INTERFEROMETRIC STUDY OF MASS TRANSFER ENHANCEMENT
BY TURBULENCE PROMOTERS

Karrie Jo Hanson
(M. S. thesis)

April 1979

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room
LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.
Interferometric Study of Mass Transfer Enhancement by Turbulence Promoters

Karrie Jo Hanson

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemical Engineering, University of California, Berkeley, California 94720

ABSTRACT

The use of small obstacles to thin the downstream mass transfer boundary layer has been investigated with a traveling, dual-beam laser interferometer. Plots of boundary layer thickness as a function of the distance from the leading edge of the electrode were developed to study the effects of obstacle shape, the distance of the obstacle from the electrode surface, and Reynolds number for the purposes of determining the optimal conditions to achieve high mass transfer rates. Parameters which characterize the efficiency of the obstacles, the minimum boundary layer thickness in the wake, and the recovery distance downstream of each obstacle have been introduced to quantitatively describe the results. In addition, the effect of local turbulence near the obstacles on the deposit morphology has been described.
To My Parents
Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>1</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. LITERATURE REVIEW</td>
<td>2</td>
</tr>
<tr>
<td>III. APPARATUS</td>
<td>12</td>
</tr>
<tr>
<td>3.1 Interferometer</td>
<td>12</td>
</tr>
<tr>
<td>3.2 Flow Cell</td>
<td>16</td>
</tr>
<tr>
<td>3.3 Flow Obstacles</td>
<td>26</td>
</tr>
<tr>
<td>3.4 Electrolyte Preparation</td>
<td>28</td>
</tr>
<tr>
<td>IV. RESULTS</td>
<td>31</td>
</tr>
<tr>
<td>4.1 Effect of Obstacles on Boundary Layer</td>
<td>31</td>
</tr>
<tr>
<td>Thickness</td>
<td></td>
</tr>
<tr>
<td>4.2 Current Distribution Around Obstacles</td>
<td>47</td>
</tr>
<tr>
<td>V. OPTICAL ERRORS</td>
<td>58</td>
</tr>
<tr>
<td>5.1 Light Deflection Errors</td>
<td>58</td>
</tr>
<tr>
<td>5.2 Surface Reflection Errors</td>
<td>68</td>
</tr>
<tr>
<td>5.3 Boundary Layer Thickness Error</td>
<td>69</td>
</tr>
<tr>
<td>VI. DISCUSSION</td>
<td>73</td>
</tr>
<tr>
<td>6.1 Interferometric Boundary Layer Measurements</td>
<td>73</td>
</tr>
<tr>
<td>6.2 Analysis of Results</td>
<td>75</td>
</tr>
<tr>
<td>6.3 Mechanism of Eddy Mixing</td>
<td>84</td>
</tr>
<tr>
<td>6.4 The Upstream Effect</td>
<td>88</td>
</tr>
<tr>
<td>6.5 Design of Electrochemical Systems Using Turbulence Promoters</td>
<td>93</td>
</tr>
<tr>
<td>VII. CONCLUSIONS</td>
<td>97</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>99</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>100</td>
</tr>
<tr>
<td>APPENDIX I</td>
<td>103</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

The rate of an industrial electrolytic process is often determined by the rate of mass transfer to the electrode surface. In a parallel plate flow cell, the non-uniform mass transfer characteristics result in uneven current distribution in the flow direction; in laminar flow on a long electrode the limiting current declines to very low values. Increasing the flow velocity in the cell is a simple method for enhancing the mass transfer rate; however, larger pumping costs may offset this advantage. To achieve a more uniform current distribution as well as enhanced mass transfer rates, small obstacles may be used in a laminar stream to break up the diffusion layer at the electrode surface resulting in only a very small increase in pressure drop. The objective of this work is to evaluate the effects of various flow obstacles on the mass transfer boundary layer downstream from the obstacle, to determine the optimum spacing, location, and shape of the flow obstacles, and to demonstrate the use of flow obstacles in achieving increased rates and greater uniformity of current distribution.

Previous investigators have studied this problem by measuring the increase in the limiting current in the presence of flow obstacles. A unique aspect of the present work is the use of a traveling dual-beam laser interferometer to directly observe the mass transfer boundary layer below limiting current. This technique permits the assessment of local mass transfer rates in the vicinity of a single obstacle in a current density range of interest for industrial applications.
II. LITERATURE REVIEW

The possibility for substantial improvement in mass or heat transport under forced convection by the use of turbulence promoters has generated considerable interest in fields ranging from desalination to nuclear reactor heat transfer. The widespread interest reflects a national trend towards improved energy efficiency as hydrocarbon fuels become increasingly scarce and expensive. Many applications have generated as many methods of studying the technique, and a unifying treatment has not yet been proposed. Literature on turbulence promoters can be separated into two broad categories. A majority of investigators have studied the effect of a large number of obstacles on the overall heat or mass transfer. The resulting flux correlations are specific to the obstacle geometry and spacing as well as the geometry of the apparatus of the particular investigation. The second experimental approach seeks a more general result. By fitting the local mixing efficiency of a single obstacle or small number of obstacles to an analytical model, the investigator extends his results to predict overall mass or heat transfer.

The most extensive work on turbulence promoters to date was done by Leitz, Marinčić et al.\textsuperscript{1,2} in a multifaceted study of both local and overall mass transfer as a function of cell geometry, obstacle size and shape, and Reynolds number. In addition, the pressure drop across the flow cell was measured for each set of promoters so that the economic benefits could be evaluated. A segmented electrode embedded in the cathode provided the necessary flexibility to determine both
local mass transfer in the difficult hydrodynamic region near the obstacle, and access the overall mass transfer using the limiting current technique. The authors studied promoters with round, square, and triangular cross-sections in three possible configurations: attached to the cathode ("attached"), suspended between the anode and cathode ("detached"), and attached to the anode ("opposed").

The resulting local current fluctuations in the vicinity of obstacles are shown in figure 2.1. Although the current variations immediately downstream from the obstacle vary with each promoter, the slow decrease in current density as the distance from the promoter increases is characteristic of turbulence promoters in general. Overall mass transfer results are given as dimensionless correlations of the Sherwood number in the form,

\[
Sh = A \left[ Sc^{1/3} Re^{a} \left( \frac{d_e}{\Delta l} \right)^b \right]
\]

(2.1)

where \( d_e \) is the equivalent diameter of the flow cell, \( \Delta l \) is the promoter spacing, and the constants \( A, a, \) and \( b \) are determined experimentally. By plotting the Sherwood number against the dimensionless pressure drop \( (f\cdot Re) \), the promoters were compared on the basis of mass transfer performance and pressure drop. By these criteria, the detached promoters of circular cross-section gave the best results.

In figure 2.2 the mass transfer in a cell with detached circular promoters of two sizes is compared to unobstructed laminar flow and turbulent flow. Compared to unobstructed laminar flow, the use of turbulence promoters doubled the limiting current.
FIGURE 2.1. Current density variation downstream of opposed rectangular turbulence promoter. From Leitz et al. 1.
FIGURE 2.2. Mass transfer characteristics of two detached circular obstacles compared with laminar flow in an open channel and the Chilton-Colburn expression for turbulent flow. $\beta$ is defined as the ratio of the open cross-section of the channel at the obstacle to the cross-section of the unobstructed cell. From Leitz et al.1.
Sutherland\textsuperscript{3} studied turbulence promoters to improve heat transfer from steam cooled nuclear reactor systems. The author modeled the reactor by air flowing past an array of heated rods. Heat transfer was determined by measuring the temperature of the inner wall of the cylinder which encased the rods. The turbulence promoter in this case was a thin wire which was wound around each rod with a carefully controlled separation distance. By disrupting the velocity field in the flow direction, the wire caused increased mixing near the rod surface, and thus increased heat transfer.

The results are presented in a graph of Nusselt number as a function of Reynolds number for different obstacle heights and rod separations, as shown in Figure 2.3. In demonstrating that promoter spacing is a relatively insensitive parameter, the study concluded that promoter height (boundary layer penetration) had the greatest effect on heat transfer. However, at high Reynolds numbers the heat transfer performance was the same for all promoter heights.

The technique of moving nets across the electrode surface was studied by Schalch and Ibl\textsuperscript{4} as a method to increase mass transfer without stirring the bulk electrolyte. Similarly to Leitz's study, the limiting current technique was used to measure the overall mass transfer of a model redox reaction. The results of the study are summarized by the following correlations:
FIGURE 2.3. Heat transfer characteristics of turbulence promoters of varying heights and separations. s/e is the ratio of promoter spacing to height, p/d is the ratio of rod separation to rod diameter, and DH is the hydraulic diameter of the flow cross-section. From Sutherland\textsuperscript{3}.
\[
Sh = 29.45 \left( \frac{Re}{d} \right)^{0.369} \quad \text{For nets moving upwards}
\]

\[
Sh = 25.07 \left( \frac{Re}{d} \right)^{0.377} \quad \text{For nets moving downwards}
\]

where \( d \) = interthread distance

\( L \) = electrode length.

To get a clearer idea of the effectiveness of the stirring produced by the moving nets, the authors compared the mass transfer performance with other well-known flow configurations. They found that the moving net correlations fell between the mass transfer predicted for fully developed laminar flow and couette flow (one plate moving). In comparison to the Leitz study, these results show a mass transfer dependence on the electrode length rather than the cell equivalent diameter. This implies that the diffusion layer increases from the leading edge of the electrode in the presence of the moving nets.

Several investigators have modeled the mass transfer enhancement produced by a single obstacle. This approach attempts a more general analysis with a goal of quantitative correlation of mass transfer rates and cell velocity. The complete mathematical description of the velocity field in the region near the obstacle is not attempted in any model. Instead, simplifying assumptions are used to model the flow pattern in the region of turbulent eddies.

The simplest model for mass transport in the presence of obstacles is the assumption of a diminished, but constant boundary layer thickness. Unfortunately, this model does not account for the effects of promoter
geometry or flow conditions, rather it simply defines an empirically
determined average boundary layer thickness. Winograd, Toren, et al.\textsuperscript{6,7}
expanded upon the constant boundary layer thickness model in developing
a "mesh step" model to describe the mass transfer in the "step" between
successive promoters (or thread separation in a net). Because complete
mixing at the beginning of each mesh step is assumed, both the hydro-
dynamic boundary layer and concentration boundary undergo a sharp
decrease. The model makes use of one experimentally determined
parameter, the "mixing efficiency", which depends on obstacle geometry
but is independent of cell velocity. In the limit of small mesh
steps, the model reduces to the assumption of constant boundary layer
thickness.

The experimental verification of the model was conducted with
net-type turbulence promoters using the limiting current technique.
Mesh steps ranging from 3 to 24 mm were tested, but only mesh steps
greater than 9 mm showed good correlation with the model. Apparently,
the assumption of complete mixing is inappropriate for short mesh
steps. On this basis, Winograd et al. conclude that within the range
of small mesh steps (less than 9 mm), the net shape and size has a
much greater impact on mass transfer than the separation distance
(mesh step).

To get quantitative information about local mass transfer coefficients
and shear stress near the obstacle, Storck and Coeuret\textsuperscript{8} studied the
effect of three suspended turbulence promoters on a row of micro-
electrodes embedded in the cathode of a rectangular flow cell. In
contrast to the Leitz work, the goal of this study was an analytical model rather than the development of a correlation, therefore only three turbulence promoters were employed in the cell. In addition, the electrolyte velocities were much smaller in the Storck experiment (0.76 cm/sec compared to 50 cm/sec). The dependence of local mass transfer coefficients on distance, obtained by limiting current measurements are shown in figure 2.4. In comparison to figure 1.2, Storck shows a much smoother variation in mass transfer along the electrode length, probably due to the smaller flow velocity. The low velocities, in fact, allow the system to be modeled by solving the convective diffusion equation with a velocity increase under the obstacles. The theory is in good agreement with experiment, but unfortunately it is not truly a turbulence promoter theory because the velocities studied are not high enough to cause eddy separation behind the obstacle. Indeed, the Storck-Coeuret model shows the greatest deviation from experiment at high flow velocity.
FIGURE 2.4. Dependence of local mass transfer coefficients on distance in a cell containing three suspended obstacles (schematic drawing of experiment is shown above). The peaks in the mass transfer coefficient correspond to the position directly beneath each cylinder. From Storck and Coeuret.8
III. APPARATUS

Laser interferometry has been used to study electrochemical mass transfer in this laboratory for many years. The original flow channel and interferometer was built by K.W. Beach⁹ in 1967 to observe concentration profiles in a cell operated in a free-convection mode. Since that time, the system has been modified many times to improve interferogram quality, facilitate alignment, and to allow greater experimental flexibility.

3.1 Interferometer

Interference patterns resulting from the local phase variation in the sample beam allows one to deduce the two-dimensional concentration fields in the object of interest. In a typical interferometer, the sample beam traverses a region of varying refractive index (an electrochemical cell, in this case), while the reference beam travels the same distance but does not undergo a phase change. When the beams are united, the curvature of the interference pattern is a result of the refractive index variation in the cell. Since the refractive index of most solutions can be easily correlated with concentration, interferometry provides a direct image of the concentration field.

A schematic drawing of the apparatus is shown in figure 3.1. The basic Mach-Zender design of the interferometer is the same as described by Beach and McLarnon⁹,¹⁰ although nearly all of the original optical elements have been replaced with components of greater capability. The light source (A) is a 5 mW continuous wave He-Ne laser (λ = 632.8 nm)
FIGURE 3.1. Side view of interferometer and flow channel.

A  dual-beam laser
B, C, F  mirrors
D, E  beam expanders
G  experimental cell
H  objective lens
I  reference lens
J  beam uniter
K  camera film plane
which has been modified to emit mutually coherent, vertically polarized beams from each end of the laser tube (C.W. Radiation Model LSR-5P). The reference and sample beams are both reflected by front surface mirrors (B and C) through Galileo-type beam expanders (Rolyne Optics) to achieve a ten-fold increase in beam diameter from 1.5 mm to 15 mm (E and D). The sample beam, rotated 90° by a third mirror (F), traverses the cell parallel to the cathode surface (upper electrode) and meets the reference beam at a partially reflecting dielectric mirror (J) which serves as a beam uniter. The recombined beams are projected onto the film plane of a Bolex 16 mm movie camera (K) where the phase change in the sample beam, a result of the varying refractive index in the cell, is indicated by the curvature and displacement of the fringes in the interference pattern.

Lenses and neutral density filters are used to focus the image and improve the fringe contrast. Located in the path of both the reference and sample beams, objective lenses (H and I) focus the light on a series of etched lines inside the glass wall of the flow cell (C). The etch marks are separated by 0.5 mm and thus serve to establish a reproducible focus as well as to provide means for a distance calibration. A neutral density filter located in the path of the reference beam compensates for the unequal intensities of the two beams and a second filter decreases the total intensity to allow a camera speed of 24 frames per second. The data are collected on Kodak Plus-X (type 7276) movie film.
Relative error in (a) interfacial concentration, (b) boundary layer thickness, and (c) interfacial concentration gradient as a function of electrode width. In each figure, $\Delta C = 0.1 \text{ M } \text{CuSO}_4$ and electrode width = 20.0 mm (a), 10.0 mm (b), 5.0 mm (c), 2.5 mm (d), and 1 mm (e). From McLarnon, et al. [11]
3.2 Flow Cell

The need for reducing optical errors, higher pressure drop and greater experimental flexibility prompted the construction of a new flow channel. Motivation for a new cell resulted primarily from operational problems with the old cell. A large (300 x 16 x 21 cm, 450 lbs) lucite and steel structure, it was unwieldy to handle and difficult to seal against leaks. Several attempts were made to improve the water-tightness of the old cell, but the unusual o-ring design (collapsible neoprene tubing under air pressure) prevented the use of a more conventional o-ring. The most successful seal resulted from a "close-cell" neoprene sponge tube that compressed as much as the previous tubing so that the glass walls could be fit into place. Unfortunately, the compression was somewhat inelastic and the o-ring required replacement after only a few runs.

A second reason for building a new cell came from past work in this laboratory demonstrating the relationship between cell geometry and optical errors in interferometry. Figure 3.2 shows how errors in interfacial concentration, concentration gradient, and boundary layer thickness diminish as the electrode width is decreased. (see section V also). For example, a decrease in electrode width from 10 mm to 5 mm results in a 60% decrease in the relative error in the boundary layer thickness at a current density of 5 ma/cm². By redesigning the channel with this new information, optical errors could be significantly reduced.
The desire to measure the effect of flow obstacles on the pressure drop in the channel provided another incentive to build a new cell. According to the Hagen-Poiseulle equation, the pressure drop in a pipe is inversely proportional to the square of the radius at a given velocity. Thus a small cell cross-section is necessary to detect small differences in pressure between experiments of different obstacle shapes and sizes. These considerations led to the following criteria for the channel design:

1. The cell should be simple and compact for efficient assembly and alignment.
2. A small electrode width is necessary to minimize optical errors and facilitate electrode polishing.
3. The electrodes should be long enough to allow the observation of the mass transfer disturbances related to at least two obstacles.
4. The cell should have a small equivalent diameter to shorten the entry length and increase the pressure drop.

With these ideas in mind, an acrylic flow channel with a 5 mm square cross-section was built.

The flow cell is pictured in figure 3.3 and illustrated schematically in figures 3.4 and 3.5. It consists of an acrylic shell which encloses copper electrodes located downstream of 55 cm long plexiglass spacers which provides an entry length to ensure fully developed flow past the electrodes. The spacers and electrodes are sandwiched between glass
FIGURE 3.3. Side view of flow channel with interferometer on the right. The cover plates are bolted together to hold the glass walls in place. The O-ring can be seen around the edge of the glass wall of the channel.

CBB 780-14870
FIGURE 3.4. Side view of channel showing spacers (A, B), copper electrodes (C, D), attached obstacle (E), and a detached obstacle (F).
FIGURE 3.5. Cross-section of channel through the electrodes.
walls to permit laser light to travel across the cell width. Plexiglass cover plates on both sides are bolted together to hold the glass walls in place.

The sealing problems encountered in the old cell were solved by restoring to the traditional design of compressing the o-rings mechanically. In the new cell, neoprene o-rings seated in grooves in the cover plates are pressed between the coverplate and the glass-plexiglass joint in the shell, as shown in figure 3.5. A conventional solid neoprene o-ring proved too rigid for this purpose, therefore a dual-wall o-ring was constructed by inserting 3/16" neoprene tube inside a 5/16" tube. This design was soft enough to press slightly into the gap between the plexiglass and glass without causing the edges of the glass to crack.

The electrodes were milled from 99.999% OFHC 3/16" copper sheets. Because their shape and alignment with respect to the laser beam have a critical effect on the interferogram image, the electrodes were subject to several requirements to minimize optical distortions. First, the working surface must be flat, and smooth, with sharp edges to prevent reflection from rounded corners. For this reason, a polishing jig was devised to hold polishing papers at a right angle to the sides of the electrode, as shown in figure 3.6. The working surface was polished to within 30 μ roughness through a sequence of silicon carbide papers (to 600 grit). The limitations of this technique can be observed in the rounded edges in the surface profile shown in figure 3.7A. Light reflection from these rounded surfaces causes an apparent concen-
FIGURE 3.6. Right angle polishing jig. The abrasive paper adheres to the wide, flat surface and the jig travels along the sides of the electrode in the Teflon® guide.
FIGURE 3.7. A. Profiles of electrode working surface obtained with right angle polishing jig and #600 grit carbide paper; surface is smooth with rounded edges.

B. Surface obtained with grinder; the edge on the light entrance side is sharp (right side), but surface is rougher.
FIGURE 3.8.  

a. High speed grinder used to finish the working edge of the electrode.

b. Close-up of abrasive tool piece and electrode.
tration gradient in the zero-current interferogram\textsuperscript{10} (see also section V). To minimize the rounding, a new polishing technique was employed that used a small high-speed grinder (figure 3.8) to finish the surface mechanically. The resulting profile, figure 3.7B, shows a slightly better edge but at the expense of greater surface roughness.

The second requirement for the electrodes was that they had to be aligned precisely with respect to the laser beam so that the sample beam crossed the cell parallel to the electrode surface. To assure this orientation, the sides of the electrodes were polished to an optically flat finish and used as a mirror for the sample beam. When the incident beam was reflected normal to the side of the electrode so that it exactly retraced its path back to the laser, the electrode was correctly aligned.

3.3 Flow Obstacles

A primary goal of this investigation was the study of the effect of turbulence promoter size and shape on the downstream concentration profile. Small promoter sizes and the wide range of shapes to be studied necessitated individual construction of each obstacle. Examples of the three obstacle shapes; round, square, and triangular, are shown in figure 3.9. For cutting ease and chemical resistance, all promoters were cut from oven-cured epoxy. Each obstacle was 0.762 mm high and 0.5 mm long so it occupied approximately 2% of the cross-sectional area of the channel.

Traditional machining techniques, albeit in miniature, were used to make the obstacles. For example, the square obstacles were made...
FIGURE 3.9. Examples of the three obstacle shapes studied: (a) round, (b) square, and (c) triangular. Each obstacle was 0.762 mm high and 5 mm long.
from epoxy sheets cut to the desired thickness with a slitting saw on a milling machine. The final trimming and polishing was done under a stereo-microscope. Triangular promoters were made in much the same way. By sanding away half of a square obstacle in specially made jig (figure 3.10), a promoter with a triangular cross-section was formed. Cylindrical obstacles were produced by turning a larger cylinder down to a 0.762 mm diameter on a conventional lathe. Obstacle diameters within 0.003" of the desired size were selected for experiments.

All of the promoters were mounted in the cell in either an "attached" or "detached" position. The attached position refers to obstacles glued to the cathode surface. Detached obstacles were sandwiched between the glass walls of the cell at distances of 0.762, 1.524, and 2.286 mm from the cathode surface. To ensure reproducibility of the detached position from one experiment to another, a locator device was constructed to hold the promoters precisely in place while gluing. The jig, pictured in figure 3.11, has three steps of 0.762 mm each and slips over the anode when one glass wall is installed in the cell. The obstacle is secured until it adheres to the glass wall.

3.4 Electrolyte Preparation

Aqueous copper sulfate (no supporting electrolyte) was prepared by mixing reagent grade CuSO₄·5H₂O crystals in distilled water. An electrolyte concentration of 0.05 M was used in each experiment.
FIGURE 3.10  Sanding jig for the construction of triangular obstacles.

XBB 792-2683
FIGURE 3.11. Positioning device for gluing detached obstacles. Steps of 0.762, 1.524, and 2.286 mm assure a precise and reproducible distance from the electrode surface.

XBB 793-2972
IV. RESULTS

Optical errors played a large role in determining the course of this investigation. Although interference techniques were sufficient to illustrate boundary layer thickness trends in general, fringe shapes in the chaotic region near the obstacle were ambiguous and current density determinations in this region were inconclusive. Photographs of the copper deposit and surface profiles were used to clarify the current distribution near the obstacles.

4.1 Effect of Obstacles on Boundary Layer Thickness

To determine overall obstacle effectiveness, the influence of the obstacle on the downstream concentration profile was measured with the laser interferometer. Raw data, in the form of interference fringes on 16 mm movie film, were reduced to plots of boundary layer thickness as a function of distance from the leading edge by tracing the projected image and measuring the profile. (Errors inherent in this procedure are discussed in section V). A typical set of interferograms, in this case showing a square obstacle at a Reynolds number of 750, is given in figure 4.1. The undisturbed profile (a), is disrupted by an obstacle of square cross-section located at a distance of 16 mm from the leading edge of the electrode (b). In the near downstream region (c), the boundary layer is thin and local turbulence causes the waviness in the appearance of the fringes in the bulk solution. As the distance from electrode increases, the disturbance subsides and the concentration profile appears similar to the undisturbed profile (d).
FIGURE 4.1. Experimental interferograms near an attached square obstacle. RE = 756, \( i = 3 \text{ ma/cm}^2 \). The electrolyte flow is from left to right.

a. 20 mm upstream of the obstacle
b. at the obstacle
c. 5 mm downstream
d. 80 mm downstream

XBB 7812-15393
To check the validity of the interferometry measurements, results from an unobstructed channel were compared to the familiar Leveque solution† for flow between two flat plates:

\[
\text{Sh}_x = 1.2325 \left( \frac{\text{Sc} \cdot \text{Re} \cdot \frac{d_e}{x}}{x} \right)^{1/3}
\]  

(4.1)

where

- \( \text{Sh} \) = Sherwood number
- \( \text{Sc} \) = Schmidt number
- \( x \) = distance from electrode leading edge
- \( d_e \) = equivalent diameter of channel
- \( \delta_N \) = Nernst boundary layer thickness.

The choice of the type of boundary layer thickness is somewhat arbitrary, as the literature reports values of either Nernst boundary layer \( \delta_N \), ninety percent boundary layer thickness \( \delta_{90} \), or the ninety-nine percent boundary layer thickness \( \delta_{99} \). The difference between these parameters is illustrated in figure 4.2. The ninety and ninety-nine percent thicknesses are defined as the distances over which ninety or ninety-nine percent of the concentration change occurs respectively between the bulk and the interface. The Nernst boundary layer thickness is defined by the intercept of the extension of the concentration gradient at the surface with the line representing the bulk concentration. In this study, the ninety-nine percent definition was chosen because in this way optical errors could be more easily eliminated. (See section 5.3).

FIGURE 4.2. Illustration of the definition of the ninety-nine percent boundary layer thickness ($\delta_{99}$), the ninety percent boundary layer thickness ($\delta_{90}$), and the Nernst boundary layer thickness ($\delta_N$). $C_b$ and $C_o$ refer to bulk concentration and surface concentration, respectively.
Figure 4.3. Boundary layer thickness ($\delta_{99}$) as a function of the distance from the leading edge of the electrode in an open channel. The deviation between theory and experiment is discussed in Section 5.3.
FIGURE 4.4. Boundary layer thickness ($\delta_{99}$) as a function of the distance from the leading edge of the electrode. $Re = 756$, $i = 3 \text{ ma/cm}^2$

Obstacles: left - square, attached
right - square, detached 0.762 mm
FIGURE 4.5. Boundary layer thickness ($\delta_{99}$) as a function of the distance from the leading edge of the electrode. $\text{Re} = 756$, $i = 3 \text{ ma/cm}^2$

Obstacles: left - round, attached
right - square, detached 1.524 mm
FIGURE 4.6. Boundary layer thickness ($\delta_{99}$) as a function of the distance from the leading edge of the electrode.

$RE = 756$, $i = 3 \text{ ma/cm}^2$

Obstacles: left - triangular, attached
right - square, detached 2.286 mm
If a parabolic concentration profile exists in the cell, the Nernst boundary layer thickness can be shown to be half the ninety-nine percent thickness. Assuming a parabolic profile, equation 4.1 can be compared to experimental results by the substitution,

\[ \delta_{99} = 2 \delta_N \]  

(4.2)

Figure 4.3 gives the results of this comparison, showing the measured boundary layer thickness to be about 7% smaller than the predicted values. The reasons for this error are discussed in section V.

The effect of promoter geometry and distance from the surface is shown in figures 4.4, 4.5, and 4.6. In each of these experiments, an obstacle of different geometry was attached to the surface at roughly 15 cm from the leading edge of the electrode and a square detached obstacle was located 20 cm further downstream. The detached obstacles were tested at 0.762, 1.524, and 2.286 mm distance from the electrode. Each obstacle was 0.762 mm high (15% of the electrode separation) to assure identical penetration of the boundary layer and each had roughly the same cross-sectional area, as shown in figure 4.6. A comparison of the results obtained with the attached obstacles shows the relative magnitude of the boundary layer disturbance to be:

triangle > square > round

All of the attached obstacles decrease the boundary layer to the resolution limit of the interferometer (see section 6.3) but the slope
FIGURE 4.7. Boundary layer thickness ($\delta_{99}$) as a function of the distance from the leading edge of the electrode. $RE = 395$, $i = 3$ ma/cm$^2$. Obstacles: left - square, attached; right - round, detached 1.524 mm.
FIGURE 4.8. Boundary layer thickness ($\delta_{99}$) as a function of the distance from the leading edge of the electrode. 

$RE = 1328$, $i = 3 \text{ ma/cm}^2$

Obstacles: left - square, attached right - round, detached 1.524 mm
FIGURE 4.9. Boundary layer thickness ($\delta_{99}$) as a function of the distance $X_{BL}$ from the leading edge of the electrode. $RE = 1903$, $i = 3\text{ ma/cm}^2$

Obstacles: left - square, attached
right - round, detached 1.524 mm
FIGURE 4.10  Experimental interferograms near an attached square obstacle at a Reynolds number of 395, $i = 3 \text{ ma/cm}^2$. Note "upstream effect" ahead of the obstacle and "kinks" in the downstream region. Flow is from left to right.

a. at the obstacle, upstream side  
b. at the obstacle, downstream side  
c. 5 mm downstream  
d. 22 mm downstream

FIGURE 4.11  Experimental interferograms near a round obstacle detached 0.762 mm from the electrode surface. RE = 395, $i = 3 \text{ ma/cm}^2$. Note the thin boundary layer directly above the obstacle compared to the upstream boundary layer. Flow is from right to left.

a. at the obstacle, upstream side  
b. at the obstacle, downstream side  
c. 22 mm downstream  
d. 152 mm downstream
of the recovery curve (boundary layer curve downstream of the obstacle) depends upon the shape of the obstacle. As the promoter becomes more streamlined, the boundary layer thickness reaches the upstream value over a shorter distance. Promoter performance declined as the obstacle distance from the surface increased. The obstacle located 0.762 mm from the surface had largely the same effect on the boundary layer as an attached obstacle (figure 4.4), while the pre-obstacle boundary layer thickness was effectively maintained (but not decreased) by the obstacle located in the center of the cell (figure 4.6).

The effect of Reynolds number in determining promoter efficiency is shown in figures 4.7, 4.8, and 4.9. In each experiment the obstacle configuration was the same: an attached square promoter was located 15 cm from the leading edge, and a round promoter, located 20 cm further downstream, was detached 0.762 mm from the surface. As expected, at higher Reynolds numbers the obstacles were more effective in maintaining a much lower boundary thickness.

In some experiments, the concentration profile near the obstacle was so complicated that determining the actual boundary layer involved great uncertainties. Figures 4.10 and 4.11 show the interferograms from an experiment at a Reynolds number of 395 with an attached square obstacle and a detached round obstacle. In the region just downstream of the attached obstacle the effect of electrolyte streaming past the obstacle can be seen. In this case the boundary layer was recorded to be the distance across the first concentration kink near the electrode.
Another problem encountered in the analysis of these results was the scatter in the data behind the obstacle. In some experiments the boundary layer appeared to grow smoothly downstream of the obstacle (for example, the attached round obstacle shown in figure 4.5), while in others (the attached triangle in figure 4.6) the recovery curve appears very jagged. When points in the jagged curves were analyzed as a function of time, it was found that they were essentially steady state profiles. To indicate this, the curves shown in figure 4.4 through 4.9 are not smoothed out behind the obstacles.

4.2 Current Distribution Around Obstacles

A closer look at figure 4.1 reveals a region of unusual interference patterns in the vicinity of the obstacle. Fringe shapes in this region, distorted by the complex and unstable flow near the obstacle, reflect an apparent zero-current concentration profile immediately upstream, and show unsteady (time-dependent) concentration variations in the near downstream region. These areas of local turbulence are particularly important in the development of optimal obstacle design. However, reflection from rounded electrode edges limits resolution and makes them inaccessible by interferometry. At first glance, the interpretation of this "upstream effect" is that this region is an area of highly effective mixing; the boundary layer is thin, and the current density is high. However, the steep concentration gradient associated with high current density, is not visible. The alternative explanation, that the upstream region is an area of stagnant flow and the current
FIGURE 4.12. Appearance of electrode deposit in the vicinity of obstacles.
RE = 756, \( i = 3 \) mA/cm\(^2\)

a. Attached square obstacle. Note effect of an adhered bubble on the deposit pattern.
b. Attached round obstacle.
FIGURE 4.13. Appearance of electrode deposit in the vicinity of obstacles.
RE = 756, i = 3 mA/cm²

a. round obstacle detached 1.524 mm
b. square obstacle detached 0.762 mm
RE = 756, \( i = 3 \text{ ma/cm}^2 \)

a. Attached triangular obstacle. Deposition on smooth electrode prepared with right angle polishing jig.

b. Attached triangular obstacle. Deposition on electrode prepared with high speed grinder
FIGURE 4.15. Appearance of electrode deposit in the vicinity of a square obstacle detached 0.762 mm from the electrode surface. \( Re = 756, \ i = 3 \text{ ma/cm}^2 \). Arrow denotes obstacle position.
density is low, is not in accordance with the narrow boundary layer thickness observed in this region. To resolve this problem, alternative methods were used to measure current distribution directly.

The deposit morphology near obstacles is a clue to the flow patterns around them. Although the experiments were run at 50% of limiting current, an organized pattern of copper ridges was deposited near the obstacle in every experiment. Several examples of deposit patterns are shown in figures 4.12 through 4.15. The outstanding features of these photographs are noted below:

1. The deposit away from the obstacle in both the upstream and downstream direction is smooth and uniform.
2. The wake fully occupies the electrode width in each experiment, but the length of the wake is a function of the obstacle shape.
3. There is a significant morphology deviation upstream of the attached and near detached obstacles. (figures 4.12, 4.14, 4.15)
4. The deposit under detached obstacles becomes smoother as the obstacle is moved further away from the surface. (figure 4.13)
5. The presence of bubbles next to the obstacle changes the deposit pattern to reflect the asymmetric flow pattern past the bubble. (figure 4.12a)

These observations suggest that the deposit ridges follow the stream lines of the flow past the obstacle.
FIGURE 4.16

XBB 793-4165
FIGURE 4.16 Illustration of the average deposit thickness near an attached square obstacle. The surface profiles at several points in the obstacle wake were integrated to measure the average deposit thickness of the active cross-section of the electrode. The arrows denote the scanning direction of the surfanalyzer stylus (from left to right on the profiles). Average deposit thickness of (a) 7.4 μ, (b) 8.2 μ, (c) 9.65 μ, (d) 10.5 μ, (e) 7.9 μ, and (f) 6.7 μ.
Observation of the deposition pattern does not allow one to distinguish areas of high and low current density. Near the obstacle, the deposit is concentrated in ridges, and the valleys appear to be relatively untouched substrate copper. Away from the obstacle, the deposit is uniform and the underlying copper is not visible. To compare these deposit zones, and to clarify the current distribution in the upstream region, a stylus surface profile analyzer (Clevite Gould Surfalyzer Model 150) was used to characterize the deposit at several locations along the length of the electrode. To determine the absolute deposit thickness, a reference surface was established by partially masking a portion of the electrode. By painting two strips of a thin coat of petroleum jelly along the length of the electrode, deposition was inhibited at the coated surface. Parallel scans across the electrode width yielded a quantitative picture of the deposit in the wake of the obstacle. The results are shown in figure 4.16. Except for the absence of deposit in the grease strips, the appearance of the electrode after deposition is similar to the deposit pattern in figure 4.12a. If a constant deposit porosity is assumed, the surface profiles show a 30% increase in deposit thickness in the upstream pattern compared to the thickness 5 cm upstream of the obstacle. On the same basis, the near-downstream zone showed an average 35% increase in deposit thickness.

When an obstacle is located at least 0.762 mm from the electrode surface, a deviation in anodic morphology was sometimes observed. Figure 4.17 shows the anodic and cathodic patterns resulting from an
FIGURE 4.17. Anodic dissolution pattern near a square obstacle detached 0.762 mm from the cathode (above) and 3.476 mm from the anode (below).
obstacle placed 0.762 mm from the cathode and 3.476 mm from the anode. Apparently, obstacle-induced turbulence alters the flow near the anode enough to interfere with dissolution. Interestingly, no anodic dissolution patterns were noted in experiments with attached obstacles.
V. OPTICAL ERRORS

If it were not for the inevitable optical errors, interferometry would be an ideal tool to elucidate concentration fields in a electrochemical cell. However, in nearly any practical situation, the non-ideal behavior of the light in the refractive index field causes errors if the interferograms are interpreted according to conventional theory. These errors have been analyzed in this laboratory in great detail and have been described elsewhere, but any study utilizing interferometry must consider the consequences of the actual light path through the cell to obtain useful results.

5.1 Light Deflection Errors

In the conventional interpretation of interferograms, one assumes that the light beam travels in a straight line across the cell. Since the geometrical path length is fixed, the changes in optical path lengths due to the boundary layer is simply the product of the change in the local refractive index and the width of the cell.

\[ \Delta p = \Delta n \cdot d \]  \hspace{1cm} (5.1)

where

\[ d \equiv \text{width of cell} \]
\[ \Delta p \equiv \text{change in optical path length} \]
\[ \Delta n \equiv \text{change in refractive index} \]

The change in optical path length of the sample beam specifies the concentration at a point in the boundary layer according to the
relationship between the refractive index and concentration of the solution. For dilute copper sulfate, the refractive index is a linear function of CuSO$_4$ concentration. At a wavelength of 632.8 nm,

$$n = 1.3311 + 0.029 \, c .$$  \hspace{1cm} (5.2)

where \( c = \) concentration (M)

However, in the presence of a refractive index gradient, instead of traveling in a straight line, the light is deflected in the direction of increasing concentration (Schlieren effect), as shown in figure 5.1. The optical path length in this case is a function of the refractive index in the cell and the actual geometric path:

$$p(x) = \int_{0}^{x} n(x,y) \sqrt{1 + \left( \frac{dy}{dx} \right)^2} \, dx .$$  \hspace{1cm} (5.3)

To solve equation 5.3, the trajectory of the beam must be calculated according to the light deflection equation,

$$\frac{d^2 y}{dx^2} = \frac{1}{n(x,y)} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right] \left[ \frac{\partial n}{\partial y} - \frac{dy}{dx} \frac{\partial n}{\partial x} \right] .$$  \hspace{1cm} (5.4)

Both equations 5.3 and 5.4 require knowledge of the refractive index in the cell, \( n(x,y) \). Hence, taking light deflection into account in the interpretation of the interferograms entails an iterative calculation involving the following steps:

1. Guess the refractive index profile.

2. Calculate the associated interferogram.
FIGURE 5.1. Schematic illustration of light deflection in a refractive index gradient. Ray DEF is deflected out of the boundary layer, while ray ABC is only deflected slightly and remains in the boundary layer. Line GH represents the edge of the boundary layer (From McLarnon\textsuperscript{6}).
Comparison of corrected and uncorrected concentration profiles in a stagnant cell. Line BF is the computed concentration profile neglecting light deflection errors. Line AE is the theoretical concentration profile corresponding to the experimental conditions of $i = 10 \text{ mA/cm}^2$, $C_b = 0.1 \text{ M CuSO}_4$, and zero flow velocity (From McLaron et al.).
3. Compare the results with the experimental interferogram and guess a new refractive index profile.

4. Repeat the process until there is good agreement between computed and experimental interferograms.

This solution technique was developed in 1975 by McLarnon using a variety of polynomial expressions for the guessed concentration profiles. The results of these calculations demonstrated that large errors in the concentration gradient, interfacial concentration, and boundary layer thickness could result if the deflection of the beam is not taken into account. (For example see figure 3.2 and 5.2). The values of interfacial concentration and concentration gradient must be obtained through the use of this iterative technique. The error in boundary layer thickness, however, corresponds to the distortion in the position of the electrode shadow (see figure 5.2). Therefore, the simplest way to correct errors in boundary layer thickness measurements is to record the position of the electrode/electrolyte interface in the zero-current interferogram and compare it to the interferogram obtained with the current on. According to figure 5.2, the error in the true boundary layer thickness \((y_F - y_A)\) is simply the difference between the apparent interfacial value, \(y_B\), and the interfacial position when the current is off.

A measure of the effectiveness of the correction techniques developed by McLarnon is given by the comparison of the corrected experimental profiles to predicted profiles based on the calculation
Comparison of experimental concentration profiles corrected by solving the light deflection equation (dotted lines) to the theoretical concentration profile (solid lines). The uncorrected concentration profiles are represented by the heavy solid lines. RE = 756, i = 3 ma/cm², D⁺ = 6 x 10⁻⁶ cm²/sec and t⁺ = 0.4.
of the current distribution below limiting current. The solution to the problem of current distribution on plane, parallel electrodes in channel flow was given by Parrish and Newman,\textsuperscript{12,13} under conditions of fully developed laminar flow, dilute solutions, single salt deposition, and a ratio of cell height to length of 0.05 or greater. This analysis was extended by Sides and Prentice\textsuperscript{14} to obtain the average interfacial concentration as a function of the distance from the leading edge of the electrode. By using the Lighthill transformation to describe the mass transfer in a thin diffusion layer, the concentration distribution was calculated from the equation of convective diffusion.

The results of these calculations at three locations along the electrode are shown in figure 5.3 for a Reynolds number of 750 and a current density of 3 mA/cm\textsuperscript{2}. As in figure 5.2, the uncorrected fringes (solid curve in figure 5.3) indicate a 50% smaller concentration gradient and a 20% higher interfacial concentration than the uncorrected data. For the most part, the computed results verify the corrected data, showing an average 5% difference in the values of the concentration gradient and predicting the interfacial concentration to within 2% of the corrected value at the center of the electrode. The largest deviation of the corrected data was an 11% difference in interfacial concentration values at a position 10 cm from the leading edge. This is probably due to the approximation of a constant light deflection error along the length of the electrode. Near the leading edge, the concentration difference between the bulk and the surface is smaller than the average, and the model tends to slightly "over-correct" the interfacial
FIGURE 5.4 Effect of focus on the appearance of the interferogram in the presence of light deflection. Location of focal plane at (a) $x = -1.1$ cm, (b) $x = -0.55$ cm, (c) $x = 0$, (d) $x = 1.1$ cm, (e) $x = 2.2$ cm, (f) $x = 3.3$ cm, (g) $x = 4.4$ cm, and (h) $x = 5$ cm. $x = 0$ is defined to be the location of the focal plane at the inside glass wall on the light entrance side of the cell. Note the appearance of the interface and the etch marks as a function of the position of the focal plane.
FIGURE 5.5.

Schematic illustration of light reflection off of rounded edges of the electrode. Ray ABC is the incoming light beam and line DBE is the tangent to the surface at the point of reflection. (From McLarnon10).
concentration. However, in general the calculated concentration profiles largely substantiate the earlier work on the problem of errors in interferometry and serve to underline the inadequacies of the conventional interpretation of interference fringes for practical problems.

In addition to the altered path length of the laser light, the curvature of the deflected beam changes the appearance of the image in different planes of focus. In the presence of light deflection, the image is determined by the virtual origin of the beam. When the lens is focused on the glass wall on the light entrance side of the cell, \((x = 0)\), the virtual origin of the deflected beam causes the electrode shadow to appear receded from the solution. As the plane of focus is moved toward the light exit side of the cell, \((x > 0)\), the interface advances into the solution. As shown in figure 5.4, this effect also changes the appearance of the fringes so that the apparent gradient and interfacial concentration are also a function of the chosen plane of focus.

5.2 Surface Reflection Errors

The appearance of a spurious concentration profile at the electrode edge in the absence of current is a result of the reflection of the sample beam from the rounded edges of the electrode. By increasing the path length and changing the direction of the incident beam, this effect causes an apparent phase change as well as distortion in the position of the interface. Figure 5.5 illustrates the way in which the beam trajectory is altered. An incoming parallel beam at \(A\) is
reflected at B at an angle of incidence (ABD) that is equal to the angle of reflection (CBE) with respect to the surface tangent (DBE). Incident beams entering the cell above \( y = 0 \) are not reflected. The severity of the distortion resulting from surface reflection depends strongly on the choice of focal planes of the imaging lens. Figure 5.6 shows the appearance of the interface, in the absence of a refractive index gradient, at various focal planes in the cell.

For a focus at \( x < 0 \), the interface seems to have receded away from the solution and the fringes are curved near the interface. As the plane of focus moves into the solution, \( x > 0 \), diffraction fringes parallel to the electrode edge appear at the interface and the etch marks, and the curvature diminishes.

The presence of these spurious concentration profiles at the interface complicates the interpretation of the boundary layer thickness near obstacles. In some experiments the actual boundary layer near the obstacle was small enough to be hidden by the apparent boundary layer caused by surface reflection. This problem of a "minimum observable boundary layer thickness", is discussed further in section 6.3.

5.3 Boundary Layer Thickness Error

Even when the error from light deflection is corrected, interferometric measurements of boundary layer thickness are approximately 10% lower than the predicted values (see figure 4.2). The magnitude of this error is relatively constant along the electrode length and cannot be attributed to scatter in the data. The most likely explanation is a systematic error in the process of data reduction. When the interferograms are projected onto a table, the fringes are at least one cm wide with a fringe spacing of approximately 2 cm. The determination
FIGURE 5.6  Effect of focus on the appearance of the electrode/electrolyte interface in the absence of current. Designations are the same as in figure 5.4. Note that the curved fringes at the interface diminish as the focal plane is moved into the solution \((x > 0)\).
of the 99% boundary layer thickness involves the choice of the fringe center, and the point at which the concentration reaches the bulk value. Since these curves are nearly parallel near this intersection, a 2% deviation in the position of the fringe center with respect to $C_0$ results in a 15% change in the value of the boundary layer thickness. Since this procedure was identical for each set of interferograms, the error is constant, and a comparison of relative boundary layer thickness is free from error.
VI. DISCUSSION

6.1 Interferometric Boundary Layer Measurements

Ideally, studies of turbulence promoters should reflect the influence of obstacles on the local current density as a function of the distance from the obstacle. In this way, the spacing between promoters can be chosen to optimize the total current and the current distribution. The direct interpretation of interferometric results as local current density is complicated by the lack of data on the concentration gradient or interfacial concentration near the obstacle. Since the relationship between the boundary layer thickness and the local current density is a function of the fraction of the limiting current, the variations in boundary layer thickness are not directly proportional to changes in the local current density.

In principle, interferometric techniques can be used to measure the interfacial concentration and concentration gradient. Under conditions of a uniform velocity field and a smooth current distribution, it is possible to correct optical errors and derive the electrolyte concentration at the surface. (See section V.) However, in the turbulent region both upstream and downstream of the obstacle, a spurious boundary layer caused by light reflection off the rounded edges of the electrode obscures the actual boundary layer.

Previous investigators have studied the effectiveness of obstacles by measuring the increase in limiting current as a function of obstacle parameters. These techniques have the advantage of measuring current
density directly, instead of inferring changes in current density from variations in the thickness of the diffusion layer. However, the use of limiting current methods restrict the study to purely mass transfer limited regimes which, due to low current efficiency, are uninteresting for industrial applications. Such techniques are useful only for overall mass transfer evaluation and isolation of the mixing contribution from a single promoter is not possible.

The local boundary layer thickness is related to the local current density for a binary electrolyte by:

\[
\begin{align*}
    \frac{i}{i_{\text{avg}}} &= \frac{nFD}{1 - t_+} \frac{dc}{dy} \bigg|_{y=0} = \frac{nFD}{1 - t_+} \frac{C_b - C_0}{\delta_N} .
\end{align*}
\]

(6.1)

Thus, to increase local current density in a mass transfer limited reactor, one must reduce the diffusion distance (boundary layer thickness) or reduce the interfacial concentration. At limiting current, the interfacial concentration drops to zero and the rise in current density in the presence of turbulence promoters is directly proportional to the decline in boundary layer thickness. Below limiting current, the magnitude of the effect of the mass transfer contribution to the current density depends upon the extent to which the reaction is diffusion controlled. A simplified expression showing the relationship between the boundary layer thickness and the kinetic contribution to the current density is given in equation 6.2. (See appendix I for the derivation of this expression.)

\[
\begin{align*}
    i &= \frac{nFD}{1 - t_+} \frac{1}{\delta} \frac{1}{C_b + \frac{1}{K'}} .
\end{align*}
\]

(6.2)
\[ K' = \frac{\text{RTD}}{i_0 \eta_s (1 - t_+)} \]

Hence, at limiting current, \( \eta_s \) is large, and the boundary layer thickness is the controlling resistance in the reaction rate,

\[ i = \frac{nF \Delta}{1 - t_+} \frac{C_b}{\delta_N}. \]  

(6.4)

However, if the cell current is well below limiting current, equation 6.2 reduces to the linear form of the Butler-Volmer equation,

\[ i = \frac{i_0 zF}{RT} \eta_s. \]  

(6.5)

Therefore, although the plots of boundary layer thickness as a function of distance are not a quantitative measure of local current density, they can be interpreted as a qualitative indication of local mass transfer.

6.2 Analysis of Results

The results of turbulence promoter experiments given in section IV show trends that can be easily visualized when they are presented as a unit. For example, figure 6.1 demonstrates the effect of three different obstacle shapes on the downstream mass transfer boundary layer at a constant Reynolds number and electrode position. Clearly, the triangular obstacle shows the greatest tendency to decrease the diffusion layer, while the round obstacle had the smallest effect as a result of its streamlined shape. Similarly, a plot of the boundary
FIGURE 6.1. Comparison of the effect of obstacle shape on the downstream mass transfer boundary layer. (A) Attached round, (B) Attached square, and (C) Attached triangle. RE = 756. $i = 3 \text{ m}^2/\text{cm}^2$.  

XBL 793-933
layer disturbance behind obstacles which are located at various distances from the electrode (figure 6.2) shows a trend towards better mass transfer as the obstacle is placed closer to the surface.

For general application, obstacle performance data should be presented in a form suitable for optimizing mass transfer in any system. The important considerations in the design of turbulent promoter networks are as follows:

1. The minimum boundary layer thickness at the obstacle
2. The distance over which the obstacle has an effect
3. The average reduction in boundary layer thickness in the obstacle wake.

Once these quantities are specified, the general shape of the downstream boundary layer thickness curve can be deduced.

The effective length of the obstacle is the "recovery distance" \( l_R \) and is defined to be the length from the leading edge of the obstacle over which the pre-obstacle boundary layer thickness is reached. To make this quantity dimensionless, the length term is divided by the height of the obstacle so that the recovery distance can be interpreted as the number of obstacle diameters necessary to re-establish the pre-obstacle mass transfer conditions. In some experiments, the electrode was not long enough to observe the entire recovery length. In these cases, the curve was extrapolated to the pre-obstacle boundary layer thickness to estimate a value for the recovery distance.
Comparison of the effect of the obstacle location on the downstream mass transfer boundary layer. Square obstacles are detached. (A) 2.286 mm, (B) 1.524 mm, and (C) 0.762 mm from the electrode. $RE = 756, i = 3 \text{ ma/cm}^2$. 

FIGURE 6.2.
Two obstacles could have an identical recovery length but show a very different current distribution in the downstream region. The rate of boundary layer recovery is described by the average boundary layer thickness over a given distance. Thus, the quantity, \( \beta \), is defined as the difference between the average unobstructed boundary layer thickness and the reduced thickness in the wake of the obstacle. This parameter was calculated by integrating both the experimental and theoretical boundary layer thickness curves (Figure 4.4 to 4.9) from the obstacle to a point fifteen cm downstream.

\[
\beta = \frac{\langle \delta_{99} \rangle \text{ unobstructed} - \langle \delta_{99} \rangle \text{ with obstacles}}{\langle \delta_{99} \rangle \text{ unobstructed}}
\]  

The minimum boundary layer thickness \( \delta_{\text{min}} \) is presented as a fraction of the obstacle height. In each experiment, the obstacle height is at least 3 times the unobstructed boundary layer thickness. Thus, this parameter is always 0.35 mm or less. The effect of obstacles having a height on the order of the boundary layer thickness is discussed in section 6.5.

The results of these calculations for all the experiments are presented in tables 1 and 2. In general, the quantitative analysis confirms the observations noted above, and data in this form facilitates further comparisons. For example, by normalizing the average boundary layer thickness measurements with the unobstructed data, the effect of the absolute obstacle position on the electrode can be largely
TABLE 6.1

<table>
<thead>
<tr>
<th>Type of Obstacle</th>
<th>$\delta_{\text{min}}$</th>
<th>$\beta$</th>
<th>$l_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Round - A</td>
<td>.033</td>
<td>37%</td>
<td>201</td>
</tr>
<tr>
<td>Square - A</td>
<td>.033</td>
<td>44%</td>
<td>216</td>
</tr>
<tr>
<td>Triangle - A</td>
<td>.033</td>
<td>50%</td>
<td>275</td>
</tr>
<tr>
<td>Square - D1</td>
<td>.033</td>
<td>67%</td>
<td>249*</td>
</tr>
<tr>
<td>Square - D2</td>
<td>.177</td>
<td>45%</td>
<td>209</td>
</tr>
<tr>
<td>Square - D3</td>
<td>.171</td>
<td>37%</td>
<td>190</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of Obstacle</th>
<th>RE</th>
<th>$\delta_{\text{min}}$</th>
<th>$\beta$</th>
<th>$l_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square - A</td>
<td>395</td>
<td>.131</td>
<td>32%</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>756</td>
<td>.033</td>
<td>44%</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>1328</td>
<td>.033</td>
<td>48%</td>
<td>393*</td>
</tr>
<tr>
<td></td>
<td>1903</td>
<td>.033</td>
<td>50%</td>
<td>380</td>
</tr>
<tr>
<td>Round - D1</td>
<td>395</td>
<td>.190</td>
<td>45%</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>1328</td>
<td>.092</td>
<td>59%</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>1903</td>
<td>.052</td>
<td>66%</td>
<td>350*</td>
</tr>
</tbody>
</table>

* extrapolated

D1 $\equiv$ detached 0.762 mm, D2 $\equiv$ 1.524 mm, D3 $\equiv$ 2.286 mm
A $\equiv$ attached
eliminated from the results. Thus, even though the detached obstacles
were located 20 cm further downstream than the attached obstacles,
the average boundary layer thickness values ($\beta$) can be compared.
This comparison extends the number of obstacles which can be evaluated
on the basis of efficiency of decreasing the boundary layer thickness.
According to table 1, if the obstacle spacing were 15 cm, the most
efficient obstacles are (1) square, detached 0.762 mm from the electrode,
(2) triangle, attached to the surface, and (3) square, detached
1.524 mm from the surface. However, if the obstacles were located
5 cm apart, the order would be (1) square, detached 0.762 mm, (2) attached
triangle, and (3) attached square.

The data from experiments at varying Reynolds numbers is presented
in table 2. The results show a strong dependence on Reynolds number,
with the highest efficiency (62%) and longest recovery distance
(350 cm) resulting from the experiment at a Reynolds number of 1903,
the highest velocity tested. The resolution of interferometry limited
the flow rates which could be tested. At Reynolds numbers higher
than 2000, the boundary layers became so thin that detection of
disturbances behind obstacles was impossible. In any case, because
the use of obstacles is not necessary at high Reynolds numbers, the
present investigation was not designed to include the turbulent bulk
flow regime.
FIGURE 6.3. Boundary layer thickness ($\delta_{99}$) as a function of distance from leading edge. An attached triangular obstacle is located 16 cm from the leading edge. $\text{RE} = 756, \text{i} = 3 \text{ m/s/cm}^2$. 
FIGURE 6.4. Comparison of theoretical and observed boundary layer thicknesses in the wake of an attached square obstacle, assuming (1) the minimum boundary layer thickness is 0.0125 mm and (2) the beginning of the new leading edge is approximately 35 mm downstream from the obstacle.
6.3 Mechanism of Eddy Mixing

The nature of the turbulence generated at the obstacles is not revealed by interferometry or limiting current techniques. One would expect, based on flow studies by Schlichting, Tani and others, that the wake contains stable and unstable vortices and stagnation points that vary according to the obstacle shape, its location, and the flow velocity in the cell. Both the interferograms and the morphology of the cathodic deposit indicate a departure from the usual fringe shape and deposit pattern at the obstacle. The "S-shaped" concentration profiles (for example, figure 4.10) and the non-uniform but highly organized deposits (figures 4.11 through 4.14) occur only near the obstacle; these effects subside as a uniform velocity profile resumes away from the turbulence source. In addition, according to figure 6.3, the boundary layer thickness does not recover to the unobstructed curve even over a distance of 40 centimeters. These results indicate that the recovery distance following the obstacle can be treated as a turbulent wake followed by a resumption of laminar flow. The turbulent wake acts to stir the solution and increase the concentration near the electrode, while in the second, laminar flow region, the mass transfer boundary layer grows as if the obstacle were the source of a new leading edge.

The presence of two hydrodynamic regions downstream of the obstacle is demonstrated in figure 6.4, which shows the theoretical expression for the development of a boundary layer from a leading edge (equation 4.1).
FIGURE 6.5. Comparison of theoretical and observed boundary layer thicknesses in the wake of an attached round obstacle, assuming (1) the minimum boundary layer thickness is 0.0125 mm and (2) the beginning of the new leading edge is approximately 10 mm from the obstacle.
FIGURE 6.6. Comparison of theoretical and observed boundary layer thicknesses in the wake of an attached triangular obstacle assuming (1) the minimum boundary layer thickness is 0.0125 mm and (2) the beginning of the new leading edge is approximately 60 mm from the obstacle.
superimposed upon the plot of the observed boundary layer in the wake of an attached square obstacle. If one assumes the boundary layer is reduced to a thickness of 0.0125 mm at the obstacle, the experimental data fits the theoretical prediction to within 3% of the theoretical height 30 cm from the leading edge. Due to the reflection from the electrode edge which prohibits the observation of any boundary layer thickness less than \( \delta_{99} = 0.025 \) mm, the assumed value of a minimum thickness of 0.0125 is somewhat arbitrary. This figure was chosen as a compromise between lowest observable thickness and a boundary layer of zero thickness associated with perfect mixing at the obstacle. The obstacle and the apparent location of the new leading edge (2.8 cm in figure 6.4), corresponds to the length of the hydrodynamic wake behind the obstacle, where continuous mixing occurs. This length is dependent on the obstacle shape, height, and distance from the surface. Hence, a more streamlined shape (round) produces almost no discernable wake (figure 6.5) and the boundary layer recovers very smoothly according to theory, assuming a thickness of 0.0125 mm at the obstacle. Similarly, a triangular obstacle has a large effect on the laminar flow, and produces a 5.9 cm long wake at the same Reynolds number as the square obstacle (figure 6.6).

In addition to the interferometric results, the unusual morphology pattern near the obstacle mirrors the turbulence in the region. Although the assignment of the precise location where the deposit becomes smooth is somewhat speculative, it is possible to correlate the length of the
apparent turbulent wake from interferometry and the wake observed from the electrode deposit. In table 6.2, the wake measured from the electrode photographs is compared to the derived wake length from interferograms. The results indicate that there is a reasonable correspondence between the deposit patterns and the turbulent wake.

Since all of these experiments were run at only 50% of limiting current, it is not obvious why the deposit ridges near the obstacle should appear at all. Several investigators have observed deposit patterns that reflect the hydrodynamic conditions at the electrode surface.\textsuperscript{18,19} It is postulated that the varying interfacial concentration in the wake of protrusions in the substrate alter the crystallization overpotential on a microscopic scale. However, a complete explanation has not yet been proposed.

6.4 The Upstream Effect

From interferometric observations, it is apparent that the region of most efficient mixing (and thus the smallest boundary layer thickness) is just upstream of the attached obstacle. Theoretical considerations and smoke tunnel experiments\textsuperscript{20,21} of flow into a wall indicate the presence of a standing vortex in the corner. According to these results, the flow in the vortex rotates in the clockwise direction (as shown in fig. 6.7), a pattern that would bring concentrated electrolyte from the bulk to the surface in a electrochemical cell. The presence of such vortices cannot be confirmed with the experimental techniques used for this study, but the interferometric results and the observed deposit morphology are consistent with this explanation.
FIGURE 6.7. Standing vortices in corner flow. Above: Vortex upstream of a corner (from a photograph by Barnes$^{21}$). Below: Vortices in flow over a rectangular step (from a photograph by Tani$^{17}$).
TABLE 6.2

Wake Correlation

<table>
<thead>
<tr>
<th>Obstacle</th>
<th>A: Wake</th>
<th>B: Upstream Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Deposit</td>
<td>Interferometry</td>
</tr>
<tr>
<td>Square - A</td>
<td>28mm</td>
<td>3.0mm</td>
</tr>
<tr>
<td>Square - A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triangle - A</td>
<td>59</td>
<td>60</td>
</tr>
<tr>
<td>Round - A</td>
<td>11.25</td>
<td>10</td>
</tr>
<tr>
<td>Square - A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triangle - A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 6.8. Upstream effect at several Reynolds numbers. $U = 3 \text{ ma/cm}^2$ in each experiment. (a) attached square, $\text{RE} = 395$; (b) round, detached 0.762 mm, $\text{RE} = 395$; (c) attached square, $\text{RE} = 540$; (d) attached square, $\text{RE} = 72$; and (e) attached square, $\text{RE} = 0$. 
The interferograms of the upstream region are shown in figure 4.1 and 4.10. Experiments at different Reynolds numbers all indicate an upstream disturbance of some kind, although the pattern of straight fringes bordered by an inclined line (as shown in figures 4.1 and 4.10) only occur at a Reynolds number greater than 75. This is demonstrated in figure 6.8, which shows fringe pattern in the upstream region at several Reynolds numbers. These figures indicate a departure from normal laminar flow at the onset of the slanted line separating the upstream region from the normal fringe pattern further upstream. Assuming a standing vortex exists in the corner, the origin of the slanted line indicates the point of boundary layer separation ahead of the vortex, as sketched in figure 6.7. The reason this effect is visible by interferometry is probably the light deflection (Schlieren) phenomenon that was discussed in section V. When the depleted region is swept past the vortex, it is surrounded on both sides by electrolyte having a higher concentration. This "sandwich" of a layer of low refractive index in between two layers of higher refractive index tends to deflect the light from the low index layer into the two high index layers. The two deflected beams interfere with the normal beam to form a slanted fringe pattern which, located between the standing vortex and the laminar region upstream, is independent of the reference beam of the interferometer. Indeed, this fringe pattern is clearly visible when the reference beam is blocked.

Many experiments (figures 4.4, 4.5, 4.7, 4.8 and figure 4.11B) showed an abnormally thick boundary layer just ahead of the upstream
region. Although originally thought to be an anomaly, this effect can be explained by assuming that the clockwise flow in the standing vortex brings depleted solution to the front of the vortex, and thus forms a thick localized boundary layer. This effect is not noted in every experiment, but since it occurs over roughly a one mm area, it could easily be missed in the interferometer scan.

The presence of a vortex upstream of the obstacle is also indicated by the deposit morphology in the region. Figures 4.11 through 4.14 show symmetric ridges in the deposit pattern that run from the center towards the sides of the electrode in all the attached and near detached obstacle experiments. The separation point indicated by interferometry can be closely correlated to the upstream effect noted in the deposit pattern. Table 6.2 shows the comparison of the interferometrically observed upstream effect and the deviation in deposit pattern measured from electrode photographs. In general, the upstream deposit pattern is larger than the deviation in the interferometry fringes, indicating that the deposit also reflects the effect of the low current density area ahead of the separation point.

6.5 Design of Electrochemical Systems Using Turbulence Promoters

The results of this study can be used to design a turbulence promoter system to maintain a predetermined average boundary layer thickness in an electrochemical flow cell. To scale these results to other flow cells, it is important to maintain a constant ratio of obstacle height to the boundary layer thickness. In this study, the
obstacle height was approximately 3.5 times the boundary layer thickness at a Reynolds number of 750. Previous studies have shown that if the obstacle height is on the order of the boundary layer thickness, the recovery distance is drastically reduced. According to equation 4.1, the boundary layer thickness is determined by the Reynolds number, Schmidt number, and the equivalent diameter of the cell. Thus, a convenient scaling parameter is the ratio of equivalent diameter to obstacle height, $\frac{d_e}{N}$ equal to 6.5 in this study.

Because the obstacles "shadow" or block the active surface of the electrode, it is advantageous to locate the obstacles as far apart as possible. However, the choice of obstacle shape and distance from the surface depends upon the consideration of the deposit morphology. If a uniform deposit is necessary, a streamlined detached obstacle will produce the smoothest deposit. However, in applications which do not require metal deposition, the best configuration to maintain the lowest boundary layer thickness over the longest area, is a square or triangular obstacle detached one obstacle height away from the surface.

The approximate shape of the recovery curve at a given Reynolds number can be deduced from curves 4.7, 4.8, and 4.9. With this information, the average boundary layer thickness in the cell is determined by the choice of obstacle spacing. For example, to maintain a boundary layer thickness of approximately 0.075 mm in a channel at a Reynolds number of 750, four attached square obstacles were placed 5 cm apart, as per figure 4.4. The results of this experiment are shown in figure 6.9.
FIGURE 6.9. Boundary layer thickness as a function of distance from the leading edge. Attached square obstacles located at 15 cm, 20 cm, 25 cm, and 30 cm from the leading edge. 
RE = 756, i = 3 ma/cm².
In the region occupied by the obstacles, the average boundary layer thickness is roughly 0.075 mm. An unexpected consequence of this experiment is the apparent decline in the recovery rate after successive obstacles. Note that the boundary layer thickness after the first and second obstacles peak at 0.125 mm, after the third obstacle the peak is 0.110 mm, and after the fourth the peak would be 0.090 mm if a fifth obstacle were included. This implies that the spacing between the first obstacles should be determined by figures 4.4 through 4.6, but subsequent obstacles could be located further apart.
VII. CONCLUSIONS

Interferometry provides a visual demonstration of the practical use of small flow obstacles to thin mass transfer boundary layers near electrode surfaces. The technique is highly sensitive to the location of the focal plane of the imaging optics of the interferometer and to the quality of the electrode surface, new polishing techniques and a reproducible setting of the focal plane were developed to achieve a measurement of the boundary layer thickness in the vicinity of the obstacle.

Results are presented in the form of plots of boundary layer thickness as a function of the distance from the leading edge of the electrode. To describe these plots quantitatively, parameters have been introduced which indicate the efficiency of the obstacles, the minimum boundary layer thickness in the wake, and the recovery distance of the downstream boundary layer. For example, at a Reynolds number of 750, the attached obstacles reduced the boundary layer over a distance ranging from 201 to 275 obstacle diameters, depending on the shape of the obstacles. Of promoters having round, square, or triangular cross-section, the latter provided the most pronounced effect on the boundary layer. Under the same conditions, detached obstacles on a square cross-section were tested at three different distances from the electrode surface. In general, the efficiency of the detached obstacles decreased as the distance from the surface increased. At the optimal distance of one obstacle diameter from the surface, the detached square shape had the greatest effect on the boundary layer.
In addition to increasing the local current density, the obstacles had a pronounced effect on the morphology of the copper deposit in the wake of the obstacle. Photographs of the electrode surface show streaks and ridges in the deposit which apparently follow the flow pattern in the turbulent region near the obstacle and subside as laminar flow is re-established. The relative length of these disturbances to some extent indicates the relative recovery distances and efficiencies of the obstacles. Thus, the most efficient attached obstacle, the triangular shape, produced a disturbed deposit pattern for nearly six cm downstream as compared to the one cm disturbance produced by the attached round obstacle. These results indicate that attached obstacles act as a source of a new pseudo leading edge for the mass transfer boundary layer at some distance downstream. This distance depends upon the intensity of secondary flows generated by the obstacle.
ACKNOWLEDGEMENTS

I am very grateful to Dr. Rolf Muller and Professor Charles Tobias for their guidance and enthusiasm throughout the course of this study. I also want to thank Professor James Evans for reviewing the manuscript.

The technical wizardry and advice of Walter Giba, Herb Riebe, and Frank Gomez was invaluable in the construction of the flow cell and the obstacles. I also want to thank Ms. Antoinette Czerwinski for drawing the figures, Ms. Carol Payne and Ms. Linda McGuire for typing the manuscript, and the entire photo lab for their patience.

I want to especially thank Peter for his perspective, advice (bear down, throw strikes), and encouragement throughout the course of this work.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Science, U.S. Department of Energy under contract No. W-7405-Eng-48.
REFERENCES


22. Suggested by K. W. Beach, private communication.

APPENDIX I

The purpose of using obstacles in electrochemical flow systems is to decrease the thickness of the mass transfer boundary layer and thus increase the rate of ionic transport to the electrode. Therefore, below limiting current the effectiveness of the obstacles depends upon the extent to which the reaction is diffusion controlled. By assuming small currents and a constant surface overpotential, an estimate can be made of the relative contribution of mass transfer to the total current density.

For a binary electrolyte, the relationship between the mass transfer boundary layer and the current density is,

\[ i = \frac{nFD}{1 - t_+} \frac{3C}{\partial y} \bigg|_{y=0} = \frac{nFD}{l - t_+} \frac{C_b - C_o}{\delta N} . \]  

(1)

Below limiting current, the surface concentration is determined by the kinetic rate of reaction. The general equation which describes electrochemical kinetics is the Butler-Volmer equation,

\[ i = i_o \left( \frac{C_o}{C_b} \right)^{\gamma} \left\{ \exp \left[ \frac{nF}{RT} \eta_s \right] - \exp \left[ \frac{-(1 - \alpha)nF}{RT} \eta_s \right] \right\} . \]  

(2)

For low currents, the surface overvoltage is small and a linear approximation is valid.

\[ i = i_c \left( \frac{C_o}{C_b} \right)^{\gamma} \frac{anF}{RT} \eta_s . \]  

(3)
To simplify equation 3, we assume $\eta_s$ is independent of the distance from the leading edge of the electrode and the current is a function of $C_o$ only.

$$i = K \left( \frac{C_o}{C_b} \right)^\gamma = K \left( 1 - \frac{\Delta C}{C_b} \right)^\gamma$$

(4)

where

$$K = \frac{i_o n F \eta_s}{RT}$$

(5)

$$\Delta C = C_b - C_o$$

(6)

The magnitude of $\gamma$ has been shown to vary between 1.2 and 1.4.23 However, for the purposes of this estimation, we will assume $\gamma$ is unity. Therefore,

$$i = K \left( 1 - \frac{\Delta C}{C_b} \right).$$

(7)

Equation 7 is a simplified expression for the kinetic relationship between the surface concentration and the current density. By solving equation 9 for $\Delta C$ and substituting into equation 1, we obtain,

$$i = \frac{n F D C_b}{(1 - t_+)^{\delta_N}} \left( 1 - \frac{i}{k} \right).$$

(8)

Solving for $i$,

$$i = \frac{n F D \frac{1}{1 - t_+} \frac{1}{\delta_N}}{C_b + \frac{1}{K'}}$$

(9)

where

$$K' = \frac{n F D}{(1 - t_+) K}.$$
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.