실관함침액막에서 코발트, 니켈이온의 분리현상에 관한 모사

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Simulation of Separation Phenomena of Cobalt and Nickel in the Hollow Fiber Supported Liquid Membrane(HFSLM)

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INTRODUCTION

Separation technique using HFSLM is the technique which can separate and concentrate materials without phase transition. In contrast to LEM, SLM has some advantages that it is one step separation process and doesn't have swelling problem at high concentration. But a planner or flat geometry SLM is not so effective to obtain high permeation rate since the ratio of surface area to permeator volume is very low. HFSLM can be applied to industrial purposes since its ratio of area to permeator volume can approach 10,000m^2/m^3.[1]

Cobalt and nickel, which are the targets of separation in this study, are commonly exist together in an ore. It is not easy to separate cobalt and nickel in the course of refinement due to the similarities of the physical characteristics so that they coexist until the final step of refinement.

In this paper, the simulation study of separation and concentration of cobalt and nickel from the inner(tube) side to the strip(shell) side through the hollow fiber membrane module is accomplished. In the first place, a mathematical model based on mass balance for a fully developed, laminar flow in a cylindrical geometry has been established. We used collocation technique as a numerical method. In order to find the unknown parameters in the model, results of simulation are compared with experimental data. So effective diffusivity of carrier-metal complex in the membrane phase can be obtained. Using these values, we performed simulation in various operating conditions and analyzed the effect of parameters which affect the extraction performance.

MATHEMATICAL MODEL

Based on the continuity equation for the solution in a constant density fluid of solute in the hollow fiber, governing equation can be represented as follows.

For bulk phase

$$\frac{\partial c}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}r\frac{\partial c}{\partial r} - 2v_0\left(1 - \left(\frac{r}{R}\right)^2\right)\frac{\partial c}{\partial z}$$

For organic phase

$$\frac{\partial \bar{c}}{\partial t} = \frac{De}{r}\frac{\partial}{\partial r}r\frac{\partial \bar{c}}{\partial r}$$

, where De is the effective diffusivity of carrier and carrier-complex of metal in the liquid membrane, C and $\bar{C}$ is the concentration of solute in the aqueous and organic phase and R is the inside radius of hollow fiber. The initial conditions are

$$0<r<R,\ \text{all } z:\ C_{Co} = C_{Co,0},\ C_{Ni} = C_{Ni,0},\ C_H = C_{H,0}$$

$$R<r<R1,\ \text{all } z:\ \overline{C_{Co}} = 0,\ \overline{C_{Ni}} = 0,\ \overline{C_{HR2}} = \overline{C_{HR20}}$$

, where R1 is the outside radius of hollow fiber module. The associated boundary conditions are

$$r = 0,\ \text{all } z:\ \frac{\partial C_{Co}}{\partial r} = 0,\ \frac{\partial C_{Ni}}{\partial r} = 0,\ \frac{\partial C_H}{\partial r} = 0$$

$$r = R,\ \text{all } z:\ D_{Co}\frac{\partial C_{Co}}{\partial r}\bigg|_{r=R^-} = De_{Co}\frac{\partial \overline{C_{Co}}}{\partial r}\bigg|_{r=R^+}$$

$$D_{Ni}\frac{\partial C_{Ni}}{\partial r}\bigg|_{r=R^-} = De_{Ni}\frac{\partial \overline{C_{Ni}}}{\partial r}\bigg|_{r=R^+}$$

$$D_H\frac{\partial C_H}{\partial r}\bigg|_{r=R^-} = De_{HR2}\frac{\partial \overline{C_{HR2}}}{\partial r}\bigg|_{r=R^+}$$

$$r = R1,\ \text{all } z:\ \overline{C_{Co}} = \overline{C_{Ni}} = 0,\ \overline{C_{HR2}} = \overline{C_{HR20}}$$

, where De_{Co}(De_{Ni}) are the effective diffusivities of cobalt(nickel)- carrier complex and De_{HR2} is the effective diffusivity of carrier in the liquid membrane. These equations may be solved using collocation method.[2,3]

RESULT AND DISCUSSION

1. Parameter Estimation

The unknown parameters in this model are De_{HR2}, De_{Co} and De_{Ni} through the liquid membrane. These unknown parameters are obtained by adjusting the model to the part of the experimental result. The ratio of each effective diffusivity values is determined based on the Wilke-Chang equation. We used the experimental data of feed phase Co^{2+} and Ni^{2+} concentration is 1g/L and 0.05g/L when carrier composition is 30(V/V(%)) and pH in the feed phase is 4.

As shown in Fig. 1, when $De_{Co}=1.55E\text{-}8cm^2/s$, $De_{Ni}=1.23E\text{-}8cm^2/s$ and $De_{HR2}=2.42E\text{-}8cm^2/s$, the simulation result was well correspond to the experimental result. Effective diffusivity values obtained by parameter estimation has the order of $10^{-8}cm^2/sec$. There values are in reasonable agreement with the effective diffusivity values obtained in other system.[4] Using these effective diffusivity values, we performed the simulation in the wide range of metal concentration.

2. Effect of Operating Parameters(pH and Carrier Composition) in the Wide Range of Metal Ion Concentration.

Fig. 3 and 4 are the result of simulation when Ni^{2+} concentration is fixed with high concentration(85mol/m^3). Each result shows the cobalt flux and separation factor when Co^{2+} concentration varies with wide range(0.01 - 100mol/m^3). Fig. 3 shows the effect of hydrogen concentration in the feed phase. Cobalt flux is highest when the pH in the feed phase is 6 in the whole cobalt concentration. In the carrier-mediated counter transport separation, the difference of hydrogen ion concentration between tube and shell side solution is the driving force of metal ion transport. When Co^{2+} and Ni^{2+} ions are transported from inner(tube)side to the external(shell) side through the liquid membrane, the H^+ ions in the shell side are transported in the opposite direction. As pH increases the concentration difference of hydrogen ion between tube and shell side solution increases, so flux increases. Separation factor also increases as the hydrogen concentration in the feed phase decreases. The increase of pH in the tube side solution may lead to the increase of separation efficiency. Fig. 4 shows the effect of carrier composition. Cobalt flux increases as the carrier composition decreases when Co^{2+} concentration is low. On the contrary when Co^{2+} concentration is high, the trend changes conversely. It is thought that low carrier composition leads to the high transport rate of carrier-complex due to the low viscosity of liquid membrane at low Co^{2+} concentration. Fig. 7 shows the relation between carrier composition and viscosity. As carrier composition increases, viscosity increases exponentially. As carrier composition increases, though the diffusion rate decreases due to high viscosity, large amount of carrier-complex transfers simultaneously through the liquid membrane. This may lead high Co^{2+} flux at the high carrier composition when Co^{2+} concentration is high. As carrier composition decreases, separation factor increases abruptly.

CONCLUSION

In this article, simulation study of HFSLM to the separation of metal ions is performed. Cobalt and nickel are chosen as a model system and are transported from tube to the shell side through the microporous hollow fiber module which contains cation carrier, HEH(EHP). A mathematical model is established based on the mass balance. Using collocation method, we can obtain the concentration profile of metals ions at collocation point in the feed and membrane phase of hollow fiber. Through the experiment of separation, we obtained the effective diffusivities of carrier-metal complexes, which are unknown parameters of simulation. Using these values, effect of operating parameters(pH, carrier composition) are examined in the wide range of metal concentration(0.01 - 100mol/m^3) when competitive separation of cobalt and nickel occur

Based on the simulation result, it is possible to predict the transport rate and effect of operating parameters on separation performance. It is thought that his study can also be used multi component separation system of more than 3 component and can be applied to obtain optimum operating conditions when designing and developing real separation system(e.q. : unit operation of multi-hollow fiber process).

REFERENCE

1. Lonsdale, H. K.: *J. Membr. Sci.*, **31**, 81 (1982)
2. Villadsen, J. V., and Michelsen, M.: "Solution of Differential Equation Models by Polynomial Approximation.", Prentice-Hall, Emglewood Cliff, NJ (1978).
3. Villadsen, J. V., and Stewart, W. E..: *Chem. Eng. Sci.*, **22**, 1483 (1967).
4. Danesi, P. R., Horwitz, E. P. and Rickert, P.: *Sep. Sci. and Technol.*, **17(9)**, 1183 (1982).

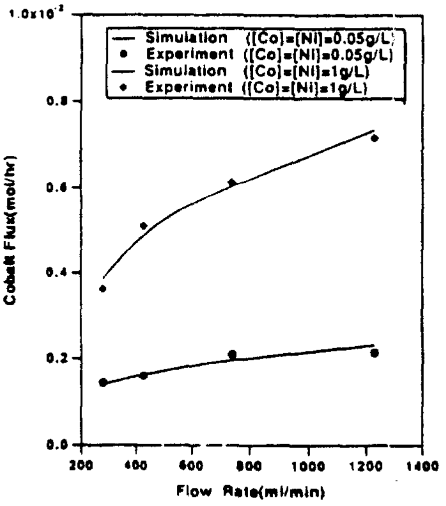

Fig. 1 Parameter estimation result

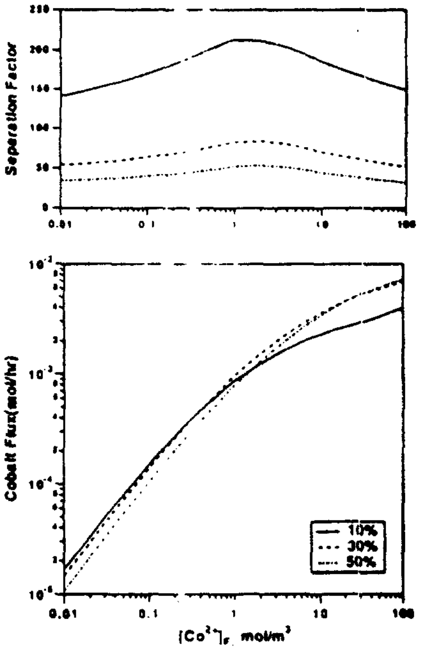

Fig. 3 Effect of carrier composition ([Ni] = 5g/L, pH = 6)

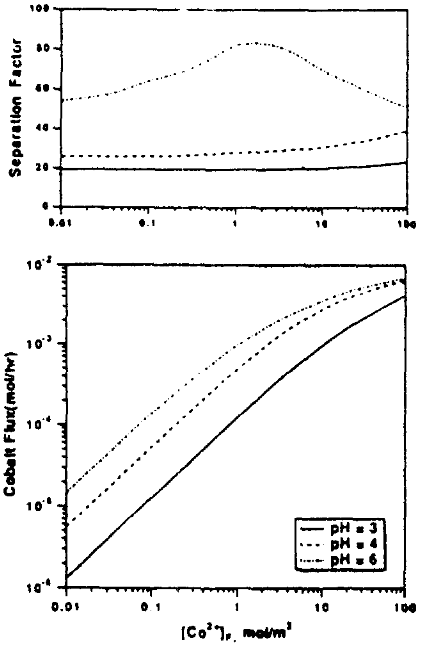

Fig. 2 Effect of pH in the feed phase ([Ni] = 5g/L, carrier : 30%)

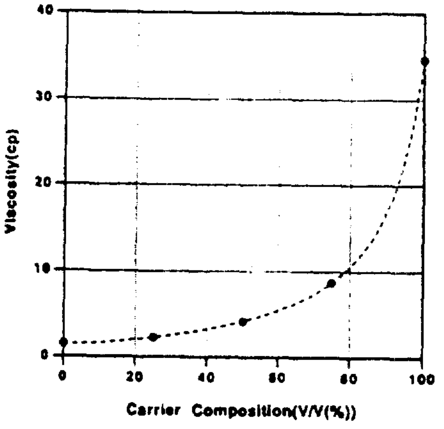

Fig. 4 Carrier composition vs. viscosity.