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Multiscale simulation of ionic fluxes through nanopores

Nanoporous membranes are a key component in many environmental and energy applications, including water treatment technology and fuel cells. As the selective transport of material through these membranes is often a performance-limiting factor in device operation, considerable effort is spent on the design of membranes for optimal throughput and selectivity. For example, for electrodesalination, membranes are needed that selectively block either anions or cations, while letting other ions move through freely. For reverse osmosis, on the other hand, membranes are desired that block all ions and contaminants, while letting water flow through.

A membrane's throughput and selectivity depend on a variety of parameters, including the membrane molecular structure, chemical composition, the structure and size of the pores, and the composition of the fluid. While significant advances have been made in the performance of nanoporous membranes, the

(Continued on page 4)

Experiments and modeling give new insight into oxy-combustion of coal

The installation of wind and solar power plants offer the possibility of lowering the carbon dioxide emissions associated with electrical power production. However, solar power is currently very expensive to produce and most of the economical wind potential lies far away from major population centers, requiring the installation of costly new high voltage transmission lines to deliver the power where it is needed. Consequently, many countries around the world are conducting research and development projects aimed at continuing electrical power production from coal while capturing and sequestering the carbon dioxide that is produced in the process. One of the most promising technologies is combustion of coal using oxygen instead of air. As shown in Figure 1, in this approach nitrogen is separated from air before combustion occurs, resulting in a flue gas that is nearly pure CO_2 and requires only a small amount of additional cleaning before it is ready for sequestration.

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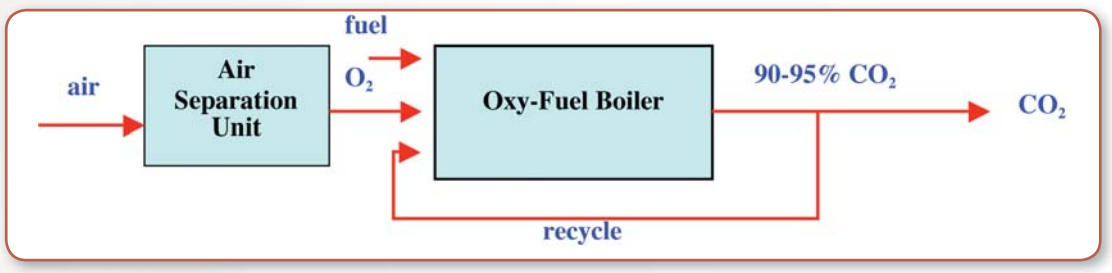

Figure 1. *Schematic of the oxy-combustion approach to capturing CO_2 when generating electricity from coal.*

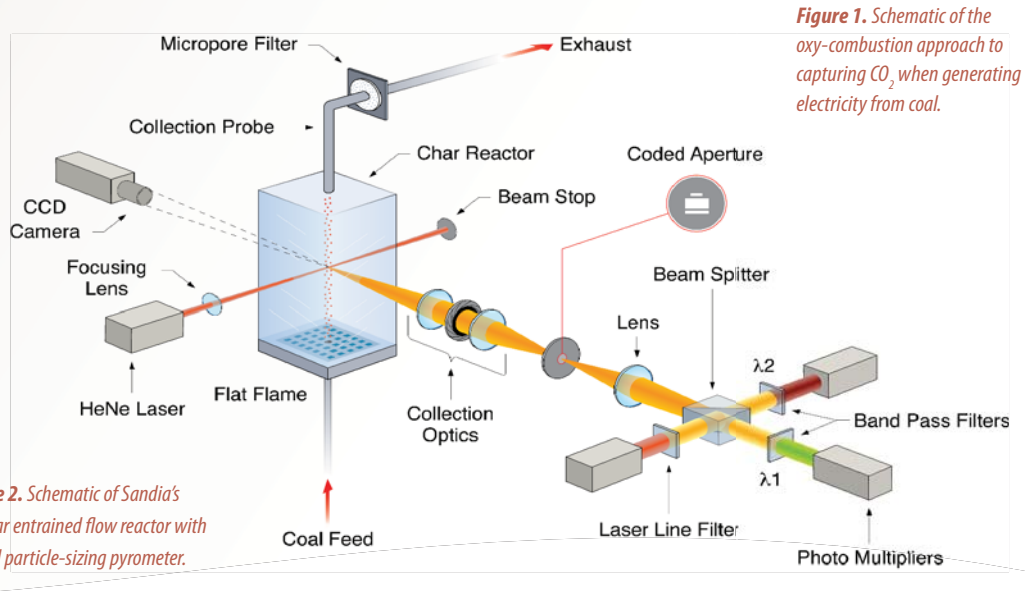

Figure 2. *Schematic of Sandia's laminar entrained flow reactor with optical particle-sizing pyrometer.*

Newsletter

Experiments and modeling (continued)

(Continued from page 1)

One of the more promising aspects of the oxy-combustion approach is the possibility of applying this technology as a retrofit to the large installed base of coal power plants, offering substantial capital cost savings relative to constructing new plants. To successfully retrofit a boiler to oxy-combustion, the heat transfer rates must be approximately matched to the original boiler design. Therefore, a large fraction of the flue gas must be recycled to the boiler to moderate flame temperatures. Exactly how much flue gas should be recycled is an important and complex question, as the high CO_2 content of the flue gas affects both radiant and convective heat transfer and may affect the coal burning rate.

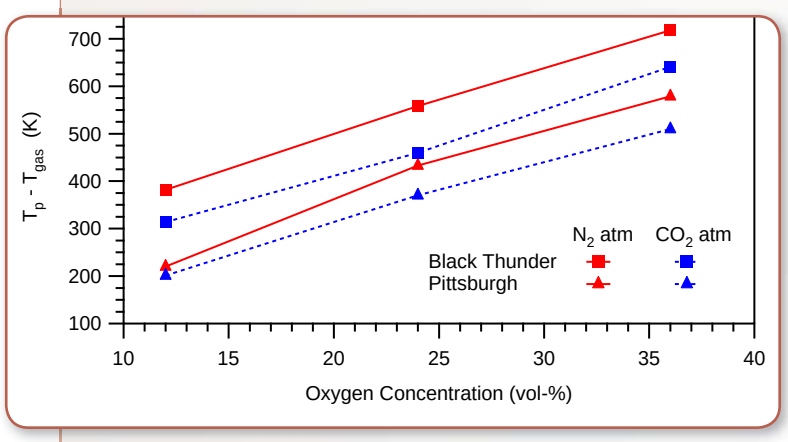

Figure 3. *Mean char particle temperature rise, relative to the surrounding gas, for Pittsburgh seam coal and Black Thunder coal as a function of the oxygen content and the use of N_2 or CO_2 background gas. Black Thunder is a lower rank coal with a higher burning rate – hence the higher measured char particle temperatures during combustion.*

CRF researchers Chris Shaddix and Alejandro Molina (now at the National University of Colombia) have been investigating oxy-combustion of coal for several years. Measurements of pulverized coal char burning rates showed that Arrhenius burning rate models used for conventional coal combustion still apply for the enhanced oxygen levels used in oxy-combustion. Measurements and analysis of devolatilizing particles showed that ignition is enhanced in the presence of higher levels of oxygen but is inhibited by CO_2 because of its high specific heat (70% larger than that of N_2). Furthermore, the reduced diffusivity of gas molecules (20% lower) in the presence of CO_2 delays the consumption of volatile gases emitted from individual burning coal particles.

Recently, measurements were made of pulverized coal char burning rates to evaluate the question of how CO_2 affects the combustion process. To investigate this effect, a laminar entrained flow reactor with a unique optical particle-sizing pyrometer diagnostic was employed, as shown in Figure 2. Burner conditions were chosen that resulted in a consistent reactor temperature of 1700 K for oxygen concentrations ranging from 12% to 36% and for either N_2 or CO_2 as the bulk diluent gas. Two different coals were investigated, representing a typical eastern U.S. medium-sulfur coal and a typical western U.S. low-sulfur coal.

Figure 3 shows the measured mean char particle temperature rise over the gas temperature. As is clearly evident, the char particles burn at a reduced temperature in the presence of CO_2, implying that the burning rate is lower. If we solve for the surface-specific burning rate of the particles, q, we find that the functional (Arrhenius) relationship between the burning rate and the inverse char particle temperature is the same for each coal whether burning in N_2 or CO_2, as shown in Figure 4. This means that the kinetic burning rate of the chars is unaffected by CO_2. Furthermore, this result implies that the observed decrease in char particle burning rate in CO_2 results from a reduction in the diffusion of oxygen through the particle boundary layer (in general, both surface kinetic rates and oxygen diffusion affect the burning rate of pulverized coal particles).

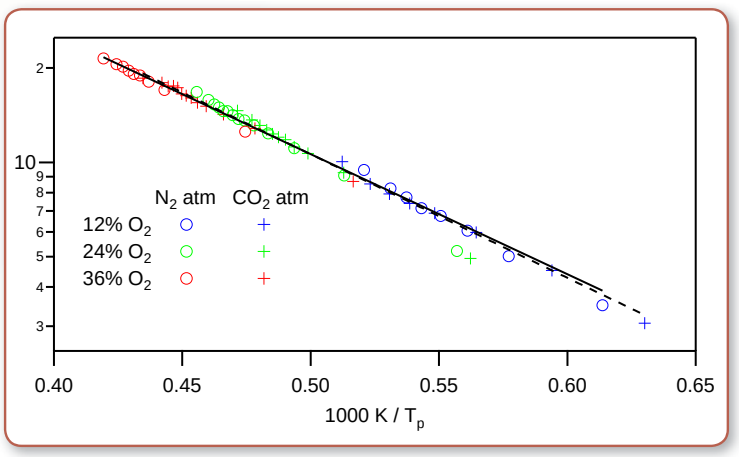

Figure 4. *Arrhenius plot of the surface-specific burning rate of Pittsburgh coal char as a function of oxygen content and background gas. The lines are best fits of the data for N_2 (solid) and CO_2 (dashed).*

To further investigate and confirm this interpretation of the data, CRF researchers employed a computational model of single-particle combustion that utilizes CHEMKIN™ algorithms. Professor Brian Haynes of the University of Sydney, a member of the CRF's External Advisory Committee, developed this model, known as SKIPPY. The model solves for detailed chemical reactions, flow, and heat transfer both

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COMBUSTION RESEARCH FACILITY

VISITOR PROGRAM

These visitors will be leaving the Combustion Research Facility at the completion of their tenure.

David Lignell

Post Doc

Affiliation: Faculty, Chemical Engineering Department, Brigham Young University

Project: Turbulence modeling for combustion stimulations

Host: Alan Kerstein

Svend Tollak Munkenjord

Visiting Researcher

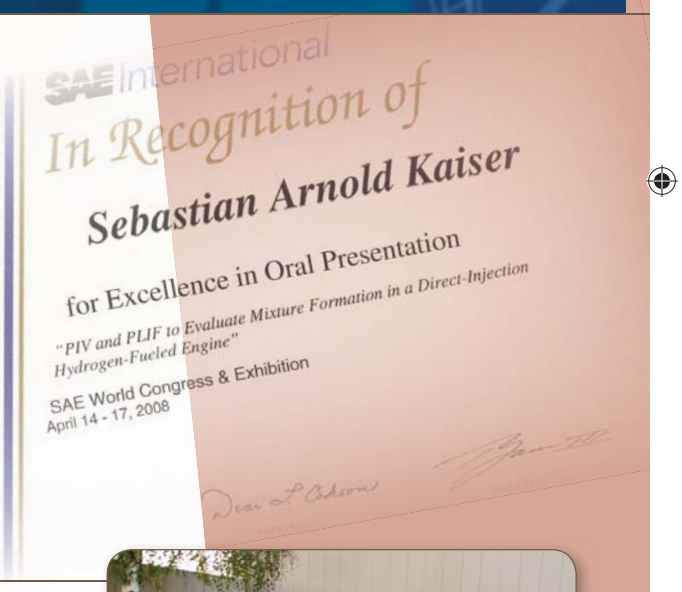
Affiliation: SINTEF Energy Research, Trondheim, Norway

Project: Computational modeling of multiphase turbulent flow

Host: Alan Kerstein

Sebastian Kaiser receives SAE award

Sebastian Kaiser received an award from SAE International for Excellence in Oral Presentation, for his paper titled, "PIV and PLIF to Evaluate Mixture Formation in a Direct-Injection Hydrogen-Fueled Engine."



Tom Settersten and Jonathan Frank host visitors

Alfred Leipertz, Sebastian Pfadler, Thomas Seeger and Johannes Kiefer from the Friedrich-Alexander-Universität Erlangen-Nürnberg and the Erlangen Graduate School in Advanced Optical Technologies (SOAT) visited the CRF in November as part of ongoing and potential future collaborations with CRF Principal Investigators Jonathan Frank and Tom Settersten. Alfred Leipertz and Sebastian Pfadler visited Jonathan Frank at Sandia to discuss future research collaborations between the University of Erlangen and the Advanced Imaging Laboratory at Sandia. Thomas Seeger and Johannes Kiefer worked with Tom Settersten and Brian Patterson during a 6-week campaign to develop time-resolved pure-rotational coherent anti-Stokes Raman scattering (CARS) for temperature and species measurements in high-pressure environments. Combining the strong rotational CARS modeling expertise in Erlangen and the unique experimental capabilities in the Picosecond Diagnostics Laboratory at the CRF, the researchers have demonstrated exquisite rejection of the resonant background from fuel molecules that typically prevents measurement in fuel-rich conditions for fuels other than methane. This fruitful collaboration will continue in 2009, when a second collaborative experimental campaign at the CRF is planned.

Multiscale simulation of ionic fluxes through nanopores (continued)

(Continued from page 1)

design of these membranes is largely based on trial and error, resulting in slow progress. In order to enable a predictive design capability, detailed insight is needed into the relationship between a membrane's structural and transport properties.

As part of a combined experimental-computational project investigating nanoporous membranes for desalination, CRF researchers Bert Debusschere and Habib Najm, in collaboration with the scalable computing R&D department, performed multiscale simulations of ionic fluxes through track-etched membranes. Track-etched membranes, as shown in Figure 1, have pores with a very repeatable, cylindrical geometry, making them more amenable to simulation with comparison to experiments.

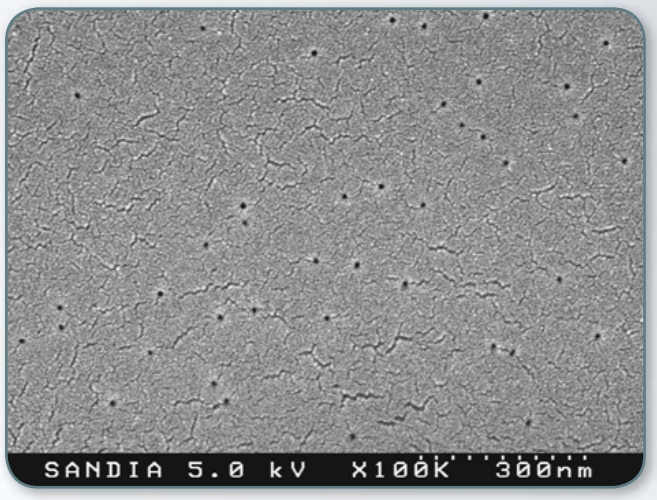


Figure 1. *SEM of track-etched polycarbonate membrane with 10 nm pore diameter.*

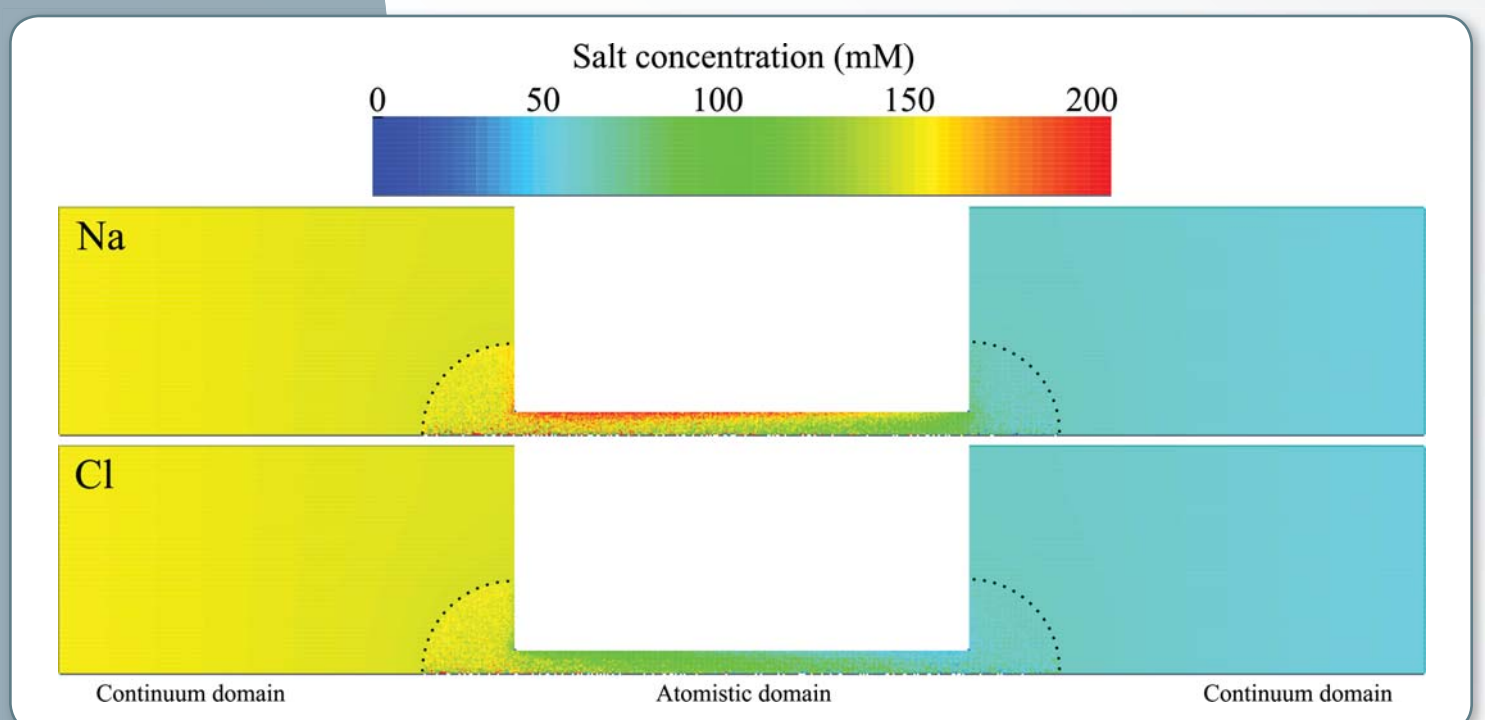


Figure 2. *Sodium (top) and chloride (bottom) ion concentration fields in electric field driven flux through a negatively charged nanopore. An axisymmetric slice is shown.*

In order to resolve the relevant transport phenomena on both the molecular and the mesoscale level, a multiscale model was used: particle methods (Brownian Dynamics or BD) inside the pore, and continuum methods (Poisson-Nernst-Planck or PNP) for the ionic transport a short distance away from the pore and for the external electric field contribution throughout the domain. The resulting multiscale model is able to take into account molecular effects such as finite ion size while at the same time accurately representing macroscale effects such as concentration polarization and the externally applied field.

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Figure 2 shows the simulated ion concentration fields for the flux of sodium chloride through a nanopore with an applied concentration and electric field. Both the field and concentration gradients are from left to right. A negative charge is applied to the pore surface. The concentration field in the pore is obtained from sampling 3D BD particle fields, while the concentrations in the far-fields are obtained from an axisymmetric PNP model. Due to the need to maintain electroneutrality in the fluid, the concentration profiles for both the sodium and chloride ions are very similar in Figure 2. Inside the nanopore, however, an excess of sodium ions is present near the pore surface in order to offset the negative charge on this surface. The chloride ions, on the other hand, are depleted in this area. This fact is confirmed in Figure 3, which shows the bulk charge density throughout the domain. While electroneutrality is maintained in most areas, an excess positive charge is present inside the nanopore.

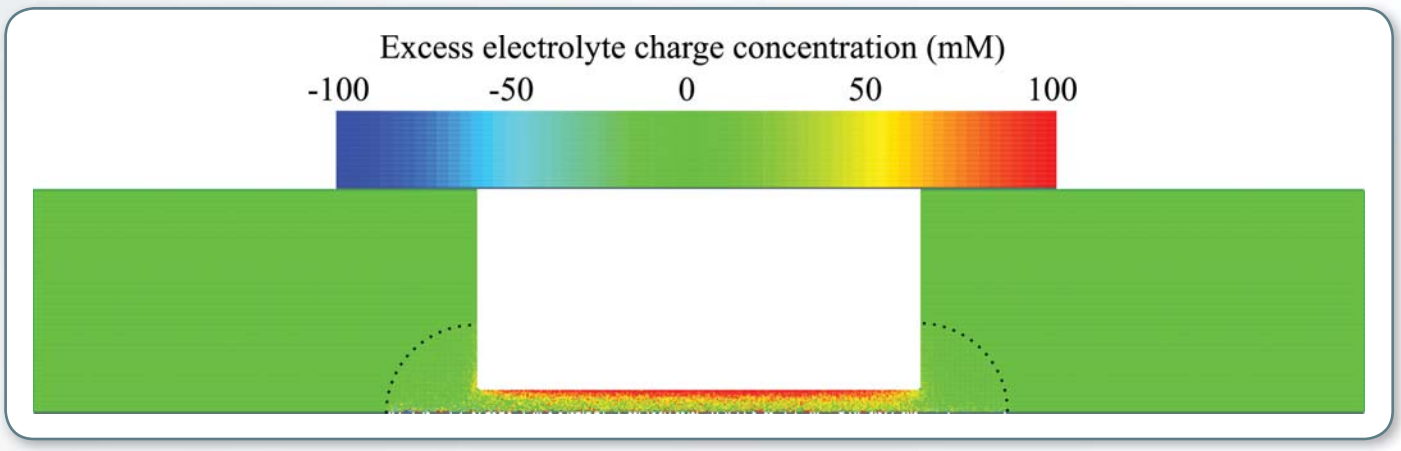

Figure 3. *Excess bulk charges inside the nanopore to shield the negative charges on the pore surface.*

As the depletion of one type of ion from the pore affects the transport selectivity, a parametric study was performed over a range of pore surface charges. Figure 4 shows the sodium and chloride fluxes for the nanopore of Figures 2 and 3, but with a pore surface charge varying from -0.1 to 0.2 C/m^2. In this context, positive fluxes are defined to be from left to right in the flow geometry (Figures 2 and 3), i.e., in the direction of the field and concentration gradients. As the surface charge increases, coions are almost completely blocked form the pore, resulting in a membrane that allows the selective transport of the counterions only, as can be seen at very low or very high wall charge density in Figure 4. The conditions for positive wall charge are representative of anion exchange membranes in electrodesalination units, where negative ions flow through an anion-selective membrane against a concentration gradient. The multiscale simulations also showed an increase of the overall throughput with wall charge magnitude.

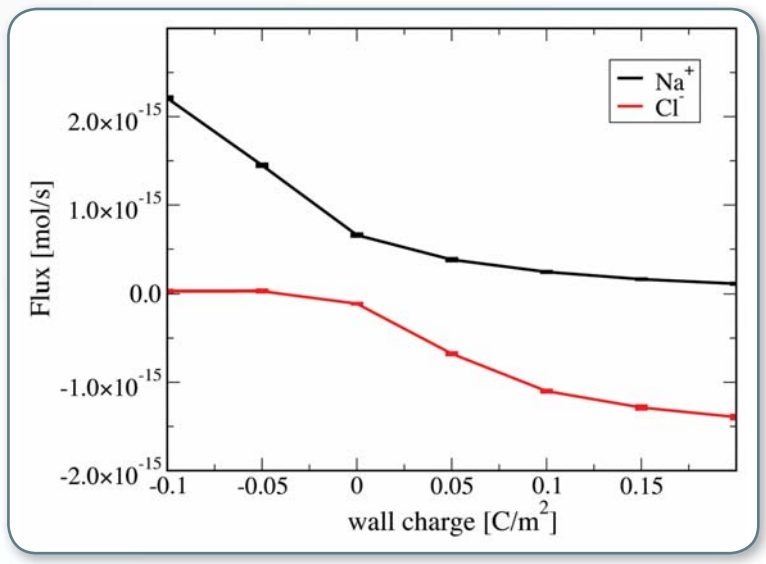

Figure 4. *Sodium and chloride ion fluxes as a function of the pore surface charge.*

Overall, the simulations showed a strong effect of surface charge on the membrane throughput and selectivity, an effect that is tied to the selective blocking of coions from the confined pore area. On the experimental side, it was demonstrated that the membrane surface charge can be tuned through UV-Ozone activation followed by thermal grafting of anionic or cationic monomers. Improved understanding of the relationship between membrane structure and transport properties will ultimately enable a science-driven predictive design capability, which will guide experimental design in order to dramatically speed up the membrane optimization process.

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Experiments and modeling (continued)

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within the particle and in the particle boundary layer. After calibrating the surface kinetic rates to match our observed char particle temperatures in N_2 atmospheres, the SKIPPY predictions for combustion in the CO_2 atmospheres show good agreement with the measured trends, as evidenced in Figure 5. In addition, if we artificially set the diffusivities of gas molecules in CO_2 to be the same as in N_2, we find that char particle temperature predictions now match those of gas molecules in CO_2 to be the same as in N_2, we find that char particle temperature predictions now match those observed for N_2. Conversely, adjusting the thermal properties of CO_2 to match those of N_2 has a negligible effect on the SKIPPY predictions.

This study has definitively established that while char combustion rates are lower in CO_2 environments, existing char kinetic expressions should still hold and CFD modeling of oxy-combustion of coal should not suffer inaccuracies in describing char combustion, as long as the diffusion of oxygen through the particle boundary layer is adequately treated. These results have been presented at several international research conferences and are currently being submitted for journal publication.

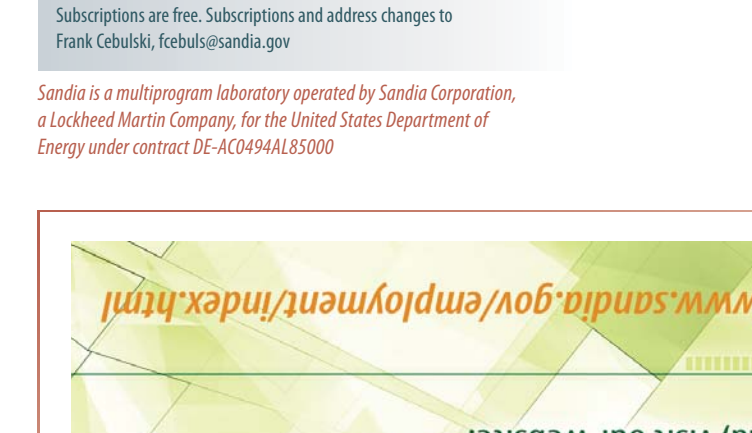

Figure 5. *SKIPPY calculation results for combustion of pulverized char particles in N_2 and CO_2 atmospheres, demonstrating how the difference in diffusivity of O_2 in N_2 and in CO_2 is responsible for the difference in measured particle temperatures (and burning rates).*