Evaluation of INL Supplied MOOSE/OSPREY Model: Modeling Water Adsorption on Type 3A Molecular Sieve

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SUMMARY

The purpose of this study was to evaluate Idaho National Lab's Multiphysics Object-Oriented Simulation Environment (MOOSE) software in modeling the adsorption of water onto type 3A molecular sieve (3AMS). MOOSE can be thought-of as a computing framework within which applications modeling specific coupled-phenomena can be developed and run. The application titled Off-gas SeParation and REcoverY (OSPREY) has been developed to model gas sorption in packed columns. The sorbate breakthrough curve calculated by MOOSE/OSPREY was compared to results previously obtained in the deep bed hydration tests conducted at Oak Ridge National Laboratory.

The coding framework permits selection of various options, when they exist, for modeling a process. For example, the OSPREY module includes options to model the adsorption equilibrium with a Langmuir model or a generalized statistical thermodynamic adsorption (GSTA) model. The vapor solid equilibria and the operating conditions of the process (e.g., gas phase concentration) are required to calculate the concentration gradient driving the mass transfer between phases. Both the Langmuir and GSTA models were tested in this evaluation. Input variables were either known from experimental conditions, or were available (e.g., density) or were estimated (e.g., thermal conductivity of sorbent) from the literature. Variables were considered independent of time, i.e., rather than having a mass transfer coefficient that varied with time or position in the bed, the parameter was set to remain constant.

The calculated results did not coincide with data from laboratory tests. The model accurately estimated the number of bed volumes processed for the given operating parameters, but breakthrough times were not accurately predicted, varying 50% or more from the data. The shape of the breakthrough curves also differed from the experimental data, indicating a much wider sorption band. Model modifications are needed to improve its utility and predictive capability. Recommended improvements include: greater flexibility for input of mass transfer parameters, time-variable gas inlet concentration, direct output of loading and temperature profiles along the bed, and capability to conduct simulations of beds in series.

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ACRONYMS

AgZ	Silver mordenite
Ag^0Z	Reduced silver mordenite
BWR	Boiling water reactor
DF	decontamination factor
GSTA	generalized statistical thermodynamic adsorption
GT	Georgia Institute of Technology
ICP-MS	inductively coupled plasma–mass spectroscopy
INL	Idaho National Laboratory
ISE	ion selective electrode
LDF	linear driving force
MOOSE	Multiphysics Object-Oriented Simulation Environment
MS	molecular sieve
ORNL	Oak Ridge National Laboratory
OSPREY	Off-gas SeParation and REcoverY
PC	personal computer
UNF	used nuclear fuel
3AMS	type 3A molecular sieve

Evaluation of INL Supplied MOOSE/OSPREY Model: Modeling of Water Adsorption onto Type 3A Molecular Sieve

1. Purpose

The purpose of this study was to evaluate Idaho National Lab's Multiphysics Object-Oriented Simulation Environment (MOOSE) software in modeling the adsorption of water onto type 3A molecular sieve (3AMS). Evaluation metrics were to include (1) comparison of calculated breakthrough curve and loading of water onto type 3A molecular sieve (3AMS) with results previously obtained in the deep bed hydration tests conducted at Oak Ridge National Laboratory; (2) clarity of documentation to map software input variables to ongoing experimental parameters, and (3) overall ease of installation and operation.

2. Background

Tritium, a radioactive isotope of hydrogen, is produced by ternary fission within the nuclear fuel of an operating nuclear power reactor. Processing of the used nuclear fuel (UNF) gives rise to off-gases containing this tritium in the form of tritiated water. Molecular sieves (MS) are being studied as a media for capturing the water vapor from these streams. Type 3A MS (or simply 3AMS) selectively sorb water from the off gas streams because the water molecule has a collision diameter slightly smaller than the pore diameter of the 3AMS crystallite, thus admitting the water and excluding other gases.[1] The sorption process is most often implemented as a packed-bed adsorber; that is, a moisture laden gas stream flows through a fixed bed of solid phase sorbent.

The INL-developed application Off-gas SeParation and REcoverY (OSPREY) is used to model gas sorption in packed beds (or columns). OSPREY is a generalized macroscale model capable of modeling the transient behavior of column adsorbers, including characteristics such as sorbate concentrations in the gas and solid phases, temperature/pressure within the column, and number of bed volumes processed. The program was initially developed and validated for krypton adsorption on hydrogen mordenite.[2]

3. Description of the MOOSE/OSPREY Program

MOOSE was developed by Idaho National Laboratory (INL) to enable scientists and engineers to solve nuclear energy-related engineering problems. It provides a framework to solve the differential equations describing a process using finite element, non-linear integration techniques. The code is described as "open-source software" capable of running on a range of platforms from desktop computers to supercomputers. An initial version was developed in 2008 and has been evolving since then. There are currently over 30 applications that are based on this system, including heat conduction, compressible flow, chemical reactors, and flow through porous media. Desktop versions are available only for the Apple MacIntosh Personal Computer (Mac PC). For more information, see http://mooseframework.org/about.

3.1 MOOSE Installation and User Tips

The MOOSE program itself is reasonably easy to download to a Mac PC. One must download each program in the following order: (1) Xcode Command Line Tools (specific to your OS) (2) XQuartz 2.7.4 (3) MOOSE Environment package. A link to each can be found on the MOOSE Framework website (http://mooseframework.org/). Following this, one must continue to steps 2-4 on the Getting Started page (http://mooseframework.org/getting-started).

To be able to access the OSPREY application, one must fill out an application with INL to gain access to the High Performance Computing repository. With granted access, follow directions in "*OSPREY Model Development Progress Update to Support Transmittal to ORNL for Evaluation.*"[2] Certain steps in this process proved difficult. For example, the setup of a username and password on the INL computing system had to be done using an offsite computer, as the port was blocked on the ORNL network. Other issues were encountered, but are addressed in the User Tips below.

User Tips:

- To access the INL server from ORNL, the "corkscrew" command must be used when logging in through the local terminal. The following line works, wherein <*username*> is the name assigned by Idaho National Lab for a particular user's High Performance Computing System account:
  - ssh -o ProxyCommand="corkscrew snowman.ornl.gov 3128 %h %p" <*username*>@hpclogin.inl.gov
- OSPREY was not operational as downloaded. Some issues that were encountered and identified solutions are listed below:
  - Errors were encountered when compiling OSPREY. Several errors were due to a mismatch of base and exponent for functions in the ". C" files. The solution to this problem was to edit the ". C" files to change the exponent to real number form; for example, changing 2 to 2.0.
  - Several warning messages were encountered after these changes were completed (primarily for "extra tokens" in some files), but the code was able to be run.
  - Errors were encountered intermittently during the "run tests" step after compiling. Sometimes there were no errors; however, when the tests were re-run, despite no changes, there were errors. An experienced user suggested this may indicate a pointer (array indexing) issue or calculated values are not reinitialized unless a new input file is used.
  - When PEACOCK was first run, this error message was encountered: "ImportError: No module named PyQt4". If this problem has not yet been removed by developers and is encountered, it is due to an old file in OSPREY – "OspreyApplication.py" – that should be eliminated. To resolve this issue, enter the following into the local terminal, wherein <*username*> is the name of the installation's profile on the operating system:
    cd /Users/<*username*>/projects/trunk/osprey/gui
    mv OspreyApplication.py OspreyApplication.bak
- After updating MOOSE ("svn update" command) and rebuilding libmesh, OSPREY often does not compile without errors. In such a case, the foregoing solutions have to be repeated.

3.2 OSPREY Variables

Design and operating parameters for the experimental system, from which a breakthrough curve was obtained, are summarized in Table 1.

Table 1. General information on experimental material and conditions

Gas to be treated: Air		Sorbent: 3AMS	
Average inlet temperature	20°C	Apparent density	47 lb/ft^3 (0.753 g/cm^3)
Average flow rate	3.558 slpm	Heat of adsorption	1800 BTU/lb water
Approximate gas pressure	740 mmHg	Maximum capacity	21% by weight
Relative humidity	6.35%	Specific heat	0.23 BTU/lb/°F
		Water content as shipped	~1.5% by weight
		Available moisture capacity	~0.18g/g
		Thermal conductivity	0.12 W/(m·K) *
		Bed diameter / length	1 in / 5 in

* Assumed same as silica sand.

Parameters and properties of the system to be modeled are fed to MOOSE/OSPREY through a set of variables called global input parameters. The interactive editor, PEACOCK, is normally used to edit or create a table-like input file containing values for these parameters. These parameters describe the sorbent (solid, 3AMS in the present case), gas stream being treated (gas), the concentration of sorbate in the gas stream (e.g., inlet water concentration in the present case), etc. and are listed by name in Table 2, along with the values used to model the 3AMS moisture sorption system.

Table 2. MOOSE/OSPREY global input parameters: known physical properties

Parameter	*Value* [a]	*Description*
max_solid_conc	**10 mol/kg**	Max amount adsorbed
mol_weight_cg	**0.02884 kg/mol**	Molecular Weight carrier gas
mol_vol_comp	12.7 m^3/mol [ref. 3]	Diffusion volume of adsorbing component
Heat_of_adsorption	**78608 J/mol**	Heat of Adsorption
Volume_pel	4.20E-09 m^3	Single pellet volume
Bulk_bed_density	**816.5 kg/m^3**	Bulk density of bed
Gas_heat_capacity	36.2 J/(mol*K) [ref. 4]	Heat capacity gas phase
Inlet_pressure	101325 Pa	Gas pressure at inlet
Solid_thermal_conductivity	0.12 W/(m*K)	Solid phase thermal conductivity
Inlet_gas_concentration	0.0666 mol/m^3	Sorbate concentration in gas phase
Wall_temp	298.15 K	Temp of column wall
Viscosity	1.80E-05 Pa*s [ref. 5]	Viscosity of gas
Flow_rate	5.88E-05 m^3/s	Gas flow rate: assumed constant
Cg_conc	41.6 mol/m^3	Concentration of carrier gas
Solid_heat_capacity	1045 J/(kg*K)	Heat Capacity solid phase
Gas_rate_const	8.314 J/(mol*K)	Ideal gas law constant
Eff_diffusivity (k_{LDF})	5.99E-04 m^2/s	Effective diffusivity, LDF
Radius_pel	1.00E-03 m	Sorbent pellet radius
Column_diameter	0.0254 m	Inner diameter
Length	0.127 m	Length of bed
Mol_weight_comp	**0.0182 kg/mol**	Molecular Wt. of sorbate
Inlet_temperature	293	Temperature of feed gas
GSTA_param	0.649 4.18 10.5 11.5 11.6 m^3/mol	Parameters for GSTA isotherm of water on 3AMS
SA_pel	1.26E-05 m^2	Surface area of a single pellet
Bed_void	**0.421 dimensionless**	Bed or bulk void fraction
Porosity	**0.678 dimensionless**	Total void fraction
Gas_thermal_conductivity	0.58 W/(m*K) [ref. 6]	Gas phase thermal conductivity
Mol_vol_cg	20.1 m^3/mol [ref. 3]	Diffusion volume carrier gas

[a] Estimated/calculated values are shown in **bold**.

3.3 Process Mathematics and Mechanics

Both the Langmuir and the generalized statistical thermodynamic adsorption (GSTA) equilibrium isotherm modeling capabilities of OSPREY were available as modules and were downloaded. It was decided to first evaluate the modeling of sorption columns using the GSTA module, because this model more closely fits the adsorption equilibria of 3AMS (i.e., water content of the solid phase as a function of gas phase water partial pressure). The GSTA model is represented by Eq. 1. Note that the K's are the temperature-dependent equilibrium parameters of the model, q_{max} is the maximum adsorption capacity, p is the partial pressure of water vapor, and m is the number of adsorption sites.[7] Solving this equation at various pressures gives the necessary GSTA parameters as shown in Table 3. There is no limit to how many values can be input into the program.

$$q = \frac{q_{\max}}{m} \frac{\sum_{n=1}^{m} n K_n p^n}{\sum_{n=1}^{m} K_n p^n} \tag{1}$$

The temperature dependent equilibrium parameters are found as follows.

$$K_n = \frac{K_n^o}{\left(p^o\right)^n} \tag{2}$$

where K_n^o, the standard state equilibrium parameter, is calculated using the van't Hoff relation as given by equation (3). H and S are the enthalpies and entropies of the monomolecular water layers on the surface of the sorbent[7] and values are given in Table 3 below.

$$\ln\left(K_n^o\right) = -\frac{\Delta H_n^o}{RT} + \frac{\Delta S_n^o}{R} \tag{3}$$

Table 3. Enthalpy and entropy values for water in the van't Hoff relation †

n	1	2	3	4
H (J/mol)	-46597.5	-125024	-193619	-272228
S (J/mol*K)	-53.6994	-221.073	-356.728	-567.459

†As found by Georgia Institute of Technology, based on data collected by Syracuse University[10]

Another important calculable parameter is the mass transfer coefficient. The original equation used in the software was determined to be equivalent to k_{LDF}, the mass transfer coefficient for the linear driving force (LDF) approximation. Given this, coding was changed such that _mass_transfr_coeff = _eff_diffusivity; this means that instead of inputting the diffusivity into Table 2, the average k_{LDF} can be inserted in its place, as determined by

$$\frac{1}{k_{LDF}} = \frac{R_p}{3k_f}\frac{q_e \rho_p}{C_b} + \frac{{R_p}^2}{15\varepsilon_p D_p}\frac{q_e \rho_p}{C_b} \tag{4}$$

C_b is the bulk gas-phase concentration, q_e is the equilibrium sorbate concentration, D_p is the macropore diffusivity, k_f is the film mass transfer coefficient, R_p is the radius of pellet, ε_p is the porosity of pellet, and ρ_p is the density of pellet.

For simplicity sake, the average bulk gas-phase concentration, C_b, was found using the experimentally measured relative humidity at the bed inlet and outlet. Assuming ideal gas behavior (a good assumption at temperatures around 25°C and pressures near 1 atm), the partial pressure was calculated at this concentration. Using equilibrium data obtained by Syracuse University[8] and the calculated partial pressure of water vapor, an average equilibrium water concentration was determined through interpolation.

The Ranz and Marshall correlation, as shown below, was used to find k_f, the film mass transfer coefficient. This method is dependent upon the calculation of the dimensionless Sherwood, Schmidt, and Reynolds numbers.[8]

$$Sh = 2 + 0.6Sc^{1/3}Re^{0.5} \tag{5}$$

$$Sh = \frac{k_f\,(2R_p)}{D_{AB}} \tag{6}$$

$$Sc = \frac{\mu_g}{\rho_g D_{AB}} \tag{7}$$

$$Re = \frac{\rho_g u\,(2R_p)}{\mu_g} \tag{8}$$

where D_{AB} is the binary gas phase diffusion coefficient, μ_g is the viscosity of the gas, ρ_g is the density of the gas and u is the velocity of gas flow in the column.

Calculated and experimental values are listed in Table 4.

Table 4. Physical properties required for correlations between dimensionless numbers 25°C.

$\rho_g[ref.8]$ (kg/m^3)	μ_g|ref.9| $(kg/m*s)$	D_{AB}[ref.3] (cm^2/s)	D_P[ref.3] (cm^2/s)	C_b (mol/m^3)	q_e (g/g)	ε_p	k_f (m/s)	R_p (m)	ρ_p (kg/m^3)	u (m/s)
1.1688	1.837E-05	0.245	0.295	0.0845	0.155	0.37	0.0504	0.001	1199	0.116

4. Results and Discussion

The resultant OSPREY output using the GSTA model is plotted in Figure 1 alongside experimental data from a deep bed hydration study to measure the moisture breakthrough curve.[11] It can be seen that the effluent concentration following breakthrough, as calculated by the model, corresponds somewhat with the experimental measured values. However, there is a variation in breakthrough time; the calculated time necessary to reach half of the maximum effluent concentration is longer than that observed experimentally. In addition, the breakthrough curve indicates a much wider adsorption band, requiring about 75 hours to reach saturation, whereas the measured data is reflective of a narrow adsorption band, taking only 5 to 10 hours to reach saturation.

One factor that could contribute to the difference between the breakthrough time predicted in the simulation and the experimental result is the initial loading in the bed. In the simulation, a value of zero loading is assumed, while there will be a nonzero loading in laboratory experiments. Further testing of the model will use estimates of the initial loading as an initial condition.

The model appears to be insensitive to the effective mass diffusivity and an increase in that parameter should sharpen the breakthrough curve, an effect that is not observed. Further investigation of this issue will require examining how the Peclet number is incorporated for modeling axial dispersion.

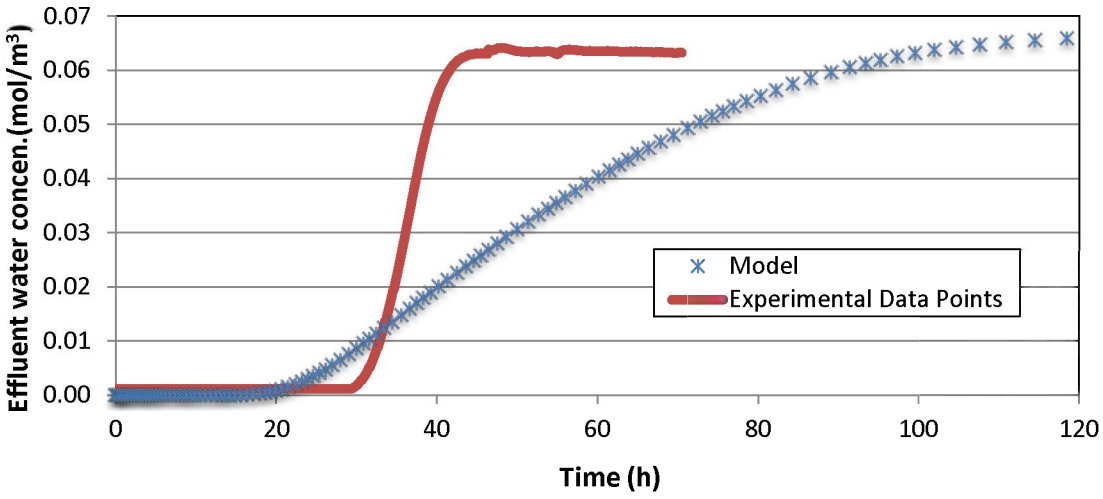

Figure 1. OSPREY output using the GSTA model compared to measured breakthrough curve

Simulations were also run using the built-in single-component Langmuir equilibria model to obtain predictions for comparison. The results are shown on Figure 2. The nearly vertical line (visually due to the large time-scale) is representative of the experimental data points. It is clear from the graph there are major discrepancies between the breakthrough times. It appears that there may have been issues in the input isotherm parameters. For example, the isotherm parameters may have been in the wrong units or the parameters did not update and the default values for the krypton-on-zeolite system may have been used.

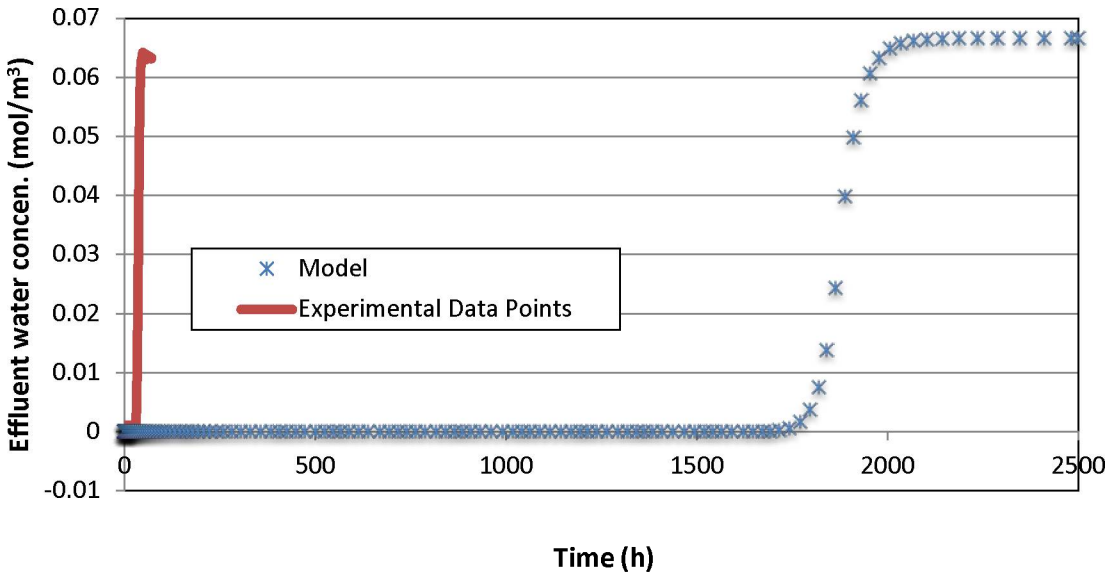

Figure 2. OSPREY output using the Langmuir Model

A further test investigated the effect of mass transfer parameters on the shape of the breakthrough curve as predicted by the GSTA model. The test was performed to ascertain if the program gave similar results if the simulation was based on the properties of a single crystallite rather than a pellet containing many crystallite particles (essentially a test to verify that the nomenclature is consistently applied). The crystallite radius, surface area, and volume were input rather than values for a single pellet. The radius was taken to be 5.0E-05 m and the resultant surface area and volume were calculated. Under these new conditions OSPREY was run at two different diffusivities, k_{LDF}, 6 orders of magnitude apart. Run 1 was conducted at 5.99E-10 m^2/s, while Run 2 was at 5.99E-04 m^2/s. Figure 3 illustrates the resultant OSPREY graphs. It is important to note that all values given in Table 1 remained the same other than volume_pel, SA_pel, eff_diffusivity (k_{LDF}), and radius_pel.

Results calculated by the GSTA model, as shown in Figure 3, illustrate no sensitivity to diffusivity over a wide range of the values—the Langmuir model was not similarly tested. The slope of the breakthrough curve is expected to change with varied diffusivity. Instead the graphs for both runs lie directly on top of one another. This could prove to be a potential coding problem within the program or a lack of reliance on diffusivity in calculations.

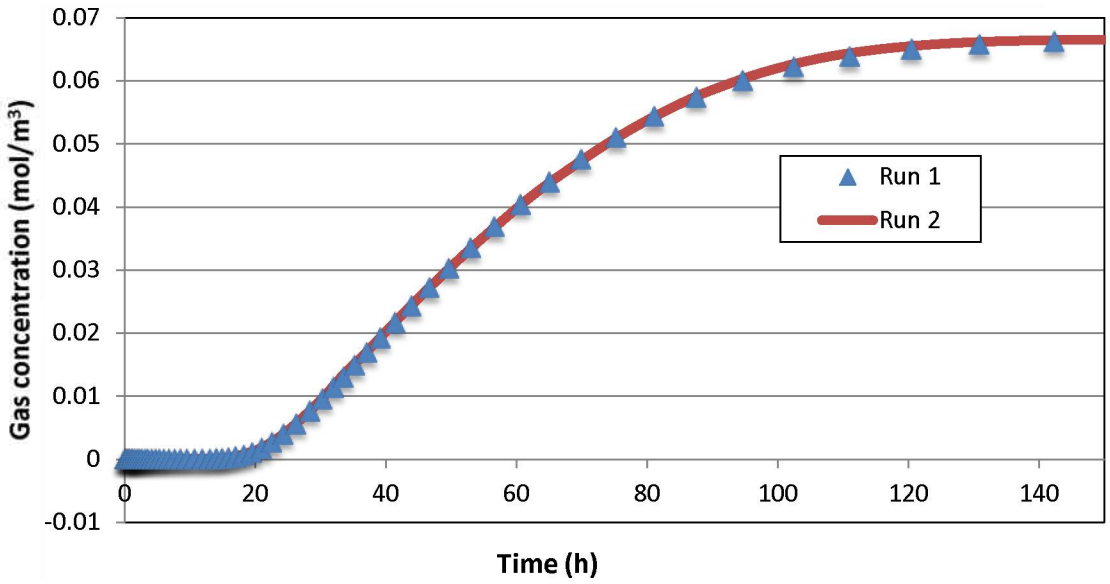

Figure 3. OSPREY gas concentration predictions comparing diffusivities six orders of magnitude apart in the GSTA model

OSPREY will also output values for temperature at the discharge end of the solids bed. This can be easily plotted by importing the `.csv` file containing the predicted temperatures into Excel. The temperature at the outlet, for conditions given in Table 2 and calculated using the GSTA model, is shown in Figure 4. As indicated, the default initial temperature was 293 K (20°C) and the temperature profile has the shape expected of a system where the pipe temperature is maintained at 298 K (25°C). To determine if the model shows a temperature rise due to adsorption, the inlet temperature was changed to 298 K, but the results of the calculation were nearly identical. It was also observed that even after changing the inlet gas temperature to 298 K, the temperature profile predicted by OSPREY nonetheless started at 293 K.

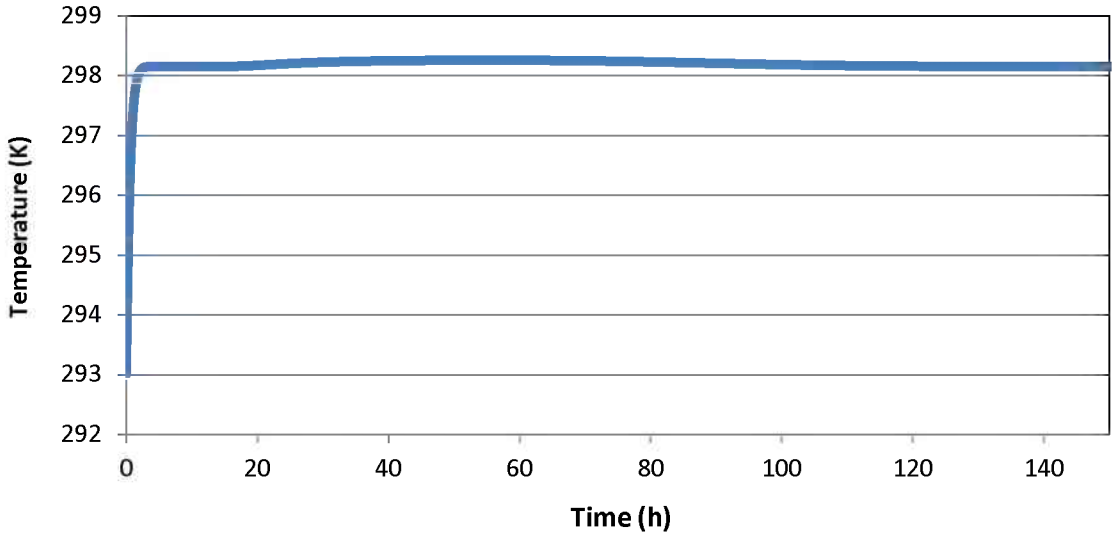

Figure 4. Temperature profile for inlet and bed temperatures at 293 K and 298 K respectively

To address this issue, the initial temperature condition must be changed to 298 K by editing a separate input file of initial conditions. The interactive editor, PEACOCK, does not address the initial conditions, so the file containing initial conditions must be changed with a standard text editor. Upon doing so and re-running the simulation, OSPREY produces the temporal temperature profile shown in Figure 5. The need to edit the file outside of PEACOCK to change the initial bed temperature makes the OSPREY program more difficult to manipulate for the user (two files to change instead of one). As shown in Figure 5, the temperature rise due to water sorption is quite small, potentially indicating that the value in Table 2 for thermal conductivity of the bed is too large.

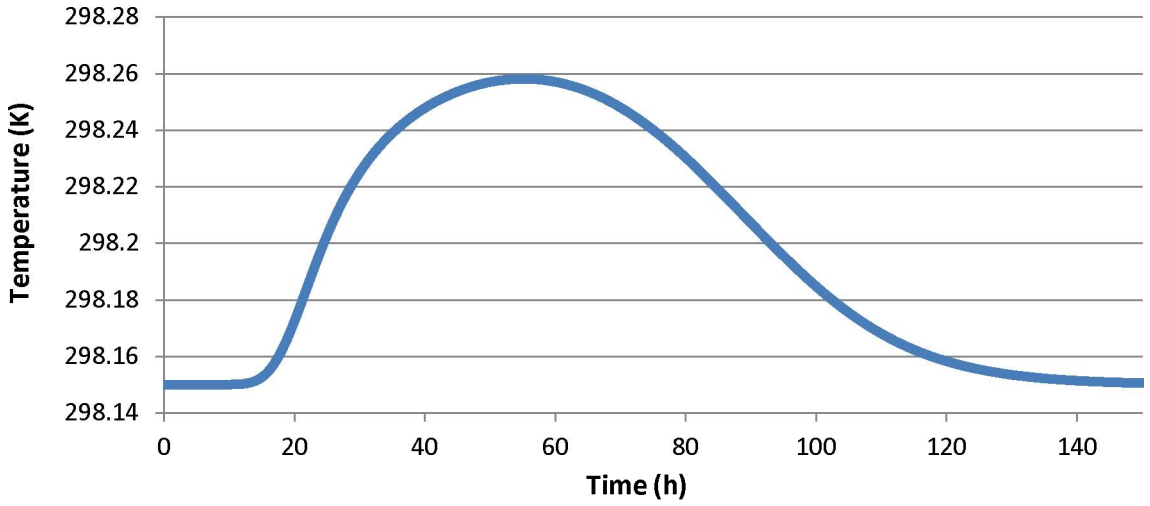

Figure 5. Temperature profile for inlet and bed temperatures at 298 K

The capability of OSPREY to analyze different processing options could be improved by providing more flexibility to the user, to plot the temperature at different points along the column as a function of time, or to plot temperature profiles across the bed at different times. This feature would require extra coding in specifying outputs.

5. Conclusions and Recommendations

OSPREY was run using both Langmuir and GSTA models of the sorption equilibira. Use of the GSTA equilibrium model results in water breakthrough predictions that compare more closely to experimental data than does use of the Langmuir equilibrium model. The model, in its present form, can predict, with moderate success, water vapor breakthrough given specific input parameters. It was found that resultant OSPREY graphs did not differ with variations in the Eff_diffusivity (k_{LDF}). Based on this evaluation the following modifications are recommended to further improve upon MOOSE's predictive capability:

- Include a user's manual with a complete description of all modules that must be installed, computer requirements, description of variables and parameters, and a test case with results so the user may run the program and verify the installation.
- Provide instructions on how to change parameters for other systems.

- Change coding such that OSPREY can recognize differences between global input parameters and initial conditions, so that the user does not have to change multiple files.
- Rather than using an average mass transfer coefficient value, the capability to change the value with position throughout the bed should be added. Also, check on the application of Peclet number for axial dispersion.
- Revise the program to enable visualization of the variation of bulk gas phase concentration, solid loading, and temperature as a function of position and time.
- Initiate the capability to use a time varying input; such that the program could process beds in series, i.e., the outlet concentration from one bed is the inlet for another.
- Code the software to more readily provide an option to model desorption from the bed. This will be useful for those systems, such as 3AMS, that can be regenerated by heating the bed and purging with a dry gas.

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