FOSSIL ENERGY PROGRAM
ORNL ACTIVITIES
FY 2003 ACCOMPLISHMENTS

1. We completed several sets of experiments on leaching of fly ash, when in combination with soils and biosolids, to examine issues with the use of fly ash to promote carbon sequestration in soil. We have submitted two papers, describing the results.[1-2] The results indicate that the minimal amounts of potentially toxic heavy metals from fly ash are further reduced in leachates, when the fly ash is mixed with soil and biosolids. Also, leaching characteristics vary in a systematic manner with the class of the fly ash. Other factors (e.g., weathering in fly ash piles and mixing with flue gas desulfurization products) also influence leaching characteristics. Boron and other light elements are significantly reduced in fly ash leachates from fly ash that was exposed to rainfall while in outdoor storage at eastern sites.[3]

2. A thermodynamic model was successfully applied to the characterization data of water-soluble organics in brine. The origin of the organics was actual crude oil samples, and the measured distributions of organic concentrations were used as input for the thermodynamic model. The model was based on an activity coefficient description of two liquid phases, one aqueous and one hydrocarbon, with coefficients derived using a UNIFAC functional group analysis. The chemical system was described in terms of a series of equilibria, subject to constraints on mole fraction. The model included acid dissociation and the Debye-Huckel expression for ionic strength. The model was used to reproduce the trends in data with pH and temperature. The work has been submitted for publication in *Chemosphere*.[4]

3. Distribution coefficients have been measured for a variety of organic compounds that represent classes of water soluble organic contaminants in produced water. Partitioning into ionic liquids and the aqueous phase were derived from bulk liquid-liquid contacts, followed by analysis of the aqueous phase by gas chromatography and high performance liquid chromatography. The extractions of a long-chain alcohol and an aromatic compound were excellent; however, results were mixed for organic acids. Hexanoic acid was extracted in the protonated form, low pH, but extraction of other acids (acetic, lactic and succinic) was negligible. The results of the tests have been prepared as a poster for the Separations Science and Technology Conference in Gatlinburg, October 2003.[5]

4. A paper[6] on methane hydrate resource characterization addresses a new method for using measured P-wave and S-wave velocities to estimate gas hydrate concentration. The method uses the Hashin-Shtrikman (HS) lower bound to provide both an upper and lower bound for mixtures of water and hydrate in unconsolidated marine sediments. The method parameterizes the region between the upper and lower bounds by using two upper bounds: HS and Voigt. Well log measurements of resistivity and the Archie equation are used to calculate hydrate concentration and quadratic functions that relate the hydrate parameters to the hydrate concentration are estimated. For this data set, neither resistivity nor velocity provides a good method for detecting values of hydrate concentration that are less than 20 percent.[7]

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[1] Palumbo, A. V., L. S. Fisher, J. C. Tarver, W. Lee Daniels, J. E. Amonette, "Influence of fly ash sources on leaching of metals from fly ash and soil combinations." Submitted to *Fuel*.
[2] Palumbo, A. V., L. S. Fisher, J. C. Tarver, W. Lee Daniels, J. E. Amonette, "Metals in leachates of soil, biosolids, and fly ash." submitted to *Proceedings of International Ash Utilization Symposium*, Lexington, KY, October 20-22, 2003.
[3] FEAA049 - Enhancing Carbon Sequestration & Reclamation of Degraded Lands with Fossil Fuel Combustion Byproducts
[4] FEAC329 - Modeling of Water Soluble Organics in Produced Water
[5] FEAC332 - Use of Ionic Liquids in Produced Water Clean Up
[6] David B. Reister (2003). "Using measured velocity to estimate gas hydrates concentration," *Geophysics*, **68**, 884-891.
[7] FEAC320 - Remote Sensing for Environmental Baselining and Monitoring

5. We completed an Environmental Assessment that evaluated potential environmental impacts associated with constructing and operating an integrated emissions control system proposed by We Energies and its project partners with cost-shared funding support by DOE. The proposed TOXECON project would be demonstrated at the existing 90-MW Units 7, 8, and 9 of We Energies' coal-fired Presque Isle Power Plant in Marquette, Michigan. The commercial-scale demonstration would allow utilities to make decisions regarding the integrated emissions control system as a viable commercial option. DOE's share of the funding for the five-year demonstration project would be about $25 million, while $25 million would also be provided by We Energies and its project partners. This project was selected by DOE under the Clean Coal Power Initiative to demonstrate the integration of technologies to reduce emissions of mercury and particulate matter, as well as to potentially control SO_2, NO_x, and hydrochloric acid emissions.[8]
6. A patent disclosure "Tough, High-Strength Dual Phase Cr-rich alloys" was submitted. This disclosure covers the invention of a new family of castable, Laves-phase strengthened Cr-rich matrix alloys with room-temperature fracture toughness in the range of 20 MPa-m$^{1/2}$ and tensile strength in the range of 250-400 MPa at 1000°C. The alloys also exhibit good high-temperature oxidation resistance in air and are resistant to the rapid Cr-nitride subscale formation that limits the use of most Cr-rich alloys in high-temperature environments containing nitrogen (e.g., air). It is anticipated that these alloys will offer an attractive alternative to ceramics in high-end specialty component applications, in aggressive environments such as thermowells, brackets, dies, and valves. This invention disclosure is the culmination of the intermetallic-reinforced Cr effort, which ended in FY 2003.[9]
7. We developed an understanding of the colloidal chemistry associated with barium cerate, as part of the process to deposit thin colloidal films of this material on porous metallic supports.[10]
8. We consistently produced thick, columnar YSZ coatings uniformly on nickel superalloy substrates via organometallic chemical vapor deposition and determined the kinetic constants for the deposition rate.[11]
9. The effects of processing conditions and crystallographic orientation of growing dendrites on stray grain formation was investigated using Rene N5 single crystal alloy welds. The extent of constitutional supercooling ahead of the growing dendrite was calculated and related to the vulnerability to stray grain formation during single crystal weld solidification. Calculations agreed well with the experimental results.[12]
10. MFIX[13] is being validated using two, table-top experiments (a 2D bed at the University of Tennessee and a very shallow patterned bed from Argonne National Laboratory) and a 9m-tall circulating fluidized bed. The results of these validation efforts were presented at an invited lecture at the GLUE workshop organized by Argonne National Laboratory, and at an ACM symposium on applied computing.[14]

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[8] FEAZ277 - Clean Coal Program Environmental Support
[9] ORNL-2(D) - Multi-Phase High-Temperature Alloys & ORNL-4(A) - Controlled Oxidation for Functional and Protective Surfaces
[10] ORNL-3(H) - Economical Fabrication of Membrane Materials
[11] ORNL-1(A) - Chemically Vapor Deposited YSZ for Thermal and Environmental Barrier Coatings
[12] FEAA064 - Welding and Weld Repair of Single Crystal Gas Turbine Alloys
[13] Multiphase Flow with Interphase eXchanges computer program
[14] FEAA046 - Computational Fluid Dynamics for Multiphase Flow

11. Dynamic Interacting Bubble Simulation (DIBS) has been used to simulate ozone conversion in fluidized beds. The time-averaged performance matches the experiments very well and the short- and long-term dynamics predicted by the model are very interesting. The results have been published in the *International Journal of Chemical Reactor Engineering*.[15]

12. An infrared convection oven was custom-designed and built to enable rigorous experimental investigations of coal/gas interactions at temperatures and pressures equal to those measured in subsurface coal beds into which CO_2 has been, or will be, injected.[16]

13. The design, construction, and testing of a stationary-autoclave densimeter system was completed this year. scoping experiments were performed to verify that the apparatus yields reference-quality density data for mixed CO_2-CH_4 gases at 25-50ºC and pressures from 0-2000 psi.[15]

14. Two articles[17,18] were published which represent important parts of a thermodynamic review of the hydrosulfurization of heavy petroleum. The reports highlight the possibility of the standard hydrosulfurization methodology failing as sulfur levels approach the single-digit ppm levels. The papers will aid refiners in the determination of the various options available to produce fuels at reasonable costs. The conclusions outline the need for a combination of technologies to produce "zero sulfur" fuels.[19]

15. A potential new coating material, calcium aluminate, was developed for protection of silicon based ceramics in high temperature, fossil environments.[20]

16. As part of the effort to optimize the compositions of iron-based alumina-forming coatings, the effect of the use of two or more reactive elements (REs) to optimize oxidation performance of alloys is being evaluated. When done correctly, such co-doping was found to improve scale adhesion and slow scale growth rates compared to similar alloy compositions with single RE additions. The addition of two or more REs did not appear to result in any significant change in the alumina scale microstructure or the amount of ionic segregation on its grain boundaries. Dopant optimization resulted in a >30% increase in the time to failure in 1h cycles at 1200°C of co-doped FeCrAl compared to FeCrAl+Y. The increased performance with reduced doping levels suggests that RE dopants are effective when located on the scale grain boundaries as ions, but when they form RE-rich oxides beneath or within the alumina scale they diminish the beneficial RE effect.[21]

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[15] FEAA313 - Real-Time Bubble Simulations for Fluidized Beds
[16] FEAA062 - Effects of Temperature and Gas Mixing on Formation Pressure, CO_2 Sequestration, and Methane Production in Underground Coal Beds
[17] R. D. Chirico, S. E. Knipmeyer, and W. V. Steele, "Heat capacities, enthalpy increments, and derived thermodynamic functions for pyrazine between the temperatures 5 K and 380 K," *The Journal of Chemical Thermodynamics* **35** (7), (2003), 1059-1072.
[18] "Possible precursors and products of deep hydrodesulfurization of gasoline and distillate fuels. Part 2. The thermodynamic properties of 2,3-dihydrobenzo[b]thiophene," *The Journal of Chemical Thermodynamics* **35** (8), (2003), 1253-1276.
[19] FEAC327 - Fundamental Chemistry for Process Development of Heavy Oil
[20] ORNL-1(B) - Corrosion-Resistant Ceramic Coatings
[21] ORNL-2(B) - Extended-Lifetime Metallic Alloys and Coatings for High-Temperature Environmental Protection

17. Corrosion testing of aluminide coatings on both ferritic (Fe-9Cr-1Mo) and austenitic (type 304L) substrates is being conducted in order to clearly define performance limitations. One area of particular concern has been the thermal expansion mismatch between Fe_3Al and the substrates. Previous testing for 2000, 1h cycles at 700°C in air with 10 vol.% water vapor had shown severe degradation of the coatings on both substrates. This degradation was attributed to the mismatch strain developed during each heating and cooling cycle. Similar coatings tested in the same environment with a 100h cycle time have reached 4,000h of total test time and show low mass gains and no evidence of degradation. Without a coating, this environment severely attacked these substrates after only a few hundred hours. By reducing the number of thermal cycles, this result supports the hypothesis that thermal cycling is detrimental to aluminide coatings in this temperature range. As power generation applications are more likely to use a long cycle time, aluminide coatings are appropriate to protect structural components in steam or exhaust environments.[22]

18. Long-term annealing tests of model aluminide coatings on ferritic and austenitic substrates have been completed and the results are being used to model the performance of coatings as a function of coating thickness, starting Al content and exposure testing. For the coating compositions commonly fabricated, the model predicts that coating lifetime above 700°C will be significantly reduced by back diffusion of Al into the substrate.[21] [In collaboration with Ying Zhang at Tennessee Tech[23]]

19. Results of initial experiments using At. ferrooxidans in contact with the different types of coal in small microcosms show that mercury is bioleached from the coal to the liquid and that the release is not dependent on the initial concentration of mercury in the coal.[24]

20. In the work to build an EMAT[25]-based Pipe Inspection Gauge for a 30-inch-diameter natural gas pipeline, the EMAT sensors are producing good signals. The instrument will be field-tested in the next few months. Wavelet-based algorithms have been developed to identify different flaw types. The algorithms will be refined based on the field-test data.[26]

21. The objective to develop thermostable oxidase enzyme, capable of transforming PAH compounds, as achieved with the development of a hybrid cytochrome P450 enzyme with melting temperature of approximately 75°C.[27]

22. We completed[28] a conceptual design for scale up of biogeochemical mineralization and sequestration of carbonates and metal species in fly ash wastes. We observed biogeochemical selenium precipitation as an advance in the art of mineral precipitation processes in fly ash ponds.[29]

23. We performed experiments with the flow-through column system and reported[30] those findings along with a description of the system.[31]

24. We developed a bench-scale process for testing ammonia removal that enables quantification of ammonia precipitated fly ash ponds.[32]

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[22] ORNL-2(B) - Extended-Lifetime Metallic Alloys and Coatings for High-Temperature Environmental Protection
[23] TTU-2 - Aluminide Coatings for Power-Generation Applications
[24] FEAA288 - Coal Biomodification to Reduce Mercury Emissions
[25] Electromagnetic acoustic transducer
[26] FEAB209 - A New Inspection Tool for Pipeline Flaw & Leak Detection
[27] FEAC326 - Bioupgrading of Heavy Crudes Using Temperature and Oil Tolerant Enzyme Catalysts
[28] Y. Roh, R. J. Lauf ,T. J. Phelps, "Biogeochemical Processes Utilizing Fly Ash for Carbon Sequestration," *Proceedings of the 2nd National Carbon Sequestration Conference*, 2003.
[29] FEAA036 - Biomineralization for Carbon Sequestration
[30] S. L. Fisher, D. Cole, J. Blencoe, G. R. Moline, J. Parker, T. J. Phelps, "High Pressure Flow-Through Column for Assessing Subsurface Carbon Sequestration," *Proceedings of the 2nd National Carbon Sequestration Conference*, 2003.
[31] FEAA045 - Geologic Sequestration of Carbon Dioxide
[32] FEAA065 - Biogeochemical Remediation of Ammonia Discharges From Power Plants

25. We successfully obtained Mallik and ODP[33] Leg 204 methane hydrate bearing sediments and initiated experimentation. We updated a patent disclosure on methods to enhance hydrate nucleation processes. We completed measurements assessing biogeochemical methanogenic properties of the Leg 204 sediments and those from Mallik.[34]

26. We completed report and draft manuscript on Net Environmental Benefit Analysis, a new assessment methodology for remediation or restoration of contaminated sites.[35]

27. We modeled badger population dynamics exposed to hypothetical brine scars at the Tallgrass Prairie Preserve in Oklahoma and began development of an ecological framework for petroleum exploration and production sites with collaborators at Lawrence Livermore National Laboratory.[36]

28. It has been demonstrated that the novel activated carbon composite removes CO_2 from gaseous mixtures of varying compositions and concentrations. In this regard, an eighteen-month investigation entitled "Modification/Development of Carbon Fiber Composite Molecular Sieve for Removal of CO_2 from a Synthesis Gas-fueled Turbine Exhaust Stream" was completed. Modified CFCMS[37] materials have been produced. These are being investigated for the separation of N_2/O_2 mixtures.[38]

29. Structural Mo-Si-B alloys contain typically 30-50 vol.% of Mo solid solution to provide adequate toughening. However, the Mo phase degrades the oxidation resistance. Mo-12Si-8.5 (at. %), which contains about 38 vol.% Mo solid solution, was $MoSi_2$-coated with a pack cementation process using Si and NH_4Cl. Its oxidation resistance was assessed by six one-day anneals at 1300°C in air. Whereas the weight loss of the uncoated material was 300 mg/cm^2, that of the coated material was only 2 mg/cm^2.[39]

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[33] Ocean Drilling Program
[34] FEAB111 - Hydrate Formation and Dissociation in Field Samples
[35] FEAC319 - Improving Tools and Methods for Ecological Risk Assessment at Petroleum-Contaminated Sites
[36] FEAB321 - Developing an Ecological Framework to Evaluate Impacts of Releases at Upstream Exploration and Production Sites: The Effect of Size and Distribution
[37] Carbon Fiber Composite Molecular Sieve
[38] ORNL-3(E) -Development of Novel Activated Carbon Composites
[39] ORNL-2(I) - Mo-Si Alloy Development