Uncertainty Quantification for Carbon-capture Simulation

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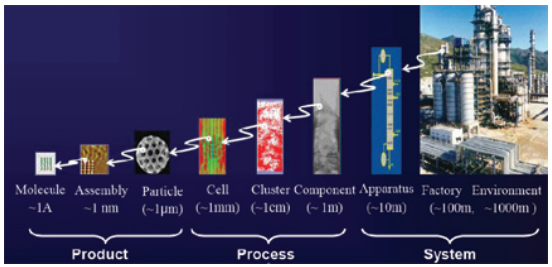
The Carbon Capture Simulation Initiative (CCSI) is developing tools to accelerate identification of reliable and affordable processes for carbon capture from coal-fired power plants using simulation. The effort includes implementation of tools for uncertainty quantification (UQ), methodology critical to simulation-based analysis of complex processes, including economic impact of incorporation of carbon capture systems in current and future commercial operations. UQ tools include input sensitivity analysis, calibration of input parameters, construction of surrogate models, and propagation of uncertainty. Here UQ use is illustrated with study of a solid sorbent process for carbon capture, using preliminary models and thermogravimetric analysis (TGA) data from the National Energy Technology Laboratory (NETL).

Carbon capture and storage (CCS) technology promises to convert fossil fuels into a reliable low carbon energy supply while remaining affordable for consumers. The Carbon Capture Simulation Initiative (CCSI) will develop a simulation toolset supporting the needs of industry to evaluate new carbon-capture technologies, scalable to commercial level with reduced physical testing, including uncertainty quantification (UQ) tools to aid in interpreting simulation results. Solid sorbent modeling was chosen to demonstrate development and validation of computer simulation approaches.

UQ includes analytical tools used to understand variable processes at all levels of a system and to focus resources on uncertainty with large impact on full-scale system performance. CCS technology and its implementation include many processes with complex impacts on energy economics and the environment, so UQ is critical. Solid sorbent adsorption of carbon dioxide ($CO_{2)}$ is a small-scale process that feeds into other CCS efforts such as basic chemistry, particle and device scale models, and plant process models (Fig. 1). UQ used in solid sorbent adsorption study supports understanding simulation performance, such as identifying parameters that induce more variation than others (sensitivity), estimating values for unknown parameters consistent with physical measurements, and quantifying parameter uncertainty from measurement error to model error sources.

Fig. 1. Scales for process engineering, showing the need for a scale-up approach to simulation.



Computer models of varying complexity simulate adsorption of CO_2 by a sorbent under well-known chemical and microstructural assumptions, with complexity dependent on extent of incorporation of chemical, microstructure, and transport phenomenon. The sorbent is a mesoporous silica backbone embedded with the amine polymer, polyethyleneimine (PEI). CO_2 is adsorbed through two chemical reactions: 1) a CO_2 molecule binds with a PEI site forming a zwitterion, and 2) a zwitterion binds with another empty PEI site forming carbamate. Diffusion of gaseous CO_2 in the sorbent is explained by a microstructural model divided into three length scales with different diffusion types. Infinitely fast gas diffusion and Knudsen diffusion occur at the large and middle length scales, while bulk-phase diffusion, where zwitterions hop between PEI sites over an energy barrier, occurs at the smallest length scale. Two computer simulation models of solid sorbent technology are explored: an ideal equilibrium model with five parameters, and a more complex second generation model implementing basic transport, kinetic, and ideal thermodynamics in a dry environment, with twelve parameters. The parameters, not measurable directly, are estimated by calibrating to thermogravimetric (TGA) experiments for a dry sorbent from the National Energy Technology Laboratory (NETL). TGA measurements are sorbent weight versus a temperature profile changing over time at specific CO_2 composition (Fig. 2 at 10 %). Many sources of uncertainty exist in this framework: data error, inaccurate modeling assumptions, boundary conditions, extrapolation, and model scaling. UQ demonstration includes parameter sensitivity assessment for a second generation model and parameter calibration illustrated for an ideal equilibrium model.

The second generation model simulates a TGA curve for a set of input parameters, an assumed temperature profile and CO_2 pressure. UQ tools in model development provide early parameter studies and identify unexpected performance of a simulation code. An initial parameter study

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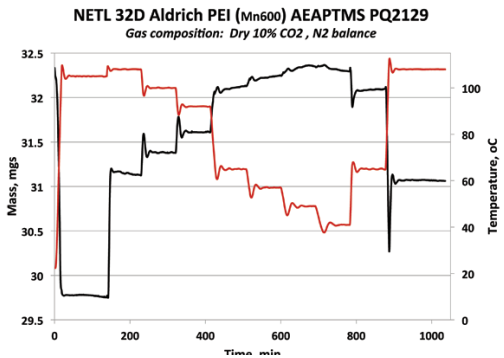

Fig. 2. Thermogravimetric analysis (TGA) response data (black) of sorbent weight measured every second, coincident with temperature profile. Temperature profile (red) includes seven temperatures and eight transitions over time, and same profile was used in model runs.

conducted with the second generation model used an ensemble of 128 sets of the twelve parameters, selected to achieve balanced representation of multiple factors at high and low levels with an orthogonal-array based Latin Hypercube Sample (LHS), a strategy in common use in computer experiments [1-3]. Sensitivity analysis was based on identifying trends in a simple scalar calculated from the TGA curves: mean weight fraction. Nearly half of the ensemble runs either did not complete or achieved very low peak weight fractions indicating model performance issues, and results were less informative of parameter values consistent with observed TGA data. Parameter sensitivity evaluation focused attention on two parameters with apparent main effects, affirming implementation of a model of sorbent kinetics controlled by number and mobility of zwitterions.

A simplified ideal equilibrium model calculates equilibrium weight for fixed temperature and five input parameters based solely on reactions of the sorbent, ignoring kinetic effects. Parameter estimation (calibration) determines the "true" input parameter set, that for which the model "best" matches observations, while accounting for model discrepancy, observation error, and any bias. Observed equilibrium weights were obtained from the seven temperature plateaus in the experimental data. A Bayesian approach [4] for parameter estimation provides a posterior probability distribution of the "true" input parameters inferred from model output, physical observations and specified prior parameter distributions. MCMC simulation produced sample-based posterior distributions. Numerically integrating over other parameters, a sample-based posterior distribution of the "true" input parameters is obtained with illustration as pairwise bivariate posterior distributions of the parameters in Fig. 3a. Predictions were obtained for each posterior sample, yielding a predictive distribution of sorbent weights at particular temperatures and pressure, with mean and 95% credible regions displayed graphically (Fig. 3b) with observed equilibrium weights in red showing model and data inadequacies.

The ideal equilibrium model is a substantive simplification of the current second generation model, itself a middle fidelity model incorporating

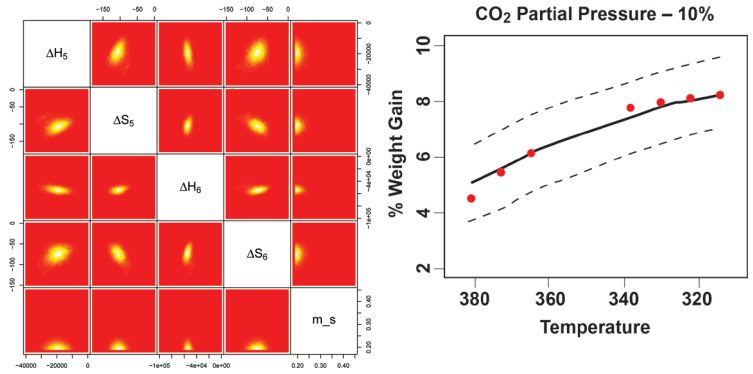

Fig. 3. a) Bivariate posterior probability densities illustrate "most likely" input parameter values. b) Simulation based prediction and bounds (95%) for 10% partial pressure, physical observations in red.

a transport model with ideal thermodynamics. Higher fidelity, more relevant models require non-ideal thermodynamics and a hydrous environment. Eventually, a solid sorbent process simulator with parameter values consistent with experimental data will be validated for use in higher-level simulations of CCS technology. UQ issues for CCS technology simulation dependent on a solid sorbent process simulator will include 1) whether the fidelity of the solid sorbent model has an important impact on CCS technology, and 2) how to quantify the impact. UQ will be used again to address such questions.

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