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FY 1986 Annual Report

ENERGY CONVERSION AND STORAGE PROGRAM

March 1987

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-22151

APPLIED SCIENCE DIVISION ANNUAL REPORT

ENERGY CONVERSION AND STORAGE PROGRAM

FY 1986

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

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ENERGY CONVERSION AND STORAGE

INTRODUCTION

The Energy Conversion and Storage Program has four main projects applying chemistry and chemical engineering to problems in the production of new fuels, their environmental impact, and energy storage and conversion. These projects are:

(1) Electrochemical energy storage and conversion
(2) Thermal energy storage and conversion
(3) Coal-related research
(4) Energy-related chemistry

Each of these projects focuses on transport-process principles, chemical kinetics, thermodynamics, separation processes, and organic and physical chemistry.

The electrochemical energy storage and conversion project provides research to develop advanced battery systems for electric vehicle and stationary energy storage applications. Topics include identification of new electrochemical couples for advanced batteries, improvements in battery components and materials, establishment of engineering principles applicable to electrochemical energy storage and conversion, and the development of metal/air cells and fuel cells for transportation. Major emphasis is on applied research that will lead to superior performance and lower life-cycle costs.

The second project is a series of research and development efforts in thermal energy storage and conversion. This project focuses on new and innovative approaches to the more efficient utilization of thermal and solar energy.

The third project involves the development of improved, energy-efficient methods for processing waste streams from synfuel plants and coal gasifiers. Also included in this project is an effort to develop an advanced model of moving-bed coal gasifiers in order to better understand their operation and improve their design.

The last project involves topics such as the use of heterogeneous metal catalysts to remove nitrogen from petroleum feedstocks, the synthesis and characterization of complex organometallic compounds, the study of cleavage reactions of compounds that have carbon-oxygen bonds in order to model the complex linkages in coal, the isolation and molecular characterization of trace heavy metal compounds in fossil materials, and the development of innovative methods to remove these trace metal compounds. In addition, an extensive data base for energy-related organic compounds is being developed, and ultra-sensitive spectroscopic techniques are being applied to detect trace amounts of materials. The conversion of biomass to liquid fuels has been an area of considerable research and development within the Chemical Process Program over the past several years. The biological conversion of wood and agricultural residues to ethanol has been examined. An enzymatic hydrolysis of these cellulosic materials has been developed to yield monomeric hexose and pentose sugars. These can be subsequently fermented to produce ethanol. Various high-rate fermentation processes have been developed, and novel processes for ethanol (and other polar organic compounds) recovery that are less energy intensive than conventional processes are being studied.

Technology Base Research Project for Electrochemical Energy Storage*

E.J. Cairns, K. Kinoshita, and F.R. McLarnon

The Lawrence Berkeley Laboratory (LBL) is lead center for management of the Technology Base Research (TBR) Project, which is supported by the Electrochemical Branch of DOE's Office of Energy Storage and Distribution. The purpose of this project is to provide the research base to support DOE efforts to develop electrochemical energy conversion systems for electric vehicle and stationary energy storage applications. The specific goal is to identify the most promising electrochemical technologies and transfer them to industry and/or another DOE program for further development and scale-up.

The general research areas addressed by the TBR Project include identification of new electrochemical couples for advanced batteries, determination of technical feasibility of the new couples, improvements in battery components and materials, establishment of engineering principles applicable to electrochemical energy storage and conversion, and the investigation of fuel cell and metal/air systems for transportation applications. Major emphasis of the project is given to applied research that will lead to superior performance and lower life-cycle costs.

The LBL scientists who participate in the program are E.J. Cairns, K. Kinoshita and F.R. McLarnon of the Applied Science Division, and L.C. DeJonghe, J.W. Evans, R.H. Muller, J.S. Newman, P.N. Ross and C.W. Tobias of the Materials and Molecular Research Division.

ACCOMPLISHMENTS DURING FY 1986

LBL conducted a vigorous in-house research program and monitored 30 subcontracts during FY 1986. A description of the research projects conducted by the subcontractors can be found in the recent annual report, *Technology Base Research Project for Electrochemical Energy Storage* (LBL-21342), and the in-house work, "Electrochemical Energy Storage," is summarized in the next article and in the *Materials and Molecular Research Division 1986 Annual Report* (LBL-22010). Highlights of the subcontracted work follow:

Exploratory Research

- Argonne National Laboratory (ANL) has achieved over 400 cycles (5000 h) at 397°C with a small prismatic $LiAl/FeS_2$ cell (25 Ah) containing a dense upper-plateau FeS_2 electrode, a Li-Al electrode, and LiCl-LiBr-KBr electrolyte (m.p. 310°C). The measurements indicate that the cell performance (coulombic efficiency >99%, utilization 89%) remains nearly constant throughout the cycle test (discharge at 50 mA/cm^2 for 4 h, charge at 25 mA/cm^2 to a cut-off voltage of 2.05 V). Based on the stable cycle life demonstrated in this cell test, at least 1000 cycles with ≤20% capacity loss should be achievable.
- Experimental measurements at the University of Pennsylvania demonstrated that the cationic transport numbers of various PEO [poly(ethylene oxide)] complexes of divalent cation salts are strongly influenced by the thermal and hydration history of the complexes. The ionic conductivity of Zn halide complexes is controlled by varying the relative fraction of crystalline and amorphous phases. At higher temperatures, crystalline components melt and dissolve in excess PEO to form mostly amorphous polymer with high conductivity. At lower temperatures, the formation of crystalline complexes is favored, and the conductivity is relatively low.
- The University of Minnesota and EIC Laboratories, Inc., were selected to investigate rechargeable lithium cells on the basis of proposals received in response to a RFP (Request for Proposals) issued by LBL. The emphasis of the research at the University of Minnesota is to investigate mechanisms occurring at the electrode/electrolyte interface of novel electrochemical cells containing thin film polymer electrolytes. The objective of the EIC program is to improve the performance and cycle life of rechargeable lithium systems containing organic electrolyte and metal-oxide cathodes.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Applied Science Research

- ANL has identified a glass composition (42 mol% Na_2O - 8 mol% Al_2O_3 - 5 mol% ZrO_2 - 45 mol% SiO_2) that has high ionic conductivity (7.1×10^{-3} ohm^{-1}-cm^{-1} at 300°C) and chemical stability (at 400°C in Na, Na_2S_3, Na_2S_4, and S) on a par with other candidate solid electrolytes, i.e., β''-alumina ceramic and Dow sodium borate glass, for use in high-temperature Na/S cells. Small-scale cells (1-3 mAh capacity) with this electrolyte were cycled at 3-6 mA/cm^2 (C/4 discharge and C/8 charge rate) for 36-40 cycles (10-20% depth-of-discharge) before the containment seals failed.
- Massachusetts Institute of Technology has observed that Ca-containing lithium borate glasses remain highly conductive, in sharp contrast to the known depressing effect of Ca additions on alkali-ion transport in alkali silicate glasses. This finding has technological importance since CaO additions are believed to improve the durability of glasses in contact with Li metal or its alloys.
- Brookhaven National Laboratory (BNL) has initiated EXAFS (Extended X-ray Absorption Fine Structure) studies of zinc bromide electrolytes. Analysis of zinc bromide electrolytes with a large excess of bromide ions (either as HBr or $AlBr_3$) revealed that the zinc ion is tetrahedrally coordinated with bromine, and the Zn-Br distance is 2.4 Å. In these electrolytes, bromide ions are also coordinated with water, and the Br-O distance is ~3.4 Å.
- Lawrence Livermore National Laboratory (LLNL) has completed isopiestic measurements of the $ZnCl_2$-H_2O system at 0.3 to 13 mol/kg (25°C). Related measurements on the $ZnBr_2$-H_2O system are underway.
- Spectroscopic studies (thermal desorption, low-energy electron diffraction, work function, Raman) are underway at Case Western Reserve University (CWRU) and Jackson State University to characterize the surface of reactive alkali and alkaline earth metals in organic electrolytes. Although these studies are still in their preliminary stages, the results indicate that propylene carbonate (PC) can undergo decomposition at close to room temperature, which is the first indication that PC can degrade at such low temperatures.

Air Systems Research

- Analytical measurements by CWRU indicate that heat treatment of transition metal organic macrocycles (phthalocyanines, tetramethoxyphenylporphyrin - TMPP) supported on carbon results in the decomposition of the macrocycle, but the pyrrole nitrogen is retained. The key catalytic role in oxygen reduction is played by the transition metal (e.g., iron, cobalt), which is bound to the carbon surface through coordination with nitrogen of the heat-treated macrocycle. These catalysts have been used in air cathodes to reduce oxygen at very high current densities (>500 mA/cm^2).
- Experiments at Pinnacle Research Institute indicate that additives show promise for enhancing the discharge performance of zinc/air cells with flowing electrolyte. The zinc discharge capacity (at 200 mA/cm^2) of a zinc/air cell using 300 g/l zinc in 12 N KOH at 55°C increased from 87.2 Ah/l to 153.8 Ah/l by the addition of 25 g/l silicate. These results are encouraging for the development of rechargeable zinc electrodes that offer high specific energy for zinc/air cells.
- Experiments at ELTECH Systems, Inc., Electromedia and CWRU have identified Norit (Ultracarbon) containing 5 to 10% CoTMPP as a promising air cathode material that exhibits long life (over 3000 cycles for a simulated drive cycle used to test electrode life). The performance of these air electrodes in KOH electrolyte is approximately 240 mV higher (at 600 mA/cm^2) than the corresponding performance in NaOH electrolyte.
- The development of aluminum/air batteries for electric vehicles has reached the stage that a review committee has recommended transfer of management responsibility of the program from LLNL to Sandia National Laboratories (SNL). As a result of this recommendation, SNL will assume management responsibility for the engineering development of the Al/air battery and its ancillary components, and LBL will retain management responsibility for research on electrodes.
- Los Alamos National Laboratory (LANL) has demonstrated that the Pt loading in proton-exchange membrane (PEM) fuel cells can be dramatically reduced by pretreating commercial

Prototech electrodes with solubilized Nafion. A factor of five improvement in oxygen reduction current density at 0.4 V was obtained with a Pt electrode (0.35 mg/cm^2) that was pretreated with Nafion. This finding suggests that the prospects for decreasing the Pt loading of PEM fuel cells are encouraging.

PROGRAM CHANGES IN 1986

Funding support for the following projects was initiated in 1986:

- Exploratory Cell Research and Fundamental Processes Study in Solid State Electrochemical Cells – University of Minnesota
- Ambient Temperature Secondary Lithium Batteries Using LiAl or Lithium Insertion Anodes – EIC Laboratories, Inc.
- *In Situ* Raman Spectroscopy of Lithium Electrode Surface in Ambient Temperature Lithium Secondary Battery – Jackson State University
- Corrosion, Passivity and Breakdown of Alloys Used in High Energy Density Batteries – Johns Hopkins University

The following work was completed in 1986:

- All-Inorganic Ambient Temperature Lithium Battery – Duracell International Inc.
- Spectroscopic Studies of Zincate Solutions – Argonne National Laboratory
- Battery Separator Research – Sandia National Laboratory
- Improved Al_2O_3 Electrolyte Through Transformation Toughening – Rockwell International
- Polysulfide Containment Materials – Argonne National Laboratory
- Microcrystalline (Amorphous) Metal/ Alloy Coatings Resistant to Molten Sulfur/Polysulfide Environments – Argonne National Laboratory

PLANNED ACTIVITIES FOR FY 1987

New initiatives include the following:

- Molten-salt battery R&D.
- Electrochemical research on aluminum anodes for Al/air cells.

Battery Electrode Studies*†

E.J. Cairns, F.R. McLarnon, T.C. Adler, M.J. Isaacson, P.M. Lessner, K.G. Miller, S.A. Naftel, K.A. Striebel, and J. Winnick‡

The purpose of this research is to study the behavior of electrodes used in secondary batteries and fuel cells, and to investigate practical means for improving their performance and lifetime. Systems of current interest include ambient-temperature rechargeable cells with Zn electrodes (Zn/air, Zn/NiOOH, Zn/AgO, Zn/Cl_2, Zn/Br_2, and Zn/$Fe(CN)_6^{-3}$); rechargeable high-temperature cells (Li/S, Li-Al/FeS_2, Li-Si/FeS_2, and Na/S); fuel cells; and liquid-junction photovoltaic cells. The approach used in this investigation is to study life- and performance-limiting phenomena under realistic cell operating conditions.

ACCOMPLISHMENTS DURING FY 1986

ALKALINE ZINC ELECTRODES

Rechargeable alkaline Zn/air and Zn/NiOOH cells can be designed to deliver high specific energy and specific power, but they typically exhibit short lifetimes. The high solubility of Zn species in alkaline electrolytes tends to enhance the various physiochemical processes (active material redistribution, filamentary Zn growths, etc.) which degrade the cell's capacity and limit its life. Modeling and experimental investigations are aimed at understanding the complex transport processes in operating Zn electrodes, and characterizing various methods to reduce Zn species solubility and extend the lifetime of the Zn electrode.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

†This project is part of a larger effort, "Electrochemical Energy Storage," described in the Materials and Molecular Research Division 1986 Annual Report (LBL-22010).

‡Department of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA.

Measurement of Concentrations in Porous Zinc Electrodes Using Micro-Electrodes

(M.J. Isaacson, E.J. Cairns, and F.R. McLarnon)

Micro-electrodes are being used to investigate chemical and transport processes that occur in secondary porous Zn electrodes. The potentials of Zn and Cd micro-electrodes are monitored as the porous electrode is charged and discharged. The micro-electrodes respond to changes in the ionic activities of the electrolyte, and ionic molalities are calculated from the micro-electrode potentials using activity coefficients derived from previously measured rest potentials.[1]

Data have been obtained in 17 wt% and 30 wt% KOH electrolyte. Examples of Zn micro-electrode data obtained in 30 wt% KOH electrolyte are shown in Fig. 1. Preliminary analyses of the results indicate that:

(1) Micro-electrodes near the edge of the electrode tend to be more negative during charge and more positive during discharge than those closer to the center of the electrode. This is consistent with a higher current density near the electrode edge.

(2) In 17 wt% KOH the micro-electrode potentials drift in the positive direction during the initial stages of discharge due to depletion of OH^- and supersaturation of $Zn(OH)_4^{2-}$. About 75% through the discharge the potentials rapidly change polarity, which may be due to precipitation of ZnO or $Zn(OH)_2$ from a supersaturated zincate solution (which releases OH^- ions).

(3) In 30 wt% KOH the rapid drop in potential is observed less often, and it is never so dramatic as that in the less-concentrated electrolyte. This may indicate that the higher KOH concentration stablizes the supersaturated zincate solution.

(4) After charging and discharging the Zn electrode, the micro-electrode potentials tend toward values positive of their original rest potentials. This is probably due to supersaturation of the zincate ions. The stability of supersaturated zincate ions has been noted by Dirkse,[2] and supersaturated solutions in Zn porous electrodes have been reported by Hamby *et al.*[3]

Hydroxide and $Zn(OH)_4^{2-}$ molalities are shown in Fig 2. For this particular cycle and location, the molalities show the following features:

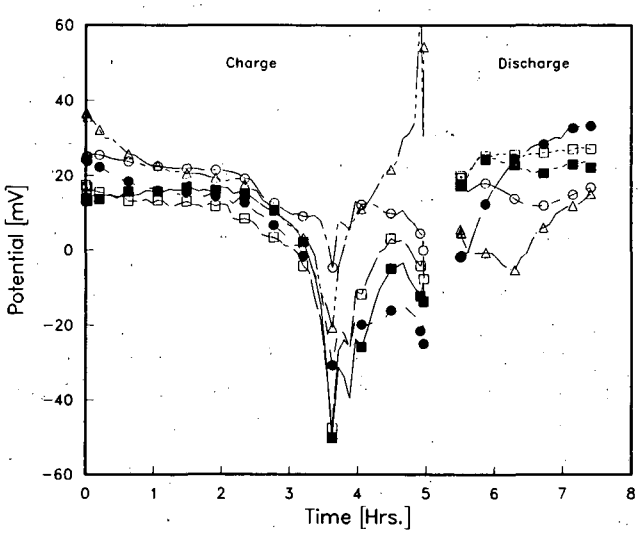

Figure 1. Zn micro-electrode potentials during the charge and discharge of a Zn porous electrode in 30 wt% KOH at cycle no. 52. Charge current is 0.1248 A, and discharge current is 0.312 A. Symbols indicate the distance of the micro-electrode from the edge of the porous electrode as follows (a negative value indicates that the probe electrode is in the electrolyte space between the cell wall and the edge of the porous electrode): ■, -.75 mm; □, +.5 mm; •, +2.5 mm; ○, +6.5 mm; Δ, +35.0 mm. (XBL 871-89)

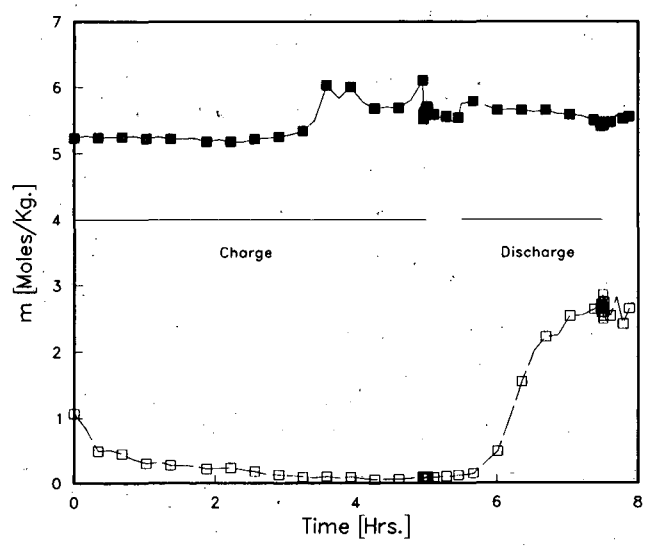

Figure 2. Molalities of OH^- and $Zn(OH)_4^{2-}$ during the charge and discharge of a porous Zn electrode in 30 wt% KOH. The cycle number and currents are the same as those in Fig. 1. Cd and Zn electrodes are +4.0 mm from the edge of the electrode. The solid horizontal lines indicate the time during which the electrode is being charged and discharged. ■, OH^- molality; □, $Zn(OH)_4^{2-}$ molality. (XBL 871-90)

(1) During charge the $Zn(OH)_4^{2-}$ molality decreases quickly.
(2) The OH^- molality is nearly constant during the first three hours of charge, but it increases during the last three hours of the charge.
(3) After the discharge begins, the $Zn(OH)_4^{2-}$ molality increases to a value that is two to three times the saturation concentration.
(4) The OH^- molality decreases only slightly during discharge.

Data similar to those shown in Figs. 1 and 2 are currently being analyzed in an effort to help elucidate the behavior of porous Zn electrodes. Also, additional experiments are being planned that will help separate chemical effects from mass transport effects.

Mathematical Modeling of the Zinc Electrode

(K.G. Miller, E.J. Cairns, and F.R. McLarnon)

A one-dimensional, time-dependent mathematical model of the Zn electrode has been formulated.[4] The model is designed to elucidate the cause of active material redistribution in the Zn electrode, and it takes into account transport of electrolyte species, heterogeneous reactions, kinetics, and current density variations. Computer implementation of the model is underway.

Cycle-life testing of a model Zn/NiOOH cell was carried out, using three different electrolytes investigated earlier in this laboratory.[5] The results can be summarized as follows (electrolyte compositions in wt %):

i) 15% KOH-15% KF electrolyte- This cell maintained more than 90% of its original capacity for 150 cycles. When the cell was disassembled, minor Zn redistribution away from the edges toward the center was visible, but there was material covering most of the electrode area.
ii) 31% KOH electrolyte- This cell reached 98 cycles, and it steadily lost capacity during its lifetime. When the cell was disassembled, the Zn electrode showed extensive redistribution of Zn from its center toward the edges.
iii) 15% KOH electrolyte- This cell reached only 38 cycles, and its Zn electrode exhibited unusual behavior. The Zn electrode showed a high overpotential during charge, and on discharge, the Zn electrode limited the capacity of the cell. When the cell was disassembled, the Zn electrode showed minor shape change (from the edges inward). However, on both the NiOOH electrode wicks and the separator, there were white (probably KOH) and metallic precipitates.

Cycle-life testing of cells using the same electrolytes, but using Zn electrodes with more-conductive current collectors (to obtain a more uniform current distribution) is underway.

Studies of the electrochemical kinetics of Zn dissolution and deposition have continued.[4] Problems arose using 1-mm Zn disc electrodes due to the low currents involved, so larger electrodes were used. Experiments using 5-25 ms pulses were carried out, and the potential step results now indicate exchange current densities of 0.75-1.0 mA/cm^2.

Open-circuit potentials of the NiOOH electrode were measured as a function of state of charge. Four discharge potential-capacity plots were obtained, all showing a similar shape. A multiple-point least squares method will be used to fit the data for use in the model.

Investigations of Methods to Improve Zinc/Nickel Oxide Cell Lifetime

(T.C. Adler, F.R. McLarnon, and E.J. Cairns)

Three factors under investigation for improving Zn/NiOOH cell cycle-life performance are: 1) electrolyte composition,[5] 2) electrode composition,[6] and 3) charging method.[7] Reductions of the rate of Zn material redistribution have been achieved by using an electrolyte composition of 15 wt% KOH- 15 wt% KF, an electrode composition in which 25 mol% $Ca(OH)_2$ is substituted for an equivalent amount of ZnO, and by using a 30-ms on/90-ms off pulse-charging regimen. For example, a 25-mol% $Ca(OH)_2$ electrode with (standard) 31 wt% KOH- electrolyte retained 90% of its original capacity after 150 deep-discharge cycles. High overpotentials associated with dendritic shorting were absent for the cell and X-ray examination of the Zn electrode showed a uniform covering of calcium zincate compound intact after 150 cycles.

A 15 wt% KOH-15 wt% KF electrolyte was used with electrodes containing 25-40 mol% $Ca(OH)_2$. Three types of charging methods were successfully employed with these cells: constant-current, constant current-voltage limited, pulsed current-voltage limited. The last two methods are preferred because they avoid high overpotentials during charge. A cell employing KF-KOH electrolyte, a Zn-Ca electrode, and a specific pulse-charging regimen (30-ms on/90-ms off, 8 mA/cm^2 peak current density) with a 1.95 V cell cutoff voltage has achieved 465 deep-discharge

cycles and still maintained 80% of its original capacity. *In situ* X-ray examinations revealed a negative electrode with a slowly-changing mottled appearance against a uniform background attributed to calcium zincate compound. The NiOOH electrodes for this cell dropped to 80% of their original capacity by cycle 435 and were replaced. Other tests demonstrated that up to 20% of the Zn transfers from the negative electrode to the NiOOH electrode early in cell life. This phenomenon may contribute to the decline of the NiOOH electrode capacity in long-lived cells.

A factorial experimental design has been developed to further investigate interactive effects among the three factors under study.

HIGH-TEMPERATURE CELLS

The high-temperature Na/S cell offers very good performance, and recent improvements to the process for manufacturing the ceramic β''-Al_2O_3 electrolytes indicate that acceptable cell lifetimes may be realized. However, the performance of the sulfur electrode has not been optimized, and the phenomena which govern its operation are poorly understood. On-going work is aimed at developing and confirming an advanced mathematical model of the sulfur electrode. Previous efforts[8-11] have focused on the characterization of metals that have been proposed for use as the current collector and/or cell-container material in the positive-electrode compartment of high-temperature alkali/sulfur cells, and on the characterization of new glass electrolytes for use in Li/S cells.[12]

Mathematical Modeling of the Sodium/Sulfur Cell

(S.A. Naftel, F.R. McLarnon, and E.J. Cairns)

A mathematical model of the sulfur electrode in Na/S cells has been developed.[13] It consists of a set of partial differential equations which describes the processes of diffusion, migration, and convection occurring during the charge/discharge of such a cell. The solution to the relevant equations will be effected on a digital computer via implementation of the Newman-IAD method [14] for the solution of two-dimensional PDE's. The results of this modeling will be compared with data from an operating cell which has been designed to allow measurement of ionic potentials throughout the sulfur electrode. An attempt will be made to predict the effect of various charge-discharge regimens upon cell operation.

FUEL CELLS AND LIQUID-JUNCTION PHOTOVOLTAIC CELLS

These cells can be designed to exhibit acceptable lifetimes for a number of applications. However, the performance of the O_2 electrode in fuel cells, and the performance of the counterelectrode in liquid-junction photovoltaic (photoelectrochemical) cells need improvement.

Oxygen Reduction In Alkaline Fuel Cell Electrolytes

(K.A. Striebel, E.J. Cairns, and F.R. McLarnon)

We are studying the reduction of O_2 on Pt electrodes in aqueous alkali hydroxide and carbonate electrolytes over a concentration range approaching practical fuel cell conditions.[15] Parallel studies of the mechanism on smooth electrodes and fuel cell behavior on gas-diffusion electrodes are being carried out.

Kinetically limited currents at an electrode potential of 880 mV vs RHE (reversible hydrogen electrode at the same conditions as the working electrode) are shown in Fig. 3 for KOH and K_2CO_3 as a function of electrolyte concentration. The right-hand scale shows the same data corrected for the large differences in O_2 solubility which occur over this concentration range. The smooth electrode studies also indicated that Pt with low oxide coverages showed negligible peroxide production when in con-

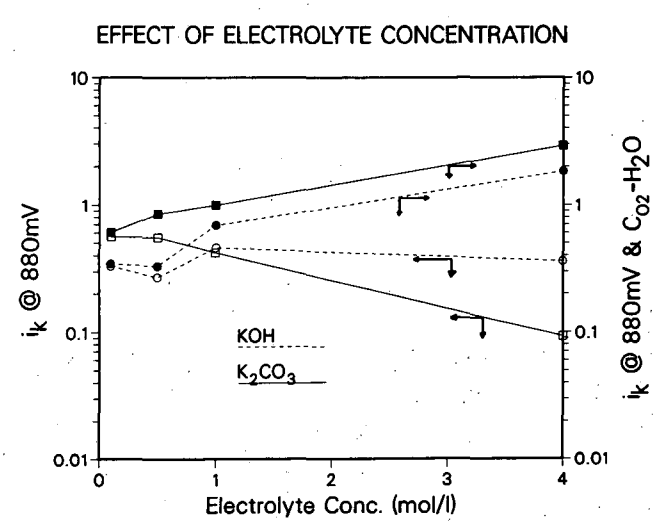

Figure 3. Kinetic current density dependence on electrolyte concentration in KOH and K_2CO_3 for O_2 reduction on Pt. (XBL 8610-3873)

tact with the carbonate electrolytes during O_2 reduction. In the higher-pH hydroxides, however, peroxide production accounted for from 2 to 15% of the total O_2-reduction current. From a kinetic point of view, therefore, carbonates are superior to hydroxides at the same concentration, showing an average of 60% higher kinetic currents and lower peroxide production rates.

Oxygen reduction currents were also measured for high-area Pt supported on carbon black porous gas-diffusion electrodes (obtained from Prototech Inc.). The area of Pt actually in contact with the electrolyte in these electrodes can be estimated from the charge associated with hydrogen desorption. The measured O_2 reduction currents can then be compared directly with the purely kinetically-limited results mentioned above. For the hydroxide electrolytes, this comparison indicated that kinetics, as opposed to mass transfer of reactants and/or products or ohmic effects, is the controlling process over most of the potential range of interest (800-1000 mV vs RHE). This is not true for the carbonate electrolytes. Local pH changes occur in the pores of the electrode due to hydroxide-ion production during operation. We believe this to be the major cause of the lower performance observed in carbonate vs hydroxide shown in Fig. 4 (solid curves). Preliminary experimental work indicates that addition of CO_2 to the O_2 feed may be a way to improve this situation by converting to carbonate some of the excess hydroxide (dashed curves). Further experimental studies and some modeling efforts are currently in progress to further our understanding of the behavior of this electrode.

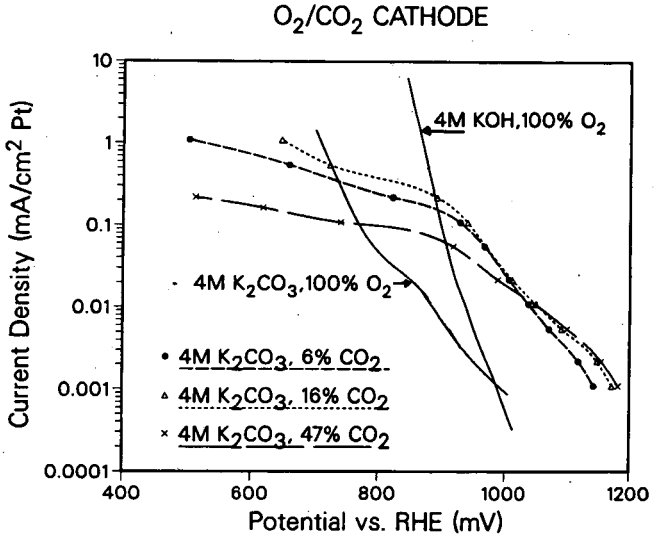

Figure 4. Performance curves for a Prototech electrode (0.3 mg Pt/cm^2) at 25°C in alkaline electrolytes with various gas compositions. (XBL 871-92)

Kinetics and Transport Processes in Aqueous Polysulfide Electrode Reactions

(P.M. Lessner, J. Winnick, F.R. McLarnon, and E.J. Cairns)

Fundamental and applied research on the aqueous sulfide/polysulfide redox couple have been carried out, motivated by its possible use in photoelectrochemical cells (PECs) and redox batteries. Recent work on PECs has concentrated on the reactions at photoelectrodes. Much less attention has been given to the development of efficient redox electrodes which can be used as a counterelectrode in a PEC or as an electrode in a redox cell. The objectives of the present work are to obtain information on the electrochemical and chemical reactions of the aqueous sulfide/polysulfide redox couple and to use that information to design a stable and efficient redox electrode.

Previous chemical and spectroscopic investigations have shown that, when an alkali metal sulfide and sulfur are dissolved in water, monosulfides (H_2S, HS^-, and S^{2-}), polysulfides (S_x^{2-}, x=2 to 5), and sulfur radicals (S_2^-) are present in equilibrium with one another. At equilibrium, the alkaline polysulfide electrochemical reactions can be represented by:

$$\frac{1}{3}S_4^{2-} + \frac{4}{3}H_2O + 2e^- \rightleftarrows \frac{4}{3}HS^- + \frac{4}{3}OH^- \quad (1)$$

We have shown that the electrochemical measurements performed by other investigators correlate well with Reaction 1 and an equilibrium model that is based on chemical and spectroscopic analyses.[16]

The kinetics of the aqueous polysulfide redox couple were investigated using a transient potential step technique in a solution 1 M in S^0 and 1.3 M in total S^{2-}, at pH 12.[17,18] This pH was selected in order to minimize the disproportionation of polysulfides to thiosulfate and sulfide. The low-overpotential region (-25 to +25 mV) was investigated for Co and Pt electrodes from 25 to 80°C. The active species concentration was found to be several orders of magnitude lower than those of any of the major (poly)sulfide ions, and its temperature dependence corresponded to an E_a of about 10 kcal/mole. These results are consistent with the idea that the electrochemically active species is S_2^-. Deviations were found between experimental data for temperatures above 45°C and the simple analytical form of

the current response for an electrode reaction with one rate-determining step. The results agree with a new model proposed here that considers two rate-determining steps, one of which is the homogeneous chemical reaction:

$$S_4^{2-} \rightleftarrows 2S_2^- \qquad (2)$$

The rate constants for this reaction determined using this new model agree with those measured for similar reactions. Exchange current densities were on the order of 1 mA/cm^2 at 60°C.

The steady-state current density-overpotential relationships for Co and Pt rotating disk electrodes were determined for a range of temperatures.[19] A model was developed to take into account the rate of Reaction 2 as well as a finite heterogeneous reaction rate. The parameters determined by the potential step method could be used with this model to explain the current density-overpotential behavior in the low-overpotential cathodic region. At higher overpotentials in the cathodic region a second cathodic reaction was evident. This second cathodic reaction was less prominent when the current densities were lower (as on Pt electrodes) or when the S_2^- concentrations were higher (as temperature increased).

The addition of 13 mol% DMF to the aqueous polysulfide solution was found to increase significantly the current density, at a given temperature and overpotential, by increasing the equilibrium concentration of the electrochemically active sulfur radical anion.[20] In the range of overpotentials studied, the first cathodic reaction wave becomes much more prominent. Although independent quantitative data are lacking for the DMF-water mixtures, the use of reasonable values for the exchange current density and the rate constant for Reaction 2 allows the quantitative prediction of the observed cathodic behavior in the temperature range of 25 to 77°C.

The results of the rotating disk work indicate that porous electrodes are required for the counterelectrode in a PEC utilizing the aqueous sulfide/polysulfide redox couple in order to meet a design goal of supporting 10-20 mA/cm^2 at less than 50 mV overpotential. A flow cell for testing flow-through porous electrodes was constructed and operated.[16] The effects of electrode material, temperature, flow rate, and the addition of DMF on electrode performance were studied. Co (plated on Ni screens) and MoS_2 (grown by reaction of sulfur vapor with Mo on expanded-metal mesh) electrodes gave similar performances which were more than adequate to meet the design goals. Flow rate variation between 0.1 liter/min and 1.6 liter/min had only a small effect on the current density-overpotential curves. Raising the temperature and/or the addition of DMF had much larger effects. These observations are in accord with the steady-state results obtained on the rotating disk electrodes. The demonstrated electrode performance is more than satisfactory for a high-performance photoelectrochemical cell or redox cell.

PLANNED ACTIVITIES FOR FY 1987

Continuing research efforts on secondary alkaline Zn electrodes will include the cycle-life testing of promising electrode/electrolyte formulations in model cells. An improved mathematical model of the Zn electrode will be developed, and cycle-life experiments to verify key features of the model, using *in-situ* microelectrode potential measurements to determine electrolyte species concentrations, will be completed. Optical microscopy and new *in-situ* spectroscopic techniques will be applied to identify the transient species formed during secondary Zn-electrode operation.

A time-dependent, two-dimensional mathematical model of the high-temperature sulfur electrode will be developed, and Na/S cell tests will be completed to verify important aspects of the model. The evaluation of a new solid Li-ion conductors in model Li/S cells will be initiated.

Experiments using porous gas-diffusion electrodes to study O_2 reduction in alkaline-carbonate electrolytes will be completed, and new ad-atom electrocatalysts for high-performance fuel-cell systems will be investigated.

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Thermochemical Energy Conversion and Storage by Direct Solar Heating*

A.J. Hunt, J. Ayer, and R. Otto

The objective of this research is to investigate the use of concentrated solar energy to drive the endothermic portion of a thermochemical energy storage cycle.[1,2] This cycle provides means to store energy collected by a solar thermal power plant on clear days and to produce electricity during the night or on cloudy days. The cycle consists of: (1) an endothermic step in which energy is supplied to dissociate the gas, and (2) an exothermic step in which the products of decomposition are combined over a catalyst to provide high-temperatures heat. The heat can be used to operate a turbine or for industrial processes.

We are investigating the decomposition reaction of gases adsorbed on the surface of small particles that act both as the solar absorber and catalyst. This is an application of the solar reactor known as the STARR (Solar Thermally Activated Radiant Reactor), described in the companion article in this Annual Report. The STARR uses a suspension of small particles (diameter less than 1 μm) as the solar absorber, heat exchanger, and, in this case, catalyst for the reaction. The advantages of using small particles are: (1) they are excellent absorbers of sunlight, (2) only a small mass of particles is required, (3) the small particle size provides a large surface area per gram of material for catalysis, (4) small particles can rapidly heat the surrounding gas to a high temperature, (5) the overall system efficiency is high because direct absorption eliminates the need for conventional heat exchangers, and (6) if the particles act as photocatalytic sites the reaction can take place at temperatures below that required for equilibrium dissociation. The specific reaction we chose to investigate experimentally is the dissociation reaction $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$. The particles are Fe_2O_3 (hematite), a known catalyst for this reaction.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ACCOMPLISHMENTS DURING FY 1986

As described previously,[3] the experimental apparatus consists of an SO_3 transfer system, a fixed-bed sealed quartz reactor, and a combination furnace/solar simulator. The hematite particles are placed on a quartz disk in the reactor and are illuminated by the simulator to heat the gas and to catalyze the reaction. To keep the SO_3 as a liquid in the storage vial, and as a gas in the reactor, the temperature controls on the transfer system were improved. The reactor vessel was redesigned to hold more SO_3 and to improve gas mixing. The SO_3 vial was found to contain SO_2 due to incomplete reaction during manufacture. It was vacuum purged until the SO_2 level was below 3%.

The experiments consisted of paired "light" and "dark" runs. The light experiments were carried out with the SO_3 reactor exposed to concentrated light from the solar simulator. The reactor was heated by the light to a certain temperature, measured by a thermocouple near the hematite particles. A sample of gas was bubbled through a water-formaldehyde solution to capture the SO_2 and SO_3. The solution was analyzed with an ion chromatograph to determine relative amounts of each. In each corresponding dark reaction, the reactor was heated following the same temperature profile but using only the furnace (no light). The same gas sampling procedure was used.

Initial results of these experiments were extremely promising. The SO_2 yield during radiant heating was approximately twelve times that during thermal (furnace) heating. Equilibrium concentrations were not reached during any of the experiments, light or dark, but the increased yield definitely indicates that radiant heating leads to (at least) a faster reaction rate. To be certain that ultraviolet light was not responsible for this effect, experiments were carried out using a glass filter to block all radiation below 310 nm. In these experiments the SO_2 yields were about five to eight times higher in the light reactions, still a significant increase. Reactions without the iron oxide particles showed no SO_2,

demonstrating that the particles are essential to the reaction.

PLANNED ACTIVITIES FOR FY 1987

The primary goal of the FY 87 effort is to determine whether SO_2 yields above equilibrium concentrations can be obtained during the light reactions. Several mechanisms can potentially play a role, and the increased reaction rates we found in FY 86 definitely point to a photo effect. Similar experiments will be performed with a cooled UV filter to allow longer run times and higher temperatures.

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Solar Energy Conversion Using Microstructured Materials: Direct Radiant Heating of Small Particle Suspensions*

A.J. Hunt, F. Miller, J.E. Noring, and D. Worth

The Microstructured Materials Group investigates the use of advanced materials for the collection and control of solar energy. Research reported here is in four areas: (1) direct radiant heating of small-particle suspensions to produce useful fuels and chemicals, (2) radiant processing of gas-particle suspensions to initiate thermochemical storage reactions, (3) development of microporous transparent materials for insulating windows, and (4) the use of sol-gel techniques to produce advanced materials. This article describes research in the first area and the other areas are reported in the following articles.

For the past eight years, we have been developing solar thermal energy conversion systems based on direct absorption of concentrated sunlight by a gas-particle mixture.[1–3] Small particles absorb concentrated sunlight to heat a gas to high temperature for electric power generation or industrial process heat. The concept was successfully demonstrated by the solar test of the air-heating, 30 kW_t Mark I SPHER (SPHER is an acronym meaning *Small Particle Heat Exchange Receiver)* at the Georgia Institute of Technology Advanced Component Test Facility in FY 1982.[4] The solar tests confirmed predictions that (1) small particles are effective solar absorbers, (2) high gas temperatures can be attained, and (3) the high-temperature zone may be isolated from the surrounding walls. In two subsequent evaluation studies of advanced high-temperature gas receivers the SPHER concept ranked first and second.[5,6]

Since FY 1983, we have been investigating the initiation of high temperature chemical reactions by directly illuminating particle suspensions with concentrated sunlight. We call such a receiver STARR, an acronym meaning *Solar Thermally Activated Radiant Reactor.*

ACCOMPLISHMENTS DURING FY 1986

Our research was divided into two main areas: (1) development of an integrated model of a gas-particle mixture subject to direct radiant heating, and (2) experimental studies of two candidate reactions for STARR, nitrogen fixation, and the CO_2 reforming of methane.

Integrated Model of Heated Suspension

In previous work we developed a model for calculating the rate of heat transfer between a single radiantly heated particle and the surrounding gas.[7] It was used to calculate the heating rate of a cloud of particles irradiated by concentrated sunlight, and the maximum temperature difference between particles and gas. The heating rate of the cloud increased rapidly as the particle diameter decreased (for the same particle mass loading) until the Rayleigh region was reached, where the heating rate was independent

*This work was supported by the Solar Fuels and Chemicals Program managed by the San Francisco Operations Office, under the Assistant Secretary for Conservation and Renewable Energy, through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the Solar Energy Research Institute.

of particle size. A second result was that the temperature difference between the submicron-sized particles and gas was essentially negligible (ie., less than 10°K) for nearly all of the conditions encountered in a small particle receiver.

To calculate temperature and flux distributions in a gas-particle suspension, we analyzed a cylindrical receiver. A window at one end admits light to heat a gas-particle mixture that flows away from (cocurrent) or towards (countercurrent) the light (see Fig. 1). The equation of radiative transfer was applied to this problem using a gray medium, two-flux approach.[8] This equation, along with an energy balance, was solved for various values of four nondimensional numbers which were found to govern this problem. The solution yielded temperature and flux profiles in the mixture for both diffuse and collimated light input.

Two major conclusions were reached from the results. First, countercurrent flow is more efficient (captures more energy) than cocurrent flow; the difference depends on the values of the nondimensional parameters, and can be substantial. Second, although scattering from the particles always reduces the efficiency in the diffuse input case, it can actually increase the efficiency for collimated input by making the path length through the mixture longer.

To investigate the chemical aspects of radiantly induced chemical reactions we have adapted and upgraded the CHEMKIN codes from Sandia National Laboratories. These codes calculate equilibrium concentrations and chemical kinetics for complex reacting systems including condensed phases. The programs were used to calculate yields for a variety of reactions for use in STARR.

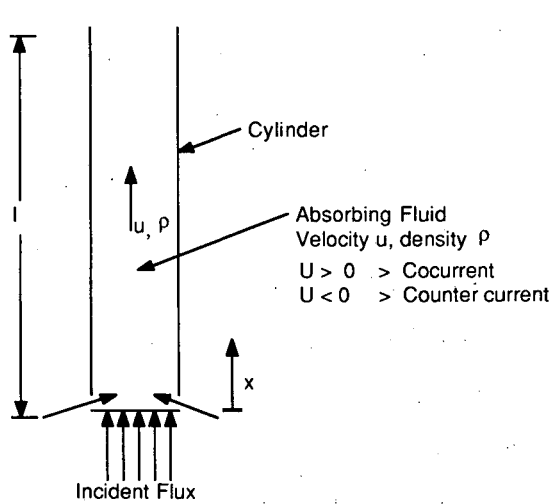

Figure 1. Receiver geometry for the two-flux model. (XBL 871-148)

Experimental Studies

Two candidate reactions for STARR were studied experimentally, nitrogen fixation and methane reforming. Nitrogen fixation is an important step for producing many useful chemicals. The reaction can be driven by the high temperatures available in a solar furnace, but may be enhanced by the high photon fluxes acting on the particles in a direct radiant receiver. In our experiments, an air stream was seeded with various particles and passed through a reactor illuminated by concentrated light from the solar simulator. The output gas stream was analyzed for NO and NO_x but, under the conditions investigated, no evidence for photoenhancement was detected.

The CO_2 reforming of methane is a highly endothermic reaction that is being developed for thermochemical transport of energy. Two types of experiments were performed. In the first, a mixture of CO_2 and CH_4 passed through the radiant reactor with different entrained particles. This reaction normally requires a catalyst to proceed at temperatures of 800°C, but the presence of high fluxes along with the particles could enhance the reaction. Unfortunately, quantitative results were not obtained due to column problems with the gas chromatograph. However, a CO monitor went off scale at 100 ppm, indicating some reaction. In the second experiment the reaction was carried out in a tube furnace to investigate carbon particle formation. Above 960°C particle formation was rapid, showing that for this reaction it is possible to form the particles directly from the reactants themselves.

PLANNED ACTIVITIES FOR FY 1987

The research in direct radiant heating of small particle suspensions will continue in FY 1987. The integrated gas-particle model will be upgraded to calculate the temperature and flux profiles in two dimensions, and to account for spectral effects. A laboratory scale cylindrical receiver will be completed and temperature measurements will be taken for a variety of conditions to compare with the model. A new project will investigate the thermal and photo effects of radiantly heating particle catalysts to react CO_2 and CH_4.

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Solid-State Radiative Heat Pump*

P. Berdahl, C. Khieu, and G. Ng

The current objective of this project is to establish the research basis for the development of a new class of heat pump. This new heat pump will be a solid-state device that accepts input energy in the form of electricity and pumps infrared (heat) radiation across a thermally insulating gap. An important potential application is the heating and cooling of buildings, including applications using thermal storage.

Semiconductor materials with direct narrow bandgaps in the range of 0.03-0.25 eV emit equilibrium thermal radiation which is in large part due to electron-hole recombination. An excess or deficit of infrared radiation, compared to the thermal equilibrium value, can be produced when the concentrations of electrons and holes are varied from their thermal equilibrium values by electrical means. Two techniques for varying the concentrations of electrons and holes are of special interest here: (1) electrical bias of a p-n junction to produce carrier injection or, for reverse bias, carrier extraction; (2) the magneto-concentration effect in which orthogonal electric and magnetic fields are used to enhance (or deplete) the concentrations of electrons and holes near the semiconductor's surface. The p-n junction technique seems particularly promising for the development of technologically mature devices, while the magneto-concentration effect offers the opportunity for the study of key recombination phenomena in a simpler experimental system.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ACCOMPLISHMENTS DURING FY 1986

A key research result was the demonstration, for the first time, of the galvanomagnetic radiative cooling effect.[1] This experiment (sketched in Fig. 1) employed the magneto-concentration effect to produce an explicit, continuous cooling and heating effect, which was measured directly with a thermocouple. With a magnetic field in the z-direction, a current imposed by an electric field is passed through the thin active indium antimonide (InSb) layer in the x-direction. The electrons and holes drift under

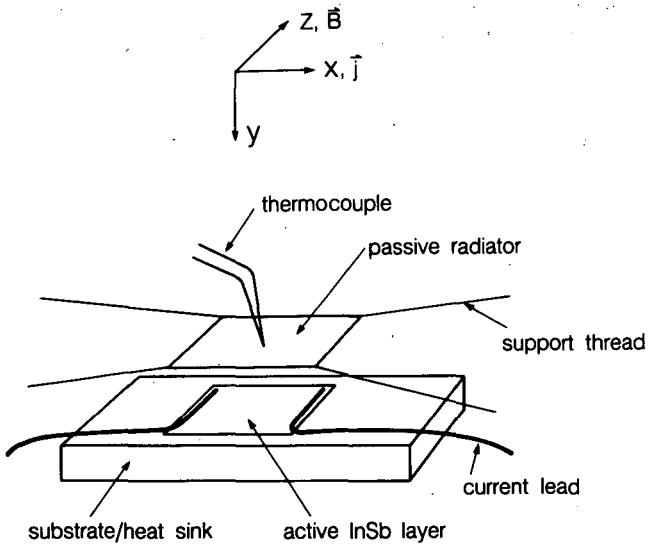

Figure 1. Apparatus used to observe the galvanomagnetic radiative cooling effect. A vacuum eliminates nonradiative heat flows. (XBL 867-11198)

the influence of the electric field and are deflected by the Lorentz force to accumulate near the crystal's surface. The accumulated electrons and holes combine to produce infrared radiation, which is absorbed by the nearby passive "radiator". In this case a radiative heating effect is observed. If either the electric or magnetic field is inverted, this heating effect is converted to the desired cooling effect, because the concentrations of electrons and holes near the layer's surface are then depleted. This depletion causes cooling of the passive radiator, because the thermal radiation emitted by the radiator is absorbed by the active layer. Measured temperatures obtained in one experiment are shown in Fig. 2. In addition to the desired temperature differences, a parasitic heating effect (proportional to I^2) is present, which causes the parabolic curve shapes shown. However, the galvanomagnetic radiative cooling effect of interest here can be easily measured as one-half the temperature difference observed for the two polarities of the magnetic field B. The magnitude of the cooling effect is in good agreement with estimates based on prior experiments and theoretical work.[2,3]

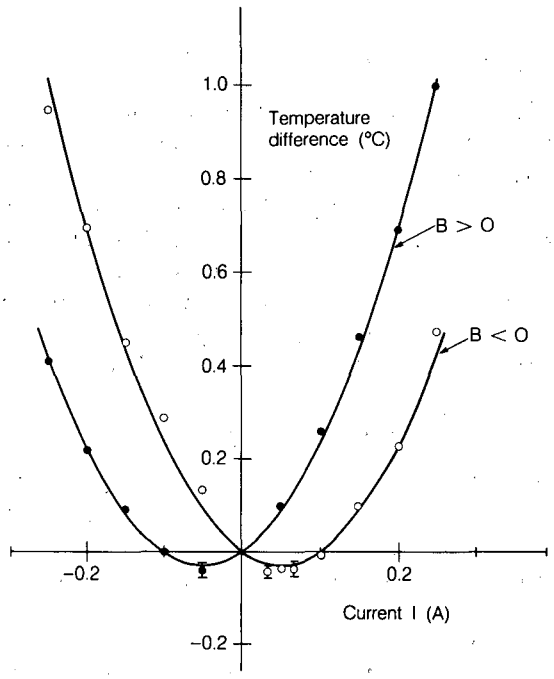

Figure 2. Measured temperature difference between the passive layer and the substrate of the active layer, for both polarities of the 1.1 T magnetic field. (XBL 867-11199)

The parasitic heating effect present in the experiment could be greatly reduced by better thermal contact between the active layer and the substrate (a coating of wax is used) and by the fabrication of thinner active layers. Nevertheless, a small absolute cooling effect is exhibited in Fig. 2 at currents of less than 0.1 amperes.

The question whether or not solid state radiative heat pumps can be constructed has now been answered in the affirmative. The question on the future utility of these devices now depends upon the ultimate achievable efficiency and cost.

PLANNED ACTIVITIES FOR FY 1987

A new activity planned for FY 1987 is the development of analytical models which represent complete solid-state radiative heat pump devices and systems. These models will be used to identify the key strengths and weaknesses of the solid-state radiative heat pump approach, and to determine which key sub-efficiencies will most greatly limit the performance of future systems. This activity is intended to ensure that, once a suitable material has been identified, it is indeed possible to develop practical heat pump systems. Also, materials research to date will be extended, focusing on the evaluation of the narrow-bandgap lead-tin-telluride materials, using the galvanomagnetic luminescence technique.[2]

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Processing of Condensate Waters from Coal Gasification*

C.J. King, J. Senetar, T. Grant, L. Poole, and R. Thompson

Large volumes of condensate water are formed when reactor effluents from coal gasification are cooled. Water from low-temperature gasification processes contains large concentrations of ammonia, acid gases, and dissolved organics – notably phenolic compounds. For both economic and environmental reasons it is necessary to process these waters sufficiently to allow recycle, probably as make-up to a cooling-tower system.

The principal objective of this project is to provide basic understanding enabling development of improved physicochemical processing methods for condensate waters formed during coal gasification. Particular attention is given to solvent-extraction, adsorption, and stripping processes. Other aspects of the project have dealt with chemical analysis of condensate waters and characterization of the mechanism and kinetics of formation of hydantoin compounds, which are produced in the quench-water circuit and tend to concentrate in the blowdown of the cooling tower.

Ongoing research focuses upon removal of organics by regenerated adsorption processes, and development of more energy-efficient approaches for removal and recovery of ammonia.

Use of carbon adsorption for condensate waters is held back by incomplete regeneration of the carbon, which typically requires replenishment of 15% or more of the carbon per cycle. A current goal is to identify the cause of this irreversibility and to identify means of overcoming or lessening the problem.

Stripping of ammonia from condensate waters is energy-intensive, because the volatility of ammonia is lowered by the presence of dissolved acids, notably carbon dioxide and hydrogen sulfide. For simple stripping it is necessary to boil about 15% of the water. For processes that isolate ammonia from the acid gases it is necessary to boil at least 25% of the water. We have been carrying out research on an innovative approach to this problem, wherein ammonia is extracted with a liquid ion exchanger, while the acid gases are simultaneously stripped. This greatly reduces the steam requirement for stripping and serves to isolate the ammonia as a product.

*This work was supported by the Morgantown Energy Technology Center, Morgantown, West Virginia, through the Assistant Secretary for Fossil Energy, Office of Surface Coal Gasification, Advanced Process Research Program of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

ACCOMPLISHMENTS DURING FY 1986

Characterization of Condensate Waters

Our concluded work on chemical analysis of condensate waters has been described in two publications.[1,2]

Formation of Hydantoin Compounds

The portion of the research dealing with identification of the mechanism and kinetics of formation of 5,5-dimethyl hydantoin in condensate waters has now been completed.[3] Hydantoins are produced from ammonia, carbon dioxide, cyanide, and ketones (notably acetone) as precursors. Formation can be reduced by minimizing the formation of hydrogen cyanide during gasification and/or by minimizing residence times in the quench-water circuit.

Adsorption of Phenols

Measurements of rates and equilibria for carbon adsorption have been carried out with aqueous solutions of phenol, and two dihydroxybenzenes, resorcinol and catechol. These solutes are present to substantial amounts in condensate waters. A number of different pieces of evidence point strongly to the loss of carbon capacity being associated with a slow, irreversible chemical reaction on the carbon surface, for which the rate increases with increasing temperature:

- The initial rates of adsorption of phenol and resorcinol are nearly the same as that for ethanol, a reversibly adsorbed solute. However, ethanol uptake readily reaches an unchanging equilibrium value, whereas the uptakes of phenol and resorcinol continue to increase slowly over time, for several weeks or longer.
- Phenol is adsorbed to a much greater extent (more moles per unit surface area) at the inter-

face between carbon and aqueous solution than at the interface between air and aqueous solution. For reversibly adsorbed solutes, adsorption densities at the two interfaces are nearly equal.

- Phenol is adsorbed by carbon to a greater extent at 80°C than at 25°C, whereas the capacity of carbon for physisorbed solutes typically decreases at higher temperature. When a carbon that has adsorbed phenol at 80°C is subsequently contacted with the same aqueous solution at 25°C, the uptake of phenol increases slightly, rather than decreasing.
- Leaching with solvents at ambient temperature removes phenol from freshly loaded carbons, removing a percentage of the phenol that corresponds roughly to the fraction that is rapidly adsorbed. The degree of reversibility is greater than that reported in the literature for regeneration with air or steam at elevated temperatures. For both methods of regeneration, the degree of reversibility is less for carbons that have aged longer since the start of adsorption.
- Adsorption capacities for resorcinol and catechol are greater than that for phenol, despite the fact that the dihydroxybenzenes have much lower activity coefficients in water. The degree of irreversibility during regeneration by solvents is much greater for the dihydroxybenzenes than for phenol. The surface reaction apparently proceeds faster and/or to a greater extent for the dihydroxybenzenes.
- When resorcinol is adsorbed onto carbon and is subsequently regenerated by leaching with alcohols, ketones or water, an additional, unidentified peak is found when the effluent solvent is analyzed by high-performance liquid chromatography (HPLC).

Isolation and Recovery of Ammonia

Our earlier work on extraction of ammonia with di-2-ethylhexyl phosphoric acid (D2EHPA)[4] has shown that there is a substantial steam requirement for regeneration of D2EHPA. Furthermore, degradation and loss of D2EHPA occurs at temperatures above 150°C. Phosphinic acids have lower acidity and potentially greater thermal stability than phosphoric acids. These properties should make phosphinic acids more effective extractants for ammonia. Cyanex 272 (American Cyanamid Company) is a phosphinic-acid extractant developed for the hydrometallurgical industry.

Extraction experiments have confirmed that Cyanex 272 possesses near-optimal acidity for regenerable extraction of ammonia. This is evidenced by the sharp rise in the equilibrium distribution coefficient for ammonia at values of pH just below those (8.0 - 9.5) typical of condensate waters.

Regeneration experiments at 126°C with Cyanex 272 have shown that the partial pressure of ammonia over 0.48 M Cyanex 272 in an alkane diluent is about 20 times that over 0.48 M D2EHPA in the same diluent, for ammonia contents of the liquid phase varying from 0.06 to 0.16 M. Thus regeneration of Cyanex 272 can be accomplished at substantially lower temperature and/or with less steam requirement.

Experiments to monitor the thermal decomposition of loaded Cyanex 272 have been complicated by the presence of a substantial phosphonic acid impurity in the extractant. Since the phosphonic acid should have lower thermal stability, it probably dominates degradation, as measured through the phosphorus content of an equilibrium aqueous phase.

PLANNED ACTIVITIES FOR FY 1987

Adsorption of Phenols by Carbon

Several different techniques will be used to characterize the surface reaction between phenols and carbon. These include controlled kinetic studies to define reaction mechanism, order, and activation energy, as well as spectroscopic studies and detection of reaction products.

Carbons are available with quite different surface chemistry, resulting from different starting materials and activation conditions. The influence of carbon surface chemistry upon the irreversibility will be investigated. This may lead to promising avenues for selection and/or pretreatment of carbons to minimize extent of the surface reaction.

Studies of adsorption and regeneration of dihydroxybenzenes will be continued, since these compounds will likely pose the most severe limitations for avoidance of capacity loss.

Promising routes for reducing the effects of the surface reaction are to reduce bed volume by means of rapid cycling and to use low-temperature means of regeneration. Both of these concepts will be explored further.

Extraction of Ammonia

The properties of the phosphinic-acid extractant, Cyanex-272, for extraction of ammonia will continue to be explored. An immediate goal is to identify the limit upon regeneration temperature imposed by thermal stability, as measured by the phosphorus content of an equilibrium aqueous phase, formation of degradation products, and/or loss of extraction ability. This limit defines the steam requirement for regeneration. For these studies it is necessary to remove the phosphonic acid impurity by selective washing. Extraction and regeneration (stripping) equilibria also require more quantitative definition.

Computer simulations of ammonia and acid-gas stripping will be continued, to gain insight into other avenues that may be effective in reducing the energy requirement for removal and isolation of ammonia.

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Removal of H_2S from Coal-Derived Gases*

S. Lynn, R. Hix, D. Neumann, S. Sciamanna, and C. Stevens

When coal is gasified, most of the organic sulfur is converted to hydrogen sulfide. The problem of removing the hydrogen sulfide varies with the nature of the gas that has been produced and with the purpose to which the gas is to be put. A new process is being developed at the Lawrence Berkeley Laboratory which consists of

- absorbing the hydrogen sulfide in a polar organic solvent;
- converting the dissolved hydrogen sulfide to sulfur by reacting it with an equivalent amount of sulfur dioxide dissolved in the same solvent;
- recovering elemental sulfur from the solvent by crystallization; and
- generating the sulfur dioxide for the process by burning hydrogen sulfide or sulfur, recovering heat from the combustion gas in a waste-heat boiler and recovering sulfur dioxide by scrubbing the gas with cooled solvent from the crystallization step.

The process under development has a number of potential advantages over conventional technology. These include reduced capital and operating costs, great design flexibility, high H_2S removal efficiency, and applicability to the treatment of a wide variety of gases.

The University of California at Berkeley's Sulfur Recover Process (UCBSRP)utilizes one step – the liquid-phase reaction between H_2S and SO_2 – that has not previously been successfully employed in a commercial process. The other unit operations in the process are all well known.

The overall objectives of this project are to obtain the physical and chemical data needed to design process configurations for treating gas streams of interest, and to evaluate these process configurations to determine their economic potential.

ACCOMPLISHMENTS DURING FY 1986

An experimental system for measuring corrosion was designed and built. In experiments completed so far, metals of interest were contacted with a liquid mixture of a polyglycol ether, sulfur dioxide, water and sulfur. The corrosion rates, of the order of 1 to 2 mil/yr at 100 to 120°C, show that ordinary carbon steel and 304 stainless steel are highly satisfactory

*This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization, Division of Surface Coal Gasification, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

materials of construction. Because it suffers a somewhat higher rate of corrosion, there is a small disincentive for using 316 stainless steel in this service.

The UCBSRP utilizes the liquid-phase reaction of H_2S and SO_2 to form elemental sulfur. The sulfur is removed from the process by crystallization from the solvent. The sulfur crystals from the crystallizer effluent must be large enough to be easily separated from the solvent using a centrifuge, i.e., greater than approximately 100 microns nominal diameter. The dependence of crystal size-distribution on crystallizer design parameters is needed for the correct design of this unit operation.

A laboratory-scale continuous crystallizer has been built to study the crystallization of sulfur from solution. Preliminary results from runs crystallizing sulfur from a polyglycol ether show that the sulfur crystals have good habit. The formation of amorphous sulfur (observed when sulfur is formed in aqueous solutions) would be a hinderance because amorphous sulfur is gelatinous, adheres to all solid surfaces, and occludes solvent. The crystals are large enough to settle rapidly in the solvent.

Tray efficiency data are needed for the design of the primary absorber in the UCBSRP, where H_2S is absorbed by a solution of SO_2 in the process solvent. The main thrust of this task is to determine the effect of various operating conditions on tray efficiencies. The experimental work involves the building and operation of an apparatus from which absorption data will be collected. The analytical work consists of developing a model for sieve-tray efficiency based on absorption with second-order, irreversible chemical reaction in the liquid for use in correlating the absorption data.

The apparatus being built consists of a 4-in. sieve tray in a closed gas-circulation loop. Construction is nearly complete. The mass-transfer rate of an absorbing gas, when not under gas-phase mass-transfer control, is enhanced when the absorbed gas reacts with a reactant dissolved in the process solvent. The mathmatical model is based on absorption in a wetted-wall column, for which the hydrodynamics are well known. The penetration model (diffusion in a semi-infinite stagnant fluid) was chosen to describe mass transport in the liquid phase, and the film model (diffusion through a stagnant film) was used for the gas-phase mass-transfer model. Limiting cases for this model agree well with those published in the literature.

A major goal of this project is to develop a process scheme that demonstrates the feasibility of using the reaction between H_2S and SO_2 in organic solvents for sweetening a sour gas stream from a coal gasifier. Since a detailed analysis of the potential flow configurations for the process was desired, a computer simulation capable of performing energy and material balances was written and has been was used to design and evaluate a number of different process configurations for this application. Figure 1 is the current flowsheet for the process; this configuration appears to have significant capital and operating cost advantages relative to conventional technology.

PLANNED ACTIVITIES FOR FY 1987

Work on the tasks outlined briefly above will continue during the coming fiscal year. The corrosion studies will investigate the rate of attack of a mixture of H_2S, sulfur and water dissolved in a polyglycol ether on carbon steel and stainless steel at elevated temperature. The kinetics of the reaction between H_2S and SO_2 at elevated temperature and in very dilute solutions will be studied with the use of a spectrophotometer. The study of reactive gas absorption will reveal its effectiveness for scavenging small quantities of H_2S from a gas stream, and the sulfur crystallization studies will yield their first results.

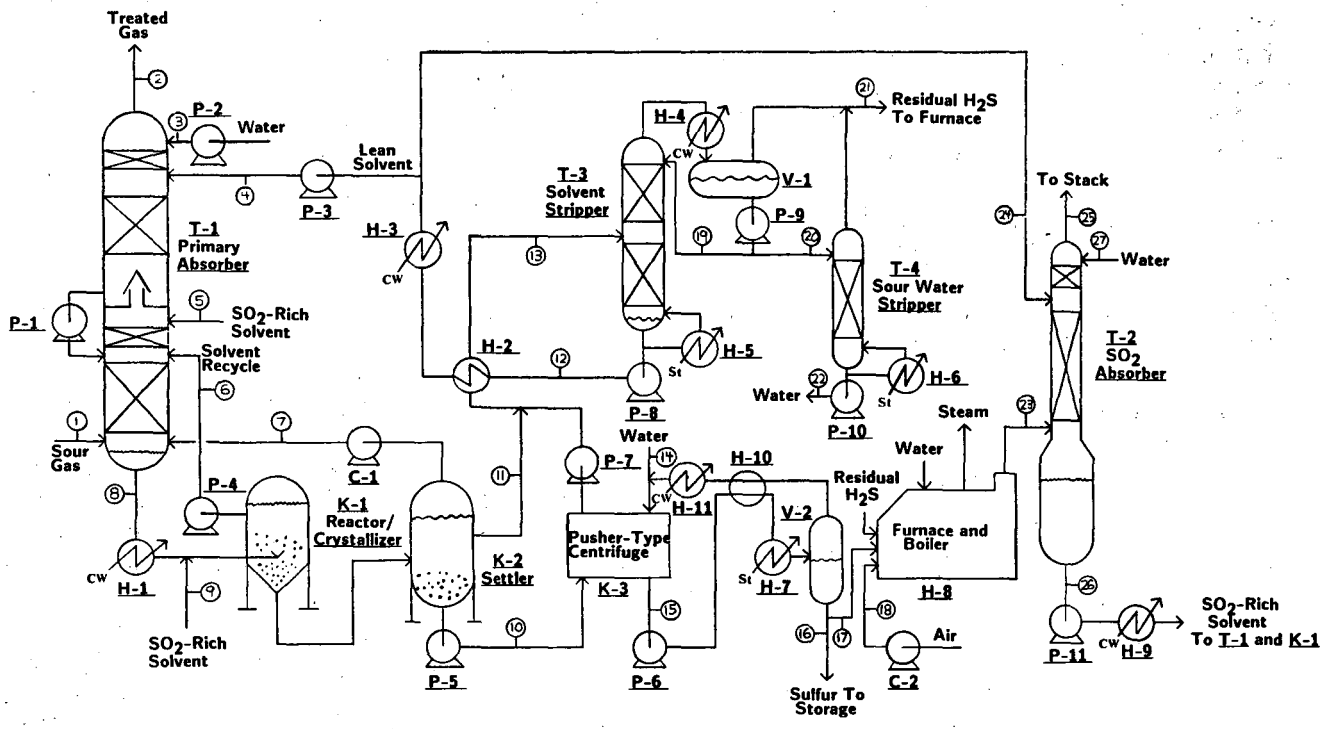

Figure 1. Flowsheet for the process to remove H_2S from a sour gas stream. (XBL 8612-4932)

Analysis of Coal Gasification Reactors*

M.M. Denn and G. Dow

Moving-bed coal gasifiers are designed to operate in either a dry-ash mode, as in the METC and commercial Lurgi gasifiers, or in a slagging mode, as in the BCG/Lurgi slagging gasifier. Dry-ash gasifiers require large amounts of excess steam for temperature moderation, and are therefore inefficient. Slagging reactors are not yet a commercial technology, and they are faced with both materials problems and problems of bed movement.

This research project has been concerned with the modeling of moving-bed gasifiers, in order to gain insight into reactor operability and design. The status of gasifier modeling is summarized in our recent book chapter.[1] All modeling efforts require the use of a single-particle model, which describes the local mass and heat transfer and chemical kinetics in the heterogeneous system. The most realistic descriptions of transport phenomena and chemical kinetics near the reactive coal surface seem to be contained in detailed single-particle models, which predict the formation of a flame front under some reaction environments. It has not been obvious how to integrate such detailed single-particle models into complete reactor models, nor what the implications of such a model would be in predictions of operating behavior. It is likely that multiple operating states would be predicted under some operating conditions. The significance of the computation of a flame front about a particle that is embedded in a densely-packed bed is itself unclear.

The focus of the work currently being carried out is to explore the way in which the assumptions made in a detailed single-particle model are integrated into a complete reactor model. The major concern is with the development of a flame front, where the point of maximum temperature leaves the solid surface and enters the bulk gas.

*This work was supported by the Morgantown Energy Technology Center, Assistant Secretary for Fossil Energy, Office of Coal Utilization, Advanced Research and Technology Development, Division of Surface Coal Gasification through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ACCOMPLISHMENTS DURING FY 1986

We have been modeling the flow pathway for reactive gases in the packed reactor as a plane channel, where the channel sides are reactive carbon. Heterogeneous reactions of oxygen and steam with carbon occur at the wall, while homogeneous oxidation reactions occur in the bulk. The partial differential equations for mass and thermal fluxes are solved using a collocation discretization in the transverse direction. Typical channel dimensions in trial calculations are 1-cm width and 100-cm length; the feed gas used to date in trial simulations is air plus steam, with a molar steam-to-oxygen ratio of 7:1.

The mathematical structure of the problem leads to a rather difficult boundary-value problem, with matching required at an unknown interior interfacial curve (the "flame front"). There are some similarities to the study of diffusion flames in combustion. Some insight was obtained from the solution to a special case in which the reaction enthalpies are set to zero, so that no "hot spot" occurs to accelerate reactions. We were then able to develop a continuation method by which the solution for realistic reaction enthalpies can be built up.

The first successful simulation has now been obtained for the air-blown case with 7:1 steam-to-oxygen ratio. The behavior is similar to what would be expected for single-particle models in which the same assumptions have been made: the carbon temperature exceeds that of the bulk gas in the oxygen-rich oxidation zone, while the location of the maximum temperature moves into the bulk gas as oxygen is depleted. Temperature differences of 100-300°K are computed between the solid and the bulk gas. The flame front development extends over a distance of about 5 cm in the flow direction. Temperature profiles in the flow direction are shown in Fig. 1.

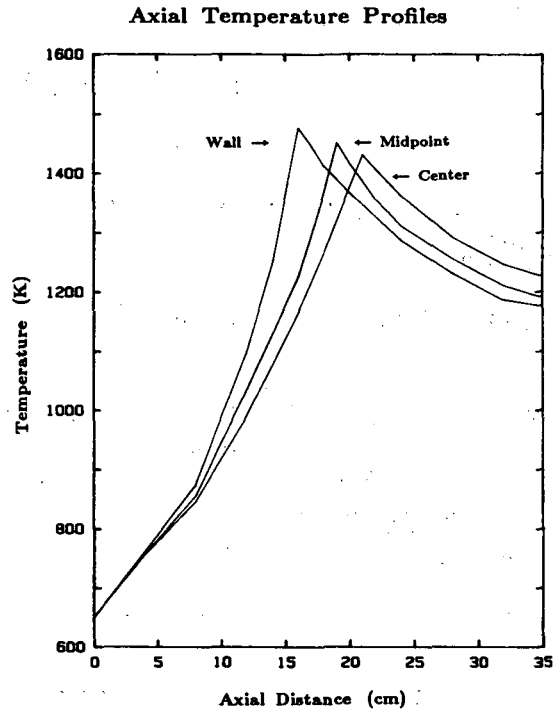

Figure 1. Temperature profile along the carbon surface and in the bulk gas for a one-dimensional channel model of flow in a moving-bed gasifier. (XBL 871-96)

PLANNED ACTIVITIES FOR FY 1987

The study will be completed during FY87. We will be exploring the effect of assumptions made in the model, particularly the kinetic assumption usually made in detailed single-particle models that the homogeneous reaction of hydrogen and oxygen to form water is rapid under gasifier conditions.

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Energy-Related Organometallic Chemistry*

The work in this area is described in the following three sections.

MOLECULAR CHARACTERIZATION OF NICKEL AND VANADIUM NON-PORPHYRIN COMPOUNDS FOUND IN HEAVY CRUDE PETROLEUMS AND BITUMENS

R.H. Fish, J.G. Reynolds, and E.J. Gallegos

We have extensively examined various crude petroleums and separated fractions to determine the characteristics of the metal-containing compounds, particularly the metallo-nonporphyrins. Recently, we reported the molecular weights (MW) of the vanadium and nickel compounds found in selected heavy crude petroleums – Boscan, Cerro Negro, Wilmington, and Prudhoe Bay – and their extracts[1,2] by size exclusion chromatography (SEC) in conjunction with graphite furnace atomic absorption (GFAA) selective metal detection. The metals distribution was found to be unique for each petroleum, while the histogrammic metals profiles may have utility for fingerprinting the heavy crude petroleums. In the case of vanadium, the majority of the metal-containing compounds falls into the 2,000 to 9,000 dalton MW range, while 3 to 7% was found in the MW range >9,000 daltons. The low MW range was calibrated by vanadyl and nickel model compounds, with 23 to 30% having a MW range of <400 daltons. Although these molecular weights may be exaggerated in the high MW range,[3,4] we feel this low MW range result provides strong evidence for the metallo-nonporphyrin coordination sphere.

Pyridine/water extractions have been applied to the same heavy crude petroleums for further identification of these metal-containing molecules.[2] The extraction procedure removes metal-containing compounds from all molecular weight ranges, placing the compounds in the size range of vanadyl and nickel model compounds. As well, 40 to 80% of the vanadium comes from the MW range >2,000 daltons. The extract consists predominantly of very small MW compounds with an average MW of approximately 350 daltons. By comparison with nickel and vanadyl model compounds of similar MW, we also feel this further substantiates metallo-nonporphyrin coordination spheres.

These pyridine/water extracts were separated by reversed-phase high-performance liquid chromatography (RP-HPLC) into three fractions based on polarity, and the fractions were monitored by element-specific detection (GFAA) and UV-vis spectroscopy.[2] Most of the nickel-containing compounds eluted in the most polar fractions. Comparison with model compound retention times indicated these compounds are nonporphyrin-bound. Most of the vanadium-containing compounds were found in the moderate polar fractions. Rapid scan (RS) UV-vis data showed a prominent Soret band in this fraction for Boscan and Cerro Negro, indicating that at least some of the vanadium is bound as petroporphyrin. This was not the case for Wilmington and Prudhoe Bay moderate-polar fractions, where the RS-UV-vis exhibited little or no Soret. At this time, we have no adequate model compounds that co-elute in this fraction. The least-polar fraction also contained vanadium (up to 30% of the total vanadium content in crude). Model compound retention times showed that the model porphyrins eluted in this fraction, but the absence of a prominent Soret in this fraction for most of the crudes suggests nonporphyrins.

The moderate- and low-polar RP-HPLC fractions from Boscan, Cerro Negro, Wilmington, and Prudhoe Bay crude petroleums were examined by electron paramagnetic resonance (EPR) spectroscopy to further elucidate the structure of the average coordination sphere around the vanadium-containing molecules.[5] Several nonporphyrin coordination spheres for the vanadyl ion were observed: 1) Boscan moderate-polar and Prudhoe Bay moderate- and low-polar fractions exhibited N_2S_2 coordination, 2) Cerro Negro and Wilmington moderate-polar fractions showed S_4 coordination, 3) Boscan low-polar fraction showed N_4 coordination, and 4) Cerro Negro had distinctively different parameters showing NOS_2 coordination.

*This work was supported by the Electric Power Research Institute; the Assistant Secretary of Fossil Energy, Office of Oil, Gas and Shale Technology, through the Bartlesville Project Office; and the Office of Technical Coordination, through the Pittsburgh Energy Technology Center, through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

We have also examined the RP-HPLC fractions by electron impact mass spectroscopy (EIMS) to further identify the metallo-nonporphyrin components. Unfortunately, the EIMS spectral studies only revealed the presence of metallopetroporphyrins in certain fractions. The metallo-nonporphyrins remained undifferentiated in the organic matrix.

We have attempted to elucidate the structure of nickel-containing molecules in the high-polar RP-HPLC fractions by using C-18 octadecylsilane column (ODS) reversed-phase and cyano normal-phase chromatography techniques to purify the pyridine/water extract of Wilmington crude petroleum. We have examined the resulting purified fractions with EIMS, positive ion fast atom bombardment (FAB+), and metal replacement FAB+ mass spectroscopies. We have also attempted to verify the existence of these highly polar nickel components in other carbonaceous materials. For example, we examined Gilsonite by RP-HPLC-GFAA and found that such highly polar nickel complex may also be present in this petroleum precursor.

Accomplishments During FY 1986

Pyridine/water extracts of selected crude petroleums were separated by polarity using HPLC with an ODS column into three fractions: low, moderate, and high polar. The moderate- and low-polar fractions were examined by EIMS to elucidate structural and behavioral characteristics of vanadyl petroporphyrin and metallo-nonporphyrin compounds. The EIMS results indicated vanadyl petroporphyrins in Cerro Negro and Wilmington moderate-polar fractions and possibly in the Wilmington low-polar fraction. These EIMS results showed the presence of petroporphyrins in the above-mentioned fractions, but provided no discrete information about the metallo-nonporphyrins.

A highly polar nickel fraction from a Wilmington crude petroleum pyridine/water extract, separated on the ODS column, was further purified on a cyano normal phase column. This fraction had a nickel concentration of approximately 15,000 wppm, and was examined by EIMS. The spectral results indicated several homologous series structures possible for the binding sites of nickel. Further examination of the same fraction by FAB+ mass spectroscopy, using a metal ion-exchange technique, showed a substantially simplified spectrum and indicated the possibility of the nickel binding sites being small molecular weight naphthenic (carboxylic) acid salts.

Gilsonite, a bitumen, was analyzed by RP-HPLC with GFAA element-specific detection, which indicated that the nickel is predominantly bound as metallopetroporphyrin, while a small portion eluted as a highly polar metallo-nonporphyrin fraction.

These results are important in the identification of nonporphyrin metal-containing compounds in heavy crude petroleums and residua, and could be beneficial for future petroleum exploration as metallo-biomarkers.

Planned Activities for FY 1987

We plan to study the chemistry of the nickel carboxylates and make further attempts to identify them by FAB+ mass spectrometry.

HYDRODENITROGENATION CHEMISTRY, 1: CLEAVAGE OF ALKYLCARBON-NITROGEN BONDS, METHANE AND AMMONIA FORMATION IN THE HDN REACTION OF 1,2,3,4-TETRAHYDROQUINOLINE WITH A NICKEL OXIDE CATALYST SUPPORTED ON SILICA/ALUMINA

R.H. Fish, A.D. Thormodsen, R.S. Moore, D.L. Perry, H. Heinemann, and J. Michaels

The hydrodenitrogenation reaction (HDN) is one of the most important industrial processes used in the refining of petroleum feedstocks and involves the removal of the nitrogen atom, as ammonia, from polynuclear heteroaromatic nitrogen compounds at high temperatures and high pressures of hydrogen gas (350-500°C and 2,000 psi).[6-12] It is interesting to note that most of the reported heterogeneous catalysts require the complete hydrogenation of both the nitrogen heterocyclic ring and the aromatic ring (e.g., quinoline to decahydroquinoline) before carbon-nitrogen bond cleavage can occur.[12] This is partly due to the thermodynamics of the aliphatic C-N bond hydrogenolysis reaction, which is more exothermic by 5 kcal/mol than the corresponding aliphatic C-C bond hydrogenolysis reaction. In contrast, the C-N multiple bond cleavage is less favorable thermodynamically than C-C multiple bond cleavage. Another factor is the thermodynamics of aromatic ring hydrogenation, which is more favorable at the higher hydrogen pressures needed to remove nitrogen from polynuclear heteroaromatic nitrogen compounds at rates necessary for the industrial HDN process.

More importantly, we have recently shown that both homogeneous and polymer-supported transition metal catalysts can regioselectively reduce the nitrogen heterocyclic ring in model coal compounds,[13-17]

providing the first step in the overall HDN reaction of polynuclear heteroaromatic nitrogen compounds. Thus, a major breakthrough in the technical and economic aspects of the HDN reaction would take place if, in fact, a catalyst could be found that would selectively cleave the C-N bond in the saturated nitrogen ring and subsequently produce ammonia, without substantial reduction of the aromatic rings, at lower temperatures as well as lower pressures of hydrogen gas.

We have studied a highly loaded nickel oxide catalyst (50% by weight Ni), supported on silica/alumina, that will effectively meet some of the criteria we have stated above for an ideal HDN catalyst. The use of a highly loaded metal catalyst for C-N bond cleavage, with a wide variety of nitrogen compounds, was recently demonstrated by Guttieri and Maier.[18] In that study, a 40% platinum on silica catalyst was used with polynuclear heteroaromatic nitrogen compounds among others (e.g., quinoline, tetrahydroquinoline); however, propylcyclohexane was the major product, i.e., aromatic ring hydrogenation again appears to precede C-N bond cleavage.

Accomplishments During FY 1986

The results clearly demonstrate that the nickel oxide catalyst supported on silica/alumina can cleave C-N bonds, form ammonia and methane (gas chromatographic analysis), while minimizing aromatic ring hydrogenation, using 1,2,3,4-tetrahydroquinoline (THQ) as the substrate, in a flow reactor at 250°C and 1 atm of H_2 gas. Pertinently, no decahydroquinoline, propylcyclohexane or other cyclohexyl derivatives were detected via capillary column gas chromatography-mass spectrometry analysis (GC-MS), even when we increased the flow rate, i.e., decreased the contact time, in our reactor. The products constitute 78% of the conversion (93%) of THQ, while methane, the only carbon-containing gas detected, presumably formed via hydrogenolysis of the products, represented the remaining 22% conversion. A significant amount of a dehydrogenated product, quinoline (21%), was formed along with a smaller amount of the only aromatic ring hydrogenated product detected, 5,6,7,8-tetrahydroquinoline (11%). The small amounts of indole derivatives probably occur via free radical intermediates from the initial C-N bond cleavage of THQ.

We then directed our attention to the reactivity of the first logical C-N bond cleavage product of THQ, o-propylaniline (OPA), with the nickel oxide catalyst. We compared the reactivity of THQ to OPA and the results strongly indicate that after C-N bond cleavage in THQ, loss of ammonia and hydrogenolysis of the propyl side chain predominates, not aromatic ring hydrogenation. It is conceivable that the presence of the nitrogen atom causes an inhibition of catalyzed aromatic ring hydrogenation and to some extent C-C bond hydrogenolysis, and this can be compared with the reactivity of propylbenzene (PB), in which methane (hydrogenolysis) is the major product with only traces of benzene detected via g.c. analysis. Additionally, aromatic ring hydrogenation would not be favorable, thermodynamically, under our relatively mild reaction conditions.

In another experiment, we studied the HDN chemistry of quinoline and found decreased amounts of products, (60%), with a higher conversion to methane (40%), as compared to the THQ results. This result clearly demonstrates that prior selective hydrogenation to THQ would enhance the overall HDN reaction to provide a more substantial conversion to substituted benzene and aniline derivatives.

X-ray photoelectron spectroscopic (XPS) studies, of both the catalyst before use and the pretreated catalyst (H_2, 350°C, 6h) that had produced the HDN reaction, showed the expected silicon and nickel photoemission lines, along with those of aluminum. The nickel $2p_{3/2}$ binding energies for both the reacted and unreacted catalysts were essentially identical (856.5 and 856.6 eV, respectively, charge referenced to the carbon 1s = 285.0 eV photoelectron line), but the "shake-up" satellite positions with respect to the main line were different (862.7 and 861.7 eV, respectively), thus showing some difference in the surfaces.

The nickel $2p_{3/2}$ binding energies of 856.5 and 856.6 eV were a full 2.5 eV higher than the 854.0 eV binding energy observed for a high-purity NiO (99.99%) standard used in this study and the values reported by other workers. The lineshapes of the nickel $2p_{3/2}$ lines were different from those reported for NiO. Rather, the binding energy data were more consistent with a ternary nickel oxide or a higher-valent nickel system. Indeed, the binding energy and satellite data for the catalyst samples are extremely close to those reported for $NiAl_2O_4$ and Ni_2O_3. These XPS studies clearly show that nickel (2+) or higher-valent nickel oxide surface species are responsible for the HDN chemistry observed and not Ni (0). A transmission electron micrograph (TEM) of this catalyst showed nickel, alumina and silica particle distributions and electron diffraction (ED) patterns revealed three nickel phases, which were tentatively identified by X-ray diffraction (XRD) as a nickel oxide and a nickel aluminate on the surface surrounding Ni(0) in the center of the 100 Å particles.

Planned Activities for FY 1987

Further studies will be directed toward rates of product formation, optimizing product yields and learning more about the active catalytic sites for C-N bond cleavage with known nickel oxides, silicates and aluminates, as well as determining the effect of sulfur on the hydrogenation-dehydrogenation and hydrogenolysis components of the HDN reaction.

CARBON-OXYGEN BOND CLEAVAGE REACTIONS OF AROMATIC ETHERS AND ESTERS WITH POTASSIUM METAL/18-CROWN-6 AS THE ELECTRON TRANSFER REAGENT: A STRUCTURE REACTIVITY RELATIONSHIP FOR MODELS IN THE DEPOLYMERIZATION MECHANISM OF COAL

R.H. Fish and J.W. Dupon

The structure of coal is highly complicated, but present knowledge indicates that the linkages that are important to cleave to depolymerize coal are those associated with aromatic ethers and aromatic esters.[19] The facile depolymerization of coal at mild temperatures would potentially allow the structure to be ascertained without thermal alterations and conceivably provide a mechanism to liquefy coal. One method that has been evaluated for the facile depolymerization of such complex matrices as coal is the use of electron transfer reagents. This includes sodium metal/liquid ammonia, lithium metal/ethylene daimine and potassium metal/18-crown-6/tetrahydrofuran (THF).[20] The problem associated with solving the structure of a polymeric material is determining the exact nature of the smaller fragments and the puzzle that occurs when the pieces are assembled for a total picture of the structure. Thus, model compound studies are highly important to conduct to determine a structure-reactivity relationship and to provide vital information that can be related to the more complex structural situation.

In determining which of the above-mentioned electron transfer systems would provide new fundamental knowledge about the structure-reactivity relationships in the facile cleavage of aromatic ethers and esters, we chose to examine these model compound coal linkages with the electron transfer reagent, potassium metal/18-crown-6/THF.[21]

Accomplishments During FY 1986

The linkages that are thought to be important in the depolymerization reactions of coal are those of aromatic ethers and esters. The facile carbon-oxygen bond cleavage reactions of a variety of aromatic ethers and esters were studied with an electron transfer reagent that consisted of potassium metal and 18-crown-6 in THF.

The relative rates of carbon-oxygen bond cleavage, with these aromatic ethers and esters under electron transfer conditions, were studied in competition with the standard, diphenyl ether. The order of relative reactivities was as follows: 2-methoxyphenyl benzoate (>2.0); 4-methoxyphenyl benzoate (>2.0); phenyl 2-hydroxybenzoate (>2.0); phenyl 2-methoxybenzoate (>2.0); phenyl 4-methoxybenzoate (>2.0); 4-hydroxyphenyl benzoate (1.6); benzyl benzoate (1.3); 4-methoxyphenyl phenyl ether (1.15); phenyl benzoate (1.04); diphenyl ether (1.0); dibenzyl ether (0.98); 2-methoxyphenyl phenyl ether (0.97); benzyl phenyl ether (0.96); phenethyl phenyl ether (0.77); and 4-hydroxyphenyl phenyl ether (<0.1).

From these relative rates, it is clear that the electron donating groups, hydroxy and methoxy, increase the relative rates of C-O bond cleavage in aromatic esters, regardless of whether these substituents are on the benzoic acid or phenol portion of the designated ester. Conversely, a methoxyl group has no apparent effect on the relative rates of aromatic ether C-O bond cleavage, while a hydroxyl group dramatically decreases the rate. Thus, electronic effects seem to be pronounced in both aromatic ester and ether C-O bond cleavage reactions. It was also found that proton donors, t-butyl alcohol and hydroquinone, decreased the rate of diphenyl ether cleavage.

Further mechanistic details were also studied, and it was shown that electron transfer is probably the rate-determining step in these C-O bond cleavage reactions, since no significant relative rate differences were seen with diphenyl ether, dibenzyl ether, benzyl phenyl ether or, in fact, the sulfur analog of diphenyl ether, diphenyl sulfide (1.02), i.e., carbon-heteroatom bond cleavage is very fast. Interestingly, diphenyl amine was not reductively cleaved, which indicates that removal of hydrogen to produce the nitrogen anion retards the rate of cleavage and could be the reason that hydroxyl substituents on ethers also retard the rate.

The regioselectivity for esters with substituents in the benzoic acid portion for carbonyl-oxygen

versus carboxyl-carbon cleavage was somewhat difficult to ascertain, since we found that under our reaction conditions benzoic acids were decarboxylated and no aldehydes were detected, i.e., decarbonylation occurred. As well, if methoxybenzene was formed from either decarboxylation or decarbonylation, it was demethylated to phenol. However, the esters that had substituents in the phenol portion clearly showed carbonyl-oxygen bond cleavage.

The regiochemistry for C-O bond cleavage reactions for the ethers showed a preference for the benzyl-oxygen bond, whereas the substitution of either a hydroxyl or methoxyl group in the ortho or para positions of diphenyl ether provided data that showed cleavage in both the substituted and unsubstituted aryl groups. The cleavage reaction of 2-methoxyphenyl benzoate was quenched with acetic acid-d_4, and gas chromatograph mass spectrometer analysis revealed no deuterated benzene. This implies that only free radical and not anionic intermediates participate in the cleavage reaction, i.e., one-electron (and not two-electron) transfer reactions are prevalent in these electron transfer reactions.

The results indicate that kinetic and possibly thermodynamic factors govern the cleavage of carbon-oxygen bonds in aromatic ethers and esters under electron transfer conditions.

Planned Activities for FY 1987

We plan to write a manuscript for publication and a report for EPRI.

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Energy-Related Organic Compounds: A Microcomputer Data Base of Chemical Properties, Structures, and Synonyms (CPSS)*

C.G. Daughton, G.W. Langlois and J.F. Thomas

Countless organic compounds representing numerous chemical classes occur in the process streams from synthetic fuel or enhanced oil recovery (EOR) operations. Chemical characterization studies of these complex, heterogeneous samples have been conducted since the mid 1800s resulting in the accumulation of a wealth of uncompiled and unexamined data. In general, similar suites of chemical classes probably occur in process streams from different fuel production technologies. Most differences in composition are a reflection of different absolute and relative concentrations of these classes rather than the presence or absence of particular classes.

Although comprehensive studies have been performed in attempts to thoroughly characterize individual process streams from particular technologies (e.g., syncrude from oil shale retorting), little has been done to unify the current state of knowledge for all process streams from one or several technologies (e.g., oil shale, tar sands, coal, EOR). A preliminary attempt has been made at presenting a unified overview of the organic compounds produced during oil shale retorting.[1] A major limitation for any discussion of chemical-class constituents, however, is the difficulty in "cataloging" individual compounds using a meaningful taxonomy. For example, a benzenoid compound with alkyl, amino, and hydroxyl substituents (e.g., amino cresols) could be classified as a substituted toluene (methyl benzene), aniline (amino benzene), or phenol (hydroxy benzene); this compound would necessarily belong under the discussion of any of these chemical classes. Such a cross-referencing problem is much more easily managed with a computerized relational data base (i.e., one that is indefinitely and readily expandable).

A major long-term goal of our current project is to establish a microcomputer data base that thoroughly categorizes each organic compound that has been identified in process streams or disposal sites for synfuel or enhanced-oil-recovery operations. When completed, this data base for energy-related organic compounds (EROC) will comprise three major realms of information: (1) the full bibliographic citations that describe the identification of a particular compound in an energy-related sample, (2) the chemical identification and quantification information presented in each citation, and (3) chemical properties, structural data, and synonyms for each compound. This report focuses on the third module of EROC: Chemical Properties, Structures, and Synonyms (CPSS). The database structure and most of the user interface for the first module, Bibliographic Citation System (BCS) has been completed;[2] the second module, Process-Stream Chemical Composition (PSCC) is under development and will be the subject of future reports.

A major objective was to make the data base widely and immediately accessible to end users, unlike some of the DOE/FE data bases that have been established on mainframe computers at various Energy Technology Centers, only some of which can be accessed on line. This was to be accomplished by implementing database software designed for microcomputers that operate under the ubiquitous MS-DOS/PC-DOS environment. To fulfill the needs of this complex application, the software needed to meet several specifications: (1) truly relational in function (i.e., unlimited numbers of files can be concurrently linked or "joined"); this is mandatory for proper "normalization" of data tables (i.e., minimization of fields and maximization of code-table use), (2) full complement of error-checking routines to minimize data-entry errors, and (3) easily queried by novice users. Only recently has software become available that could meet these criteria, one of the most revolutionary of which is Paradox™ (Ansa Software Corp., Belmont CA 94002), a true relational database program that uses the straightforward system of "query by example".

ACCOMPLISHMENTS DURING FY 1986

The LBL Synfuels Program has been involved in numerous aspects of synfuels and the environment since the late 1970s. Major research areas have included waste treatment, methods of chemical analysis, and physicochemical aspects of environmental pollution. All of these tasks have involved critical reviews of the extensive and often confusing literature on chemical composition of waste streams from synfuel production facilities. A pioneering attempt at unifying this information suffered from the lack of a detailed compilation of all compounds that have been identified.[1] This need has led to the

*This work was supported by the Assistant Secretary for Fossil Energy, Office of Oil, Gas, and Shale Technology through the Bartlesville Project Office, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

development of the Energy-Related Organic Compounds (EROC) data base.

The third module of EROC – the Chemical Properties, Structures, and Synonyms (CPSS) data base[3] – was designed to contain a wide spectrum of information for each organic compound. The current CPSS data base contains information (when available) for over 1700 compounds, all of which have been identified in process streams from oil shale retorting; a majority of these compounds has been identified in the most extensive chemical characterization study ever undertaken for any synfuel-related sample (which was an oil shale retort water).[4] Each compound is assigned an arbitrary but unique identification number. This ID number is necessary for linking the many different data tables together, a result of constructing a truly "normalized" relational data base. The following is a brief summary of the organization and types of information that are contained in CPSS, together with example entries.

Organization of CPSS

(1) *Synonyms.* All known names are entered for each compound. This information greatly facilitates finding a compound since several different names can often exist. Synonyms include: CAS (Chemical Abstracts Services), IUPAC, alternate, common, trivial, trade, obscure, and acronyms. For the 1700 compounds currently in CPSS, there are over 5300 names. Using the synonyms alone, it is usually possible to locate any other data in EROC for any compound of interest. For example, a query for all the synonyms for 4-hexylresorcinol gives the following names: 1-hexyl-2,4–dihydroxybenzene, 4-hexyl-1,3-benzenediol, 4-hexyl-1,3-dihydroxybenzene, 4-hexylresorcinol, Ascaryl, Caprokol, Crystoids, Gelovermin, ST37, Sucrets, and Worm-agen. This query only requires several keystrokes to construct from scratch and requires merely 4 seconds to execute (for the current file of 5300 records) using an 80286 microprocessor and 640K of RAM. Just from these synonyms, with little experience in chemical nomenclature, one could surmise that this compound has several commercial uses (including sore-throat lozenges and as an anthelmintic) and that resorcinols are also called benzenediols or dihydroxylated benzenes. A unique feature of Synonyms is that one can query for a particular type of synonym (e.g., CAS vs. trade name). One can query using any portion of a name (e.g., ..diol..) or even on the basis of an approximation of a name. If one does not know the spelling for a particular compound, the Paradox "like" operator can often be useful. For example, the query "like acidanalid" finds "acetanilide", "like pipperdene" finds "piperidine", and "like pthallazene" finds "phthalazine". The synonyms capability is extremely powerful, allowing one to access the data for a compound by using any of its names, fragments, or likenesses.

(2) *Unique identification number (ID#).* Each compound is assigned an arbitrary, unique identification number. For example, 4-hexylresorcinol has ID# LAL-0857. All numbers begin with a three-letter prefix followed by four digits. This will allow future users of CPSS to add their own compounds (beginning with number one) by using their own alphanumeric designator prefix. Since the ID# field is a keyed field (i.e., unique), all compounds are automatically sorted according to ID#. All compounds that would be added to CPSS by a particular research group would therefore be grouped together (because of their common prefix) and sorted in increasing numeric order. Every distinguishable form of a compound (e.g., stereoisomers and unidentified isomers) receives a different ID#.

(3) *Elemental composition.* Contains molecular formula (including individual numbers of atoms of C, H, N, O, and S, and other relevant elements such as As and Hg needed for the organometallics), molecular weight, and line structure (where appropriate). Using 4-hexylresorcinol as an example, the following information was retrieved from a single query (less than 4 seconds): MF: C12H18N00O02S00; MW: 194.27; line formula: CH3(CH2)5C6H3(OH)2.

(4) *Various physical properties (when available).* Includes boiling point, melting point, density, water solubility, vapor pressure, values for pK_a/pK_b, odor index, and 100% odor recognition concentration. Using 4-hexylresorcinol as an example, the following information was retrieved from one query (less than 4 seconds): bp (°C): 334; mp (°C): 66; water solubility (mg/L): 500.

(5) *Toxicological information.* Includes LD_{50} values, other effects (e.g., carcinogenicity), and whether the compound appears on the Toxic Substances Control Act (TSCA) list.

(6) *Miscellaneous information.* Includes descriptions of odor, taste, and color, notation as to

whether the compound is hygroscopic or volatile with steam, and descriptions of general chemical reactivity (e.g., polymerization, autooxidation, etc.).

(7) *Various reference handbook numbers.* Includes Chemical Abstracts (CAS) registry, Merck Index (10th edition), Beilstein, Aldrich Chemical Co., Registry of Toxic Effects of Chemical Substances (RTECS), Manufacturers Safety Data (MSD),* and Chemical Rubber Corporation (CRC). With these reference numbers, one can readily find additional, detailed information. We know of no other single literature source where all of these reference numbers are collectively available.

(8) *Reactions.* Includes routes of chemical synthesis for formation and destruction. Possible reactants and reaction conditions that can lead to the formation of an EROC compound are included in CPSS. Emphasis was placed on simple reactants that commonly occur in synfuel process streams, often at high concentrations (e.g., NH_3, CO_2, CO, H_2S). Using this information, one can search for all compounds that may have been produced by the reaction of particular starting materials. For example, a query for formaldehyde and ammonia as reactants showed a number of possible products in EROC, including 2,6-dimethylpyridine, methylamine, imidazole, and hexamethylene tetramine. Reactions that the EROC compounds can undergo themselves are also included. Emphasis was put on reactions with commonly occurring compounds (e.g., alcohols, aldehydes, ketones, amines) and on reaction types having significance to synfuel process waste streams (e.g., polymerization, pyrolysis). For example, results from a query for compounds that self react included cyanamide (dicyanamide), ethyl acrylate (transparent, elastic material), and formaldehyde (trioxymethylene).

(9) *Structural information.* The structural information in CPSS is perhaps the most useful aspect of this system. An unpublished method was used to encode the chemical structure of each compound. Compounds can be queried using the Structures Query System (SQS) on the basis of a wide variety of structural information, including ring number and sizes, type of fused-ring system (cata-condensed acenes/phenes or peri-condensed), N-O-S heteroatoms (total numbers and ring positions), alkyl substituents (total number, chain lengths, and positions), and type of substituent (alkyl group or any of numerous functional groups) and its position. A more detailed discussion of the structural information contained in SQS follows.

*Sigma-Aldrich Library of Chemical Safety Data, edition 1.

CPSS Structures Query System (SQS)

Commercial software for microcomputers has recently become available that displays two-dimensional chemical structures (e.g., Molecular Presentation Graphics™, Hawk Scientific Systems, Inc., Kinnelon, NJ) and that also allows queries on the basis of graphically displayed structural fragments (e.g., ChemBase™, Molecular Design Ltd., San Leandro, CA). The query capabilities of this software are limited, however, especially in its inability to search for compounds containing particular numbers of like groups (e.g., benzenediols versus phenols; diaromatics versus triaromatics) or for those that do not contain a particular group (e.g., all nonalkylated aromatics).

In SQS, although there is no graphics mode for displaying chemical structures, the structural information has been encoded using an unpublished hierarchical method that allows for very detailed and complex queries. The hierarchy is arranged according to structural relatedness. For example, ketones, aldehydes, acids, esters, lactones, and amides are all related to one another since each contains a carbonyl bond; lactones and esters are further related by having carbonyl and ether bonds shared by the same carbon. The user does not need to understand the encoding method since an extensive interface has been written to enable queries on the basis of chemical-class names. This interface is a menu system of hierarchical filters, each of which selects all of the compounds that possess a particular structural attribute. By iteratively passing the answer from one query back through the system of filters, one can query for the compounds that meet any number of detailed criteria. For example, one can select for all aromatic compounds containing three fused, six-membered rings with only one nitrogen heteroatom, two amino groups, and no alkyl groups; the result of this query was 3,6-acridinediamine (proflavin).

The SQS menu system is designed with redundant paths, so that several different pathways can lead to the same result. In this manner, the user simply picks the route that seems most obvious at the time. The following is an example of one pathway through the menus for finding all of the unsubstituted acyclic mono ketones.

The SQS main menu gives the three general choices "acyclics – cyclics – substituents". Although we could start by choosing "acyclics", we choose

"substituents" since we know from the outset that we are interested in compounds with a keto functionality. We are immediately prompted for the number of like substituents. We answer "1", since we only want ketones with one carbonyl group (i.e., we are not interested in multi-keto functionalities such as diones). The next submenu is a list of possible functional group substituents: "hydroxyl – ether – carbonyl – amine – cyanide ..." When "carbonyl" is selected, another submenu appears that displays the possible functional groups containing the carbonyl group: "ketones – aldehydes – esters – carboxylic acids – amides..". When "ketones" is selected, the user is prompted for acyclic, alicyclic, aromatic, or all ketones. Choosing acyclic then gives two choices: "all – unsubstituted" (the latter refers to the absence of any other functional group). Choosing "unsubstituted" initiates a query for unsubstituted acyclic mono ketones, for which there were 36, all of which were unbranched, and most were 2-keto substituted; the molecular weights ranged from 58.08 (2-propanone) to 436.83 (2-triacontanone). The data tables from these queries can be linked to any other module of CPSS for retrieval of other information.

Sorting and Calculational Queries Using CPSS

The sort capabilities of CPSS can be illustrated using the physicochemical properties for the current CPSS data base containing 1700 records. Ascending or descending sorts are readily performed. A sort on any of these fields required 1′20″. A sort according to melting points gave a range from -189°C (propane) to 440°C (1,2,8,9-dibenzpentacene); only 69% of the compounds have published MPs. Molecular weights ranged from 30.03 (formaldehyde) to 578.44 (1-tetracontanol). The maximum number of respective atoms for a compound were 40 carbons (five different derivatives of tetracontane), 6 nitrogens (melamine), 7 oxygens (picric acid), and 4 sulfurs (tetramethylthiuram disulfide and 2,2′-dithiobis[benzothiazole]). Considering all the compounds, 41% contained nitrogen, 52% contained oxygen, and 10% contained sulfur. Using the Paradox menu selection, queries for the compounds that contain nitrogen, oxygen, or sulfur in various combinations required less than 18 seconds to execute; 264 contained both N and O; 40 contained N and S; 35 contained O and S; and 9 contained N, O, and S (e.g., 1-acetyl-2-thiourea). These are but a few of the nearly limitless queries that can be run by a novice user with no programming experience.

Calculational queries can also be easily run. For example, using the fields that specify the number of atoms comprising each compound, one can readily construct a query that calculates the weight percentages for each element. This query required 3′20″ to execute. Sorting the compounds according to weight percent for each element (1′40″ per element) gave the following minimum and maximum percentages, respectively, for each element: carbon (methanesulfonic acid: 12%; large fused-ring systems such as coronene: 96%); hydrogen (picric acid: 1%; propane: 18%); nitrogen (tetracontanenitrile: 2%; melamine: 67%); oxygen (various aliphatic, $>C_{30}$, alcohols and aldehydes: 3%; ethanedioic acid: 71%); and sulfur (1-triacontanethiol: 7%; s-trithiane: 70%).

PLANNED ACTIVITIES FOR FY 1987

Organic compounds will continue to be added to CPSS, with emphasis being placed on those identified in process streams from coal conversion and EOR. Considerable effort will be devoted to the second module of the EROC data base (PSCC): actual concentrations of individual compounds that have been identified, together with complete data on the method of chemical analysis and description of the process stream in which they occurred. The user interface for CPSS will continue to be developed and improved, and considerable effort will be devoted to checking the internal consistency of the CPSS data.

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Separations by Reversible Chemical Association*

C.J. King, A.S. Kertes, D. Arenson, J. Tamada, and W. Rixey

Separations of polar organic substances from aqueous solution consume a large amount of energy industrially. Examples include recovery of ethanol, butanol, acetic acid, glycols, phenols, adipic acid, sugars, and corn-starch products. Needs for recovering such substances will increase still further and become more complex with the advent of bioprocessing technology, since most of the methods for production of chemicals from biomass generate products in dilute aqueous solution.

For the most part, these separations are presently accomplished by distillation and evaporation. Reversible chemical association, or complexation, provides a low-energy alternative, and should be particularly attractive for those solutes which have volatilities lower than or comparable to that of water. Separations by reversible chemical complexation utilize selective and reversible chemical interactions between the solute and functional groups on a liquid extractant or solid polymeric sorbent.

This research concerns measurement, interpretation and modeling of phase equilibria and transport for these separations. Further goals are to define rational selection criteria for complexation reagents, to develop suitable methods for regeneration and process integration, and to define the most likely applications. The solutes of particular interest are those potentially important as chemicals obtained by fermentation of biomass – carboxylic acids, alcohols, and multifunctional compounds containing the -COOH and -OH groups.

The initial phases of the project have included literature surveys of the extraction chemistry of carboxylic acids and alcohols[1,2] and measurement and chemical modeling of phase-equilibrium behavior for extraction of carboxylic acids by amine extractants in various diluents, and for extraction of alcohols by phenolic extractants in various diluents.

Another part of the project concerns use of non-functionalized, and therefore non-wetting, solid polymeric adsorbents for recovery and fractionation of carboxylic acids, alcohols and glycols from aqueous solution. Non-wetting adsorbents have air-filled pores, which reduce concomitant uptake of water and provide uptake that is rate-limited by vapor-phase diffusion along the pores. Solutes can thereby be fractionated according to volatility over aqueous solutions, and solutes of surprisingly low volatility can be adsorbed because of the very short transport paths.

ACCOMPLISHMENTS DURING FY 1986

Extraction of Carboxylic Acids

Experimental measurements have focussed upon extraction of succinic acid and malonic acid by Alamine 336, a commercial tertiary amine mixture with 8- to 10-carbon alkyl groups (Henkel Corp.). Methyl isobutyl ketone (MiBK, a Lewis base), chloroform (a Lewis acid), and n-heptane (inert) have been used as diluents for the amine. The chloroform diluent gives the largest equilibrium distribution coefficients, reflecting complexation or solvation between the acid-amine complex and chloroform. MiBK gives substantially higher distribution coefficients than heptane.

These results have been successfully rationalized through chemical modeling, allowing for complexation between the amine and one or more acid molecules and, for higher amine concentrations, association between these complexes and the diluent.[3] These postulated complexes are consistent with spectroscopic data in the literature for related systems; however, independent spectroscopic confirmation is still desirable.

Equilibrium data have also been obtained for extraction of malonic acid with Alamine 336 as extractant. These data clearly show stoichiometric overloading of the amine extractant; molar ratios of extracted malonic acid to amine are as high as 1.5. This result is important from the viewpoints of both chemical interpretation and process implementation, since stoichiometric overloading probably leads to more facile regeneration of the extractant.

Data have been obtained for co-extraction of water during extraction of succinic and malonic acids by Alamine 336 in chloroform and alkane diluents. Water is co-extracted in rough proportion to the amount of acid extracted, but the mole ratio of water to acid varies considerably from system to system.

Initial data have been obtained for loss of nitrogen to the aqueous phase during extraction of succinic acid by Alamine 336 in the different diluents.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Conversion and Utilization Technologies (ECUT) Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

However, these results are dominated by dissolution of lower-molecular-weight and/or secondary- or primary-amine impurities, as has been confirmed by a series of reuses of the extractant following washing.

Extraction of Alcohols

As has been shown in earlier work by our group,[4] Lewis acidity is a useful property in an extractant for lower alcohols. Among Lewis acids (hydrogen-bond donors), we have found that phenols are effective extractants for alcohols. For extraction of ethanol from dilute aqueous solution, m-cresol provides a weight-fraction-based equilibrium distribution coefficient of 2.17, whereas no other common solvents give equilibrium distribution coefficients above 1.0.[4] Non-interacting diluents reduce the equilibrium distribution coefficient in rough proportion to cresol concentration. However, chloroform as a diluent is synergistic, keeping the distribution coefficient high. Apparently the electron-acceptor characteristic of chloroform serves to solvate the cresol-ethanol complex.

Equilibrium measurements have been made at 25°C and 40°C for extraction of ethanol from water by m-cresol in n-octane. The change of equilibrium distribution coefficient with temperature is very small, thereby ruling out back-extraction following a temperature change as a means of regeneration.

Equilibrium data have also been obtained for extraction of ethanol from water by t-butyl catechol and n-hexyl resorcinol, both in toluene diluent. Equilibrium distribution coefficients (weight-fraction basis) for tert-butyl catechol are slightly higher than those for m-cresol as extractant, at the same concentration in the same diluent. Equilibrium distribution coefficients for hexyl resorcinol are substantially higher.

Phase-equilibrium data have been obtained for extraction of the four butanol isomers (n-, s-, i-, and t-) by m-cresol in n-octane diluent. Vapor headspace analysis has been used to determine activity coefficients of n-butanol in aqueous phases saturated with m-cresol. These data enable interpretation of the extraction equilibrium data in terms of chemical effects in the two separate phases. The presence of m-cresol at saturation level has only a minor effect on the activity coefficients of n-butanol in the aqueous phase. Therefore literature data for activity coefficients of the different butanol isomers in aqueous solution can be used together with the measured distribution coefficients to infer activity coefficients of the isomers in the organic phase. When this is done, the organic-phase activity coefficients do not differ much, indicating that isomeric effects reside much more in the aqueous phase than in the organic phase.[5]

Non-Wetting Adsorbents

A series of runs has been carried out fractionating aqueous solutions of succinic acid, acetic acid, and ethanol by adsorption onto fixed beds of Rohm & Haas Amberlite XAD-4 (a styrene-divinylbenzene macroreticular resin) and Ambersorb XE-340 (a pyrolyzed sulfonated styrene-divinylbenzene macroreticular resin), both of which are non-wetting adsorbents. The results demonstrate that adsorption is dominated by rate effects based upon differences in solute volatility, with succinic acid adsorbing to a very small extent because of its low volatility. These results confirm earlier experiments in agitated vessels which indicate that the rate-controlling step for adsorption with these adsorbents is Knudsen diffusion in the pores.[6]

PLANNED ACTIVITIES FOR FY 1987

Measurements will be made of the effect of temperature on equilibria for extraction of various carboxylic acids, in order to identify opportunities for regeneration by back-extraction following a temperature change. These measurements and additional measurements for alcohol extraction by phenolic extractants will also provide indications of enthalpy and entropy changes, which are useful for understanding of extraction mechanism.

Studies of other regeneration methods will be initiated. For extraction of carboxylic acids by tertiary amines, one method to be explored is back-extraction with aqueous ammonia, followed by thermal decomposition of the ammonium salt to give ammonia and the free acid. If workable, this approach avoids the consumption of chemicals associated with neutralizing back-extraction with other chemical bases.

Other phenolic extractants for alcohols will be examined, with the goals of enhancing extraction equilibria through steric effects and minimizing extractant solubility in the aqueous phase. Chemically active diluents will be explored further as well, with the same goals.

Spectroscopic measurements will be made where appropriate and useful for confirming association stoichiometry.

For extraction of carboxylic acids, measurements will be made to characterize further the coextraction of water and loss of extractant to the aqueous phase, with emphasis on quantitative modeling of the underlying phenomena.

Our studies of separations by reversible chemical association will be extended to include solid polymeric sorbents, as well as liquid extractants. Initial efforts will be directed toward identifying basic groups effective for regenerable sorption of carboxylic acids, and assessing the utility of sorbents with pendant phenolic groups for recovery of alcohols.

Further studies of the use of non-wetting polymeric adsorbents will involve use of higher temperatures and smaller particles (Porapak Q, Waters Associates), both of which should serve to increase rates of adsorption. Measurements will be made of breakthrough curves and fractionation among mixed solutes during adsorption onto non-wetting polymeric sorbents in a fixed bed. These results will be interpreted in terms of the underlying transport and equilibrium conditions.

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Sub-Micromolar Actinide Detection Via Photoacoustic Spectroscopy*

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Photoacoustic spectroscopy (PAS) is an ultrasensitive absorption technique capable of providing non-destructive characterization of atomic and molecular systems. PAS measurements are based on a periodic optical absorption in a sample followed by non-radiative conversion of the absorbed energy into heat.[1,2] A subsequent heat-induced thermal expansion produces a pressure or acoustic wave in the sample medium whose amplitude is measured by a suitable transducer. The amplitude of this photoacoustic wave is directly related to the optical absorption of the sample, and therefore the concentration of absorbing species. In this work, PAS was demonstrated as a sensitive technique for measuring micromolar and lower concentrations of rare earth and actinide ions in aqueous solution. In near-neutral solutions, actinide ions are sparingly soluble ($< 10^{-7}$ M); chemical methods used for the measurement of actinides at submicromolar concentrations, such as extraction and ion exchange, disturb the natural equilibria.[3,4] An optical technique such as PAS facilitates direct measurement without disturbing the chemical equilibria.

ACCOMPLISHMENTS DURING FY 1986

The experimental system developed consisted of a repetitively pulsed Nd:YAG pumped dye laser, sample cell assembly, boxcar integrator and chart recorder. The photoacoustic cell consisted of two identical quartz cuvettes acoustically coupled to cylindrical quartz flats. The quartz flat was found to reduced the photoacoustic amplitude by approximately 40%. Without the quartz flat, it was difficult to change samples because the piezoelectric transducer (PZT) was coupled directly to the cuvette. We

*This work was supported by Office of Civilian Radioactive Waste Management, Nevada Nuclear Waste Storage Investigations Project, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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believe the 40% reduction in amplitude is acceptable considering the simplicity of design. Standard Suprasil fluorescence cuvettes (1x1x5 cm) were employed because the high-quality quartz exhibits minimum absorption of the laser radiation and produces negligible window-noise signals. The transducer chosen for this work was a lead-zirconate-titanate 5A PZT because of its high sensitivity to small pressure fluctuations. The signal from the PZT was amplified by a charge-sensitive preamplifier and conditioned by a shaping amplifier before it was transmitted to a boxcar integrator.

The absorption coefficient of water in the 500-nm range is approximately 10^{-5} cm^{-1}, and can change according to purity.[5] Therefore, the PAS signal caused by the absorption of the water can be large at the low sample concentrations expected for the actinide ions. Using a differential technique, the solvent effect was subtracted and the detection sensitivity increased.

Pulsed Versus Modulated CW PAS

There are two excitation modes that can be employed in PAS; modulated continuous wave (cw) and pulsed.[1,2] We chose pulsed PAS because the acoustic propagation distance during the pulse is typically much smaller than the dimensions of the sample. For our PAS configuration, the acoustic propagation distance during the laser pulse was approximately 15 μm, which is much smaller than the cuvette sample cell dimensions. Therefore, the photoacoustic response was independent of boundary reflections. The use of pulsed laser sources also avoids problems arising from heating and convection in liquids.[6] In addition, the photoacoustic generation efficiency (acoustic energy generated/light energy absorbed) for thermal expansion (typically on the order of 10^{-12} to 10^{-8}) is proportional to laser pulse energy. The calculated photoacoustic pressure, using characteristics of our system, was approximately 1.37 x 10^{-8} atm. Assuming 10% coupling to the PZT, and the 3 V/atm sensitivity of the PZT, the photoacoustic signal was only about 4 nV.

PAS Measurements of Rare Earth and Actinide Ions

Nd^{3+} solutions were used to optimize the photoacoustic experimental configuration. The coordination chemistry of Nd^{3+} is similar to that of trivalent actinide ions in solution. The amplitude of the PA signal was strongly dependent on the vertical position where the laser beam entered the cuvette (the horizontal position did not influence the PA response). For the unfocused beam, we obtained the maximum photoacoustic signal amplitude when the center of the beam was approximately 19 mm above the surface of the PZT.

For the Nd^{3+} measurements, the dye laser wavelength was set at 521 nm. Using this absorption peak (molar absorptivity = 4.7 L/mole-cm) and the optimized photoacoustic detection configuration, we measured 1 x 10^{-6} M Nd^{3+} in 0.001 M HCl. Our detection limit (S/N ratio = 3) was calculated to be 8.4 x 10^{-7} M. These data indicated the ability to measure sub-micromolar actinides because of their higher molar absorptivities.

Figure 1 shows the americium spectrum obtained for a concentration of 5.5 x 10^{-8} M in 0.01 M HCl, at the 503 nm absorption band (molar absorptivity = 278 L/mole-cm). This detection represents an equivalent absorbance of 2 x 10^{-5}, which is several orders of magnitude lower than that for commercial absorption spectrometers. Our measurement of 5.5 x 10^{-8} M americium is not the minimum level detectable with our system, but represents the lowest *clean* solution available. Solutions must be filtered when working at these low concentration levels because the influence of light scattering becomes significant. However, an americium spectrum at this level had never been achieved before this work.

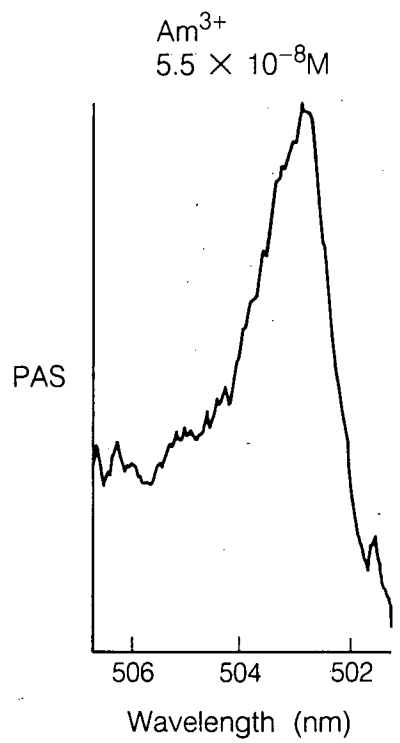

Figure 1. Photoacoustic spectrum obtained from 5.5 x 10^{-8} M americium in 0.01 M HCl. (XBL 871-348)

PLANNED ACTIVITIES FOR FY 1987

Improvements in our electronics (better preamplifiers) and signal processing (computer averaging) are planned in FY 1987 in order to detect lower levels than those reported here and provide broad wavelength spectra for several actinides and their complexes. In addition, we will be investigating thermal lensing and photothermal deflection for such measurements because of an expected reduced influence of sample volume.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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