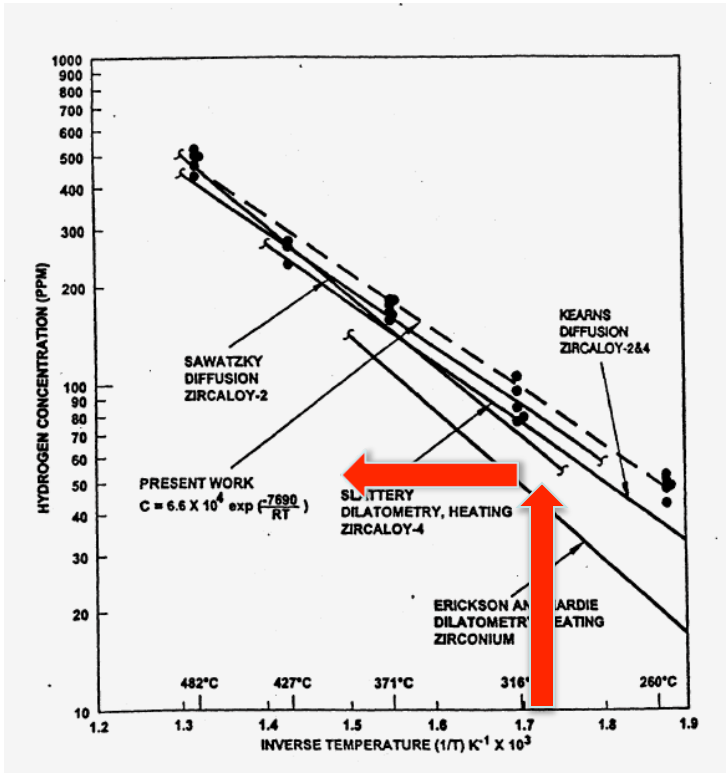
Problem Data



- **H content dependence on radiation**

A. McMinn et al., "The Terminal Solubility of Hydrogen in Zirconium Alloys", 1998, ASTM-STP-1354, pp173-195.



- **H solubility**

B. F. Kammenzind et al., Hydrogen Pickup and Redistribution in Alpha-Annealed Zircaloy-4, WAPDT-3047, Bettis Atomic Power Laboratory, 1995.

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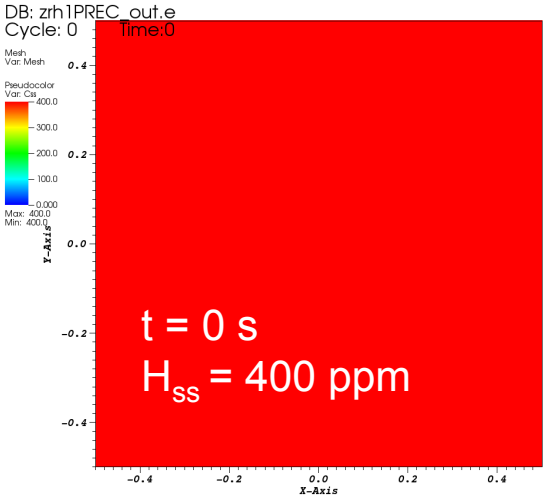
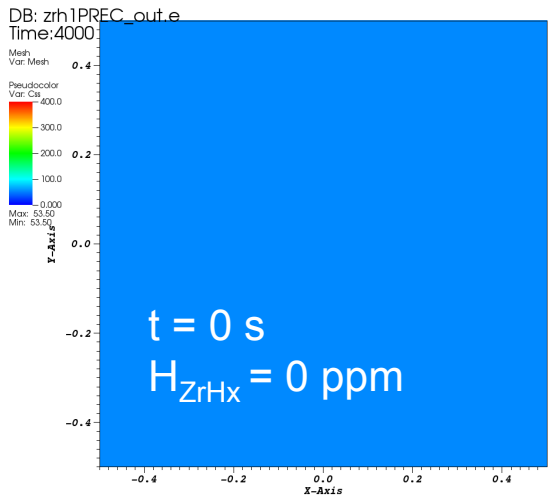
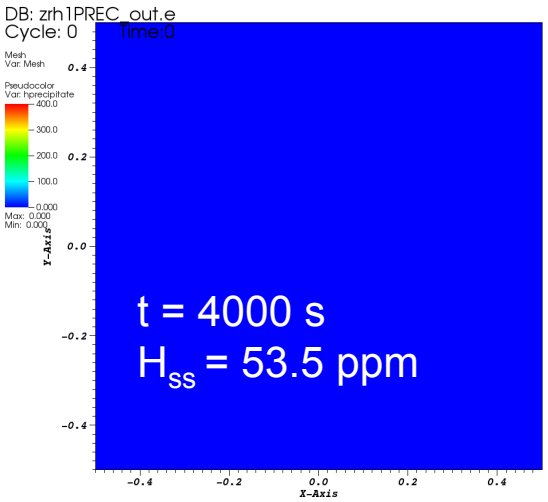
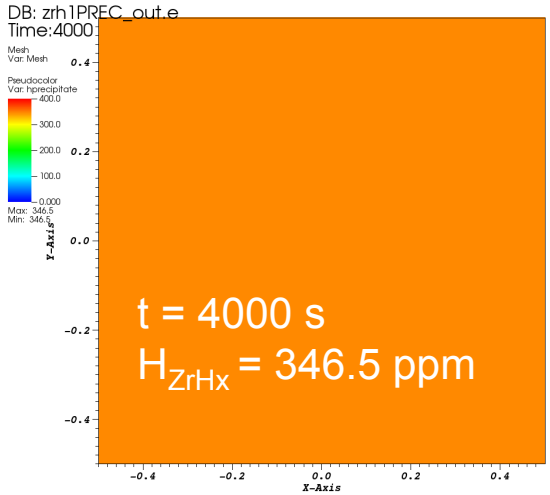
Single Element Test









- **Boundary Condition**
  - T=573K
- **Initial Condition**
  - H_{ss}= **400** wppm
  - H_{ZrHx}= 0 wppm
- **End result**
  - H_{ss}= **53.5** wppm
  - H_{ZrHx}=346.5 wppm

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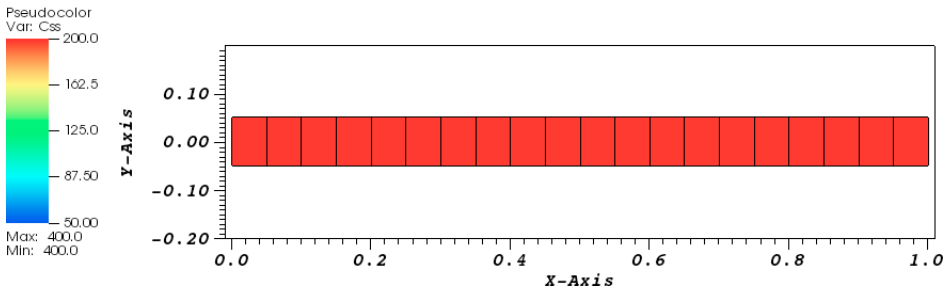
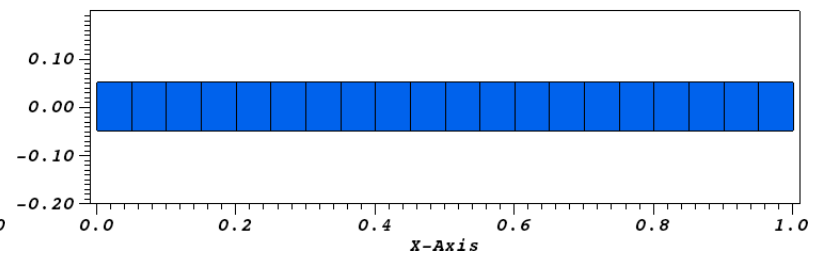
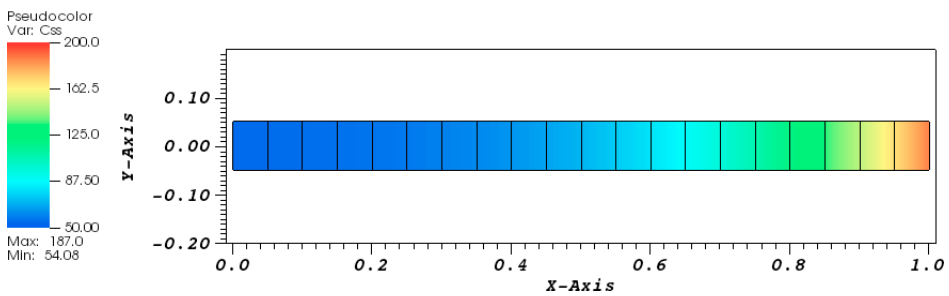
Element Strip, 20 elements



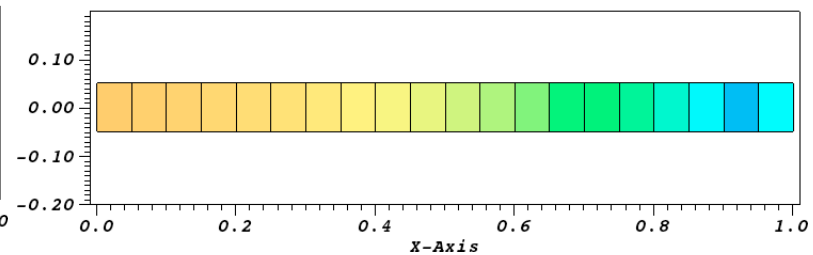
- t=0s, H_{ss}=400 ppm



- t=0s, H_{ZrHx}=0ppm



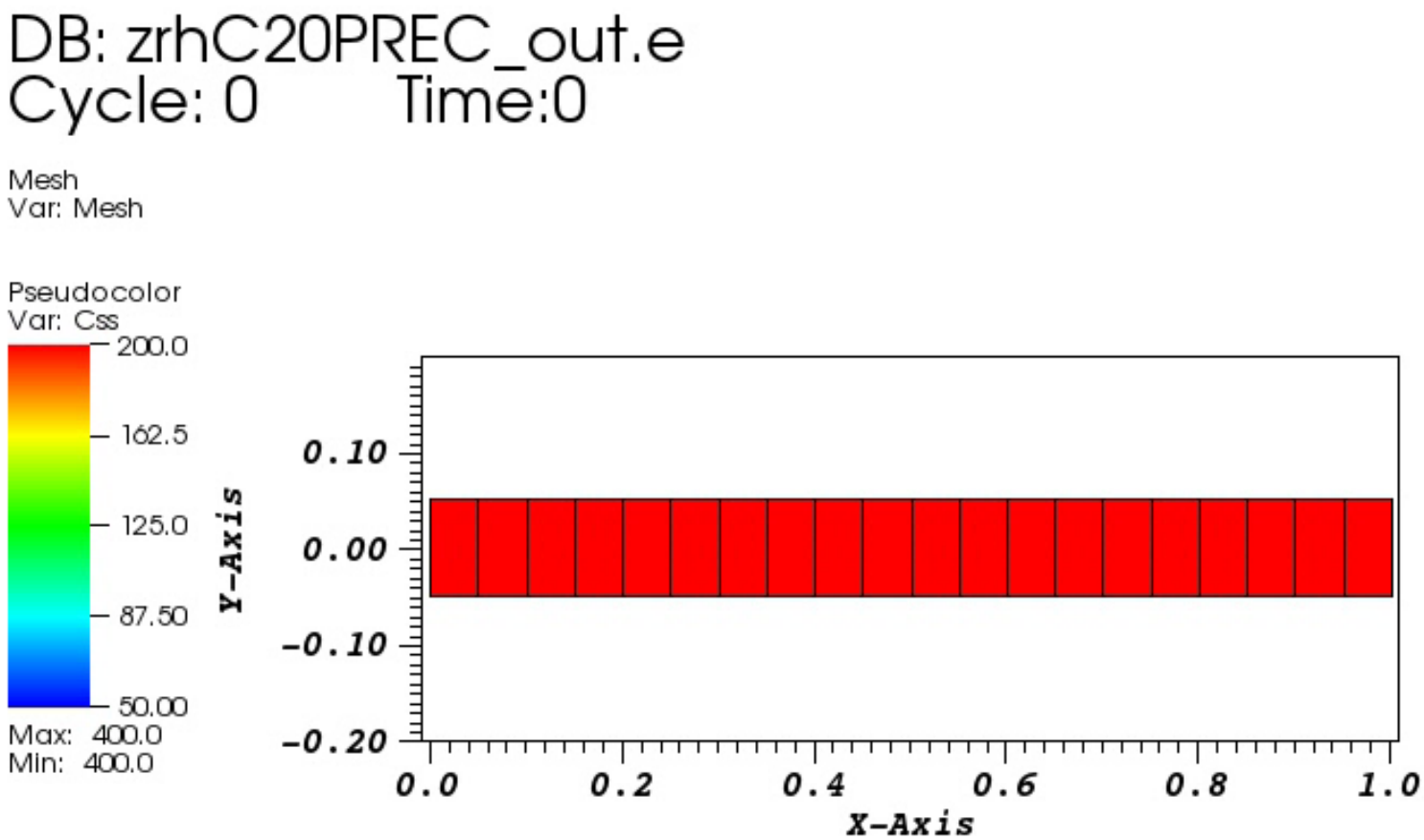
- t=10000s, H_{ss}



- t=10000s, H_{ZrHx}

- **Boundary Conditions**
  - Left T=573K, Right T=673K
- **Initial Condition**
  - t=0s, H_{ss}=400 wppm

Animation of H in Solid Solution



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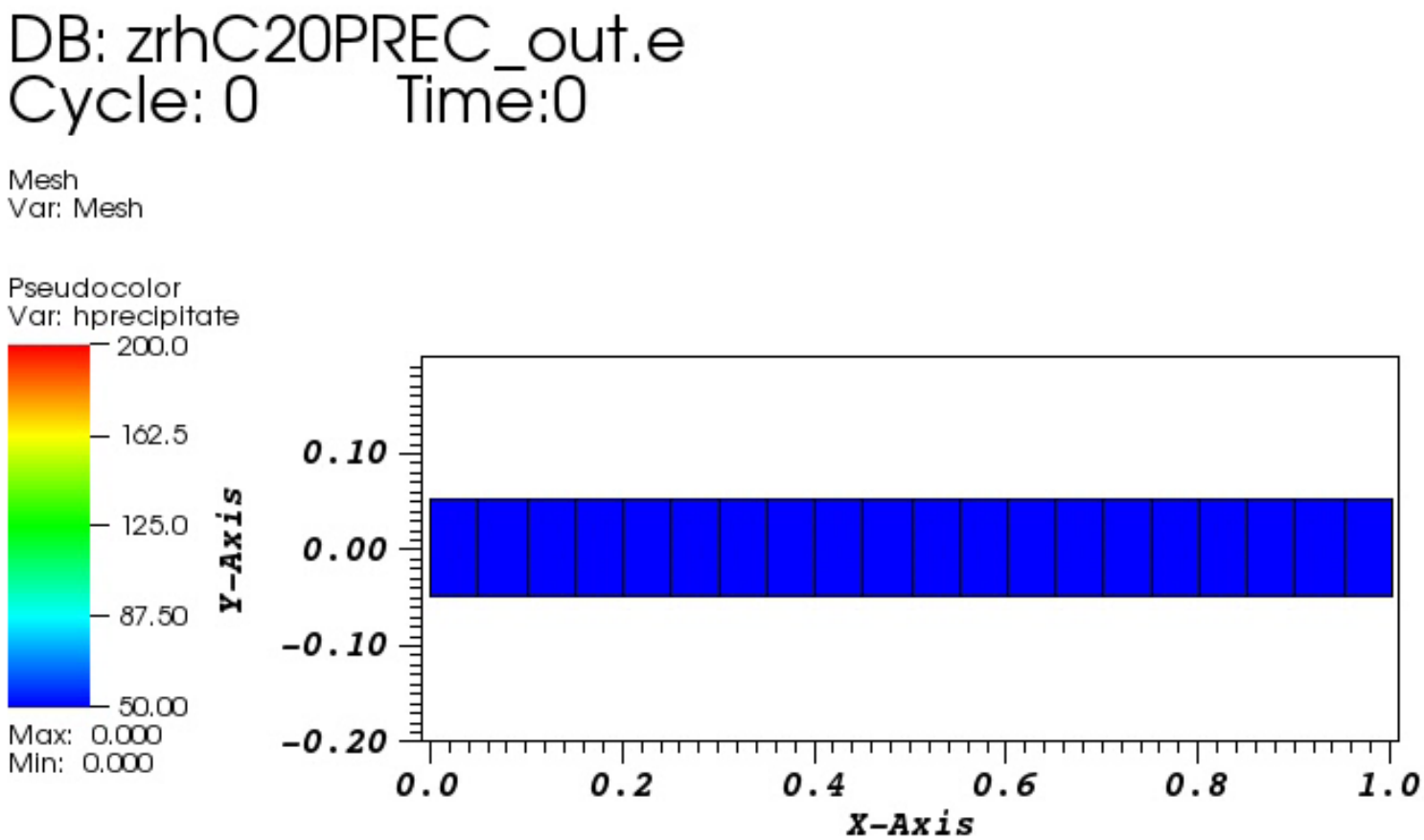
Animation of H in ZrH_{x-2} δ



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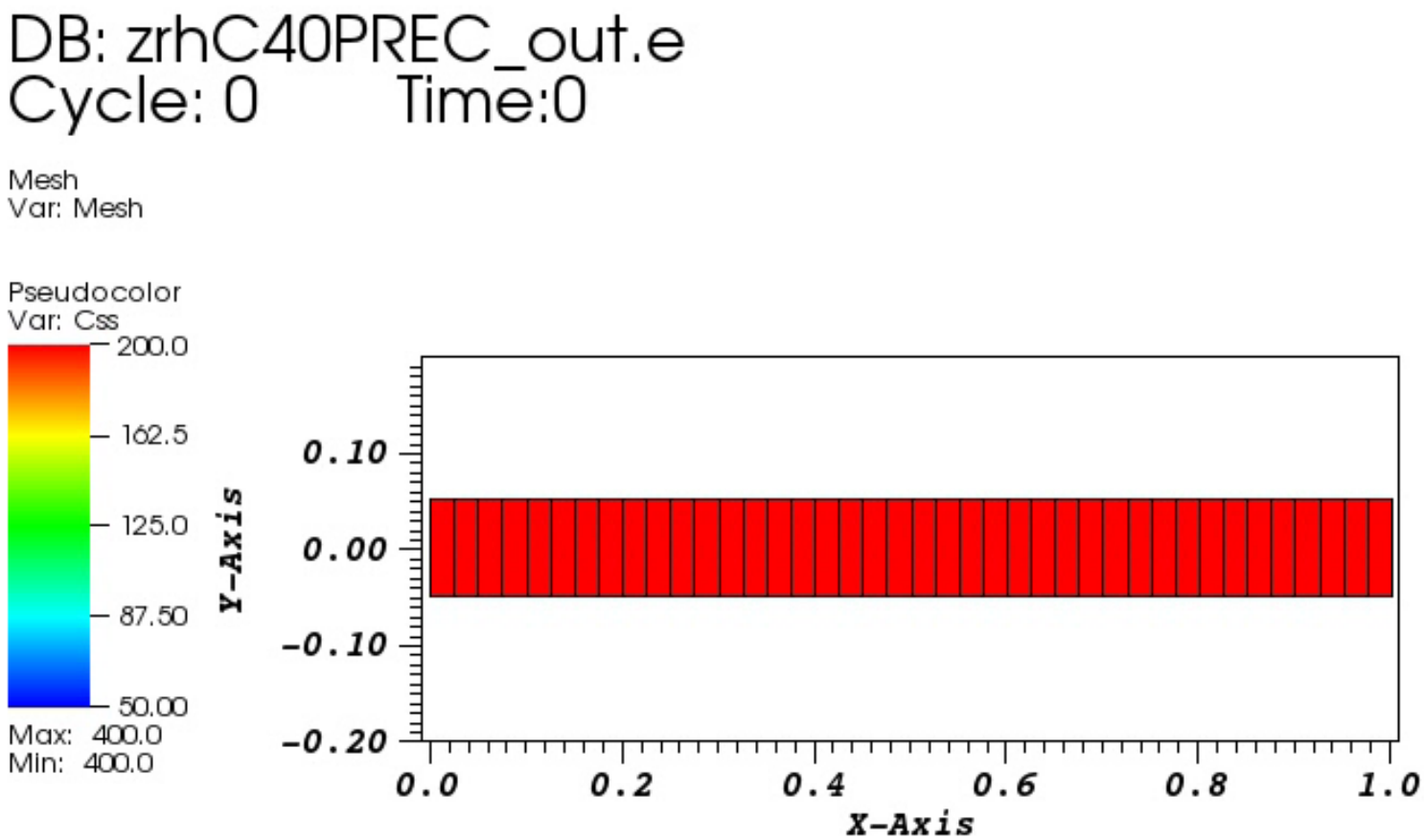
Animation of H in Solid Solution Double FEM Discretization



Solution is the same as for 20 element model.

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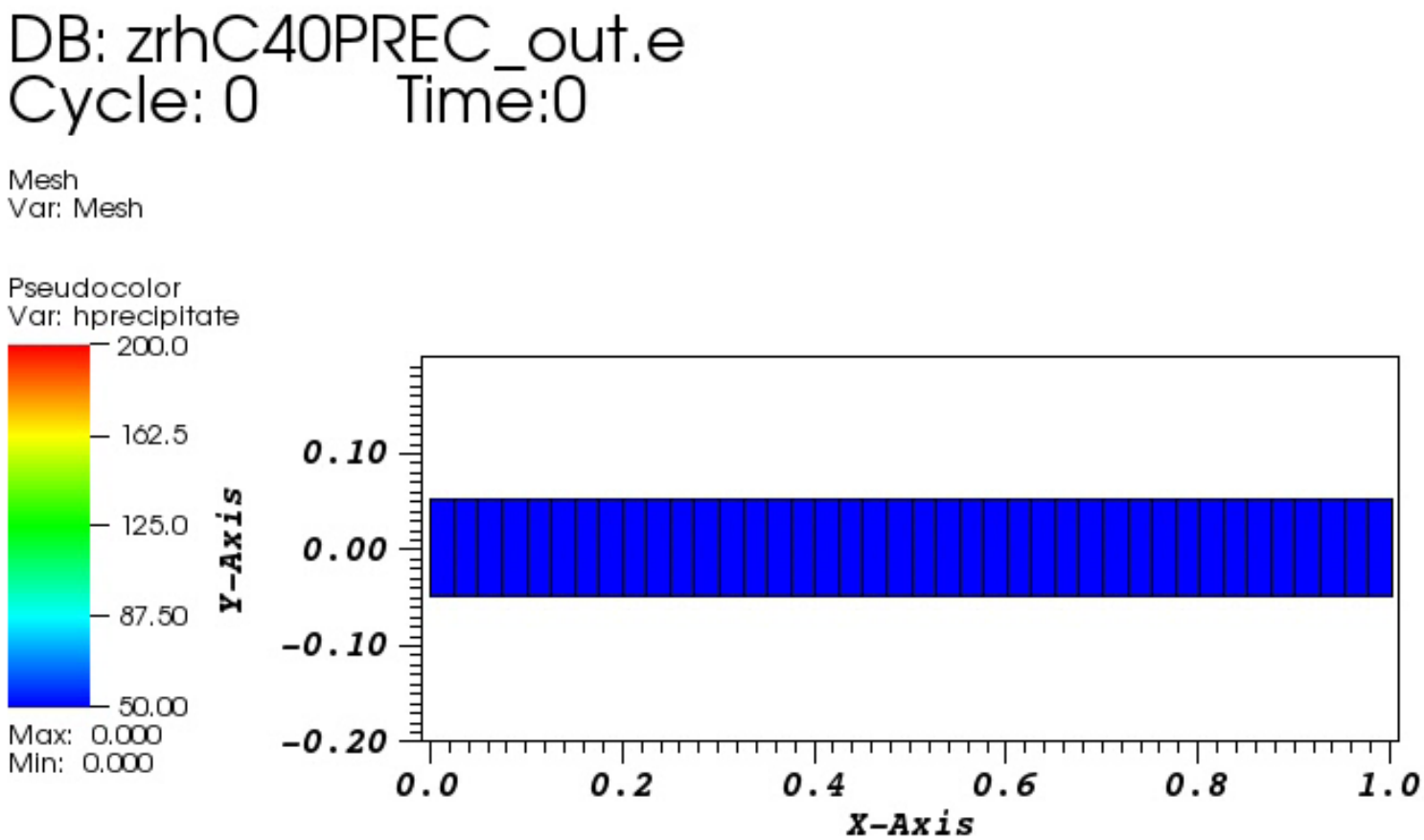
Animation of H in ZrH_{x-2} δ Double FEM Discretization



Solution is the same as for 20 element model.

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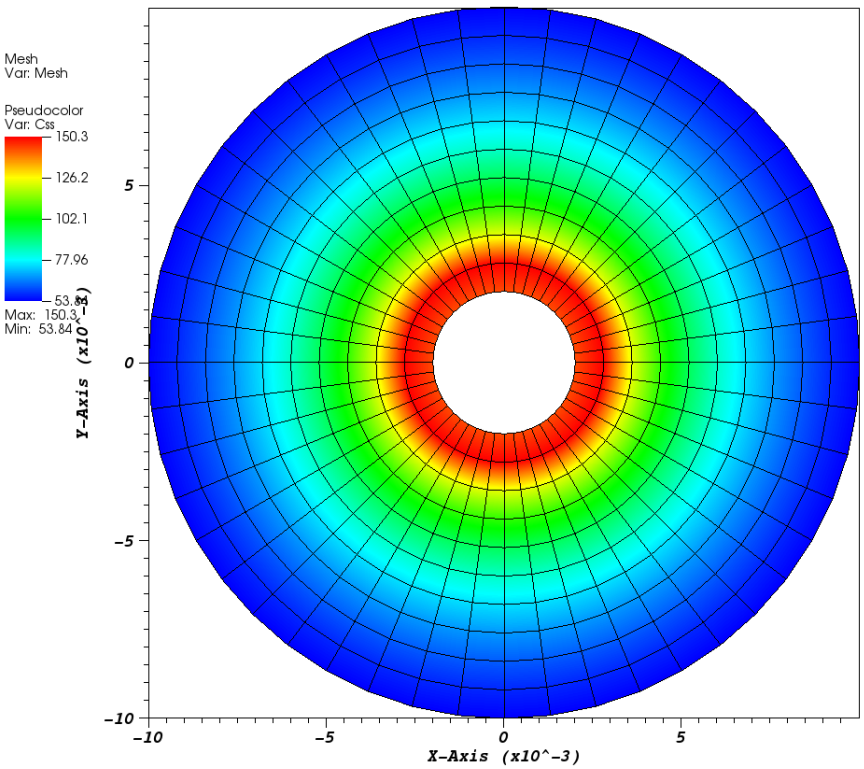
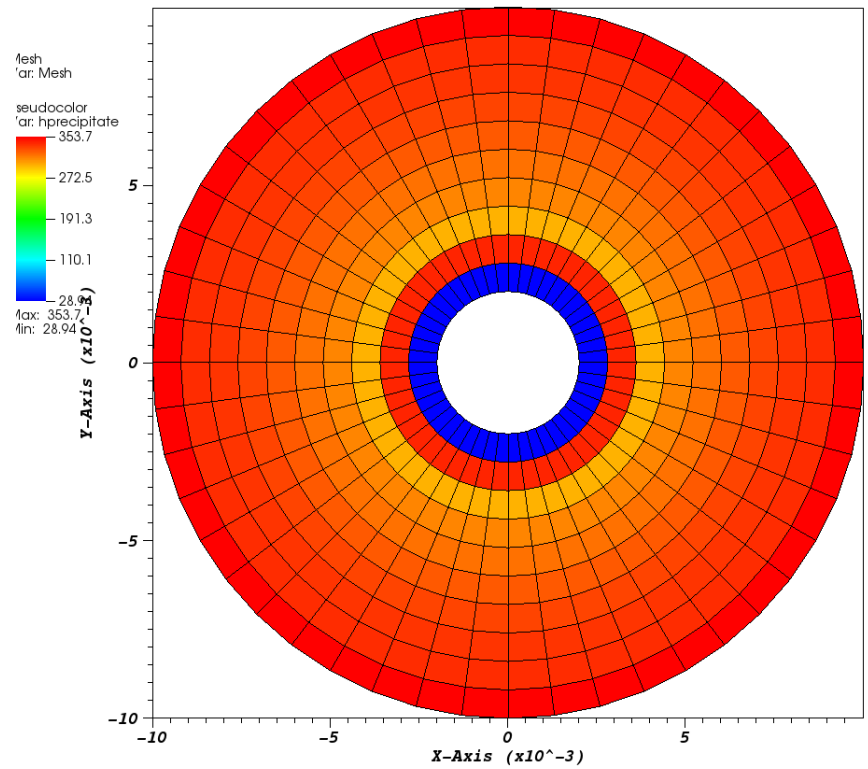
Circular Strip Simulation Distribution at t=10000s



■ H_{ss}



■ H_{ZrHx}

- **Boundary Conditions**
  - Outer T=573K, Inner T=673K
- **Initial Condition**
  - H_{ss}=400 wppm

NEAMS

NUCLEAR ENERGY ADVANCED MODELING & SIMULATION PROGRAM

Summary

- **New implementation of THERMOCHIMICA in Bison enables transport and reaction simulations**
  - Can provide material data to support other physics models
- **The approach is also applicable to the systems with larger number of diffusing species as long as the thermodynamic calculations are done only as needed.**
- **Thermodynamic model gives results similar to the ones reported in the literature**
- **New models are being developed for the fuel chemistry**
- **Fuel chemistry models will be implemented with the transport models using the same approach**