Gas-Liquid Mass Transfer and Pressure Drop in Pulp Bed with Flexible Fibers as Solid Supports

The volumetric mass transfer coefficients between oxygen and water in a pulp bed have been determined by the gas-liquid reaction method with an enhancement factor approximately equal to one. The coefficients ranged from 0.08 s^{-1} at 13% to 0.34 s^{-1} at 19% solids content in the pulp bed, values that are close to those for comparable trickle beds. No liquid flow over the pulp bed (13-19% solids content) occurred under the operating conditions. The results showed that gas-liquid mass transfer was affected only by the solids content of the pulp bed rather than by the oxygen superficial velocity (0.4 to 1.2 cm/s). The gas pressure drop across the pulp bed was also predicted by Ergun's equation using an estimated effective diameter for the fiber flocs.

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Introduction

Multiphase transfer phenomena have been the subject of intensive chemical engineering research. Most of the correlations on the volumetric mass transfer coefficients are based on systems with a rigid solid phase, such as gas-liquid absorption, catalytic hydroprocessing, and other polymerization and chemical processes with the solid phase as reactants.

Very little research has been directed at the system with a flexible solid phase, in spite of its importance in industrial pulping and bleaching applications. The flexible structure of fibers, the irregular manner of water-fiber absorption, and different types of pulp-gas mixing apparatus make the application of available mass transfer coefficient correlations impractical. Quantification of gas-liquid mass transfer in the pulp bed is essential to the final reactor design.

The objective of this study was to establish oxygen-water volumetric mass transfer coefficients in a pulp bed. The oxygen absorption rate in the pulp bed varied linearly with equilibrium oxygen concentration in the liquid phase and was found to be unaffected by the rate of chemical reaction. Therefore, the gas-liquid chemical reaction method with an enhancement factor approximately equal to one was used. The enhancement factor is defined as the ratio of the average rate of gas absorption into liquid with reaction to the rate without reaction (Danckwerts, 1970).

The results also showed that oxygen gas superficial velocities ranging from 0.4 to 1.2 cm/s had no impact on the gas-liquid mass transfer. The volumetric mass transfer coefficient was found to increase linearly with the solids content of the pulp bed over the range from 13 to 19%. The relationship is correlated by $k_L a_L = 0.033\, S_c - 0.35$ ($13\% \leq S_c \leq 19\%$). In addition, the pressure drop across the pulp bed can be predicted by Ergun's (1952) correlation with an estimated effective fiber floc diameter.

Background

In the pulp and paper industry, the conventional chemicals used to bleach the pulp from the pulping process are chlorine, chlorine dioxide, and hypochlorite. Due to pollution problems and chemical costs, oxygen gas was applied before the chlorination stage to bleach pulp beginning in 1970. This procedure can reduce wastewater effluent COD (chemical oxygen demand) by 50% and BOD (biochemical oxygen demand) by 25–50%. In addition, chemical cost reductions of more than 25% can be achieved through the lower use of conventional bleaching chemicals (Croon and Larsson, 1983).

Oxygen bleaching is a heterogenous reaction that occurs in a system comprising solid (fiber), liquid (water), and gas (oxygen). In the current commercial process, the slow oxygen transfer is improved by increasing solids content and using high oxygen pressure. Because of the associated high capital and operation costs, these high solids content processes are not widely adopted. Recent developments on medium and low solids content processes have led to use of a high shear mixer to blend oxygen with the pulp slurry.

Regardless of the commercialization of these processes, the basic oxygen transport phenomenon is not thoroughly investigated in this area. Pulp, unlike rigid solids, can absorb water and swell. Its structure varies at different levels of solids content. Current high solids content processes are operated at 22–30%. In this range, most of the water is absorbed inside fibers. In the medium solids content of 8 to 16%, pulp forms an enclosed structure in which water can be removed only by external force.

A pulp bed with solids content below 13% formed a discontinuous gas phase, and a uniform pulp bed could not be tested. With solids content above 19%, the amount of solution from the pulp was insufficient to determine its solute concentration. Therefore, our study on pulp beds was limited to solids content from 13 to 19%.

Most of the available gas-liquid mass transfer correlations were related to the rigid solid structure. The trickle bed was considered to be similar to the pulp bed. However, in a trickle-bed reactor liquid flows over the packing in the form of a thin liquid film and gas flows between the packing. In a pulp bed, liquid does not flow but is absorbed in the fibers whereas the gas continuously flows through the voids in the bed. Comparison of the volumetric mass transfer coefficients in pulp bed to those in a trickle bed showed similar orders of magnitude.

Experimental

In a packed bed, solid packings are often introduced into the bed by gravity; a uniform porosity of the bed is obtained through shaking. However, in a pulp bed with 13 to 19% solids content, fibers tend to flocculate and form nonuniform porosity. The pulp must first be dispersed at low solids content. Then a vacuum dewatering system is used to adjust the water content in the pulp bed.

A 2.54 cm OD stainless steel tube with a fine screen at the bottom was mounted to a 1,000 mL volumetric flask. The surge tank was vacuumed to 4.8×10^4 N/m^2 before turning on the valve connected to the volumetric flask. The pulp slurry was poured into the tube and the valve to the surge tank was opened simultaneously. A uniform pulp bed was formed in the tube through the use of a vacuum from the surge tank.

The pulp bed was divided into three sections—upper, middle, and bottom—for checking its uniformity. Their solids content distribution is shown in Figure 1 with two portions from each section. The maximum deviation was around 5%.

Sodium sulfite is one of the most commonly used chemicals to study the oxygen gas-liquid mass transfer. The enhancement factor of oxygen-sulfite reaction is around one under very low catalyst concentrations. According to Linek and Vacek's review paper (1981), the concentration of sulfite must be above 0.5 M so that the rate of reaction of the dissolved oxygen is second-order with respect to the oxygen concentration and is independent of the sulfite concentration. Through trial and error, 25.21 g of sodium sulfite dissolved in 200 mL of distilled water was found to be sufficient to maintain the sulfite concentration above 0.5 M at the end of each run.

The sulfite oxidation rate is greatly accelerated by transition metals such as cobalt, copper, and iron. Therefore, the pulp sample was washed repeatedly with hydrochloric acid and EDTA. The treated pulp was washed again with distilled water to remove the residual acid and EDTA. Analysis of the solution in the pulp slurry by a Perkin-Elmer 2380 atomic absorption spectrophotometer showed that concentrations of these metals were below 0.05 ppm.

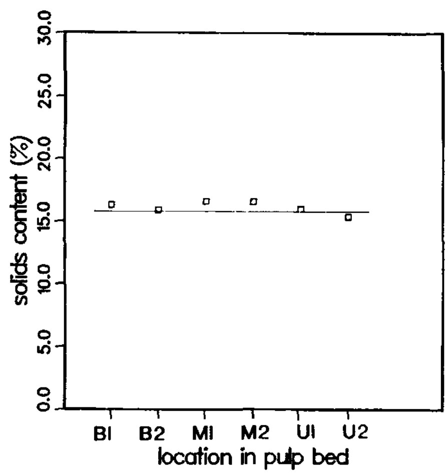

Figure 1. Pulp bed uniformity.

After complete dissolution of sodium sulfite in water, 3.23 g of the washed, unbleached (93% solids content) kraft pulp was introduced. The pulp was prepared from loblolly pine in a laboratory digester at 170°C with NaOH and Na_2S as the pulping chemicals. The lignin content of the pulp was 5.5% and the yield was 49.7%.

The sulfite concentration was determined by titration with iodine solution. The differences between sulfite concentrations in the pulp bed and those in the excess water were determined in several samples and were found to be around 0.01 M.

A schematic diagram of this experimental apparatus for the mass transfer study is shown in Figure 2. A 2.54 cm OD tube with packed pulp bed was placed horizontally in a constant-temperature bath. An inlet copper coil to the reactor was used to preheat the inlet gas. A thermocouple and a manometer were used to measure the temperature and the pressure drop across the pulp bed, respectively.

Nitrogen was used to purge residual oxygen in the pulp bed at the beginning of each run. When the temperature reached the set point, the nitrogen flow was switched to the oxygen-nitrogen mixture. The system was operated at 1 atm (101.3 kPa). The partial pressure of oxygen was controlled by varying the ratios of nitrogen and oxygen flows. All the experiments were performed at 37°C in the pulp bed for 20 min.

The weight differences of the tube between the beginning and the end of each run were found to be within 0.5%, which was considered to be within experimental error.

High alkali concentrations and temperatures up to 100°C must be used for oxygen to bleach the pulp. Our experiments were performed at 37°C and no alkali. Therefore, it is assumed that pulp is inert to oxygen at this condition.

Theory

Linek and Vacek (1981) pointed out that under conditions

$$
\begin{gathered}
C_{\mathrm{Co}^{++}} < 10^{-4}\ \mathrm{M} \\
C_{\mathrm{SO}_3^{-}} \geq 0.5\ \mathrm{M} \\
C^{*}_{\mathrm{LO}_2} \leq 3.6 \times 10^{-4}\ \mathrm{M}
\end{gathered}
\tag{1}
$$

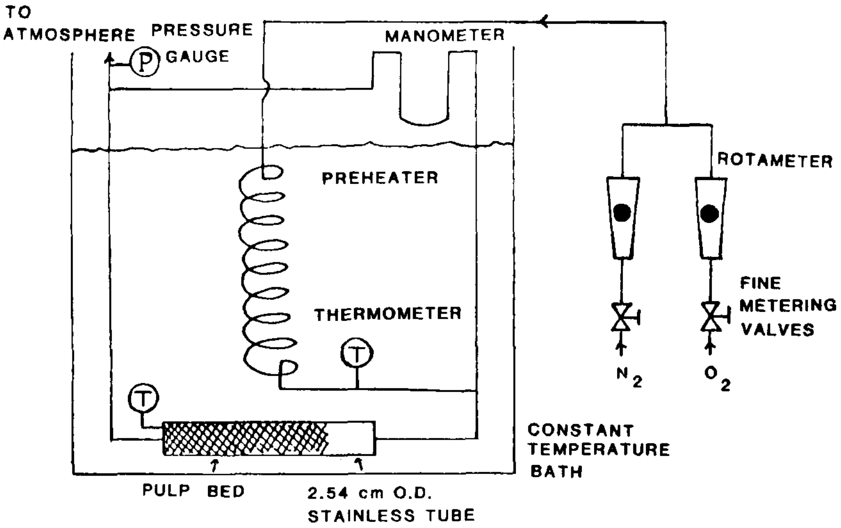

Figure 2. Experimental apparatus for mass transfer and pressure drop study

the oxidation reaction rate of sulfite with dissolved oxygen

$$SO_{3(aq)}^{=} + \tfrac{1}{2} O_{2(aq)} \rightarrow SO_{4(aq)}^{=} \tag{2}$$

is second-order with respect to the oxygen concentration:

$$r_{O_2} = k_2 C_{LO_2}^2 \tag{3}$$

In the film model, the oxygen mass transfer resistance is assumed to be principally in the interfacial film. The consumption of dissolved oxygen molecules is completed in this thin film by sulfite ions, and oxygen concentration outside this film in water is zero. The equation for oxygen diffusion and reaction in the film is

$$D_{O_2} \frac{d^2 C_{fO_2}}{dx^2} - k_2 C_{fO_2}^2 = 0$$

with the boundary conditions:

$$C_{fO_2} = C^*_{LO_2}, \qquad x = 0$$

$$C_{fO_2} = 0, \qquad x = \delta = \frac{D_{O_2}}{k_L} \tag{4}$$

Danckwerts (1970) obtained an approximation of the exact solution for the above equation with 8% deviation.

$$Na_L = a_L \left[\tfrac{2}{3} k_2 C^*_{LO_2} D_{O_2} + (k_L)^2\right]^{1/2} C^*_{LO_2} \tag{5}$$

If the concentrations of the catalysts cobalt, copper and, iron are very low, the reaction rate for oxygen-sulfite is negligible in comparison with the physical absorption rate. Equation 5 can be rewritten as

$$Na_L = k_L a_L C^*_{LO_2} \tag{6}$$

Equation 6 was used by Fukushima and Kusaka (1977) to determine the gas-liquid mass transfer in a packed column with downward cocurrent flow. It was verified that at very low catalyst concentrations, the volumetric mass coefficients determined by the physical absorption were consistent with those determined by the oxygen-sulfite reaction method. The system studied here has similar characteristics.

Results and Discussion

With the low solubility of oxygen in water, the equilibrium oxygen concentration can be expressed by Henry's law as

$$C^*_{LO_2} = \frac{P_{O_2}}{H_{O_2} RT} \tag{7}$$

The maximum oxygen partial pressure drop in the pulp bed was estimated to be within 10%. It was calculated from the difference between the oxygen gas inlet flow rate and the oxygen absorption rate into water. If a linear oxygen partial pressure gradient in the pulp bed was assumed, only a 5% deviation would occur. Thus, the oxygen partial pressure was assumed constant.

The Henry's law coefficient used for oxygen in the liquid tested was given by Miller (1983) as:

$$H_{O_2} = \exp\left(12.907 - 2.832/T - 9.665\, C_{SO_3^=} + 3{,}181\, C_{SO_3^=}/T\right) \tag{8}$$

The total oxygen transfer into the liquid films surrounding the fibers was calculated as the sulfite concentration decrease in the liquid divided by a stoichiometric factor, 2.

In order to show that Eq. 6 can be used to determine the volumetric mass transfer coefficients, several runs with different oxygen partial pressure were performed. The gas absorption rate vs. oxygen equilibrium concentration at 17% solids content in the pulp bed is shown in Figure 3. It shows a linear fit with a correlation coefficient of 0.92.

The filled-square data points in Figure 3 represent the runs with additions of the same amounts of transition metals. It might be assumed that if the chemical reaction rate dominated the physical absorption rate, doubling the amount of the catalysts in solution would increase the reaction rate twofold or more. The data did not support this argument. The data points

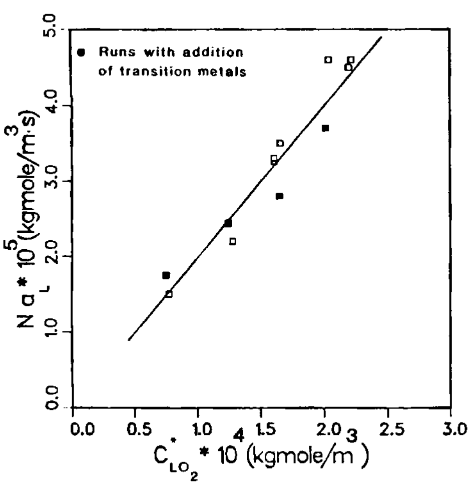

Figure 3. Effect of oxygen partial pressure on gas absorption rate.

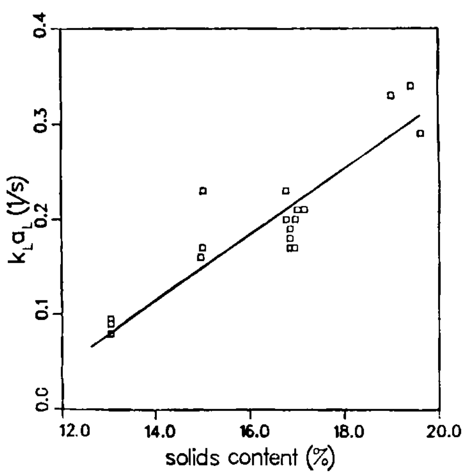

Figure 5. Effect of solids content on k_La_L.

with transition metals (filled squares) still fall at the same line. Therefore, it is concluded that in this system, the gas absorption rate was controlled by the physical absorption and Eq. 6 is valid for the volumetric mass transfer coefficients determination.

The effect of gas flow rate on the gas-liquid volumetric mass transfer coefficient in the pulp bed was also studied. In a packed bed with rigid solids, the liquid flow rate and the gas flow rate play major roles in the gas-liquid mass transfer. At a high liquid flow rate, the turbulent motion generated in the liquid phase can decrease the liquid-side mass transfer resistance. At a high gas flow rate, the gas-side mass transfer resistance can be decreased in a similar manner.

The plot of volumetric gas-liquid mass transfer coefficients in the pulp bed vs. gas flow rate is shown in Figure 4. It can be seen that gas flow rate had an insignificant effect on the mass transfer coefficients. The reason is that the liquid phase was trapped inside the fibers of the pulp bed and did not flow. The gas flowed through the porous space in the pulp bed and could not activate the liquid. In the oxygen-water system, the gas-liquid mass transfer is controlled by the liquid-side resistance due to its low solubility, as suggested by Sherwood et al. (1975). Therefore, the gas flow rate should not have an effect on the gas-liquid mass transfer in the pulp bed.

Figure 5 shows volumetric mass transfer coefficient vs. solids content in the pulp bed. The best fit of the relationship yields a straight line represented by

$$k_La_L = 0.033\,S_c - 0.35\ (13\% \leq S_c \leq 19\%) \tag{9}$$

with a correlation coefficient of 0.82.

The transfer of oxygen into the liquid phase of the pulp bed was carried out mainly by diffusion because no agitation was applied to the liquid phase. The oxygen transfer coefficients did not vary much for the small range of different solids content (13–19%). The differences in volumetric mass transfer coefficients could be due to the differences in interfacial area, a_L, at various solids content in the pulp bed.

The calculated porosity vs. solids content is shown in Figure 6. With the same amount of oven-dry fibers in the pulp bed, porosity is greater at higher solids content. Thus the interfacial area between gas and liquid is increased with higher solids content in the pulp bed.

In addition, an effective particle diameter in the pulp bed was further estimated from the gas pressure drop across the pulp

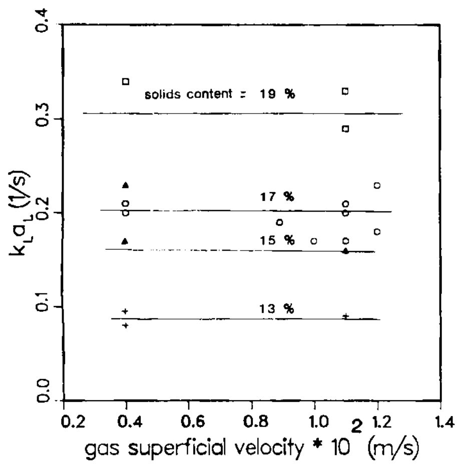

Figure 4. Effect of gas superficial velocity on k_La_L.

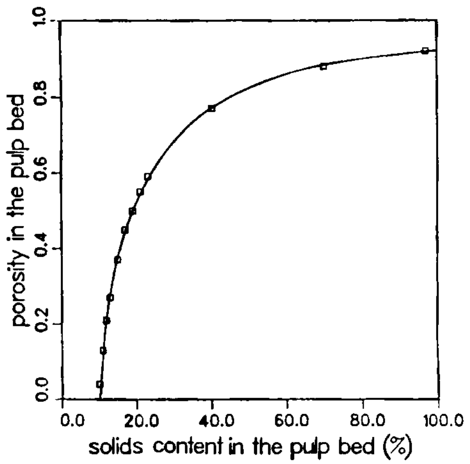

Figure 6. Relation between porosity and solids content in pulp bed.

Table 1. Numerical Values of d_p and ϵ at Various Pulp Bed Solids Content

	Solids Content, %			
	13	15	17	19
d_p, mm	0.09	0.084	0.079	0.075
ϵ	0.27	0.37	0.45	0.50

bed. Fibers in the pulp bed agglomerated into many fiber flocs. It is reasonable to assume that oxygen flows through the void space between each fiber floc. A pulp bed can be considered as a solid, fixed, packed bed with fiber flocs as rigid structure.

Ergun has proposed the following relationship for pressure drop through a fixed packed bed of uniform-size solids.

$$\frac{\Delta P_E}{l} = 150\frac{(1-\epsilon)^2}{\epsilon^3}\frac{\mu u_o}{(\phi_s d_p)^2} + 1.75\frac{(1-\epsilon)\rho_g u_o^2}{\epsilon^3\,\phi_s d_p} \tag{10}$$

At the conditions used in these experiments, the second term is negligibile in comparison with the first term.

In the above equation, the particle (fiber floc) size is not measurable. Initially, it was assumed that each fiber was covered by a thin water film. The numerical values of d_p and ϵ are shown in Table 1 for different solids content pulp beds. The fiber floc was considered to be spherical ($\phi_s = 1$). An empirical factor f was incorporated into Ergun's equation to account for fiber flocculation.

$$\Delta P_{\text{pulp bed}} = \Delta P_E^* f \tag{11}$$

The factor f was estimated to be approximately 0.33 from the data. Figure 7 shows the pressure drop measured in the pulp bed vs. the predicted values by the Ergun correlation corrected for variations introduced by fiber flocculation with a correlation coefficient of 0.95.

The effective fiber floc diameters can be estimated from the d_p values used above divided by the square root of 0.33; they are in the range of 0.16 mm (13% solids content) to 0.14 mm (19%).

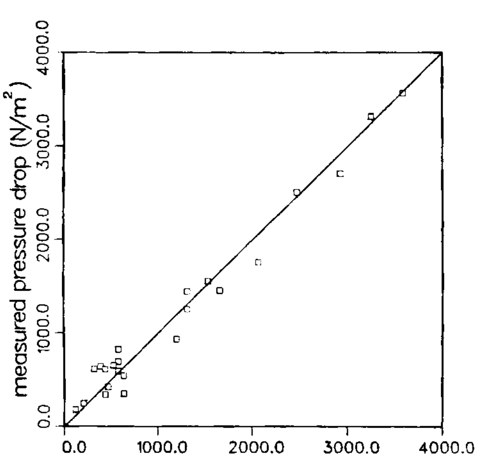

Figure 7. Pressure drop across pulp bed, experimental vs. prediction by Ergun's equation.

Table 2. Magnitude Comparison of k_La_L Values in Pulp Bed and Trickle Bed

k_La_L s^{-1}	Type of Packing	Reference
0.08–0.3	Flexible pulp bed with fibers, 0.13–0.16 mm	This study
0.1–3.0	Raschig rings, 12.7–76.2 mm	Reiss (1967)
0.006–0.14	Berl saddles, 19.0 mm Raschig rings, 6.35–12.7 mm	Ufford and Perona (1973)
0.1–1.0	Cylinders 3.2 × 3.2 mm	Sylvester and Pitayagulsarn (1975)
0.007–1.6	Spheres, raschig rings and saddles, 6 mm	Gianetto et al. (1973)
0.02–3.0	Glass spheres, 2.95–12.2 mm	Hirose et al. (1974)
0.002–0.014	Saddles, 2.9 mm Spheres, 4.1 mm	Goto and Smith (1975)

The experimental volumetric mass transfer coefficients in the pulp bed were further compared with those in a trickle bed, as shown in Table 2. The wide ranges of k_La_L values in the trickle bed resulted from different gas and liquid flow rates in the various studies. It was observed that the magnitude of the volumetric mass transfer coefficients in the pulp bed was between those in a trickle bed with rigid solids.

It is noted that the volumetric mass transfer coefficients could be smaller since there is no liquid flowing in the pulp bed. In fact, the volumetric mass transfer coefficients in the pulp bed were increased due to the much larger interfacial area resulting from the smaller particle (fiber floc) size between the gas phase and the liquid phase in the pulp bed.

Acknowledgment

The authors would like to thank the Georgia Tech Foundation for support of this work.

Notation

a_L = gas-liquid interfacial area per unit packed volume, m^{-1}
C_{fO_2} = oxygen concentration in diffusion film, kmol/m^3
C_L = solute concentration in bulk liquid phase, kmol/m^3
$C_{LO_2}^*$ = equilibrium oxygen concentration in liquid phase, kmol/m^3
D_{O_2} = diffusivity of dissolved oxygen, m^2/s
d_p = particle diameter, m
f = empirical factor to correct fiber overlapping
H = Henry's law constant, kmol/m^3 in gas per kmol/m^3 in liquid
k_L = mass transfer coefficient for physical absorption, m/s
k_2 = second-order rate constant for reaction, m^3/kmol · s
k_La_L = volumetric mass transfer coefficient for physical absorption, s^{-1}
l = packed bed length, m
N = oxygen absorption rate, kmol/m^2 · s
P = pressure, N/m^2
R = gas law constant, N·m/kmol · K
r = rate of reaction per unit volume, kmol/m^3 · s
Sc = solids content in the pulp bed, %
T = temperature, K
t = time, s
u_o = superficial gas velocity, measured on an empty tube basis, through a bed of solids, m/s

Greek letters

δ = thickness of diffusion film, m
ϕ_s = sphericity of a particle

ϵ = porosity
μ = gas viscosity, kg/m · s
ρ_g = gas density, kg/m^3

Subscripts

Co^{++} = cobaltous ion
E = Ergun
f = diffusion film
O_2 = oxygen
$SO_3^=$ = sulfite ion

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Manuscript received Sept. 10, 1985, and revision received Mar. 25, 1986.