Enhancement of Mass Transfer in the Fluidized Bed Electrode Reactors

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Abstract–With the view of developing the fluidized bed electrode system, mass transfer coefficient, overpotential distribution, and copper degradation have been observed in this investigation. Particles whose diameters were one of 327, 388, 510, 548, 750, and 960 μm were fluidized by the 1,000 ppm copper sulfate electrolyte. This study used two types of the experimental reactor. One had 5×5.5 cm bed-dimension with various thickness in a rectangular side-by-side configuration; the other 3.2 cm bed-diameter with various height in a cylindrical flow-through configuration. Mass transfer coefficient increased with increasing particle diameter, and the optimum fluidization was obtained at the condition of bed porosity near 0.65. For processing a large fluidized bed reactor, the expansion of bed height at a distance between electrodes was found to be more effective than the enlargement of bed thickness between electrodes. By replacing a three-dimensional current-feeder with a plane feeder, degradation and residual concentration of copper ion in a batch recycling mode could be achieved to be higher than 99% and less than 5 mg/L, respectively.

Key words: Fluidized Bed Electrode, Mass Transfer Coefficient, Copper Degradation

INTRODUCTION

From the early 1970s considerable attention has been given to the research on packed and fluidized bed electrodes for the attraction of high space-time yields. As the dispersed phase is dense in the packed bed, charge can easily flow through bed from feeder. But agglomeration among packed particles brings not only a break of continuous operation but also interruption of the detachment of produced species. The fluidized bed has several desirable characteristics. A great amount of fluid can be continuously treated due to small hold-up of the dispersed phase. Circulation of the fluidized particles reduces the diffusion layer of reactive species. Contrary to these advantages the distance between particles makes low collision-frequency of particles. It causes poor charge transfer and/or dead zone in the fluidized bed. From both aspects of the two reactors, it is predictable that the packed bed is advantageous to the extent of less conductive solution and the fluidized bed more [Genders and Weinberg, 1992].

Fluidized bed electrode is commonly known as one of the best reactors for the application to metal removal from waste and leach effluent [Goodridge and Vance, 1979; Vatistas and Bartolozzi, 1990; Fleck and Bautisa, 1991]. To produce a developed configuration of a fluidized system, preceding studies should be performed on mass transfer rate and reactor performance. The past decade in particular has shown that some researchers devoted themselves to the enhancement of mass transfer rate [Ali and Gomes, 1989; Kim and Kim, 1990; Bouzek et al., 1996]. Little thorough work has been done on systems with a batch recycling operational mode to obtain quantitative infor-

mation on how reactant depletion rates depend on operating parameters and on what final depletion level can be achieved [Byun et al., 1986]. The information that allows an engineer to produce a reasonable commercial plant of the fluidized reactor system is obviously important in process design.

The investigation represented here was undertaken with these deficiencies in the current state of engineering knowledge of fluidized bed electrodes. It has been concerned with the effects of particle size (d_p), bed porosity (ε), bed thickness (S), bed length (L), and reactor's configuration on mass transfer coefficients. Particles whose diameter was varied from 327 μm to 960 μm were fluidized at a bed porosity in the range from 0.48 to 0.85 by the 1,000 ppm copper sulfate electrolyte. Electrolyte passed through one of two reactors composed of a 5×5.5 cm rectangular bed or 3.2 cm cylindrical bed. An attempt also has been made to measure the degradation of copper concentration in the duration of electro-deposition on the platinized titanium cathode from copper sulfate electrolyte using a batch recycling operational mode. The aim was to propose an appropriate current-feeder satisfied with the significant final depletion.

EXPERIMENTAL

Mass transfer coefficient can be calculated by reading limiting current from overpotential-current voltammogram measurable at working electrode.

$$K = \frac{I_L}{zFaALC} \tag{1}$$

In Eq. (1), K, I_L, z, F, a, A, L, and C mean mass transfer coefficient, limiting current, number of charge transferred, Faraday's constant, specific surface area, cross-sectional area of reactor, length of fluidized bed, and bulk concentration of re-

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active species, respectively. Specific surface area means the reactive surface area of particles per unit volume of reactor, expressed as follows.

$$a=\frac{6(1-\varepsilon)}{d_p} \qquad (2)$$

In which ε and d_p mean bed porosity and particle diameter, respectively. As indicated in Eqs. (1) and (2), major parameters influencing mass transfer include limiting current, bed length, bed porosity, and particle diameter.

Limiting currents have been measured in a cross-flow rectangular reactor and in a parallel-flow tubular reactor. The former is called a flow-by side-by-side reactor and the latter a flow-through cylindrical reactor [Genders and Weinberg, 1992]. The obvious cathodic compartment of the side-by-side reactor had dimension of 35×5.5 cm (H×W) with various thickness of 1.2, 3.2, and 5.2 cm. The bed of copper particles was supported on a distributor consisting of porous sintered glass with a pore size 120 μm and 0.3 cm thickness. A cathode and anode made of platinized titanium were situated at either side of a porous separator with a pore size 30 μm.

The inside diameter of the flow-through reactor was 3.2 cm. The upward flow of electrolyte fluidized the particles packed on a mesh cathode. Cylindrical anode was inserted at a distance of 2 cm on the top surface of fluidized bed. The height of fluidized bed was sometimes described as bed length between electrodes in this investigation.

Electrolyte consisted of copper sulfate and 1.0 M sulfuric acid. It maintained the normal concentration of 1,000 mg Cu^{2+}/ L for the experiment to obtain mass transfer coefficients. A centrifugal magnetic pump drove catholyte from a reservoir of 25 L to the reactor. Cooling coil dripped into catholyte in reservoir maintained solution temperature to be constant at 25 °C. Nitrogen purged into catholyte for 30 minutes before experimentation and a bleed was left on throughout the course of the experiment to reduce oxygen overpotential. A rotameter connected to the flow circuit gave a continuous variation of flowrate from 1.0 L/min to 9.6 L/min.

The luggin capillary shaped from fine bore glass tubing of 0.3 cm outside diameter was connected to the saturated calomel electrode (SCE) by soft polyethylene tubing. The opposite end tip of the luggin capillary placed on the current-feeder, 0.2 cm below the top surface of bed. Sweeping overpotential by the increment of 20-40 mV with respect to SCE, voltammogram was recorded on a x-y chart to determine limiting current. A 40 V/5 A potentiostat using as a power source controlled the sweep rate of overpotential.

To investigate degradation rate, copper deposition was carried out from catholyte of 10 L continuously passing through the batch recycling circuit. A plane feeder welded with two vertical fins replaced the ordinary plane feeder as a three-dimensional electrode for the purpose of comparison how to effect on degradation at constant overpotential operation. Samples of catholyte were taken from the reservoir at intervals of 20-40 min during 6 hour runs. An Atomic Absorption spectrophotometer and an Inductively Coupled Plasma-mass spectrometer analyzed the dissolved copper concentration in the sam-
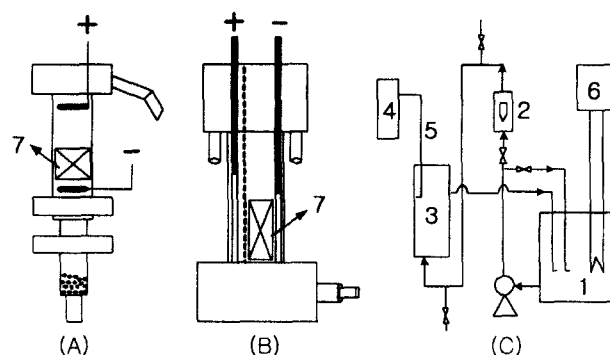

Fig. 1. Schematic diagrams of the experimental reactors and system apparatus.

(A): cylindrical flow-through reactor, (B): rectangular side-by-side reactor, (C): system apparatus

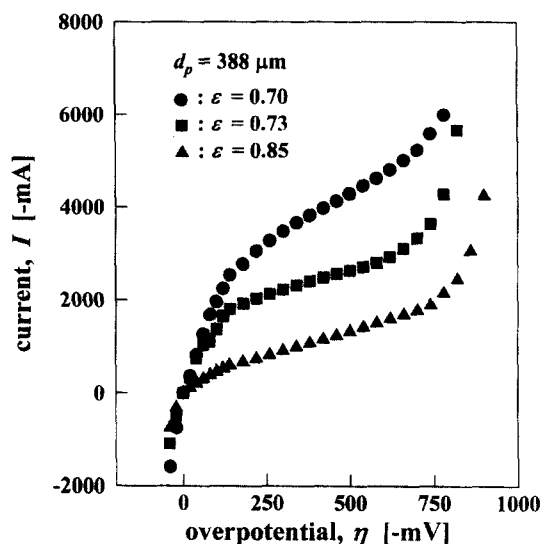| 1. Solution reservoir | 5. Luggin capillary |
2. Rotameter	6. Temperature controller
3. Reactor	7. Fluidized bed
4. SCE	

Fig. 2. Typical voltammograms measured in a side-by-side reactor.

ples. Fig. 1 shows the schematic diagrams of the experimental reactors and system apparatus used in this investigation.

RESULTS AND DISCUSSION

Fig. 2 represents typical voltammograms obtained at some extent of high velocity of electrolyte in a side-by-side reactor. The increment of current progressively declined till current reached a plateau called the limiting current [Walker and Wragg, 1981]. Overpotential corresponding to limiting current was placed from 150 mV to 850 mV between two points of curvature at all experimental conditions. This investigation adapted current at higher point to Eq. (1) as the limiting current. Mass transfer coefficient calculated from the limiting current density on the basis of particle surface increased with increasing particle size, as shown in Fig. 3. It can be expected from the substitution of Eq. (2) into Eq. (1) that mass transfer coefficient is in propor-
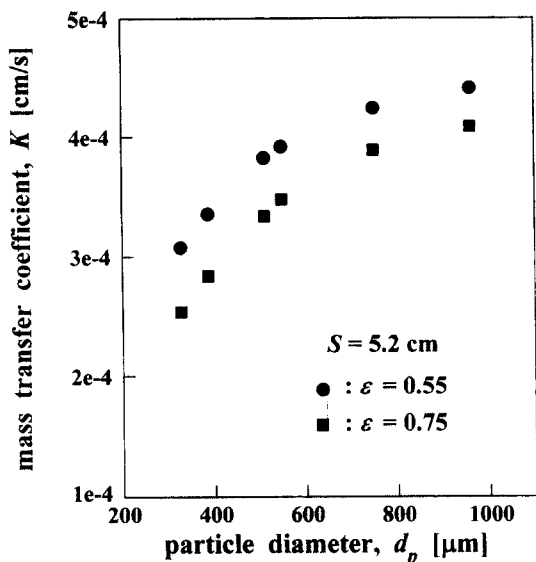
Fig. 3. Effect of particle size on mass transfer coefficient in a side-by-side reactor.
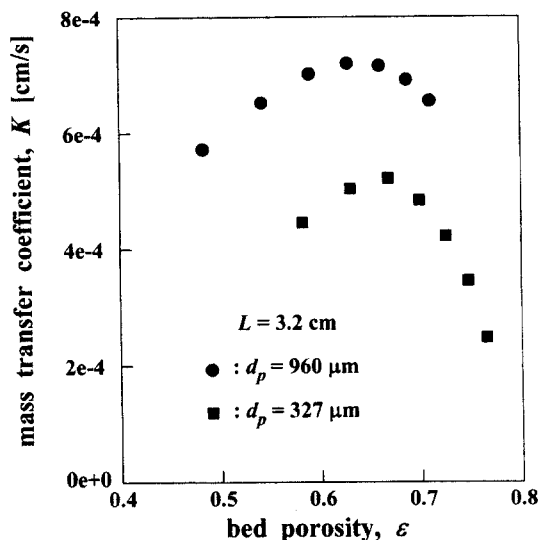

Fig. 4. Effect of bed porosity on mass transfer coefficient in a side-by-side reactor.

high resistance of solution. Owing to these contrary aspects, maximum mass transfer should be found. Although fluidization is known as the property of perfect mixing exhibits, particle aggregation can be observed at low expansion in this investigation. Mass transfer would increase up to maximum until the whole aggregates are broken down in reaching enough expansion. Walker and Wragg [1981] and Smith and King [1975] introduced the bed porosity corresponding to maximum mass transfer was 0.55-0.70 and 0.65, respectively.

It is in general possible to scale-up the fluidized bed height in the space between anode and cathode for a side-by-side configuration, but scaling-up the radius of tubular reactor is not convenient. To confirm whether enlargement could be available along axial flow direction, mass transfer coefficients were measured at various bed length of the fluidized particulate. Fig. 5 came from the cylindrical bed fluidized on the bottom feeder, and Fig. 6 from the rectangular bed fluidized between elec-
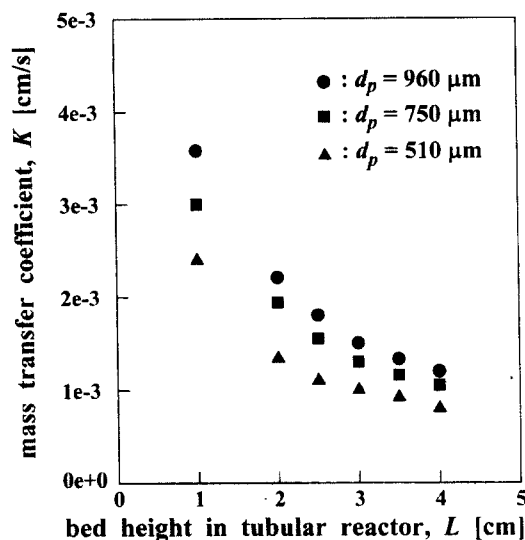

Fig. 5. Effect of bed height on mass transfer coefficient in a tubular reactor.

tion to particle diameter. But the increment of mass transfer coefficient progressively declined because the expansion rate at constant porosity increased with particle size. As big particles tended to take good mass transfer in Fig. 3, the variation of mass transfer coefficient with bed porosity was observed for the biggest size of 960 μm among experimental particles. The smallest size of 327 μm was also used in order to compare with the biggest one. Fig. 4 shows the significant result for both sizes that mass transfer reveals its maximum at the bed porosity near 0.65. Interstitial velocity passing through particles would be higher at a large porosity than at a small one. Flow channel of fluid is staggered fast at higher velocity, which brings a decrease of the concentration gradient and that of diffusion resistance at the interface between dispersed phase and solution phase. But particles would be far from one another at a great extent of porosity, which makes the charge transfer poor because of the
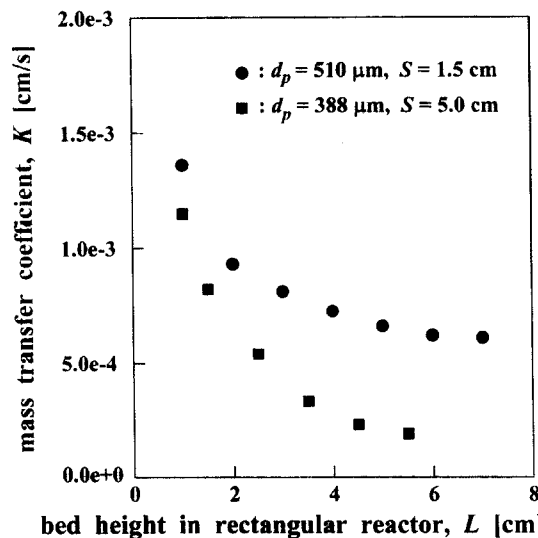

Fig. 6. Effect of bed height on mass transfer coefficient in a side-by-side reactor.

trodes. The result of Fig. 5 clearly shows that mass transfer coefficient was inversely proportional to the bed length expanded; which indicates it might be undesirable to expand axial length in the tubular reactor. In order to compare this result from the cylindrical configuration with the influence of bed height in the rectangular configuration, mass transfer coefficient was measured along bed height that was the same coordinate with axial fluid flow in a side-by-side reactor. Fig. 6 conspicuously shows the result that mass transfer was interrupted somewhat at small height bed, but no serious depletion occurred due to the enlargement of bed height. Carbin and Gabe [1974] and Roy and Pintauro [1993] carried out similar research relating limiting current density to the electrode length. They found the limiting current was highest at entrance of reactor either in the presence or in the absence of particles. It is apparent from the above experimental results that the expansion of bed height is more convenient and more effective for commercial scale-up than that of bed thickness.

Alternative research examined the overpotential distribution from feeder electrode to separator across the particulate bed in the side-by-side reactor. As shown in Fig. 7 obtained under the condition of activation-controlling current density, the overpotential of the particles adjacent to feeder and separator was higher than that of the particles in the inner bed [Chun and Kang, 1981; Lee et al., 1988]. Magnitude of cathodic polarity on the basis of unit thickness increased with decreasing the thickness of the fluidized bed. Integrated overpotential was found to be −10.3 mV, −20.8 mV, and −23.1 mV for the whole bed, and the value divided by the thickness was −8.6 mV, −6.5 mV, and −4.4 mV for 1.2 cm, 3.2 cm, and 5.2 cm thickness, respectively. High driving force of particle makes the reactive species transfer well to diffusion layer, particularly to the particles adjacent feeder. Therefore the structure of the feeder electrode should be altered to a three-dimensional configuration to improve mass transfer at the particles in inner fluidized bed.

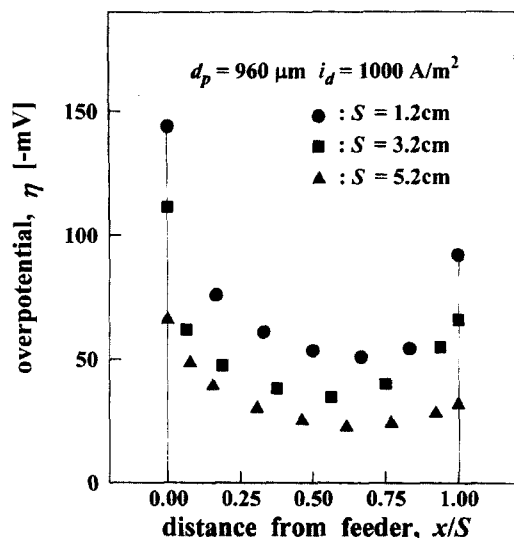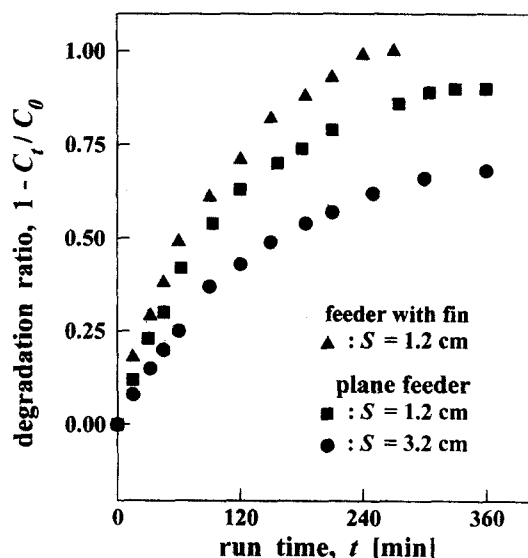To compare the reactor performance, this investigation used

Fig. 8. Degradations of copper concentration after 6 hour run in a batch recycling operation mode.
▲ : 2 series of 1.2 cm thick reactor installed with a fin-feeder, ■ : 2 series of 1.2 cm thick reactor installed with a plane feeder, ● : 3.2 cm thick reactor installed with a plane feeder

3.2 cm and 1.2 cm thick reactors situated in the batch recycling flow circuit. Two series of 1.2 cm thick reactor to make 2.4 cm thickness was used with two modes in which a flat feeder and a plane welded with two vertical fins were inserted alternatively. Under the condition of constant overpotential at 700 mV, copper concentration decayed exponentially so that the degradation increased progressively. The degradation was 69% after a 6-hour run using 3.2 cm thick reactor, and 93% using two series of 1.2 cm thick reactor, as shown in Fig. 8. Residual concentration was 155 mg/L for the 3.2 cm thick, and 35 mg/L for the two series of 1.2 cm thick. By replacing a three-dimensional current-feeder with plane feeder in 1.2 cm thick reactor, degradation approved above 99% and residual concentration decayed less than 5 mg/L. These results are similar with the recent research [Yen and Yao, 1991] indicating the depletion of copper to be 90-98%. The fluidized bed electrode reactor has been evidently found to be applicable to removing copper ion especially when a series of thin reactors installed with a three-dimensional feeder electrode is applied.

CONCLUSIONS

In this investigation, the measurements of overpotential-current voltammograms, overpotential distributions, and degradation of copper ion have been performed at various conditions for the purpose of the enhancement of mass transfer in fluidized bed electrodes. Mass transfer depended upon particle size, bed porosity, bed height, bed thickness, and reactor's configuration. It increased with increasing particle diameter in the range examined in this study. But its increment progressively declined with particle size. The optimum fluidization was observed at the condition of bed porosity nearby 0.65. The thickness of

Fig. 7. Overpotential distributions across fluidized bed from feeder for three kinds of thickness.

particulate bed could not be expendable effectively, but the height of bed could be possible to extend by using a three-dimensional feeder electrode. In a batch recycling operational mode using a side-by-side reactor installed with a fin-feeder, degradation and residual concentration of copper ion were achieved to be higher than 99% and less than 5 mg/L, respectively. From the experimental results, this investigation concludes that a fluidized bed electrode reactor is an applicable system for the removal of copper ion from waste effluent.

ACKNOWLEDGMENT

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