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SCHOOL OF CHEMICAL ENGINEERING PRACTICE
BROOKHAVEN STATION

SUMMARY OF PROJECTS
1983 — 1986

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1. INTRODUCTION

THE MIT Graduate School of Chemical Engineering Practice stresses engineering problem solving. The Practice School program, as it is commonly called, develops in a unique and particularly effective way the student's ability to apply fundamentals to problems in the chemical industry and thus accelerates one's professional development.

Graduate students participating in the three-term Practice School Master's degree program complete their chemical engineering course work at the Institute in Cambridge before participating in three or four one-month projects at Practice School stations such as Brookhaven. The scope and intensity of the program is such that completion of one-semester of Practice School is accepted in lieu of a Master's thesis.

The program was created to assist students in making the transition from their life in academia to one in industry. Practice School emphasizes:

- Organization and Planning: the development of a plan of attack and its implementation within a carefully defined time schedule.

- Leadership: the responsibility for group organization and action toward the solution of problems.

- Engineering judgment: the development of analysis skills by exposure to a wide range of chemical engineering operations with active review by station personnel and MIT staff.

- Communication: effective oral and written presentation of ideas.

- Economic-Technological Interaction: the role of technical and economic factors and their interaction in determining commercial feasibility.

The MIT Practice School has maintained a part-time station at Brookhaven National Laboratory from 1983 to 1986. Groups of twelve students completed one set of four projects at BNL during August of 1983 and 1984. Another group of twelve students completed nine projects during July and August of 1985. In 1986, the MIT Practice School was held at BNL during the spring term rather than summer as in previous years. A group of seven students completed five projects at BNL between January and March 1986, and a different group of eight students completed six projects between March and May.

Because of the part-time nature of the Practice School at BNL, the MIT staff has changed more often than other stations operating on a year-round basis. T. A. Hatton was Director and A. D. Richards, Assistant Director, during the first summer. R. K. Helling as Associate Director, and J. C. Erickson as Assistant Director ran the station during the second summer with assistance from Directors, T. A. Hatton and J. W. Tester. In 1985 and 1986, R. D. Sproull served as Director, and F. J. Hrach as Assistant Director.
To attain the Practice School goal of training chemical engineering graduate students for their transition from academia to industry, the students are assigned four-week projects proposed by various divisions at Brookhaven National Laboratory. In selecting projects the directors of the Practice School seek problems that will utilize the students' chemical engineering background, imagination and judgment in a group approach (two to four members) to an area of national importance. The Laboratory staff members who propose the projects serve as technical consultants, while everyone concerned (students, consultants, and practice school directors, as well as visiting MIT faculty) works cooperatively toward the resolution of the proposed problem.

At the completion of their projects, the participants write comprehensive reports for distribution at BNL and present their results at seminars to which the Laboratory staff is invited. During the three-year period from the summer of 1983 to the summer of 1986, 28 projects were completed, which involved a total of 51 students. BNL divisions that have worked with the Practice School include:

- Biomedical and Environmental Assessment
- Chemical Sciences
- Fuels and Catalysis
- Energy Applications and Analysis
- Environmental Chemistry
- Materials and Electrochemistry
- Medical
- Metallurgy and Materials Science
- Plant Engineering
- Process Sciences
- Safety and Environmental Protection
- Terrestrial and Aquatic Ecology

The themes of atomization, methanol production and utilization, hydrogen production and compression, localized electrochemical corrosion and biochemical engineering reflect some of the major programs at the Laboratory. The titles of all the projects are listed in chronological order in the index at the end of this document. Brief summaries are presented for each project with related projects grouped together. Detailed reports on these projects can be obtained from the Practice School Coordinator at BNL, M.F. Bonner (ext. 3340).

Funding support for the cooperative BNL/MIT Program was provided by several technical divisions within the Department of Energy, as well as the Office of Energy Systems Research, and the Office of Field Operations Management (University/Industry). One project received support from the Office of Nuclear Regulatory Research, Nuclear Regulatory Commission.
Coal water mixtures (CWM) are liquid-like fuels that may someday replace petroleum-derived fuels in industrial oil burners and electric power generators. One critical factor for CWM combustion is atomization, which is governed by the rheological properties of the fluid as well as the fuel flow rate and nozzle geometry. CWM additives (stabilizers and dispersants) alter the rheological properties of the fluid and, hence, affect atomization quality.

For the past three years at BNL a series of CWM-atomization studies have been undertaken by MIT Practice School groups, with each study being more fundamental than the previous. In the 1984 study, CWM were atomized, while in 1985 homogeneous fluids, without the coal, were atomized. Then in 1986, a single atomization jet was studied using homogeneous fluids. The surfactants used in the first and third studies included (a) anionic aerosol OT-75 and sodium dodecyl sulfate and (b) nonionic Triton X-100 and X-705. Aqueous solutions of glycerine, xanthan gum and carboxymethyl cellulose were used in the second study.
Coal-water mixtures (CWM) are liquid fuels which may replace petroleum-derived fuels in industrial burners. Surfactants improve the stability and reduce the viscosity of CWM, but their effect on atomization, which is a critical factor influencing combustion, is unknown. The goal of this work was to determine the effect of two surfactants, one anionic, and the other nonionic, on the atomization process.

The anionic surfactant, Aerosol OT-75, and the nonionic surfactant, Triton-X100, were chosen because they differ significantly in chemical composition and the proposed mechanisms by which they may improve the fluid properties of CWM. Other experimental variables included atomizing air pressure (20 and 30 psig), liquid/air mass flow ratio (1-16) and surfactant loading (0-4% by weight). All slurry experiments were performed with a 45% (by weight) mixture of coal in water. Droplet-size distributions were fit to the two parameter Rosin-Rammler distribution to characterize atomization quality. The liquid/air mass ratio was the most significant variable affecting the atomization of fluids; atomization decreased with increasing liquid/air mass flow ratio. Pressure had a lesser effect but in general atomization quality improved with nozzle pressure.

The anionic surfactant, Aerosol OT-75, did not affect the atomization of pure water at any of the loadings tested (0.5, 2, and 4% by weight). Triton-X, however, decreased the quality of water atomization with increased loading. The median-mean diameter of water mixture containing 4% surfactant at a mass flow ratio of 5 was 40 μm greater than water with 2% surfactant. This may have been caused by the molecules forming a gel-like network with water containing a large degree of hydrogen bonding, thereby, preventing break-up of the droplets. No consistent trend was observed between changes in fluid low-shear viscosity or surface tension and atomization of water.

The atomization of a 45% coal/55% water mixture apparently produced a bimodal distribution of droplet sizes consisting of smaller pure water droplets and larger coal particles, surrounded by a water layer of variable thickness. Concentrations of either surfactant of up to 4% by weight of coal in suspension produced no effect on mean droplet size and no systematic effect on the distribution breadth, despite the significant changes in physical properties.

Future work should investigate means to measure fluid properties at the conditions in the atomizer nozzle, clarify the effect of the coal particle-size distribution on atomization, and characterize the nature and importance of surface properties of the coal.
ATOMIZATION OF NON-NEWTONIAN LIQUIDS

MIT/BNL-85-2

BNL Consultant: C.R. Krishna

Coal water mixtures (CWM) are liquid-like fuels that may someday replace petroleum-derived fuels in industrial oil burners and electric power generators. One critical factor for complete CWM combustion is atomization, which is governed by the rheological properties of the fluid as well as the fuel flow rate and nozzle geometry. Commercial CWM are non-Newtonian fluids that contain stabilizers and dispersants that alter the rheological properties (viscosity and surface tension) of the fluid. These additives affect atomization quality.

The goal of this project was to model the atomization of homogeneous, non-Newtonian fluids with rheological properties similar to CWM. This work relates droplet mass mean diameter to the rheological properties of liquids that did not contain any coal particles.

Newtonian fluids were atomized to provide baseline droplet size distributions for low and high viscosity fluids. Water and glycerine/water mixtures of 50, 90, and 300 cp were used. Aqueous Xanthan gum (0.05, 0.1, 0.25 wt%) and carboxymethyl cellulose (0.2, 0.35, 0.85 wt%) solutions were the non-Newtonian working fluids. Air-blast atomizations were conducted at air pressures of 20 and 30 psig, and liquid to air mass flow ratios from 1 to 40.

Estimate of shear rates near the nozzle orifice were based on a laminar fully developed tubular flow model. Since the estimated shear rates of the non-Newtonian fluids in this study follow power law behavior, the power law assumption is the basis for data analysis.

Air-blast atomization results showed that for both Newtonian and non-Newtonian fluids, the following general expression described the relation between droplet size and its dependent parameters:

\[
\text{droplet mass mean diameter} \propto \eta^{0.1} (L/A)^{0.5}
\]

where viscosity, \(\eta\), for power law non-Newtonian fluids was calculated from the shear rate estimated at the nozzle. Droplet size was mainly dependent on \(L/A\), liquid-to-air mass flow ratio, and only weakly dependent on fluid viscosity. The results suggest that the shear rates for non-Newtonian fluids were overestimated; probably because of the many assumptions involved in the shear rate estimation.
Atomization, the breakup of a liquid stream into fine droplets, has applications in a variety of industrial processes including anti-misting, spray drying, and liquid-fuel combustion. Coal-water mixtures (CWM) are suspensions of coal in water which serve as liquid fuels when atomized. Surfactants are commonly mixed with CWM to improve the flow properties by better dispersing the coal particles. However, the effect of surfactants on the atomization quality is difficult to predict because of the randomness of the atomization process and the complexity of surfactant behavior.

In this project, the lengths of breakup of cylindrical water jets were examined for four surfactants with varying physical properties. Surfactants lower the surface tension of aqueous jets by diffusing to and adsorbing on the fresh water surface, which creates a dynamic surface tension. The Rayleigh equations accurately predicts the breakup length of pure fluid jets but over-predicts the jet breakup length for surfactant solutions because of this dynamic surface tension phenomenon.

The objective of the project was to experimentally determine the effect of surfactants on the jet breakup of aqueous jets. Specifically, the jet length and the length fluctuations were determined as a function of the jet velocity, nozzle diameter, surfactant, and surfactant concentration.

Distilled water and four surfactant solutions of nonionic Triton X-100 and X-705 and anionic sodium dodecyl sulfate (SDS) and Aerosol OT-75 were used in both 0.58 and 0.30 mm ID nozzles at velocities between 60 and 800 cm/sec. The concentrations chosen were 0.1, 0.2, and 1.0 wt% for all the surfactants tested. The jet lengths were measured by first recording the jet on videotape and then taking ten readings by freezing the playback at random. The mean jet length was determined as was the length fluctuation, which is determined as the width of the region of 95% confidence about the sample mean.

Rayleigh plots of mean jet length versus the square root of the Weber number were made for each run. The plots were linear in the laminar region for distilled water and were slightly concave downward for the surfactant solutions. From the slopes of the distilled water runs, the initial amplitude of the disturbance was calculated and was found to increase for the smaller nozzle. More surfactant transport (i.e., less deviation from Rayleigh predicted behavior) was observed in the smaller nozzle, which may have been due to enhanced radial convection caused by greater velocity profile relaxation. Aerosol OT-75 was found to have the fastest transport, and deviated from the Rayleigh prediction the least of the surfactants studied.

A single-parameter surfactant flux equation was developed to relate the jet breakup length to the jet velocity and surfactant equilibrium surface tension. The flux was considered to be the product of a mass transfer
coefficient, \( K \), and a driving force, which is the difference between the surfactants actual surface concentration and the equilibrium surface concentration that corresponds to the surfactant's bulk concentration. The jet was modeled as a series of discrete wavelengths, each having a constant surface tension and particular amplitude of disturbance. A marching procedure was used to calculate the surfactant surface concentration along the jet and its effect on the growth in amplitude of the disturbance. Jet breakup occurred when the amplitude of the disturbance equaled the radius of the jet. The predicted jet length was accurate to within 5\% of the experimentally determined jet-breakup length in the laminar region regressed. The \( K \) values for each experimental run were slightly dependent on the jet velocity.
3. THE EFFECT OF SURFACE TENSION ON LIQUID WAVE DYNAMICS

MIT/BNL-85-5

MIT Group: T. Foo
BNL Consultants: J.R. Saunders and C.R. Krishna

Experiments conducted during space shuttle flights under microgravity conditions have shown that many physical phenomena take on a different perspective when the dominant gravity factor is removed. Research to explore these unusual effects is a prerequisite to conducting manufacturing operations in space. BNL has an interest in determining the types of experiments, equipment, and facilities that would be required to support a microgravity research program. This study was directed toward the basic understanding of surface tension-gradient driven fluid flows believed to be encountered in the growth of single crystals under conditions of reduced gravity. The eventual goal of such a venture is the control, reduction, or elimination of undesirable fluid behavior to eradicate crystal defects, which are critical in semiconductor materials.

Surface tension flows isolated from gravitational effects can be simulated under the earth's gravitational field by producing surface capillary waves, whose primary surface-flatness restoring force is surface tension. The objectives of this project were to ascertain the relationship between fluid surface tension and surface wave dynamics, and to suggest means of refining the mechanical wave generating apparatus and optical wavelength measurement system to obtain more accurate and precise measurements.

The wavelength of dispersive water waves was measured as a function of wave generating frequency for distilled water in the frequency range of 800 to 3000 rpm. The measured values of wavelength agreed within 12% to values calculated from elementary wave theory for fluids. The surface tension of water was then lowered by 56.5% to 0.0322 N/m with the addition of sodium dodecyl sulfate (SDS), a soluble surfactant, to a concentration of $5.67 \times 10^{-3}$ M. A decrease in wavelength of approximately 20% was observed for the aqueous SDS solution compared to distilled water results. As predicted by elementary wave theory for surface waves in the capillary regime, a 24% decrease in wavelength was observed for the aqueous SDS solution over distilled water. The accuracy of measurements is within the precision limit of 10 to 15% for the experimental apparatus. The loss in precision is a result of problems with focusing a clear image of the waves onto a projection screen. At higher frequencies and shorter wavelengths (<5 mm), the lack of sharp wave images introduces errors of greater than 10% in measurement.

Another limitation of the apparatus was the range of frequency available for study. The range was restricted to the gravity-to-capillary wave transition region by the limitations of the wave generating motor. In addition, the unsteadiness in the speed of the motor and the vibration of the motor on its stand created undesirable frequencies that interfered with wavelength measurements at the desired frequency.
4. METHANOL PRODUCTION

Methanol is currently used almost entirely for the manufacture of synthetic chemicals. It is also widely regarded as the best substitute for gasoline. Modern methanol plants produce a crude methanol from synthesis gas, a 2:1 mixture of hydrogen and carbon monoxide. The conventional heterogeneously catalyzed processes, which are operated at a high temperature (250°C) and pressure (750 psig), suffer from low conversions, low yields, and poor selectivity. Presently, synthesis gas used in methanol production is prepared by the partial oxidation of natural gas or by the gasification of coal. Both processes use pure oxygen because of the already high pressure in the conventional processes and, hence, require expensive air separation plants. Economic analyses by EPRI (AP-1962 and AP-3749) have shown that the cost of the air separation plant amounts to approximately one-third of the total cost of producing methanol from raw materials. As a result, the development of an economic process for the production of methanol from synthesis gas which overcomes the drawbacks of the current processes will make methanol more viable as an alternative fuel.

The Fuels and Catalysis Division of BNL has developed a novel catalyst for the production of methanol from synthesis gas. This catalyst, a solution of a base and a transition-metal compound in an appropriate solvent, overcomes many of the disadvantages of conventional, solid-phase, methanol synthesis catalysts. Using the BNL catalyst, the reaction can be conducted at low temperatures (110°C) and pressures (150 psia), where the equilibrium conversion is high (94%).

The Practice School projects at BNL on methanol production have included: (1) a batch-reactor kinetic study (85-4); (2) a process design study (85-9); and (3) analysis of the operation of a continuous stirred tank reactor.
In this project a data base was developed to be used to design a commercial process using the BNL catalyst to produce methanol from synthesis gas.

Experiments were conducted in batch reactors using p-dioxane, methanol, and p-dioxane/methanol mixtures as the solvent for the catalyst system. The reaction was studied at temperatures ranging from 70 to 120°C. The total pressure in the reactor varied from about 765 psia at the start of each run to about 100-150 psia when the reaction was terminated; this final pressure is equivalent to the desired operating pressure of a continuous reactor.

The reaction rate was modeled as dependent upon carbon monoxide partial pressure, \( P_{CO} \), and liquid methanol concentration, \([\text{MeOH}]\), using the expression:

\[
- \frac{dp_{CO}}{dt} = k_1 P_{CO} \exp(-k_2 [\text{MeOH}])
\]

where \( k_1 \) and \( k_2 \) are dependent upon the base concentration. In methanol/p-dioxane mixtures ranging from 6 to 50 vol% methanol (1.5-12 M), at a temperature of about 110°C, and \( k_2 \) are 1.71 min\(^{-1}\) and 0.443 M\(^{-1}\), respectively. In methanol/p-dioxane mixtures ranging from 25 to 100 vol% methanol (6.5-24.7 M), at a higher catalyst concentration and the same temperature of about 110°C, \( k_1 \) and \( k_2 \) are 7.71 min\(^{-1}\) and 0.208 M\(^{-1}\), respectively. The activation energy for the reaction was determined to be 23.3 kcal/g-mole for 1.5-2.3 M methanol in p-dioxane solution. As much as 86% of the hydrogen was converted into methanol during the experiments.

Kinetic studies showed that at high catalyst concentrations, the reaction proceeds at a reasonable rate using pure methanol as the solvent for the catalyst system. However, the possibility of using a co-solvent other than p-dioxane was also examined. Solvent selection criteria were based on the assumptions that in a commercial process: (1) the solvent would be separated from methanol by distillation, and (2) the heat generated by the reaction would be used to drive this distillation. On this basis, most saturated hydrocarbons and esters are unsuitable solvents because they are azeotropic with methanol. Among the alcohols that are zeotrophic with methanol, butanol and iso-butanol are the best solvents, based on the additional criteria of solvent price and ease of separation from methanol.
The liquid-phase catalyst system developed at Brookhaven National Laboratory (BNL) for the production of methanol permits the use of milder operating conditions (110-120°C, 150 psia) than the conventional solid catalyst systems. Methanol and p-dioxane have been identified as suitable solvents for the catalyst system. This study was directed toward determining the feasibility of using the BNL catalyst system for the commercial production of methanol from synthesis gas based on earlier kinetic studies at BNL.

Three processes were considered: (a) Case I - the use of methanol as solvent with pure syngas as feed, (b) Case II - the use of p-dioxane as solvent with pure syngas as feed, and (c) Case III - the use of methanol as solvent with nitrogen-containing syngas as feed. A plant located on the Gulf Coast and producing 3000 tons per day of 99.85% pure methanol was chosen as the basis of design. The reactor design was based on a reactor pressure of 150 psia for Cases I and II and 250 psia for Case III. A rate constant equal to 0.51 min⁻¹ was used in all cases, corresponding to a reactor temperature of 100°C. The design for Cases I and II was based on syngas containing 67% H₂ and 33% CO being delivered at reaction conditions. Syngas for Case III contained 40% H₂, 40% N₂, and 20% CO. Overall conversions of 100% and conversions per pass equal to 90% were used for Cases I and II; whereas, a single-pass conversion of 90% was used for Case III.

Packed columns, tray columns, static mixers, stirred tanks, and bubble columns were evaluated as possible reactor configurations for this unique gas absorption, which would be followed by the liquid phase reaction. Kinetics, heat and mass transfer, and pressure drop through the reactor were the main criteria used in selecting the reactor. Stirred tanks and bubble columns seemed to be the most promising, but more quantitative data was needed in order to choose between the two.

Design equations were developed for both the bubble column and stirred tank. Due to the uniqueness of these systems, the required liquid volumes were identical for both reactors when nitrogen-free syngas was used. Total required volumes were calculated using mass transfer correlations and gas hold-up considerations. When nitrogen is present in the syngas, the equations showed that bubble columns require smaller total volumes than stirred tanks; with pure syngas the volumes are almost equal. Smaller liquid volumes in the reactor were predicted if p-dioxane is used as a co-solvent than if pure methanol is, even when the same value of the rate constant was used in both designs.

Process flowsheets along with material balances were developed for Cases I and III. Both flowsheets are similar, with the major differences being in the gas flow rates through the reactor, and the total pressure in the reactor. In the presence of nitrogen (Case III), the molar flow rate increases...
by two-thirds and the required pressure necessary to maintain the same CO partial pressure increases from 150 psia in Case I to 250 psia. Additionally for Case III, the unconverted gas is not recycled to prevent a build-up of nitrogen in the reactor. The increased gas flow rates cause about 70% of the product methanol to leave in the vapor phase. Energy balance calculations showed that for Case I, the heat of reaction was sufficient to supply all the heat requirements. This results in an annual saving of $6 million per year in utilities.

The purchased equipment cost, as well as fixed capital cost and operating costs, were estimated for Case I by using the ASPEN-PLUS costing routines. Economic calculations were based on the following: (1) a plant life of 15 years, (2) an annual interest rate of 15%, (3) an inflation rate of 7%, (4) nitrogen-free syngas price of $0.95/MSCF, and (5) cooling water price of $0.10/1000 gal. The distillation equipment accounted for 53% of the total purchased equipment cost. The total investment was estimated to be approximately $130 million for the current selling price of 50¢/gal, the calculated ROI was 40%. A sensitivity analysis was performed on the selling price of methanol and on the cost price of syngas in order to determine their effect on the ROI. It was found that the breakeven point for the plant occurred at a methanol selling price of around 35¢/gal. This economic analysis indicates that the proposed process using the BNL catalyst system with methanol as solvent and pure syngas as feed is not only economically viable, but very favorable.
BENCH-SCALE APPARATUS FOR THE CONTINUOUS LOW TEMPERATURE PRODUCTION OF METHANOL FROM SYNTHESIS GAS

MIT/BNL-86-11

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The BNL liquid-phase catalyst system for the production of methanol from synthesis gas (carbon monoxide and hydrogen) has a number of novel features that include low temperature (120°C) and pressure (185 psia) operation, high conversion (80-90%) for batch operation and high selectivity towards methanol. BNL has built a continuous bench-scale stirred tank reactor system to demonstrate the commercial viability of this process. The continuous system has had trouble attaining steady-state operation and achieving high conversion. The objective of this project was to suggest modifications that will permit this goal to be achieved.

Six experimental runs were conducted on the continuous bench-scale reactor using pure methanol and a p-dioxane/methanol mixture as the catalyst solvent. The reactor pressures were varied from 163 to 300 psia, while the temperature was held constant at 120°C. Several syngas feed compositions used were: pure syngas (33.3% CO and 66.6% H₂), syngas with nitrogen (20% CO, 40% H₂ and 40% N₂) and syngas with excess CO (50% H₂ and 50% CO).

Steady-state was defined as a constant temperature (within 2°C of the set point) and instantaneous conversion (within 2% of the final value) for a period of two hours. Excellent temperature control was achieved for five of our six experimental runs. Runs where excellent temperature control was exhibited all contained 300 ml of solution in the reactor. The run conducted with 140 ml in the reactor exhibited poor temperature control (fluctuations up to 35°C about the set point were observed). The reason for improved temperature control at higher liquid levels was due to the improved liquid contact with the cooling coil in the reactor. Of the six experimental runs performed, only three achieved steady state. Their steady-state syngas conversions were 10, 12 and 20%. All three steady-state runs were conducted with excess as in the feed and indicate that this condition might be necessary to achieve steady state with the present reactor system. Three runs were conducted with pure syngas as feed. One operated at 100% syngas conversion for two hours and was shut down due to excessive accumulation of liquid in the reactor; the other two runs had continuously declining conversions (final instantaneous conversions were approximately 15 and 20%).

High initial conversions (80-100%) were achieved for all the runs with the conversion decaying to its final value after 1-2 hours. The initial high conversions indicate that the present reactor does not limit the maximum syngas conversion and that selection of a suitable set of operating parameters and procedure will permit high conversions at steady-state.

Analysis of the reactor products indicated that a significant amount of dimethyl ether was produced during all of the experiments. In four of the six runs, production of dimethyl ether was so large, there was a net consumption
of methanol. A possible cause for the formation of dimethyl ether was the high concentration of methanol in the reactor during the run. This results with the use of pure methanol as the solvent.

In addition to the formation of dimethyl ether, methyl formate was also found in the product from the reactor. Methyl formate is formed from the reaction of carbon monoxide and methanol. For all the runs conducted, high methanol versus methyl formate selectivities were obtained (75-100%).

Suggestions have been made for modifying the present reactor system so that eventual steady-state operation may be achieved with high conversions.
5. THE PRODUCTION OF METHYL FORMATE USING CO₂-RICH FEED GAS

MIT/BNL-86-3

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The Fuels and Catalysis Division of BNL is currently interested in examining the potential use of methanol as an intermediate in the production of important industrial chemicals, such as methyl formate. A conventional methyl formate process, developed by the UCB Corporation in Belgium, uses carbon monoxide and methanol, to produce methyl formate at 100 atm and 90°C. The process uses a sodium methoxide catalyst, some of which must be continuously added to overcome a poisoning reaction with carbon dioxide, which forms insoluble sodium methyl carbonate. The UCB process is believed to operate with a carbon dioxide scrubber and a catalyst regeneration system where the spent catalyst is flashed to recover methoxide.

One alternative to the UCB process is based on the decomposition reaction that potassium methyl carbonate (PMC) undergoes to produce methoxide anion and carbon dioxide. This process offers several advantages over the UCB process since it is carbon dioxide tolerant, thus eliminating the need for the scrubber and the catalyst regeneration system. Since the potassium catalyst produces methyl formate at a faster rate than the sodium catalyst, the proposed process may operate at a lower pressure as well. Potassium methoxide is a better catalyst than sodium methoxide; however, for economic reasons associated with the relative costs of these two compounds, UCB chose the sodium catalyst for their process.

Batch experiments verified that methyl formate can be produced in the presence of carbon dioxide, starting with PMC, methanol, and carbon monoxide. The PMC decomposed to form the methoxide catalyst and carbon dioxide, which was measured with a gas chromatograph. The reactions were carried out at temperatures between 80 and 150°C and at pressures between 200 and 1000 psia in a zipper-clave batch reactor. The rate of methyl formate production was found to increase with increasing temperatures. For an initial CO partial pressure of 900 psia at 150°C, 35% conversion of methyl formate and 7% decomposition of the PMC to carbon dioxide and methoxide were obtained.

An economic analysis was performed to determine the economic feasibility of producing methyl formate in the PMC process based on 10 million lb/yr of methyl formate production. The economics of UCB and PMC processes were compared for a synthesis feed gas from the air partial oxidation of natural gas, containing 10% carbon dioxide. For a plant capacity of 10 MM lb/yr of methyl formate, the return on investment (ROI) was found to be roughly 17% for both processes.
The performance of an iron-copper Fischer-Tropsch catalyst was studied in a slurry continuous stirred tank reactor (CSTR) at 227°C and 790 kPa (100 psig). While extensive Fischer-Tropsch studies have been published with iron-based catalysts in fixed-bed, fluidized-bed, and slurry reactors, no published work was found for an iron-copper catalyst in a slurry CSTR. The objectives of this study were to evaluate the catalyst performance on the basis of carbon monoxide conversion and product distribution, and to determine if methanol could be incorporated into the Fischer-Tropsch reaction by adding it continuously to the feed.

Conversion and product distribution data were obtained from gas chromatography and nuclear magnetic resonance analysis, flow contraction measurements and mass balances. The conversions and product distributions obtained with the iron-copper catalyst were within the range reported by other investigators using iron-based catalysts. Overall mass balance closures were between 88 and 94% for carbon and 91 and 99% for oxygen.

Carbon monoxide conversion decreased from 92 to 58% when the flowrate was increased from 0.3 to 0.9 liters/min, corresponding to an increase in space velocity from 488 to 1570 hr\(^{-1}\). The decrease in CO conversion was caused by a decrease in the average residence time of the gas in the reactor. Product distributions were identical for both 1:1 and 2:1 hydrogen to carbon monoxide ratios in the feed gas, and could be described by a Flory model with an average chain-growth probability (α) of 0.67 ± 0.02, indicating that most of the products (on a weight basis) were in the gasoline range.

While changing the hydrogen to carbon monoxide feed ratio from 2:1 to 1:1 did not affect the product distribution, the CO conversion dropped from 77 to 50% at a space velocity of 950 hr\(^{-1}\). The decrease in CO conversion may have been caused by the lower hydrogen partial pressure in the reactor, but this could not be confirmed due to a partial catalyst deactivation, possibly during the change over from 1:1 back to 2:1 H\(_2\)/CO feed gas.

To determine if Fischer-Tropsch reaction products could be incorporated into the production of higher molecular weight products, methanol was added continuously to the reactor feed at a rate of 0.072 ml/min. No noticeable incorporation was observed, and the methanol slowly oxidized and deactivated the catalyst over a period of approximately 12 hr.

Future Fischer-Tropsch studies using this iron-copper catalyst should be carried out over a range of temperature and pressure to fully characterize catalyst performance in the slurry reactor. In addition, the reactor should be operated for longer periods of time (>50 hr) to allow the larger molecular weight products to come to vapor-liquid equilibrium in the slurry phase.
Metal-hydride hydrogen compressors are being considered for the replacement of mechanical hydrogen compressors because they have few moving parts and can be powered by low-grade heat. The energy source for metal-hydride compressors is potentially very inexpensive because low-grade heat normally has limited applications and is often not utilized.

Metal hydrides absorb hydrogen exothermically at low temperature and pressure and desorb it endothermically, in a reversible reaction, at higher temperature and pressure. Specific metal hydrides may be developed for service between desired pressure and temperature ranges, and by staging several hydride beds of different composition, a high compression ratio can be achieved. Cycling hot and cold water in two sets of jacketed beds provides a continuous compression operation.

In the 1984 and 1985 hydrogen-compression Practice School studies, two different Ergenics, Inc. metal-hydride hydrogen compressors were tested at the BNL Hydrogen Technology Evaluation Center. The effects of hot water temperature, hot and cold water flowrate, cycle time and outlet pressure on average hydrogen flowrate were studied. The development of computer programs for the modeling of metal-hydride compressors met with little success.
EVALUATION OF THE PERFORMANCE AND APPLICATIONS
OF A METAL HYDRIDE HYDROGEN COMPRESSOR

MIT/BNL-84-2

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Hydrogen can be compressed with devices using chemical reactions of metal hydrides instead of mechanical action to increase the gas pressure. These compressors have the useful characteristic of being powered by heat exchange from low-cost, low-grade heat. Metal hydrides absorb hydrogen exothermically at low temperature and pressure and desorb it endothermically, in a reversible reaction, at higher temperature and pressure. Specific metal hydrides may be developed for service between desired pressure and temperature ranges, and by staging several hydride beds of different composition, a high compression ratio can be achieved. Cycling hot and cold water in two sets of jacketed beds provides a continuous compression operation.

A prototype compressor built by Ergenics Incorporated was evaluated by operating it over a wide range of water flowrates, hot water temperatures, inlet hydrogen pressures, and compressor cycle times. It was designed to operate with a 75°C hot stream and a 20°C cold stream to compress hydrogen from 0.30 MPa (50 psia) to 3.5 MPa (500 psia) at average flowrates of about 28 standard liters per minute (1 SCFM). The criteria in the performance evaluation were the average hydrogen flowrate, cycle efficiency (fraction of low-grade heat converted to work) and utilization efficiency (fraction of the available work in the two water streams converted to work).

The performance of the compressor was well below that reported previously for the same compressor. The measured maximum cycle efficiency was 2.14%, compared to 5.5% previously, and the maximum atomic ratio of hydrogen to metal (H/M ratio) in the LaNi₅ hydride bed was 0.47, previously reported as 0.65. The poor performance was probably due to alloy deactivation, with possible contributions from surface contamination (O₂ and H₂O), faulty hydrogen check valves, or faulty water check valves.

Various hydrogen power cycle applications of the compressor were examined. The high temperature (>350°C) heat conversion efficiency in a Brayton gas cycle increased from 40% with a mechanical compressor to over 85%. Large quantities of free hot water (70-90°C) and cheap cooling water must be available for this process to be economical. Electrical power generation, using the hydride compressor and a multi-stage, isothermal turbine, and requiring only low-grade heat input, is a possible application in remote areas where electricity is not available. Economically favorable application to hydrogen compression (compared to a conventional mechanical compressor) depends on the availability of low cost hot and cold water streams.
Hydrogen is an attractive energy source because it has the highest energy density per unit mass of any chemical fuel. The International Energy Agency has predicted that the direct use of hydrogen as a fuel will grow and eventually surpass all other uses of hydrogen. As a result, the need for reliable, inexpensive, and efficient hydrogen compressors will increase. Ergenics, Inc. has developed a new and potentially more reliable hydrogen compressor that utilizes the thermally activated reversible reaction between hydrogen and rare earth metal alloys to form metal hydrides. For large-scale commercial applications, the capacity of the Ergenics compressor must be increased from 3 SCFM to as much as 50,000 lb/day (6,240 SCFM) hydrogen output.

Public Service Electric and Gas Co. of New Jersey has purchased a four-stage Ergenics metal hydride hydrogen compressor; this compressor was located at the Hydrogen Technology Evaluation Center (HTEC) at BNL. Closed cycle tests were performed on this compressor and a Hamilton Standard solid-polymer electrolyzer was tested as a potential source of hydrogen for open cycle operation of the compressor.

Experiments were conducted on the integrated SPE electrolyzer/hydride compressor system at HTEC. A shakedown of the system was performed, followed by 19 experimental runs. The ranges of conditions studied were: 75-85°C for hot water temperature, 3-5 GPM for water flow rates, 2-5 min for cycle time, and 800-1000 psia for outlet pressure. The optimal operating conditions suggested by Ergenics were 85°C hot water, 16°C cold water, 4 GPM water flow rates, and 3-min cycle time; at these conditions, the rated capacity of the compressor is 3 SCFM.

The computer program, written by a previous MIT group (MIT/BNL-84-2) to model metal hydride compressor performance, was rewritten to improve its clarity and efficiency, i.e., to allow input of process conditions, bed properties, and compressor dimensions; and to enable the use of different bed properties for each stage in the compressor. At present, the model seems to correctly predict bed temperature variations but fails to predict reasonable bed pressure variations or hydrogen flow rates.

The results of this project can be summarized as follows:

1. Of the variables studied, hot water temperature had the largest effect on throughput and cycle and utilization efficiencies. Throughput increased with increasing hot water temperature and water flow rates and was maximized at a cycle time of 3 min. Cycle efficiency increased with hot water temperature, water flow rates, and cycle time; a maximum of 2.3% was
obtained. Utilization efficiency increased with increasing hot water temperature, decreased with increasing water flow rates, and was maximized at 7.1% at the cycle time of 3 min.

2. For the operating conditions suggested by Ergenics, the throughput obtained was 25% below the rated value of 3 SCFM. Increasing the water flow rates from 4 to 5 GPM increased throughput to 6% below rated flow.

3. The amortized cost for the hydride compressor with a closed heating stream is less than that for a diaphragm compressor if electricity costs are less than $0.07/kWh or if waste heat is used instead of electricity to reheat the hot water. The amortized cost of the hydride compressor with an open heating stream is less than that of the diaphragm compressor if hot water costs are below $3.50/1000 gal.

4. Scale-up of the current Ergenics compressor to 50,000 lb/day capacity presents extreme manifolding and control problems. Operating costs for this design are high ($70,000/day) because power and water requirements are large.
9. HIGH-TEMPERATURE STEAM ELECTROLYSIS

Due to finite fossil fuel reserves, interest exists in finding alternate fuel forms (such as hydrogen) that are storable and easily transportable. One of the major goals of the Chemical/Hydrogen Energy Systems (CHES) group at BNL is the development of technologies for producing hydrogen gas from non-petroleum feedstocks.

In particular, since water is an abundant resource CHES has been working on processes for producing hydrogen by the electrolysis of steam. The cost of producing hydrogen can be reduced by using high-temperature steam electrolysis (HTE) rather than conventional electrolysis because a larger portion (over one-quarter) of the endothermic heat of reaction can then be applied thermally rather than electrically.

Three Practice School projects have been conducted in the area of high-temperature steam electrolysis. In 1983, preliminary process designs that integrated a HTE unit with a thermal energy source and a heat recovery system were developed and economically analyzed. The 1985 project studied the mechanism of ion transport in the solid electrolytes BaSO₄ and AlPO₄. In 1986, the effect of Pr₂O₃ doping on the mechanism of the water decomposition reaction on the evolution of hydrogen was studied.
Manufacturing hydrogen by electrolyzing water vapor at higher temperatures has potential cost advantages over lower temperature processes because a portion of the endothermic heat of reaction can be supplied thermally rather than electrically. The feasibility of using high-temperature solid-oxide electrolytes for electrolysis of water vapor has been demonstrated by Westinghouse Electric Corp. Preliminary experiments performed by Westinghouse at 1000°C in ceramic electrolyte cells showed that high-temperature steam electrolysis (HTE) can be carried out at much lower cell potentials than those required by conventional electrolysis.

The first objective of this project was to develop preliminary process designs that integrated a HTE unit with a thermal energy source and heat recovery equipment. The thermal energy source selected was a coal-fired furnace operating at about 2000°C. The average electrolyzer operating temperature was assumed to be 1000°C. Heat exchangers were used to preheat the electrolyzer feed stream while cooling the hot product streams. Several alternative HTE process flowsheets were developed with particular emphasis being given to the replacement of electricity derived from coal with the less expensive direct use of coal-fired heat.

The second objective of this project was to analyze the economics of alternative HTE processes. To accomplish this, material and energy balances were made for the three process flowsheets selected. Electrolyzer steam conversions of 15 to 90% and hydrogen product pressures of 3 to 10 atm were considered. Operating and equipment costs were estimated based on the material and energy balance results. Finally, HTE hydrogen production cost estimates were compared with production costs obtained from the literature for other hydrogen manufacturing processes.

The major conclusions that can be drawn from this study are: (1) High-temperature electrolysis coupled with thermal and electrical energy derived from coal is not yet competitive with processes that make hydrogen from hydrocarbons. (2) Electrical power cost is the major component of HTE hydrogen production cost. (3) Replacement of electrical power input with thermal energy reduces HTE hydrogen production cost. (4) High electrolyzer steam conversions give the best thermodynamic efficiency in converting coal-fired heat into hydrogen. (5) The degree of heat recovery obtained has a strong effect on the thermodynamic efficiency of a HTE process.
Hydrogen production from steam electrolysis at high temperatures (HTE) require solid electrolytes. Previous work at BNL indicates that barium sulfate (BaSO₄) and aluminum phosphate (AlPO₄) might be suitable as solid electrolytes for steam electrolysis because of their relative stability to high temperatures and high pressure steam. Furthermore, earlier studies suggest that the conducting species in these solids may be protonic in nature. The use of a proton-conducting solid electrolyte in HTE is desirable because it would result in the production of a pure hydrogen stream rather than a steam-hydrogen stream.

The objective of this project was to determine the mechanism of ion transport in AlPO₄ and BaSO₄. Since the conducting species was suspected to be protonic, normal steam was substituted with deuterated steam (D₂O) to ascertain the effect of ionic mass on conductivity. If diffusion of an ionic species is responsible for conduction, then classical diffusion theory predicts that the conductivity is inversely proportional to the square root of the mass of the migrating species.

The conductivities of AlPO₄ and BaSO₄ wafers pressed at 40,000 psig were studied from 200 to 600°C in the presence of 100 psig steam. The conductivities were measured at 1000 Hz using an impedance bridge. Experimental results indicate that BaSO₄ may dissolve in high temperature steam; hence, BaSO₄ is an unsuitable electrolyte for HTE. Experimental results with AlPO₄ wafers showed a minimum conductivity (σ) at temperatures between 300 and 350°C. Modeling of the conductivity of AlPO₄ wafers at temperatures above 450°C (high temperature region), using an Arrhenius-type expression, yielded an activation energy of 1.0 eV. Conductivity has a strong negative dependence on temperature for temperatures between 200 and 300°C.

No isotope effect was observed in the high temperature region, which suggests that bare protons were not the primary conducting species, while scatter in the low temperature region masked any observable isotope effect. The change observed in conductivity as a function of temperature indicates that different conduction mechanisms operate in high and low temperature regions. Previous work at BNL showed that conductivity in the low temperature region is strongly dependent on steam pressure, which indicates that the conducting species in this region is water-related. This evidence, along with the strong negative dependence of conductivity on temperature, suggests that ion transport in the low temperature region is the result of conduction pathways created by adsorbed water on the surface of the AlPO₄ granules. Conduction along the surface is postulated to occur by a Grotthuss-type mechanism, which involves proton jumping from a H₃O⁺ molecule to an adjacent H₂O molecule, coupled with successive reorientations of the H₂O and H₃O⁺ molecules. The conduction mechanism is common in hydrated ionic solids containing long
channels. The observed decrease in conductivity with increasing temperature may be due to the loss of adsorbed water.

The relatively high activation energies (0.7 eV and 1.0 eV) of the high temperature region suggests that conduction at high temperatures occurs in the bulk of the crystal lattice. The absence of an isotope effect in this region indicates that conduction is the result of a defect transport mechanism and not bare proton migration.
The tubular high-temperature (1000°C) steam electrolysis (HTE) cells developed by Westinghouse are sealed at one end and use oxygen-ion conducting yttria-stabilized zirconia (YSZ) as the electrolyte. A steam/hydrogen gas stream flows continuously outside the HTE tubular cell, where it contacts the cathode and decomposes to hydrogen gas and oxygen ions when an external potential is applied. The oxygen ions migrate through the YSZ electrolyte to the anode, located on the inner side of the tubular cell, where they release electrons to form oxygen gas. Porous electrodes have been designed to maximize the creation of tri-phase boundaries that are junctions of the electrode, YSZ electrolyte, and gas. The overall rate of processes occurring at tri-phase boundaries greatly influences the efficiency of the electrolyzer. Work at both Westinghouse and BNL has shown that doping the cells with praseodymia (Pr$_2$O$_3$) enhances hydrogen evolution rates.

The primary objective of this project was to investigate the effect of Pr$_2$O$_3$ on the evolution of hydrogen and on the mechanism of the water decomposition reaction. A secondary objective was to propose HTE cell design modifications that would result in high steam utilization without excessive efficiency losses. To identify the mechanism of the reaction, cyclic voltammetry was performed on doped and undoped YSZ wafers by a single-point contact technique. The effects of steam/fraction Pr$_2$O$_3$ concentration, and depth of the dopant layer were studied.

Electrolytic wafers were prepared from a 6.9 mol% YSZ powder. Platinum paste was used for counter and reference electrodes, and a platinum-rhodium ball was used as the working electrode. Four wafers were tested: an undoped YSZ wafer; as 1 and a 5 mol% Pr$_2$O$_3$ doped wafer, each doped to 5% of the total wafer thickness; and a 5 mol% Pr$_2$O$_3$ doped wafer doped to 10% of the total wafer thickness. All wafers were examined under five steam/hydrogen atmospheres, which varied from 92 to 42% steam. Reaction atmosphere was controlled by passing a hydrogen/nitrogen mixture through water bubbler kept at 75°C. Cyclic voltammetry was performed at two scan rates (200 and 5 mV/s) with the voltage varying from -1.5 V to +1.5 V.

Under all experimental conditions, the cyclic voltammograms showed a hysteresis in the cathodic region, the current was greater on the return path than on the forward path. This can be explained by the presence of a region of reduced zirconia, which was observed around the point of contact on the YSZ wafer. Reduced zirconia also increases the number of vacancy sites in the YSZ lattice. Both of these factors enhance reaction rates and suggest that the reaction mechanism involves adsorption of water molecules onto vacant sites in the zirconia surface. This does not indicate, however, that water is adsorbed only onto the electrolyte.
Both doped and undoped wafers showed an unexpected trend during cyclic voltammetric runs under the fast and slow scan. The expected decrease in current at a given potential with decreasing steam fraction was not observed. Rather, the undoped wafer showed an increase in current (measured at -0.3 V) with decreasing steam fraction, and the doped wafers showed a current maximum at some steam fraction between 92 and 42%. This was also explained by the formation of reduced zirconia, which is favored at greater hydrogen concentrations.
9. STREAMING POTENTIALS IN CONDUCTIVE AND NONCONDUCTIVE TUBING

MIT/BNL-84-4

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Electroarteriogram (EAG) signals are being investigated as a noninvasive technique to analyze blood flow, artery characteristics, and electrolyte concentration. EAG signals were believed to be generated by streaming potentials caused by blood flow in the arteries. The relationship between blood flow and streaming potential is not fully understood; these interactions must be quantified before EAG signals can be used as a diagnostic tool.

The governing equations of streaming potentials for the laminar flow regime were first derived by Helmholtz in 1879. Recent work has extended the equations into the turbulent regime and verified them in experiments with non-conductive tubing. Blood flow can be either laminar or turbulent, and artery walls are conductive. Thus the objective of this project was to extend earlier studies to include systems that better model blood flow in arteries by quantifying the effects of hydrodynamics and electrolyte concentration on streaming potentials with both nonconductive (polyethylene) and conductive (Nafion, and both cationic and anionic exchange materials) tubing.

Experiments were performed with $10^{-4}$ and $10^{-5}$ M sodium chloride solutions. The results in experiment with nonconductive tubing supported the known hydrodynamic model, and streaming potentials were observed to decrease with increasing concentration. Experimental difficulties were encountered in experiments using conductive tubing due to the development of erratic potentials when the tubing was subjected to an applied stress. The apparatus was modified to minimize the stress exerted on the tubing and to reduce the level of noise in the signal. Neither Nafion nor cationic exchange tubing exhibited a measurable streaming potential, which may have been too small to detect due to the high surface conductivity of the tubing. Potentials measured on anionic exchange tubing appeared to increase with flow rate. The decrease in streaming potentials with electrolyte concentration and the existence of large stress potentials in conductive tubing suggest that the origin of EAG signals are probably not streaming potentials and should be reevaluated, since blood has a high electrolyte concentration and blood vessels are both flexible and conductive.
10. LOCALIZED ELECTROCHEMICAL CORROSION

The Practice School has participated in one project on localized electrochemical corrosion for each of the four years that it has been at BNL. Of interest to BNL is the fact that localized electrochemical corrosion of metals presents a problem in pressurized nuclear reactor steam generators and in containment vessels for radioactive wastes that are to last for up to 1000 years. Pitting, one of the most rapid types of corrosion, can lead to the breaching of vessel walls in periods of time much shorter than anticipated. The goal of the pitting corrosion program at BNL is to fundamentally understand the mechanism of localized electrochemical corrosion so that localized corrosion can be minimized in steel vessels. If this can be achieved, the rate of corrosion will be uniform and predictable, enabling designers to estimate the life of containment vessels.
In the presence of chloride ions, pitting corrosion of alloys such as stainless steel occurs only when a voltage difference between the metal surface and the bulk solution exceeds a minimum value called the critical pitting potential. This critical potential depends mainly on alloy composition, chloride concentration, pH value, and temperature. The corrosion rate at potentials just above the critical pitting potential is frequently diffusion controlled. (This was experimentally verified for potentiostatic metal dissolution conditions above the critical potential using a one-dimensional artificial pit consisting of a wire mounted in an inert support with the top surface exposed to a stagnant chloride solution. Current-time behavior showed that dissolution rate was diffusion-controlled with a concentration driving force and a diffusion length equivalent to the pit depth. In later experiments, the potential was suddenly lowered below the critical value, after establishing quasi-steady dissolution of the wire.) Nonlinearities in the shape of experimentally determined current-time decay curves at constant potential suggest the possible existence of multiple steady-states, where the rates of diffusion and dissolution are balanced.

The primary objective of this project was to experimentally establish the existence of multiple steady-states, by achieving different rates of corrosion (current density) under the same operating conditions (type of metal, bulk solution composition, applied potential, and temperature). A secondary objective was to model mathematically the rates of diffusion and electrochemical reaction in the system to predict the conditions under which multiple steady states would occur.

Experimentally, a steady-state current value for 304L stainless steel was reached at a 0.8 mm pit depth and a potential of -100 mV SCE. Experiments conducted at pit depths greater than 1.5 mm indicated the existence of two different steady states: an upper steady state corresponding to a high current density and an intermediate steady state corresponding to a lower current density (about 45% of the upper value). With respect to potential perturbations, the upper steady state was stable, whereas the intermediate steady state was unstable and moved towards the upper one under potentiostatic conditions. Microscopic observations of the metal surface at the intermediate steady state revealed the coexistence of two different surface morphologies: an active region and a passive region. The different surface morphologies caused nonuniform pitting and increased the effective surface area of the wire.

The computer model that was developed overpredicts the steady-state pit depth and underpredicts the value of the current density at the onset of a multiple steady state. This is possibly due to nonuniform pitting which tends to increase the surface area of the wire electrode.
Localized electrochemical, or "pitting," corrosion of metals has been an observed problem on the secondary side of pressurized nuclear reactor steam generators. Pitting occurs in aqueous solutions in the presence of an aggressive anion (chloride) and an oxidant (dissolved oxygen) at an electrical potential above a minimum potential called the critical pitting potential. Potential changes were monitored in this project to investigate specific conditions for the initiation and continued propagation of pits in Alloy 600 (75% Ni, 15% Cr, 10% Fe).

The results obtained using different Alloy 600 samples exhibited only limited reproducibility, most likely because of differences in the surface condition of the samples. The effect of the alloy surface condition on pitting should be studied in the future. Nevertheless, in general, its corrosion potential increased with increasing oxygen level, and decreased with temperature or when chloride was added.

The pitting potential for initiation decreased with increasing Cl\(^-\) concentration from +560 mV at 0.01 M to +230 mV at 1.0 M at 25°C and with increasing temperature from +560 mV at 25°C to 170 mV at 95°C for a 0.01 M NaCl solution. The pitting potential for propagation was approximately 40 to 130 mV above the pitting potential for initiation and showed comparable trends.

A theoretical model was developed which predicts ion concentrations within the pit, pit growth, and current density changes over time. A hemispherical pit geometry was assumed and the electromigrational and diffusional transport of the metal and chloride ions were considered. Additional assumptions were constant diffusivities and mobilities, Nernst-Einstein transport, and diffusion-controlled pit growth.

An explicit finite difference method was used to solve the model equations numerically. Because the explicit method of finite differences is not unconditionally stable, step sizes on the order of 1 x 10\(^{-10}\) sec and 10 Å were needed to obtain a stable, convergent solution. A large number of iterations were required to reach times of interest.

Based on diffusivities of the order 10\(^{-5}\) cm\(^2\)/sec and a constant 0.5 V potential driving force, the model predicts that ion concentration in the pit and current density increase exponentially with time until the solution in the pit became saturated with metal chloride. This occurred 2 x 10\(^{-7}\) sec after initiation. At saturation, a maximum current density of 7.2 x 10\(^4\) A/cm\(^2\) was attained. To reduce the number of iterations, an implicit or analytical method should be used to solve the model equations.
DISSOLUTION KINETICS OF IRON WITHIN ARTIFICIAL PITS

MIT/BNL-85-1

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BNL Consultant: H.S. Isaacs

A major problem in the disposal of radioactive wastes is the design of a container that will last 300 to 1000 years, as required by federal regulations. Pitting, one of the most rapid types of corrosion, could lead to perforation of the container walls in a shorter time period. The kinetic and mass transfer characteristics of the pitting corrosion process must be understood before radioactive waste containers can be accurately designed.

Tester and Isaacs (1975) have developed a mass transfer model valid for one-dimensional diffusion-controlled pitting corrosion of nickel and stainless steel in a variety of metal chloride solutions. According to their model, the current (the rate of corrosion) varies inversely with the square root of time in the diffusion controlled regime. This one-dimension diffusion model can be used to estimate the product of the metal ion diffusivity, D, and the saturation concentration of the metal ion at the metal-solution interface in the pit, C_{sat}, from potentiostatic current-time data.

The applicability of this model to the diffusion-controlled pitting corrosion of iron in 1 N sodium chloride and sodium sulfate solution was investigated at temperatures ranging from 25 to 85°C. An artificial pit apparatus and an experimental technique similar to that of Tester and Isaacs was used and the current was monitored as a function of time for a constant applied potential. Fitting this data to the Tester-Isaacs model, regressed values for ferrous ion diffusivity (D) were obtained over the experimental temperature range. For repeated runs, the scatter in D was around 100%. On examining the pitting process with a microscope, frequent but random occurrence of bubbles were observed within the pit along with the formation of a precipitate near the top of the pit. When the solution was deaerated by heating and purging with argon and the experiments repeated, the precipitate disappeared and reproducibility improved with the scatter dropping to 10%.

Gordon's correlation was then used to predict the diffusivity of the ferrous ion as a function of temperature, and the resulting values were compared with the diffusivities determined from the experimental data. For both chloride and sulfate solutions, the theoretically predicted and experimentally determined diffusivities increased with temperature but Gordon's correlation consistently predicted diffusivities greater than those experimentally determined. For chloride solutions, the predicted diffusivity was more than twice the experimentally determined value at 25°C; however, this discrepancy steadily increased by more than a factor of four at 85°C. This could be attributed to the numerous assumptions made in estimating the parameters in Gordon's equation for chloride solutions. For sulfate solutions, diffusivities compare better at high temperatures than for chloride solutions; data suggested the presence of different hydration states in the temperature range 60 to 70°C.
Pitting, the most common form of localized corrosion, occurs via the formation of a galvanic cell at the iron surface exposed to an electrolytic solution. Iron dissolution occurs at the bottom of the pit (anodic reaction) while a cathodic reaction, oxygen or hydrogen reduction, occurs at the surrounding metal surface. The iron ions in the pit solution hydrolyze to form hydrogen ions, lowering the pH locally. The decrease in pH inside the pit accelerates the growth of the pit by enhancing the dissolution of the metal. The cathodic reaction results in an increase in pH at the surface of the metal surrounding the pit due to the production of hydroxide ions or consumption of hydrogen ions. Therefore, the pH varies from the bottom of the pit to the surrounding metal surface. The objective of this project was to determine the influence of pH changes in unbuffered chloride and sulfate solutions on the localized corrosion of iron.

Two experimental apparatuses were used to determine the magnitude of pH in the solution adjacent to the bottom surface of an artificial pit. The first apparatus simulated a pit 16 mm in diameter and 41 mm deep. A flat-bottomed glass membrane pH probe of diameter 12 mm was inserted into the pit to measure the pH approximately 1 mm from the iron surface. The solutions used in the apparatus were 1 N and 2 N NaCl and 1 N and 2 N Na$_2$SO$_4$. Current densities used were 0.5, 5.0 and 10 mA/cm$^2$. After applying current, the pH and potential were recorded with time. The bulk pH of the electrolytic solution was in the range 6.5 to 7.5, and the pH measured after 2 hr was in the range 5 to 6. The runs were reproducible to approximately 0.5 pH unit.

Two separate simplifications were made for the first system in order to calculate to Fe$^{2+}$ concentration profiles in the bottom of the pit. First the iron which had dissolved was assumed to be uniformly contained in the volume beneath the probe. Second, an estimate of the rate of diffusion out of the region near the probe was made. The first simplification resulted in calculated Fe$^{2+}$ concentrations above that expected from the equilibrium at the measured pH. The second simplification accounted for the removal of Fe$^{2+}$ by diffusion and resulted in a good estimate of the Fe$^{2+}$ concentration at the measured pH.

In the second pit apparatus, which incorporated an antimony pH microprobe (tip diameter = 0.4 mm) so that the effect of the probe on the pH profile in the pit was effectively eliminated, the variation in pH was measured as a function of height above the pit bottom. The simulated pit had dimensions of 6 mm diameter and 18 mm deep; the probe was moved vertically in the pit by increments of 0.6 mm and the pH measured at each point after the system had reached a "quasi-steady state." Although the antimony probe was carefully calibrated in a series of standard buffer solutions, its response in the solutions studied was incorrect, indicating a pH of 3 to 4 in a neutral solution.
However, the small size of the probe did allow pH differences to be measured over distances less than 1 mm.

A one-dimensional transport model was derived to predict pH variations around the mouth of a pit. Because comparisons of the predicted and experimental profiles indicated the poor accuracy of the antimony probes, the validity of the model could not be verified.

The model outside the pit accounted for the presence of a cathode and predicted the pH variation with radial distance from the pit. For a bulk solution of pH 10, there is a critical value of pit radius (10⁻⁶ cm) above which there is a sharp pH decrease from the bulk pH to the pH at the pit mouth (pH=5). This critical radius, which does not exist for a solution of pH 7, indicates that in basic solutions pits greater than 10⁻⁶ cm in radius will exhibit a tendency to spread rather than deepen.
11. THE SEPARATION OF HELIUM-METHANE MIXTURES BY SINGLE-COLUMN PRESSURE SWING ADSORPTION

MIT/BNL-83-2

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In pressure swing adsorption (PSA) gas mixtures are separated in a packed column. PSA takes advantage of the different amounts of a heavy component that are adsorbed at different pressures: impurities are adsorbed during the high pressure steps (pressurization, constant feed/product recovery), which provides separation, and are subsequently desorbed during the low pressure step (blowdown). PSA has several advantages over alternative separation techniques for gas streams, such as removal of multiple impurities in a single column, high product purity, operation at ambient temperature, and high bed productivity associated with short cycle times. Unfortunately, there is no general model of PSA which can be used for preliminary process design at short cycle times. Previous investigators have developed both equilibrium and mass transfer limited models that agree with experimental results to within 10-15%. However, no comprehensive model has been developed to account for the combined effects of cycle time, pressure gradients across the bed during each cycle step, the adsorption of a nondilute species of the gas mixture, flow rates, feed composition, and a nonlinear equilibrium adsorption isotherm. The objectives of this project were: (1) to evaluate the performance of a single column pressure swing adsorption process for the separation of helium-methane mixtures with an activated carbon adsorbent using a three-step (pressurization, feed, and blowdown) cycle and (2) to develop a comprehensive mathematical model for the PSA process.

Experiments were conducted to determine the effect of the various operating parameters on PSA. Final product purity (He fraction) increased as feed time, product stream flowrate and methane mole fraction in the input stream were decreased. The lack of change in product purity indicates that the PSA process is equilibrium controlled. Mass transfer studies support this conclusion. The variation of average particle size of the adsorbent indicated no important intra-particle mass transfer resistance. Finally, the flow characteristics of the PSA column follow Darcy's law and a bed permeability was calculated from experimental results.

A theoretical model describing the three-step single column PSA cycle was based on overall and methane-component material balances. Using a Langmuir isotherm to describe the equilibrium between phases and Darcy's law to describe the bed flow characteristics, these governing equations were solved using the finite element method and the Galerkin method of weighted residuals. Oscillations inherent in the numerical approximation were damped using upwind dispersion and peak averaging. The solution algorithm did not converge quickly to a cyclic steady state. Model predictions of product purity were typically higher than observed experimental values.
In flash pyrolysis, coal particles are rapidly heated to reaction temperatures of about 900°C and the reaction is then rapidly quenched to prevent decomposition and reforming of the products. When flash pyrolysis is carried out in a methane atmosphere (a process termed flash methanolysis), gaseous hydrocarbons (ethylene, ethane and propane) and aromatics (benzene, toluene and xylene) are produced. Although the product yields are small, they are of potential commercial significance. Earlier research has indicated that the addition of nonreacting gases, such as helium or nitrogen, leads to an increase in product yields in flash methanolysis.

A 1/4-fractional factorial experiment at two levels was done to determine the effects of helium and nitrogen in the feed gas, system pressure, coal particle size, and methane-to-coal ratio on the yields of ethylene and benzene-toluene-xylene (BTX). The experiments were carried out in an 8-foot-long, 1-inch-diameter entrained downflow tubular reactor at 950°C using New Mexico subbituminous coal. Gas samples, which were taken from one of five sampling ports, were analyzed by an on-line gas chromatograph. This permitted the determination of gas composition as a function of residence time in the reactor, and provided a check on the consistency of our readings with time. Product char composition was determined by microanalytic elemental analysis.

Total yields of ethylene and BTX of up to 20% were obtained. Carbon balances of all runs closed to within 10%. Pressure, particle size and methane-to-coal ratio were found to have a significant effect on ethylene yields; however, any effect of helium or nitrogen composition in the feed gas was obscured by the standard error of the experiments. Ethylene yields increased at low pressure, small particle size and high methane-to-coal ratios. None of the variables studied has a significant effect on BTX yields.

The flash methanolysis process is transport limited, and not equilibrium controlled. The overall process appears to be exothermic. The heat of reaction correlates well with the ratio of methane conversion to coal conversion.

A preliminary economic analysis indicates that the flash methanolysis of coal to produce ethylene and BTX is currently not economically feasible and has a negative return on investment of 4.9%. A 19% percent increase in gaseous product value would be required for the process to break even, which corresponds to an ethylene price of $0.26/lb. However, commercial viability will depend on how quickly ethylene prices increase. An ethylene price of $0.39/lb is required for a 15% return on investment. Recent fluctuations in the price of petroleum feedstocks make the prediction of future ethylene prices extremely difficult.
13. BIOLEACHING AND BIOACCUMULATION

All three of the projects in this area were carried out by the 1986 Practice School groups. Each group worked on a bioleaching project and then one of the groups undertook the bioaccumulation project.

In the context of these BNL projects, bioleaching refers to the dissolution or solubilization of metals catalyzed by microorganisms. *Thiobacillus* bacteria were used in these studies because of their ability to oxidize insoluble heavy-metal compounds into more soluble forms. In particular, *Thiobacillus ferrooxidans*, which derives energy by catalyzing the solubilization of inorganic sulfur compounds was used in both the removal of metals from geothermal sludge and from coal. In the latter case, the *ferrooxidans* primarily promoted the oxidation of ferrous ions from pyrite to ferric ions, which produced sulfuric acid and more ferrous ions.

Bioaccumulation refers to the surface adsorption of metals on microorganisms. In such a biophysical process, the organisms can be in a dormant state, so no nutrients need to be supplied. Bioaccumulation occurs much faster than bioleaching, on the order of minutes rather than days. The adsorption of metals by microorganisms tend to be a species-specific process, that is, certain organisms adsorb certain metals better than others.

Bioleaching and bioaccumulation are complimentary processes. Bioleaching preferentially solubilizes metals from a solid while bioaccumulation preferentially removes metals from a solution to a solid. Both processes are necessary in the biological decontamination of a solid, whether it be geothermal sludge, coal or some other metal-laden solid. The end result is that a small amount of toxic metals from a large quantity of contaminated solids is concentrated in a small amount of biomass.
BIO-LEACHING OF TOXIC METALS FROM GEOTHERMAL WASTE

MIT/BNL-86-1

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BNL Consultants: L.E. Kukacka and E.T. Premuzic

Brines from the Salton Sea area in the Imperial Valley contain total dissolved solids up to 350,000 ppm, which lead to the generation of solid wastes in geothermal power plants. Currently, the disposal of these wastes can cost over $1 million per year for a 50-MW geothermal power plant operating in the Salton Sea area. High disposal costs and the long-term liability associated with hazardous waste disposal motivate this study of a biological solid-waste treatment facility.

The objective of this project was to estimate the economic impact of a biological solid-waste treatment facility on a base-case 50-MW double-flash geothermal power plant operating in the Salton Sea area. The bacteria Thio- bacillus thiooxidans and ferrooxidans were used to study the effect of sludge concentration, initial nutrient concentration, non-sterile conditions, agitation and air bubbling on the rate of bio-leaching of chromium and zinc contained in solid geothermal waste. (The sludge waste used in these experiments was given to BNL by a geothermal source in the Imperial Valley.) All experiments were performed in batch flasks and monitored daily for bacterial growth. The leachate was analyzed for chromium and zinc using an atomic absorption spectrometry.

Experimental results indicate that T. thiooxidans leached out 36% of the zinc in the sludge after 288 hr but leached little chromium. T. ferrooxidans leached out 60% of the chromium in the sludge after 250 hr but did not leach zinc. The acidity of the medium must be low (less than 1.7) for zinc to be leached from the sludge. Air-bubbling has little effect on the rate of bio-leaching and sludge to medium ratios of greater than 10% are toxic to the microorganisms. Both strains of bacteria survived under non-sterile conditions, and for a limited period (5 days) in temperatures as high as 120°F. In all the successful leaching experiments, the maximum amount of metals were leached after 10 days. The ferrooxidans leached out chromium to below the California threshold limits for chromate. However, within the time frame of the experiments, the thiooxidans did not leach zinc to below the California threshold limits.

These experimental results were used to design a biological solid-waste treatment plant, using as a basis 80,000 lb/day of geothermal sludge generated from a 50-MW double-flash plant located in the Salton Sea area of the Imperial Valley. In the proposed process, the 65 wt% solid waste slurry is sent to a thickener where nutrients, water and inoculum are added so that the solids liquid ratio is 5%. Based on the experimental results, a residence time in the thickener of about ten days was chosen. The leachate from the thickener containing the dissolved metals is neutralized, filtered, and reinjected. The resulting waste from the filter press should be a small fraction of the original amount of waste generated by the double-flash plant. The nonregulated solids remaining in the thickener are pumped through a second filter press.
where they are concentrated to 65 wt%. These nonregulated solids can be used as landfill or for construction materials, such as concrete.

The cost of a biological waste treatment plant (0.17-0.23¢/kWh) is about the same as the current cost of hauling the solid waste to a hazardous disposal site ($1,022,000 per year or 0.23¢/kWh). Either cost accounts for about 5% of the cost of generating electricity from geothermal power (about 4¢/kWh in 1986).
ENHANCEMENT OF COAL QUALITY BY MICROBIAL DEMETALIZATION AND DESULFURIZATION

MIT/BNL-86-8

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Precombustion desulfurization processes are being considered as a means of utilization of high-sulfur coals. While the level of sulfur in coal is very important, coal quality is also dependent on the quantity of ash in the coal. When coal is burned, ash that is carried out of the furnace with the hot combustion gases tends to foul heat exchange surfaces, thereby reducing furnace efficiency. The removal of metals from coal reduces the ash content, which reduces fouling.

Bioleaching with the bacterium Thiobacillus ferrooxidans results in the solubilization of inorganic sulfur compounds, mainly pyrite (FeS₂). The bacterium promotes oxidation of ferrous ions to ferric ions, which attack the pyrite, producing sulfuric acid and more ferrous ions. The acid and ferric ions may also enhance the solubilization of other metals in coal, including Ca, Mg, Al, Na, K, and Ti.

The effectiveness of microbial leaching with Thiobacillus ferrooxidans as a method of coal benefication was investigated. Particular emphasis was placed on the demetalization of coal by this bacterium, since little is known about this potentially beneficial aspect of bioleaching. Additionally, the economic feasibility of a commercial-scale microbial leaching process for coal desulfurization/demetalization was estimated. The proposed process was based on a newly constructed 500-MW power plant in Ohio and on 90% pyritic sulfur removal.

To characterize the effect of Thiobacillus ferrooxidans on the desulfurization/demetalization of coal, two experiments were conducted: the first focused on the influence of coal type and slurry concentrations, while the second investigated the effects of degree of agitation, particle size, temperature, nutrient concentration, and CO₂ concentration.

Slurries of Illinois #6, Pittsburgh #8, and Ohio Quarto #8 coals were prepared in concentrations of 10, 20, and 30% (g coal/100 ml nutrient solution). Inoculated and control (no bacteria) samples for all nine variable combinations were shaken mechanically and maintained at 27°C for 16 days. Samples were removed every two days to monitor pH and total iron and sulfate concentrations in the leachate. After 16 days, leachate metal concentrations were determined using atomic absorption spectroscopy.

Thiobacillus ferrooxidans enhanced the rate and extent of sulfur and iron leaching for all coals and slurry concentrations studied. The maximum amount of inorganic sulfur removed, as a fraction of the amount of inorganic sulfur, was 79%, and as a fraction of total sulfur was 41% for the 10% slurry of Ohio #8 coal, while the maximum amount of iron removed was 45% for the 10% slurry of Pittsburgh #8 coal. The Ohio coal showed the earliest onset of bacterial
activity (5-6 days). As the coal slurry concentration increased, the percent removal of inorganic sulfur and iron decreased, possibly due to insufficient mixing at the 20 and 30% slurry concentrations.

*Thiobacillus ferrooxidans* also slightly enhanced aluminum leaching, although in absolute terms, little aluminum was removed with or without bacteria. All coal types exhibited roughly the same percentage of aluminum removal at a given slurry concentration. Aluminum removal was again inversely related to slurry concentration, decreasing from about 0.65% for 10% slurries to about 0.49% for 30% slurries. *Thiobacillus ferrooxidans* had no effect on the leaching of magnesium, calcium, and sodium, which were removed by solubilization. The Illinois #6 had far greater removal of magnesium, calcium, and sodium (roughly 60, 70, and 75%, respectively) than the other two coals.

In a second set of experiments, particle size, temperature, degree of agitation, nutrient concentration, and CO₂ concentration were varied independently for 20% slurries of the Ohio Quarto #8 coal. The CO₂ concentration was varied by bubbling air or a 10 mol% CO₂ mixture through an agitated/ventilated slurry.

After 11 days, a 20% (absolute) reduction in inorganic sulfur removal was observed at 37°C versus 27°C, and 15% (absolute) less sulfur removed at the higher (fivefold increase) nutrient concentration. Increased agitation independently increased sulfur removal, supporting the conclusion that poor mixing had occurred in the 20% and 30% mechanically shaken slurries. Decreased particle size increases sulfur removal. The CO₂ concentration had no effect on sulfur or iron removal, while the bubbling increased iron and sulfur removal significantly, and also improved aluminum removal. However, the bubbling had no effect on the removal of sodium, magnesium, calcium, or potassium.

The effect of bacterial demetalization of coal was also investigated by considering the changes in ash content and ash fusion temperature, which is a function of ash composition. Bacterial treatment reduced ash content for all three coals. Pittsburgh coal showed the largest percentage ash removal -27% reduction with *T. ferrooxidans* compared to 18% without. The hemispherical ash fusion temperature of Pittsburgh and Ohio coal samples increased between 150°F and 450°F due to bacterial leaching. For the Illinois #6 coal, there was no effect of bacterial leaching on the hemispherical ash fusion temperature.

A commercial microbial leaching process was proposed to remove 90% of the inorganic sulfur in Ohio Quarto #8 coal at a new 500 MW utility in Ohio. Capital costs estimated for this process include the costs of land, equipment, installation, and working capital. Annual operating costs consist of the costs of electricity, steam, nutrients, lime, sulfuric acid, lost coal, labor, and maintenance. The total capital cost is $27 million; the annual operating cost is $26 million. The total cost of the proposed process is $9.58 per ton of coal treated, which compares well to the costs of other proposed coal beneficitation processes. This cost is not sensitive to the capital cost, but is highly sensitive to annual operating costs.
Microorganisms such as bacteria, algae, and fungi can adsorb and concentrate metals from their environment. During this biophysical process, termed bioaccumulation, the biomass is in a dormant state, so no nutrients need to be supplied. The objective of this project was to determine the feasibility of an industrial process using bioaccumulation for the metal detoxification of dilute wastewater. In particular, an actual 720,000-GPD industrial waste stream containing Cr (as chromate), Cu, Mn, Ni, and Zn was chosen as a basis. The amount of Ni and Zn present was less than the maximum allowed in discharges to drinking water by Federal and New York State regulations; thus, only the removal of Cr, Cu, and Mn was examined.

The ability of five microorganisms to remove Cr (as chromate), Cu, and Mn from solution was quantified by exposing single-metal solutions of known concentrations to different amounts of biomass. The mixture was filtered after 30 min of exposure, and the filtrate was analyzed by atomic absorption spectroscopy (AA) to determine the amount of metal remaining in solution. Two bacteria, Escherichia coli and Sphaerotilus natans; two algae, Synechococcus and Cyanidium caldarium; and a yeast, Saccharomyces cerevisiae, were studied. The experiments were conducted at 25°C and at pH 5 to 6 under nonsterile conditions. Metal removal was complete within 30 min. Agitation had no effect on the removal rate.

Escherichia coli was the most effective microorganism studied in removing Cu and Mn: at a concentration of 500 mg/l, E. coli removed 75% of the Cu from a solution of 3.23 mg/l Cu and 95% of the Mn from a solution of 0.67 mg/l Mn. The least effective microorganism was Saccharomyces cerevisiae. A concentration of 10,000 mg/l of S. cerevisiae was required to remove 73% of the Cu from a solution of 3.41 mg/l Cu and 58% of the Mn from a solution of 0.82 mg/l Mn. None of the microorganisms tested was able to remove significant amounts of chromate. However, the amount of chromate removal increased as the pH was lowered; at pH 3.2, 500 mg/l of E. coli removed 18% of the chromate from a solution of 1.58 mg/l Cr and at pH 2.25, 10,000 mg/l of S. cerevisiae removed 42% of the chromate from a solution of 1.39 mg/l Cr. At very low pHs (1.8), the removal of chromate decreased, possibly due to the destruction of the cellular surface by the acidic environment. The removal of Cu, however, was hindered by lowering the pH.

Due to the inability of the chosen microorganisms to remove chromate, an initial chemical treatment step is required to reduce chromate to chromic, Cr(III), which precipitates from solution at pH 6.0. The waste stream would then contain Cu, Mn, Ni, and Zn, which could be treated successfully with E. coli. To determine the approximate amount of biomass required to reduce the metals content of the waste stream to meet environmental standards, bioaccumulation experiments were performed on a simulation of the industrial wastewater. The solution used contained 2.48 mg/l Cu, 1.29 mg/l Mn, 1.0 mg/l Ni,
and 2.19 mg/1 Zn. At a concentration of 500 mg/1 of E. coli, Cu was removed in the greatest quantity (1.6 mg/1 removed), also 0.28 mg/1 Mn was removed but no Zn was removed. At 1500 mg/1 of E. coli, both Cu (2.35 mg/1 removed) and Mn (0.99 mg/1 removed) met their respective environmental limits.

An industrial bioaccumulation process has been proposed to detoxify the industrial waste stream using E. coli. The concentrations of metals in the waste stream were determined to be: 1.6 mg/1 Cr (as chromate), 3.3 mg/1 Cu, 0.8 mg/1 Mn, 0.7 mg/1 Ni, and 0.8 mg/1 Zn. The flow rate of the waste stream is 720,000 GPD. Chromate is first removed by SO2 reduction to chromic at pH 2 and precipitation by raising the pH to 6; the remaining metals are removed by treatment with 1500 mg/1 E. coli at pH 6. The bacteria is grown in a fermenter and filtered to remove the growth media before being mixed with the waste stream. The biomass contacts the wastewater for 10 min in a baffled vessel and is removed by rotary drum vacuum filtration. The waste biomass is dried, drummed, and trucked to a landfill site. The treated water is analyzed for metals content, and discharged if it meets environmental standards; otherwise it is retreated.

The capital cost of the process was estimated to be $8.67 million. Operating costs were estimated to be 0.56¢/gal of treated water, plus 0.40¢/gal for the amortization of capital. The total cost of 0.96¢/gal compares favorably with the criterion of 1.0 to 1.5¢/gal specified by the generator of the basis waste stream.

The use of conventional chemical precipitation was also investigated as a means of treating the basis waste stream. It was experimentally confirmed that the metals in the waste could be precipitated at pH 10 to meet environmental regulations. The total cost of the chemical precipitation plant was estimated at 0.67¢/gal, which is about one-third less than the cost of bioaccumulation. For this particular waste stream, chemical treatment will always be less expensive than bioaccumulation because of the additional nutrient and solid-waste disposal costs associated with bioaccumulation. Therefore, on a purely economic basis, chemical treatment is recommended for this particular industrial waste stream; however, the moderate cost of bioaccumulation suggests that it may be the more economic alternative for streams of different compositions. Also, for other reasons, including environmental concerns, bioaccumulation may be preferred.

The results of this study suggest that bioaccumulation is a feasible method for metal detoxification of aqueous waste, although it is not the most economic method for the industrial waste stream of primary interest in this report. The discovery or development of a microorganism that could remove chromate has the potential for decreasing operating costs; the chromate-reduction facility could then be eliminated. Bioaccumulation also shows promise for waste streams containing metals that are difficult to precipitate. Therefore, it is recommended that: (1) research continue with efforts directed toward obtaining a microorganism that is an effective accumulator of chromate and (2) experiments be conducted with solutions of metals that preclude removal by conventional methods.
14. CONTROL AND TREATMENT OF AQUEOUS LOW LEVEL RADIOACTIVE WASTE

MIT/BNL-86-7

MIT Group: T.F. Morse and T-C. Lee

The annual average level of radioactivity in the BNL discharge to the Peconic River has always been below the EPA Drinking Water Standard; however, last year's daily fluctuations in activity show that the limit was exceeded once for 3 days by a factor of 3 to 4. Even on those days when the discharge contained activity in excess of the EPA's Drinking Water Standards, the DOE limit for surface water discharges ($2.4 \times 10^{-9}$ Ci/ml) was not exceeded. Nevertheless, as part of its civic responsibility, BNL would like to eliminate its aqueous radioactive discharges.

BNL facilities that routinely discharge large volumes of low level aqueous waste are provided with a dual waste handling system to segregate the "inactive" F waste (below $9 \times 10^{-11}$ Ci/ml) from the "active" D waste (between $9 \times 10^{-11}$ and $7 \times 10^{-9}$ Ci/ml). F waste is checked for radioactivity before being sent to the Laboratory Sewage Treatment Plant (STP), while D waste is sent to the Waste Concentration Facility (WCF) for the removal of radioactive cations. While nonvolatile radioactive contaminants in the D waste stream are removed by the WCF tritiated water (HTO) is not because the vapor pressures of HTO and $H_2O$ are very similar. As a result, the discharge to and from the STP contains tritiated water. Concern over tritiated water emissions at BNL has recently increased due to the discovery of HTO in off-site ground water monitoring wells. As a result, tritiated water discharge to the Peconic has been discontinued, causing a large backlog of D waste being held in BNL's limited storage facilities.

The objectives of this project were (1) to analyze the Waste Concentration Facility and determine the costs of repair or replacement of expensive parts deemed most likely to fail, (2) to evaluate the potential of alternative processes for concentrating D waste, and (3) to analyze various alternatives for disposing tritiated water. In order to achieve these objectives, the problem was divided into two parts; examination of the WCF processes and evaluation of the tritiated water disposal methods.

The components that were considered in the failure analysis of the WCF were the blower and the evaporator. (The feed preheater was discarded from the analysis because it is in excellent condition and not prone to failure while the mesh filter and pumps were discarded because they are inexpensive to replace or repair.) The WCF blower, a Read-Standard straight lobe rotary blower, can be replaced with an equivalent-sized unit for approximately $10,000. The current evaporator was installed in 1956 after the original one failed. The total expense for repairing the evaporator calandria, which consists of a cluster of 865 heat exchanger tubes, is $14,500 plus an additional $164 per tube. Since the installed replacement cost of the evaporator calandria is less than four times the repair cost, replacement of the calandria should be considered whenever repairs are required.
Among the alternative processes considered as replacements for the WCF are ion exchange, reverse osmosis and flocculation. Since all of these processes would be much more expensive than the existing system for the treatment of D waste, the WCF should be repaired as required rather than replaced.

Three alternatives for tritiated water disposal have been investigated in detail. They include an evaporation process using a sloped pond, an atomization system to vaporize the water, and another evaporation process which utilizes a covered pond. The evaporation process with the sloped pond offers the most politically attractive alternative since its location is not highly visible. The tritiated water disposal capacity of this system is about 170,000 gal/yr and its total installed cost is approximately $115,000. Evaporation with the covered ponds by adapting two existing structures would cost about $50,000; however, the evaporative capacity would only be 94,000 gal/yr. Construction of an additional covered pond to increase the evaporative capacity to 141,000 gal/yr would cost an additional $51,000. If the existing structures cannot be used, the cost of constructing three covered ponds would be about $153,000.
BNL currently uses two methods to measure trace amounts (0.1-5 ppbv) of \( \text{H}_2\text{O}_2 \) that occur in the atmosphere. These methods involve the use of a diffusion scrubber or an impinger to absorb \( \text{H}_2\text{O}_2 \) from a controlled air stream into an aqueous phase, which is later analyzed for \( \text{H}_2\text{O}_2 \) content by (p-hydroxyphenyl) acetic acid (PHOPA) fluorescence. The liquid absorption techniques facilitate analysis for \( \text{H}_2\text{O}_2 \) by concentrating the small amounts of gaseous \( \text{H}_2\text{O}_2 \) in the atmosphere, but are limited by the reactive nature of \( \text{H}_2\text{O}_2 \). Sulphur dioxide or ozone in the sampled air can interfere with the peroxide measurement by destroying \( \text{H}_2\text{O}_2 \) or creating artifact \( \text{H}_2\text{O}_2 \) in the aqueous phase. Reduction of these interferences is difficult and inconvenient.

The cryogenic removal of \( \text{H}_2\text{O}_2 \) from air into a solid phase may reduce reactivity of \( \text{H}_2\text{O}_2 \) and thereby minimize interferences. Hydrogen peroxide is expected to be co-collected with ice, which can then be melted and analyzed fluorimetrically. The objectives of this project were to design and optimize the performance of a cryogenic sampler for co-collection of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) from ambient streams into the ice phase for subsequent analysis, and to compare the performance of the designed cryogenic method with the existing BNL impinger sampling method.

Thirty centimeter glass U-tubes of 0.5, 1, and 2-cm ID were considered as possible sampler designs; helical tubes of 0.5 and 1-cm ID and 3 and 1.2-meter lengths, respectively, were also examined in an attempt to increase interior surface area. These prototypes were evaluated on the basis of water collection efficiency.

Clean tank air was humidified to 50% relative humidity by water bubblers and passed through the U-tubes and helical tubes immersed in Dewar flasks filled with an acetone-dry ice mixture. The 1-cm diameter U-tube achieved a water collection efficiency of 62.6 ± 2.9% for seven 45-min runs at an air flow rate of 8 l/min. The 0.5 cm helix consistently clogged with collected ice midway through the run, and therefore, did not collect a sufficiently large water sample. While water collection efficiency for the 1-cm helix (84% for one run) was higher than for the 1-cm U-tube, the collected water was difficult to remove quantitatively from the sampler because of the geometry and the high surface area; the amount of water recovered from helix was therefore smaller than for the U-tube. The 1-cm U-tube design was selected for further characterization because of the consistency of the observed water collection efficiencies.

The effectiveness of the U-tube at removing hydrogen peroxide from air under laboratory conditions was investigated by introducing a 30 ml/min air
stream with an approximately 450 ppbv H$_2$O$_2$ content into the 3 l/min flow used in the water collection experiments; the resulting prepared air contained 1.5 ppbv H$_2$O$_2$ at 50% humidity. The hydrogen peroxide source consisted of a porous Teflon tube immersed in 0.018 M H$_2$O$_2$ in water, which was maintained at 19°C. Teflon tubing was used for all lines after peroxide introduction to minimize adsorption losses of H$_2$O$_2$. The 1-cm U-tube achieved 107% H$_2$O$_2$ collection efficiency, indicating complete removal of peroxide within experimental error. This compared well with the collection efficiency obtained by the standard BNL water impinger (116%) in tests under the same conditions. The difference between observed water and H$_2$O$_2$ collection efficiencies indicates that water and peroxide are collected by different mechanisms.

The U-tube sampler was modeled as a cylindrical tube by assuming that the air entered the sampler with uniform H$_2$O concentration, at a uniform temperature, and with a flat velocity profile. The model indicates that the temperature difference between the bulk air stream and the wall decreases exponentially with axial distance, as does the water/H$_2$O$_2$ concentration. For the conditions of the water collection experiments, the model predicts a temperature at 30 cm of -15°C, which is in good agreement with the observed value of -15°C. The model predicts water collection efficiencies of 54%, somewhat lower than the observed 63%, partly due to conditions which were not included in the model. Importantly, the model also predicts the occurrence of condensation and sublimation in the U-tube, supporting experimental observations.
Conducting polymers are of interest because of their possible uses in batteries and electrochromic devices. Many of these materials exhibit a hysteresis effect when a cyclic potential is applied. Particular attention has been focused on polyaniline because it displays a clean, sharp hysteresis that is scan rate independent. The redox behavior of polyaniline is being studied to provide a better understanding of the hysteresis in the redox switching of electrically conducting polymers.

Earlier studies showed the scan rate independence of hysteresis characterized by the constant anodic and cathodic peak separation in a cyclic voltammogram. To verify this result, polyaniline was galvanostatically synthesized on a platinum electrode in a 2 N HCl solution. A cyclic voltammogram was generated by ramping the applied potential from -0.3 to 0.6 V vs. SCE at scan rates between 5 and 100 mV/s. These results confirmed that the peak separation was scan rate independent.

In addition, an attempt was made to improve the experimental protocol used in previous studies. The platinum electrode was replaced with an indium tin-oxide coated glass slide. This replacement reduced the apparent capacitive current in the reduced state of the polyaniline, which was probably due to hydrogen evolution on the platinum surface.

The hysteresis of polyaniline was also studied using spectroelectrochemical techniques. By applying a tungsten light source and measuring absorbance at various optical wavelengths while generating a cyclic voltammogram, the absorbance versus total charge behavior was investigated, which indicated the presence of at least three different charge domains within the polyaniline. These charge domains each have N-shaped free energy curves similar to the N-shaped pressure/composition isotherms that can explain the hysteresis observed in metal hydride systems. With this model, the spectroelectrochemical behavior of polyaniline could be completely explained.
17. CONTROL OF TOXIC GAS RELEASE DURING THE PRODUCTION OF CuInSe$_2$
PHOTOVOLTAIC CELLS

MIT/BNL-86-4

MIT Group: P.K. Fowler, D.G. Dobryn and C.M. Lee
BNL Consultants: V.M. Fthenakis and P.D. Moskowitz

A number of processes are currently being investigated for mass production of CuInSe$_2$/CdS heterojunction photovoltaic (PV) cells. Reactive sputtering deposition of the CuInSe$_2$ and CdS layers which uses two highly toxic gases, H$_2$Se and H$_2$S, is a leading candidate. The deposition process for the CuInSe$_2$ and CdS layers is only about 40% efficient; the remaining unreacted gases (~60%) must be reduced to safe levels before release to the atmosphere. In addition, massive release of H$_2$Se and H$_2$S could be life threatening to nearby population centers. Toxic gas control systems are therefore needed for treating the routine amounts of unreacted gases and possible accidental releases.

The basis for designing such a toxic gas control system in this study was a PV cell plant with an annual production of modules capable of generating 10 MWp of power at AM1 conditions. It was assumed that each module had a solar to electric conversion efficiency of 12% and 0.65-m$^2$ active surface area so that the facility produced 128,000 modules/annually.

In the production of these cells, CuInSe$_2$ (and CdS) are deposited on the cell substrate by reactive sputtering sources in a vacuum chamber under an argon and H$_2$Se (and H$_2$S) atmosphere. The concentrations of H$_2$Se (and H$_2$S) in unreacted streams depend on the amount of argon used in the process, the material requirements of the PV cell, and the conversion efficiency. Based on assumptions about these parameters, routine emission flows to a treatment facility of 2.2 and 0.9 g/min at concentrations of 10,300 and 4,200 ppm were estimated for H$_2$Se and H$_2$S, respectively. The accidental release scenarios considered in this study assume the release of one cylinder (one-half week's inventory) of each gas, 16 kg of H$_2$Se and 6.5 kg of H$_2$S.

Treatment alternatives investigated for routine and accidental releases were caustic scrubbing, carbon adsorption, and combustion. Scrubbing and adsorption are viable options, but the toxicity of H$_2$Se and H$_2$S combustion products eliminated combustion from further consideration.

Both venturi and packed-bed scrubbers were designed for routine releases. A venturi scrubber has a low removal efficiency (50 to 80%) but is useful for treating high gas concentrations since precipitating salts are not a problem. The packed-bed scrubber has a high removal efficiency (90 to 99.9%) but cannot handle high gas concentrations because precipitating salts would clog the bed. Caustic-impregnated activated carbon adsorption has the highest removal efficiency (>99.99%) and can reduce gas concentrations to below 0.004 ppm; however, inlet gas concentrations must be kept below 100 ppm.

Routine and accidental release treatment facilities should be separate for safe and optimum performance. Routine emissions from the base case 10-MWp
CuInSe$_2$ plant are best handled by a series of systems: (1) venturi scrubber, (2) packed-bed scrubber, and (3) activated carbon adsorption bed. This series of treatment systems can effectively reduce the toxic gas concentration of the unvented gases from 14,500 ppm to less than 0.004 ppm; the incremental production cost for such a routine release facility was estimated to be 0.62¢/Wp.

The strategy used for treating accidental releases of toxic gases is to contain the released gases and then divert them to a treatment facility. A ventilation system comprising gas storage cabinets, ducts enclosing toxic gas lines, and enclosures around the manufacturing equipment has been proposed. Purge air pulled through this system would automatically take toxic gas releases to the accidental release treatment facility. Two alternative facilities are considered. One is a 425-SCFM packed-bed scrubber and adsorption bed for continuously treating the purge with caustic solution at a high recirculation rate, with provision for adding more NaOCl to the caustic storage tank in case of an accidental release. The other was a containment scheme whereby the toxic gases would be compressed into a pressure vessel and caustic solution would be sprayed into the vessel to neutralize them; when the concentration is down to 100 ppm, the gas can be treated by an activated carbon adsorption bed. The incremental production cost was estimated to be 0.91¢/Wp for the packed-bed scrubber alternative and 1.25¢/Wp for the containment scheme.
The staff of the MIT Practice School and the BNL Coordinator would like to graciously acknowledge the efforts of all the BNL secretaries and administrative assistants who made the publication of the 28 MIT/BNL reports possible, including Betty Ivero, Francine Donnelly, Marguerite Marsch, Paula Appling, Trudi Neuhoff, Pat Towey, and various members of the DAS Micom Group under Catherine Tierney's direction.
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