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EFFECTS OF SUSPENDED PARTICLES ON THE RATE OF
MASS TRANSFER TO A ROTATING-DISK ELECTRODE

David Jeffries Roha
(M.S. thesis)

June 1981

MASTER

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EFFECTS OF SUSPENDED PARTICLES ON THE RATE OF MASS TRANSFER
TO A ROTATING DISK ELECTRODEContents

ABSTRACT	v
INTRODUCTION	1
Literature Review	3
EXPERIMENTAL	18
Description	18
Experimental Procedure	25
Properties of Glass Beads	28
Experimental Error and Reproducibility	29
The Limiting Current and Physical Properties of the Solution without Glass Beads	39
EXPERIMENTAL DATA	43
0.564 cm Disk—Limiting Current Versus Volume Fraction . .	44
1.413 cm Disk—Limiting Current Versus Volume Fraction . .	51
0.564 cm Disk—Limiting Current Versus Rotation Speed . .	58
1.413 cm Disk—Limiting Current Versus Rotation Speed . .	71
0.564 cm disk—Limiting Current Versus Particle Diameter .	84
1.413 cm Disk—Limiting Current Versus Particle Diameter .	91
DISCUSSION OF EXPERIMENTAL RESULTS	98
Increase in Limiting Current	98
The Offset in Particle Concentration	98
Effect of Electrode Size on Limiting Current	108
Effect of Disk Rotation Speed on Limiting Current	112
Effect of Particle Size on Limiting Current	117

MASS TRANSFER MODELS	120
Surface Renewal Model	120
Conclusions of the Surface Renewal Model	129
Particle Film Model	146
The Practical Particle Film Model	239
MECHANICAL POWER CONSUMPTION FOR A RDE	243
ACKNOWLEDGMENTS	249
APPENDIX A. TEMPERATURE CORRECTION FOR A RDE	250
APPENDIX B. EFFECT OF BULK SLURRY PHYSICAL PROPERTIES ON LIMITING CURRENT	253
APPENDIX C. CALCULATING PARTICLE SURFACE CONCENTRATION, c_s , AND PARTICLE CROSS-SECTION, σ	260
APPENDIX D. THE MEAN VOLUME FRACTION, OCCUPIED BY UNIFORMLY DISPERSED SPHERES, WITHIN ONE DIAMETER OF A WALL	262
APPENDIX E. THE RELATIVE VELOCITY OF A PARTICLE TRAVERSING THE SURFACE OF A RDE	266
APPENDIX F. CALCULATION OF THE MASS TRANSFER BOUNDARY LAYER THICKNESS, δ , AND THE EFFECTIVE DIFFUSICITY, D'	274
APPENDIX G. INTEGRATION I	277
APPENDIX H. INTEGRATION II	282
APPENDIX I. INTEGRATION III	289
APPENDIX J. THE AREA, a_T , AND WIDTH, w , OF INTERACTION OF THE PARTICLE FILM WITH THE ELECTRODE SURFACE	292
APPENDIX K. INITIAL SURFACE CONCENTRATION, C_0	296
REFERENCES	298

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TO A ROTATING DISK ELECTRODE

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ABSTRACT

Limiting currents for the reduction of ferric cyanide at a rotating disk were determined in the presence of 0-40 percent by volume of spherical glass beads. Experiments were conducted with six different particle diameters, and with rotation speeds in the range of 387-270 rpm, using both a 0.56 cm and a 1.41 cm radius disk electrode.

It was established that at a given rpm upon addition of glass beads the limiting current, i_L , may increase to more than three times its value without solids. This increase in limiting current density is greater at high rotation speeds and with the larger disk electrode. i_L as a function of particle diameter yields at maximum at $\sim 10 \mu\text{m}$.

Two mass transfer models are offered to explain this behavior, both of which assume that the beads are in contact with the disk electrode and moving parallel to its surface. In the "surface renewal" model it is assumed that complete mixing takes place with the passage of each bead and the boundary layer is replaced with fresh bulk solution. While with the "particle film" model it is assumed the bead and a clinging film of fluid rotate together. The film promotes mass transfer by alternately absorbing and desorbing the diffusing species. The "particle film" model best explains the observed behavior of the limiting current density.

Calculations of stirring power required verses i_L observed, show that adding beads to increase i_L consumes less additional power than simply increasing the rotation speed alone and even permits a decrease in the amount of stirring energy required per unit reactant consumed, at limiting current conditions.

INTRODUCTION

This thesis describes an efficient method of increasing the rate of mass-transfer between a moving fluid and a solid surface in contact with the fluid. This is achieved by suspending small particles in the flow which somehow "disturb" or "disrupt" the mass-transfer boundary layer and thus speed the exchange of chemical species between surface and fluid. In particular we used a rotating disk electrode contacting an alkaline ferro-ferricyanide solution, to which various particles were added. The rate of mass-transport was determined from the limiting current of the electrochemical reduction of ferricyanide ion to ferrocyanide ion.

The basic idea of this investigation arose from considering the problems of high-speed electroforming, in which entire metallic objects are "formed" by the process of electrodeposition. This differs from electroplating mainly in that after deposition the deposit is intended to come off the substrate cathode instead of adhering firmly to it, and in that the deposit is usually much thicker than an electroplate.

What are the problems of electroforming? They include problems of current distribution, surface finish of product, properties of the electrodeposited material, how to form complex geometric shapes, and the overall energy efficiency of the process. But what is of utmost importance from the economic standpoint as well as of interest to the chemical engineer is the rate of electroforming. Unfortunately, with current technology it is a very slow process.

Electrodeposition of copper at 100 mA/cm^2 (considered a respectable rate for electroplating) yields $2.2 \text{ } \mu\text{m}$ of metal deposit per minute. If one wants to electroform an article 1 mm thick, he must deposit for 7-1/2 hrs. Compare this to sheet metal stamping operations which typically produce pieces every few seconds. Therefore the process of electroforming has been limited to such low-volume specialty items as mesh for very fine sieves, metal-working dies made of hard nickel-cobalt alloy, the stampers used to make phonograph records, precision mirror surfaces for reflective optics (1) and thrust chambers for rocket engines (2).

Electroformed parts appear wherever minute surface detail or precise irregular surfaces are required. Electrodeposited metals are typically harder, stronger and more finely grained than those formed by crystallization from a melt. Some electro-nickels even rival the tempered alloy steels in hardness and strength (3). Scores of composite materials, with interesting properties, have been formed through the codeposition of hard submicron particles or high strength fibers into the metal matrix (3,4).

Although the new amorphous or "glassy" metals have attracted much attention recently (5,6), it is not well known that amorphous alloys such as NiS (7), NiP (8), FeP (9) and CoP (10) have been produced by electrodeposition. However, whereas the conventional ultra-fast quenching technique can only produce thin wires or ribbons, there is no limit to the thickness of amorphous alloys produced by electrodeposition.

These two dissimilar methods of producing the same "glassy" material may be really quite similar in basic principle. A rapidly quenched melt will pass through the temperature region, where phase segregation and crystal formation are possible, within about 10^{-3} sec. Not enough time is available for ordered phases to form and the melt becomes a super-cooled liquid.

Likewise during electrodeposition at 1 A/cm^2 , an atom remains on the surface about 10^{-3} sec before being covered up by the next layer of atoms. Not enough time is available for the atoms to move into the correct crystallographic positions by surface diffusion. Therefore the deposit is amorphous.

The advantages of a high-speed electrodeposition process can be easily seen. Not only would it form the product in less time, but it would also decrease the "quench" time, permitting new meta-stable or unstable materials with superior properties to be formed.

Literature Review

The rate of electrodeposition is limited by the mass transport of the metal ion in the solution to the cathode. More of the metal ion is consumed at the cathode surface than can be replaced by electromigration alone. Therefore, more ions must be transported through a mass-transfer boundary layer by diffusion, essentially a very slow process. When, for given mass-transport conditions, the concentration of metal ions at the surface goes to zero and diffusion can not supply ions any faster, the cathode is said to be at a "limiting current."

Once at the limiting current, that part of the current due to metal ion deposition alone, has reached its limit, regardless of the applied voltage, although other electrochemical reactions, like hydrogen evolution, can then take place.

Nearly all the methods of achieving high current densities involve disrupting the boundary layer or reducing its thickness to make the diffusion process faster. Six major ways of doing this are found in the literature.

- (1) Use of spray jets,
- (2) high-speed channel flow,
- (3) mechanical wiping
- (4) sonic and ultrasonic vibration
- (5) electromagnetic stirring effects
- (6) agitation by a dispersed phase

Use of Spray Jets

It is possible to increase the rate of electrodeposition through the use of spray nozzles which direct jets of electrolyte towards the cathode surface, penetrating the boundary layer and bringing in fresh electrolyte. Blackmore (11) patented such a system for electrotyping and claimed a maximum current density of 320 mA/cm^2 from a lead-tin fluoborate solution. Kawasaki and Mizumoto (12) reported a current density of 1.0 A/cm^2 with a jet velocity of 20 cm/s . Butter and Wittich (13) used agitation from spraying in their oxygen-free electroplating method.

Zarb (14) deposited 2 microns of gold in 15 sec using a jet flow rate of 100 liters/min. Such a growth rate corresponds to 126 mA/cm^2 . Bok and St. Onge (15) directed their spray jets so as to create flow parallel to the surface being plated. No current densities were given in their patent. Reidel (16) plated gold at 400 mA/cm^2 by directing electrolyte streams at the cathode.

High-Speed Channel Flow

Quite high limiting current densities may be obtained by simply pumping the electrolyte at high speeds between the closely spaced anode and cathode. Spaulding et al. (17) of General Motors patented an automatic plating system, which among other things can plate a metal piece by enclosing it with a lead anode which conforms to the shape of the piece, and pumping electrolyte between them at a high rate during electrolysis. Nickel can be plated out at 1.29 A/cm^2 with the electrolyte moving at 40 ft/s, and up to 2.69 A/cm^2 at even higher flow velocities.

Safranek (18,19) used similar means in his investigation of the physical properties of metals, such as copper, lead, nickel, zinc and chromium, deposited at high rates. Current densities of up to 8.0 A/cm^2 were reported, with the electrode gap ranging between 2.5 and 6.25 mm, and the flow velocity between 1.2 and 3.6 m/s. Jacob and Maestri (20) have achieved plating rates between 13 and 22 $\mu\text{m/min}$, with inter-electrode fluid flows from 3.3 to 13.3 m/s.

Der-Tau Chin (21) deposited chromium at up to 70 A/cm^2 by forcing electrolyte at high speeds through a 1.14 mm thick flow channel. It

should be noted however, that his current densities for chromium deposition from chromic acid solution are somewhat inflated due to the fact that it takes six electrons to reduce chromium instead of two for copper or nickel. Also keep in mind that the current efficiencies of chromium deposition are notoriously low (10-15 percent), although Chin was able to raise the efficiency to about 50 percent in his high speed cell.

Mechanical Wiping

Some of the largest current densities reported in the literature are from systems utilizing mechanical wiping. Mechanical wiping involves direct contact of the cathode with moving cloth, brushes, wipers, honing stones or abrasive belts; all of which are driven by some external mechanical force.

Marculla (22) has patented a system in which the anode is covered with three layers of cloth and continuously rubs the cathode surface. Patat (23) reviewed the high speed brush plating of metals.

Ellis and Gavasso (24,25) have received patents on electrochemical honing, where the inside of a cylinder is subject to abrasion from a set of rotating, expandable honing stones. The rotating shaft holding the stones may be made anodic and the workpiece cathodic for electrodeposition, or the shaft cathodic and the workpiece anodic for electrodisolution, or both may be neutral for conventional honing. The inventers claim to be able to plate 0.001 in. of copper in 1 min (1.15 A/cm^2).

Watts (26) takes this idea a step further by using in place of the nonconductive honing stones a material of non-conducting abrasive particles embedded in a matrix of electrically conducting material,

typically metal. Electrodes are kept from touching by the protruding abrasive particles which maintain a separation of 0.0005 to 0.050 in. (0.0127 to 1.27 mm) between anode and cathode. No maximum current densities were given.

The most astounding results come from the experimental work of Eisner. Using abrasive belts moving through the anode-cathode gap, or a rotating cathode perpendicular to a rotating abrasive disk anode (27), he reported current densities as high as 60 A/cm^2 . This highest current density was achieved with a $\text{SnSO}_4/\text{H}_2\text{SO}_4$ solution containing no additives. However, the metal was brittle and contained 8.7 percent SnO_2 . At 2 A/cm^2 and with the same electrolyte a ductile deposit of 99.4 percent tin was produced. Eisner points out that this electrolyte had not hitherto been used without additives because of its tendency to produce dendrites. With abrasion such dendrites would be worn away before they can fully form.

According to the above report, chromium was deposited from a $\text{H}_2\text{CrO}_4/\text{H}_2\text{SO}_4$ solution at 23.5 A/cm^2 , with roughly 40 percent C.E. (current efficiency). Copper was deposited from a pyrophosphate bath at 10.8 A/cm^2 , but due to low current efficiency the growth rate was only 0.001 in./min, corresponding to an effective current density of 1.15 A/cm^2 . With acid-sulfate electrolyte copper was deposited at 4.6 A/cm^2 at 4.6 A/cm^2 with 100 percent current efficiency.

Nickel plated out at 4.6 A/cm^2 with 100 percent C.E. from a $\text{NiSO}_4/\text{H}_3\text{BO}_3$ solution. However the conventional Watts bath and a proprietary nickel sulfamate bath fared less well, both yielding a maximum

of 2.15 A/cm^2 with roughly 50 percent C.E. Zinc, iron, and a nickel-copper alloy were also plated.

From a three-to-one copper-to-zinc sulfate solution, a 21 percent Zn brass was deposited at 2.3 A/cm^2 and close to 100 percent C.E. To this author's knowledge this has never been done from an acid sulfate solution before due to the large (1.1 V) difference in reduction potential between these two metals. It could be that at high current densities the surface and concentration overpotentials for copper is high enough to allow zinc to codeposit. Another possibility is that the dislocations produced in the metal by abrasion may make it easier for zinc atoms to fit into the distorted copper lattice and form a solid solution.

In a subsequent article (28), Eisner concedes the high power consumption due to abrasive friction and the high electrical resistance of his previous methods and discusses a method of light abrasion in which less force was applied on the cathode by the abrasive. This time he obtained current densities of only up to 2.15 A/cm^2 . From his experimental data, one can calculate a resistance 5-10 times higher than what should be expected without an abrasive pad between electrodes.

In his patent (29) Eisner claimed very high current densities, including 18.8 A/cm^2 for depositing aluminum from what appears to be an $\text{AlCl}_3\text{-H}_2\text{O}$ solution. However, his figures on the actual thickness of metal deposited per unit time seem to indicate very low current efficiencies.

Sonic and Ultrasonic Vibration

It is possible to increase mass-transfer to electrodes by causing them to vibrate, either normal or parallel to the plane of the electrode surface. Al-Taweel, Ismail and El-Abd (30,31) have investigated enhanced free-convective mass-transfer for a vertical planar electrode vibrating in the up-and-down direction from 0 to 48 Hz, and up to 8 mm in amplitude. The increase in limiting current over the free-convective limiting current is found to increase with frequency to the 1.09 power and with amplitude to the 0.42 power. However, at certain frequencies, "resonance" peaks are found, where the limiting current is two or three times higher than outside the "resonance" region. In a later paper (32) Al-Taweel and Ismail discuss various mass-transfer models to explain the enhancement of mass-transfer and compare them with experimental results.

Much work has been done on the effects of ultrasonic vibration (13 kHz-100 kHz) on electrodeposition. This field is reviewed by Walker (33). In general ultrasound increases the rate of mass-transfer, and reduces the grain size of the deposit. However, the energy dissipated for most of the cited experiments is comparatively high. For example Enchev et al. (34) applied 1.5 watts/cm^2 ultrasonic energy while depositing at 200 mA/cm^2 . This is equivalent to an incremental voltage drop of 7.5 volts across the cell.

If the effect of a given ultrasonic intensity is to increase the limiting current by a certain percentage of the original limiting current, for example by 100 percent, we could increase the limiting current density by some other means, say by using a high-speed

turbulent flow channel, to 1.0 A/cm^2 and then apply ultrasonic vibration to increase the limiting current to 2.0 A/cm^2 . In this case the additional energy of ultrasound would only be equivalent to $(1.5 \text{ W/cm}^2)/(2.0 \text{ A/cm}^2)$ or 0.75 volts. Therefore the sonic or ultrasonic method might be quite practical if combined with other methods of increasing mass-transport.

Electromagnetic Stirring

If an electrolytic solution conducts current normal to a magnetic field it will experience a body force normal to both the field and current vectors. The body force can then make the solution flow and cause convection to occur.

Mohanta and Fahidy (35) have deposited copper from an acid-sulfate bath in a uniform magnetic field. Although they seem to have been unable to get good limiting current curves at higher current densities, at lower currents we can see a 25 percent increase in mass-transfer. Sunderman and Fahidy (36) have also investigated electrolyte flow under alternating magnetic and electric fields. No data of the combined effects upon limiting currents were given.

An electric current, of course, establishes its own magnetic field, which in turn can influence neighboring lines of flux causing them to twist and curve. Again, as with an external magnetic field, body forces on the electrolytic solution may cause it to flow. Such an effect in aluminum smelting cells was investigated by Evans, Zundelovich et al. (37). The molten cryolite solution swirls at about 10 cm/s , helping bring dissolved aluminum metal to the anode, thereby

reducing the cell's current efficiency. Since a current's magnetic field is proportional to its intensity, and the force on a conductor is proportional to its current density times the magnetic field, one would then expect this self-induced magnetic effect to vary with the square of the current density. If this effect is just noticeable in aluminum cells at 1 A/cm^2 , how much greater would it be in electrochemical machining, for example, at 100 A/cm^2 ? It is not clear at this point whether electromagnetic effects might in the future be economically utilized to raise the limiting current or if they will remain only curious annoyances.

Dispersed Phase Agitation

Dispersed phase agitation involves small elements of a suspended phase, which cause disturbances in the motion of the fluid surrounding them, and in so doing cause mixing and promote mass-transfer.

Bobrov et al. (38) have patented a method of making copper foil, one side of which is microscopically rough. Using bubbles of compressed air for agitation, they deposited smooth metal at 50 mA/cm^2 , and to produce a rough surface, increased the current density as far as 5 A/cm^2 . Harvey et al. (39), working for Kennecott Copper, sparged copper electrorefining cells with air bubbles so as to utilize current densities (226 mA/cm^2) ten times higher than those possible with just natural convection.

The earliest use, in the literature, of solid particles in electroplating is a 1902 patent by Reed (40). The plating bath holds an agitated slurry of sand particles suspended in the plating solution,

and the cathodic workpiece is moved around in the slurry while being plated. He mentioned no current densities, just that the deposit had a better and smoother appearance.

Fluidized bed electrodes, of the type in which one or both of the electrodes are immersed in a fluidized bed of solid non-conducting particles, have attracted attention over the past 15-20 years. Le Goff and co-workers (41) have increased the limiting current by a factor of 4.3 through the use of this kind of fluidized bed, over that for the same flow rate without a bed. Carbin and Gabe (42,43) confirm this increase with a similar experiment and also provide a mass-transfer correlation of their own. Their experiments show a slight increase in limiting current with glass particle diameter, from 184 to 354 μm . It would be interesting to know whether this is because agitated large particles are innately more effective in disrupting or thinning boundary layers, or if it is because the greater flow rates needed to fluidize large particles cause more turbulent convection.

They found that increasing the flow rate temporarily increases the limiting current as the bed becomes more fully fluidized and then decreases it as the bed expands and the concentration of glass beads falls off. Maximum mass-transfer occurs just below a superficial velocity of 1 cm/s and at a 60 percent bed expansion. Even with saturated CuSO_4 solution I do not see this system being able to go much higher than about 1 A/cm^2 unless some way is found to increase the fluidization velocity and hence the degree of agitation at the optimum degree of bed expansion. Using denser particles, such as plastic coated lead shot, is one possible solution.

Thangappan et al. (44) used a fluidized bed to deposit PbO_2 on graphite electrodes. Giles and Waller (45) used a fluidized bed of metal powder as a sacrificial anode in metal deposition, separated from the cathode by a porous membrane.

On a slightly different principle than fluidization, Eisner and Wisdom (46) immersed objects to be plated in vibrating tubs full of abrasive particles. The optimum particle size was reported to be about 800 μm . Current densities ranged from 270 mA/cm^2 to 970 mA/cm^2 and voltage drops were between 3 and 97 V. This indicates a very high resistance through the bed of abrasives.

To reduce this electrical resistance, Eisner (47) coated copper wire with alumina and cut the wire up into short segments. These particles were subsequently etched in nitric acid to recess the copper, and used in place of the abrasives in the vibrating tubs. The particles decreased the bulk resistance of the slurry by conducting electrons, with copper being deposited on one end and anodically dissolved on the other. A current density of 810 mA/cm^2 was reported, no voltage drop was given.

Since the basic transfer mechanisms are the same, it is well to also consider heat and mass-transport in dispersed phase agitated systems besides those for electrodeposition. Dworak and Wendt (48,49) prepared emulsions of CCl_4 and n-hexane in caustic ferro-ferricyanide solution, which was pumped through an electrochemical flow cell. Hexane had no effect while CCl_4 increased the limiting current by 20-30 percent.

Ibl et al. (50) have studied mass transfer at electrodes evolving gas and also with bubbles introduced externally by sparging. When H_2 or O_2 was evolved on platinum electrodes at about 10 A/cm^2 , the bubbles thinned the boundary layer to approximately $1.0 \text{ }\mu\text{m}$. Such agitation corresponds to a $20\text{--}30 \text{ A/cm}^2$ limiting current for Cu deposition from a concentrated solution. However as Ibl and co-workers themselves point out, Cu deposition cocurrent with H_2 evolution produces loose or powdery deposits. Another drawback is that unless the gas itself is a desired product, one wastes about as much energy evolving the gas as in the intended electrochemical reaction itself. Since Ibl and co-workers show that limiting current density is a function of volume of gas produced per unit time per unit area, perhaps it would be possible to circumvent this last problem by pulling a partial vacuum on the system or by heating the electrolyte to just below the boiling point where the solvent vapor pressure is high, in order to get a greater bubble volume per mole of evolved gas.

When they sparged a vertical electrode with gas bubbles the boundary layer was reduced only to the extent of $16 \text{ }\mu\text{m}$. Therefore it appears that the greatly enhanced mass transfer with gas evolution has more to do with the actual formation process of the bubbles, than the presence of bubbles moving past the electrode surface.

It has been found that metals corrode much faster in flowing water containing particulates in suspension. This was sometimes blamed on the enhanced mass-transfer due to the motion of particles. In their study of slurry-pipeline corrosion, Postlethwaite and Holdner (51,52)

measured the transport rate of dissolved oxygen to the surface of the pipe by finding the limiting current of the oxygen reduction reaction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). They added sand, iron ore and iron ore concentrate, 40 to 430 μm diameter, to their pipeline flow system in concentrations up to 23 percent by volume. The tubular flow cell was oriented either horizontally or vertically; aerated 0.1 M NaOH solution and particles flowed through it at 1.0–3.5 m/s. The maximum limiting current with the slurry was found to be almost twice that without.

Along similar lines Pini and DeAnna (53) studied the effect of SiC abrasive particles (40–75 μm diameter) on mass-transport to a rotating cylinder, using the I^-/I_3^- redox system. Again, the maximum limiting current obtained was almost twice that without particles.

The same problem of concentration polarization presents itself in the case of ultrafiltration. Only this time it is not a matter of too little but of too much solute concentration at the surface. Those molecules too large to go through the membrane must be transferred by diffusion or convection back into the bulk fluid. Bixler and Rappe (54) patented a means to increase this transfer by introducing small glass or polymeric beads (10–500 μm) suspended in the flowing fluid. They achieved a maximum 112 percent improvement in mass flux at 10 percent volume beads.

Avtar Singh Ahuja (55,56) investigated the effect of suspended particles on heat transfer to the walls of a thin metal tube as the slurry flowed through it. Maximum heat fluxes were 2.8 times those without particulates.

Zeilmaker and Barendrecht (57) have investigated the effect of CaCO_3 particles, of unspecified size, on mass transfer to a rotating disk electrode in a caustic ferro/ferricyanide solution. The limiting current increased by up to 2.5 times that without particles.

It can be seen from this review that many approaches to this problem have been tried on empirical bases with little fundamental understanding of how they work. The mathematically treatable laminar flows, for the most part, do not give high transport rates. Therefore the experimenter seeks to introduce some kind of random mixing or chaotic disruption to the well-ordered layers of fluid, with a consequent dissipation of external energy. The practical problem the engineer tries to solve is how to get the greatest rate of mass-transfer for a given amount of energy.

EXPERIMENTAL

Description

The rotating disk electrodes used are shown in Figs. 1-3. Both electrodes were made from a central metal core, which was tapped on one end to screw onto the spindle of the rotating disk apparatus, and faced with nickel on the other end to form the active area of the rotating disk electrode (RDE). In the case of the smaller area electrode a nickel disk was attached to a brass core using silver-epoxy adhesive, while the copper core of the larger area electrode was electroplated with nickel from a standard Watts bath. Around these central cores, epoxy resin was cast and then machined down to produce the same external shape for both electrodes. Thus, the two disks effectively differ only in their active electrode areas.

The experimental cell, shown in Figs. 4 and 5, was made from a 350 ml lab beaker cut to 6.5 cm height. A 78.8 cm^2 anode made of nickel foil covered about $3/4$ the circumference of the cell from top to bottom. That sector of the cell not covered by the anode served as a window to observe what was happening inside. A lucite top-cap was made to fit over the top of the cell and help prevent spillage. The rotating disk entered the cell through a hole in the center of the cap. Rubber gaskets sealed the gap between the inside glass wall of the cell and the top-cap, and also the gap between the top-cap and the lucite spindle-housing above it. The term spindle-housing refers to the large cylindrical block shown in Fig. 7 above the RDE. The cell was raised up towards the disk and the spindle-housing until a seal was made

Fig. 1. The smaller of the two disk electrodes used, shown in cross section facing up. The radius of the nickel active electrode area is 0.564 cm. Including the electrically insulating epoxy plastic material, the total disk diameter is 38.1 mm, the same as for the larger disk (Fig. 2).

XBL 8011-2361

Fig. 2. The larger of the two disk electrodes used, shown in cross section facing up. The radius of the nickel active electrode area is 1.413 cm. Including the electrically insulating epoxy plastic material, the total disk diameter is 38.1 mm, the same as for the smaller disk (Fig. 1).

XBB 800 12297

Fig. 3. Photograph of the two rotating disk electrodes shown facing up. The 1.413 cm disk is on the left and the 0.564 cm disk on the right.

XBL 8010-2261

Fig. 4. Cutaway exploded diagram of the experimental cell. The rotating disc electrode screwed onto the spindle (not shown) of the rotating disk apparatus.

XBB 800 12299

Fig. 5. Photograph of the experimental cell. The top scale of the ruler is in centimeters, the bottom is in inches.

between the top-cap and the flat bottom surface of the spindle-housing to prevent the highly agitated suspension from escaping.

Four small lucite baffles projected down from the top-cap into the solution around the edge of the cell. These baffles served to keep the contents of the cell from swirling around as a whole, in the direction of the rotating disk. When this happened an air-filled vortex formed around the axis of rotation and interfered with the mass transfer to the RDE. Experiments both with and without baffles, in which the solution level was carefully adjusted so that practically no air was in the cell when the RDE was fully inserted, showed that the baffles have no significant effect (<1 percent) on limiting current.

The cell was stirred by a magnetic stirrer to keep the particles from settling out on the bottom of the cell. The stirrer rotated opposite the direction of the RDE. Experiments with particle-free solution showed that the effect of the stirrer was to decrease the limiting current by only a very small (<0.2 percent) amount.

For a reference electrode, a thin strip of nickel foil was used. The strip was inserted into a hook-shaped 7 mm pyrex tube, drawn to a tip at the end. The electrochemical reaction was the same for the cathode, anode and reference electrode ($\text{Fe}(\text{CN})_6^{-3} + e^- = \text{Fe}(\text{CN})_6^{-4}$). The reference tube was led in through a hole in the top-cap and terminated a few millimeters from the plane of the RDE, but far enough away from the center so as not to interfere with the fluid flow to the disk.

The electrical setup is shown in Fig. 6. The rotating disk apparatus, Fig. 7, consisted of a spindle, driven by a variable speed electric motor, with an electrical brush contact to the spindle. The spindle drove the rotating disk which screwed onto it via a left-handed thread.

Power was supplied by a PAR Model 371 Potentiostat-Galvanostat equipped with a Model 178 Electrometer Probe. The potentiostat was made to operate galvanostatically by means of a current control resistor. A PAR Model 175 Universal Programmer controlled the potentiostat and caused it to increase the cell current linearly with time. Cell current was measured both by a Keithley 179 TRMS Digital Multimeter and on the Y axis of an HP 7001 AM X-Y Recorder. The over-voltage as measured by the potential difference between the reference and rotating disk electrode was recorded on the X axis.

Experimental Procedure

On either the day of an experimental run or the day before, 500 ml fresh solution, without particles, was prepared of the following composition.

NaOH	1.97 N	40.0 gms	98.6 percent purity
$K_4Fe(CN)_6 \cdot 3H_2O$	0.20 F	42.241 gms	Reagent grade
$K_3Fe(CN)_6$	0.04 F	6.5852 gms	Analytical reagent grade

Both electrodes were polished before each run on a canvas covered polishing wheel coated with 1 μ m diamond paste.

XBL 8010-2263

Fig. 6. The experimental electrical set up. The potentiostat is configured to act in the galvanostatic mode through the use of the current control resistor.

Fig. 7. Rotating disk apparatus with RDE and cell. The apparatus rotates the disk at constant speed while maintaining electrical contact between the RDE and the potentiostat.

The cell was filled with 218 ml of the ferri-ferrocyanide solution and the magnetic stirrer under the cell was turned on. The cell was raised up by means of a Lab-Jack until the electrode was immersed and the cell sealed against the spindle-housing by means of the top gasket.

Limiting current measurements were then made at different rotation speeds of the RDE. The current scan rate near the limiting current plateau was always less than 1 mA/sec, slow enough that no unsteady state mass transfer effects were observed. After these measurements were made for both size electrodes, a weighed quantity of particulate material was added to the cell and solution removed to maintain the same level. Limiting currents were again determined and the procedure repeated until 35-40 percent volume solids was reached. At this point the experimental run was stopped because the slurry tended to froth and limiting current plateaus were hard to identify.

During the run the temperature inside the cell was maintained close to 30°C, by elevating it off the magnetic stirrer, which proved to be a source of heat, with popsicle sticks. The temperature of the suspension was repeatedly checked by thermometer and later used to make corrections to the obtained data according to Appendix A.

Properties of the Glass Beads

The glass beads were purchased from Potters Industries, Hasbrouck Heights, NJ. They are made of soda-lime glass with density 2.46-2.49 gm/cm³. Four subsieve sizes (1-5 μ m, 5-10 μ m, 8-20 μ m and

0-25 μm) were procured directly from the vendor. The two larger sizes (44-53 μms and 61-74 μms) were obtained by classification through sieves from a large undifferentiated quantity of technical grade glass spheres.

Electron and photomicrographs were made of these sizes and are shown in Figs. 8-13. For each size-range the diameters of a large number of particles were measured from the micrographs. Then a mean particle diameter was calculated with each diameter weight by volume of particle. The volume of a given size range of particle was more significant in mass transfer than their numbers. The diameters computed are presented in Table 1.

Most beads are virtually perfect spheres although a few fragments and other irregular shapes can be seen. Also note that the greatest deviation of diameter from the mean is in the small sizes while the large sizes are nearly uniform.

Experimental Error and Reproducibility

There are many sources of experimental error. The largest and most vexing is that of the decomposition of the ferri-ferrocyanide solution during the course of the experimental run. This phenomena is characterized by a drop in the height of the limiting current plateau with time for the same particle concentration and disk rotation speed, rapid fluctuations in overpotential near limiting current, and the transition from a sharp flat plateau to a less well defined sloping curve. After experimental runs which showed this behavior a fraction of the residual

XBB 800 13961A

Fig. 8. Electronmicrograph of "1-5 μm " glass beads. Volume mean diameter is 3.96 μm . Note the large variation in particle size.

10 μm

XBB 800 13962A

Fig. 9. Electronmicrograph of "5-10 μm " glass beads. Volume mean diameter is 8.36 μm .

Fig. 10. Electronmicrograph of "10-25 μm" glass beads. Volume mean diameter is 12.39 μm.

20 μm

XBB 800 13963A

Fig. 11. Electronmicrograph of "8-20 μm " glass beads. Volume mean diameter is 13.71 μm .

Fig. 12. Photomicrograph of "44-53 μm " glass beads. Volume mean diameter is 55.96 μm .

100 μm

XBB 800 13966A

Fig. 13. Photomicrograph of "61-74 μm " glass beads. Volume mean diameter is 74.94 μm .

Table 1. Properties of glass beads.

Nominal Size	Volume Mean Diameter	Settling Velocity (In ferro-ferricyanide solution)
1-5 μm	3.96 μm	32.7 $\mu\text{m/s}$
5-10	8.36	146.
8-20	13.71	392.
10-25	12.39	320.
44-53	55.96	6530.
61-74	74.94	11700.

solution was filtered from the suspension, diluted to the cell volume and used to obtain limiting currents without particles. These limiting currents were lower, sometimes by as much as 27 percent or more, than for the same dilution made with fresh solution. For this reason this behavior is taken to be a chemical decomposition of the ferri-ferrocyanide solution. Making the RDE anodic or saturating the solution with finely divided $K_3Fe(CN)_6$, or other possible causes, appear to start the decomposition process which then proceeds by itself.

In any case, using fresh $K_4Fe(CN)_6$ from Matheson Coleman and Bell instead old reagent from Baker decreased the incidence of decomposition. The results of any experimental run showing obvious decomposition were disregarded.

During the experiments the solution temperature was as low as 21.3°C or as high as 33.5°C. For the most part though, temperature was within 2°C of the reference temperature of 30°C. Despite the corrections of Appendix A, temperature variations are still a possible source of error. The volume fraction occupied by the particulates is also uncertain due to occasional leakage of the slurry from the cell, inability to keep the cell filled to exactly the same level with each addition of glass beads and the tendency of the beads to settle in quiescent areas such as behind the anode and inside the reference tube. The particle size is subject to statistical sampling errors and deviations in the magnification of the electron microscope. Adsorbed chemical species or dirt on the RDE could have reduced the effective

Fig. 14. Reproducibility of experimental limiting current measurements, illustrated by the results of three different experimental runs using the same size of glass beads.

electrode areas. In addition the entrained bubbles seen at high speeds could have influenced the rate of mass transfer.

Instead of quantifying all these errors and determining their combined effect upon the data, as a more meticulous study would do, I shall simply examine the reproducibility of experimental runs made with the same particle size. Figure 14 shows the data from three separate runs with the 8.36 μm beads, for which the solution decomposition was not excessive. Most limiting currents lie within ± 8 percent of their mean value. This deviation of course does not account for determinate errors, unknown factors which may uniformly increase or decrease limiting current in all the experimental runs.

The Limiting Current and Physical Properties of the Solution without Glass Beads

The density and viscosity of the caustic ferro-ferricyanide solution used were obtained from the empirical equations of Boeffard (58):

$$\begin{aligned} \rho(\text{gm/cm}^3) &= 0.99702 + 0.04423 C_{\text{NaOH}} + 0.17118 C_{\text{Ferri}} \\ &\quad + 0.23119 C_{\text{Ferro}} - 0.00133 C_{\text{NaOH}}^2 - 0.00787 C_{\text{NaOH}} C_{\text{Ferri}} \\ &\quad - 0.00978 C_{\text{NaOH}} C_{\text{Ferro}} \\ \nu(\text{cps}) &= 0.96714 + 0.09622 C_{\text{NaOH}} - 0.20528 C_{\text{Ferri}} \\ &\quad + 0.090255 C_{\text{Ferro}} + 0.05404 C_{\text{NaOH}}^2 + 0.53303 C_{\text{Ferri}}^2 \\ &\quad + 0.43505 C_{\text{Ferro}}^2 + 0.23546 C_{\text{NaOH}} C_{\text{Ferri}} \\ &\quad + 0.302585 C_{\text{NaOH}} C_{\text{Ferro}} + 0.99923 C_{\text{Ferro}} C_{\text{Ferri}} \end{aligned}$$

Knowing the viscosity, the diffusivity of Ferricyanide ion is determined from the equation of Gordon et al. (59)

$$\frac{D_{\mu}}{T} = (0.234 + 0.0014 \Gamma) 10^{-9} \frac{\text{cm}^2 \text{ poise}}{\text{s} \cdot \text{K}},$$

where Γ is the ionic strength. Using the classical relation for mass transfer to a rotating disk (60) we find the limiting current from

$$i_L = 0.62048 \text{ nFC}_B (\nu \Omega)^{1/2} \text{ Sc}^{-2/3}.$$

A comparison of the above equation to the experimental values is made in Fig. 15 and 16. The data points are linear with a standard deviation of 3.2 percent for the 0.564 cm radius cathode and 1.6 percent for the 1.413 cm cathode. However, the straight line they lie upon intersects the ordinate near $i_L = 1 \text{ mA}$ and is below the theoretical line. In general the limiting currents for the 0.564 cm electrode are 96 percent of theoretical and for the 1.413 cm electrode 93 percent.

These discrepancies might be attributed to inaccuracies of concentrations, physical properties, electrode areas or to deviation from the theoretical rotating disk hydrodynamics due to the presence of baffles or the small volume of the cell. In any case the deviation from theoretical is not larger than the experimental error itself and does not greatly invalidate the theoretical interpretation of the results which follows.

XBL 815-857

Fig. 15. Experimental limiting current densities with no beads present compared with limiting current density calculated using classical RDE theory.

42

XBL 815-854

Fig. 16. Experimental limiting current densities with no beads present compared with limiting current density calculated using classical RDE theory.

EXPERIMENTAL DATA

The following pages display the experimental data in graphical form. The dashed lines drawn through the data points represent a cubic spline function, which expresses limiting current as a function of three independent variables: log of particle size, volume percent of particulate material and the rotation speed of the disk electrode.

The three dimensional independent variable space was divided into 96 rectangular solids by passing three sets of orthogonal planes through it. The first set consists of six planes at -8.0, 2.6, 13.2, 23.8, 34.4 and 45.0 percent volume solids. The second set of planes were at the logarithms of 1.00 μm , 6.81 μm , 46.4 μm and 316 μm particle diameter. The third set divided the dimension of disk rotation speed at 30.0, 130, 230 and 330 radians per second. Each rectangular solid or "box" had a separate cubic function which gave limiting current density as a third order polynomial in the three variables such that the limiting current density and its first and second derivatives at the boundaries with neighboring boxes were continuous. The parameters of the spline function were adjusted to provide a least-squares fit, but due to variations over one or more of the hidden dimensions, the dashed lines may appear not to match the data points well. Two separate spline functions were made, one for the 0.564 cm radius cathode disk and one for the 1.413 cm radius cathode disk.

0.564 cm Disk—Limiting Current Versus Volume Fraction

Figures 17-22 plot limiting current density in mA/cm^2 versus percent of suspension volume occupied by glass beads. The various disk rotation speeds in radians/second are found to the right of the spline lines. Points for alternate disk speeds are plotted with alternating symbols for clarity. Each figure presents the data of one experimental run with the specified disk and size of glass bead, proceeding in time, during the course of the experiment, from zero to the maximum amount of particulates.

XBL 8011-7526

Fig. 17. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

XBL 8011-7523

Fig. 18. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

XBL 8012-12913

Fig. 19. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

XBL 8011-7543

Fig. 20. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

56.0 Micron Beads

XBL 8011-7546

Fig. 21. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

XBL 8011-7545

Fig. 22. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

1.413 cm Disk--Limiting Current Versus Volume Fraction

Figures 23-28 plot limiting current density in mA/cm^2 versus volume percent glass beads. The disk rotation speed in radians/second is found to the right of the spline lines.

XBL 8011-7525

Fig. 23. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

8.4 Micron Beads

XBL 8011-7524

Fig. 24. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

12.4 Micron Beads

XBL 8011-7528

Fig. 25. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

XBL 8011-7530

Fig. 26. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

56.0 Micron Beads

XBL 8011-7527

Fig. 27. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solus at each disk rotation speed.

XBL 8011-7529

Fig. 28. Experimental data points and cubic spline curves expressing limiting current density as a function of volume concentration solids at each disk rotation speed.

0.564 cm Disk--Limiting Current Versus Rotation Speed

Figures 29-40 plot limiting current density in mA/cm^2 versus disk rotation speed in radians/second. The percent volume occupied by the specified size of glass bead is displayed to the right of the spline line. Data points and spline lines for alternate volume percents are represented by alternating symbols and types of line. The points represented by circles correspond to the dashed lines; the points represented by plus signs correspond to the dotted lines.

XBL 815-9497

Fig. 29. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

4.0 Micron Beads

XBL 815-9498

Fig. 30. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9499

Fig. 31. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9500

Fig. 32. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9501

Fig. 33. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9502

Fig. 34. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9503

Fig. 35. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9504

Fig. 36. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9505

Fig. 37. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

56.0 Micron Beads

XBL 815-9506

Fig. 38. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9507

Fig. 39. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9508

Fig. 40. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

1.413 cm Disk--Limiting Current Versus Rotation Speed

Figures 41 through 52 plot limiting current density in mA/cm^2 versus disk rotation speed in radians/second. The percent volume occupied by the specified size of glass bead is displayed to the right of the spline line.

Fig. 41. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9510

Fig. 42. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9511

Fig. 43. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9512

Fig. 44. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

12.4 Micron Beads

XBL 815-9513

Fig. 45. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9514

Fig. 46. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9515

Fig. 47. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

1.413 cm radius Cathode

13.7 Micron Beads

XBL 815-9516

Fig. 48. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9517

Fig. 49. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9518

Fig. 50. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

74.9 Micron Beads

XBL 815-9519

Fig. 51. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

XBL 815-9520

Fig. 52. Experimental data and cubic spline curves expressing limiting current density as a function of disk rotation speed, at every other volume concentration particulates.

0.564 cm Disk--Limiting Current Versus Particle Diameter

Figures 53-58 plot limiting current density in mA/cm^2 versus the volume mean particle diameter in micrometers on a logarithmic scale. The rotation speeds in radians/second are shown to the right of the spline lines. Actually the specified percent volume particulates of the data points is not exact. The computer was programmed to display all data within 2.5 percentage points of the nominal percent volume glass beads. Thus 0 percent is actually 0-2.5 percent and 8 percent is really 5.5-10.5 percent, etc. Because of this, some places two sets of data can be seen superimposed, elsewhere no data appears at all.

Fig. 53. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 54. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 55. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

XBL 8011-7556

Fig. 55. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 57. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

XBL 8011-7558

Fig. 58. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

1.413 cm Disk--Limiting Current Versus Particle Diameter

Figures 59-64 plot limiting current density in mA/cm^2 versus the volume mean particle diameter in micrometers on a logarithmic scale. The rotation speeds in radians/second are shown to the right of the spline lines.

Fig. 59. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 60. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 61. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 52. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 63. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

Fig. 64. Cubic spline curves and experimental data points within 2.5 percent volume of the above labeled particle concentration. This graph displays limiting current density as a function of particle size for each disk rotation speed.

DISCUSSION OF EXPERIMENTAL RESULTS

Increase in Limiting Current

Notice that in general, when the glass beads are added to the solution the limiting current increases. This is not predicted by what is known of the bulk behavior of slurries. When particulates are added to a solution, the bulk diffusivity normally goes down, the suspension viscosity increases and the concentration of reacting species is diluted by the particles. As shown in Appendix B and illustrated in Fig. 65, all these changes in bulk, macroscopic physical properties should decrease limiting current. The fact that it does not decrease but in fact increases, indicates by the process of elimination that something must be happening on the microscopic level, on the scale of the particles themselves, that is responsible for this phenomenon.

The Offset in Particle Concentration

Another feature to notice in Figs. (14-25) is the small "threshold step" in the limiting current when glass bead concentration is low. From 0 percent volume to 5-10 percent or sometimes even higher, practically no increase in limiting current occurs. Zeilmaker and Barendrecht (57) have investigated the effect of CaCO_3 particles, of unspecified size, on mass transfer to a rotating disk electrode. When their data are plotted as limiting current versus volume percent solids, Fig. 66, one sees the same effect.

A possible explanation for this phenomenon is that the particles are settling under the influence of gravity, away from the electrode surface, which faces down, into the solution.

Fig. 65. Calculated RDE limiting current with suspended particles divided by that without. Based on changes in bulk density, solute concentration, viscosity and diffusivity with increased solids concentration.

Fig. 66. Limiting current of a RDE as a function of volume concentration CaCO_3 particles, according to the data of Zeilmaker and Barendrecht.

Figure 67 shows the results of some numerical calculations to find the "static approach distance," or the distance from the disk surface where all the forces acting on a single particle, gravitational and buoyancy forces, pressure gradient and hydrodynamic interaction with the surrounding fluid assuming Stoke's flow, are in static equilibrium. The pressure gradients and fluid velocities towards the disk were evaluated at the point of the center of the sphere. In actuality the momentum of the glass bead can be expected to carry it past the static approach distance, perhaps even to the extent of contacting the electrode, until it settles down to the equilibrium point.

From inspection of Fig. 67 one can surmise that whether this settling effect is significant depends upon the magnitude of the "interaction distance" or the maximum distance from the particle's surface to the electrode over which the particle can have an effect on mass transfer. Even a very small particle traveling very quickly past the electrode will settle somewhat. If the interaction distance is very small, this slight amount of settling may be enough to keep the solid particle from affecting mass transfer.

As the concentration of solids increases, they collide with each other more often and some get pushed up towards the disk's surface. When they finally touch it the sharp increase in limiting current, seen in Figs 17-28, begins.

To develop a semi-quantitative model as to how the beads reach the rotating disk when they are highly concentrated, imagine layers of slurry shearing past each other, as in Fig. 68. Each layer may have a

XBL 815-853

Fig. 67. Particle size vs static approach distance (the distance from the disk at which all hydrodynamic and gravitational forces on a glass bead balance) is plotted with the solid line. The circles represent the size of beads on the scale of the abscissa.

XBL 815-850

Fig. 68. Mechanism of particulate diffusion through shear induced collisions.

different concentration of spheres. The middle layer is taken as the frame of reference. The difference in the number of "collisions" any given sphere in the middle layer experiences from below versus those from above, is proportional to the difference in particle concentration between the top and bottom layers. The net downward (positive z -direction) flux of spheres due to collisions should be

$$N_c = -K c_p \frac{dc_p}{dz}$$

where c_p is the concentration of particles, and K is a proportionality constant which depends primarily upon the shear rate, and particle size. The downward flux of spheres due to settling is

$$N_G = c_p U$$

where U is the settling velocity. At steady state the sum of the fluxes must be zero.

$$c_p U - K c_p \frac{dc_p}{dz} = 0$$

or

$$\frac{dc_p}{dz} = \frac{U}{K}$$

Assume also that there is some arbitrary distance, S , from the disk, where the fluid updraft towards the disk no longer suffices to counter the settling velocity. As shown in Fig. 69, the particles can be considered to be well mixed and at their bulk concentration when $Z > S$. For $Z < S$, only transport by inter-particle collision can occur.

When the particle concentration is below the threshold, the particle concentration profile would look something like the solid line in Fig. 69. The particle concentration drops to zero below the surface of the rotating disk, and the electrode in effect "sees" no particles. Above the threshold the particle concentration profiles would resemble the heavy dashed lines. Thus the surface concentration of beads is offset by $\frac{US}{K}$ from the bulk concentration but, of course, is never less than zero.

When the surface renewal model developed below was fitted to the experimental data a 7 percent offset was used that not only gave a level region at low particle concentrations in plots of i_L versus percent volume particulates, but also made the maxima of both the experimental and theoretical curves coincide. However for some experimental curves, such as those for the larger particles at the slow speeds it is apparent that the offset is much larger. The derivation above is offered as a semi-quantitative justification for a rather

XBL815-856

Fig. 69. Concentration of particles, C_p , as a function of distance from the rotating disk, z . Three possible concentration profiles are shown.

arbitrary "constant offset" assumption made further on. It does not account for how the offset might vary with particle size, volume fraction, disk speed or diameter.

This threshold effect is more or less constant except for the two larger particle sizes, where it increases for the larger radius disk and at the slower rotation speeds. A more accurate empirical correlation (although by no means understood) was found to be

$$p_{os} = k_1 + k_2 \frac{a^2}{\Omega R} \quad (1)$$

where p_{os} is the offset in particle concentration expressed in volume fraction, k_1 and k_2 are arbitrary constants, a is the particle radius in cm, R is the radius of the active area of the RDE in cm and Ω is the rotation speed in radians/s.

This equation was used in the particle film models developed in the following pages. The constants k_1 and k_2 were adjusted along with other adjustable parameters to give the least squares fit. For the particle film model, $k_1 = 0.0340$ and $k_2 = 352010$, and for the practice particle film model, $k_1 = 0.0354$ and $k_2 = 98445$.

The fact that the threshold is constant for the small particles, whose settling velocities are very low, as shown in Table 1, and the fact that Eq. (1) is a sum of two distinct parts suggest that there might be another mechanism at work keeping the glass spheres from the RDE, perhaps a fluid dynamic mechanism having nothing to do with gravity.

Ibl, Kind and Adam (50) have taken time-lapse pictures of sparged bubbles flow past a vertical electrode and have found that the bubbles tend to concentrate near the solid surface. The inverse phenomenon, called the tubular pinch effect, is reported by Porter (61) in the course of his work with mass transfer in ultrafiltration systems; dense particles flowing through tubes tend to concentrate along the axis. Rouhani (62) attributes this effect to rolling vortices which appear around the bubbles or particles in velocity gradients close to the wall. A bubble, being less dense than its vortex, will be stabilized in its center, while a particle, denser than the surrounding fluid will get spun out of its own vortex and tend to stay in regions of low velocity gradient.

In any case it appears this investigation has stumbled upon some very complex phenomena of two-phase flow. A future investigation would do well to try to circumvent particle concentration offsets by using neutrally bouyant spheres (for example polystyrene beads sulfonated on the surface to render them hydrophilic). For this work let us simply use the above semi-empirical estimates, recognizing that the volume fraction particulate concentration at the rotating disk may be off by roughly ± 0.05 .

Effect of Electrode Size on Limiting Current

Two different sizes of electrodes were used in these experiments. With conventional rotating disk electrodes, it is known (60) that the local limiting current density is constant over the disk. This is true because the axial flow velocity, $V_z = (\nu\Omega)^{1/2} H(\zeta)$, (63), which brings

fresh reactant to the surface, is constant with respect to r and θ . The cylindrical coordinates r and θ are defined as in Fig. 70. V_r and V_θ can be ignored because no concentration gradients exist in the r and θ directions (in the plane of the disk).

However it is V_r and V_θ which cause the particles to move across the surface and disrupt or perturb the boundary layer. Moreover both V_r and V_θ are proportional to r .

$$V_r = r\Omega F(\zeta)$$

$$V_\theta = r\Omega G(\zeta)$$

If the surface area per second, disrupted by a particle, is proportional to its velocity, then we might loosely postulate without knowing the exact mass transfer mechanism that the larger disk, which has 2.5 times the radius of the smaller disk, should show an increase in limiting current 2.5 times that of the smaller.

Figure 71 shows R , the ratio of increase in limiting current density for the larger disk over that of the smaller, as a function of particle size. More precisely for each rotation speed and particle size, the limiting current density without any particles was subtracted from the maximum limiting current density in the i_L versus percent volume plot, to form the increase in limiting current density. R is simply the maximum increase for the 1.41 cm disk divided by the maximum increase for the 0.56 cm disk ($R = (i_{L,Max,1.41} - i_{L,0}) / (i_{L,Max,0.56} - i_{L,0})$).

One can see that for the most part R lies below 2.5, the ratio of the electrode radii, but above 1.0 where limiting current densities are independent of r . Coincidentally the mean R value for the 8.4 μm

XBL 815-888

Figure 70 - Cylindrical coordinate system for rotating disk electrode. Axial displacement, z , is measured from the disk surface down. Radial displacement, r , is measured out from the axis. The angle θ measures rotation about the z -axis.

XBL 815-855

Fig. 71. Relative increase in limiting current density of the larger disk over that for the smaller, $R = (i_L - i_{L,o})_{\text{Large Disk}} / (i_L - i_{L,o})_{\text{Small Disk}}$, is plotted as a function of particle size. The dots represent the R values at different disk speeds, the circles, the mean R for each particle size.

beads, which also happen to give the largest absolute limiting currents, lies exactly on 2.5.

There is an implicit assumption buried in this simple analysis: that of a "background" steady-state limiting current, upon which the non-steady-state fluctuations in local limiting current, caused by the passage of a particle, are superimposed. Can we suppose that it is the same as the zero-solids limiting current? Or must we take into account the changes with particulate concentration of bulk diffusivity, viscosity and overall concentration of the slurry as in Appendix B? This latter approach is not perfect either, considering that the mass transfer boundary layer thicknesses (6-40 μm), and the particle diameters (4-75 μm) are about the same size. That part of the boundary layer closest to the surface of the electrode may experience practically no reduction in diffusivity because it contains so little particulate volume. Or the high viscosity of the slurry could suddenly drop near the smooth electrode surface, causing a "slip" in velocity gradient to occur.

Being aware of the uncertainties involved, let it just be said for now that the above "proportional to parallel velocity" hypothesis might explain part of difference in limiting current density between the two disk sizes.

Effect of Disk Rotation Speed on Limiting Current

As shown in Figs. 29-52, not only does i_L increase monotonically with Ω , as one might well expect, but the shape of the curve changes when particles are added. In accordance with classical rotating disk

theory, when no solids are present the i_L versus Ω curve is parabolic ($i_L \propto \Omega^{1/2}$). However, as glass beads are added the curve tends towards a straight line ($i_L \propto \Omega$). This "curve straightening" effect is most apparent for the smaller particles and progressively lessens as the particle size increases. In fact, for the 56 and 75 μm beads, Figs. 37-40 and 49-52, with increasing volume fraction solids the curves go from a parabolic to a "kinked" shape. The plot of i_L with increasing Ω is almost linear until about 150 r/s, where it "kinks" and proceeds as another approximately straight line of lesser slope.

How does this i_L vs Ω behavior compare to the "proportional to parallel velocity" hypothesis put forth in the previous section? To calculate the particle velocity it is assumed the particle is touching the electrode and has the velocity of the surrounding fluid at $z = a$, where a is the particle radius. Very close to the disk the velocity gradients may be considered constant so

$$V_\theta = a \frac{\partial V_\theta}{\partial z}, \quad V_r = a \frac{\partial V_r}{\partial z}$$

$$V_\theta = a \frac{\partial V_\theta}{\partial \zeta} \frac{\partial \zeta}{\partial z}, \quad V_r = a \frac{\partial V_r}{\partial \zeta} \frac{\partial \zeta}{\partial z}$$

$$\text{but } \zeta = \frac{\Omega^{1/2}}{\nu^{1/2}} z, \quad V_\theta = r\Omega F \text{ and } V_r = r\Omega G.$$

$$V_\theta = \frac{ar\Omega^{3/2}}{\nu^{1/2}} F' \quad \text{and} \quad V_r = \frac{ar\Omega^{3/2}}{\nu^{1/2}} G'$$

where

$$F' = \frac{dF}{d\zeta} \quad \text{and} \quad G' = \frac{dG}{d\zeta}$$

The absolute value of velocity over the surface is

$$|v| = \frac{ar\Omega^{3/2}}{v^{1/2}} (F'^2 + G'^2)^{1/2},$$

therefore the "proportional to parallel velocity" hypothesis predicts an $\Omega^{3/2}$ dependence.

Figures 72 and 73 show the exponents of Ω which best fit the observed increases in limiting current above the limiting current without particles. N best fits the data with $i_L = i_{L,0} + K\Omega^N$, where K is an arbitrary constant. As in Fig. 71 above, the data seem to match the "proportional to parallel velocity" hypothesis, $N = 1.5$, at about 8.4 microns diameter.

However, some other mechanism might be dominant at the 4.0 μm ($N = 1.8$) size and still another at the 56 and 75 μm ($N = 0.7$) sizes. A possible explanation for the larger beads is the "proportional to perpendicular velocity" hypothesis, wherein the particles are brought up towards the disk surface by the axial velocity, $V_z = v^{1/2}\Omega^{1/2}H(\zeta)$. Each bead which contacts the surface, hits it only once and then settles down from the boundary layer. It may be reasonably assumed that the increase in mass transfer is proportional to the number of "hits" per second made on the electrode surface by the impinging particles, which in turn is proportional to V_z . This theory would predict an N value of 0.5 in Figs. 72 and 73, and an R value of 1.0 in Fig. 71. The

Figure 72 - Values of N which give least squares fit to experimental limiting current density with $i_L = i_{L,0} + K\Omega^N$. The small dots represent the "best N " values at different volume fractions beads. The circles indicate the mean N for each particle size.

XBL 815-889

Figure 73 - Values of N which give least squares fit to experimental limiting current density with $i_L = i_{L,0} + K\Omega^N$. The small dots represent the "best N " values at different volume fractions beads. The circles indicate the mean N for each particle size.

actual values of R and N for large particles are intermediate to those predicted by the "proportional to parallel velocity" and the "proportional to perpendicular velocity" hypothesis, indicating that both mechanisms may be at work simultaneously.

This combined mechanism explanation although plausible has not been developed further by this author. It remains an alternative to the "particle film" model below which explains the variations in limiting current density with electrode size, rotation speed, particle size and particle concentration by a single mechanism.

Effect of Particle Size on Limiting Current

As can be seen in Figs. 53-64, there is usually a maximum in the limiting current versus particle size curve. At the higher rotation speeds it occurs close to the 8.4 micron size, but as speed decreases it shifts to the larger sizes.

Figure 74 compares the optimum particle size for a given rotation speed with, δ , the mass transfer boundary layer thickness. Two values of δ are calculated, one assuming no particles are present and the other using the bulk suspension treatment of Appendix B. Limiting current is calculated first, and then δ according to $\delta = DnF/i_L$.

The optimum particle sizes were obtained from the maxima in the cubic spline fit to the experimental data at 32 volume percent solids. For the 1.41 cm radius disk, the optimum size was about 1.40 times the clear solution boundary layer, except below ~170 radians/second where the optimum size was much larger. With the 0.56 cm disk the highest

XBL815-922

Fig. 74. Boundary layer thickness, δ , compared with bead size giving maximum limiting current density, as a function of rotation speed Ω .

limiting currents occurred with bead diameters 2.06 times δ , except below 220 r/s were again the optimum beads were much larger.

One might theorize then, in a qualitative sense, that the large glass beads are never able to fully penetrate the boundary layer. They either fall away from it or have such a small fraction of their spherical volume inside the boundary layer that they can not disrupt it effectively. As the particles get smaller they enter more fully into the depleted regions of the boundary layer and the augmentation of mass transfer reaches a maximum. However, as particles become smaller than the boundary layer the mixing length of the particle vortex becomes smaller and less effective. The concentration difference over the diameter of a bead inside a linear concentration boundary layer is proportional to particle size in this case. Whereas a bead much larger than δ mixes the bulk concentration with the electrode surface concentration, regardless of size. For this reason one would expect the enhancement of mass transfer to decline approaching very small particle sizes.

MASS TRANSFER MODELSSurface Renewal Model

Consider a rotating disk electrode in a homogeneous fluid having a mass transfer boundary layer of thickness δ . Then, conceptually, introduce a few suspended particles introduce, some of which reach the electrode surface and penetrate the boundary layer. The flow of the surrounding fluid and various body forces cause the particles to move across the surface of the electrode. For purposes of this model, it is assumed each particle causes complete mixing. It leaves in its wake fresh bulk solution all the way to the very surface of the electrode. The limiting current at a point on the electrode surface will increase sharply as the sphere passes over it and then decay gradually, approaching the steady state corresponding to diffusion through an undisturbed boundary layer, until it is again disturbed by another sphere.

Now imagine a line segment of length w , as in Fig. 75, perpendicular to the direction of flow of the particles, where the particles are represented by line segments of width σ , all moving in the same direction with velocity V . If c_s is the surface concentration of particles on the electrode (particles/cm²) then the mean number of particles crossing line w per second is

$$(\text{particles crossing per second}) = w c_s V$$

Conceptualization of Surface Renewal Model

XBL 815-886

Figure 75 - Surface renewal model. Randomly dispersed particles of thickness σ , travel across disk surface with uniform velocity V . In their wakes they replace the old boundary layer with fresh bulk solution.

Given that a particle crosses line w the probability that any one particular point on line w is crossed over is

$$(\text{probability of being passed over}) = \frac{\sigma}{w} \quad .$$

The mean number of times per second a point on the surface is "renewed" or passed over by a particle is given by s and

$$s = (wc_s V)(\sigma/w) = c_s V \sigma$$

The determination of c_s and σ is described in Appendix C. The value of V is obtained from Appendix E. These spherical particles are placed randomly about the surface of the electrode, except they cannot be any closer than just touching each other, as in Fig. 76, (less than $2a$ distance between centers, where a is the spherical radius). This means that a point on the surface must wait at least $\frac{2a}{V}$ between surface renewals.

Imagine at time $t = 0$, we have a large number, N_0 , of freshly renewed points, and over the course of time the number of original points remaining un-renewed is termed N . The variation of N with time is derived as follows

XBL 815-887

Figure 76 - Closest approach permitted of two spherical particles of radius a .

For $t < 2a/V$:

$$\frac{dN}{dt} = 0, \quad N = N_0$$

For $t > 2a/V$:

$$-\frac{dN}{dt} = sN$$

$$\int_0^N \frac{dN}{N} = -s \int_{\frac{2a}{V}}^t dt$$

$$\ln\left(\frac{N}{N_0}\right) = -s\left(t - \frac{2a}{V}\right)$$

$$N = N_0 \exp\left[-s\left(t - \frac{2a}{V}\right)\right]$$

Any given point on the surface will have the probability time-density, $P(t)$, of renewal between t and $t + dt$ of

$t < 2a/V$:

$$P(t) = -\frac{1}{N_0} \frac{dN}{dt} = 0$$

$t > 2a/V$:

$$P(t) = -\frac{1}{N_0} \frac{dN}{dt} = s \exp\left[-s\left(t - \frac{2a}{V}\right)\right] \quad (2)$$

Except for the $2a/V$ correction factor this is the same surface-age distribution as used in Danckwerts' surface renewal theory (64),

$$\phi = se^{-st}.$$

However as Danckwerts modeled his theory on unsteady state diffusion through a semi-infinite slab, we shall base our model on unsteady state diffusion through a finite boundary layer as derived by Roseburgh-Miller (65) where

$$\frac{i}{nF} = \frac{D}{\delta} (c_b - c_0) \left(1 + \sum_{m=1}^{\infty} \exp[-m^2(4\alpha\theta)] \right)$$

The instantaneous current density as limited by mass transfer conditions is i , n the number of electrons transferred per molecule reactant, F is Faraday's constant, 96,487 coulombs/equivalent, D the diffusivity evaluated in Appendix F, δ is the thickness of the mass transfer boundary layer also evaluated in Appendix F, c_b and c_0 the bulk and surface concentration of reactant respectively. The time constant α is given by $\alpha = \frac{\pi^2 D}{4\delta^2}$, and θ is the time since surface renewal when $c = c_b$ throughout the boundary layer. Under limiting current conditions $c_0 = 0$ and the mean limiting current density $\bar{i}_L$ for a point with surface age t is

$$\frac{\bar{i}_L}{nF} = \frac{Dc_b}{\delta t} \int_0^t \left(1 + 2 \sum_{m=1}^{\infty} \exp[-m^2(4\alpha\theta)] \right) d\theta$$

$$\frac{\bar{i}_L}{nF} = \frac{Dc_b}{\delta t} \left(t - \frac{1}{2\alpha} \sum_{m=1}^{\infty} \frac{1}{m^2} [\exp(-m^2 4\alpha t) - 1] \right)$$

Next we must average this mean limiting current for one surface age, over the whole distribution of surface ages.

$$\bar{i}_L = \int_0^\infty \frac{\bar{i}_L}{nF} \cdot P(t) dt$$

$$\bar{i}_L = \int_0^{\frac{2a}{V}} \frac{\bar{i}_L}{nF} \cdot 0 dt + \int_{\frac{2a}{V}}^\infty \frac{\bar{i}_L}{nF} \cdot s e^{-s(t-2a/V)} dt$$

$$\bar{i}_L = \frac{Dc_b}{\delta} \left[\int_{\frac{2a}{V}}^\infty s e^{-s(t-2a/V)} dt - \frac{1}{2\alpha} \sum_{m=1}^\infty \frac{1}{m^2} \int_{\frac{2a}{V}}^\infty \frac{s}{t} \exp\left(-m^2 4\alpha t - s\left[t - \frac{2a}{V}\right]\right) dt \right]$$

$$\bar{i}_L = \frac{Dc_b}{\delta} \left[1 - \frac{s e^{-\frac{s 2a}{V}}}{2\alpha} \sum_{m=1}^\infty \frac{1}{m^2} \int_{\frac{2a}{V}}^\infty \frac{\exp(-[m^2 4\alpha + s]t) - \exp(-st)}{t} dt \right]$$

So far I have not been able to evaluate the above integral exactly so we shall use a more approximate expression that is developed in Appendix G.

$$\bar{i}_L = \frac{Dc_b}{\delta} \left[1 - \frac{s e^{-\frac{s 2a}{V}}}{2\alpha} \sum_{m=1}^\infty \left(\frac{\ln\left[\frac{s}{m^2 4\alpha + s}\right]}{m^2} + \frac{12\alpha}{m^2 4\alpha + 2s} \left[1 - \frac{1}{\left(\left[\frac{m^2 4\alpha + 2s}{6} \right] \frac{2a}{V} + 1 \right)^2} \right] \right) \right]$$

or

$$\frac{\bar{i}_L}{nF} = \frac{Dc_b}{\delta} \left[1 - \frac{se^{c_s \sigma 2a}}{2\alpha} \sum_{m=1}^{\infty} \left(\frac{\ln \left[\frac{m^2 4\alpha}{s} + 1 \right]}{m^2} - \frac{12\alpha}{m^2 4\alpha + 2s} \left[1 - \frac{1}{\left(\left[\frac{m^2 4\alpha + 2s}{6} \right] \frac{2a}{V} + 1 \right)^2} \right] \right) \right]$$

The above expression gives the local time-average limiting current density at a point on the disk. To find the over-all limiting current density we integrate over the area of the disk.

$$\frac{i_{OL}}{nF} = \frac{1}{\pi R^2} \int_0^R \frac{\bar{i}_L}{nF} 2\pi r dr$$

i_{OL} is the overall limiting current density, R the outer radius of the electrode and r is the radial distance from the center to any point on the electrode surface.

The only variables that are functions of r are

$$V = r\Omega[F^*{}^2 + (1 - G^*)^2]^{1/2} = rQ$$

(where Q is just the proportionality constant for a fixed Ωv , etc., as developed in an Appendix E) and $s = c_s \sigma V = c_s \sigma Q r$

$$\frac{i_{OL}}{nF} = \frac{Dc_b}{\delta\pi R^2} \cdot 2\pi \left[\int_0^R r dr + \frac{c_s \sigma Q e^{c_s \sigma 2a}}{2\alpha} \sum_{m=1}^{\infty} \left(\frac{1}{m^2} \int_0^R r^2 \ln \left[\frac{m^2 4\alpha}{c_s \sigma Q r} + 1 \right] dr \right. \right. \\ \left. \left. - \int_0^R \frac{12\alpha r^2}{m^2 4\alpha + 2c_s \sigma Q r} \left[1 - \frac{1}{\left[\frac{m^2 4\alpha + 2c_s \sigma Q r}{6} \left(\frac{2a}{Qr} \right) + 1 \right]^2} \right] dr \right) \right]$$

which reduces to

$$\frac{i_{OL}}{nF} = \frac{Dc_b}{\delta} \left[1 + \frac{c_s \sigma Q e^{c_s \sigma 2a}}{\alpha R^2} \sum_{m=1}^{\infty} \left(\frac{1}{m^2} \int_0^R r^2 \ln \left[\left(\frac{m^2 4\alpha}{c_s \sigma Q} \right) \frac{1}{r} + 1 \right] dr \right. \right. \\ \left. \left. - \frac{1}{m^2} \int_0^R \frac{(12\alpha) r^2}{(m^2 4\alpha) + (2c_s \sigma Q) r} \left[1 - \frac{r^2}{\left[\frac{m^2 4\alpha + 2c_s \sigma Q r}{6Q} + r \right]^2} \right] dr \right) \right]$$

The first integral is evaluated in Appendix H and the second in Appendix I. We use the notation

$$A = \frac{m^2 4\alpha}{c_s \sigma Q} \quad \text{and} \quad B = 1 + \frac{3}{2\alpha c_s \sigma}$$

$$\frac{i_{OL}}{nF} = \frac{Dc_b}{\delta} \left[1 + \frac{c_s \sigma Q e^{c_s \sigma 2a}}{\alpha R^2} \sum_{m=1}^{\infty} \left(\frac{1}{m^2} \right) \left[\frac{R^3}{3} \ln \left(\frac{A}{R} + 1 \right) + \frac{A^3}{3} \ln \left(\frac{R}{A} + 1 \right) \right. \right. \\ \left. \left. + \frac{R^2 A}{6} - \frac{R A^2}{3} \right] - \frac{3\alpha}{m^2 c_s \sigma Q} \left[R^2 - AR - \frac{(B-1)^2 R^2}{B^2} + \frac{(B-1)^2 (B+2) AR}{B^3} \right. \right. \\ \left. \left. + \frac{(4B-3) A^2}{2B^4} \ln \left(\frac{2BR}{A} + 1 \right) - \frac{(B-1) A^2 R}{B^3 (A + 2BR)} \right] \right]$$

or alternatively

$$\begin{aligned} \frac{i_{OL}}{nF} = \frac{Dc_b}{\delta} & \left[1 + \frac{4e^{c_s \sigma 2a}}{3R^2} \sum_{m=1}^{\infty} \left(\frac{R^3}{A} \ln \left(\frac{A}{R} + 1 \right) + A^2 \ln \left(\frac{R}{A} + 1 \right) \right. \right. \\ & + \left. \left. \frac{R^2}{2} - AR \right) - \frac{3e^{c_s \sigma 2a}}{R^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \left(R^2 - AR - \frac{(B-1)^2 R^2}{B^2} \right. \right. \\ & + \left. \left. \frac{(B-1)^2 (B+2) AR}{B^3} + \frac{(4B-3) A^2}{2B^4} \ln \left(\frac{2BR}{A} + 1 \right) - \frac{(B-1) A^2 R}{B^3 (A + 2BR)} \right) \right] \quad (3) \end{aligned}$$

Conclusions of the Surface Renewal Model

The surface renewal model developed above was implemented via a FORTRAN subroutine. When it was assumed that all particles which touch or enter the boundary layer cause surface renewal ($\Delta = \delta$, where Δ is the interaction distance), the limiting currents calculated were up to 12 times higher than those observed experimentally. I then postulated that the steady state boundary layer thickness calculated in Appendix F might not be appropriate due to unsteady state effects which cause the steepest concentration gradients to be closest to the electrode surface.

A computer program was written which matched the limiting currents predicted by the model to the experimental data by varying the fraction of the steady state boundary layer thickness the particles must penetrate, to have an effect. However, these boundary layer fractions had different values for different rotation speeds. For example at 2870 rpm a 13.7 μm glass bead must come within 4.32 percent

of δ from the surface to have an effect, while at 387 rpm it must come within 1.38 percent. If most of the mean unsteady state concentration gradient occurs very close to the surface, as these figures suggest, due to repeated surface renewals, then one would intuitively expect the region of depleted solution to extend out further at the lower speeds because the particles come by less frequently. Strangely enough, the absolute distance the particles must penetrate to have effect, Δ , was found to be remarkably constant (for example, $\Delta = 0.428 \mu\text{m}$ at 2870 rpm, $\Delta = 0.411 \mu\text{m}$ at $\Delta = 1440$ rpm and $0.340 \mu\text{m}$ at 387 rpm) with rotation speed.

Also, the value of Δ , being less than half a micron seems unusually small. How does this compare with distance the concentration depletion actually extends into the bulk solution between surface renewals? Let us take a point on the outer rim of the 1.41 cm radius disk, turning 300.5 r/s in a 30 percent volume suspension of $13.71 \mu\text{m}$ glass beads. According to the model, the surface is covered with 9516 beads/cm^2 , each of which scrapes a path $1.96 \mu\text{m}$ s wide as it moves over the surface at 23.1 cm/s. On the average there are 23.2 milliseconds between renewals. Using the concentration profile for transient diffusion in a semi-infinite solid,

$$\frac{c_i - c}{c_i - c_0} = \text{erf} \left(\frac{z}{2(Dt)^{1/2}} \right) ,$$

we calculate the point of half the bulk concentration to be 3.32 μm s from the electrode, 7.8 times Δ .

At 40.5 r/s, the lowest speed, the model predicts 7559 beads/ cm^2 , cutting swathes 1.75 μm s across, as they travel at 1.13 cm/s. The mean time between renewals is 666 milliseconds, during which time the half bulk concentration point extends 16.7 μm s into the suspension, 49 times Δ . Therefore the supposition that Δ corresponds to an actual mean nonsteady boundary layer thickness seems to be not quite correct.

Figure 77 gives an example of the matching of the surface renewal model to the experimental data. For each disk size, particle diameter and rotation speed, Δ was adjusted to make a least squares fit. The ordinate is the augmentation factor or the limiting current with beads divided by the limiting current without beads. As mentioned above in discussing the threshold step, a 7 percent offset in particle concentration is used in the model.

Figure 78 shows those values of Δ which give the best fit. It can be seen that the values for the smaller disk (represented by squares connected with dashed lines) are only slightly higher than those for the larger disk (represented by circles joined with solid lines). In all cases the variation of Δ with rotation speed, Ω , is also slight. The most noticeable variation of Δ , however, is that with particle size. Large particles have high Δ values, smaller have small ones. Figure 79 shows particle diameter divided by the mean optimum Δ value

XBL 815-915

Fig. 77. Augmentation factor ($i_L/i_{L,0}$) from experiment (symbols) and from surface renewal model (dashed lines).

XBL 815-894

Fig. 76. Interaction distances, Δ , which yield least squares fits of surface renewal model to observed limiting currents, for all particle sizes used.

XBL 815-890

Figure 79 - Particle diameter, d , divided by the interaction distance, Δ , deduced through the surface renewal model, as a function of particle size. The mean value (d/Δ) used in figures 81 and 83 is 43.

as a function of particle size. The mean value of Δ is 1/43 the particle diameter.

Figures 80-83 compare some of the experimental data as expressed by the cubic spline function with the surface renewal model utilizing the 1/43 Δ to particle diameter ratio and the 7 percent particle concentration offset. The convexness of the i_L versus percent solids curves and the straightening of the i_L vs Ω curves is born out by the model. Also the relative magnitude of limiting current density between the two different sized disks is reproduced. However the model shows almost no change of i_L with particle size.

This scaling of Δ to the particle diameter (or radius) is reminiscent of the classic creeping flow about a sphere solution by Stokes (66):

$$u_r = U \cos\theta \left[1 + \frac{1}{2} \left(\frac{a}{r} \right)^3 - \frac{3}{2} \left(\frac{a}{r} \right) \right]$$

$$u_\theta = U \sin\theta \left[-1 + \frac{1}{4} \left(\frac{a}{r} \right)^3 + \frac{3}{4} \left(\frac{a}{r} \right) \right]$$

Radial distance relative to spherical radius, a , is the significant independent variable. Although I am not aware of any hydrodynamic solutions to creeping flow about a free sphere in a velocity gradient next to a wall, it is likely that if such a solution did exist, velocity would be a function of r/a .

XBL 8011-12779

Fig. 80. Experimental limiting current density as expressed by the cubic spline function of volume amount solids and particle size at 304 radians/s disk rotation speed. Compare with Fig. 81.

XBL 8011-12769

Fig. 81. Limiting current density as a function of volume amount solids and particle size as predicted by the surface renewal model. Compare with Fig. 80.

EXPERIMENTAL SPLINE FIT
10.7 micron Beads radius 1.41 cm

XBL 8011-12767

Fig. 82. Experimental limiting current density as expressed by the cubic spline function of volume amount solids and disk rotation speed with 10.7 μm beads. Compare with Fig. 83.

XBL 8011-12773

Fig. 83. Limiting current density as a function of volume amount solids and disk rotation speed as predicted by the surface renewal model. Compare with Fig. 82.

The facts that Δ is invariant with Ω , the rotation speed, and R , the electrode radius, but is scaled to a , the particle radius, strongly suggest a different physical picture (Fig. 84). In this Δ represents the thickness of a layer of stagnant solution clinging to the surface of the sphere which absorbs reactant as the particle cartwheels over the electrode surface, and transfers it as it contacts the electrode. Of course the electrode also has a thin layer of solution adhering to it, and what results when the two layers impinge must be a melding of the two and not a step function of concentration as the surface renewal model assumes.

One might argue that we are now destroying the very assumptions upon which the surface renewal model was founded. This is true. However, the surface renewal model, despite its deficiencies, can still be used to point the way to an improved model which might do a better job of explaining the behavior of the system. For example in the discussion sections "Effect of Electrode Size on Limiting Current" and "Effect of Disk Rotation Speed on Limiting Current" the proposition was put forth that the enhancement of limiting current was proportional to the surface area covered by the particles per unit time. From the viewpoint of a fixed spot on the electrode surface, each time a particle passes near it a fixed amount of extra mass is transferred, regardless of how fast the particle is traveling. However, Figs. 71-73 show that this theory holds only for the mid-size particle range. What happens with particles that are either too large or too small?

XBL 815-892

Fig. 84. Particle surrounded by a film of solution, Δ thick, being rolled over the electrode by a velocity gradient.

In transient diffusion problems a measure of the time scale in which mass transfer takes place is the time constant:

$$\frac{1}{\alpha} = \frac{4x^2}{\pi^2 D} \quad .$$

The variable x is the distance over which mass is transferred. In our case it is equal to the layer thickness, Δ .

Imagine a $3.96 \mu\text{m}$ particle traveling at its maximum experimental speed (outer rim of large disk at 300.5 r/s). We compute $\Delta = 6.0 \times 10^{-6} \text{ cm}$, $1/\alpha = 2.8 \times 10^{-6} \text{ sec}$. However, the time it takes the particle to pass over and interact with the surface is $6.0 \times 10^{-6} \text{ sec}$. If we can use the transient diffusion in a semi-infinite slab model for the stagnant layer of thickness, Δ , then 90 percent of the concentration in the layer has been discharged in that time. Keep in mind this is the shortest time of interaction case with the particle traveling at its highest velocity over the surface. At lower speeds the local limiting current might appear as in Fig. 85. A fixed amount of reactant, essentially all that is stored in the particle's surface layer, is transferred at once. Then a period follows in which limiting current is held below the steady state limiting current because the particle is blocking the surface.

As shown in Appendix C, c_s , the surface concentration of interacting particles at a given volume fraction is proportional to $1/a^2$, when Δ is scaled with a . However, the mass contained in each surface layer around the particle is proportional to its volume which

XBL 815-914

Fig. 85. Transient in local limiting current density with the passage of a small or slow moving particle.

XBL 815-885

Figure 86 - Local limiting current transient experienced when a relatively large or fast moving particle passes by.

is in turn proportional to a^3 . Therefore if all the mass in the particle film is released as it contacts the electrode, the augmentation of mass transfer is proportional to a . This explains why limiting current decreases with the smaller particle sizes.

At the other extreme, consider a $75\text{ }\mu\text{m}$ bead with $\Delta = 1.7\text{ }\mu\text{m}$, traveling at a very slow speed ($r = 0.28\text{ cm}$, $\Omega = 40.5\text{ r/s}$, $V = 1.26\text{ cm/s}$). Using a quarter sine wave concentration distribution, which as dealt with below is not such a bad assumption, it is calculated that by the time the particle breaks contact with the surface its surface layer is still diffusing reactant to the surface at 73 percent its initial rate. This is a longest time of interaction case. A point on the surface being passed over by a $75\text{ }\mu\text{m}$ bead will experience an i_L versus time plot like Fig. 86.

In other words, the surface layer is so large it does not have enough time to fully discharge itself. A fixed amount of mass is no longer transferred to each point. The amount transferred is now also dependent on the time a particle remains in contact with a point on the electrode. As shown in Figs 72 and 73, this causes the limiting current not to increase so readily as Ω is increased, when larger particles are used. This slow discharge of the particle film coupled with a low initial concentration gradient explains why the limiting currents decrease with increasing particle size.

Particle Film Model

The discussion of the surface renewal model above points the way to a new model. This "particle film model," assumes that a liquid film of thickness Δ adheres to the particle as shown in Fig. 84. The hydrodynamic velocity gradient causes the particle and its film to rotate. Through the process of diffusion the particle film alternately absorbs reactant from the bulk solution and desorbs it to the electrode surface. Outside the particle film, flow is laminar and no turbulent mixing takes place. For this reason this extra mass transfer to a point on the electrode lasts only as long as it contacts the particle film.

As before, we base our model on a well known analytic solution to a one-dimensional transient diffusion problem. When the particle film first contacts the electrode, a certain initial concentration profile exists in the space between the electrode and particle as shown in Fig. 87, which then decays with time. Since the electrode is at limiting current, $c = 0$ at $y = 0$. At $t = 0$, the concentration at the particle surface is c_0 , further since the particle itself is neither a source nor a sink of matter,

$$\frac{dc}{dy} = 0 \quad \text{at} \quad y = y_0 \quad .$$

The solution of Fick's second law,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2} \quad ,$$

147

XBL 815-891

Fig. 87. The decay of an arbitrary concentration profile between the electrode and particle with time.

subject to the above boundary conditions, through separation of variables, is well known (67,68), and is given by

$$c = b_1 e^{-\alpha t} \sin\left(\frac{\pi y}{2y_0}\right) + b_2 e^{-9\alpha t} \sin\left(\frac{3\pi y}{2y_0}\right) + b_3 e^{-25\alpha t} \sin\left(\frac{5\pi y}{2y_0}\right) + \dots$$

where $\alpha = \pi^2 D / 4y_0^2$, and b_n are the Fourier coefficients needed to describe the concentration profile at $t = 0$.

For the particle film model only the first four terms of this infinite series are considered.

$$c = \frac{c_0}{(1 - C_2 + C_3 - C_4)} \left[e^{-\alpha t} \sin \frac{\pi y}{2y_0} + C_2 e^{-9\alpha t} \sin \frac{3\pi y}{2y_0} + C_3 e^{-25\alpha t} \sin \frac{5\pi y}{2y_0} + C_4 e^{-49\alpha t} \sin \frac{7\pi y}{2y_0} \right]$$

where c_0 is the initial ($t = 0$) concentration at the particle surface, and C_2 , C_3 and C_4 are empirical constants to be determined latter by fitting the model to the experimental data. In order that, $c = c_0$ at $t = 0$, $y = y_0$, the expression is divided by $(1 - C_2 + C_3 - C_4)$.

To find the amount of reactant, $M(t)$, contained in the gap between particle and electrode, expressed in moles per unit surface area, as a function of time, we integrate over y .

$$M(t) = \int_0^{y_0} c dy \quad .$$

$$M(t) = \frac{c_0}{(1 - c_2 + c_3 - c_4)} \left[e^{-at} \int_0^{y_0} \sin\left(\frac{\pi y}{2y_0}\right) dy + c_2 e^{-9at} \int_0^{y_0} \sin\left(\frac{3\pi y}{2y_0}\right) dy \right. \\ \left. + c_3 e^{-25at} \int_0^{y_0} \sin\left(\frac{5\pi y}{2y_0}\right) dy + c_4 e^{-49at} \int_0^{y_0} \sin\left(\frac{7\pi y}{2y_0}\right) dy \right]$$

$$M(t) = \frac{c_0}{(1 - c_2 + c_3 - c_4)} \left(\frac{2y_0}{\pi} \right) \left[e^{-at} + \frac{c_2}{3} e^{-9at} + \frac{c_3}{5} e^{-25at} + \frac{c_4}{7} e^{-49at} \right]$$

The amount of reactant transferred to the electrode in time t is $M(0) - M(t)$ which is given by

$$M(0) - M(t) = \frac{c_0}{(1 - c_2 + c_3 - c_4)} \frac{2y_0}{\pi} (1 - e^{-at}) + \frac{c_2}{3} (1 - e^{-9at}) \\ + \frac{c_3}{5} (1 - e^{-25at}) + \frac{c_4}{7} (1 - e^{-49at}) \quad (4)$$

It is necessary now to relate this simple one-dimensional analysis to the motion of the particle and the fluid surrounding it. As depicted in Fig. 88 the spherical particle is rolling over the electrode impelled by the fluid velocity gradient. The sphere need not be touching the electrode but it is assumed there is no slip between the lower surface of the sphere and the electrode. In effect the sphere "rolls" over the electrode. Also as the particle rotates solution is "squeezed" out from beneath it, around its sides and is "sucked" back under it again as it rolls by. A plausible flow field under the bottom of the sphere is shown in Fig. 89.

XBL815-924

Fig. 88. Sphere with particle film rolling over electrode.

XBL 815-921

Fig. 89. Possible flow field between particle and surface, from the particle's frame of reference looking from the electrode's side.

Conceptually one can follow a column of solution in the particle film, extending from the sphere to the electrode, as the particle moves by. In actuality, an originally straight column of solution will get bent and distorted by the flow field underneath the sphere, but to apply the above one-dimensional analysis it is necessary to disregard this effect. It is assumed that although the columns of fluid may be shortened and uniformly widened they will not skew or buckle sideways.

In Fig. 88 we can follow the progression of such columns as they pass under the particle (or as the particle passes over them depending on the frame of reference). $\overline{ABC}$ traces the path of a column that passes directly under the center of the sphere. At point A the particle film first touches the electrode and transient mass transfer begins ($t = 0$). As time goes on the distance between sphere and electrode, y_0 , gets less until point B where it reaches a minimum. The distance y_0 then increases until point C, where the particle film breaks contact with the electrode and the transient diffusion to it has stopped. A column located more to the side of the sphere would follow a path like $\overline{DEF}$ with generally larger y_0 values and a shorter contact time.

It can be easily shown, by breaking time into infinitesimal segments of duration, dt , that when y_0 changes with time, the at exponential terms in Eq. (4) can be replaced by β , defined as

$$\beta = \frac{\pi^2 D}{4} \int_0^t \frac{dt}{[y_0(t)]^2} \quad ,$$

where for this model, the upper limit of integration, t , is the contact time for any given column of solution in the particle film.

Each particle, therefore, has a whole range of β values corresponding to different parts of the particle film with various degrees of mass depletion. However, rather than solving this horrendous problem analytically, it was decided to arbitrarily chose a single contact time and several y_0 values, constant in time, to represent the spherical particle and then assign relative weights to each y_0 value empirically.

Figure 90 shows the theoretical representation of the particle, a solid with three distinct levels. If the distance of the level farthest from the electrode, level 0, is y_0 , the next, level 1, is $y_0/9$, and the third, level 2, $y_0/81$ from the electrode. The choice of multiples of $1/9$ is purely arbitrary. This mathematical formulation stipulates that a column of solution is either on one level or the other. Usually one level dominates mass transfer. Level 0 with its large volume of solution but small concentration gradient is pre-dominant at small particle sizes and low velocities. level 2 is dominant at large particle sizes and high speeds, while level 1 is intermediate. Figure 91 shows the contributions of the three levels to the limiting current as a function of particle size, in the final model below. A model based on one level alone, would yield an i_L vs particle diameter curve that is too sharp, too high in the middle of the curve and too low at the large and small particle extremes to match the experimental limiting currents. Thus it is necessary to introduce

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Fig. 90. The particle film model's simplification of the 3-dimensional rotating sphere.

Figure 91 - Relative contribution of the three levels in the particle film model and the total calculated limiting current density (solid line).

a multiplicity of levels, both to account for the spherical geometry of the particles and to "smear out" the curve.

If m represents the number of a level then the amount of mass transferred to a unit area electrode surface is derived from Eq. (4) as

$$M(0) - M(t) = \frac{c_0}{(1 - c_1 + c_3 - c_4)} \left(\frac{2y_0}{\pi a_T} \right) \sum_{m=0}^2 \frac{a_m}{9^m} \left[1 - \exp(-81^m \beta) \right. \\ \left. + \frac{c_2}{3} (1 - \exp(-81^m 9\beta)) + \frac{c_3}{5} (1 - \exp(-81^m 25\beta)) \right. \\ \left. + \frac{c_4}{7} (1 - \exp(-81^m 49\beta)) \right]$$

where a_m is the surface area of the m th level and $a_T = a_0 + a_1 + a_2$, is the total area of all three levels. β is defined as

$$\frac{\pi^2 D t}{4 y_0^2}$$

since the levels are all constant with respect to time. At any given point on the surface of the rotating disk electrode, the transient component of limiting current, i_{LT} , is given by

$$i_{LT} = n F N_p w V [M(0) - M(t)] \quad (5)$$

where N_p is the number of particles per unit area within Δ of the electrode as calculated in Appendix C. The width of the particle, w ,

as seen by its interaction with the surface is obtained from Appendix J. The velocity of the particle V is obtained from Appendix E, assuming $z = a + \frac{1}{2} \Delta$. The product $N_p w V$ then represents the area per unit time swept out by all particles per given electrode surface area. $[M(0) - M(t)]$ is the mass transferred per unit area swept out. The time of interaction, t , can be defined as w/V , assuming the particle is as long as it is wide.

The distance of the highest level, y_0 , was set at the height of the center of the mean interacting particle or $y_0 = a + \frac{1}{2} \Delta$. The initial concentration at the surface of the particle, c_0 , is taken to be the average concentration across the diameter of all spheres interacting with the electrode, as developed in Appendix K. Thus the smaller glass beads have less of an effect because they are immersed too deeply in the mass transfer boundary layer and contact a lower concentration of reactant species. As in the surface renewal model, the thickness of the particle film is proportional to the sphere's radius.

$$\Delta = C_1 a \quad ,$$

where C_1 is the proportionality constant.

The steady state component of limiting current, i_{LS} , is taken to be the classical limiting current density for a RDE, $i_{L,0}$, taking into account the increase in bulk viscosity and decrease in diffusivity and bulk concentration (Appendices B and F), multiplied by the fraction of the surface not interacting with a particle film, or

$$i_{LS} = i_{L,0}(1 - N_p a_T)$$

Finally the total limiting current density is given as the sum of the transient and steady state components.

$$i_L = i_{LS} + i_{LT}$$

Using the above mathematical formulation, the empirical parameters were varied to provide a least-squares fit to the experimental data. The values of the limiting currents for each particle and disk size were adjusted upwards by as much as 7.6 percent or downwards as much as 0.7 percent to make the limiting currents with no particles added match classical RDE theory. This accounts for discrepancies due to solution composition varying from one run to the other and for uncertainties in measuring cathode area. Thus in effect we are looking at the proportionate relative increase in limiting current not its absolute value. The optimum C_1 value was 1.146, much larger than 0.023 for the surface renewal model. In otherwords the particle film appears to be not so much a thin film as a volume of liquid more than 8 times the volume of the sphere itself. Would such a large particle film be hydrodynamically stable under these flow conditions? A future hydrodynamic analysis may be helpful in this regard. In any case the value of the thickness of the particle film should be considered as approximate, seeing how C_1 varied from 0.4 to 1.4 during the course of the convergence on the best fit.

The least squares values of the level areas are

$$a_0 = 2.711 a^2$$

$$a_1 = 0.846 a^2$$

$$a_2 = 0.770 a^2$$

The relative proportions of these areas are shown in Fig. 90. The cross section of the figure is not exactly suggestive of a sphere, but it need not be either. It is possible that the large area assigned to level 0 represents large reserves of reactant in those parts of the particle film not contacting the electrode, but which can be drawn upon if the time available for diffusion is long enough.

The values of C_2 , C_3 and C_4 were 0.395, 1.013 and -0.165 respectively. This yields the initial concentration profile shown in Fig. 92. This "two humped" concentration curve is plausible if one considers that the particle film is exposed repeatedly to alternating high and low concentrations as it rotates. It takes time for reacting species to diffuse inward, causing a spiral concentration pattern.

On the other hand, one must note that the higher order sine functions used to define initial concentration and those that reflect the different levels of the particle are mathematically identical. The choice of the 3rd, 5th and 7th harmonics to describe concentration and 1st, 9th and 81st to account for spacing distance is purely arbitrary. Most likely these two effects meld together in such a way to make their separate determination from experimental data impossible.

The constants C_1 , a_0 , a_1 , a_2 , C_2 , C_3 and C_4 derived from the curve fitting process should not be considered to be accurate. The many degrees of freedom and imprecise data allow for a wide range of "solutions." Rather, the important information to be gleaned from this analysis is that by postulating a region of fluid around the spherical particle which moves with it, we can then proceed to predict

Fig. 92. The initial concentration profile that gives the least squares fit between the particle film model and experiment.

the limiting current density to a degree of accuracy about equal to experimental error. However, by assuming complete mixing in the wake of the particle, as in the surface renewal model, we cannot.

Comparison of the particle film model with experimentally determined limiting current densities is made in Figs. 93-164. The following observations can be made:

1) In the i_L versus percent volume solids curves (Figs. 93-116), the slope of the lines decreases with increasing particle concentration. For the most part this is due to the increasing viscosity of the slurry which cause the glass beads to move more slowly and thus cover less surface area per unit time. However the slopes for the two largest beads (Figs. 101-104 and 113-116) change very little. Their particle films are so large and discharge mass so slowly that they are virtually insensitive to velocity. Until the fractional depletion of their layers becomes significant, they will diffuse mass to the surface at close to the initial rate ($t = 0$). In contrast the surface renewal model yields the same shape i_L versus percent solids curve regardless of the particle size.

2) Figures 117-140 show limiting current density as a function of the disk rotation speed. For the same basic reasons as in paragraph 1) above, with increased concentration of smaller particles, the curves progress from parabolic to linear. The particle films of these particles are so small that most of their reactant concentration is discharged on a single contact with the electrode. For this reason the enhanced mass transfer is proportional to the rate at which they

roll over the electrode surface. The insensitivity of larger particles to velocity causes their lines to remain curved. In the extreme of largeness and speed they are offset from the parabolic curve of 0 percent solids, by a constant amount. Again the surface renewal model does not account for the curves of the big glass beads.

3) The particle diameter versus limiting current density curves are shown in Figs. 141-164. The particle film model reproduces the experimental curve with a peak in the middle and the smaller diameter side dropping off faster than the larger because of the lesser concentration on the surface of the small glass beads, which are inside the boundary layer. In contrast the surface renewal model shows virtually no change with particle size.

4) The particle film model also replicates the shift in the maxima of the i_L versus size curves towards the larger sizes as rotation speed decreases and particle films have more time to discharge their reactants before moving to a new spot on the electrode surface.

5) Both surface renewal and particle film models do a fair job of explaining the difference in limiting currents between the 0.564 cm and 1.413 cm radius disks. The difference seems to be due to the different particle velocities relative to the electrode which are approximately proportional to radial distance.

The fact that the particle film model explains the observed limiting currents better than the surface renewal model implies that the hydrodynamic flow around a particle is essentially laminar with little if any mixing from turbulent vortices outside of the particle

film itself. The key assumption of the particle film model is that no permanent mixing has occurred in the wake of the particle. The fluid elements of the boundary layer separate and displace to allow the particle and its film to roll by and then flow back to their same original positions as if the particle had not passed through them. Therefore, it appears that a particle in a fluid velocity gradient forms an "artificial eddy" under conditions, such as a low Reynolds number or within the laminar sublayer, where a vortex of fluid alone is not stable.

Limiting Current versus Volume Percent Particles

Limiting current density was plotted as a function of percent volume solids in Figs. 93-104 for the 0.56 cm disk and in Figs. 105-116 for the 1.41 cm disk. The points represent the experimental limiting currents. The dashed lines are the limiting currents predicted by the particle film model. The disk rotation speed in radians per second is found immediately to the right of the dashed lines. For greater clarity each figure shows every other rotation speed.

XBL 815-9671

Fig. 93. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9670

Fig. 94. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9672

Fig. 95. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

8.4 Micron Beads

XBL 815-9673

Fig. 96. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

12.4 Micron Beads

XBL 815-9675

Fig. 97. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

12.4 Micron Beads

XBL 815-9677

Fig. 98. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9674

Fig. 99. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

13.7 Micron Beads

XBL 815-9676

Fig. 100. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

56.0 Micron Beads

XBL 815-9678

Fig. 101. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

56.0 Micron Beads

XBL 815-9680

Fig. 102. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9679

Fig. 103. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

74.9 Micron Beads

XBL 815-9681

Fig. 104. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

4.0 Micron Beads

XBL 815-9634

Fig. 105. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

4.0 Micron Beads

XBL 815-9635

Fig. 106. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

8.4 Micron Beads

XBL 815-9636

Fig. 107. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9640

Fig. 108. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

12.4 Micron Beads

XBL 815-9641

Fig. 109. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

Fig. 110. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9642

XBL 815-9637

Fig. 111. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9638

Fig. 112. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9639

Fig. 113. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9643

Fig. 114. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

Fig. 115. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9644

Fig. 116. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

Limiting Current versus Disk Rotation Speed

Limiting current density as a function of the angular velocity of the RDE is shown in Figs. 117-128 for a 0.56 cm disk and in Figs. 129-140 for the 1.41 cm disk. The points represent the experimental limiting currents. The lines represent the values of limiting current density predicted by the particle film model. The dashed lines correspond to the same percent volume solids as the circles and the dotted lines to the asterisks. The value of the percent volume solids is found to the right of the end of each line. A staggered presentation was used to prevent overlap. For clarity each figure displays every other concentration of particles.

XBL 815-9682

Fig. 117. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9683

Fig. 118. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9684

Fig. 119. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

Fig. 120. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9686

Fig. 121. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

Fig. 122. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9688

Fig. 123. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9689

Fig. 124. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9690

Fig. 125. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9691

Fig. 126. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9628

Fig. 127. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

XBL 815-9629

Fig. 128. Experimental data points and the limiting current density predicted by the particle film model as a function of volume concentration glass beads.

Fig. 129. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9648

Fig. 130. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9647

Fig. 131. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9651

Fig. 132. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

Fig. 133. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9653

Fig. 134. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9649

Fig. 135. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

13.7 Micron Beads

XBL 815-9654

Fig. 136. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9650

Fig. 137. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9655

Fig. 138. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

XBL 815-9657

Fig. 139. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

74.9 Micron Beads

XBL 815-9656

Fig. 140. Experimental data points and the limiting current density predicted by the particle film model as a function of disk rotation speed.

Limiting Current Versus Particle Diameter

Limiting current density as a function of particle diameter is displayed in Figs. 141-152 for the 0.56 cm disk and in Figs. 153-164 for the 1.41 cm disk. The points represent those experimental limiting currents with particle concentrations closest to the nominal concentration of each figure. The lines are the limiting current densities predicted by the particle film model at the nominal particle concentration. Disk rotation speeds are found to the right of each line. For clarity every other rotation speed is displayed in each figure.

XBL 815-9627

Fig. 141. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9625

Fig. 142. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9623

Fig. 143. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9622

Fig. 144. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9626

Fig. 145. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9624

Fig. 146. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9620

Fig. 147. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9630

Fig. 148. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9621

Fig. 149. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9632

Fig. 150. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9631

Fig. 151. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9633

Fig. 152. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9659

Fig. 153. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9658

Fig. 154. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9660

Fig. 155. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9663

Fig. 156. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9662

Fig. 157. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9661

Fig. 158. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9664

Fig. 159. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9665

Fig. 160. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9666

Fig. 161. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9668

Fig. 162. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9667

Fig. 163. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

XBL 815-9669

Fig. 164. Experimental data points and the limiting current density predicted by the particle film model as a function of particle size.

The Practical Particle Film Model

The particle film model evokes seven arbitrary constants, excluding those to evaluate the particle concentration offset, and draws on twelve exponential functions to evaluate one limiting current density. It is desirable to have a simpler function with fewer arbitrary constants, both to make engineering applications of this model more feasible and to counter the possible allegation that I have introduced so many adjustable parameters I could fit any shaped curve I liked.

To do this the concept of a variable "predominant level distance" is introduced. It stipulates that under a given set of conditions one level dominates mass transfer and the contributions from all other levels may be ignored.

The particle diffuses mass to the electrode at the same rate as if it were one flat surface a given distance from the electrode. The predominant level distance, y_L , divided by the particle radius, a , is arbitrarily expressed as

$$\frac{y_L}{a} = k_2 = k_{2,0} \left(\frac{aV}{D} \right)^b$$

where $k_{2,0}$ and the exponent, b , are to be determined empirically.

The dimensionless group (aV/D) is a Peclet number for the spherical particle which indicates the extent of discharge of the particle film. When the Peclet number is large only a small amount of the available mass has been transferred and the predominant level distance is very small. When the Peclet number is small most of the particle film's

solute has reacted with the electrode and y_L is large. It can be shown that for a linear velocity profile (av/D) is proportional to the inverse of at in Eq. (4).

The concentration profile is assumed to be a simple 1/4 wave sine function. In this case Eq. (4) reduces to

$$M(0) - M(t) = c_o \left(\frac{2y_o}{\pi} \right) (1 - e^{-at}) \quad (6)$$

The term y_o is a measure of the amount of solution in the gap available for transfer and is identical to Δ , the thickness of the particle film. While y_L determines the fraction of mass in the gap discharged after contact time t , y_o determines the volume solution available. y_o is proportional to the spherical radius

$$y_o = \Delta = C_1 a$$

The area a_T is determined analytically from Appendix J instead of empirically. Equation (5) becomes

$$i_{LT} = nFN_p w V c_o \left(\frac{2y_o}{\pi} \right) \left[1 - \exp \left(- \frac{\pi^2 D}{4y_L^2} \left(\frac{w}{V} \right) \right) \right] \quad (7)$$

Except for these changes, limiting current density was calculated the same way as in the previous particle film model. At optimal fit the empirical constants were

$$C_1 = 1.183$$

$$k_{2,0} = 2.478$$

$$b = -0.1829$$

The graphs of this model are essentially the same as Figs. 93-164 in their basic features and are therefore omitted for the sake of brevity. Table 2 compares the standard deviations of the cubic spline functions, the partial film model and the practical particle film model. The practical model fits the data almost as well as the original particle film model. Both models correlate experimental data with slightly more error than the reproducibility of the limiting current measurements themselves, ± 8 percent. The cubic spline functions fit the data better than 8 percent in part by twisting and curving to match spurious deviations not significant to the overall trends in the data. More accurate data are needed to develop models more refined than those above.

Table 2. Deviations from experimental limiting currents.

Function	Disk Radius	Standard Deviation	Std. Dev. as percent of i_L
Cubic Spline	0.56 cm	0.998 mA/cm ²	4.5 %
	1.41	1.673	5.3
Particle Film Model	0.56	2.50	12.3
	1.41	2.51	8.2
Practical Particle Film Model	0.56	2.57	12.2
	1.41	2.51	9.4

MECHANICAL POWER CONSUMPTION FOR A RDE

The circumferential (θ -direction) shear stress on a surface element of a rotating disk electrode is given by Newton's viscosity law.

$$\tau_{z\theta} = \mu \left. \frac{dv_{\theta}}{dz} \right|_{z=0}$$

Since the disk moves only in the θ -direction the other stress components may be ignored. We introduce the customary dimensionless velocity and displacement (61) using

$$v_{\theta} = r \Omega G(\zeta)$$

and

$$\zeta = \left(\frac{\Omega}{\nu} \right)^{1/2} z$$

Newton's law becomes

$$\tau_{z\theta} = \frac{\mu \Omega^{3/2} r}{\nu^{1/2}} \left. \frac{dG}{d\zeta} \right|_{\zeta=0}$$

The value of the derivative is given in the literature (69) as

$$G'(0) = -0.61592$$

The work done by that surface element on the fluid per unit time is $-\tau_{z\theta} r \Omega$. Therefore the power consumption over the entire disk is

$$\begin{aligned}
 \text{Power} &= - \int_0^R \tau_{z\theta} r \Omega 2\pi r dr \\
 &= \frac{0.61592 \mu \Omega^{5/2} 2\pi}{\nu^{1/2}} \int_0^R r^3 dr \\
 &= \frac{0.3080 \mu \Omega^{5/2} \pi R^4}{\nu^{1/2}}, \quad (8)
 \end{aligned}$$

where R is the outer radius of the disk.

The limiting current density for a rotating disk electrode (60) is

$$i_L = 0.62048 \text{ nF } c_i \Omega^{1/2} \nu^{-1/6} D_i^{2/3},$$

or put in another way, if the limiting current is given, then the rotational speed is given by

$$\Omega^{1/2} = \frac{i_L \nu^{1/6}}{0.62048 \text{ nF } c_i D_i^{2/3}} \quad (9)$$

Now we can answer the question, "Given the limiting current, what must the power consumption be?" by substituting Eq. (9) into Eq. (8):

$$\text{Power} = \frac{3.3485 \nu^{1/3} \mu \pi R^4 i_L^5}{D_i^{10/3} (\text{nF } c_i)^5} \quad (10)$$

Figures 165 and 166 plot the power consumption calculated by Eq. (8) divided by the experimentally observed limiting current, as a function of volume fraction solids. The increased viscosity and density of the slurry is taken into account after the treatment in Appendix B. Power divided by limiting current has units of volts and can be useful in looking at the overall energy consumption of an electrochemical process (i.e., so many volts reversible reaction, plus volts surface overpotential, volts concentration polarization, volts IR drop and volts agitation energy).

However, the bulk concentration of reactant ($\text{Fe}(\text{CN})_6^{-3}$) in these experiments is only 0.04 molar, which makes the limiting current low and in turn P/i_L seems excessive. Also one might want to operate the process below limiting current (to obtain a smooth electrodeposit for example), in which case agitation power divided by operating current is the relevant measure of energy loss. In any case it can be seen that at high velocities suspended particles can cut the agitation energy per Faraday of material produced in the cell while at the same time increasing the maximum allowable current density.

Figure 167 compares the energy cost associated with achieving a higher limiting current density by rotating the disk faster without particles present, Eq. (8), with that for keeping the speed constant but adding 8.4 μm glass beads to obtain the same increase in limiting current. This approach might be used in high-speed flow cells and other high rate electrochemical systems of practical importance to reduce the power needed for convective mass transport.

XBL 8011-12762

Fig. 165. Agitation power, P , in watts/cm² divided by limiting current density, i_L , in amps/cm². This quantity represents the minimum energy to effect mass transfer per unit reactant, and is shown as a function of volume fraction solids.

XBL 8011-12766

Fig. 166. Agitation power, P , in watts/cm² divided by limiting current density, i_L , in amps/cm². This quantity represents the minimum energy to effect mass transfer per unit reactant, and is shown as a function of volume fraction solids.

XBL 8012-12936

Fig. 167. A comparison of the increased power consumption incurred to raise limiting current by keeping the disk speed at 300.5 r/s and adding 8.4 μ m beads against that incurred by rotating the disk faster without particulates.

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APPENDIX A. TEMPERATURE CORRECTION FOR A RDE

In order to compare many different limiting current measurements, it is necessary to correct them to the same standard temperature. 30°C was chosen as the standard temperature because the cell usually approached this value asymptotically during the course of the experimental run. Classical Rotating Disk Theory (63) tells us

$$i_L = [0.62048 n F c_i \Omega^{1/2}] \nu^{-1/6} D_i^{2/3} \quad (A1)$$

Only kinematic viscosity, ν , and diffusivity, D_i , depend on temperature; all the other terms are constant.

We shall assume this $\nu^{-1/6} D_i^{2/3}$ temperature dependency for the case of a RDE with suspended particles as well, since no known relationship yet exists. The root-mean-square of the correction was 3.36 percent, with the largest corrections being at the beginning of the run, before the cell came up to temperature, and the particulate concentrations were still low.

The temperature dependency of kinematic viscosity was determined experimentally using an Ostwald viscometer.

$$\frac{\nu_{T+\Delta T}}{\nu_T} = \exp \left[1996.75 \left(\frac{1}{T + \Delta T} - \frac{1}{T} \right) \right] \quad (A2)$$

fits the data best, with T being absolute temperature in °K. ΔT is the actual temperature minus the reference temperature. The variation of density, ρ , with T is expressed as

$$\rho_{T+\Delta T} = \rho_T + C\Delta T$$

where C , as determined from literature (70) values for 2N NaOH, is $-4.3 \times 10^{-4} \text{ gm/cm}^3\text{ }^\circ\text{C}$. Since $\mu = \nu\rho$, the temperature dependence of viscosity is

$$\frac{\mu_{T+\Delta T}}{\mu_T} = \left(\frac{\rho_T + C\Delta T}{\rho_T} \right) \exp \left[1996.75 \left(\frac{1}{T + \Delta T} - \frac{1}{T} \right) \right] ,$$

The diffusivity of ferricyanide ion can be estimated by (59)

$$D_{\text{Ferri}} = \frac{T}{\mu} (2.34 + 0.014\Gamma) \times 10^{-10} \frac{\text{cm}^2}{\text{s}} ,$$

where Γ is the ionic strength. The variation of diffusivity with temperature would then be

$$\frac{D_{T+\Delta T}}{D_T} = \left(\frac{T + \Delta T}{T} \right) \left(\frac{\mu_T}{\mu_{T+\Delta T}} \right)$$

or

$$\frac{D_{T+\Delta T}}{D_T} = \left(\frac{T + \Delta T}{T} \right) \left(\frac{\rho_T}{\rho_T + C\Delta T} \right) \exp \left[1996.75 \left(\frac{1}{T} - \frac{1}{T + \Delta T} \right) \right] \quad (\text{A3})$$

The change in limiting current itself, with temperature is obtained from Eq. (A1).

$$\frac{i_L(T + \Delta T)}{i_L(T)} = \left(\frac{D_{T+\Delta T}}{D_T} \right)^{2/3} \left(\frac{v_T}{v_{T+\Delta T}} \right)^{1/6}$$

substitution of Eqs. (A2) and (A3) yields

$$\frac{i_L(T + \Delta T)}{i_L(T)} = \left[\frac{1 + \frac{\Delta T}{T}}{1 + \frac{C\Delta T}{\rho_T}} \right]^{2/3} \exp \left[1663.96 \left(\frac{1}{T} - \frac{1}{T + \Delta T} \right) \right]$$

or using the solution properties at 30°C

$$\frac{i_L(30^\circ + \Delta T)}{i_L(30^\circ)} = \left[\frac{1 + 3.30 \times 10^{-3} \Delta T}{1 - 3.98 \times 10^{-4} \Delta T} \right]^{2/3} \exp \left[1663.96 \left(\frac{1}{303.15} - \frac{1}{303.15 + \Delta T} \right) \right]$$

APPENDIX B. EFFECT OF BULK SLURRY PHYSICAL PROPERTIES
ON LIMITING CURRENT

The physical properties of solid-liquid suspensions have been fairly well worked out. Using what we know about how diffusivities, kinematic viscosities etc., change with the volume fraction solids, ϕ , how might we expect the mass transfer rate to a rotating disk to also change assuming that the slurry acts like a continuous medium?

Intuitively:

(I) The effective viscosity increases sharply with concentration solids, decreasing the Reynolds number and therefore lessening the extent of convective mass transport.

(II) The diffusing species in the liquid phase must diffuse around the dispersed solid particles. As the number of particles increases the cross-sectional area normal to the mass flow decreases and the mass transport path becomes longer and more tortuous. The effective diffusivity through the boundary layer should therefore decrease.

(III) As the solids displace more and more solution the effective concentration for convection or the amount of reacting substance per unit volume slurry gets less. So the effect of convection is weakened.

Most correlations of suspension physical properties take the form:

$$A_s = X_A(\phi) A_0$$

where the clear solution property A_0 is multiplied by some function, X_A , of the volume fraction solids to yield the appropriate property of the suspension, A_s . We are primarily interested in density:

$$\rho_s = X_\rho(\phi) \rho_0 \quad ,$$

viscosity:

$$\mu_s = \chi_\mu(\phi) \mu_0 \quad ,$$

kinematic viscosity:

$$\nu_s = \chi_\nu(\phi) \nu_0$$

and diffusivity:

$$D_s = \chi_D(\phi) D_0$$

Let us now derive a mass-transport relationship for a rotating disk in an uniform suspension of spherical inert particles along the same general lines as the derivation of mass-transport to a rotating disk in a single phase newtonian fluid (60). The concentration function, c_i , is governed by the law of convective diffusion.

$$\frac{\partial c_i}{\partial t} + \mathbf{V} \cdot \nabla c_i = D_i \nabla^2 c_i$$

The velocity field about a rotating disk has been mathematically determined (71-73). A cylindrical coordinate system depicted in Fig. 70 is used. Most remarkable is the result that the z-velocity component, V_z , is completely independent of r and θ , and is a function of z only.

$$V_z = (\nu\Omega)^{1/2} H\left(z\left(\frac{\Omega}{\nu}\right)^{1/2}\right)$$

where H is a dimensionless velocity function of dimensionless z-distance, $\zeta = z(\Omega/\nu)^{1/2}$.

By arguments of symmetry, c_i is also a function of z only, and at steady state the equation of convective diffusion reduces to

$$v_z \frac{dc_i}{dz} = D_i \frac{d^2 c_i}{dz^2}$$

However for our suspension of inert spheres we must modify this equation to take into account the reduced concentration available for convection (effect III) and the hindered diffusion around the particles (effect II).

$$v_z (1 - \phi) \frac{dc_i}{dz} = x_D D_i \frac{d^2 c_i}{dz^2}$$

Integration yields

$$\frac{(1 - \phi)}{x_D D_i} \int_0^z v_z dz = \int_0^z \frac{d\left[\frac{dc_i}{dz}\right]}{\left[\frac{dc_i}{dz}\right]}$$

$$\frac{dc_i}{dz} = \left[\frac{dc_i}{dz} \Big|_{z=0} \right] \exp \left[\frac{(1 - \phi)}{x_D D_i} \int_0^z v_z dz \right]$$

And integrating a second time and introducing dimensionless variables

$$c - c_0 = \left[\frac{dc_i}{dz} \Big|_{z=0} \right] \frac{x_v^{1/2} v^{1/2}}{\Omega^{1/2}} \int_0^\omega \exp \left[\frac{(1 - \phi) x_v v}{x_D D_i} \int_0^\eta H(\zeta) d\zeta \right] d\eta$$

where η is an arbitrary value of ζ . The rate of mass transfer at the surface is then

$$N_i = x_{D_i} \frac{dc_i}{dz} \Big|_{z=0} = \frac{x_{D_i} D_i (c_\infty - c_0)}{\left[\frac{x_v^{1/2} v^{1/2}}{\Omega^{1/2}} \right] \int_0^\infty \exp \left[\frac{(1 - \phi) x_v v}{x_{D_i} D_i} \int_0^\eta H(\zeta) d\zeta \right] d\eta}$$

Formed into dimensionless groups it becomes

$$\frac{N_i R}{(c_\infty - c_0) x_{D_i} D_i} = \frac{\left(\frac{\Omega R^2}{x_v v} \right)^{1/2}}{\int_0^\infty \exp \left[S'_c \int_0^\eta H(\zeta) d\zeta \right] d\eta} \quad (B-1)$$

where R is the radius,

$$S'_c = \left[\frac{(1 - \phi) x_v}{x_D} \right] \left(\frac{v}{D_i} \right)$$

is a solid suspension Schmidt number,

$$\left(\frac{1}{x_D} \right) \left(\frac{N_i R}{(c_\infty - c_0) D_i} \right) = Sh'$$

the solid suspension Sherwood number and

$$\left(\frac{1}{x_v} \right) \left(\frac{\Omega R^2}{v} \right) = Re'$$

the solid suspension Reynolds number.

The integral in the denominator of Eq. (B-1) has already been evaluated in classical rotating disk theory for $Sc > 1000$. Therefore mass transfer to a rotating disk in a suspension of inert particles should be correlated as

$$Sh' = 0.62048 Re^{1/2} Sc^{1/3} \quad (B-2)$$

This is completely analogous with the clear fluid rotating disk correlation and reduces to it as $\phi \rightarrow 0$.

One might have been tempted just to use the suspension-corrected values of D_i and ν in the conventional correlation and avoid this lengthy derivation. But then the $1 - \phi$ term, to account for the reduced concentration available for convection, would have been omitted from the Schmidt number.

The limiting current density can now be expressed explicitly as

$$i_L = 0.62048 nF c_{\infty} D_i \left(\frac{\Omega}{\nu} \right)^{1/2} \left(\frac{\nu}{D_i} \right)^{1/3} \left[\frac{x_D^{2/3}}{x_v^{1/6}} (1 - \phi)^{1/3} \right]$$

$$i_L = i_{L,0} \left[\frac{x_D^{2/3}}{x_v^{1/6}} (1 - \phi)^{1/3} \right] \quad (B-3)$$

Where $i_{L,0}$ is the limiting current without particulates. For the relative viscosity of spherical particles let us use the correlation of Thomas (74).

$$X_{\mu} = 1 + 2.5 \phi + 10.05 \phi^2 + 0.00273 \exp(16.6 \phi) \quad (\text{B-4})$$

and

$$X_{\rho} = (1 - \phi) + \frac{\rho_{\text{solid}}}{\rho_{\text{solution}}} \phi = 1 + \left[\frac{\rho_{\text{solid}}}{\rho_{\text{solution}}} - 1 \right] \phi$$

for soda glass spheres ($\rho_{\text{solid}} = 2.475 \text{ gm/cm}^3$) suspended in the Ferri-Ferrocyanide solution ($\rho_{\text{solution}} = 1.126 \text{ gm/cm}^3$).

$$X_{\rho} = 1 + 1.199 \phi$$

and therefore

$$X_{\nu} = \frac{X_{\mu}}{X_{\rho}} = \frac{1 + 2.5 \phi + 10.05 \phi^2 + 0.00273 \exp(16.6 \phi)}{1 + 1.199 \phi}$$

The relative diffusivity X_D is obtained by analogy from the relative electrical conductivity through a suspension of non-conducting spheres where $\nabla^2 \phi = 0$ (75).

$$\text{relative conductivity} = (1 - \phi)^{3/2}.$$

For transport by molecular diffusion alone, $\nabla^2 c_i = 0$. In addition the geometry and boundary conditions (e.g., at particle surface and normal to surface $\partial \phi / \partial r = \partial c_i / \partial r = 0$) are the same therefore

$$x_D = (1 - \phi)^{3/2} .$$

Finally,

$$\frac{i_L}{i_{L,0}} = \left[\frac{(1 - \phi)^{\frac{3}{2} \cdot \frac{2}{3}} (1 - \phi)^{1/3}}{x_v^{1/6}} \right]$$

$$\frac{i_L}{i_{L,0}} = (1 - \phi)^{4/3} \left[\frac{1 + 1.199 \phi}{1 + 2.5 \phi + 10.05 \phi^2 + 0.00273 \exp(16.6 \phi)} \right]^{1/6} \quad (B-5)$$

This function is plotted in Fig. 65. The limiting current should drop precipitously with increasing concentration of suspended solids.

APPENDIX C. CALCULATING PARTICLE SURFACE CONCENTRATION, c_s , AND
PARTICLE CROSS-SECTION, σ

Not all the particles traversing the electrode surface physically touch the surface, but a particle can still disrupt the boundary layer from a distance. Also the part of the boundary layer which is disrupted is significant. In both the steady state and transient concentration profiles alike replacing the solution near the wall with fresh bulk solution, will have a greater effect on the mass transfer rate than replacement further away.

Much could possibly be said about the precise microscopic way these particles might disrupt the boundary layer. But for this model let us handle the issued by just postulating a few crude assumptions:

(I) Any particle whose surface penetrates to within a certain distance, Δ , from the electrode is considered "on the surface;" any wholly outside that distance is not.

(II) The volume occupied by X spheres in the $0 < z < \Delta$ region is transformed into the same volume occupied by X cylinders of length Δ of diameter σ with their bases resting on the surface.

The volume particle density is

$$\frac{\phi}{\frac{4}{3} \pi a^3} \text{ (particles/unit volume) } .$$

Therefore the surface concentration is

$$c_s = \frac{3\phi\Delta}{4\pi a^3}$$

If Δ is proportional to the particle radius, $\Delta = c_1 a$, then

$$c_s = \frac{3\phi c_1}{4\pi a^2}$$

The mean volume occupied by spheres within Δ , per unit surface area is $\bar{\phi}(\Delta)$ which is obtained by integrating the expression D2 from Appendix D.

$$\begin{aligned}\bar{\phi}(\Delta) &= \phi(\infty) \int_0^\Delta \left(\frac{3}{4} \left(\frac{z}{a} \right)^2 - \frac{1}{4} \left(\frac{z}{a} \right)^3 \right) dz \\ &= \phi(\infty) \left[\frac{(\Delta)^3}{4a^2} - \frac{(\Delta)^4}{16a^3} \right]\end{aligned}$$

and

$$\left(\text{Volume occupied per particle in } \Delta \right) = \frac{\phi(\infty) \left[\frac{(\Delta)^3}{4a^2} - \frac{(\Delta)^4}{16a^3} \right]}{\frac{3\phi(\infty)\Delta}{4\pi a^3}} = \pi \left(\frac{\sigma}{2} \right)^2 \Delta$$

$$\sigma = \left[\frac{4}{3} a(\Delta) - \frac{(\Delta)^2}{3} \right]^{1/2}$$

APPENDIX D. THE MEAN VOLUME FRACTION, OCCUPIED BY UNIFORMLY
DISPERSED SPHERES, WITHIN ONE DIAMETER OF A WALL

A plane penetrates a distance x inside a sphere of radius a , and their intersection is a circle of radius r (Fig. D-1). The area of this circle is derived using the pythagorean theorem.

$$\text{Area} = \pi r^2 = \pi(a^2 - [a - x]^2) = \pi(2ax - x^2) \quad (\text{D1})$$

Now to consider the situation at hand, we have a wall, and spheres whose centers cannot approach closer than distance, a , from the wall, but which are otherwise dispersed in a perfectly even and random way in the space permitted them (Fig. D-2). Consider also a plane a distance y from the wall that can be anywhere from 0 to $2a$.

The mean area $\bar{A}$ intersected by the y -plane per sphere with center from a to $3a$ is

$$\bar{A} = \frac{\int_{y-2a}^0 \text{Area } dx + \int_0^y \text{Area } dx}{2a}$$

where we integrate over x , the distance the y -plane penetrates a sphere. Of course when x is negative the plane does not even intersect the sphere, so the first integral goes to zero and we get.

$$\bar{A} = \frac{\pi}{2a} \int_0^y (2ax - x^2) dx = \frac{\pi}{2a} \left(ay^2 - \frac{y^3}{3} \right)$$

XBL 815-917

Fig. D1. Cross section of sphere intersected by plane.

XBL 815-919

Fig. D2. Spherical particles of radius a , randomly dispersed next to a solid wall.

If $\phi(y)$ is the volume fraction (or the cross-sectional area fraction) occupied by spheres at y then

$$\phi(y) = \frac{\left(\begin{array}{c} \text{number of spheres} \\ \text{between } a \text{ and } 3a \end{array} \right) \times \left(\begin{array}{c} \text{mean area intersected by} \\ \text{y-plane per sphere with} \\ \text{center between } a \text{ and } 3a \end{array} \right)}{A_{\text{cross-section}}}$$

$$\phi(y) = \frac{\left(\frac{\phi(\infty)}{\frac{4}{3}\pi a^3} \cdot 2a \cdot A_{\text{cross-section}} \right) \left(\frac{\pi}{2a} \left[ay^2 - \frac{y^3}{3} \right] \right)}{A_{\text{cross-section}}}$$

where $\phi(\infty)$ is the volume fraction occupied by spheres in the bulk, far away from the wall, and $A_{\text{cross-section}}$ is any cross-sectional area of wall surface large enough for studying this population of spheres statistically. Finally,

$$\phi(y) = \phi(\infty) \left[\frac{3}{4} \left(\frac{y}{a} \right)^2 - \frac{1}{4} \left(\frac{y}{a} \right)^3 \right] \quad (D2)$$

APPENDIX E. THE RELATIVE VELOCITY OF A PARTICLE TRAVERSING THE SURFACE OF A RDE

Our particles are not of the same density as the solution, so besides just being swept around with the solution they will also move under the influence of the "centrifugal force" and the "coriolis force." Such forces might not be trivial. For example, at $r = 1.41$ cm and $\Omega = 300.5$ r/s, the centripetal acceleration, $\Omega^2 r$, is 130 times the force of gravity. In the treatment below we shall neglect gravitational force.

The motion of a homogeneous viscous fluid near a rotating disk has been well analyzed (71-73). The fluid velocity components are:

$$V_r = r\Omega F$$

$$V_\theta = r\Omega G$$

$$V_z = (\nu\Omega)^{1/2} H$$

where V_r , V_θ and V_z are the radial, circumferential and axial velocities respectively, and F , G and H are functions of the dimensionless distance from the disk,

$$\zeta = z \left(\frac{\Omega}{\nu} \right)^{1/2},$$

only. The cylindrical coordinates of Fig. 70 are used.

Let us postulate that a similar velocity field exists for the particles, which we shall distinguish from the homogeneous fluid by the superscript, *.

$$V_r^* = r\Omega F^*$$

$$V_\theta^* = r\Omega G^*$$

$$V_z^* = (\nu\Omega)^{1/2} H^*$$

We consider only those spheres touching the surface, $z = a$, which makes the problem two dimensional, $V_z^* = 0$. As a first approximation, the fluid dynamic force exerted on the particle by liquid flowing past it, is Stokesian.

$$F = -6\pi\mu aU$$

where U is the velocity of the particle relative to the bulk fluid. Since we are concerned specifically with particles touching the surface the Stokes flow assumption may not be exact, but is suitable. Because of the linear velocity-force relation, we can resolve the force and velocity vectors into θ and r components as

$$F_\theta = -6\pi\mu a(V_\theta^* - V_\theta)$$

$$F_r = -6\pi\mu a(V_r^* - V_r)$$

Technically this is the only force acting on the particle since "centrifugal force" and "coriolis force" are really accelerations that arise from choosing a non-newtonian frame of reference. The accelerations the particle experiences are given by

$$\left(\text{Radial Acceleration} \right)^{\dagger} = \frac{dV_r^*}{dt} + V_r^* \frac{dV_r^*}{dr} + \frac{V_\theta^*}{r} \frac{dV_r^*}{d\theta} - \frac{V_\theta^{*2}}{r} + V_z^* \frac{dV_r^*}{dz}$$

$$\left(\text{Circumferential Acceleration} \right)^{\dagger} = \frac{dV_\theta^*}{dt} + V_r^* \frac{dV_\theta^*}{dr} + \frac{V_\theta^*}{r} \frac{dV_\theta^*}{d\theta} + \frac{V_r^* V_\theta^*}{r} + V_z^* \frac{dV_\theta^*}{dz}$$

Since we are considering steady state flow the time derivatives are zero. Due to symmetry the circumferential derivatives drop out. And because the particles are touching the surface V_z^* is zero.

This leaves us with

$$\left(\text{Radial Acceleration} \right) = V_r^* \frac{dV_r^*}{dr} - \frac{V_\theta^{*2}}{r}$$

$$\left(\text{Circumferential Acceleration} \right) = V_r^* \frac{dV_\theta^*}{dr} + \frac{V_r^* V_\theta^*}{r}$$

Newton's second law for a particle is

$$-6\pi\mu a(V_r^* - V_r) = \frac{4}{3} \pi a^3 (\rho_s - \rho_L) \left[V_r^* \frac{dV_r^*}{dr} - \frac{V_\theta^{*2}}{r} \right]$$

$$-6\pi\mu a(V_\theta^* - V_\theta) = \frac{4}{3} \pi a^3 (\rho_s - \rho_L) \left[V_r^* \frac{dV_\theta^*}{dr} + \frac{V_r^* V_\theta^*}{r} \right]$$

[†] These are taken from the substantial time derivative part of the Navier-Stokes equations in cylindrical coordinates (76).

It is possible to find a series solution to these coupled differential equations of the form:

$$\frac{V_r^*}{\Omega} = F_1^* r + F_2^* r^2 + F_3^* r^3 + \dots$$

and

$$\frac{V_\theta^*}{\Omega} = G_1^* r + G_2^* r^2 + G_3^* r^3 + \dots$$

Substitution yields

$$\begin{aligned} -K[F_1^* r + F_2^* r^2 + F_3^* r^3 + \dots - Fr] = \\ ([F_1^* r + F_2^* r^2 + F_3^* r^3 + \dots][F_1^* + 2F_2^* r + 3F_3^* r^2 + \dots] \\ - [G_1^* r + G_2^* r^2 + G_3^* r^3 + \dots][G_1^* + G_2^* r + G_3^* r^2 + \dots]) \end{aligned}$$

and

$$\begin{aligned} -K[G_1^* r + G_2^* r^2 + G_3^* r^3 + \dots - Gr] = \\ ([F_1^* r + F_2^* r^2 + F_3^* r^3 + \dots][G_1^* + 2G_2^* r + 3G_3^* r^2 + \dots] \\ + [F_1^* r + F_2^* r^2 + F_3^* r^3 + \dots][G_1^* + G_2^* r + G_3^* r^2 + \dots]) \end{aligned}$$

where

$$-K = \frac{-9\mu}{2a^2(\rho_s - \rho_L)\Omega}$$

Equating the first power of r:

$$-K(F_1^* - F) = F_1^{*2} - G_1^{*2}$$

and

$$-K(G_1^* - G) = 2F_1^* G_1^* ,$$

which can be transformed to

$$G_1^{*2} = F_1^{*2} + K(F_1^* - F)$$

$$F_1^* = \frac{K(G - G_1^*)}{2G_1^*} .$$

Combining the two yields

$$G_1^{*2} = \frac{K^2(G - G_1^*)^2}{4G_1^{*2}} + \frac{K^2(G - G_1^*)}{2G_1^*} - KF$$

or

$$G_1^{*4} + \left(\frac{K^2}{4} + KF\right) G_1^{*2} - \frac{K^2 G^2}{4} = 0 .$$

By means of the quadratic equation applied twice we get

$$G_1^* = \left[\frac{-\left(\frac{K^2}{4} + KF\right) + \left[\left(\frac{K^2}{4} + KF\right)^2 + K^2 G^2\right]^{1/2}}{2} \right]^{1/2} . \quad (E1)$$

And once having G_1^* then

$$F_1^* = \frac{K(G - G_1^*)}{2G_1^*} \quad (E2)$$

When we equate the coefficients of the second power of r ,

$$-KG_2^* = 3G_2^*F_1^* + 2G_1^*F_2^*$$

$$-KF_2^* = 3F_1^*F_2^* - 2G_1^*G_2^*$$

and

$$G_2^* = \frac{-2F_2^*G_1^*}{(K + 3F_1^*)}$$

$$F_2^* = \frac{2G_1^*G_2^*}{(K + 3F_1^*)} \quad (E3)$$

Combining the last two equations gives

$$\left[1 + \frac{4G_1^{*2}}{(K + 3F_1^*)^2} \right] G_2^* = 0$$

Therefore $G_2^* = 0$. And from Eq. (E3)

$$F_2^* = 0$$

In general for $n > 1$

$$\left[1 + \frac{4G_1^{*2}}{[(n+1)F_1^* + K]^2} \right] G_n^* = 0 \quad \text{and} \quad G_n^* = 0$$

$$F_n^* = 0$$

The absolute value of velocity, V , of the particle relative to the surface is

$$V = [V_r^{*2} + (r\Omega - V_\theta^*)^2]^{1/2}$$

or

$$V = r\Omega[F^{*2} + (1 - G^*)^2]^{1/2} \quad (E4)$$

Therefore V , V_r^* and V_θ^* , like V_r and V_θ , are proportional to r . To justify some of our original assumptions, let us take a worst case example, that of the largest particle size (75 μm) on the edge of the larger disk ($r = 1.41$ cm) at the highest speed (300.5 radians/s). Under these conditions ($\zeta = 0.5812$, $K = 11.12$, $F = 0.1637$ and $G = 0.6654$), $F^* = 0.1973$ and $G^* = 0.6426$. In other words, the particles are traveling 20.5 percent faster in the radial direction than the fluid surrounding them and 6.8 percent slower in the circumferential direction. The surrounding fluid is moving 158 cm/s relative to the disk overall, with the particles moving 17.2 cm/s relative to the surrounding fluid. The particle Reynolds number ($Re_D = 5.2$) indicates creeping flow is still dominant, and because the particles'

velocity relative to the fluid is an order of magnitude below the velocity relative the electrode surface, this crude assumption of stokes flow might be overlooked.

APPENDIX F. CALCULATION OF THE MASS TRANSFER BOUNDARY LAYER
THICKNESS, δ , AND THE EFFECTIVE DIFFUSIVITY, D'

In this system of suspended spheres, δ and D' are closely intertwined. One cannot compute one without knowing the other. Let us base our reasoning upon the homogeneous suspension model developed in Appendix B. The mass transfer relationship is Eq. (B1).

$$Sh' = 0.62048 Re'^{1/2} Sc'^{1/3}$$

But since $Sh' = R/\delta$, where R is the electrode's outer radius, we can express the boundary layer thickness as

$$\delta = \frac{R}{0.62048 Re'^{1/2} Sc'^{1/3}}$$

or in terms of the homogeneous suspension properties

$$\delta = \frac{1.6117 v'^{1/6} D'^{1/3}}{\Omega^{1/2} (1 - \phi)^{1/3}} \quad (F1)$$

This leaves us still to find D' , the effective diffusivity through the boundary layer. Very close to the electrode (within one particle diameter) the effective void fraction decreases because the particles can get no closer than just touching the electrode. The fraction solids versus distance relationship is derived in Appendix D. For mathematical simplicity let us just use a linear function:

$$\phi(z) = \phi_{\infty} \frac{z}{2a} \quad \text{for } z < 2a$$

and

$$\phi(z) = \phi_{\infty} \quad \text{for } z > 2a$$

The distance from the electrode is z , and ϕ_{∞} is the bulk particulate fraction in the suspension.

At steady state the mass flux, N_i , is constant with respect to z and

$$N_i = \frac{D_i^* \frac{dc_i}{dz}}{\delta} = \frac{D_i c_b}{\delta}$$

where D_i^* is the local diffusivity, a function of ϕ and therefore of z also. Separating variables and integrating

$$\frac{\delta}{D_i c_b} \int_0^{c_b} dc = \frac{\delta}{D_i} = \int_0^{\delta} \frac{dz}{D_i^*}$$

Using $D_i^* = (1 - \phi)^{3/2} D_i$

$$\frac{\delta}{D_i} = \frac{1}{D_i} \int_0^{\delta} \frac{dz}{(1 - \phi(z))^{3/2}}$$

if $\delta < 2a$ then

$$\frac{\delta}{D_i} = \frac{1}{D_i} \int_0^{\delta} \left[1 - \frac{\phi_{\infty}}{2a} z \right]^{-3/2} dz = \frac{4a}{D_i \phi_{\infty}} \left[\frac{1 - \left(1 - \frac{\phi_{\infty} \delta}{2a} \right)^{1/2}}{\left(1 - \frac{\phi_{\infty} \delta}{2a} \right)^{1/2}} \right] \quad (F2)$$

and if $\delta > 2a$

$$\frac{\delta}{D_i} = \int_0^{2a} \frac{dz}{D_i^*} + \int_{2a}^{\delta} \frac{dz}{D_i^*} = \frac{1}{D_i} \int_0^{2a} \left(1 - \frac{\phi_{\infty}}{2a} z\right)^{-3/2} dz + \frac{1}{D_i (1 - \phi_{\infty})^{3/2}} \int_{2a}^{\delta} dz$$

$$\frac{\delta}{D_i} = \frac{4a}{D_i \phi_{\infty}} \left[\frac{1 - (1 - \phi_{\infty})^{1/2}}{(1 - \phi_{\infty})^{1/2}} \right] + \frac{\delta - 2a}{D_i (1 - \phi_{\infty})^{3/2}} \quad (F3)$$

Using Eqs. (F2) and (F3) together with Eq. (F1) we can use an iterative numeric technique to calculate both δ and D_i^* . Actually D_i^* is used only for the steady state diffusion term in Eq. (3). The clear solution diffusivity D_i is used for the nonsteady state part since most of the nonsteady state effects happen very close to the electrode where for all practical purposes $\phi = 0$.

APPENDIX G. INTEGRATION I

In evaluating the integral from page 126,

$$\sum_{m=1}^{\infty} \frac{1}{m^2} \int_{\frac{2a}{V}}^{\infty} \frac{\exp(-[m^2 4\alpha + s] t) - \exp(-st)}{t} dt \quad (G1)$$

we are faced with an indefinite integral of the type:

$$\int \frac{e^{-ax} - e^{-bx}}{x} dx$$

which to my knowledge has not been solved yet in close form. However

(77)

$$\int_0^{\infty} \frac{e^{-ax} - e^{-bx}}{x} dx = \ln \frac{b}{a}$$

And we can therefore write our integral as

$$\sum_{m=1}^{\infty} \frac{1}{m^2} \left[\ln \left(\frac{s}{m^2 4\alpha + s} \right) - \int_0^{\frac{2a}{V}} \frac{\exp(-[m^2 4\alpha + s] t) - \exp(-st)}{t} dt \right]$$

Since $2a/V$ is a small number, for our experiments, we need now to only find an approximation to the integral. Let us use

$$\frac{e^{-at} - e^{-bt}}{t} = \frac{\alpha}{(\beta t + 1)^3}$$

The constants α and β shall be determined from the conditions:

$$\left. \frac{e^{-at} - e^{-bt}}{t} \right|_{t=0} = \left. \frac{\alpha}{(\beta t + 1)^3} \right|_{t=0}$$

and

$$\left. \frac{d\left(\frac{e^{-at} - e^{-bt}}{t}\right)}{dt} \right|_{t=0} = \left. \frac{d\left(\frac{\alpha}{(\beta t + 1)^3}\right)}{dt} \right|_{t=0}.$$

We shall evaluate these expressions using L'hospital's rule and direct substitution.

$$\lim_{t \rightarrow 0} \frac{e^{-at} - e^{-bt}}{t} = \lim_{t \rightarrow 0} (be^{-bt} - ae^{-at}) = b - a$$

$$\lim_{t \rightarrow 0} \frac{\alpha}{(\beta t + 1)^3} = \alpha$$

Therefore $\alpha = b - a$

$$\frac{d\left(\frac{e^{-at} - e^{-bt}}{t}\right)}{dt} = \frac{1}{t} (be^{-bt} - ae^{-at}) - \frac{1}{t^2} (e^{-at} - e^{-bt})$$

$$\begin{aligned} \lim_{t \rightarrow 0} \frac{d\left(\frac{e^{-at} - e^{-bt}}{t}\right)}{dt} &= \lim_{t \rightarrow 0} [(a^2 e^{-at} - b^2 e^{-bt}) - \frac{1}{2} (a^2 e^{-at} - b^2 e^{-bt})] \\ &= \frac{1}{2} (a^2 - b^2) \end{aligned}$$

$$\frac{d}{dt} \left[\frac{\alpha}{(\beta t + 1)^3} \right] = \frac{-3\alpha\beta}{(\beta t + 1)^4}$$

$$\lim_{t \rightarrow 0} \frac{d}{dt} \left[\frac{\alpha}{(\beta t + 1)^3} \right] = -3\alpha\beta$$

Equating the two first derivatives at $t = 0$

$$-3\alpha\beta = \frac{1}{2} (a^2 - b^2)$$

$$\beta = \frac{(b + a)}{6}$$

Some plots of

$$\frac{e^{-at} - e^{-bt}}{t}$$

and

$$\frac{(b - a)}{\left[\left(\frac{b + a}{b} \right) t + 1 \right]^3}$$

are shown on Fig. G1.

It can be seen that the approximation fits quite well for $(a/b) = 0$, but gets progressively worse as $(a/b) \rightarrow 1$. In any case the approximate function fits well for $t < 0.1$. For our experiments the particle diameters $(2a)$ are quite small and the relative velocities (V) are large so $(2a/V)$ is usually well below 0.1 sec and the approximation is good.

XBL 815-895

Fig. G1. Approximations to $(e^{-at} - e^{-bt})/t$.

$$\int_0^{\frac{2a}{V}} \frac{a}{(\beta t + 1)^3} dt = \frac{a}{\beta} \int_{t=0}^{t=\frac{2a}{V}} (\beta t + 1)^{-3} d(\beta t + 1) = \frac{a}{\beta (-2)} \left[(\beta t + 1)^{-2} \right]_{t=0}^{t=\frac{2a}{V}}$$

$$\int_0^{\frac{2a}{V}} \frac{e^{-at} - e^{-bt}}{t} dt = \frac{(b - a) 6}{(b + a) (-2)} \left[\frac{1}{\left(\left(\frac{b + a}{6} \right) \frac{2a}{V} + 1 \right)^2} - 1 \right]$$

But $a = m^2 4\alpha + s$ and $b = s$, therefore

$$\int_0^{\frac{2a}{V}} \frac{\exp(-[m^2 4\alpha + s] t) - \exp(-st)}{t} dt \approx \frac{-m^2 4\alpha 3}{m^2 4\alpha + 2s} \left[1 - \frac{1}{\left(\left[\frac{m^2 4\alpha + 2s}{6} \right] \frac{2a}{V} + 1 \right)^2} \right]$$

Returning to Eq. (G1) then we have as an approximation:

$$\sum_{m=1}^{\infty} \left(\frac{\ln \left(\frac{s}{m^2 4\alpha + s} \right)}{m^2} + \frac{12\alpha}{m^2 4\alpha + s} \left[1 - \frac{1}{\left(\left[\frac{m^2 4\alpha + 2s}{6} \right] \frac{2a}{V} + 1 \right)^2} \right] \right)$$

APPENDIX H. INTEGRATION II

We have a function to integrate from page 128:

$$F(r) = \sum_{m=1}^{\infty} \frac{r}{m^2} \ln \left[\frac{m^2 A}{r} + 1 \right]$$

This function is finite for $r > 0$; to prove this we first find its limit as $r \rightarrow 0$; by L'hospital's rule

$$\lim_{r \rightarrow 0} \frac{\ln \left(\frac{m^2 A}{r} + 1 \right)}{m^2 r^{-1}} = \lim_{r \rightarrow 0} \frac{\left(\frac{m^2 A}{r} + 1 \right)^{-1} \cdot -\frac{m^2 A}{r^2}}{-\frac{m^2}{r^2}} = \lim_{r \rightarrow 0} \frac{A}{\left(\frac{m^2 A}{r} + 1 \right)}$$

$$\lim_{r \rightarrow 0} \frac{A}{\left(\frac{m^2 A}{r} + 1 \right)} = \lim_{r \rightarrow 0} \frac{0}{\left(-\frac{m^2 A}{r^2} \right)} = 0$$

Therefore $F(r) \rightarrow 0$ as $r \rightarrow 0$.

It must also be shown that this series converges as $m \rightarrow \infty$. This can be done through the integral test. If

$$\int_1^{\infty} \frac{r}{m^2} \ln \left(\frac{m^2 A}{r} + 1 \right) dm$$

exists and is finite then the series converges. Using integration by parts where:

$$u = \ln \left[\frac{m^2 A}{r} + 1 \right] \quad ; \quad du = \frac{2m dm}{\left[\frac{m^2 A}{r} + 1 \right]}$$

$$dv = \frac{r dm}{m^2} \quad ; \quad v = -\frac{r}{m}$$

$$\begin{aligned} \int_1^\infty \frac{r}{m^2} \ln \left[\frac{m^2 A}{r} + 1 \right] dm &= -\frac{r}{m} \ln \left[\frac{m^2 A}{r} + 1 \right] \Big|_1^\infty - \int_1^\infty -\frac{r}{m} \cdot \frac{2m}{\left[\frac{m^2 A}{r} + 1 \right]} dm \\ &= -\frac{r}{m} \ln \left[\frac{m^2 A}{r} + 1 \right] \Big|_1^\infty + \frac{2r^2}{A} \int_1^\infty \frac{1}{m^2 + \left(\frac{r}{A} \right)} dm \\ &= -\frac{r}{m} \ln \left[\frac{m^2 A}{r} + 1 \right] \Big|_1^\infty + \frac{2r^2}{A} \left(\frac{A}{r} \right)^{1/2} \tan^{-1} \left[\frac{m}{\left(\frac{r}{A} \right)^{1/2}} \right] \Big|_1^\infty \end{aligned} \quad (H1)$$

to evaluate the upper limit on the first term

$$\begin{aligned} \lim_{m \rightarrow \infty} \frac{-r \ln \left(\frac{m^2 A}{r} + 1 \right)}{m} &= \lim_{m \rightarrow \infty} -r \left[\frac{m^2 A}{r} + 1 \right]^{-1} \cdot \frac{2A}{r} m = \lim_{m \rightarrow \infty} \left(\frac{-2Am}{\frac{m^2 A}{r} + 1} \right) \\ &= \lim_{m \rightarrow \infty} \left(\frac{-2A}{\frac{2A}{r} m} \right) = 0 \end{aligned}$$

Substituting back into Eq. (H1)

$$\int_0^{\infty} \frac{r}{m^2} \ln \left(\frac{m^2 A}{r} + 1 \right) dm =$$

$$r \ln \left[\frac{A}{r} + 1 \right] + \frac{2r^{3/2}}{A^{1/2}} \left[\frac{\pi}{2} - \tan^{-1} \left(\left[\frac{A}{r} \right]^{1/2} \right) \right]$$

which is finite so the series converges. We can average this function over the area of a disk as

$$\bar{F}(r) = \frac{\int_0^R F(r) 2\pi r dr}{\pi R^2}$$

where R is the outer radius of the disk, and r is just the radial distance from the center to a point on the disk.

One would expect that since $F(r)$ is finite $\bar{F}(r)$ is also finite.

$$\bar{F}(r) = \frac{2}{R^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \int_0^R r^2 \left[\ln \frac{m^2 A}{r} + 1 \right] dr \quad (H2)$$

let us introduce a change in variable:

$$Y = \frac{m^2 A}{r}, \quad dY = \frac{-m^2 A dr}{r^2}$$

$$\int_0^R r^2 \ln \left[\frac{m^2 A}{r} + 1 \right] dr = - \frac{1}{m^2 A} \int_0^R r^4 \ln \left[\frac{m^2 A}{r} + 1 \right] \left[\frac{-m^2 A}{r^2} \right] dr =$$

$$-(m^2 A)^3 \int_{\infty}^{\frac{m^2 A}{R}} \frac{\ln(Y + 1)}{Y^4} dY$$

According to the table of integrals in the CRC Handbook (78)

$$\int \frac{\ln(ax + b)}{x^m} dx = - \frac{1}{m-1} \frac{\ln(ax + b)}{x^{m-1}} + \frac{1}{m-1} \left(-\frac{a}{b}\right)^{m-1} \ln \frac{ax + b}{x}$$

$$+ \frac{1}{m-1} \left(-\frac{a}{b}\right)^{m-1} \sum_{r=1}^{m-2} \frac{1}{r} \left(-\frac{b}{ax}\right)^r, \quad (m > 2)$$

Therefore

$$\int_0^R r^2 \ln \left[\frac{m^2 A}{r} + 1 \right] dr = (m^2 A)^3 \left[-\frac{1}{3} \frac{\ln(Y + 1)}{Y^4} - \frac{1}{3} \ln \left(\frac{Y + 1}{Y} \right) \right. \\ \left. - \frac{1}{3} \left(-\frac{1}{Y} + \frac{1}{2Y^2} \right) \right]_{\frac{m^2 A}{R}}^{\infty}$$

Obviously

$$\lim_{Y \rightarrow \infty} \ln \left(\frac{Y + 1}{Y} \right) = \lim_{Y \rightarrow \infty} \frac{1}{Y} = \lim_{Y \rightarrow \infty} \frac{1}{Y^2} = 0$$

Not quite so obvious is

$$\lim_{Y \rightarrow \infty} \frac{\ln(Y+1)}{Y^3} = \lim_{Y \rightarrow \infty} \frac{1}{(Y+1) 3Y^2} = 0$$

All the upper limit is zero.

$$\begin{aligned} \int_0^R r^2 \ln\left(\frac{m^2 A}{r} + 1\right) dr &= \frac{(m^2 A)^3}{3} \left[\frac{\ln\left(\frac{m^2 A}{R} + 1\right)}{\left(\frac{m^2 A}{R}\right)^3} + \ln\left(\frac{\frac{m^2 A}{R} + 1}{\frac{m^2 A}{R}}\right) \right. \\ &\quad \left. + \left(\frac{R^2}{2(m^2 A)^2} - \frac{R}{m^2 A} \right) \right] \\ \int_0^R r^2 \ln\left(\frac{m^2 A}{r} + 1\right) dr &= \frac{R^3}{3} \ln\left(\frac{m^2 A}{R} + 1\right) + \frac{(m^2 A)^3}{3} \ln\left(\frac{R}{m^2 A} + 1\right) \\ &\quad + \frac{R^2(m^2 A)}{6} - \frac{R(m^2 A)^2}{3} \end{aligned}$$

Substituting back into Eq. (H2)

$$\begin{aligned} F(r) &= \frac{2R}{3} \sum_{m=1}^{\infty} \frac{\ln\left(\frac{m^2 A}{R} + 1\right)}{m^2} + \frac{2A^3}{3R^2} \sum_{m=1}^{\infty} m^4 \ln\left(\frac{R}{m^2 A} + 1\right) \\ &\quad + \frac{A}{3} \sum_{m=1}^{\infty} 1 - \frac{2A^2}{3R} \sum_{m=1}^{\infty} m^2 \end{aligned}$$

The first series,

$$\sum_{m=1} \frac{\ln\left(\frac{m^2 A}{R} + 1\right)}{m^2}$$

converges by the same integral test performed previously.

It appears that the next three series diverge to plus, plus and minus infinity as $m \rightarrow \infty$. However, if we make the substitution $X = (R/m^2 A)$ then

$$\frac{(m^2 A)^3}{3} \ln\left(\frac{R}{m^2 A} + 1\right) + \frac{R^2 (m^2 A)}{6} - \frac{R (m^2 A)^2}{3} =$$

$$\frac{R^3}{3} \left[\frac{1}{X^3} \ln(X + 1) + \frac{1}{2X} - \frac{1}{X^2} \right]$$

Using a Mc'Laurin series

$$\ln(X + 1) = X - \frac{X^2}{2} + \frac{X^3}{3} - \frac{X^4}{4} + \dots$$

and

$$\frac{\ln(X + 1)}{X^3} = \frac{1}{X^2} - \frac{1}{2X} + \frac{1}{3} - \frac{X}{4} + \dots$$

Upon addition the reciprocal terms cancel out and

$$\frac{R^3}{3} \left[\frac{\ln(X+1)}{X^3} + \frac{1}{2X} - \frac{1}{X^2} \right] = \frac{R^3}{3} \left[\frac{1}{3} - \frac{X}{4} + \frac{X^2}{5} - \dots \right]$$

$$= \frac{R^3}{3} \sum_{n=0}^{\infty} \frac{(-1)^n X^n}{n+3}$$

as, $m \rightarrow \infty$, $X \rightarrow 0$ and this series approaches $R^3/9$. The greater series

$$\sum_{m=k}^{\infty} \frac{1}{m^2} \frac{R^3}{9}$$

where k is suitably large is known to converge so therefore

$$\sum_{m=1}^{\infty} \frac{R^3}{3m^2} \sum_{n=0}^{\infty} \frac{(-1)^n X^n}{n+3}$$

converges.

APPENDIX I. INTEGRATION III

We have from page 128

$$\int_0^R \frac{(12\alpha) r^2}{(m^2 4\alpha) + (2c_s \sigma Q) r} \left[1 - \frac{r^2}{\left[\left(\frac{m^2 4\alpha}{3Q} \right) - \left(\frac{2}{3} ac_s \sigma + 1 \right) r \right]^2} \right] dr$$

which could also be written

$$\frac{12\alpha}{2c_s \sigma Q} \int_0^R \frac{r^2}{\frac{1}{2} A + r} dr - \frac{12\alpha}{2c_s \sigma Q \left(\frac{2}{3} ac_s \sigma \right)^2} \int_0^R \frac{r^4}{\left(\frac{1}{2} A + r \right) \left(\frac{1}{2} A + Br \right)^2} dr$$

The first integral may be evaluated by making the substitution:

$$Y = \frac{1}{2} A + r$$

$$\begin{aligned} \int_0^R \frac{r^2}{\frac{1}{2} A + r} dr &= \int_{\frac{1}{2} A}^{\frac{1}{2} A + R} \frac{Y^2 - AY + A^2/4}{Y} dY \\ &= \left[\frac{Y^2}{2} - AY + \frac{A^2}{4} \ln(Y) \right]_{\frac{1}{2} A}^{\frac{1}{2} A + R} \\ &= \frac{R^2}{2} - AR + \frac{A^2}{4} \ln \frac{2R}{A} + 1 \end{aligned}$$

The second integral can be evaluated through the method of partial fractions

$$\frac{r^4}{\left(\frac{1}{2}A + r\right)\left(\frac{1}{2}A + Br\right)^2} = \frac{K_1 r^4}{\frac{1}{2}A + R} + \frac{K_2 r^4}{\frac{1}{2}A + Br} + \frac{K_3 r^4}{\left(\frac{1}{2}A + Br\right)^2}$$

where $K_1 = 4/(A^2 (B - 1)^2)$, $K_2 = -4B/(A^2(B - 1)^2)$, $K_3 = 2B/(A(B - 1))$.

It can be shown through change of variable and other standard techniques that

$$\begin{aligned} \int_0^R \frac{r^4}{\left(\frac{1}{2}A + r\right)\left(\frac{1}{2}A + Br\right)^2} dr &= \frac{R^2}{2B^2} - \frac{(B + 2)AR}{2B^3} + \frac{A^2}{4(B - 1)^2} \ln\left(\frac{2R}{A} + 1\right) \\ &+ \frac{(3 - 4B)A^2}{4B^4(B - 1)^2} \ln\left(\frac{2BR}{A} + 1\right) + \frac{A^2 R}{2B^3(B - 1)(A + 2BR)} \end{aligned}$$

This result has been verified by differentiation. The net integral might be expressed as

$$\frac{12\alpha}{2c_s \sigma Q} \left[\int_0^R \frac{r^2}{\left(\frac{1}{2}A + r\right)} dr - (B - 1)^2 \int_0^R \frac{r^4}{\left(\frac{1}{2}A + r\right)\left(\frac{1}{2}A + Br\right)^2} dr \right]$$

or

$$\begin{aligned} \frac{6\alpha}{c_s \sigma Q} &\left[\frac{R^2}{2} - \frac{AR}{4} + \frac{A^2}{4} \ln\left(\frac{2R}{A} + 1\right) - \frac{(B - 1)^2 R^2}{2B^2} + \frac{(B - 1)^2 (B + 2) AR}{2B^3} \right. \\ &\left. - \frac{A^2}{4} \ln\left(\frac{2R}{A} + 1\right) + \frac{(4B - 3)A^2}{4B^4} \ln\left(\frac{2BR}{A} + 1\right) - \frac{(B - 1)A^2 R}{2B^3(A + 2BR)} \right] \end{aligned}$$

which simplifies to

$$\frac{3\alpha}{c_s \sigma Q} \left[R^2 - AR - \frac{(B-1)^2 R^2}{B^2} + \frac{(B-1)^2 (B+2) AR}{B^3} \right. \\ \left. + \frac{(4B-3) A^2}{2B^4} \ln\left(\frac{2BR}{A} + 1\right) - \frac{(B-1) A^2 R}{B^3 (A + 2BR)} \right]$$

APPENDIX J. THE AREA, a_T , AND WIDTH, w , OF INTERACTION OF THE
PARTICLE FILM WITH THE ELECTRODE SURFACE

All particles whose surfaces come within Δ of the electrode are considered to interact with it. Δ , in turn, is proportional to the radius of the spheres, $\Delta = c_1 a$. If, as shown in Fig. J1, Δy is the closest distance between a sphere and the electrode and Δx is the radius of the area of interaction, then by the pythagorean theorem

$$(1 + c_1)^2 a^2 = \left(1 + \frac{\Delta y}{a}\right)^2 a^2 + \Delta x^2,$$

or

$$\left(\frac{\Delta x}{a}\right)^2 = (1 + c_1)^2 - \left(1 + \frac{\Delta y}{a}\right)^2 = 2\left(c_1 - \frac{\Delta y}{a}\right) + c_1^2 - \left(\frac{\Delta y}{a}\right)^2$$

To find the mean interaction area over all possible values of Δy , we integrate

$$a_T = \frac{\pi}{c_1 a} \int_0^{c_1 a} (\Delta x)^2 d(\Delta y)$$

$$a_T = \frac{\pi a^2}{c_1 a} \int_0^{c_1 a} \left[2c_1 - 2\left(\frac{\Delta y}{a}\right) + c_1^2 - \left(\frac{\Delta y}{a}\right)^2 \right] d(\Delta y)$$

$$a_T = \frac{\pi a}{c_1} \left[2c_1 \Delta y + c_1^2 \Delta y - \frac{2\left(\frac{\Delta y}{a}\right)}{2} - \frac{\Delta y^3}{3a^2} \right]_0^{c_1 a}$$

$$a_T = \pi a^2 \left[2c_1 + c_1^2 - c_1 - \frac{c_1^2}{3} \right] = \pi a^2 \left(c_1 - \frac{2}{3} c_1^2 \right)$$

XBL 815-920

Fig. J1. Particle film intersecting electrode surface.

Another approach is to determine a_T from the sum of the empirically determined level areas, a_0 , a_1 and a_2 . In any case, once a_T is determined, w is derived by resolving the area of interaction into a square of equal area as shown in Fig. J2. The side of the square is w or

$$w = \left[\pi \left(c_1 - \frac{2}{3} c_1^2 \right) \right]^{1/2} a$$

XBL 815-918

Fig. J2. Circle of intersection resolved into a square of equal area.

APPENDIX K. INITIAL SURFACE CONCENTRATION, c_0

The interacting particle is 0 to Δ from the electrode and is assumed to be exposed to a steady state concentration profile, given by $y < \delta$:

$$c = c_B \left(\frac{y}{\delta} \right)$$

$y > \delta$:

$$c = c_B$$

where c_B is the bulk electrolyte concentration, and δ the boundary layer thickness. Since the spherical particle is exposed to a whole range of outside concentrations, the initial surface concentration, c_0 , is taken to be the mean over that range. In particular, the range is considered to extend from $y = 0$ to $y = 2a + \Delta$.

$2a + \Delta < \delta$:

$$c_0 = \frac{1}{(2a + \Delta)} \int_0^{2a+\Delta} c dy = \frac{c_B}{(\Delta + 2a) \delta} \int_0^{2a+\Delta} y dy$$

$$c_0 = \frac{c_B}{\delta} \left[a + \frac{1}{2} \Delta \right]$$

$$2a + \Delta > \delta:$$

$$c_o = \frac{1}{(2a + \Delta)} \int_0^{2a+\Delta} c dy = \frac{c_B}{(2a + \Delta) \delta} \int_0^{\delta} y dy + \frac{c_B}{(2a + \Delta)} \int_{\delta}^{2a+\Delta} dy$$

$$c_o = \frac{c_B}{(2a + \Delta) \delta} \cdot \frac{\delta^2}{2} + \frac{c_B}{(2a + \Delta)} (2a + \Delta - \delta)$$

$$c_o = c_B \left(1 - \frac{\delta}{2(2a + \Delta)} \right)$$

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