

## DIVISION OF ENVIRONMENTAL CHEMISTRY

238th ACS National Meeting

Washington, DC

August 16-20, 2009

### THURSDAY MORNING

#### Emerging Environmental Technologies towards a Cleaner and Sustainable Society

P. Bishop, *Organizer*

V. Shah, *Organizer, Presiding*

**8:30** — Introductory Remarks.

**8:35 —207.** *In situ* controlled-release systems (CRS) for lower-cost, target-specific, and 'greener' treatment of pollutants in water resources. **E. S. Lee**, G. Liu, F. W. Schwartz, Y. Kim

**8:55 —208.** Development of a sustainable catalytic treatment process for perchlorate-contaminated water. **T. J. Strathmann**, J. K. Choe, J. Liu, Y. Zhang, C. J. Werth, J. R. Shapley

**9:15 —209.** Dual isotope fractionation ( $^{15}\text{N}$ ,  $^{18}\text{O}$ ) in catalytic nitrate reduction. **J. R. Shapley**, K. A. Guy

**9:35** — Intermission.

**9:45 —210.** Dual-mode detection of *E. coli* and total coliforms. **L. Su**, K. Venkitanarayanan, Y. Lei

**10:05 —211.** Electrode-based reactive capping of contaminated sediments for *in situ* redox control. **M. Sun**, F. Yan, D. D. Reible, G. V. Lowry, K. B. Gregory

**10:25 —212.** Nucleation statistics of carbon dioxide hydrate: Enhancement of the underwater sequestration safety. **K. Lee**, W. Lee, S -H. Lee

**10:45 —213.** Quantum chemistry applications for environmental science: Evaluation of military produced contaminants. **Y. Kholod**, L. Gorb, F. Hill, J. Leszczynski

## ABSTRACTS

### ENVR 207

#### ***In situ* controlled-release systems (CRS) for lower-cost, target-specific, and 'greener' treatment of pollutants in water resources**

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This paper illustrates new possibilities for using the controlled-release system (CRS) for lower-cost, target-specific groundwater remediation, and more generally in greener treatment of pollutants in urban and rural water resources. The CRS approach utilizes reaction-diffusion modes, which effectively add the highly soluble treatment chemicals slowly in reactive barriers. Our paper first examines a variety of practical approaches to employ the controlled release forms in groundwater remediation. This work has involved manufacturing prototype CRS forms, developing a generalized reaction-diffusion code capable of modeling CRS, performing proof-of-concept experiments of variable scales, development of well-based controlled-release permeable reactive barriers (CR-PRB), and development of a code capable of describing release, reactive transport, and mixing of treatment chemicals/pollutants in the CR-PRB systems in complex aquifer settings. Outcomes of this integrated work suggest that the minimal dispersion in the well-based CR-PRB system provided unique challenges in the mixing of treatment chemicals with pollutants. The second part of our paper then examines several possibilities of mixing the treatment chemical with a contaminant plume in the CR-PRB settings. One example utilizes strategic pumping downstream of the CR-PRB in cyclical patterns to create a well-mixed, stable zone of treatment chemical with predetermined size and concentration ranges. Size of the mixing zone can be expanded by attaching several CR-PRB systems and the mixing zone can be maintained for years with periodic well mixing and replacements of exhausted CRS forms. Another promising approach couples funnel-and-gates with CR-PRB. In this scheme, the CR-PRB system is designed to achieve mixing and agent concentrations optimized for target treatment plume of contaminants. This paper concludes with presentations of preliminary results for using the CRS for low-cost and target-specific treatment of urban nonpoint source pollutants and acid mine drainages.

**Development of a sustainable catalytic treatment process for perchlorate-contaminated water**

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Novel catalysts combining palladium (Pd) and rhenium (Re) on carbon-based support materials have recently been developed in our laboratory that are capable of rapidly reducing perchlorate ( $\text{ClO}_4^-$ ) to chloride ( $\text{Cl}^-$ ) using hydrogen as an electron donor. Reaction rates under ambient temperature and pressure are much faster than chemical reduction processes (e.g., zerovalent iron) at comparable conditions, and no toxic oxyanion intermediates ( $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}^-$ ) are detected during the process. Although initial studies suggest a promising approach for treating this widespread and persistent groundwater pollutant, the controlling interfacial reaction mechanisms and surface speciation of the active metals remains poorly understood. This contribution describes recent efforts to (i) correlate the activity of Pd-Re catalysts with the speciation of Re, (ii) improve stability of catalysts during operation through modification of Re coordination and redox status, and (iii) enhance catalyst activity by modifying Re coordination. Results of surface spectroscopic studies indicate that while Pd is present predominantly in the metallic state, Re is present in a mixture of oxidation states that are influenced by solution conditions (e.g., dissolved oxygen, hydrogen). Immobilization of Re on catalyst surfaces and overall catalyst activity are heavily influenced by the redox status of Re. Catalyst activity is also significantly influenced by the prevailing coordination environment of Re on the catalyst surface. Efforts to improve catalyst activity and stability by depositing Pd-Re within a polymeric microporous supports and by coordinating Re with oxazoline and amine ligand groups will be described along with key opportunities and challenges for technology adoption.

## ENVR 209

### Dual isotope fractionation ( $^{15}\text{N}$ , $^{18}\text{O}$ ) in catalytic nitrate reduction

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Relationships between  $^{15}\text{N}$  and  $^{18}\text{O}$  isotope fractionation have been observed to characterize nitrate reduction in natural systems. In order to provide a basis for mechanistic comparison, analogous measurements have been made for reduction of aqueous nitrate with hydrogen over a synthetic, alumina-supported Pd-Cu catalyst. Fundamental prediction of the relative magnitudes of fractionation factors for oxygen atom transfer reactions will be discussed.

## ENVR 210

### Dual-mode detection of *E. coli* and total coliforms

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A dual-mode (amperometric and colorimetric) method was developed for the simultaneous detection of *Escherichia coli* and total coliform in aqueous system. Flow injection analysis (FIA) system (or CNT-modified FIA) was applied for amperometric detection of *E. coli* based on  $\beta$ -D-glucuronidase, while spectrophotometer was used for colorimetric detection of total coliforms based on the universal enzyme  $\beta$ -D-galactosidase. The current signal and the light absorption value (ABS) of the enzymatic products were measured and correlated to the initial concentration of *E. coli* and total coliforms, respectively. The detection of 100 cfu/ml *E. coli* and total coliforms have been demonstrated within six hours and eight hours, respectively.

## ENVR 211

### **Electrode-based reactive capping of contaminated sediments for *in situ* redox control**

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Reactive capping has emerged as a potential method for minimizing releases from contaminated sediments through emplacement of material in the cap which serves as an active barrier for sequestration or transformation of target contaminant. We demonstrate proof of concept for a novel, reactive cap technology which electrochemically controls the redox gradient and supplies electron donor to the subsurface. Moreover, we explore important geochemical parameters which may affect the redox gradient and evolution of hydrogen as an electron donor for contaminant degradation. Application of low potentials (2.5-5V) between graphite electrodes in a simulated sand cap produced a redox gradient through the cap. Cathodic hydrogen evolution rates were proportional to the applied potential and not greatly affected by pH. Hydrogen evolution rates were increased by ionic strength but not significantly impacted by organic matter. Electrodes may be employed for real-time control of redox conditions and electron donor supply in sediment caps.

## ENVR 212

### **Nucleation statistics of carbon dioxide hydrate: Enhancement of the underwater sequestration safety**

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The induction time of CO<sub>2</sub> hydrate has been reported to be irreproducible. In this research, we have investigated the stochastic characteristics of hydrate induction time for a safer CO<sub>2</sub> sequestration. The experimental system was composed of a high-pressurized vessel having four independent cells and a data acquisition system for collecting the temperature readings. CO<sub>2</sub> hydrate has been repeatedly formed in soil mineral suspensions at temperatures between 273.4 and 274.6°K and pressures ranging from 2.0 to 3.0 MPa. Each data set consisting of more than 30 induction times

has been obtained under different temperature, pressure, soil mineral, and electrolyte conditions. We have generated an empirical cumulative distribution function (CDF) for each data set and chosen a normal distribution for the hydrate induction time in montmorillonite suspension as a best-fit. As pressure increased, distribution parameters (mean and variance) decreased significantly. We are testing the effect of other experimental factors on stochastic patterns in the hydrate induction time.

## ENVR 213

### Quantum chemistry applications for environmental science: Evaluation of military produced contaminants

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High-energetic nitro compounds are widely used for a range of military and industrial purposes. Nitroaromatic, nitrogen-rich compounds and nitramines, as well as products of their chemical transformations, are toxic contaminants to various terrestrial and aquatic receptors. An understanding of complex chemical processes, and estimation of the influence of different factors on the properties and reactivity of those compounds, is essential for design of efficient, environmentally nontoxic applications for their synthesis, storage, utilization, and remediation from the environment. In the present work, we demonstrate how quantum chemical methods can serve for these goals. We employed *ab initio*, semi-empirical and statistical computational techniques to predict the physico-chemical properties which determine sufficiency of synthesis, storage and utilization of potential contaminants; to model the distribution of a wide range of nitro compounds into the environment; to design degradation pathways of decomposition of contaminants.