Continuous Removal of Heavy Metals by the Lime Sulfurated Solution (Calcium Polysulfide) Process

Toshiro ARATANI,* Shigeki YASUHARA,† Hitoshi MATOBA†† and Takeo YANO
Department of Chemical Engineering, College of Engineering, University of Osaka Prefecture, Mozu-Ume, Sakai, Osaka 591

(Received July 1, 1978)

A continuous wastewater treatment system was developed for the Lime Sulfurated Solution Process which had already been tested in a batch, stirred tank and ascertained to be an effective chemical precipitation process. The removability of heavy metals was investigated with the continuous treatment system, consisting of a plant composed of H_2S desorber, reactor, thickener, sand filter, and H_2S desorber. The sulfide ion dissolved in treated water was desorbed as H_2S by a mixed gas of air and CO_2 and recycled in the reactor to precipitate heavy metals. It has been found that: (1) by the recycling use of H_2S, the continuous treatment system can remove heavy metals with less coagulant than in the batch, stirred vessel, (2) desorption of the dissolved sulfide ion by the mixed gas decreases the sulfide ion concentration in the treated water below 0.2 ppb, and (3) the conditions for the removal of heavy metals can be detected immediately by a sulfide ion electrode meter.

The development of a continuous processing system is of great practical importance to economically treat wastewater. In previous work,[1–3] an effective heavy metal removal process, *i.e.*, the CaS_x process, which utilized the lime sulfurated solution as a single coagulant, had been proposed and investigated kinetically,[1] for the removal condition for heavy metals,[2] and the simultaneous removal of heavy metal, phosphate, and COD substances.[3] These investigations had, however, been conducted in a batch, stirred vessel. On the engineering scale, *i.g.*, the wastewater treatment plant, continuous operation has been desirable, since continuous processing reduces the operating costs. It is, therefore, necessary to devise a suitable continuous processing system for the CaS_x process. The removal of heavy metals from the system also needs investigation.

According to a previous work,[1] reaction scheme for the CaS_x process is represented by Eqs. 1 to 4.

$$CaS_x + 3/2\,O_2 \longrightarrow CaS_2O_3 + (x-2)S, \quad (1)$$

$$CaS_x + CO_2 + H_2O \longrightarrow CaCO_3 + H_2S + (x-1)S, \quad (2)$$

$$M^{2+} + CaS_2O_3 + H_2O \longrightarrow MS + CaSO_4 + 2H^+, \quad (3)$$

$$M^{2+} + H_2S \longrightarrow MS + 2H^+. \quad (4)$$

In the batch operation, the H_2S liberated by Eq. 2 is partly lost to the gas (air or CO_2) blown into the water to decompose the coagulant (CaS_x),[2] and so an amount of coagulant, more than the stoichiometric amount calculated from Eqs. 1 to 4 is required. In the present study, a continuous treatment system suited to the CaS_x process was realized on the bench scale. The plant was devised to recycle the H_2S in Eq. 2. In the plant, the H_2S liberated was scrubbed by the wastewater, and the dissolved sulfide ion recovered as H_2S from the treated water and re-used to precipitate heavy metals. The efficiency of the H_2S recycling plant was investigated with regard to the removal of heavy metals and the recycling of H_2S. The desorption of the dissolved sulfide ion from the treated water was also investigated.

Experimental

Continuous Processing Plant. Figure 1 shows the total system for the continuous CaS_x process. Simulated wastewater containing heavy metal was continuously fed to the top of the reactor. The reactor was made of a multistage vibrating disc column (MVDC) consisting of 15 stages (100 mm in height pet stage and 100 mm in inner diameter). The MVDC was used as the reactor, since it had excellent gas-liquid contacting ability even in the presence of suspended solid particles.[4] The coagulant, CaS_x solution was continuously injected into the 7th stage of the MVDC reactor. At the upstream stages from the injection point (1st to 7th stage), H_2S gas generated at the downstream stages (8th to 15th stage) was scrubbed by the wastewater and caught on reacting with the heavy metals in the wastewater. The CaS_x decomposed when it came into contact with the gas introduced from the bottom of the reactor. The precipitation of heavy metals by the decomposed CaS_x proceeded mainly at the downstream stages. The suspended solid particles were sedimented in the thickener of 300 mm both in diameter and height. The supernatant liquid was further clarified by a sand filter (150 mm diameter and 200 mm depth), packed with 120 mesh silica sand of 100 mm thickness. The clarified water was stripped of dissolved sulfide ions in the desorber, where the clarified water was contacted in countercurrent with the gas blown for the CaS_x decomposition. The gas used for the desorption was a mixture of air and CO_2 at predetermined volume ratio. The effluent water (treated water) from the desorber was removed as regards heavy metals and sulfide ions. The desorber was made up of an irrigated packed bed with 1/2″ Rasching ring.[5] The bed had a diameter of 150 mm and a height of 1 m. Air, according to a previous paper,[2] requires 60 to 90 min to decompose the CaS_x solution. The long processing time in the batch operation was known to require a large volume of the reactor for continuous operation. A mixed gas of air and CO_2 at various volume ratios was tested to determine the optimum conditions for heavy metal precipitation. The exit gas from the H_2S desorber was blown into the bottom of the reactor, and with this flow of gas, the H_2S, which was recovered by blowing gas into the desorber, was re-used to precipitate the heavy metals in the reactor. The other gas exiting from the top of the reactor was removed perfectly for H_2S, at the

---

† Present address: Matsushita Electric Works Co., Ltd., Kitashinkai, Yokkaichi 510.

†† Present address: Ataka Kogyo Co., Ltd., Sueyoshibashi, Minami-ku, Osaka, 542.

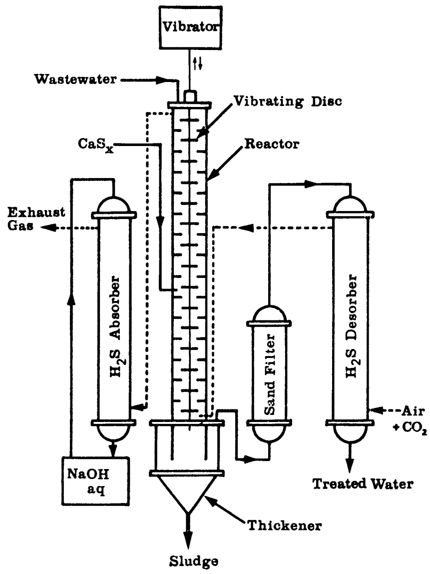

Fig. 1. Continuous heavy metal treatment system for the CaS_x process.

H_2S absorber (the same dimension of irrigated packed bed as the H_2S desorber was used). As the absorbing liquor, 5% NaOH aqueous solution was used.

Method. The simulated wastewater was prepared by dissolving the heavy metal nitrates into ordinary water, and stored in a tank (500 dm^3). The simulated wastewater was not temperature controlled, since the removal of heavy metals with the CaS_x process had already been found to be not severely affected by temperature.[2] First, the whole space of the plant, except the absorber and desorber, was filled with ordinary water. Continuous operation was started by the injection of the coagulant (CaS_x solution), followed by blowing of the gas for the CaS_x decomposition. Finally, the simulated wastewater was introduced. Samples were taken at predetermined time intervals from the outlets of the reactor, thickener, sand filter, and desorber. The samples from the reactor and thickener were filtered by membranes of various pore sizes, and the heavy metal concentrations were determined on an atomic absorption spectrophotometer. Samples from the sand filter and the desorber were directly determined for heavy metal concentrations. The sulfide ion concentration was measured by an ion meter with sulfide ion electrodes (Orion Research Inco., Model 94-16 and 90-02). Since the pH of the sample affects the detected sulfide ion concentration, the pH's of the samples were adjusted by adding a portion of 2 M-NaOH to give a pH of 10.0. The ion meter was calibrated with Na_2S of known concentration at pH=10.0. The flow rates of the wastewater and the blowing gas were set at 500 cm^3/min and 14 dm^3/min respectively. Liquid hold-up's in the reactor, thickner, sand filter, and desorber were measured to be 20, 20, 5, and 1 dm^3, respectively. With the base of these flow rates, the retention times of the reactor, thickener, sand filter, and desorber were calculated, respectively, as 40, 40, 10, and 2 min (the sum total was 92 min). The vibrating frequency of the disc in the MVDC reactor was set at 1.5 Hz with an amplitude of 19 mm, that is, at a vibrating speed of 2.85 cm/s, effective for the fine dispersion of the gas.[4]

Results and Discussion

The preliminary investigation was with simulated wastewater contaminated solely with Cd^{2+}. Figure 2 shows the change in Cd^{2+} concentration in the treated water from the start of the operation. Approximately four times the total retention time (92 min×4=368 min=6 h) was found sufficient for the steady state to be attained. In Fig. 3, the steady state concentration of Cd^{2+} has been plotted against the CO_2 vol % to air of the blowing gas. 8.5 vol % of CO_2 was found to be the optimum condition for the removal of Cd^{2+}, when R_m (the mole ratio of sulfur in the injected CaS_x per Cd^{2+} in the simulated wastewater) was 10 or 15, for C_{in} (the inlet concentration of Cd^{2+})=75 ppm. Consequently, the blowing gas containing 8.5 vol % of CO_2 was utilized in the following experiments. Figure 4 shows the steady state concentration of Cd^{2+} in the treated water plotted against R_m. The continuous plant can remove Cd^{2+}, even with R_m=5.0 for C_{in}=100 ppm, *i.e.*, closely at the stoichiometric amount of the coagulant (R_m=4.7 to 5.4).[2] This compares to the batch processing which needs more units of coagulant as shown by the dotted line in Fig. 4, for C_0=100 ppm. The economization of coagulant is mainly attributed to the recycling of H_2S.

Figure 5 shows the sulfide ion concentration detected by the ion meter against R_m. The keys in Fig. 5, *i.e.*, R_0, T_0, and O indicate the samples taken from the reactor, thickener, and desorber, respectively. The treated water (key: O) was found to be desorbed as

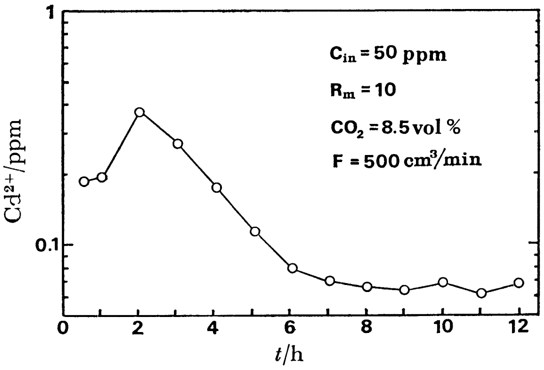

Fig. 2. Attainment to the steady state concentration with the continuous processing of Cd^{2+}.

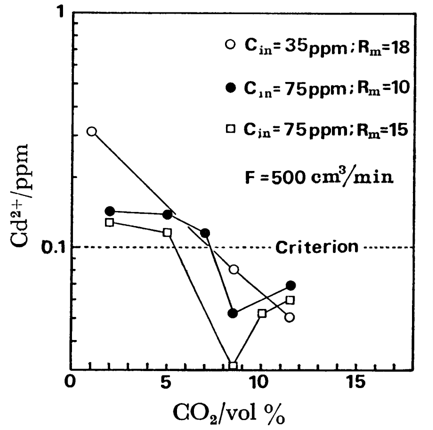

Fig. 3. Steady state concentration of Cd^{2+} *vs.* CO_2 vol % in the blowing gas.

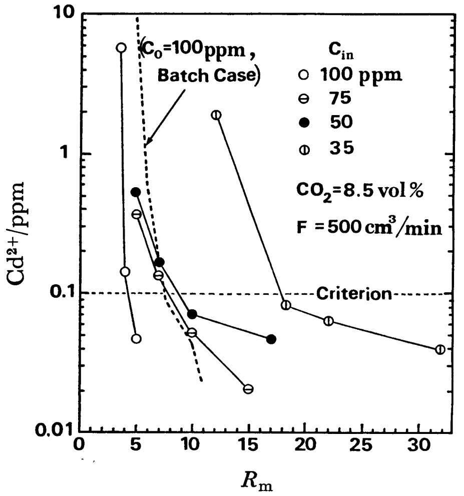

Fig. 4. Steady state concentration of Cd^{2+} *vs.* R_m.

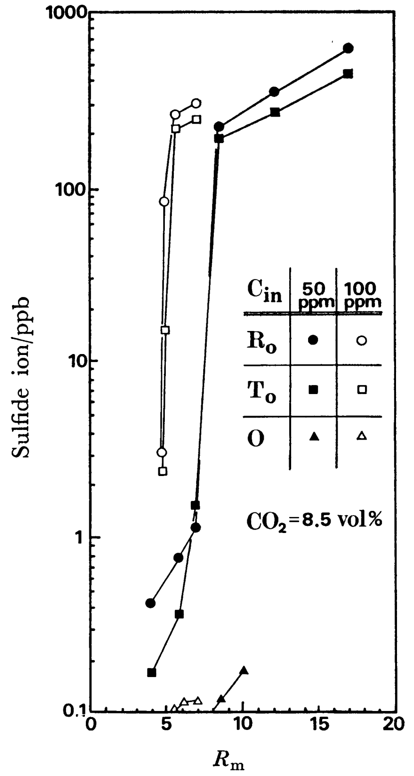

Fig. 5. Detected sulfide ion concentration by ion meter *vs.* R_m.
R_0: reactor outlet, T_0: thickener outlet, O: desorber outlet.

to have the sulfide ion concentration below 0.2 ppb. In water, H_2S is known to dissociate as shown by Eqs. 5 and 6, with dissociation constants of $K_1=[H^+][HS^-]/[H_2S]_{aq}=10^{-7.1}$ and $K_2=[H^+][S^{2-}]/[HS^-]=10^{-12.4}$ at 20 °C.[6]

$$(H_2S)_{aq} \underset{}{\overset{K_1}{\rightleftharpoons}} HS^- + H^+, \quad (5)$$

$$HS^- \overset{K_2}{\rightleftharpoons} S^{2-} + H^+. \quad (6)$$

From Eqs. 5 and 6, the mole fractions of $(H_2S)_{aq}$, HS^-, and S^{2-} are represented as functions of pH;

$$[H_2S]_{aq}/C_{TDS} = 1/Q, \quad (7)$$

$$[HS^-]/C_{TDS} = 10^{-7.1+pH}/Q, \quad (8)$$

$$[S^{2-}]/C_{TDS} = 10^{-19.5+2pH}/Q, \quad (9)$$

where $Q=1+10^{-7.1+pH}+10^{-19.5+2pH}$ and C_{TDS} is the total molar concentration of the dissolved sulfides ($C_{TDS}=[H_2S]_{aq}+[HS^-]+[S^{2-}]$). The pH of the treated water with the blowing gas with 8.5 vol % of CO_2 was measured as 6.1. At pH=6.1, the mole fractions of $(H_2S)_{aq}$, HS^-, and S^{2-} calculated from Eqs. 7, 8, and 9 are 0.909, 0.09, and 10^{-7}, respectively. As reported by Ohkawa and Sakai,[7] H_2S in water can be desorbed better on the acidic side, since $(H_2S)_{aq}$ is more readily stripped than HS^- and S^{2-} which need to pass through the associating reaction to $(H_2S)_{aq}$ (Eqs. 5 and 6). 90.9% of C_{TDS} was found to be $(H_2S)_{aq}$ at pH=6.1; the low pH is a direct consequence of the acidity of the CO_2 gas. Thus, the use of CO_2 mixed gas for the CaS_x decomposition is desirable from the view point of H_2S desorption. The reason for the adjustment of the samples pH to 10.0 can be explained from Eqs. 7, 8, and 9 as follows. At pH=10.0, the mole fractions of $(H_2S)_{aq}$, HS^-, and S^{2-} are estimated as 0.001, 0.995, and 0.004, respectively. Therefore, the detected sulfide ion by a pair of electrodes can be said to be almost equal to C_{TDS}.

Figure 5 indicates that the R_m values crossing down the criterion for Cd^{2+} in Fig. 4 for $C_{in}=50$ and 100 ppm agrees closely with the R_m values of Fig. 5 when the sulfide ion concentration shows steep increase. This good agreement of R_m values suggests that the optimum conditions for Cd^{2+} removal can be detected immediately by measuring the sulfide ion concentration at the outlet of the reactor.

The agglomeration of precipitates is known to be accelerated by the solid particle concentration, or the number of particles existing in the water. To increase the solid particle concentration in the reactor, the precipitated sludge was recycled from the thickener to the top of the reactor by a peristaltic pump at 30 cm^3/min. Figure 6 shows a result of Cd^{2+} removal with and without the sludge recycle. The sludge recycle was found to be effective in reducing the amount of coagulant as can be seen from Fig. 7. In Fig. 7, the abscissa is converted from R_m in Fig. 4 to $C_s=R_m \times C_{in}$, C_s being defined as the total sulfur atom concentration injected with the coagulant. Since the sulfur atoms added give rise to equivalent moles of metal sulfide and solid sulfur particles, as seen from Eqs. 1 to 4, C_s can be interpreted as the solid particle concentration generated by the CaS_x process. Since the Cd^{2+} concentration in Fig. 7 shows a single correlation with the solid particle concentration, C_s, the precipitation of heavy metals may depend solely on the solid particle concentration of the water. The recycling of the sludge will increase the solid particle concentration and may work effectively to precipitate heavy metals with less coagulant.

Figure 8 shows the result of the continuous processing of wastewater simultaneously contaminated with 25 ppm of Cd^{2+}, 100 ppm of Pb^{2+} and Zn^{2+}, 40 ppm of Cu^{2+}, and 5 ppm of Cr(VI) and Hg^{2+}. Figure 8 indicates that R_m=5.0, *i.e.*, nearly stoichiometric

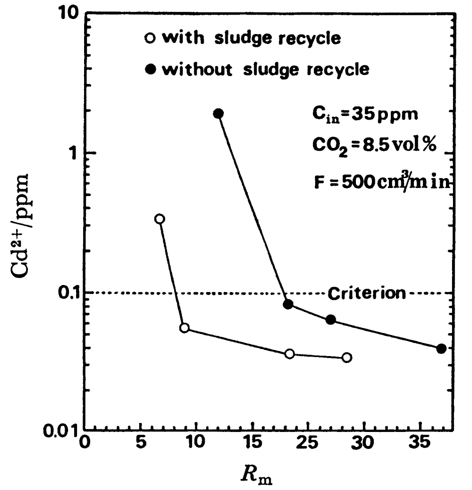

Fig. 6. Removal of Cd^{2+} with and without sludge recycle.

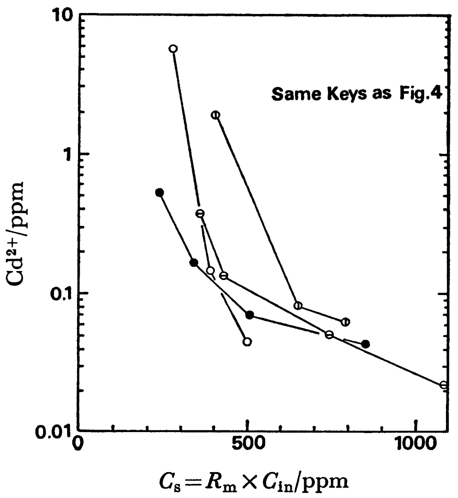

Fig. 7. Cd^{2+} *vs.* solids particle concentration or the sulfur atom concentration.

amount of coagulant is sufficient for the removal of contaminants. The removal concentrations are approximately proportional to the solubilities of the respective sulfides; 6.0×10^{-18} ppb for HgS, 1.62×10^{-10} ppb for CuS, 2.58×10^{-6} ppb for CdS, 2.0×10^{-6} ppb for PbS, 1.1×10^{-3} ppb for ZnS, and 8.3×10^{-2} ppb for Cr(OH)$_3$ at pH=7.0.[6] Cr(VI), Pb^{2+}, and Zn^{2+} show deviations from the order of solubility. The batch processing data shows a higher residual concentration for Zn^{2+}; the reason for this is not evident at present, but it is felt that the particle size of the precipitate may be concerned.

The samples taken from the outlets of the reactor and the thickener were filtered by membranes of various pore sizes, and the residual heavy metals concentrations were determined by atomic absorption, the results of which are shown in Fig. 9. Cr(VI) and Pb^{2+} are found to be finer in gain size. The growth of precipitates was shown to take place in the thickener. Figure 9 also shows that the precipitates grow to about 8 μm and this is thought sufficient for sand filtration.

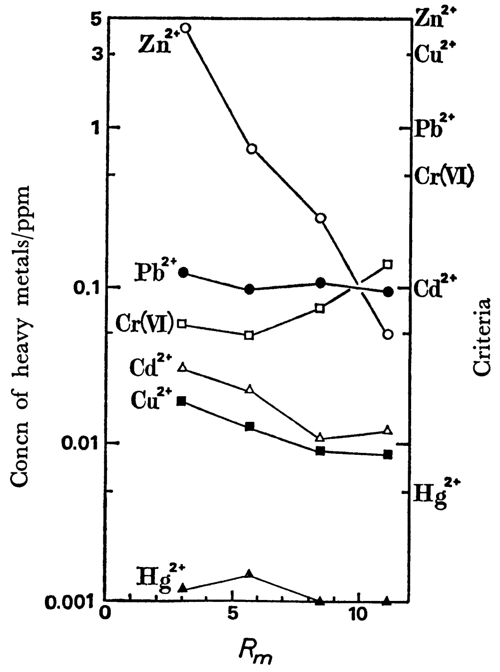

Fig. 8. Simultaneous removal of heavy metals by the continuous CaS$_x$ process.

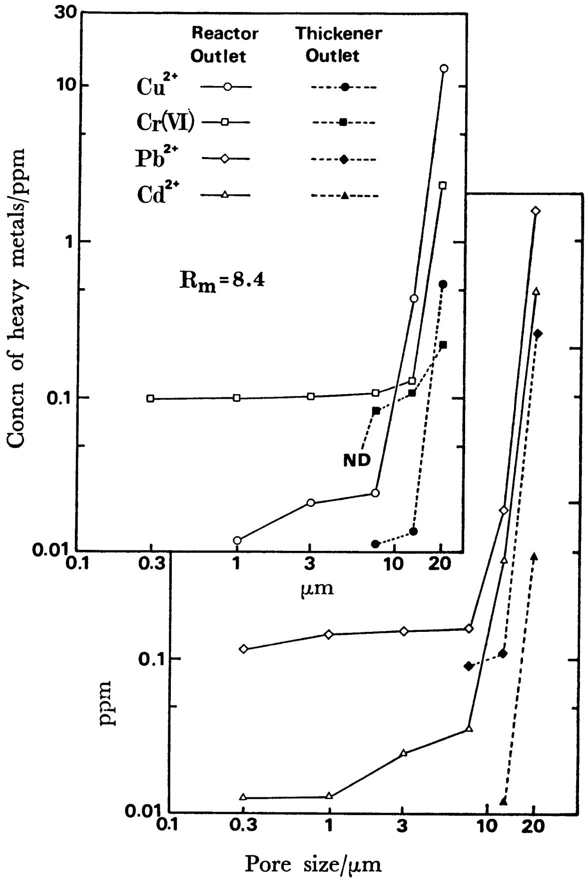

Fig. 9. Residual concentration of heavy metals *vs.* pore size of membrane filter.

Conclusion

Continuous CaS$_x$ process study has lead to the following conclusions.

1) The amount of coagulant needed for the heavy metal removal can be lowered by recycling H_2S in the continuous operating plant.

2) The solid particle concentration in the reactor depends on the removability, which may explain the effective precipitation of Cd^{2+} by the recycling of the sludge.

3) The condition for removal of heavy metals can be detected by an electrode type ion meter. This simple method may enable the plant to be operated automatically with the least amount of coagulant.

4) The desorption of sulfide ions from the treated water can be effectively attained by the blowing gas or air containing CO_2.

The authors wish to thank Assoc. Prof. Kei Miyanami of the University of Osaka Prefecture, Prof. Ryuzo Ito of Osaka University, Profs. Takataro Suda, Yoshiki Sanoh, and Mr. Kiyochika Yahikozawa of Shinshu University for their useful discussions.

The present work was partially supported by a Grant-in-Aid for Developmental Scientific Research from the Ministry of Education, No. 185210.

References

1) K. Yahikozawa, T. Aratani, R. Ito, T. Suda, and T. Yano, *Bull. Chem. Soc. Jpn.*, **51**, 613 (1978).

2) T. Aratani, K. Yahikozawa, H. Matoba, S. Yasuhara, and T. Yano, *Bull. Chem. Soc., Jpn.*, **51**, 1755 (1978).

3) T. Aratani, Y. Nakata, H. Matoba, S. Yasuhara, and T. Yano, *Bull. Chem. Soc. Jpn.*, **51**, 2705 (1978).

4) K. Miyanami, K. Tojo, and T. Yano, *J. Chem. Eng. Jpn.*, **6**, 518 (1973).

5) "Chemical Engineers' Handbook," 4th ed, ed by J. H. Perry, McGraw-Hill, New York (1963).

6) "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964).

7) H. Ohkawa and N. Sakai, Presentation No. A302, the 40th Annual Meeting of the Soc. of Chem. Engr. of Japan, Nagoya, April 1975.

8) V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, N. J. (1962).