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SUMMARY

During the processing of used nuclear fuel, volatile radionuclides will be discharged to the atmosphere if no recovery processes are in place to limit their release. The volatile radionuclides of concern are ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. Methods are being developed, via adsorption and absorption unit operations, to capture these radionuclides. It is necessary to model these unit operations to aid in the evaluation of technologies and in the future development of an advanced used nuclear fuel processing plant. A collaboration between Fuel Cycle Research and Development Offgas Sigma Team member INL and a NEUP grant including ORNL, Syracuse University, and Georgia Institute of Technology has been formed to develop off gas models and support off gas research. This report is discusses the development of a tritium specific adsorption model. Using the OSPREY model and integrating it with a fundamental level isotherm model developed under and experimental data provided by the NEUP grant, the tritium specific adsorption model was developed.

CONTENTS

FIGURES

ACRONYMS

HZ-PAN	Hydrogen engineered form sorbent
INL	Idaho National Laboratory
K	Kelvin (°C + 273.15)
Kr	krypton
UNF	Used Nuclear Fuel
ORNL	Oak Ridge National Laboratory
SU	Syracuse University
GIT	Georgia Institute of Technology
MOOSE	Multi Object Oriented Simulation Environment
OSPREY	Offgas SeParation and RecoverY
GSTA	Generalized Statistcal Thermodynamic Adsorption
LDF	Linear Driving Force
SC	Shrinking Core
NEUP	Nuclear Energy University Program

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1. Introduction

The reporocessing of used nuclear fuel (UNF) generates off-gas containing several radioactive gases including $^{129}I_2$, ^{85}Kr, ^3H_2O, and $^{14}CO_2$. The unit operations of adsorption and absorption are being developed for the removal of these off-gas constituents. It is necessary to model complex series of unit operations simulating the off gas treatment system of a UNF reprocessing facility. These simulations will aid in the future design of advanced U.S. reprocessing plants as well as minimize waste, proliferation risk, environmental impact, process complexity and cost.

In support of the DOE Fuel Cycle Research and Development Offgas Sigma Team and a Nuclear Energy University Program (NEUP) grant including Oak Ridge National Laboratory (ORNL), Syracuse University (SU), and Georgia Institute of Technology (GIT), a tritium specific model has been developed within the MOOSE application OSPREY for the adsorption of water vapor on molecular sieve 3A. The delivery of this report satisfies milestones M4FT-13IN03120212 and M3FT-13IN03120211.

2. Purpose and Scope

The purpose of this work was to update and maintain OSPREY and to add a tritium specific model to the OSPREY application while improving OSPREY as more Kr data became available and integrating the Sigma Offgas Team INL modeling effort with the NEUP grant offgas work. Throughout FY-13, OSPREY has been modified to comply with changes and upgrades to MOOSE. These modifications include generating tests with tighter tolerances to verify that OSPREY remains functional while the modeling environment improves and provides a higher fidelity. Also, in support of the krypton portion of the OSPREY model, more experimental data for krypton adsorption were provided to further validate this krypton specific model; however without having experimentally determined kinetic data and parameters for krypton to complement the equilibria data, no validatation graphs are shown in this report.

Additional updates to OSPREY, which are discussed within this report, include integration with a GIT developed isotherm model and collaboration with SU for the provision of experimental data and kinetic parameters. This report does not include any tritium specific model validation graphs as a result of the dew point meter at SU providing incorrect readings for the data initially collected and provided to INL for model support. This error was not detected in time to correct the data and parameters provided prior to this report; however, the model will be validated early in FY-14 as updated data become available.

3. Tritium Specific Adsorption Model

The OSPREY model provides the necessary framework for the tritium specific adsorption model because the governing equations are generalized for adsorption and do no change based on the gas/sorbent system. A detailed description of the OSPREY model was previously reported[1]. Changes that were necessary due to the change of the gas/sorbent system were the isotherm model and the kinetic equations.

3.1   Equilibrium Model

Due to the fact that the OSPREY model was initially generated as a krypton specific model, the equilibrium model used was the Langmuir Isotherm model. According to literature[2], tritium adsorption does not fit the Langmuir Isotherm model. Therefore, to accurately model the equilibrium for the tritium specific model the Langmuir Isotherm model has been replaced with a Generalized Statistical Thermodynamic Adsorption (GSTA) Isotherm model that was created by GIT. Since this is a generalized isotherm model, it will work for a wide variety of isotherms, including the Langmuir Isotherm. Therefore, integration of OSPREY with the GIT developed isotherm model broadens the use of OSPREY beyond simply Langmuir type adsorption. OSPREY, integrated with the GSTA isotherm model will work for krypton adsorption as well as tritium adsorption.

3.1.1 GSTA Isotherm Model

The Generalized Statistical Thermodynamic Adsorption (GSTA) isotherm model, summarized in equations 1 through 3, was originally developed by Llano-Restrepo and Mosquera[2] as an alternative presentation of Hill's statistical isotherm model of adsorption. This recast version of Hill's model allows for a simpler physical interpretation of the parameters as follows: q_{max} represents the theoretical maximum adsorption capacity, m is the number of adsorption sites (or subsystems) available to adsorbate molecules, K_n is the equilibrium constant relative to the adsorption of n molecules in the network of available adsorption sites, K_n^o is the dimensionless equilibrium constant which is relative to the standard state pressure (P^o) of 100 kPa, ΔH_n^o is the standard molar enthalpy of the adsorption of n molecules in a network of sites, and ΔS_n^o is the standard molar entropy of adsorption of n molecules in the same network of sites.

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

(1)

$$K_n = K_n^o / (P^o)^n$$

(2)

$$\ln K_n^o = -\frac{\Delta H_n^o}{RT} + \frac{\Delta S_n^o}{R}$$

(3)

The dimensionless constant is related to temperature by the van't Hoff equation (equation 4). Integration of this equation with temperature results in equation 3 above. Once the parameters of the GSTA model are determined, the corresponding enthalpies and entropies are found by performing a linear regression across temperature for all K_n^o values. With the determination of the appropriate enthalpies and entropies for a specific adsorbent-adsorbate system, it is then possible to predict the isotherm curves at temperatures for which data was not obtained.

$$\left(\frac{\partial \ln K_n^o}{\partial T} \right)_n = \frac{\Delta H_n^o}{RT^2}$$

(4)

Some notable properties of the GSTA isotherm model are linear low pressure behavior, adaptability to represent various degrees of heterogeneity of adsorbents, and flexibility to

describe a wide variety of data sets. One of the more rigorous measures of an adsorption isotherm model is the behavior displayed at low pressures in the so called Henry Regime of adsorption. As the pressure in a system approaches zero, the isotherm is expected to display a linear relationship, equation 5, between solid and gas phases (i.e. Henry's Law). Equation 6 below shows the determination of the Henry's Law constant that results by taking the limit of the GSTA isotherm as pressure approaches zero.

$$q = K_H p \tag{5}$$

$$K_H = \lim_{p \to 0} \frac{q}{p} = \frac{K_1^o q_{max}}{mP^o} \tag{6}$$

The adaptability and flexibility of the GSTA model is immediately apparent by simply considering the *m* parameter from equation 1 above. When *m* is increased, the physical interpretation is that more adsorption sites are available and therefore the adsorbent is more heterogeneous. At the same time, allowing the *m* parameter to be flexible when performing an equilibrium analysis will allow the polynomial section of the model to expand, thus resulting in tighter agreement between the model and the collected data. Under the condition in which the *m* parameter is equal to one, then the form of the GSTA model is the exact same form of the Langmuir model, which is a homogeneous isotherm model.

Upon integration of the GSTA isotherm model with OSPREY, it was verified using the krypton specific model for the case mentioned in the previous paragraph of m equal to one. Since the krypton specific model was originally generated using the Langmuir Isotherm model the results from this were compared to the results generated after replacing the Langmuir Isotherm model with the GSTA model when m is equal to one. This comparison is shown in Figure 1.
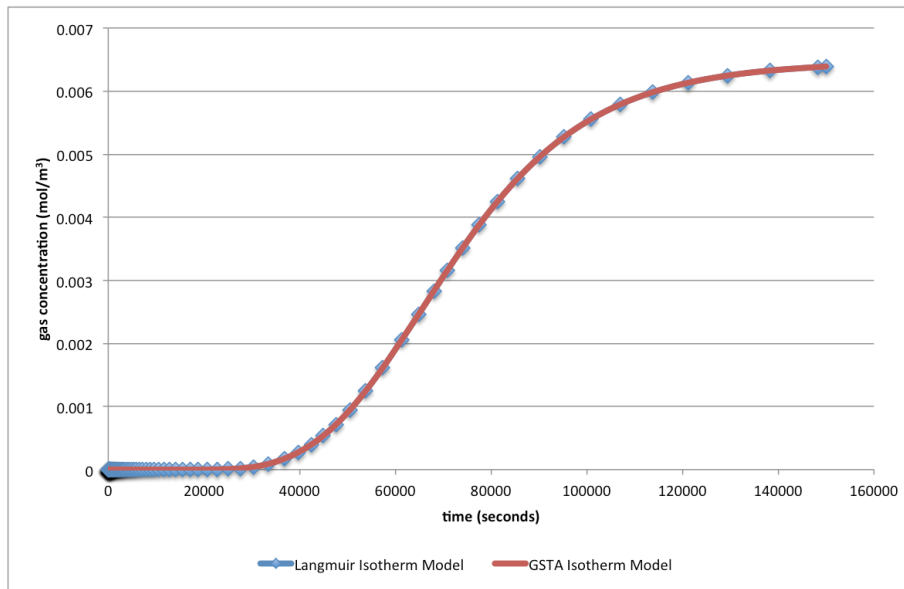

Figure 1: Krypton adsorption at 191 K on HZ PAN. Comparison of using Langmuir Isotherm model vs. GSTA Isotherm model with m=1 for verification that GSTA isotherm model works when integrated with OSPREY model.

Figure 1 shows that, when compared, the use of the Langmuir Isotherm model and the GSTA Isotherm model with m equal to one do not generate different OSPREY model output. This provides verification that when integrated with OSPREY, the GSTA Isotherm model works. For the tritium specific model, the GSTA Isotherm model parameter m is greater than one in order to better fit the isotherm and determine the equilibrium parameters.

3.2 Kinetics

The kinetic parameters for tritium adsorption were experimentally determined by SU. SU performed water vapor adsorption testing on molecular sieve 3A. Uptake curves for water adsorption on molecular sieve 3A were obtained at adsorption temperatures of 25, 40, 60 and 80°C and over a dew point range from -70 °C to 10°C. Selected uptake curves were fitted with several adsorption kinetic models including the Langmuir model, the xth-order kinetic model, the Elovich model, the Weber-Morris model, the Double Exponential model, the Linear Driving Force (LDF) model and the Shrinking Core (SC) model[3-6]. It was found that the LDF and SC models best fit the experimental data. Therefore, the LDF and SC models were used to correlate all water uptake curves and the corresponding kinetic parameters were determined. The initial tritium specific model has been generated using the LDF model for the kinetics.

3.2.1 Linear Driving Force Model

Originally proposed by Gleuckauf and Coates in 1947, the linear-driving force (LDF) model has been widely used in modeling adsorption kinetics due to its analytical simplicity[7]. According to the LDF model, the average sorbate uptake rate is proportional to the amount still required to reach equilibrium, as given by:

$$\frac{dq}{dt} = k\left(q_e - q\right) \tag{7}$$

where q is the average sorbate concentration in sorbents, q_e is the equilibrium sorbate concentration in sorbents and k is the lumped LDF mass transfer coefficient. Integrating Equation 7 results in:

$$\ln\frac{q_e - q}{q_e} = -kt \tag{8}$$

The LDF mass transfer coefficient can be determined by plotting $\ln\dfrac{q_e - q}{q_e}$ versus t.

Assuming a linear isotherm $q=KC$, it can be shown that the LDF mass transfer resistance has the following expression [6]:

$$\frac{1}{k} = \frac{R_p}{3k_f}\frac{q_e\rho_p}{C_b} + \frac{R_p^2}{15\varepsilon_p D_p}\frac{q_e\rho_p}{C_b} + \frac{R_c^2}{15D_c} \tag{9}$$

where, C_b – bulk gas-phase concentration
  D_c – micropore diffusivity
  D_p – macropore diffusivity

k_f – film mass transfer coefficient
R_c – radius of micropore
R_p – radius of pellet
ε_p – porosity of pellet
ρ_p – density of pellet

The three terms (from left to right) in the right-hand side of Equation 9 are external film resistance, macropore resistance and micropore resistance, respectively.

The overall mass transfer resistances ($1/k$) were determined in the order of magnitude from 10^{-1} to 10^2 hr. The micropore diffusivity (D_c) in zeolite is usually in the order of magnitude of 10^{-8} cm^2/s (ref. 8), which leads to a micropore resistance of $\sim 4 \times 10^{-5}$ hr^{-1}, which is much smaller than the overall mass resistance and therefore can be neglected. Accordingly, Equation 9 can be simplified as:

$$\frac{1}{k} = \frac{R_p}{3k_f}\frac{q_e\rho_p}{C_b} + \frac{R_p^2}{15\varepsilon_p D_p}\frac{q_e\rho_p}{C_b} \tag{10}$$

The film mass transfer coefficient (k_f) in Equation 10 can be estimated by the Ranz and Marshall correlation[9]:

$$Sh = 2 + 0.6Sc^{1/3}Re^{0.5} \tag{11}$$

where Sh, Sc and Re are the dimensionless Sherwood number, Schmidt number and Reynolds number. It should be mentioned that the current water uptake curves were obtained in a single-layer adsorption bed where the single layer of sorbents was sitting on a screen pan suspended on a microbalance arm. Equation 11 is for mass transfer to unobstructed spheres and we assume that the effect of the support screen used to hold the single-layer of sorbents was negligible. For correlating deep bed data, the Wakao and Funazkri correlation[10] is recommended:

$$Sh = 2 + 1.1Sc^{1/3}Re^{0.6} \tag{12}$$

The water molecular diffusivity required for the calculation can be estimated by the Fuller et al. correlation[11].

$$D_{AB} = \frac{0.00143T^{1.75}}{PM_{AB}^{1/2}\left[\left(\Sigma_v\right)_A^{1/3} + \left(\Sigma_v\right)_B^{1/3}\right]^2} \tag{13}$$

Finally, the macropore diffusivity can be determined from Equation 10.

3.2.2 Shrinking Core Model

The shrinking-core model is also frequently used in modeling adsorption kinetics. This model simplifies the adsorption process in three steps[3,8]: (1) diffusion through external gas film, (2) diffusion through saturated shell, and (3) adsorption at the surface of the sorbate-free core. Assuming that the third step occurs sufficiently rapidly, the sorbate uptake curve can be expressed by:

$$t = \frac{q}{q_e}\tau_1 + \left(1 + 2(1 - \frac{q}{q_e}) - 3(1 - \frac{q}{q_e})^{2/3}\right)\tau_2 \tag{14}$$

$$\tau_1 = \frac{R_p q_e}{3\varepsilon_p k_f C_b} \tag{15}$$

$$\tau_2 = \frac{R_p^2 q_e}{6\varepsilon_p D_p C_b} \tag{16}$$

The first and second terms in the right-hand side of Equation 14 correspond to steps (1) and (2), respectively. This model has been successfully used for the analysis of water uptake curves at or near ambient temperature in molecular sieve adsorbents[8].

It is reasonable to assume that the adsorption kinetics is controlled by the external film mass transfer in the very beginning of the adsorption process. Therefore, τ_1 was determined by plotting q/q_e versus t at q/qe <0.1. τ_2 was then determined by plotting $1 + 2(1 - \frac{q}{q_e}) - 3(1 - \frac{q}{q_e})^{2/3}$ versus $t - \frac{q}{q_e}\tau_1$ at q/qe <0.9. Finally, k_f and D_p were determined by Equations 15 and 16, respectively.

4. Conclusions and Future Work

In conclusion, an initial tritium specific adsorption model has been developed within the OSPREY model. Also, a beneficial collaboration with the NEUP grant has been established and will continue along with the INL off gas modeling effort. The tritium model will be validated early in FY-14 using data generated by SU. Additional future work for the OSPREY model includes validation of multiple component models and integration with a fundamental level kinetic model developed by GIT. Kinetic data for krypton adsorption is needed to further develop and validate the krypton specific model more accurately.

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