

## **Intercalation of CO<sub>2</sub> and H<sub>2</sub>O in Na-hectorite under geological carbon sequestration conditions using GCMD simulations**

OZGUR YAZAYDIN\*<sup>1,2</sup>, NARASIMHAN LOGANATHAN<sup>2</sup>,  
GEOFFREY M. BOWERS<sup>3</sup>, ANDREY G. KALINICHEV<sup>4</sup>, R.  
JAMES KIRKPATRICK<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, University College  
London, London WC1E 7JE, UK (\*correspondance:  
ozgur.yazaydin@ucl.ac.uk)

<sup>2</sup> Department of Chemistry, Michigan State University, East  
Lansing, Michigan 48824, USA (naresh20@msu.edu,  
rjkirk@msu.edu)

<sup>3</sup> Department of Chemistry and Biochemistry, St. Mary's  
College of Maryland, St. Mary's City, Maryland 20686,  
USA (gmbowers1@smcm.edu)

<sup>4</sup> Laboratoire SUBATECH, Institut Mines-Télécom  
Atlantique, 44307 Nantes, France  
(kalinich@subatech.in2p3.fr)

We report computer simulations using grand canonical molecular dynamics (GCMD) to understand the intercalation of CO<sub>2</sub> and H<sub>2</sub>O at different combinations of temperature and pressure relevant to petroleum reservoirs and geological carbon sequestration. The simulations are based on the smectite mineral hectorite with Na<sup>+</sup> as the charge compensating cation. In the GCMD simulations the interlayer spacings were fixed at values from 9.5Å (dry state) to 18.0Å (3-layer hydrate) at intervals of 0.2Å. The interlayer mole fractions imposed by the chemical potential of the CO<sub>2</sub>/H<sub>2</sub>O bulk phase were quantitatively analyzed using equilibrium adsorption isotherms. The results agree well with experiments and confirm the notion that the presence of H<sub>2</sub>O aids CO<sub>2</sub> intercalation, which is inhibited under dry conditions. Maximum CO<sub>2</sub> adsorption occurs at 12.2Å which is in the range of monolayer structures. The adsorbed CO<sub>2</sub> molecules exhibit parallel orientations with respect to basal hectorite surface and are coordinated to the basal surface. The interlayer species exhibit significant redistribution between different coordinations as the temperature and pressure changes. The orientation of the structural hydroxyl groups plays an important role in determining the interlayer CO<sub>2</sub>/H<sub>2</sub>O content. The variation in adsorption structure, nearest neighbour coordinations, residence time correlation functions, and diffusional mobility of H<sub>2</sub>O and CO<sub>2</sub> as functions of interlayer spacing are consistent with available experimental and simulation data and provide a detailed structural and dynamical understanding of CO<sub>2</sub> and H<sub>2</sub>O intercalation on a molecular scale.