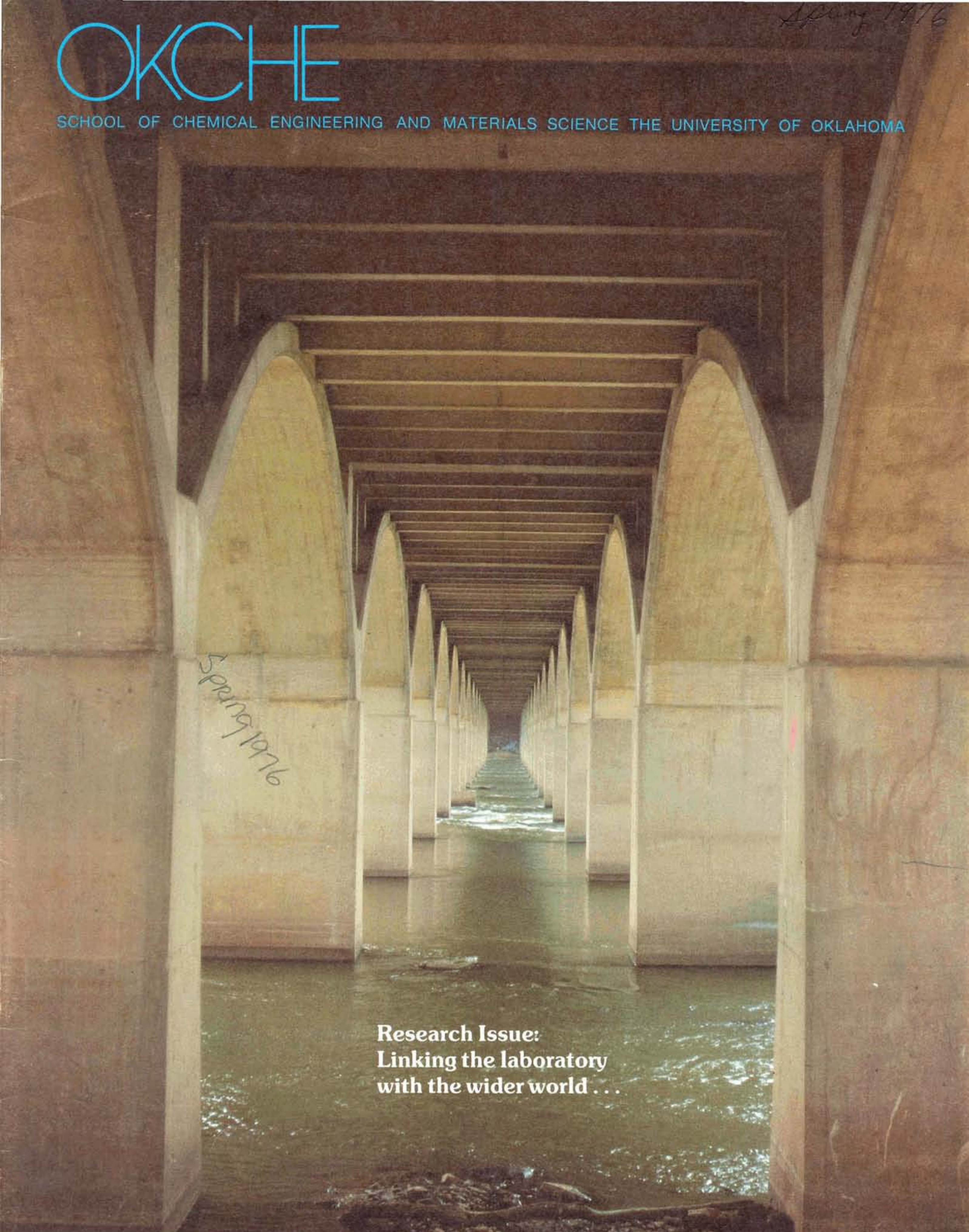
# OKCHE

SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE THE UNIVERSITY OF OKLAHOMA

Spring 1976



Spring 1976

**Research Issue:**
**Linking the laboratory with the wider world . . .**

***On the cover:***
*A new way of looking at it! Twenty-first Street bridge over Arkansas River, Tulsa, as shot by University Publications Director Bill Williams. A more traditional view, shown above. For research update on bridge deck deterioration in the state, see page five.*

# CONTENTS

SPRING, 1976

# The Cycle of Research . . .

The CEMS Faculty of the University of Oklahoma is not content to sit and observe. Much time and effort is spent in seeking the new, the undiscovered—through research.

To those of us who spend our days . . . and an occasional night . . . bent over potentiostats or calorimeters, the rationale for the laboratory life seems apparent. Research activity complements our teaching role. Therefore, the students—especially those who play a vital role in the experiments—become the first benefactors.

There is a slightly selfish aspect for the researcher, too: the personal reward of knowing that he has added a jot or digit of significance to the accumulation of knowledge in his special field.

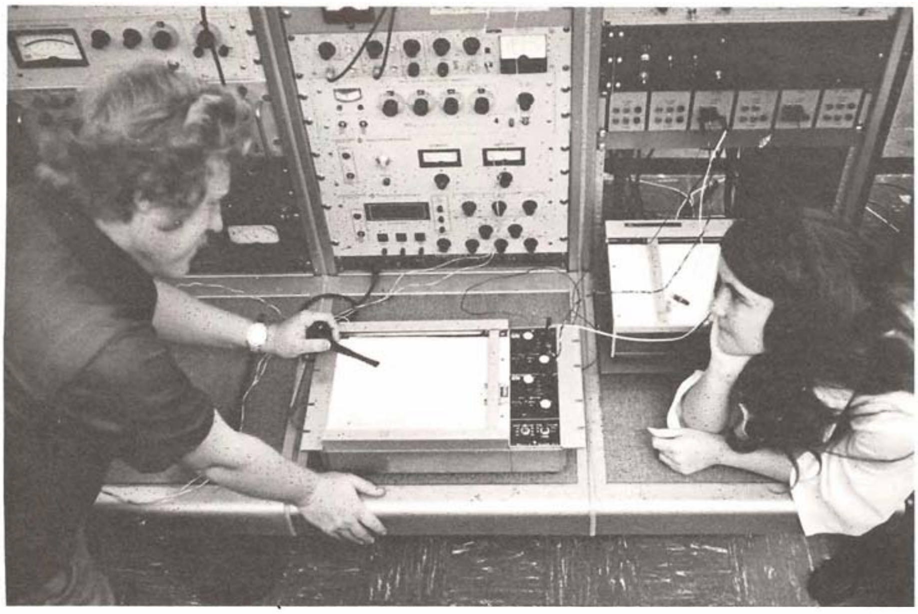
But what of the world Out There . . . beyond the Engineering Center? How does this activity link us together?

The best answer to that question is offered in the wide spectrum of subjects covered in the progress reports that follow. They range from studies on the feasibility of alternate energy sources (geothermal, ocean thermal) to the development of a substitute material cheaper than gold used to crown a tooth.

Call it technology development, if you like; the term is apt. But whether it be the analysis of materials to use in building stronger bridges, or the refinement of a compound to produce a pill without side effects . . . the ultimate goal is the same—finding a better way.

The next eleven pages of this Research issue will give you an inkling of how we are seeking that better way . . . here and now.

*Dr. Arthur Aldag, analyzing Auger spectra of nickel-crystals after forming acid decomposition, as junior Sheila Stuckey looks on.*



*Arthur W. Aldag*
*Associate Professor*
*Chemical Engineering*
*and Materials Science*

## Olefin Disproportionation

The first olefin disproportionation (poly-olefin) catalysts were discovered in the Phillips Petroleum research laboratories in the 1950's. The process was commercialized and licensed by Phillips and is still used to produce small volume specialty olefins. The list of catalysts that have been found to be active for this reaction has grown rapidly over the past few years and includes a number of metal oxides and sulfides as well as a wide range of homogeneous metal complex catalysts.

We have been studying the disproportionation reaction of olefins on supported rhenium oxide catalysts. We have used both alumina and silica gel to support or disperse the metal oxide and find that the alumina supported samples are very active, even at room temperature for the disproportionation of propylene. However, under otherwise identical reaction conditions the silica supported samples were found to be inactive. These results emphasize that the carrier, which is sometimes considered inert. can have a profound effect on catalytic activity of the "active" component particularly when this component is dispersed into very small particles.

We also found significant differences in the degree to which the metal oxide could be reduced by hydrogen when dispersed on alumina and silica gel. The silica supported sample could be reduced quite readily, possibly to the metallic state by hydrogen or even the reactant olefin. By contrast, the alumina supported catalyst could be reduced only with $H_2$ at 500°C and then only to an intermediate oxide level.

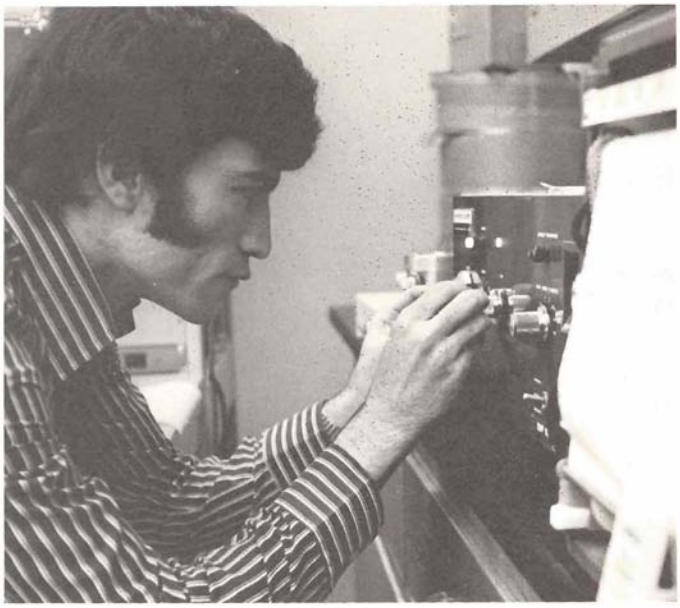
Finally, we have measured the extent of adsorption and the disproportionation rate for ethylene on the alumina supported rhenium oxide catalyst. Our results suggest that the reaction proceeds through an elementary step involving the interaction of two adsorbed olefin molecules. We are also able to obtain values for the rate constant and activation energy for the elementary step occurring on the surface.

We plan to continue this work to include the disproportionation of 2-butene which is another molecule for which we can independently measure extents of adsorption and reaction rates. Hopefully we can gain some better insight into the relationship between molecular properties and the kinetic parameters. We would also like to include other catalyst supports to better define the interaction between the catalytically active component and the carrier material.

## Surface Studies Laboratory

Of critical importance in achieving a better understanding of those factors that control the activity and selectivity of a catalyst is an accurate characterization of the surface composition. All catalysts are affected by the presence of poisons and surface contaminants such as carbon, oxygen, and sulfur. In addition, with metal alloy catalysts, the percentage of the metal components at the surface may differ appreciably from that of the bulk. Until very recently the composition of a catalyst surface could be estimated at best only by indirect means. There are now available a number of non-destructive research techniques that allow for a close scrutiny of the catalyst surface. Most of these techniques involve an energy analysis of scattered or emitted electrons and x-rays from the metal surface. We have currently been engaged in a project to study the decomposition of formic acid on nickel catalysts using Auger Electron Spectroscopy (AES) to monitor the surface composition. In the application of AES, the catalyst surface is bombarded with electrons in the energy range of 1-2 kev. The atoms present at the metal surface will re-emit secondary electrons at an energy level that is well documented for each element. Thus we can obtain a quantitative and qualitative analysis of the surface.

We are using formic acid as a test molecule to assess the dependence of the decomposition activity and selectivity of nickel on the crystallographic orientation of the surface and the level of surface contamination. We have currently completed the study of the clean Ni(100) and find that formic acid adsorbs on clean nickel with close to unit probability (i.e., every molecule that hits will adsorb) as long as there are available sites. The rate of decomposition also appears to be about two orders of magnitude greater than the rate on a conventional "dirty" surface. With reference to similar studies that were recently completed on clean Ni(110), it would appear



*Abdoulrasoul Malboubi adjusting differential scanning calorimeter to determine crystallinity.*

that there are profound differences in the decomposition kinetics on the different nickel planes and that the activity on Ni(100) is about an order of magnitude greater than the value on Ni(110) under comparable conditions. We plan to continue these studies and include carbon and sulfur contaminated surfaces. We also plan to extend this work into the area of hydrogenolysis and hydrogenation of simple hydrocarbons on single crystal platinum and nickel catalysts. □

*C. M. Sliepcevich*
*George L. Cross Research Professor of Engineering*

### TGA and DSC Analysis of Thermal and Kinetic Parameters for the Pyrolysis of Representative Coals

A study of the kinetics and energetics of the thermal pyrolysis of coal by means of thermogravimetric analyses and differential scanning calorimetry. Phase I will develop and utilize TGA and DSC techniques on "standard" or representative coals to develop gross kinetic parameters and quantitative energetics data and to identify differences in properties of coals within a seam as well as across geographical areas. Phase II will involve analysis of the principal U.S. coal beds. The resultant catalog of basic data will be invaluable for heat and material balances to improve efficiencies in coal combustion, gasification, and liquefaction processes and for insight for innovating coal pyrolysis techniques. □

*Carl E. Locke*
*Assistant Professor,*
*Chemical Engineering and Materials Science*

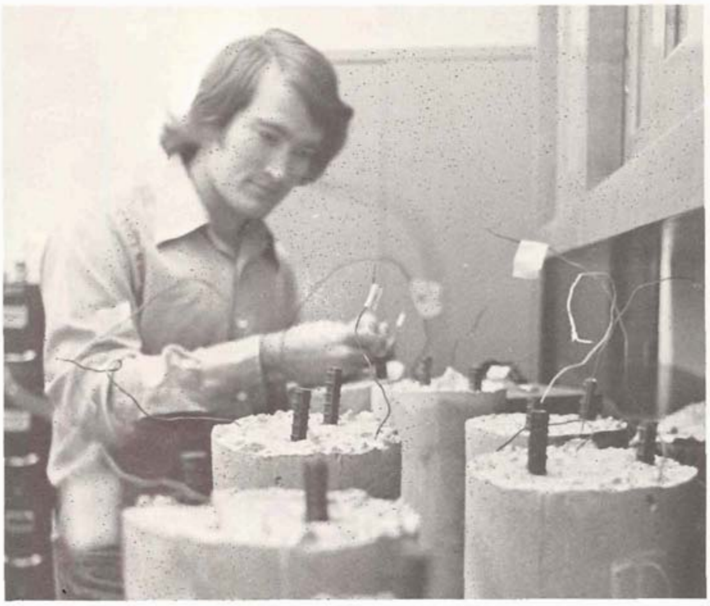
### Auger Electron Spectroscopy

The passive film is very important to mankind since it is responsible for the corrosion resistance of many metals and alloys. Stainless steels, nickel, chromium and titanium are some of the materials that derive their corrosion resistance from this film. This film is very thin, 10-100 Å thick, and is not well understood even though widely utilized. It can also lead to severe difficulties when disrupted. As an example, the stainless steels are subject to pitting when the film is disrupted by ions such as chloride. A better understanding of the composition of the passive film should help to design alloys which will produce an even better film.

We are studying the elemental composition of the passive film using the surface analysis technique, Auger Electron Spectroscopy (AES). A sample is bombarded by electrons which can cause transitions which lead to ejection of secondary electrons which are called Auger Electrons. The energies of these secondary electrons are unique since they result from transitions between quantitized energy levels. The element from which they are ejected can be determined by analyzing the energy levels of these electrons. The energies of the Auger electrons are low so that only those emitted from the top one or two atomic layers of the surface can be detected. Thus, AES has become a surface analysis tool in a number of technical areas. However, AES has only recently been applied to corrosion.

We have completed a study of the passive film on nickel and Inconel X-750. The passive film was formed electrochemically in sulfuric acid under controlled potential conditions. Mohammed Afzal passivated these two materials at three different electrode potentials. There was some scatter in his data but he was able to outline the proper experimental procedures which allowed Oladis Rincon to obtain some very good data. Oladis repeated the work Mohammed had done and also examined the effect of chlorides on the film.

We have found that the passive film is about 30 - 40 Å thick on nickel and $>90$ Å on Inconel X-750. The nickel film thickness data is about the same as found by other investigators using ellipsometry. Ellipsometry is an optical technique using elliptically polarized light. The concentration of elements in the film and the thickness is somewhat dependent on electrode potential. There is evidence that the ions in the solution contacting the metal are also included in the film. Surprisingly, the chloride ion does not seem to be extensively incorporated in the film. Other investigators using other techniques have postulated the chloride ions would replace other species in the film. This work was reported at the ACS National meeting in



*Junior Terry Stone checks samples of concrete used in bridge decks sent to Dr. Locke by the Oklahoma Highway Department for his studies on corrosion.*

New York City on April 6, 1976. It will be published in the proceedings of the symposium.

This area of work is far from being complete. We want to examine other alloys and solution compositions. As stated above, the ultimate goal is to better understand the film composition. We hope to equip the surface studies laboratory with other techniques such as x-ray photoelectron spectroscopy, known as ESCA. This technique will help in determining the way in which the elements are combined in the passive film.

There has been no financial support of this work except through some University funds. We have plans to submit proposals to several governmental agencies for funds to continue the work.

## Bridge Deck Deterioration

Any of you who have occasion to drive in Oklahoma City during the next few months may experience the discomfort furnished by bridge deck deterioration. The elevated expressway that carries I-40 through downtown Oklahoma City is closed for repairs, in fact—complete rebuilding. This rehabilitation work has been made necessary by deterioration caused by the use of deicing salts. These salts, mostly sodium chloride, have an extremely important function in keeping bridge decks safe for travel in icy weather. They also have an insidious side effect. The chloride ion is carried through the porous concrete to the reinforcing steel by the melted ice and rain water. The steel reinforcing bars (rebars) normally do not corrode while imbedded in concrete. Chloride ions cause a change in this condition. The rebars corrode and the corrosion products are less dense than the steel which causes the concrete to delaminate at the rebars. This effect coupled with the mechanical forces induced by normal traffic can cause severe damage to the concrete deck of the bridge.

This problem is widespread across the U.S. Since the usage of deicing salt, there were 8 million tons per year in 1973. This has resulted in a cost of in excess of 70 million dollars per year to repair existing bridge decks. Therefore, the mitigation and prevention of this damage is of great interest to the Oklahoma Department of Highways.

We are working on two projects both supported by the Highway Department which are aimed at solving this problem. Corrosion can be halted on the rebars using cathodic protection. This technique which has been used for many years for pipelines and items in the sea has only recently been considered for bridge decks. The salt can be prevented from contacting one rebar if the pores in the concrete can be sealed. They can be sealed by incorporating polymers with the concrete. These two projects will be discussed in greater detail below.

## Cathodic Protection of Bridge Decks

Cathodic protection of bridge decks is applied by laying electrodes (anodes) on the surface of the concrete and connecting a DC power source between the rebars and the electrodes. The rebars are made the cathodes, the negative poles. (Sacrificial anodes such as magnesium or zinc can be used but the impressed current method seems to be more practical.) There are several problems inherent in bridge deck application, such as current distribution, potential measurement and deterioration of the concrete by the impressed currents.

We have worked with the Highway Department on these problems during the summer of 1975 and will begin another series of studies during the summer of 1976.

Current distribution is a problem in bridge decks since the anodes must be placed on the deck which is only inches from the rebars. In pipelines, the anodes are placed several to hundreds of feet from the structure. Due to the limited conductivity of the concrete and the economic necessity of using only a few anodes, it is desirable to increase the conductivity of a surface layer on the concrete. Some investigators have placed the anodes in a two inch layer of coke breeze atop the deck. Coke breeze even when blended with asphalt is not a very good paving material. The anodes are usually covered by an overlay paving material made of asphaltic concrete. In order to prevent freeze thaw damage, which can be severe under the overlay, a polymer membrane is usually installed between such an overlay and the bridge deck. We have studied the possibility of

*Larry Watters, graduate student, removing a polymer blend from the blending chamber of the Brabender Plasticorder in the Polymer Lab.*

making this membrane electrically conductive. Our laboratory studies indicate it is possible to make the materials conductive but with some loss in flexibility. We will continue this study on a pilot scale slab. In addition, we plan to look for other methods of making the surface of the deck more conductive.

The best method of determining the operating status of a cathodic protection system is to measure the potential of the structure with respect to a standard electrochemical half cell. The copper-copper sulfate reference electrode is commonly used for pipelines and bridge decks. Those electrodes must be touched to the surface of the deck and a meter connected to the rebar and electrode to make a potential measurement. It is necessary to stop traffic flow in order to make these measurements on a bridge deck.

It would be most helpful to install reference electrodes in the deck and leave them there on a permanent basis. It would then be possible to monitor potentials with a recorder or at least connect a meter to the electrode and rebars without stopping traffic. We are working on this problem and have a possible solution. There are a few difficulties which remain, but those should be able to be solved during the next phase of the project.

When DC current flows through concrete, ions migrate with the current flow. If the rebar potential is made sufficiently negative, gaseous hydrogen will be evolved at the rebars. As you would expect this is not a desirable condition for the concrete. In addition, some work has shown that the concrete is softened adjacent to the rebar even at potentials above the hydrogen evolution potential. The currents used in this study were higher than those expected in a cathodic protection installation. We plan to design and construct an apparatus for long term tests of the ion migration due to cathodic protection currents. Rebar pull-out tests and chemical analysis of the concrete near the rebar will be utilized to determine the effect of the currents.

We hope this work will assist the Highway Department in applying cathodic protection to several bridge decks in the State of Oklahoma.

## Dental Alloy Corrosion

Several manufacturers have been introducing many new alloys to the dentists around the country. These alloys are being used to replace the previous metals for crowns, bridges and other implants. The rising cost of gold has accelerated the introduction of these non-precious alloys into dental practice. (There is little information available concerning the corrosion behavior of these alloys.) Dr. M. G. Duncanson of the College of Dentistry is working with us on a project to help fill this information void. Dr. Duncanson has supplied us with the alloys and also has specified the solutions which can be used to simulate saliva. Deepak Pareekh is now working on this project using a potentiostat to study the electrochemical behavior of these alloys. He will use another electrochemical technique, linear polarization, to determine the corrosion rates of the metals in the selected solutions. He has been studying the structures of the metals through the use of metallography techniques. The Research Council has given us a small grant to purchase the necessary chemicals and miscellaneous laboratory glassware for the present work. We hope to expand the work and use these results to help in obtaining funding from outside the University.

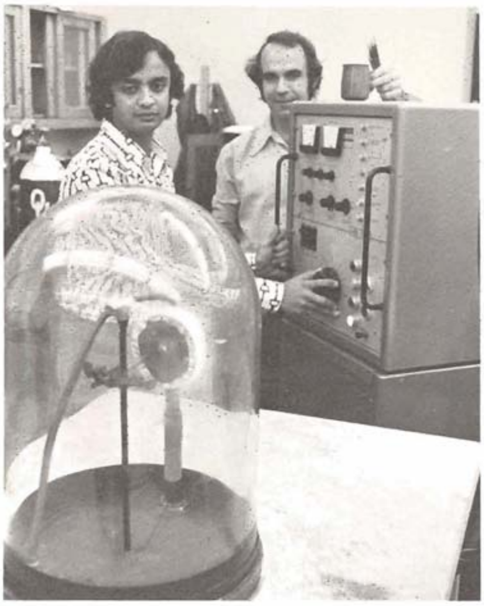
## Miscellaneous Polymer Projects

We are studying the properties of blends of polyphenylene sulfide (Ryton[1]) and polytetrafluorethylene (Teflon[2]). These blends are used for coating molds since they have very good release properties. Abdoulrasoul Malboubi is using differential scanning calorimeters and dynamic mechanical testing to study the interaction of these materials when blended together.

Glow discharge initiated polymerization is a very specialized method of producing polymers. Glow discharge produced highly ionized gasses which in turn produce active sites on monomers or other polymers. These active sites can then interact with other monomer molecules to produce the polymer. Gopal

[1]Trademark of Phillips Petroleum
[2]Trademark of Dupont

*Graduate student Gopal Rahti and Dr. Locke operating the glow discharge apparatus employed in producing a surface coating of styrene on a polymer substrate.*



Rahti is beginning a study supported by ACS-PRF in this area. We will point our study toward producing a surface coating on a polymer by a second polymer by exposing the base material to the glow discharge. The polymer will then be exposed to the monomer and the active sites will initiate polymerization and produce the coating. These materials have interesting applications as body implants.

Larry Watters is studying the synthesis and properties of a graft copolymer of chlorinated polyethylene (CPE) and styrene. The chlorinated polyethylene is attacked by a free radical from the decomposition of benzoyl peroxide. The resulting active sites on the chlorinated polyethylene can then initiate polymerization of the styrene. The styrene is attached to the CPE as a branch. These materials have interesting properties and can be used as modifiers of blends of polyethylene and styrene or polyvinyl chloride and styrene. The modified blends should have much better mechanical properties than the unmodified blends which have very poor mechanical properties.□

*Kenneth E. Starling*
*Professor, Chemical Engineering and Materials Science*

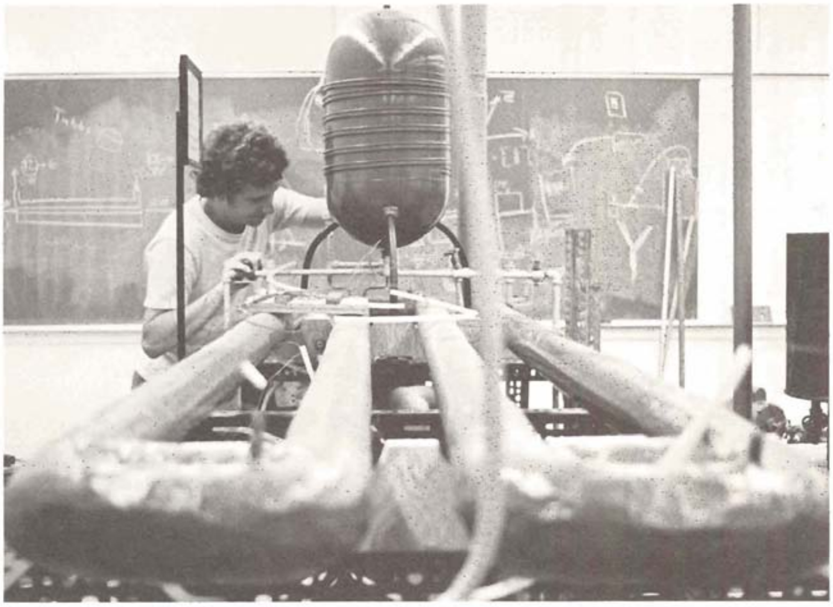
## Self-Consistent Correlation of Thermodynamic and Transport Properties

The objective of this research is to develop self-consistent correlations of the thermodynamic and transport properties of fluids of interest to the gas industry, including natural gas, liquified natural gas and synthetic gases. The project is supported by the American Gas Association, AGA Project BR-111-1, Kenneth E. Starling and Kingtse C. Mo, principal investigators.

The method of multiproperty analysis is being used for simultaneous correlation of thermodynamic and transport properties. This research is of both theoretical and practical interest. The research is of theoretical interest because thermodynamic and transport properties are known to be interrelated at the most fundamental molecular level. The research is of practical interest because the accuracy of design of industrial processing equipment is very dependent on the self-consistency as well as accuracy of property values used in the design.

The initial attack on the problem of self-consistent correlation has focused on three areas, (1) thermodynamic properties correlation, (2) transport properties correlation and (3) interrelationships between properties. It was realized at the outset that simultaneous correlation of properties is valuable only if common parameters occur in the correlation framework for each property. On the basis of the initial effort, a general correlation framework has been developed which can be described as a multiparameter corresponding states methodology for simultaneous correlation of both thermodynamic and transport properties. A first order perturbation expansion is used for the reduced properties for nonpolar polyatomic fluids, denoted for generality by R, where $R = R_0 + \gamma R_1$, in which $R_0$ is the value of the reduced property R of a monatomic fluid, such as argon, and $\gamma R_1$ is a polyatomic correction (perturbation) term (polar effects can be treated as an additional perturbation, but have not been considered to date). The orientation parameter $\gamma$ is a characteristic constant for each fluid. Both $R_0$ and $R_1$ are universal functions of reduced temperature and reduced density.

Perturbation equations have been developed for the thermodynamic functions and transport coefficients. Interrelationships between the coefficients of viscosity, thermal conductivity and self diffusion have been derived theoretically. Results to date for pure hydrocarbons have demonstrated the feasibility of simultaneously correlating thermodynamic and transport properties. Research has been initiated to correlate mixture properties, with good initial results for prediction of hydrocarbon mixture viscosities.



*Charles Thomas, senior in Chemical Engineering, checks out the double-pipe heat exchanger in the Unit Operations Lab.*

## Resource Utilization Efficiency Improvement of Geothermal Binary Cycles

Geothermal energy is an alternate energy source which potentially can contribute significantly to intermediate and long range energy problem solutions in the United States as well as other parts of the world. Assessments of U.S. geothermal resources vary, depending on the data and estimation methods used. In the western U.S., alone, it is estimated that there is a geothermal capacity for generation of 400,000 Mw, which is comparable to the present total U.S. generating capacity.

A number of geothermal energy resource types are known, including (1) liquid dominated, (2) vapor dominated, (3) hot rocks, (4) geopressured and (5) magma. The earliest geothermal power plants utilized the vapor dominated geothermal resource because the stem could be expanded directly in conventional steam turbines. The first geothermal power project was the Larderello, Italy dry steam project started in 1904 and still in operation. The Pacific Gas and Electric Company's dry steam geothermal power project at the Geysers, California has been under continued development since started in 1960 and is expected by 1980 to exceed 1000 Mw generation capacity. Liquid dominated geothermal reservoirs also have been used for commercial electrical generation, for example in Wairakei, New Zealand (160 Mw) and Cerro Prieto, Mexico (75 Mw); both plants flash the liquid and use the steam produced for power generation. There also have been

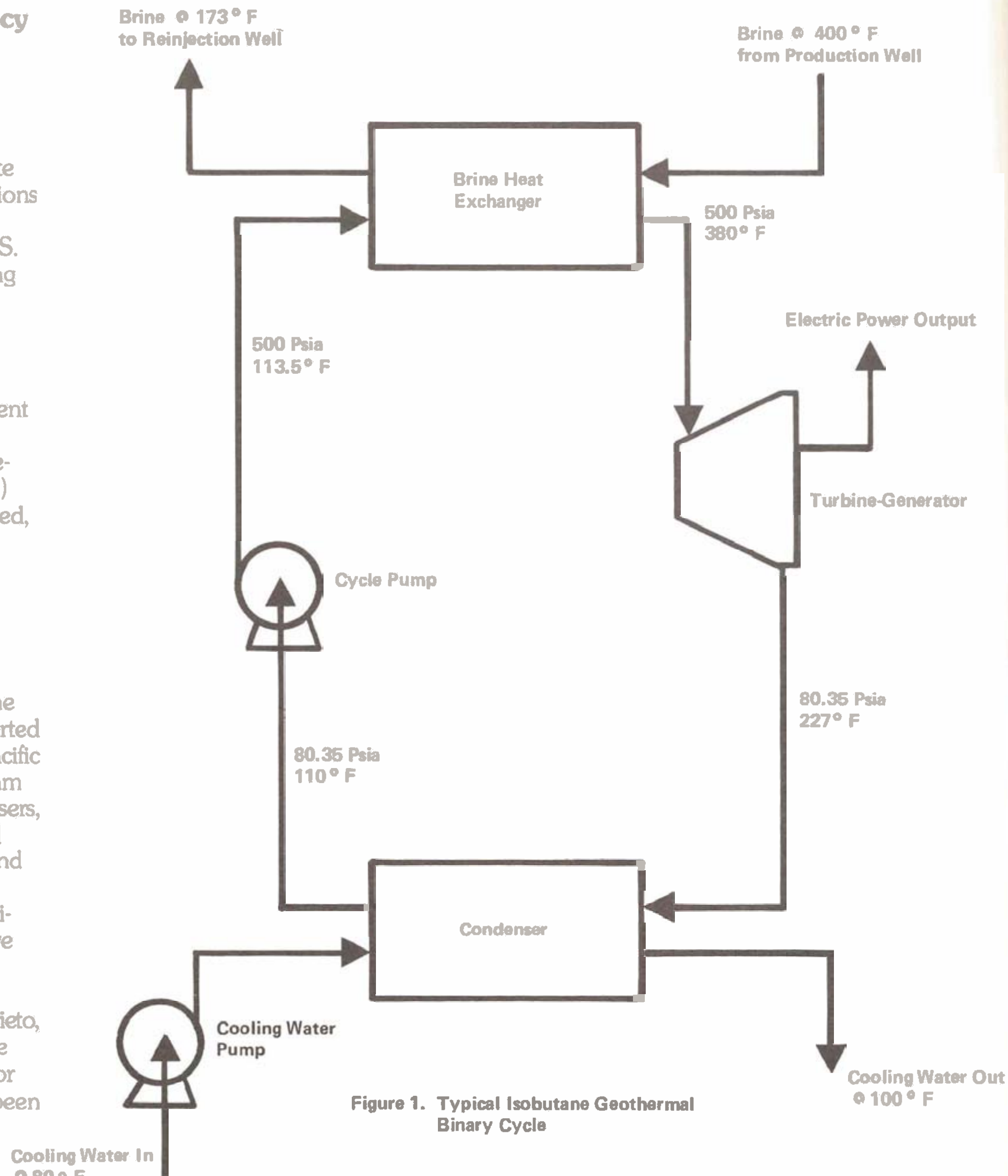



**Figure 1. Typical Isobutane Geothermal Binary Cycle**

*Research Technician, Joan Shelton, performing extractions.*

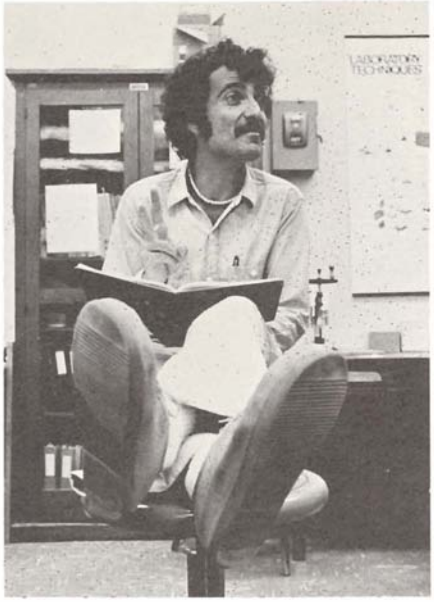
geothermal power projects in the Soviet Union, Japan and other countries. No power plants using hot rocks, geopressured reservoirs or magma have been built to date, although projects on utilization of these resources are in progress. Projects involving hot rock reservoirs are in progress in the Valles Caldera region in New Mexico, by the Los Alamos Scientific Laboratory and in Marysville, Montana by Battelle Northwest Laboratories, Southern Methodist University and Rogers Engineering Company. Projects involving geopressured reservoirs are in progress in the Gulf Coast region by the University of Texas and McNeese State University, with ERDA support. A project which may reveal magma flows is in progress in Hawaii by Hawaii and the Colorado School of Mines. A number of geothermal projects sponsored by USGS and ERDA are in progress to obtain pertinent geological, geophysical and geochemical data for resource assessment. Projects studying environmental effects are under support by NSF. Economic model development for geothermal energy is being supported by ERDA at Battelle Memorial Institute.

Liquid dominated geothermal reservoirs presently are the most attractive geothermal resource, after vapor dominated reservoirs, which are much less abundant. Both of these resource types have been attractive because little technology development has been required (e.g., conventional steam turbines have been utilized). However, utilization of the resource geothermal fluid for liquid dominated reservoirs is low when the liquid is flashed because often no more than 20% of the resource is converted to steam. Basically, two approaches are being pursued to achieve greater resource utilization of liquid dominated reservoirs, the total flow concept and the binary cycle concept. In the total flow method, the geothermal liquid is expanded directly through a turbine especially designed to tolerate brine precipitates. The total flow method appears feasible for the high temperature, high salinity brines for which other methods presently appear infeasible. A total flow project aimed for application in the Salton Sea area in California is in progress by the Lawrence Livermore Laboratory as part of the ERDA program. In the binary cycle method, a secondary fluid (such as isobutane), rather than the geothermal fluid, is used as the working fluid which passes through the turbine and the geothermal fluid is used as a heat source for the cycle. Both direct and indirect contact heat exchange methods for the heat exchange between the geothermal fluid and the working fluid are under consideration. Direct contact heat exchange projects are in progress at the University of Utah and elsewhere. A number of geothermal binary cycle projects involving indirect contact heat exchange have been in progress over the past few years, as discussed below.

The first geothermal binary cycle system made available for commercial sale (before 1973) was the Magma Company's process. The Ben Holt Company's process was developed subsequently and during 1974 design work was in progress by Holt (with Magma) for a proposed plant (low salinity) near Mammoth, California for Southern California Edison Electric Company (however, this project has not progressed much beyond the design work). San Diego Gas and Electric Company has a project underway in the Imperial Valley of California, with heat exchanger test loop and other studies in progress at their test facility. A number of other geothermal binary cycle projects supported by ERDA are in progress. A project for utilization of low temperature (300ºF), low salinity brine in the Raft River Valley of Idaho is in progress by the Aerojet Nuclear Company. A project for utilization of medium temperature brines (300ºF to 450ºF) in the region of northern Nevada is in progress by the Lawrence Berekely Laboratory. A project for study of utilization of medium salinity brines has been carried out by TRW Systems for NSF.

The above projects still must be considered in their preliminary stages with respect to optimal cycle design development. For the most part, these projects cannot put a large effort into cycle design development nor working fluid properties correlation development because of the demands of other project components, such as the geological, geophysical and geochemical components, as well as the drilling of wells, reservoir engineering and production engineering. Ultimately, however, the maximization of utilization of the geothermal resource will require improved geothermal binary cycle designs.

Geothermal energy research activities at the University of Oklahoma encompass a broad spectrum of activities ranging from resource assessment to energy



*CEMS Director Sam Sofer employs body language to answer age-old scientific query: "What comes after one?"*

conversion. The Oklahoma Geological Survey and the School of Geology and Geophysics, under the direction of Professor Charles Mankin, recently have been involved in the development of geological information and the assessment of geothermal potential in the United States. The School of Petroleum and Geological Engineering has initiated projects in the development of drilling fluids for the higher temperatures (300°F to 700°F) encountered in geothermal wells, under Professor Martin Chenevert, and in the simulation of geothermal reservoir behavior, under Professor Henry Crichlow.

The School of Chemical Engineering and Materials Science is carrying out a research program titled "Resource Utilization Efficiency Improvement of Geothermal Binary Cycles." This project is sponsored by the United States Energy Research and Development Administration, with Professor Kenneth E. Starling as Program Manager and Mr. Larry W. Fish as Principal Investigator. The objective of this research is to optimize binary cycle working fluid compositions and operating conditions for maximum utilization of liquid dominated geothermal resources and minimum cost net energy production. Because economic geothermal resource liquid temperatures vary continuously from about 300ºF to 700ºF, no single working fluid is appropriate for all binary cycle power plants. In fact, optimal performance for a given pure working fluid generally occurs only over a small temperature range. On the other hand, given a specified geothermal resource temperature, it is anticipated that a mixture composition can be determined which will provide optimal cycle performance. Thus, a major aspect of our research is involved with the study of working fluid composition effects on geothermal binary cycles. Results to date indicate that mixtures offer definite potential advantages over pure working fluids, particularly when no pure working has optimal performance at the geothermal resource temperature.

## Use of Mixtures as Working Fluids in Ocean Thermal Energy Conversion Cycles

Potentially, a significant portion of the world's future energy needs can be supplied by ocean thermal energy. In ocean thermal energy conversion schemes, the objective is to utilize the 30 to 40ºF temperature differences between hot surface sea water and cold 1000 and 4000 feet deep sea water which occur in numerous regions in the oceans. Although this resource is large and continuously available, the problems of low power plant efficiency and location in the ocean environment create technical and economic problems for the development of OTEC (Ocean Thermal Energy Conversion) schemes.

The early history of ocean thermal energy conversion technology has been discussed by Samuels (*Mechanical Engineering, 93,* No. 10, p. 21, 1971), who noted that the utilization of ocean temperature differences was proposed before 1900 by D'Arsonval, a Frenchman. The first technically successful ocean thermal energy conversion plant was built onshore at Matanzas Bay, Cuba, in 1926 by another Frenchman, Georges Claude. An open cycle using sea water as the working fluid was used by Claude to obtain power from the temperature difference between the warm surface water and the cold deep water. Claude's plant was uneconomic and was abandoned because it was of low efficiency and subject to severe corrosion problems. A major factor in its inefficiency was the fact that the cold water warmed up in coming approximately 7000 feet to shore in pipes. By 1966 the closed cycle concept had been formulated. This concept uses a fluid such as propane in a closed cycle and locates the plant in the ocean on a floating semi-submersible platform, much nearer the cold water source than would be possible with an onshore plant. Current studies of ocean thermal energy are based primarily on the closed cycle concept.

Conceptual design studies of ocean thermal energy systems have been supported at the University of Massachusetts at Amherst and at Carnegie-Mellon University, Pittsburgh. Both of these conceptual design studies have indicated that the problem which will probably be most critical to the development of ocean thermal energy conversion systems is the development of low cost and/or high efficiency heat exchangers for undersea duty.

Cost estimates using state-of-the-art technology have recently been developed for ocean thermal energy systems. Two projects for engineering evaluations

*Dr. Jerry Peavey replaces oscili-scope in Surface Studies Lab.*

of proposed conceptual designs supported by NSF during FY 75 have estimated the capital cost of ocean thermal energy plants to be $2000 to $2600 per Mwe using present-day technology. One project is with Lockheed Missiles and Space Company, Inc. (teamed with Global Marine Development, Inc. and United Engineers and Constructors). Besides the engineering evaluations and cost determinations, these two projects specify test program requirements for ocean thermal energy development.

Additional projects were initiated by NSF during FY 75 for advanced research and technology on key program elements. Those program elements related to total system development include resource assessment and ecological and environmental impacts, legal considerations, product mix studies, such as electricity, hydrogen, fresh water, mariculture, etc. combinations, open cycle feasibility, energy delivery, and test facilities program elements directed toward proof-of-concept experiments including heat exchanger studies, energy conversion, pumps, materials studies, including corrosion, mooring and positioning.

An acknowledged major research problem in development of ocean thermal energy conversion systems is the development of low cost and/or efficient heat exchangers for undersea duty. Not only problems of materials selection and design are involved but also problems regarding biofouling and corrosion control as well as servicing of heat exchangers. In addition, because the working fluid selected affects the heat exchange system and cycle performance, working fluid selection is an important problem. The design and positioning of the semi-submersible hull and related marine support system and the cold water inlet pipe also may be major problems. Energy delivery also is a major problem, with plant-to-shore electrical transmission and transportation of other plant products such as hydrogen, fresh water and other energy intensive products requiring consideration.

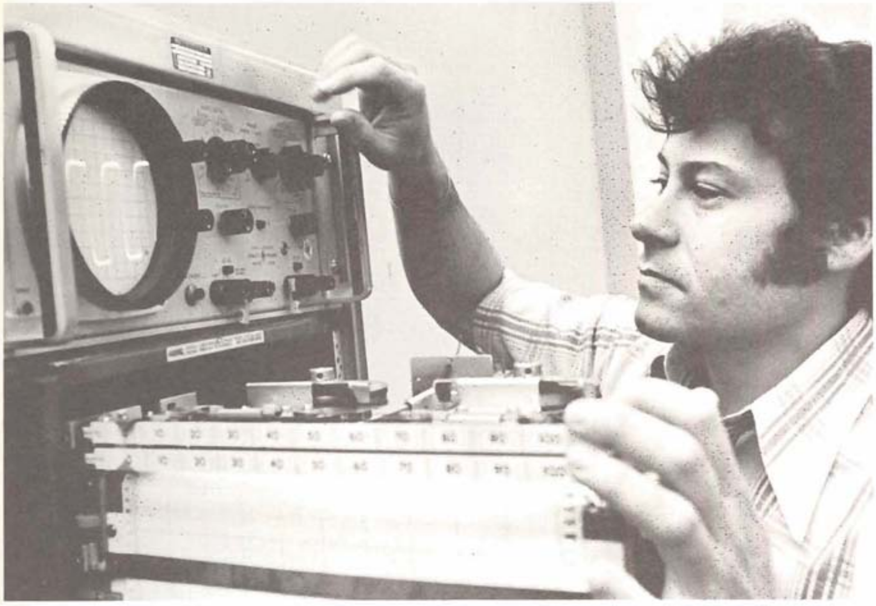
OTEC research at the University of Oklahoma has as its thrust the selection of working fluids and cycle operating conditions for improved efficiency and/or economics. This project is being supported by the Energy Research and Development Administration, ERDA Project E-(40-1)-4918, Kenneth E. Starling and Larry W. Fish, principal investigators. Research performed to date indicates that mixtures have potential advantages over pure working fluids in OTEC cycles. Cost calculations performed in this project show that with present technology, OTEC heat exchangers are more than 50% of total plant cost, so that there are virtually no trade-offs with other major equipment components. Therefore, optimal cycle design presently corresponds essentially to minimum heat exchanger size, which in turn corresponds to maximum temperature difference driving force for heat exchange and therefore to minimum temperature change for sea water passing through the heat exchangers. Mixtures therefore have only a small advantage over pure working fluids with present technology. However, cost calculations show that an increasing advantage of mixtures over pure working fluids should occur as OTEC technology becomes increasingly advanced (mainly through reductions in heat exchanger costs). □

*Jerris H. Peavey*
*Visiting Professor of Materials Science*

## Basic Research on the Correlation of Superconducting Properties with Surface Properties on Both Thin Film and Bulk Superconductors

Basic research to attempt to correlate the superconducting properties of materials is being carried out. In order to enhance the effects of the surface properties on the superconducting properties the research is being done on thin films. The surface properties being measured are (1) surface roughness, (2) film thickness, and (3) elemental chemical composition. The superconducting properties being measured are (1) critical temperature, (2) critical current, and (3) critical magnetic field.

The goals of this work are to be able to (1) vary the surface parameters in order to optimize the appropriate superconducting parameters, and (2) suggest new and unusual techniques to fabricate and analyze these materials. Possible applications are in the areas of electric power generation and transmission, higher magnetic fields, and higher operating temperatures of existing devices. □



*Dr. Robert J. Block adjusting output on CRT.*

*Robert J. Block*
*Professor of Metallurgical Engineering*

## Metallurgical Evaluation of Rail Sections Department of Transportation

It has been established that failures of railroad rails are generally associated with plastic deformation of the rail head during service. Failures generally take the form of spalling off of large sections of the working portions of the rail and have been responsible for a large number of train derailments. Experiments in the Department of Aerospace and Mechanical Engineering of The University of Oklahoma have demonstrated that acoustical wave propagation rates are directly related to the nature and degree of plastic deformation in the rail head. In principle, measurements of the propagation characteristics of acoustical waves in rails could provide a method to gauge the disposition toward failure before evidence had presented itself at the surface of the rail head.

Metallographic analysis has been carried out on rail heads which have seen varying degrees of service. The thickness of the heavily deformed layers at the surfaces are clearly evident in the photomicrographs which have been obtained. Rails which show anomalies in their wave propagation characteristics are being examined to determine whether evidence of incipient failure can be detected microscopically. If such evidence can be found then a correspondence between propagation characteristics and failure may be demonstratable.

Final stages of the work will include direct determinations of the residual stresses in deformed rail heads and a study of the relationship between defects or unusual microstructural characteristics and the disposition toward failure.□

*Sam S. Sofer*
*Director, Assistant Professor*
*School of Chemical Engineering and Materials Science*

## On Pharmaceuticals

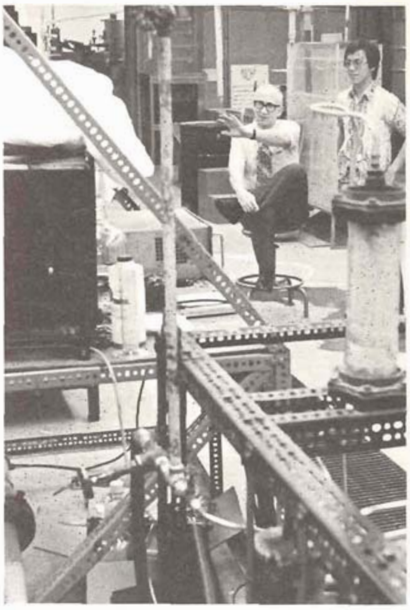
The search for psychoactive drugs has led to a dramatic decrease in the number of mental patients in hospitals. It has been shown that many of these drugs, used with advice from community mental health organizations, aid patients to live and work in society relatively freely. Chlorpromazine, for example, is one such drug—it has been used with remarkable success by millions of patients. However, many of these psychoactive drugs have undesirable side effects. Consequently the search continues for modifications of these compounds in order to obtain more specific responses and fewer unpleasant side effects.

A good many drugs are modified or metabolized in the liver, and some of these metabolites are also interesting as drugs. For example codeine, commonly found in cough syrup, is metabolized by the liver to morphine, a common narcotic. Obviously, both of these compounds are interesting as drugs. A similar logic may be used that the psychoactive phenothiazines may have metabolites that are also interesting as drugs.

It turns out that organic and pharmaceutical chemists have been devilishly creative in coming up with ways to synthesize related compounds and metabolites. It also turns out that enzymes can compete with the most devilish of the creative. The problem has been that many of the important drug-metabolizing enzymes are bound firmly to membranes (microsomes) within the liver cell and that the isolation of these enzymes has not been particularly easy. As a matter of fact, only one of these enzymes, which we shall call oxidase, had been purified until recently. The purification was done by the fancy maneuvers of an excellent enzymologist at the University of Texas.

In any case, we mounted this enzyme on porous solids such as glass and found the half-life to increase by a hundredfold. Subsequent optimization with respect to pH, temperature, and other parameters led to large increases of product yield. Soon enough, instead of thinking of yields in the microgram region, we began thinking of producing gram quantities. With backing from NSF, we have produced five new compounds—N-oxides of various phenothiazine drugs. We have also produced three other related new compounds—glucuronides of phenothiazine drugs. We have plans for more.

*Senior Dennis Yieh and Dr. F. Mark Townsend discuss experimental tests to be made on the kinetics apparatus.*



## On Chemical Carcinogens

The NCI (National Cancer Institute) Biological Models and Carcinogenesis people have been interested in pancreatic carcinogenesis since 1971. The basic proposition, considered as early as 1929, is that the gall bladder may contribute to carcinogenesis in the human pancreas. Since in most humans the common bile duct and pancreatic duct join before emptying in the duodenum, it is possible that a reverse flow of bile (bile reflux) or duodenal contents would introduce a wide variety of drugs and chemical carcinogens in the head of the pancreas. This area is said to be the location of the origination of the majority of adenocarcinomas.

The NCI further postulates that the bile, rich in conjugated substances such as glucuronides, may either contain directly carcinogenic conjugates or compounds rendered carcinogenic upon deconjugation *in situ*. Consequently the NCI has recently announced an RFP for the study of deconjugation in the pancreas and its secretions.

Clearly the ability to conjugate certain chemical carcinogens is very critical to the NCI program.

We have recently developed a technique to insolubilize whole liver microsomes on porous glass. This was the system used to produce the glucuronides mentioned above. The glucuronide synthesis is called conjugation. This is one of the conjugation mechanisms which is of interest to the NCI. Our work here is only at a starting phase.

## On Artificial Livers

In the field of clinical detoxification, past work has largely focused on physical removal of unwanted compounds; for example, by adsorption or dialysis. To duplicate liver function, however, a replication of biochemical pathways is called for—a goal that has not been reached clinically primarily due to a lack of purified liver microsomal enzymes, and secondarily to the necessity of using toxic (and expensive) cofactors in *in vivo* systems.

The immobilized microsomal enzymes mentioned above are of logical value as a first step towards an artificial liver. However, many, many problems due to instability and required coenzymes come into play due to the very complex nature of the liver. Our plans are to incorporate this microsomal system with a closed-loop dialysis unit to mimic at least one detoxification pathway.

## On Agricultural Wastes

There's a lot of engineering to be done in agriculture. For some reason, and everyone here tells me (with a giggle) what that reason is, I have been concentrating on cow manure. The source is plentiful and the grantors are generous.

The biogasification of cow manure to methane gas described in the last OkChE issue is continuing, so I won't go into it (pardon the expression) here.

Given 100 million cows and a very low efficiency of conversion of feed, even a small increase in efficiency would feed millions of people. As a result, it pays to look at a cow's stomach as a reactor (in my kinetics class, we compared it to four continuous stirred-tank reactors in series) in which microbes are doing the actual work. The production of single-cell protein from wastes is thus a reasonable engineering project. We have just begun investigating the possibility of growth of a special fungus on these wastes for possible feeding to cattle or to fish.

The fungus is edible for humans, but so far, I don't have any volunteers. Do I? □

*F. Mark Townsend*
*David Ross Boyd Professor,*
*Chemical Engineering and Materials Science*

## Recovery of Sulfur from Hydrogen Sulfide

The recovery of sulfur from hydrogen sulfide is being investigated in a constant volume reactor. Hydrogen sulfide is mixed with sulfur dioxide in a 2:1 molar ratio in a vertical Pyrex-glass column 2 inches in diameter, 2 feet long. Reaction occurs forming liquid water and solid elemental sulfur. The rate is followed by noting the drop in pressure in the reactor as the reaction occurs. The effects of various solutions such as triethylene glycol on the rate of reaction are also being studied. Data obtained are compared with data from industrial columns and used to make improvements in the performance of those units. □

*Zane Q. Johnson, B.S. '47, former board president of OkChE, is the 1976 recipient of the College of Engineering Hall of Fame award. Zane was elected by students on the basis of his accomplishments in engineering, management and the community. He is president of Gulf Science and Technology Company.*

## Alumni Notes

"Educational relations make the strongest tie . . ." Cecil J. Rhodes

And we want to keep these ties with you. We are interested in knowing where you are and what you are doing. Please fill out one of the enclosed information cards and send it to us. We will publish the information in our Fall Newsletter.

*Larry D. Airington*, B.S. '72, M.B.A. '75, lives in Oklahoma City and is presently employed with Phillips Petroleum Company as an engineering trainee.

*Colonel Hugh R. Bumpas, Jr.*, B.S. '51, M.S. '71, is serving as Chief of Staff and Senior Advisor, Ministry of National Defense, with the USMC. He is stationed in Taipei, Taiwan.

*Donald W. Evans*, B.S.'70, M.S.,'75, lives in Metairie, Louisiana, and is the environmental control supervisor for Monsanto's Luling Plant.

*David E. Fields, Jr.*, B.S. '51, is president of his own company, Fields Company of Tulsa, with branches in Pinehurst, North Carolina, (Fields Industries) and Tulsa (A-OK Supply). He resides in Pinehurst with his wife and three sons, and is active in community life there as a member of Sandhills Chamber of Commerce, director of Southern Golf Association, director of Boy Scout Regional Council and chairman of a Boy Scout troop.

*Larry E. Glasgow*, B.S. '58, lives in Tyler, Texas, where he is senior engineer for Howe-Baker Engineers, Inc. He also serves as a regional professional engineer—Texas Major—U.S. Air Reserve.

*Don W. Green*, M.S. '59, Ph.D. '63, is professor of chemical and petroleum engineering at the University of Kansas, Lawrence. He served as chairman of that department from 1970-1974. He is married and has three sons.

*Monte D. Hart*, B.S. '73, lives in Milwaukee with his wife Valarie. He currently is employed with Ladish Company of Cudahy, Wisconsin, as a metallurgical engineer.

*Manford R. Haxton*, B.S. '51, received his Juris Doctor of Law degree from the University of Houston in 1963 and is now serving as assistant general counsel—patents for R. J. Reynolds Industries, Inc., Winston-Salem, North Carolina. He is currently chairman of the County Department of Social Services and secretary of the County Board of Elections. Prior to joining Reynolds, he was employed with the Standard Oil Company of Indiana for 15 years.

*Robert L. Hedworth*, B.S. '52, resides in Smoke Rise, Kinnelon, New Jersey. He is now director of process engineering for GAF in Wayne, New Jersey.

*Jerry M. Hobbs*, B.S. '62, M.S. '63, lives in Wilmington, Delaware, where he is production supervisor for E.I. DuPont de Nemours & Company, Inc.

*Wayne Montgomery*, B.S. '48, is living in Gibsonia, Pennsylvania, and is employed as manager of powder sales with the Aluminum Company of America, Pittsburgh.

*Thomas G. Norris*, B.S. '56, M.S. '57, residing in Pittsburgh, Pennsylvania, is vice president of mining, Washington Operation, Consolidation Coal Company, a division of Continental Oil Company, Library, Pennsylvania.

*G.M. Olds*, B.S.'50,M.S. '51, is manager, Nuclear Service Department, Nuclear Power Generation Division of Babcock & Wilcox, Co., Lynchburg, Virginia. He lives in Lynchburg with his wife, Gerry (B.F.A. '51), who is a counselor at E. C. Glass High School there.

*Clare Hachmuth Patterson*, B.S. '62, is currently employed as a buyer with Northern Natural Gas Company of Omaha, Nebraska. She has two children, Jay, 12, and Suzy, 10.

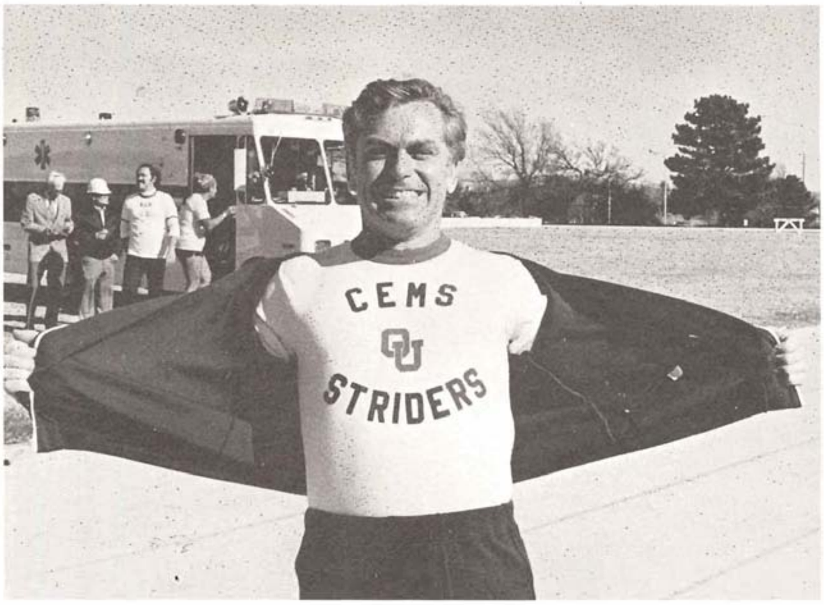
*Howard L. Pilat*, B.S. '44, is vice president of technology for Celanese Chemical Company, New York. He received his Ph.D. from the University of Pittsburgh and has been with Celanese 24 years, working with the licensing of outside, world-wide technology. He lives in Larchmont, New York, with his wife, Elaine; his daughter, Marsha, a Cornell graduate in architecture; and his son, William, an architecture major at Cornell.

*Joe A. Porter*, M.S. '49, is married, has two sons, and lives in Whittier, California. He is a senior project engineer with Uniloc, Inc., Irvine, California. He has served as past Commander, Rio Hondo Power Squadron, and is Staff Commodore of the Hollywood Yacht Club.

## CEMS Trackers Win National Trophy

*In all CEMS Land, the Fastest Four-Fleet-Feet-Flashers*
*Have captured the F. J. Antuerpen Trophy by being the fastest dashers.*
*With a four-mile time of 22:08,*
*"Soupy Sofer," "Catfish Fish," "Furbelly Locke" and "Tweety'bird Starling" weren't a second too late.*

*They're proud of their victory as right you can see—*
*And these intelligent trackers have pledged that the trophy*
*With OU CEMS will forever stay,*
*Till blisters, aching muscles and age snatch it away.*




*Relayman Kenneth E. Starling*

*John Charles Ray*, B.S. '72, is a process control engineer with Phillips Petroleum Company in Borger, Texas. He lives there with his wife, Nancy, and son, Joel.

*Larry B. Reams*, B.S. '65, lives in Marshalltown, Iowa, with his wife, Kendall (B.S. '65) and their two daughters. He has received his M.B.A. from Drake University and is sales manager for Fisher Controls Co., Marshalltown.

*Alan D. Robertson*, B.S. '58, lives in Hixson, Tennessee, and is process super-intendent with E. I. DuPont, Chattanooga.

*Kenneth E. Sanders*, Ph.D. '73, is a process engineer for the International Atomic Energy Agency, Vienna, Austria.

*Paul F. Tapp*, B.S. '40, lives in Houston, Texas, where he is a registered professional engineer and a member of the American Chemical Society. He is self-employed as the owner of an investment company.

*J. Barry Wilder*, M.S. '65, is now living in Tulsa and is employed as senior engineer with E. I. DuPont Company.

*Ken Wolfe*, B.S. '65, is a development representative for DuPont in Wilmington, Delaware. Presently, he is assigned to new product and market development for the Plastic Products and Resins Department.☐

## CEMS notes

"The keen spirit seizes the prompt occasion; makes the thought start into instant action, and at once plans and performs, resolves and executes . . ." Hannah More

We have discovered two such "keen spirits" in our recent search for new faculty members.

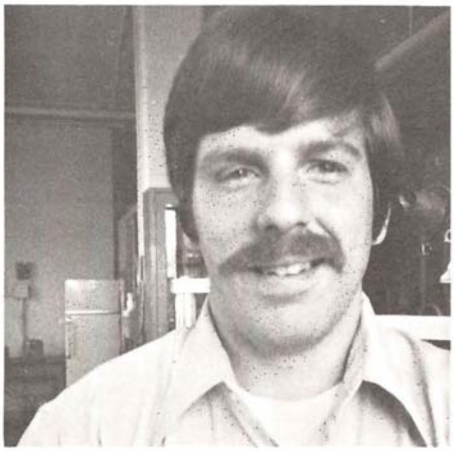
John Michael Radovich (Jay) will join our faculty as assistant professor this September. Jay comes to us from Washington University where he was instructor in the Department of Chemical Engineering. He received his B.S. from the University of Notre Dame; M.S., Stanford University; and D.Sc. from Washington University with a 4.0 G.P.A.

He has worked in both the academic and industrial realms and his areas of specialty include transport phenomena, unit operations and biomedical engineering. He is a member of the American Institute of Chemical Engineers, and the American Chemical Society.

Jay brings with him his wife, Ann, and daughters, Amy and Julie (9-month-old twins), and 3-year-old Camille.

We are also fortunate to have Lloyd L. Lee join us from Cleveland State University where he served as visiting assistant professor. He will join our faculty as assistant professor. Lloyd received his Ph.D. from Northwestern University and continued in research and development with E. I. DuPont, the University of Paris, National Central University, Taiwan, and the Chinese Petroleum Company of Taiwan. He is a member of AIChE, Sigma Xi, and Phi Lambda Mu.

His areas of special interest include statistical mechanics of fluids, thermodynamics, and polymer technology.



*Jay Radovich*

*Lloyd L. Lee*

*Celebrating ourselves . . . students, faculty, friends of CEMS gather at Awards Banquet.*

## Top CEMS students honored

It was "a CEMS first!"

This spring, four students were rewarded for their outstanding scholastic achievements by scholarships presented at the school's first annual awards banquet.

Mark A. McDonald of Bartlesville was the evening's biggest winner. He received both the Phillips Petroleum Company award for outstanding junior-senior in Chemical Engineering, and the Dresser Engineering scholarship. Mark was further honored by being named outstanding student by the American Institute of Chemical Engineers.

Michael A. Caldwell of Tulsa was winner of the Celanese Award for outstanding freshman in Chemical Engineering; Paul H. Spangler of Ponca City won the Pamela Pesek Johnson Award for outstanding senior in Chemical Engineering Design; and Donald L. Jordan of Newton, Kansas, was given the Frank Maginnis Award for outstanding student in Metallurgical Engineering. The Maginnis Award has been newly established by Frank Maginnis, president of Research Instrument Company of Norman.

The school also recognized 28 recipients of its Program of Excellence scholarships during the ceremonies.

Representatives from several of the companies and organizations which sponsor the awards were on hand to assist in the presentation.

*And the winner is . . . Mark McDonald, center, flanked by admiring faculty members Arthur Aldag, left, and Sam Sofer.*

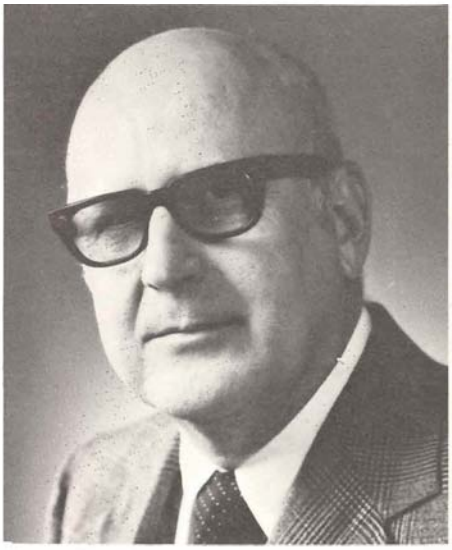
Ruskin once said that when we fail to praise a man who deserves praise, two sad things happen; we run a chance of driving him from the right road for want of encouragement, and, we deprive ourselves of one of the very happiest of our privileges, the privilege of rewarding labor that deserves a reward. . . .

So, we would like to acknowledge the work of faculty members who are leaving us at the end of this academic term. Some will be traveling to other institutions, and some will be engaged in private industry. To all, we wish the best of luck and success in their new endeavors. . . .

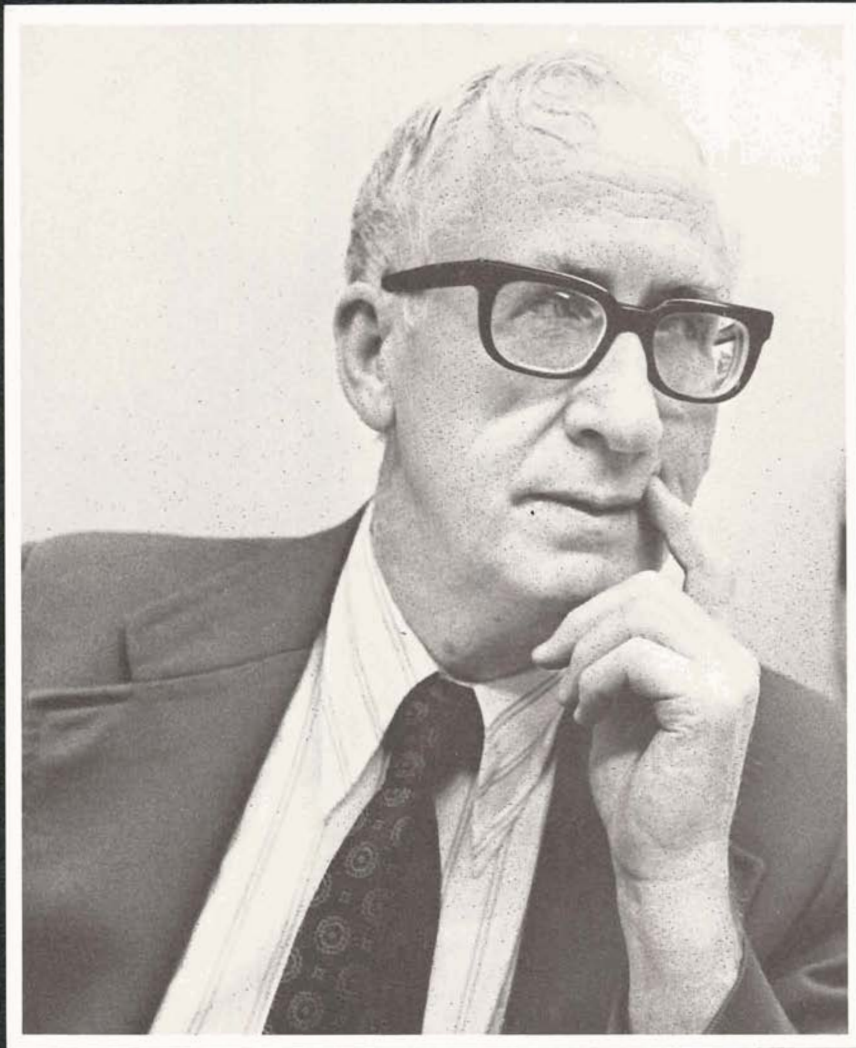
*Jerris H. Peavey*
*James H. Christensen*
*Charles Phillip Colver*
*Kingtse C. Mo*

The Spring '75 edition of OkChE introduced the establishment of the Harry G. Fair Memorial Lectures. The second annual lectureship was presented on the afternoon of April 21, with this year's honored guest speaker, Harry L. Blomquist, Jr., president of Coastal States Gas Corporation, Houston, Texas. This is the company which Mr. Fair served as President until his death in 1974.

Mr. Blomquist spoke to a large gathering of students, faculty, and interested public on the subject "Engineering in the Business Environment." This annual event carries out the wish of Harry Fair to give future engineers exposure to persons with backgrounds in corporate engineering.



*Harry M. Blomquist, Jr.*



The recent naming of Dr. F. Mark Townsend as David Ross Boyd Professor of Chemical Engineering and Materials Science adds yet another honor to a distinguished career. As recipient of the Boyd professorship, Dr. Townsend has been recognized by the University of Oklahoma Board of Regents for his continued performance and leadership in teaching, counseling and guidance of students.

A native of Purcell, Dr. Townsend received his B.S., M.S., and Ph.D degrees from the University's College of Engineering. He has been a member of the faculty since 1957, and served for four years as chairman of the School of Natural Gas Engineering.

Dr. Townsend's enthusiasm for his subject and his ability to transmit this to his students have not only made him a popular faculty member, but also earned him the Regents' Award for superior teaching in 1972, the same year he was given a full professorship. Aside from classroom duties, he has donated many hours to academic counseling as advisor to the senior class, and for students in the school's scholarship program.

The entire CEMS faculty shares in the pride of Dr. Townsend's accomplishments over his more than twenty years of dedication to the University, and to its "most important products" . . . . the countless students he has inspired.