Award Lecture

A RANDOM WALK IN POROUS MEDIA

The ASEE Chemical Engineering Division Lecturer for 1989 is J. L. Duda of Pennsylvania State University. The 3M Company provides financial support for this annual lectureship award, and its purpose is to recognize outstanding achievement in an important field of ChE theory or practice.



A native of Donora, Pennsylva-

nia (a small steel mill town near Pittsburgh) Larry earned his BS in chemical engineering in 1958 from Case Institute of Technology and his PhD in chemical engineering from the University of Delaware in 1963. After graduation he joined the Process Fundamentals Laboratory at Dow Chemical Company in Midland, Michigan, as a research engineer. Eight years later he joined the chemical engineering department at The Pennsylvania State University as an associate professor and subsequently became head of the department in 1983.

He has conducted research in a wide range of fields including polymer processing, enhanced oil recovery, arctic engineering, molecular diffusion, rheology, numerical analysis of coupled transport processes, and tribology. Although these activities appear to be unrelated, most of his research involves the application of transport phenomena principles to problems involving polymers and macromolecules. He has conducted research with fifteen different members of Penn State's faculty in chemical engineering and related fields, and this work has resulted in over one hundred research articles.

Professor Duda has taught a wide range of classes in chemical engineering, including specialty courses in the polymer field and advanced transport phenomena. In addition to teaching undergraduate and graduate students, he has been the advisor or co-advisor of 35 MS and 15 PhD graduate students.

In 1980 Professor Duda received the Penn State Engineering Society's Award for Outstanding Research Achievement, and in 1981 he and a colleague (James Vrentas) were the joint recipients of the William H. Walker Award of the AIChE. He also was the recipient of a NSF Visiting Scholar grant to National Taiwan University in 1978. J. L. DUDA Pennsylvania State University University Park, PA 16802

WHEN I WAS NOTIFIED that I was the recipient of the 1989 3M Lectureship Award, I was very pleased and surprised. After the initial euphoria, however, I panicked when I realized I also had to give a lecture at the ASEE National Meeting. I looked up the past lectures published in Chemical Engineering Education. This was a mistake! Not only did the list of authors read like "Who's Who in Chemical Engineering," but the lectures also covered a wide range of subjects. However, they could be put into two broad classifications: many were reviews of the research fields of the lecturers, while others dealt with a philosophy of education and teaching. Like most researchers, I enjoy talking about my research field, but most of my audience would probably be bored since the subject is outside the area of expertise of a general engineering audience. On the other hand. I am sure that the average engineering educator would also be bored by an hour of my philosophy on education. Consequently, I decided to combine these two general subjects in my lecture.

University professors are in the knowledge business. First, through our teaching, we transfer knowledge to our students; second, we produce knowledge for the world through our research; and third, we transfer a knowledge of how to produce more knowledge. That is, we teach undergraduate and graduate students how to conduct research. Of these three activities, I feel the third has the greatest potential for payback, yet it is the one that we essentially neglect when we discuss our profession and when we seek ways to improve our effectiveness.

The philosophical component of my lecture involves teaching students how to conduct research. To present this philosophy, I have decided to incorporate it as part of a discussion of one of my research projects. Throughout the discussion, I will utilize quotes from many other individuals which mirror my own philosophical point of

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view. I hope to present more than just information concerning my subject matter. I agree with J. Epstein's observation that

What great teachers teach is not just subject matter but an attitude toward it, an approach to it.

My main premise is that students often initiate their first research project with a distorted view of the research process. Students are aware of the scientific method and usually feel that research closely follows that method. However, I feel that research more closely resembles a random walk than an idealized scientific method. Students usually do not realize this when they initiate a research project, and unfortunately we educators do not attempt to dispel their illusions.

In the title to this lecture, a "random walk" refers to the reality of many research projects, and "porous media" refers to the specific topic I will be discussing—a study of the flow of polymer solutions in porous media. Many individuals contributed to the scientific content of this lecture and the most prominent were my graduate students S. K. Fan, S. A. Hong, and H. L. Wang, and my colleague, E. E. Klaus. More details of the technical aspects of this paper are available [1–4]. However, I have no one to blame except myself for the philosophical components of this lecture.

I feel that most educators fail to prepare students for their first encounter with research. Perhaps we are embarrassed by the fact that our research programs do not progress in a systematic manner paralleling scientific methods as perceived by the general public. There is no question that the body of scientific knowledge is very well-systematized. However, the production of new scientific knowledge is clearly related to artistic creativity. While we use the scientific approach to test results, when we start a project, all kinds of hurdles and false leads present themselves, and the overall process often resembles a random walk towards our well-defined objective. Nobel Prize winner Szent-Gyorgyi stated it succinctly:

Research means going out into the unknown with the hope of finding something new to bring home. If you know in advance what you are going to do, or even to find there, then it is not research at all.

Similarly, W. P. Schmitt stated:

Most studies prove that almost all truly significant inventions come outside the formal planning process. Unfortunately, many bureaucrats who control research funding do not understand these facts. While we cannot do much about them, we *can* do a better job of preparing the researchers of the future to take on the challenge of creative research.

There is a dichotomy which new researchers have difficulty in reconciling. Although the actual process of doing research usually does not follow the idealized scientific method, we always report our results as if it did. We feel a need to report our results in the most succinct and logical manner; including all the false starts, failed experiments, and theories would only confuse and detract from the new knowledge that we want to add to the scientific and engineering base. When writing up the first research project, a young researcher should be made aware of the advice of O'Conner and Woodford:

Remember, a thesis or any scientific paper should not be the history of an inquiry, but its outcome.

In this paper, however, I am going to ignore that good advice and present the account of a project involving the flow of polymer solutions in porous media. By chronicling the actual history of this project, I hope to make new researchers more aware of the actual research process.

The main objective of this program was to develop an ability to predict the pressure drop vs. flow relationship for the flow of polymer solutions in porous media by independently characterizing the porous media and the rheology of the fluid. In essence, we wanted to develop an analog of Darcy's Law for polymer solutions. In Darcy's Law for Newtonian fluids, the porous media is characterized by the permeability, and the Newtonian fluid is characterized by the viscosity. In the flow of Newtonian fluids, the porous media is usually modeled by some sort of capillary model, and the most commonly followed approach is the one represented by the Blake-Kozeny equation as presented in Table 1. Because of the success of this approach for Newtonian fluids, it was natural that the analogous approach be considered for non-Newtonian solutions of polymers. One of the first attempts along this line was the work of Christopher and Middleman [5], presented in Table 2, in which the power law was used as a model for the fluid.

When my group at Penn State initiated this work, we developed an experimental technique in which we could actually measure the flow rate as a function of pressure drop for the flow of non-Newtonian solutions in porous media. We initiated experiments with a wellcharacterized porous media and beds of uniform spherical glass beads. Review of the literature indicated that the main problems associated with the study of flow in packed beds were a result of the complications due to end effects. First of all, excess pressure drops occurred at the entrance and exit of packed beds, and the increase in porosity near the walls containing the bed caused channeling. Both of these problems were addressed in the experimental technique shown in Figure 1. By subtracting the total pressure drop across the 3-inch packed column from the pressure drop across the 6-inch packed column, the pressure dropped through 3 inches of fully





developed flow in the center of the 6-inch column could be determined. Similarly, a layer of glass beads was incorporated into an epoxy coating on the walls of the column to eliminate radial variations in porosity. This experimental technique resulted in excellent pressure drop vs. flow rate measurements for Newtonian fluids as presented in Figure 2. The straight diagonal line in the figure represents predictions of the flow behavior based on the capillary model for the porous media. The slight deviation of the data from the prediction at high Reynolds numbers is probably due to inertial effects which are not included in the capillary model.

Most young researchers would be quite pleased with results such as those presented in Figure 2 and would be ready to wrap up the project. However, two quotes are apropos at this point:

If an experiment does not hold out the possibility of causing one to revise one's views, it is hard to see why it should be done at all.

Peter B. Medawar

To limit oneself to what one can be rigorous about is



FIGURE 1. Experimental Apparatus Used to Study Flow in a Packed Column of Glass Beads.

often to limit oneself to trivial questions. M. C. Bateson

Too often young researchers design experiments to test well-documented theories, and it is not clear what they would conclude if their experimental results did not agree with the theory. For example, if the experimental results presented in Figure 2 did not agree with the capillary model theory, would they conclude that the capillary model approach for describing the flow of Newtonian fluids in porous media is incorrect? Since that model has been evaluated by numerous investigators. I doubt that they would be willing to make such a bold statement. Instead, disagreement between the experiment and theory would probably cause them to reconsider and to modify the experiment until agreement was attained. In this case, the results of Figure 2 were used to show the validity of the experimental technique, and then the technique was used to study the flow of polymer solutions in the beds of glass spheres. Some very interesting results were attained for polymer solutions which appear to behave as purely viscous solutions and others which show elastic effects. These results are available in the literature and are not reproduced here since they would distract from the main theme of this paper.

At this point, the research group at Penn State was very pleased with the program and was prepared to



FIGURE 2. Friction Factor-Reynolds Number Relationship for Flow of Newtonian Fluids in Packed Column.

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spend more time elucidating the flow of polymer solutions in the well-characterized beds of glass spheres. However, it turns out that most young researchers are not cognizant of the fact that in the shadow of every research project there lurks a sponsor. In this case, the Department of Energy was sponsoring the research (which was related to enhanced oil recovery) and the project had an industrial advisory group. This industrial advisory committee pointed out that they did not feel the study of the flow of polymer solutions through pristine packed beds of uniform glass spheres shed much light on the practical problems which involved the flow of complex mixtures of polymers, oil, electrolytes, etc., in porous rock containing clay and minerals in addition to wide variations in porosity and other characteristics. It became very clear that in order to maintain our funding we would, at the minimum, have to study flow in sandstone.

The unwanted interference of a sponsor is a reality that every researcher has to face, and the sooner a young researcher becomes aware of this the better. The key is to appreciate the interesting scientific and engineering challenges encountered along the way. In fact, in the work being reviewed here, it could be argued that the net result of unwanted sponsor interference was a greater contribution to our scientific knowledge base.

Consultations with our petroleum engineering colleagues who routinely study flow in sandstone under conditions simulating oil recovery conditions indicated that extensive new equipment would be required. The velocities in oil reservoirs are an order of magnitude of a foot a day, requiring sophisticated pumps and expensive apparati to measure the very low associated pressure drops. Naturally, the required funds were not available in our contract! Another truism that young researchers must quickly assimilate is that sponsors always want more than they are willing to pay for!

The project faced the dilemma which is characteristic of many research programs across the country: the equipment and instrumentation were not sufficient to meet the challenge of the research. Although I would be the last to disagree with the point of view that the instrumentation and experimental infrastrucIt is like "keeping up with the Joneses"! I feel we must warn our young researchers not to let a profusion of instruments, apparati, computers, *etc.*, constrain their creativity or the direction of their research. The main constraint for scientific progress has been, and will continue to be, the limitations of the ingenuity and creativity of the researchers.

ture of America's colleges and universities are in critical need of an infusion of resources, I do feel that there is a tendency for hardware to take too prominent a position in our scientific endeavors. Sometimes it seems that everyone has to have a SEM, FTIR, HPLC, and a supercomputer, *etc.*, before they can make any progress. It is like "keeping up with the Joneses"! I feel we must warn our young researchers not to let a profusion of instruments, apparati, computers, *etc.*, constrain their creativity or the direction of their research. The main constraint for scientific progress has been, and will continue to be, the limitations of the ingenuity and creativity of the researchers.

In the project I am dissecting, the lack of funds for the "essential" equipment resulted in a breakthrough. To meet the challenge of studying flow in porous sandstone under conditions simulating oil reservoirs, my colleague, E. E. Klaus, developed a simple, inexpensive technique illustrated in Figure 3. Basically, this apparatus is analogous to an Ostwald capillary viscometer where the capillary has been replaced by a piece of porous media. The flow rate is measured by the time the fluid requires to fill a calibrated efflux bulb. The low pressure drop required to simulate re-

servoir conditions is easily attained by utilizing the head of the fluid in the reservoir above the efflux bulbs. This apparatus could be easily calibrated with Newtonian fluids to produce results which are in excellent agreement with theory. However, once these experiments were initiated with polymer solutions, several complications arose. It became apparent that large quantities of solution had to flow through the porous sandstone before steady state conditions were realized, and the permeability of the sandstone was irreversibly changed by exposure to the polymer solution. To eliminate the cost of the preparation of sandstone samples during the preliminary experiments and to enhance the probability of reproducible results. well-characterized filter paper was utilized as porous media. The permeability of the porous media was determined with a Newtonian saline solution, and then the media was exposed to a flowing polymer solution until steady state conditions were attained. Finally. the polymer solution was replaced with the original saline solution and the reduction in the permeability of the porous media was determined. Although the new experimental technique seemed to be accurate and reproducible, the preliminary results with filter



FIGURE 3. Porous Media Viscometer.



FIGURE 4. Relationship Between Initial Permeability and Residual Permeability for Flow of 500 ppm Xanthan Gum Solution Through Filter Paper.

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FIGURE 5. Relationship Between Initial permeability and Residual Permeability for Flow of 500 ppm Xanthan Gum Solution Through Three Different Porous Media.



FIGURE 6. Influence of the Hydrodynamic Size of Polymer Molecules in Solutions on Residual Permability of Bradford Sandstone. ○ 500 ppm Xanthan Gum and 200 ppm NaCl; ○ 500 ppm Xanthan Gum and 2% NaCl; △ Ultrasonic Degraded Solution of 1000 ppm Xanthan Gum and 200 ppm.

paper as presented in Figure 4 did not seem to be correct. Although the students conducting the experiments swore by the accuracy and reproducibility of the results, I concluded that the data in Figure 4 were ridiculous. Everyone agreed that the polymer molecules were irreversibly absorbing on the walls of the porous media channels and that this caused a reduction in the permeability. However, these results appeared to indicate that thicker polymer coatings were associated with larger pores. The natural extension of this data would indicate that if we conducted experiments on a sewer pipe, we would plug off the pipe! As D. J. Boorstin said,

The greatest obstacle to scientific discovery is not ignorance but the illusion of knowledge.

Will Rogers stated the same point of view more succinctly:

It ain't what you don't know that hurts you—it's knowin' what ain't so.

Progress on this project was held up for months because of our preconceived notions of what was occurring in the porous media. Because of the limited range of the filter paper, data could not be extended beyond the range covered in Figure 4. Finally, we decided to take the bull by the horns, and we conducted experiments in actual sandstone. As the results in Figure 5 clearly show, the initial trend, which seemed to go against logic, was reversed at higher initial permeabilities, and the behavior followed the anticipated trend after a maximum was attained. Although everyone associated with the project was finally convinced that these results were real, they did not represent a contribution until a mechanism consistent with this behavior was envisioned. I think Einstein said it best:

Knowledge cannot spring from experience alone, but only from the comparison of the inventions of the intellect with the observed facts.

Like most new knowledge, the explanation for behavior shown in Figures 5 and 6 appeared trivial once it was stated. The polymer molecules could not enter the pores which were smaller than the hydrodynamic volume of the polymer chains in solution. Since the polymer did not enter the small pores, these pores did not become coated with a layer of adsorbed polymer molecules. The selective flow of polymer molecules was analogous to the phenomena which was the basis of exclusion chromatography. If this mechanism was correct, then the maximum occurring in Figure 5 should have shifted towards smaller initial per-

meabilities if the hydrodynamic volume of the polymer molecules was reduced. Since the xanthan gum used in this study was not synthesized at different molecular weights, the size of the chains of this polymer in solution were modified by two techniques. By subjecting the polymer solutions to severe mechanical agitation, the covalent bonds of the polymer chain were broken. A lower molecular weight polymer resulted from this mechanical degradation. The effective hydrodynamic size of the polymer molecules in solution was also reduced by increasing the electrolyte concentration of the solutions. The confirmation of xanthan gum chains in solution was enlarged by repulsion forces between ionized groups on the molecules. An increase in electrolyte concentration formed a double layer around these charge groups and reduced the repulsion and the effective size of the polymers in solution. The data presented in Figure 6 qualitatively confirmed this mechanistic point of view. The curve with the maximum was that obtained for the flow of the unaltered xanthan gum polymer molecules in Berea sandstone. The upper curve shows the results when the size of the polymer chains were reduced by mechanical degradation, and the third curve shows that the behavior associated with the flow of xanthan gum molecules had been contracted into smaller hydrodynamic volumes by a significant increase in the electrolyte concentration. It is interesting to note that this behavior had not been observed previously, and probably would not have been observed if this research program had the experimental equipment which was generally believed necessary to study flow in sandstone under reservoir conditions.

At this stage in the project, we decided that a comprehensive understanding of flow in porous media could not be realized when the complications due to the complex rheology of the solution were coupled to the complications associated with polymer-wall interaction. Consequently, the next set of experiments was conducted in porous media of high permeability where polymer chain-pore wall interactions were not significant. The original plan was to study the flow of polymer solutions under conditions where they behaved as purely viscous fluids, and then to move on to the more interesting area of viscoelastic solution. We anticipated that we would guickly confirm the applicability of capillary models to describe the flow of purely viscous, non-Newtonian fluids in porous media. The utility of capillary models for such systems had been confirmed by numerous investigators, including our own earlier studies with packed beds of glass beads. However, these elegant plans were quickly scuttled by new experimental data, and the

random-walk nature of the project continued. As T. H. Huxley stated,

The great tragedy of science—the slaying of a beautiful hypothesis by an ugly fact.

It is interesting that playwright Eugene O'Neill perhaps best describes a pitfall which is most dangerous for the older researcher:

A man's work is in danger of deteriorating when he thinks he has found the one best formula for doing it. If he feels that, he is likely to feel that all he needs is merely to go on repeating himself.

All our elegant plans and preconceptions were wiped out by the new data produced with the porous media viscometer depicted in Figure 3. Instead of following the advice and the procedure which his advisors had suggested, a new student on the project started to present the data in raw form (as shown in Figure 7) rather than presenting dimensionless friction factor as a function of Reynolds number. As Figure 7 indicates, when the pressure drop (as represented by the head of the fluid between the reservoir and efflux bulb) was plotted as a function of velocity through the porous media, the experimental measurements did not agree with the model based on the capillary model and a power law rheology.

At first, this was not disturbing since the model prediction could be modified by changing adjustable parameters such as tortuosity. However, there were no



FIGURE 7. Velocity as a Function of Pressure Head in a Porous Media Viscometer for Flow of a 3000 ppm Xanthan Gum Solution Through Sandstone With a Permeability of 7.0 Darcy. Predicted Line Based on Power Law Model.

adjustments in the power law model to change the slope of the prediction lines when presented in the form of Figure 7. In other words, the line representing the prediction of the model could be raised or lowered by adjusting some parameters in the model, but the conventional model could never be adjusted to give a slope which agreed with the experimental data. At first, we assumed that this problem was due to the inadequacy of the power law model in describing the rheology of the fluid. It is a well-known fact that all polymer solutions exhibit Newtonian behavior at low shear rates and then a transition to shear thinning and power law behavior is observed at higher shear rates. Consequently, to reconcile the difference between the experimental data and the theory based on the capillary model, an Ellis model was used to describe the rheology of the polymer solutions, and the capillary model approach was coupled with this rheological equation to develop a new model. A comparison of this new model with the experimental data is presented in Figure 8. These data are representative of data obtained from many different polymer solutions. In this log-log plot, the model based on the Ellis model rheology is a curve which comes closer to fitting the experimental data but still does not represent an adequate description of the flow of purely viscous polymer solutions in porous media.

After much effort, we concluded that the limitations of the overall model were not due to the limitations of the rheological model describing the viscosity-shear be-



FIGURE 8. Velocity as Function of Pressure Head in a Porous Media Viscometer for Flow of a 5000 ppm Carboxy Methylcellulose Solution Through Sandstone With a Permability of 7.0 Darcy. Predicted Line Based on Ellis Model.

havior of the solutions, but were somehow inherent in the basic capillary model. This study showed that the excess pressure drops associated with the converging and diverging flow regions of any porous media must be included in a model of flow of non-Newtonian fluids in porous media. The assumption of fully developed flow. which is characteristic of all capillary models, eliminated the utilization of these models for accurately describing non-Newtonian flow in porous media. Fortuitously, capillary models can describe the flow of Newtonian fluids in porous media since the pressure drops associated with fully developed flow and the excess pressure drops in the entrance and exit regions are linearly related. Consequently, a constant tortuosity factor can incorporate the effects of the excess pressure drops and the tortuosity of the flow path. However, a constant tortuosity factor is inadequate for the description of the flow of purely viscous polymer solutions or viscoelastic solutions in porous media. Finally, we concluded that two criteria were required to describe the flow of a purely viscous polymer solution in porous media.

- 1. The model of the porous media must include the converging and diverging nature of the porous media.
- 2. The rheological model of the fluid must include the transition from Newtonian behavior at low flow rates to shear thinning behavior at higher shear rates.

From these studies, we concluded that to describe the flow of polymer solutions in porous media, the model of the porous media must include converging and diverging sections. However, to describe the flow, the complete equations of motion for the non-Newtonian fluid would have to be solved for this two-dimensional flow field. If such a problem were offered to a new group of chemical engineering graduate students, it would be a very popular project indeed since it involves extensive utilization of the computer to solve a non-linear set of partial differential equations. Today we see more and more research which is based on complex numerical analysis of well-established partial differential equations such as the Navier-Stokes equations. Computers have had a very significant impact on science and engineering, and this impact will probably increase in the future. As tools, modern computers are a wonderful contribution to research. However, I feel there are problems associated with the utilization of computers (particularly by students) which are sometimes overlooked in the present environment of computer euphoria. A few quotes clearly present this point of view:

The more computer power we have, the less students

know what they're doing.

Alvin White

Computers can raise a barrier to intuition.

E. Block

Several years ago, James Wei published a humorous paper in *Chemtech* concerning the number of parameters it would take to fit an elephant. A cliche among researchers is that the number of parameters in some correlations would fit an elephant. So Professor Wei went on to determine the number of parameters needed to fit the shape of an elephant. An interesting experiment is to assign the following problem to a group of students: Determine the minimum number of parameters required to produce a shape which can be recognized



FIGURE 9. Conventional Least Square Fit of an Elephant.



FIGURE 10. A Different Point of View!

as an elephant. Students love such a challenge since it enables them to use all the power of the computer, and it gives a sense of great accomplishment without the stress of really thinking about a problem. The students are ingenious in their ability to come up with new spline fitting techniques, the use of parallel processes, *etc.* However, they will inevitably come up with a result similar to that shown in Figure 9, and the number of parameters for all of the students will be approximately the same. Computers are touted as a great contribution to our theoretical ability. However, J. Willard Gibbs stated

The purpose of a theory is to find that viewpoint from which experimental observations appear to fit the pattern.

In other words, the purpose of theory is to find a different point of view. Computers can provide a more detailed vision, but they very seldom change a point of view. To make a breakthrough in the problem stated above, the student must think about an elephant, do a coordinate rotation, and find a line of symmetry. The resulting different point of view is presented in Figure 10. Either the front or the back of an elephant has a line of symmetry and the number of parameters needed to represent those points of view are significantly less than the usual point of view (Figure 9).

In conclusion, I feel that computers are very useful tools, but that we must train our students to recognize the danger of allowing computers to set the pace and direction of their work. They need to take time for reflection on their problems. Only then can they enjoy the benefits of the computer without falling into its empirical clutches.

I would like to express my appreciation to the 3M Company, to members of the Selection Committee, and to all those who were involved with my nomination for the opportunity to present my point of view. My collection of quotes is not well documented, and I apologize if I misquoted anyone or if I failed to give appropriate credit for material I used in this presentation.

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