Welcome to another edition of EECO News! The faculty, staff and students of the Department have been very busy over the past year. Another new faculty member was recruited: Dr. Yinjie Tang who will join the Metabolic Engineering/Systems Biology Cluster in the Department after a very successful post doctoral stint at the University of California, Berkeley. 30 students graduated with B.S. degrees in Chemical Engineering and 10 students received their doctoral degrees. The Department has also seen an increase in the number of UG students with the incoming class – with approximately 50 interested in majoring in ChE. 18 new doctoral students have accepted our offers of admission and will join us this Fall to take the total number of enrolled doctoral students to 75. One of them is a new McDonnell Academy Scholar who will join us from India.

We are excited about several new initiatives that have been launched. You can read about some in this Newsletter – the International Experience Class in EECE, and others. Research projects and efforts in the Energy and Environmental arenas are mushrooming. Through the University initiatives of ICARES and MAGEEP – several seed projects have been initiated. Preparation is underway for launching a clean coal research consortium. Planning is underway in earnest for the Second International Symposium on Energy and Environment – see www.mageep.wustl.edu/symposium08 for details.

We look forward to hearing from you!
Pratim Biswas
The Stifel and Quinette Jens Professor
Chair, Department of Energy, Environmental and Chemical Engineering

Useful websites:

Department:  www.eec.wustl.edu
ICARES:  http://i-cares.wustl.edu/
MAGEEP:  www.mageep.wustl.edu
McDonnell International Scholars Academy: http://mcdonnell.wustl.edu/
<table>
<thead>
<tr>
<th>Name</th>
<th>Degree Year</th>
<th>Institution</th>
<th>Position</th>
<th>Research Areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muthanna Al-Dahhan</td>
<td>Ph.D., 1993</td>
<td>Washington University</td>
<td>Professor</td>
<td>Chemical Reaction Engineering, Multiphase Reactors, Mass Transfer, Process Engineering</td>
</tr>
<tr>
<td>Richard L. Axelbaum</td>
<td>Ph.D., 1988</td>
<td>University of California</td>
<td>Full Professor</td>
<td>Nanoparticle Synthesis, Combustion</td>
</tr>
<tr>
<td>Pratim Biswas</td>
<td>Ph.D., 1985</td>
<td>California Institute of Technology</td>
<td>Stiffl and Quintette Jens Professor Chair and Professor</td>
<td>Aerosol Science and Engineering, Air Quality and Pollution Control, Energy &amp; Environmental Nanotechnology</td>
</tr>
<tr>
<td>Da-Ren Chen</td>
<td>Ph.D., 1997</td>
<td>University of Minnesota</td>
<td>Associate Professor</td>
<td>Particle Measurement and Instrumentation, Particle Filtration and Separation, Aerosol Dynamics Modeling, Aerosol Science &amp; Tech.</td>
</tr>
<tr>
<td>Milorad P. Dudukovic</td>
<td>Ph.D., 1972</td>
<td>Illinois Institute of Technology</td>
<td>Professor</td>
<td>Laura and William Jens Professor of Environmental Engineering Multiphase Reaction Engineering, Tracer Methods, Environmental Engineering</td>
</tr>
<tr>
<td>Daniel Giammar</td>
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<td>Aquatic Chemistry, Water Quality Engineering, Fate and Transport of Inorganic Contaminants</td>
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<td>John Gleaves</td>
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<td>Heterogeneous Catalyst, Surface Science, Microstructured Materials</td>
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<td>Rudolf B. Husar</td>
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<td>University of Minnesota</td>
<td>Directed, Center for Air Pollution &amp; Trends Analysis, (CAPITA) Environmental Informatics, Aerosol Pattern &amp; Trend Analysis</td>
<td></td>
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<tr>
<td>Young-Shin Jun</td>
<td>Ph.D., 2005</td>
<td>Harvard University</td>
<td>Assistant Professor</td>
<td>Aquatic Processes, Molecular issues in Chemical Kinetics</td>
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<tr>
<td>Cynthia Lo</td>
<td>Ph.D., 2005</td>
<td>Massachusetts Institute of Technology</td>
<td>Assistant Professor, Biomineral Structure and Reactivity at Environmental Interfaces</td>
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<tr>
<td>Himadri Pakrasi</td>
<td>Ph.D., 1984</td>
<td>University of Missouri, Columbia</td>
<td>Professor of Energy Director, International Center for Advanced Renewable Energy and Sustainability Systems Biology</td>
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<tr>
<td>Palghat Ramachandran</td>
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<td>University of Bombay</td>
<td>Professor</td>
<td>Chemical Reaction Engineering, Boundary Element Methods</td>
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<tr>
<td>Radhakrishna Sureshkumar</td>
<td>Ph.D., 1996</td>
<td>University of Delaware</td>
<td>Associate Chair, Professor</td>
<td>Complex Fluids Dynamics, Interfacial Nanostructures, Multiscale Modeling &amp; Simulations</td>
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<tr>
<td>Yinjie Tang</td>
<td>Ph.D., 2004</td>
<td>University of Washington</td>
<td>Assistant Professor</td>
<td>Metabolomics, Systems Biology</td>
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<td>Jay R. Turner</td>
<td>D.Sc., 1993</td>
<td>Washington University</td>
<td>Associate Professor</td>
<td>Air Quality Management</td>
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<tr>
<td>Dong Qin</td>
<td>Ph.D., 1996</td>
<td>University of Pennsylvania</td>
<td>Associate Dean of Research</td>
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<tr>
<td>Stephan Falke</td>
<td>D.Sc., 1999</td>
<td>Washington University</td>
<td>Research Assistant Professor</td>
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<tr>
<td>Gregory Yablonsky</td>
<td>Ph.D., 1971</td>
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<td>Research Associate Professor</td>
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<td>Research Associates</td>
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<tr>
<td>Ruth Chen</td>
<td>D.Sc.</td>
<td></td>
<td>Research Associate</td>
<td>Toxicology</td>
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<tr>
<td>Ray Ehrhard</td>
<td>P.E., BCEEE</td>
<td></td>
<td>Research Associate</td>
<td>EPRI, Global Energy Partners</td>
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</tbody>
</table>
As students in the Department of Energy, Environmental and Chemical Engineering, our days are full of long hours and hard work as we pursue our various degrees. But, we also take time out to have some fun while we learn about our prospective fields outside the classroom setting.

In addition to our regular meetings, this semester our WEF chapter had a wonderful opportunity to take a plant tour of the Metropolitan St. Louis Sewer District, Coldwater Creek Waste Water Treatment Plant (WWTP). Project manager, David Flushing, Plant Manager, Ken Gambaro, and WEF student liaison, Tom Ratzki, also joined us. This waste water plant is currently undergoing a massive expansion project. This allowed us to see many components of the system that are typically covered with wastewater, in addition to the older facilities that were still in operation. Seeing the “guts” of the WWTP instilled a more practical understanding for each of us. Its experiences like these that make our WEF membership so invaluable. We are looking ahead to another exciting semester with other facility tours, conferences and partnerships.

Members of WEF during a tour of the Metropolitan St. Louis Sewer District, Coldwater Creek WWTP.

**OUR NEWEST ALUMNI ~ 2007**

**Doctoral Graduates (Advisor)**
- Swapnil Dhumal (Biswas, Khomami)
- Zhen He (Angenent)
- Debangshu Guha (Dudukovic)
- Anatha Koppol (Khomami, Sureshkumar)
- Shaohua Hu (Biswas)
- Ashfaq Shaikh (Al-Dahhan)
- Vidya Venkataramani (Khomami)
- Lu Han (Al-Dahhan)
- Chaolong Qi (Chen)
- Liyun Xie (Giammar)

**2007/2008 STUDENT CHAPTERS EXECUTIVE COMMITTEES**

**AIChE**
- President: Adam Webb
- Treasurer: Jeff Packer
- Social Coord: Adam Grimm
- Advisor: Dr. Cynthia Lo

**WEF**
- President: Sarah Dryden
- Vice Pres.: Hui Zeng
- Secretary: Matt Agler
- Treasurer: Abhas Singh
- Advisor: Dr. Dan Giammar

**AWMA**
- President: James Noel
- Vice Pres.: Achariya Suriyawong
- Secretary: Matt Agler
- Treasurer: Abhas Singh
- Advisor: Dr. Pratim Biswas

**AAAR**
- Coordinator: Chris Hogan
- Advisor: Dr. Pratim Biswas

**ENVESA**
- President: Alyssa Smith
- Advisor: Dr. Dan Giammar
The American Institute of Chemical Engineers (AIChE) is the world’s leading organization for chemical engineering professionals, with more than 40,000 members from 93 countries. AIChE not only works to apply chemical expertise to meet societal needs, but also provides opportunities for professional and personal growth. To that end, AIChE student chapters on campus are important resources for promoting the professional development of undergraduate students, through networking with fellow ChemE majors as well as faculty on campus and practicing chemical engineers in industry.

The AIChE student chapter at Washington University in St. Louis has been very active this year. The chapter officers: President Adam Webb, Treasurer Jeff Packer, and Social Coordinator/Brewmaster Adam Grimm, have been working hard to organize a variety of educational and social events. At the beginning of the year, Adam Webb spoke to the incoming freshmen at the EECE department’s undergraduate social, encouraging them to be involved in AIChE from the beginning of their academic careers. To follow up, the chapter has held monthly meetings, often featuring nationally recognized experts in engineering and related disciplines, and organized periodic brewing sessions that utilize the conservation laws and unit operations of chemical engineering. In March 2008, Washington University hosted AIChE Ambassador Alan Rossiter, of Rossiter and Associates in Bellaire, TX, who spoke on “Professional Experience- Beyond Technical Competence”. Dr. Rossiter spoke about his background in industry and consulting, and exhorted the students to invest in their profession and society, as well as to carefully consider their professional responsibilities, workplace interactions and balance between work and home life.

AIChE also spearheaded the formation of an Undergraduate Advisory Board, which meets twice a semester with department chair Dr. Pratim Biswas to discuss the undergraduate student experience. Two students from each undergraduate class (freshman, sophomore, junior, and senior), as well as two graduate students, are members of the board. Topics of conversation have included the undergraduate curriculum and ideas for increased faculty-student interactions. One of the fruits of these meetings has been the organization of a faculty-student softball game and picnic, to occur later this spring.

In November 2007, Adam Webb attended the AIChE Annual Meeting and National Student Conference in Salt Lake City, UT. There, he met the presidents of student chapters around the country, and came away with some new ideas for organizing chapter activities and increasing participation. In March 2008, Adam Webb, along with Jim Wexler, Brent Sensenich, Jeff Packer, Paul Northrop, and Adam Grimm, attended the AIChE Mid America Regional Conference in Lincoln, NE. There, they mingled with fellow students from chapters in Arkansas, Iowa, Kansas, Missouri, Nebraska, and Oklahoma, and discussed ideas for new chapter projects related to renewable energy, including the ChemE-Car competition.

Finally, AIChE members have been honored with several national awards. Current junior, Jay Werber, was honored last year with the Donald F. Othmer Sophomore Excellence Award, for which he received a certificate and a copy of Perry’s Handbook. This year, sophomore, Cameron Smith, will receive the Othmer Award.

Membership in AIChE, which includes online access to the AIChE eLibrary powered by Knovel as well as exclusive job search and career management services, is free for students thanks to ScaleUP, a new initiative sponsored by BP, Rohm & Haas, DuPont, Praxair, Merck, Dow and UOP. We encourage every undergraduate to join AIChE and visit their website: http://www.aiche.org/Students/
EECE students participated in the 2007 MAEEC Conference held at University of Missouri, Columbia.

CONGRATULATIONS TO:

- Dr. Richard L. Axelbaum on his promotion to Full Professor.
- Dr. Daniel Giammar on his promotion to rank of Associate Professor with tenure.

GO BEARS!

Engineering Sophomore, Cameron Smith, helps lead Bears to their first NCAA Division III men’s basketball national championship with a 90-68 victory. The Bears defeated defending national champion Amherst College March 22nd at the Salem Civic Center in Salem, Va.

Cameron is one of the first students to be selected for the International Experience in Energy, Environmental & Chemical Engineering. These students will be visiting Beijing, China in the summer of 2008 where they will study with partner schools of the McDonnell International Scholars Academy. In addition, he is an excellent student, with a GPA of 4.0.

Department Statistics 2007

- Total External Research Awards in 2007 = $3.1 million
- Total number of doctoral students = 65
- Total number of undergraduate students = 88
- Full-time faculty in Energy, Environmental and Chemical Engineering = 16
- Major Program Endowments are:

  Ahmann, Browne, Jens, Lopata and Stuckenbuerg professorships.
  Ahman, Buescher, Dubois, EVIRSAN, Homeyer, Lue-Hing,
  McGrath, McKelvey, Olin, Schwartz, Sproul, Stein, Sverdrup, and
  Jens Laboratory endowments.
DEPARTMENT Launches International Experience in Energy, Environmental & Chemical Engineering Program for Undergraduate Students

There is an increased interest amongst students to gain experience by working overseas. To ensure that maximum benefits could be gained by the students, and with faculty interest in collaborative programs with 24 partner Universities of the McDonnell Academy (http://mcdonnell.wustl.edu); a new course was launched in the Department.

Each year, students will be selected for this program that will be guided by faculty from the Department of Energy, Environmental and Chemical Engineering. The highlight of the class is a Summer visit to a city where partner schools of the McDonnell Academy are located. Students then register for the class in the following Fall Semester and engage in project discussions, presentations and report writing. This program will not only provide an International Experience to the student, but promote teamwork and leadership skill development.

The inaugural program will be led by Profs. Jay Turner and Ruth Chen, and they will be visiting Beijing, China in Summer 2008; and the focus will be on air quality monitoring and air quality studies. The 2009 Program will be led by Profs. Pratim Biswas and Ruth Chen, and the students will be visiting Seoul, Korea; and the focus of the program will be on nanotechnology, energy and environmental technologies. The 2010 Program will be led by Profs. Da-Ren Chen and Ruth Chen, and the students will visit Mumbai, India; and the focus will be on aerosol science and technology, and visiting rural areas where nanotechnology projects have been implemented.

For more details, please look up: http://eec.wustl.edu/Academics/InternationalExperience.asp

Highlights:
- Pre-visit orientation meetings and lectures in Spring Semester prior to Summer International visit
- Students visit a McDonnell Partner University School for 2 or 3 weeks during summer
- Engage in a project to enhance teamwork and knowledge of the field of Energy, Environment or Chemical Engineering
- Field Trips to local industries, regulatory agencies and national laboratories
- Social Programs
- Analysis of experience, projects, discussions and presentations in subsequent Fall Semester
WU TEAM Goes to Conference

By: Matthew Agler

A group of Washington University graduate and undergraduates are working on a sustainable water desalination design. They are competing in early April against teams from across the country in a design competition at the WERC conference at New Mexico State University. The team, primarily funded by the department of Energy, Environmental, and Chemical Engineering, is doing construction in the Jens lab where they are combining their classroom knowledge with their skills in building.

The team is comprised of graduate and undergraduate students from the department, as well as a student from the WU law school. Team members are Matt Agler, Kate Nelson, Alexandria Palensky, Alyssa Smith, and Megan Wright. Each of these students bring their own specialty to the table - or lab bench - that creates quite a formidable team with a good chance to take home the gold-or at least some clean and refreshing \( H_2O \)!
REFEERED JOURNAL PUBLICATIONS


**Continued on next page**


Yablonsky G.S., Constales D., Shekhtman S., Gleaves J.T., “Y-Procedure: How to Extract the Chemical Transformation Rate from the Reaction-Diffusion Data with no Assumption on the Kinetic Model.” Chemical Engineering Science, online (2007)


Microbial reduction of soluble uranium(VI) generates U(IV) oxide solids that are less soluble, and thus has been proposed for in-situ remediation of contaminated sites. The intrinsic reactivity of biogenic UO₂, which forms nanoparticles <5 nm, is unknown; however, this property is crucial to predict the migration of uranium in aquifers. A research project at Washington University (PI: Daniel Giammar) aims at quantifying the solubility and dissolution rate constants of biogenic UO₂ in comparison to its abiotic analog, taking into account the structural properties of the materials.

Abiotic UO₂ was synthesized by reducing U(VI) peroxide in a heated hydrogen atmosphere. Bacteriogenic UO₂ was isolated from *Shewanella oneidensis* after bioreduction, and provided by cooperation partners at Ecole Polytechnique Federale de Lausanne (EPFL), Switzerland. The abiotic UO₂ was identified as highly crystalline cubic uraninite using powder X-ray diffraction (XRD) on a Rigaku D-MAX/A diffractometer (Fig. 1). A specific surface area of 5.93 m²/g was derived from multipoint N₂-BET (Quantachrome Autosorb). Images of the UO₂ particles (Fig. 2) were gained from field emission scanning electron microscopy (SEM, Hitachi S-4500) and high resolution transmission electron microscopy (HR-TEM, at EPFL). Synchrotron-based spectroscopy and diffraction techniques were applied at Stanford Synchrotron Radiation Laboratory to investigate the molecular and nano-scale structures.

Dissolution experiments were carried out in custom-built continuously stirred flow-through reactors using a gas-tight influent reservoir (Fig. 3). The low solubility of UO₂ under reducing conditions requires low detection limit for U analysis (10 ppt), provided by ICP-MS (Agilent Series). Results show that equilibrium solubility and dissolution rates of biogenic and abiotic UO₂ were similar under anoxic conditions at neutral pH. However, the dissolution of biogenic UO₂ accelerated substantially in the presence of carbonate, and more than for the abiotic UO₂. A similar phenomenon was observed in systems with low dissolved oxygen concentration. The dissolution process is driven by oxidation of U(IV) on the particle surface, limited by the availability of sites and thus by the detachment of U(VI) from the surface, unless carbonate is supplied to accelerate the detachment reaction. The same mechanism can explain the results obtained under anoxic conditions, where oxidants are formed by α-radiolysis of water. Because groundwater carbonate concentrations are usually significant, the stability of biogenic UO₂ nanoparticles will be controlled by surface reactivity with carbonate and solubility of U(VI) phases rather than U(IV). Bioremediation strategies for uranium immobilization should carefully consider the impact of carbonate on the reactivity of the products formed.
The Jens Environmental Molecular and Nanoscale Characterization Laboratory, established in 2001, is located in Urbauer Hall, Washington University in St. Louis. The Laboratory is a shared Instrumentation facility supported by the core faculty in the Department of Energy, Environmental and Chemical Engineering. The instruments in the laboratory are also made available to all university researchers and the scientific community for performing analysis at the molecular and nanometer scales.

SEM
The SEM image (A) of a scalpel tip shows the machining lines that are formed in the scalpel cutting edge during the manufacturing process of breast implants. The image was obtained by the Field Emission Scanning Electron Microscope, Hitachi S-4500. The next image (B) shows the edges of a ruptured implant. The striations that were formed by the machining grooves in the blades are quite visible. Electron microscopy is being used to determine if implant failure is caused by surgical instruments. This project is under the direction of Professor Harry Brandon, Plastic Surgery, Mechanical Aerospace and Structural Engineering Department.

Following is a list of Instruments that are currently available in the Laboratory:

1. BET Surface Area and Pore Volume Measurement Instrument, Quantachrome Autosorb-1
2. HPLC-High performance Liquid Chromatography, HP 110 with diode array & UV detector
3. Humidity Controlled Microbalance Facility (Precision weighing of samples, conditioned to a specific humidity level)
4. ICP-MS – Inductively Coupled Plasma Mass Spectrometer-Agilent 7500ce Series
5. TOC-Total Organic Carbon Analyzer, Shimadzu TOC-500
6. GC-Gas Chromatography with TCD, FID-HP5890 Series
7. SEM-Scanning Electron Microscope, Hitachi model s-4500 Field Emission Scanning Electron microscope, a NORAN Instruments Energy Dispersive X-ray (EDX) microanalysis system, a back scatter detector and mechanical straining stage.
8. 96 Well Plate Reader, BIO-TEK SYNERGY HT
9. Fourier Transform Infrared Spectrometer (FTIR), Nicolet Nexus 470 instrument with mid-IR source and DTGS detector. Attenuated total reflectance (ATR) and diffuse reflectance (DRIFTS) accessories for the analysis of solids liquid, and aqueous suspensions.
10. Molecular Imaging Pico Scan AFM
11. AFM/MFM Digital Instrument Dimension 3000 Multimode IIIA Microscope

Synthesis of γ-Al₂O₃ powders of with different size, shape and morphology using spray pyrolysis method in a furnace aerosol reactor (FuAR) by researchers in the Aerosol and Air Quality Research Laboratory (AAQRL). By controlling process conditions, different shape materials can be readily produced. Fourier transformed infrared spectroscopy (Thermo Nicolet, Model: Nexus-470) is used to analyze for shift in bond stretching frequency by in the infrared region to identify the surface property and identify certain type of bonding. Thermogravimetric analysis (TGA), differential scanning calorimetric (DSC) and differential thermal analysis (DTA) is utilized to understand decomposition kinetics and estimate heat of reactions. The work is done by doctoral student Soubir Basak.
Recognizing the potential for using novel or non-model microbes for bioremediation or the production of alternative energy sources has fostered studies on the cellular metabolism of environmentally relevant microorganisms such as Geobacillus metallireducens, Shewanella oneidensis and Geobacter metallireducens.

To understand these microbial metabolisms, a high-throughput technology, metabolic flux analysis via $^{13}$C labeling, is applied to quantitatively track carbon flux through metabolic pathways.

Measurement of metabolic fluxes allows us to observe the functional output of the combined transcriptomic, proteomic and metabolomic changes and bridges contemporary analyses to the cellular phenotype. For example, when cells are exposed to certain environmental stresses or genetic manipulations, changes in gene expression and protein function are often observed. The ultimate outcome of such gene regulation encompasses activity alteration of various cellular enzymes in a network, which are in turn responsible for the overall changes in cellular metabolism and energy production. Such a response can be assessed using the $^{13}$C isotopic labeling approach (Figure 1). When a carbon substrate (e.g., glucose) is labeled with a certain pattern of non-radioactive $^{13}$C, the resultant labeling pattern of cellular metabolites, isotopomers, (e.g., amino acids) permits the accurate determination of the metabolic reaction rates (fluxes) through all related pathways. By knowing the isotopic patterns of only 10–20 key metabolites, it is possible to derive the flux distributions in the entire central metabolic network (comprising hundreds of enzymatic reactions) under the specific growth condition.

Two core techniques are used for metabolic flux analysis: 1) precise measurements of the labeling pattern of targeted metabolites (at concentrations as low as 10 nM) using high-resolution, highly sensitive mass spectrometers (such as GC-MS, LC-MS, or FT-ICR) and 2) interpretation of large data sets given by mass spectrometry spectra via an \textit{in silico} model of thousands of cellular enzymes. This technique has diverse applications: 1) Discover or validate gene functions involved in central metabolic pathways; 2) Provide information of the bottleneck pathways for biomass or metabolite synthesis in engineered microorganisms; 3) Identify pathogen-specific metabolic pathways for drug targets.

**Figure 1:** $^{13}$C metabolic flux analysis in cellular central metabolisms
PROJECT HIGHLIGHTS

BIOENERGY FROM ANIMAL AND FARM WASTES VIA ANAEROBIC DIGESTION TREATMENT

By Dr. Muthanna Al-Dahhan

The growth of livestock industry provides a valuable source of affordable, sustainable, and renewable bioenergy, while also requiring safe disposal of large quantities of animal wastes (manure) generated at dairy, swine, and poultry farms. For example, the U.S. produces 1.8 billion tons of cow manure annually (USDA 2002/2003). If these biomass resources are mishandled and underutilized, major environmental problems will be created, such as surface and ground water contamination, odors, dust, ammonia leaching, and methane emission. Methane emission notably results in a greenhouse gas effect that is considered 22 times worse than carbon dioxide (Sheffield, 2002). Anaerobic digestion of animal wastes, in which microorganisms break down organic materials in the absence of oxygen, is one of the most promising waste treatment technologies. This process produces biogas typically containing ~65% methane and ~35% carbon dioxide. The production of biogas through anaerobic digestion from animal wastes, landfills, and municipal waste water treatment plants represents a large source of renewable and sustainable bio-fuel. Such bio-fuel can be combusted directly, used in internal combustion engines, converted into methanol, or partially oxidized to produce synthesis gas that can be converted to clean liquid fuels and chemicals via Fischer-Tropsch synthesis.

Different design and mixing configurations of anaerobic digesters for treating cow manure have been utilized commercially and/or tested on a laboratory scale. Among the types of farm-based digesters actually built, the failure rates for mechanically mixed and plug flow technologies are staggering, 70% and 63%, respectively. For covered lagoon digesters, the failure rate is 22% (Lusk, 1998). Such high failure rates have been attributed to poor design, insufficient mixing, and in sufficient understanding of hydrodynamics. Mixing is an important parameter for successful performance of large scale anaerobic digesters. It enhances substrate contact with the microbial community, improves pH, temperature and substrate/microorganism uniformity, prevents stratification and scum accumulation, facilitates the removal of biogas from the digester, reduces or eliminates the formation of inactive zones (dead zones), prevents settling of biomass and inert solids, and aids in particle size reduction. Unfortunately, information and findings in the literature on the effect of mixing in anaerobic digestion are contradictory. All the published studies on cow manure anaerobic digestion have been performed using small laboratory scale digesters (~4 liter or less). No reported investigations have been conducted in pilot plant and/or commercial scale digesters. Therefore, design and variables on the performance of large digesters are unknown. One reason is the lack of measurement techniques for opaque systems such as digesters. Better understanding of the mixing and hydrodynamics of digesters will result in appropriate design, configuration selection, scale-up, and performance, which will ultimately enable avoiding digester failures.

As shown in Figure 1 below, the project systematically studied parameters affecting cow manure anaerobic digestion performance, in different configurations and sizes by developing and implementing advanced imaging techniques such as computational fluid dynamics (CFD), and a novel multiparticle computer automated radioactive particle tracking (MP-CARPT) and a novel dual source computed tomography (DSCT) techniques. It is hoped that the findings can be applied to promote bioenergy production and eliminate major environmental pollution problems.

The following investigations have been performed:
• Studies of anaerobic digesters performance and kinetics using various configurations, modes of mixing, and scales (laboratory, pilot plant, and commercial sizes) were conducted. It was found that mixing significantly affected the performance (~97 liter). It was also found that in a pilot plant digester, as the energy input (in terms of the gas recirculation rate) increased, the energy output also increased (in terms of the biogas production) up to an asymptote. Such finding is the only of its kind which has not yet been reported in open literature. This important finding indicates that a minimum power input that maximizes energy output can be determined for large scale digesters.
• A novel multi radioactive particle tracking technique has been developed which is capable of tracking the flow of two or more phases simultaneously.
• Development of a novel dual source computed tomography to image phase distribution in three phase systems.
• Investigation for the first time the flow held and phase distribution using these techniques.
• Development, evaluation and validation of the computational fluid dynamics (CFD) models and closures have been achieved to model and simulate the hydrodynamics and mixing intensity of the anaerobic digesters.
Energy issues are of paramount importance – and there is tremendous interest in all sectors of society (globally) to address this issue. One reason for this is because energy fuels the economy, and there is a strong correlation between GDP per capita of a nation to the energy consumed per capita! Clearly, the interest in energy issues is not new – one has to only look back 30 years or so in this country and note the mushrooming of activities due to the oil embargo. While interest in energy research waned in the early 80’s, attention to this arena is expected to be more “sustainable” this time around. There are several reasons for this – the first and foremost being the “energy-environment nexus”. The environmental attributes of the energy equation, primarily the impact on global climate issues is a very important factor. Issues that are also discussed include energy-security, the population growth, and eventual availability of fossil fuels.

A review of the projections of the energy consumption patterns and energy sources points out that Energy R&D is one of temporal dimensions. Clearly, fossil fuels will be used for at least the next 50 years; however we have to ensure that they are used in an environmentally benign manner. These include new modalities of fossil fuel combustion, novel ways of preventing release of toxic pollutants (such as mercury from coal combustion), and methods of carbon dioxide sequestration. The interim energy scenario is the increase use of carbon neutral fuels, hybrid transportation vehicles, and use of devices such as fuel cells. The long term temporal dimension is that our energy sources and generating methods must be completely environmentally benign, renewable and sustainable. One still expects a mixed bag of methodologies in the foreseeable future – and R&D efforts need to be vigorously initiated and continued. The socio-cultural dimensions will also be an important factor – with technological development accounting for such factors so that adaptation of new technologies is seamless. Issues of distributed energy production and the energy demands of the large population bases will be key considerations in the future.

The Aerosol and Air Quality Research Laboratory has initiated projects in all temporal dimensions outlined above. A brief description of current research work underway is provided:

1) Oxy-coal combustion and Emissions Reduction: A new modality of combustion is the oxy-fuel method wherein the oxygen and nitrogen are separated from air. As a result of this, the concentration of carbon dioxide in the exhaust increases from about 18% to more than 98% - allowing for more effective sequestration methods to be applied. Collaborative work on this project has been initiated with Prof. R. Axelbaum, and funded by a USDOE Project. Some additional details can be viewed in the two publications:


2) Coupling algal biofilm systems to coal combustion exhausts for carbon dioxide capture: Nano-biotechnology based systems are being developed for effective conversion of carbon dioxide to products of value – such as bio-diesel. Post doctoral fellow, Dr. Ying Li is leading these efforts in AAQRL.

3) Novel Nanostructured Systems for Solar Energy Applications: Solar energy has been touted as the “holy grail” in the Energy sector. A key requirement for these systems is the fabrication of systems using low cost and robust semiconducting materials. AAQRL Doctoral Student Elijah Thimsen has developed and patented a novel system of depositing such structures (see Figure) in a single step process. Finally, collaborations with Prof Blankenship’s group has allowed the integration of antenna complexes from microorganisms (see page 19 for details). For more details:


4) Other interesting projects include one with an international dimension: “Taking Nanotechnology to the Villages” [http://www.aerosols.wustl.edu/aaqrl/Projects/cookstoveproj.htm/] – a joint project with the Dr. Gautam Yadama of the School of Social Work. The initial project is focused on development of energy efficient stoves that have minimal, adverse public health impacts. Initial work is being done in India with the assistance of the Foundation for Ecological Security (http://www.fes.org.in/) The work in AAQRL is led by McDonnell Scholar and doctoral student, Manoranjan Sahu.

SEM and TEM image of nanostructured films of titanium dioxide deposited in a single step process for solar energy applications. The process could be scaled up to deposit similar films over large areas for use in photovoltaic devices. (work by Elijah Thimsen)
By Dr. Da-Ren Chen

Particle charging plays an important role in both scientific studies and practical applications related to aerosols, especially for those in the nanometer range (i.e., <100 nm). Charging of nanoparticles has been applied in a number of different areas, such as material synthesis, nano-structure patterning, contamination control, and particle instrumentation. A variety of aerosol charging methods have been proposed and studied for different applications.

To electrically charge high percentages of submicron particles, ion diffusion charging and photoionization are the most used methods. The former exposes sampled particles in an ion-rich environment and charges them by their collisions with ions. The latter ionizes particles using photons emitted from UV or soft X-ray light sources. Although photoionization achieves a higher charging efficiency than diffusion charging for particles smaller than 20 nm, it is often associated with the issues of diffusion discharging and material dependence, limiting its practical applications. Diffusion charging, on the contrary, is less dependent on the particle composition and more stable if a stable ion generation source is used.

In ion diffusion charging, particles can be exposed to either bipolar or unipolar ion environments. Bipolar chargers, with bipolar ions often produced by the ionization of gas molecules using the radioactive decay of an isotope, such as Kr85 or Po210, have been widely used in the characterization of particle size distribution. However, because of increasingly tight safety regulations on the use of radioactive material, alternatives for producing bipolar ions by corona discharge (dual corona jets or AC corona) or by soft X-rays have been explored. In bipolar chargers, charged particles may discharge themselves by capturing ions of the opposite polarity, while neutral particles can acquire electrical charges. Thus bipolar chargers are suited for applications requiring charged particles in only moderate concentration, or for neutralizing highly charged particles. Because both charging and discharging mechanisms are involved in bipolar chargers, their charging efficiency for nanoparticles is, however, quite low (typically below 1% at 3 nm). To improve the percentage of charged nanoparticles, it is better to electrically charge them by unipolar ions.

At the Particle Laboratory directed by Dr. Chen, a new corona-based, unipolar aerosol charger has been constructed, and its performance has been systematically evaluated. Figure 1 shows the image and schematic diagram of the prototype charger. The prototype consists of completely separated corona ionization and charging chambers. With this configuration the electrostatic loss of charged particles is eliminated, and particle loss by diffusion and the space charge effect is minimized by the angular injection of the ionizer flow and the rapid exit of charged particles. The charger performance was optimized by varying different operational parameters, i.e., total and ionizer flowrates, and ion concentration. It was found that operating the charger at a total flowrate of 5 lpm, with 1.0 lpm flow in each of the two ionizers, gave the highest extrinsic charging efficiency. Further, the performance of prototype charger was not compromised even at a total flowrate of 10 lpm. The charger provides higher extrinsic charging efficiency than other corona-based unipolar chargers existed.
INFLUENCE OF WATER CHEMISTRY ON LEAD CONCENTRATIONS IN DRINKING WATER DISTRIBUTION SYSTEMS

By Dr. Daniel Giammar

Lead release from pipes in distribution systems is a serious threat to public health. The recent observations of high lead levels in Washington D.C. tap water illustrate the current importance of this problem. Lead concentrations in drinking water are affected by chemical reactions that occur within the distribution system. Lead may be released directly from the pipe or from lead-containing corrosion products on the pipe surface. While several studies have evaluated the equilibrium solubility of lead corrosion products, there have been few studies of dissolution rates. Information on dissolution rates is particularly valuable as water suppliers consider process changes that affect water chemistry. Changes in water chemistry may lead to the dissolution of corrosion products or to the transformation of one corrosion product into another.

In my research group, the Aquatic Chemistry Laboratory, I am working with three graduate students to evaluate the impact of water chemistry on the dissolution rates of important lead corrosion products. The overall organization of the project is shown in Figure 1. We are studying three important solid phases that have been identified in scales on lead pipe: the lead carbonate hydrocerussite, the lead phosphate hydroxy-lpyromorphite, and the lead(IV) oxide scrutinyite. James Noel leads the efforts on hydrocerussite, Yanjiao Xie on scrutinyite, and Katherine Nelson-Nguyen on hydroxylpyromorphite. As a McDonnell Academy Scholar, Yanjiao Xie is also active in international collaborations and cross-departmental activities organized by the academy. In addition to her research, Ms. Nelson-Nguyen is teaching local public school students about water quality and water treatment as a National Science Foundation Graduate Fellow in K-12 Education. This research project is supported by the American Water Works Association Research Foundation.

Through our collaboration with the Massachusetts Water Resources Authority, we have identified several lead carbonate phases in the scales of pipes (several over 100 years old) removed from their distribution system. We have synthesized pure forms of the three solid phases of interest, and we are now quantifying their dissolution rates using custom-designed flow-through reactors. Our work is developing predictive models for lead release as a function of solid composition and important water quality parameters of pH, dissolved inorganic carbon (DIC), dissolved orthophosphate, and the presence of choramines as a disinfectant residual. The effect of DIC on the dissolution rate of hydrocerussite is illustrated in Figure 2. With increasing DIC, the thermodynamic driving force for dissolution decreases and consequently so does the dissolution rate.

With research support from the McDonnell Academy Global Energy and Environment Partnership (MAGEEP), we have initiated an exciting collaboration to incorporate real-time analysis of the solid phases as they react and heterogeneous reaction modeling into this project. Together with Professor Jill Pasteris’ (Earth and Planetary Sciences) we are applying an in situ Raman spectroscopic technique to probe the transformation of hydrocerussite to other solid phases in real time. We are then working with Professor A.K. Suresh (Indian Institute of Technology – Bombay in Chemical Engineering) to interpret our experimental data using heterogeneous reaction modeling. We will present the results of our collaboration in Hong Kong in December at the second McDonnell Academy Symposium on Energy and Environment.

The results of this project will benefit the water supply community as it manages lead concentrations in distribution systems. Knowledge of lead release rates as a function of water chemistry will be useful for evaluating potential effects of treatment process changes on water quality in the distribution system. This new knowledge can be used to evaluate alternative strategies for controlling lead concentrations (e.g., adjusting pH or adding an inhibitor) and to assess the impacts of other process changes (e.g., switching disinfectant) on dissolved lead concentrations.

![Figure 1: Organization of project focused on the dissolution and transformation rates of lead corrosion products.](image1)

![Figure 2: Hydrocerussite dissolution rate as a function of dissolved inorganic carbon (mg-C/L) at pH 7.5.](image2)
Environmental nanoparticles are often poorly-crystalline or metastable structures, whose kinetics of formation and growth are poorly understood. Further, the sorption or growth of nanoparticles on mineral surfaces may control the mineral surface’s reactivity and modify its ability to influence contaminant transport. Due to the characteristic length scale, a holistic understanding of the nucleation mechanisms and kinetics of nanoparticle formation on mineral surfaces is difficult to achieve with traditional methodology. While I have worked as a postdoctoral scholar at University of California, Berkeley and Lawrence Berkeley National Laboratory (2005-2007), the research goal is to determine the molecular nature of nucleation on surfaces, the kinetics of surface nucleation and growth, and the effect of crystal surface topology using new synchrotron-based techniques.

I have approached these objectives by: (1) combining state-of-art crystal-truncation rod diffraction (CTR) and grazing incidence x-ray absorption fine structure spectroscopy (GIXAS) techniques to investigate the three-dimensional molecular-scale geometry of silicate monomer sorption on the r-plane of hematite; and (2) developing a new grazing-incidence small angle x-ray scattering (GISAXS) setup at Stanford Synchrotron Radiation Laboratory and Argonne National Laboratory to explore the initial development of environmental nanoparticles on various mineral surfaces. This study also includes complementary techniques such as atomic force microscopy (AFM), bulk SAXS, dynamic light scattering (DLS), X-ray Diffraction (XRD), and transmission electron microscopy (TEM).

From both non-specular and specular CTR data and GIXAS, the silicate adsorption geometry on hematite surfaces can be obtained in three-dimensions. Our work indicated that the complexed silicate on the hematite (1-102) surface is linked by a single oxygen to surface Fe, i.e. a monodentate connection, with an interatomic Si-Fe distance close to those observed in the nontronite and acmite structures (which are natural Si-Fe containing minerals). This is the first evidence that identifies silicate as a well-defined sorption complex rather than only as an amorphous surface precipitate. These findings have important significance for the nature of passivation processes on Fe oxides and other important reactive natural surfaces.

In the other part of my study, the initial GISAXS work with iron oxide nanoparticles on quartz constitutes the first environmental application of GISAXS, and demonstrates our ability to detect low concentrations of sorbed 7.2 ± 0.6 nm diameter nanoparticles. The results agree with simulations of nanoparticle GISAXS on substrates, and is further confirmed via DLS, bulk SAXS, and AFM. Most recently, using in-situ GISAXS, we have been able to observe the nucleation and growth of iron oxide nanoparticles on quartz surfaces real-time. This is the first kinetic data to resolve the nucleation and growth of nanoparticles in situ in aqueous systems (with better statistics than any techniques and shorter data acquisition time). This technique can provide statistically improved morphological information of environmental nanoparticles compared with AFM and SEM, and allow real-time geochemical kinetics analysis of nanoparticle growth and reactions.

By using this arsenal of newly developed state-of-art techniques, our research group (Environmental NanoChemistry Laboratory at Washington University in St. Louis) aims to explore the environmental impacts of human activities through improved understanding of the fate and transport of contaminants and nanoparticles, and the biogeochemical cycling in complex environmental systems from nanoscale to macroscale, with a view to conserving sound environmental systems.

In addition, our group research involves a more comprehensive analysis of the risks associated with CO2 sequestration strategies related to climate changes and the development of new treatment techniques and new catalysts for purifying drinking water, remediating contaminated sites related to fresh and coastal water and soil, and developing new energy alternatives.

Figure 1. GISAXS setup allows us to observe the in situ real time early nuclei evolution (at nanoscale, a very short measurement time: seconds) of nanoparticles at mineral-water interfaces. D: particle distribution (spacing); h: height of nanoparticles; d: lateral size of nanoparticles; k: incident x-ray; k: scattered x-ray by newly formed nanophase.
There is a pressing and global need for abundant and affordable energy solutions that minimize harm to the environment. Solar power is a renewable and sustainable energy source that may be the only one capable of significantly mitigating global climate change. Currently, about 120,000 terawatts of power from the sun reaches the earth; as a point of reference, the amount of sunlight reaching the continental United States is more than 2,500 times the amount of the nation’s daily electricity consumption. Despite this potential, solar energy has been relatively untapped, making up only 0.066% of the U.S. energy portfolio. Thus, there is a growing interest in harvesting solar energy in an inexpensive manner.

Photovoltaic devices are used to convert light energy into electricity. These devices have traditionally been manufactured using doped silicon, which have high light-to-energy conversion efficiencies. Unfortunately, the prohibitive cost of crystalline silicon has to date hindered the widespread adoption of photovoltaic technology.

In an effort to find low-cost alternatives to silicon, we have turned to semiconducting oxide materials such as nanostructured titanium dioxide (TiO$_2$), which in its pristine state absorbs in the ultraviolet region of the solar spectrum. However, both transition-metal doping of the oxide and adsorption of photosensitive dye molecules onto the TiO$_2$ surface have been demonstrated to improve the visible-light performance of TiO$_2$.

We are working with Pratim Biswas and his group to simultaneously perform density functional theory calculations of the structural and electronic properties in both pristine and doped bulk TiO$_2$, and synthesize doped nanostructured thin films with controlled morphology and composition using a premixed methane-oxygen flame reactor, in order to predict the effect of transition metal dopants on the visible-light performance. Furthermore, we are both modeling the structural and electronic properties of, and synthesizing, layered oxide semiconductors that may be used for photovoltaic devices (figure 1).

We have also recently begun a new collaboration with Drs. Robert Blankenship of the Departments of Biology and Chemistry, and Pratim Biswas, EECE, to design improved high-efficiency solar photovoltaic devices. We will couple light-harvesting antenna complexes (chlorosomes) from the green photosynthetic bacteria Chloroflexus aurantiacus with photosensitive ruthenium-based dye-sensitized solar cells. Chlorosomes consist of multiple pigments that absorb light and transfer excitation energy to a photochemical reaction center (dye). The use of chlorosomes effectively increases the cross section for photon absorption, and hence, the density of light-harvesting molecules available for photon capture, making these solar cells well-suited for effective performance even under low-light conditions (figure 2).
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