Conditions for the Precipitation of Heavy Metals from Wastewater by the Lime Sulfurated Solution (Calcium Polysulfide) Process

Toshiro ARATANI, Kiyochika YAHIKOZAWA,* Hitoshi MATOBA,**
Shigeki YASUHARA, and Takeo YANO

Department of Chemical Engineering, College of Engineering, University of Osaka Prefecture, Mozu-Ume, Sakai, Osaka 591
**Department of Chemical Engineering, College of Textile Science and Technology, Shinshu University, Tokida, Ueda, Nagano 386*

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A new chemical precipitation process utilizing CaS_x solution as a single coagulant was tested for the removal of heavy metals from a batch stirred vessel. The precipitation of heavy metals from the simulated wastewater was investigated under varing conditions of pH, temperature, and heavy metal concentrations. Several agitating speeds were studied for the gases (atmospheric air and CO_2 gas) blown into the water to decompose the coagulant (CaS_x). The findings are as follows: Heavy metal removal in keeping with the water quality standards in Japan was achieved for the simulated wastewater having pH's between 3 and 11, and the temperatures from 10 to 85 °C. The agitating speed for optimum removal was found to be 10 Hz. More than 250 ppm of the initial heavy metal concentration gives sufficient removal at stoichiometric quantities of coagulant, while less than 50 ppm of the initial concentration results in rather poor removal owing to the colloidal properties of the metal sulfide or hydroxide. For low concentrations of heavy metals, several units of the coagulant over stoichiometric amount are necessary for sufficient precipitation to achieve the water quality standards.

The effluent from the industry and the cities known as wastewater has various pH's, temperatures and concentrations of contaminants. Therefore, in designing and operating wastewater treatment plants, information about the properties of the wastewater to be treated and the precipitating conditions are of great importance. For the removal of heavy metals, there have been many processes with high efficiency.[1] Among these, the chemical precipitation processes are most widely put into practice.[2,3] The temperature and pH of the wastewater, the initial concentration of heavy metals, the amount of coagulant to be injected, and the agitating speed of the stirrer are known to adversely affect the heavy metal removal by chemical precipitation.[1]

In the previous work,[4] a new chemical precipitation process has been developed to cope with the severe water quality standards in Japan for Hg^{2+}, Cd^{2+}, and Cr(VI). This process utilizes "Lime Sulfurated Solution" as a single coagulant to precipitate the heavy metals from wastewater as metal sulfides or hydroxides. Kinetic studies on this process have already been done for the removal of heavy metals: Hg^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, and Cr(VI).[4,5]

In the present study, optimum precipitating conditions have been discussed. The conditions for effective coagulation were investigated experimentally in a batch stirred vessel for the removal of Cd^{2+} and Cr(VI) from simulated wastewater at various pH's, temperatures, and initial concentrations of the heavy metals.

Lime Sulfurated Solution (Calcium Polysulfide) Process

According to previous studies on the apparent kinetics,[4,5] the principal reactions for the precipitation of heavy metals by this process may be summarized as follows.

$$CaS_x + \frac{3}{2}O_2 \longrightarrow CaS_2O_3 + (x-2)S, \qquad (1)$$

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

CaS_x which is the main component of the lime sulfurated solution reacts with O_2 or CO_2 which is blown into the wastewater, and this liberates CaS_2O_3, H_2S, and S (solid sulfur particles), as shown in Eqs. 1 and 2. Bivalent heavy metals denoted by M^{2+} are precipitated as metal sulfides by CaS_2O_3 and H_2S according to Eqs. 3 and 4.

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

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

Trivalent heavy metals, the sulfides of which are usually unstable in water as is the case of Cr^{3+}, may be precipitated as metal hydroxides by the alkaline base of the lime sulfurated solution. Sexi-chromium Cr(VI) (dichromate) is reduced to Cr^{3+} by H_2S or CaS_2O_3 and precipitated as $Cr(OH)_3$.

$$Cr(VI) + \frac{3}{2}H_2S \longrightarrow Cr^{3+} + \frac{3}{2}S + 3H^+, \qquad (5)$$

$$Cr(VI) + \frac{3}{2}CaS_2O_3 + \frac{3}{2}H_2O \longrightarrow Cr^{3+} + \frac{3}{2}CaSO_4 + \frac{3}{2}S + 3H^+. \qquad (6)$$

The experimental findings of previous studies[4,5] may be summarized as follows;

(1) Heavy metals, especially Hg^{2+}, Cd^{2+}, and Cr(VI) may be treated below the water quality standards in Japan within 60 min of processing time (fixed temperature of 25 °C, initial pH of 5.0, initial heavy metal concentration of 25 ppm with the amount of the coagulant: $R_m=25$). R_m is defined as the mole ratio of sulfur in CaS_x per M^{2+}.

2) The processing time is dependent on the kinds of

** Present address: Ataka Kogyo Co. Ltd., Sueyoshibashi, Minamiku, Osaka 542.

heavy metals and gases (air and CO_2) used for the decomposition of CaS_x, and varies from 5 to 60 min. The rate of precipitation for the bivalent heavy metals is determined by that of the CaS_x decomposition, which is accelerated by CO_2 blowing. The rate of $Cr(OH)_3$ floc formation can be favored by aeration. The pH values of the water treated with aeration or CO_2 blowing were found to change to 7 and 6, respectively.

Experimental

The precipitation of heavy metals at various conditions by CaS_x solution was carried out in a batch stirred vessel with gas (air or CO_2) blowing. The vessel was made of glass and cylindrical in shape and had a flat bottom. The diameter and height of the vessel were, respectively, 15 and 22 cm. Four baffles were positioned symmetrically on the inside wall of the vessel. The vessel contents were agitated by a six-bladed turbine driven by a variable speed electric motor. The vessel was immersed in a constant temperature bath, maintained between 10 and 85 °C by set of control systems consisting of a contact thermometer and a heater or cooler. The gas (air or CO_2) for the decomposition of CaS_x was blown through a pipe of 1 mm inner diameter attached just below the center of the turbine. Simulated wastewater containing heavy metals as soluble salts (nitrates were used for bivalent metals and potassium dichromate was used for sexi-chromium) was poured into the vessel. After ensuring steady state conditions in the vessel, removal of the heavy metals was started by injecting the coagulant (CaS_x solution). The sample liquor taken from the vessel at predetermined time intervals was filtered on a No. 5C filter paper and, if necessary, by a membrane filter and analyzed by an atomic absorption spectrophotometer according to JIS-K0102.

Results and Discussion

Effect of the Injected Amount of the Coagulant. Removal experiments were undertaken for Cd^{2+} as the representative of the bivalent heavy metals which were precipitated as metal sulfides, and for Cr(VI) as one of the multivalent heavy metals precipitated as metal hydroxides after reduction to the trivalent state.

Figure 1 shows the concentration of Cd^{2+} in the filtrate plotted against the processing time for the various mole ratios (R_m) of sulfur in CaS_x solution per metal (at 25 °C, agitating speed of 10 Hz, and initial heavy metal concentration (C_0) of 25 ppm). The CO_2 gas was blown in at the rate of 0.5 dm^3/min. The steady state concentration is likely to be realized after 80 to 120 min of the processing time and enough removal was found to be attained for R_m over 25. The steady state concentrations of Cd^{2+} after 120 min were measured for various values of C_0 and R_m (the same operating conditions as the data in Fig. 1). The result is shown in Fig. 2. For the highest value of $C_0=1000$ ppm, $R_m=5.9$ was found sufficient to achieve the water quality standard (criterion). Since x atoms of sulfur in the polysulfide are necessary to precipitate an ion of Cd^{2+} if the reactions proceed as described by Eqs. 1 to 4, then $R_m=x$ is the theoretical stoichiometric amount of the coagulant. x in CaS_x is reported as $x=4.7$ to 5.4.[6] The higher R_m value observed here, *i.e.*, $R_m=5.9$ is a little more than the stoichiometric amount for $C_0=1000$ ppm. One explanation for this may be that the sulfur from the CaS_x partly leaks as H_2S from the liquid phase to the exhaust gas phase, though the H_2S generated is in relatively smaller quantities under aeration than CO_2 blowing. Figure 3 illustrates the precipitation of Cd^{2+}, when CO_2 gas is used as the blowing gas instead of air. For the same values of C_0, R_m values increased a little with CO_2 blowing, in comparison with aeration. This increase may be due to the fact that CO_2 blowing generates H_2S which tends to leak from the liquid phase to the exhaust gas phase without any precipitating reaction with Cd^{2+}. Aeration generates mainly CaS_2O_3 which does not leak from the liquid phase. This leakage may explain the higher R_m values in Fig. 3 (CO_3 blowing) than that in Fig. 2 (aeration). CO_2 blowing had the advantage over aeration in that it shortened the processing time.[4] Aeration was found to utilize the sulfur from CaS_x more effectively than CO_2 blowing in the batch process. With decrease in C_0 from 1000 ppm, values of R_m (to achieve the same standard) increased gradually as shown in Figs. 2 and 3 for both cases of aeration and CO_2 blowing. A reason for this increase may be the generation of finer particles of metal sulfide for the lower values of C_0. These finer particles may pass the No. 5C filter paper and may be detected as apparent liquid phase concentration by atomic absorption to give high concentration of Cd^{2+} in the filtrate.

The behavior of these suspended fine particles was investigated by the following experiments. The sample liquors were filtered by membrane filters of various pore sizes. The filtrates were acidified with HCl to dissolve the metal sulfides and the atomic absorption was measured. Figures 4 and 5 show the apparent particle size distributions of the suspended colloidal CdS. These distributions are calculated from the filtrate concentrations based on the assumption that the membrane filter works like a standard mesh. As may be seen from

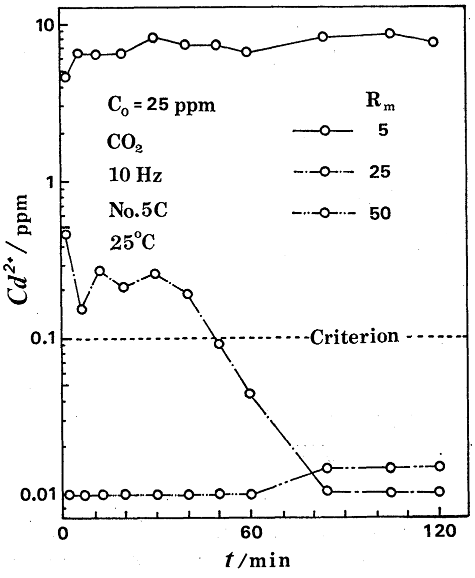

Fig. 1. Concn of Cd^{2+} in filtrate *vs.* processing time (CO_2 blowing, at initial concn of Cd^{2+}; $C_0=25$ ppm, agitating speed of 10 Hz, filtered on No. 5C, for mole ratio of coagulant to heavy metal; $R_m=5$, 25, and 50).

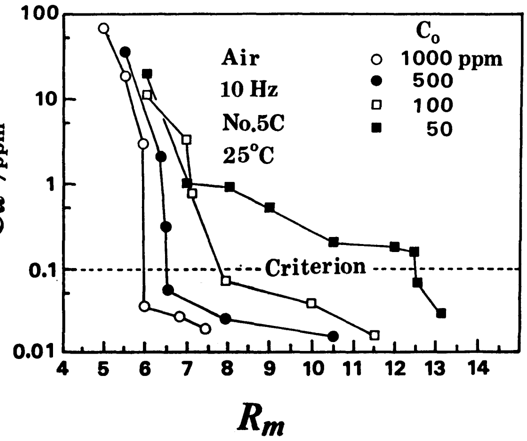

Fig. 2. Concn of Cd^{2+} in filtrate after 120 min of aeration *vs.* R_m (at 25 °C, 10 Hz, by No. 5C, for C_0=1000, 500, 100 and 50 ppm).

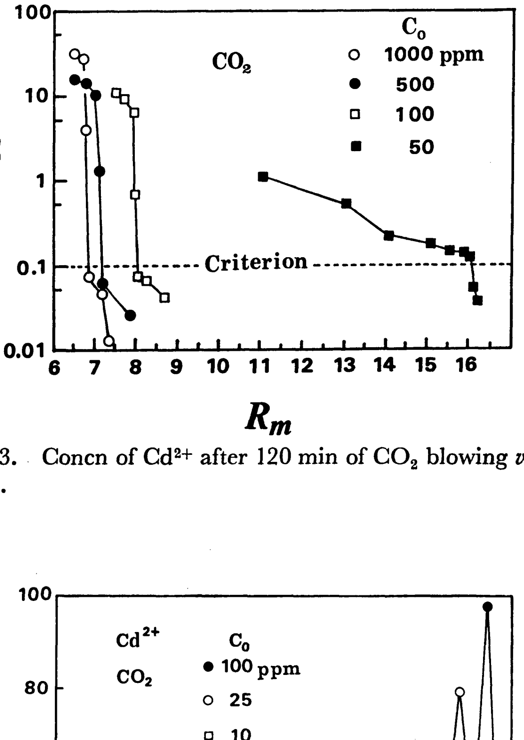

Fig. 3. Concn of Cd^{2+} after 120 min of CO$_2$ blowing *vs.* R_m.

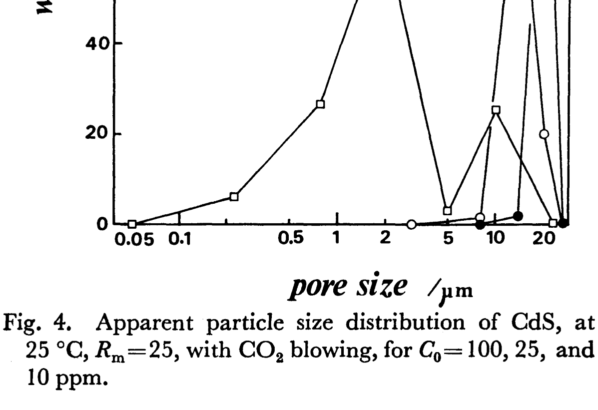

Fig. 4. Apparent particle size distribution of CdS, at 25 °C, R_m=25, with CO$_2$ blowing, for C_0=100, 25, and 10 ppm.

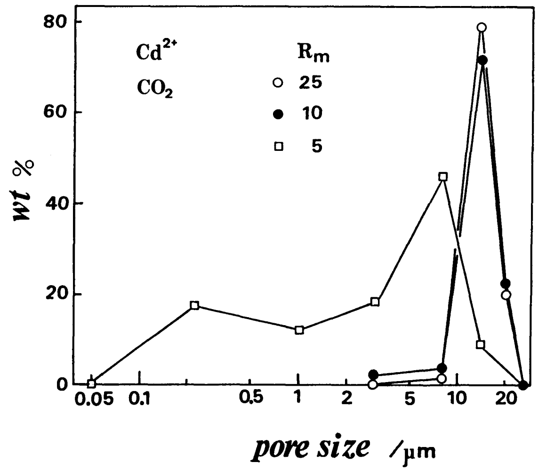

Fig. 5. Apparent particle size distribution of CdS, at 25 °C, C_0=25 ppm, with CO$_2$ blowing, for R_m=25, 10, and 5.

Fig. 4, decreases in C_0 gives rise to the generation of fine particles for R_m=25. Increase in R_m results in the generation of the big particles, as shown in Fig. 5. To separate the precipitated CdS completely for R_m=25 and C_0=25 ppm, a filter having a maximum pore size of 3 μm was suitable as may be seen from Figs. 4 and 5. The mean particle size of this process was found to be over 8 μm from Figs. 4 and 5, for R_m greater than 10 and C_0 greater than 25 ppm.

Processing results of Cr(VI) by CaS$_x$ are shown in Fig. 6 with aeration and in Fig. 7 with CO$_2$ blowing. The residual concentration of total chromium in the filtrate after 180 min of the processing time is shown as the ordinate. As observed with Cd^{2+}, the concentration decreases critically near the theoretical stoichiometric injection of CaS$_x$ only for aeration. If the reducing reactions follows Eqs. 1 to 5 or 6 and x is taken as 4.7 to 5.4,[6] the theoretical stoichiometric amount of CaS$_x$ needed to treat Cr(VI) is $R_m=(3/2)x$, that is, R_m=7.1 to 9.1. Figure 8 shows the apparent particle size distribution of Cr(OH)$_3$ flocs. CO$_2$ blowing was found to give a finer particle size than aeration. On comparing Figs. 6 and 7, values of R_m (to achieve the standard) are observed to differ more evidently with aeration and CO$_2$ blowing than those with Cd^{2+} (see Figs. 2 and 3). CdS flocs have almost the same particle size distribution both for CO$_2$ blowing and aeration. On the other side, Cr(OH)$_3$ flocs formed by the CaS$_x$ process with CO$_2$ blowing are relatively fine and need more processing time to flocculate than with aeration. This slow flocculation was observed as a gradual decrease in the amount of the light green particles (Cr(OH)$_3$) (the suspension was held in the filtrate for about 60 min with the CO$_2$ blowing).

Effect of Temperature. Figure 9 shows the concentration of Cd^{2+} in the filtrate (No. 5C) after 120 min of the processing time plotted against the temperature of the simulated wastewater (CO$_2$ blowing for C_0=25 ppm). For large values of R_m and C_0, the removal of Cd^{2+} is almost independent of the temperature. The temperature may not have such an effect on the precipitation of Cd^{2+} with large values of R_m and C_0 when

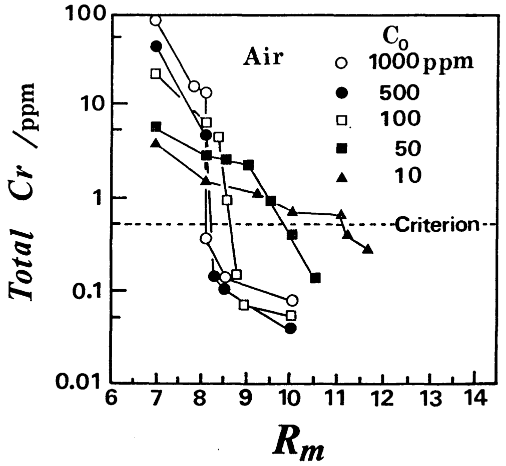

Fig. 6. Concn of total Cr after 180 min of aeration *vs.* R_m, at 25 °C, 10 Hz, by No. 5C, for C_0=1000, 500, 100, 50, and 10 ppm.

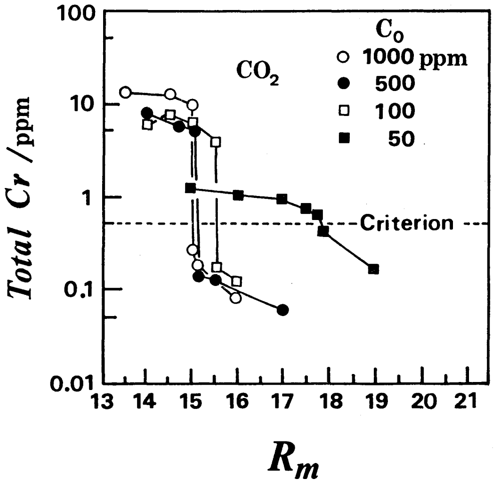

Fig. 7. Concn of total Cr after 180 min of CO_2 blowing *vs.* R_m.

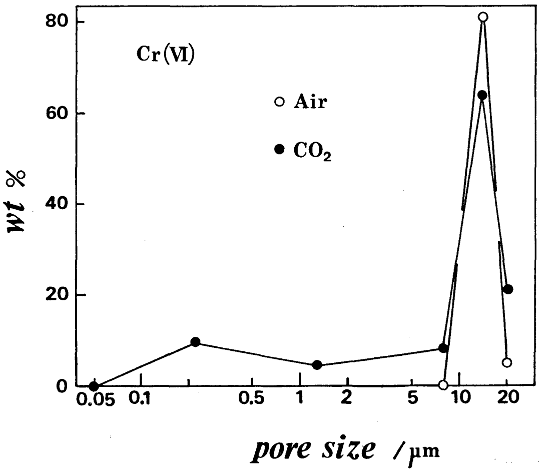

Fig. 8. Apparent particle size distribution of $Cr(OH)_3$, at 25 °C, C_0=25 ppm, after 15 min from the start of run with aeration or CO_2 blowing.

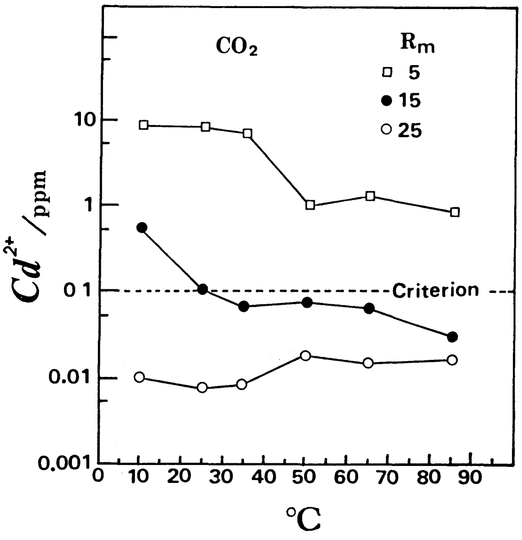

Fig. 9. Effect of temperature: Concn of Cd^{2+} *vs.* processing temperature, with CO_2 blowing, at 25 ppm, by No. 5C, for R_m=5, 15, and 25.

the particle size is large. The precipitation seems to be related to the temperature of the wastewater for R_m=5 which gives fine particles as shown in Fig. 5. Removal meets the criterion conditions for wastewater between 10 and 85 °C. Thus the CaS_x process is able to cope with variations in the temperature of the wastewater to be treated.

Effect of Agitating Speed. The removal of Cd^{2+} is shown plotted against the agitating speed of the impeller for C_0=1000 ppm and 50 ppm in Figs. 10 and 11, respectively. For C_0=1000 ppm which produces a precipitate of large particle size, the removal is almost independent of change in the agitating speed. For C_0= 50 ppm which generates the fine suspended particles, the agitation affects the removal. The removal is thought to be promoted by the agitation which accelerates the flocculation. However, removal at an agitation higher than 10 Hz results in adverse removal, and this may be due to the fragmentation of the flocs, once

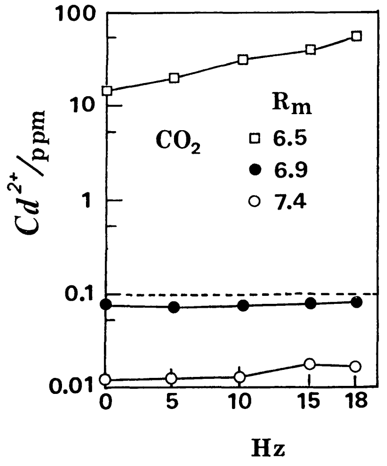

Fig. 10. Effect of agitating speed: Concn of Cd^{2+} after 120 min of CO_2 blowing *vs.* Hz, at C_0=1000 ppm, 25 °C, by No. 5C.

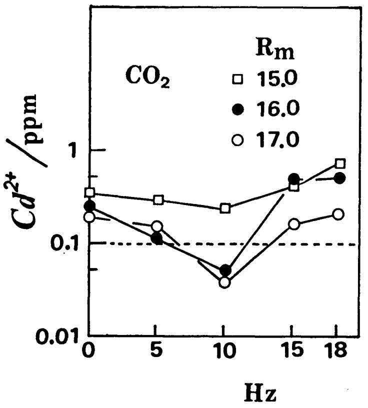

Fig. 11. Concn of Cd^{2+} with CO_2 blowing *vs.* Hz, at $C_0=50$ ppm.

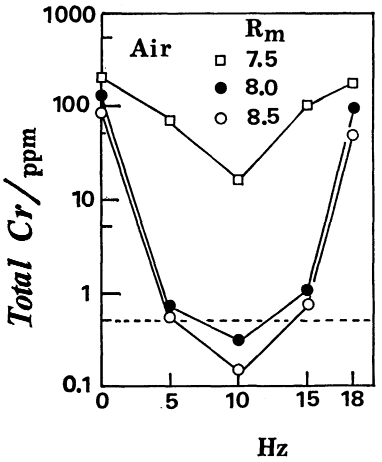

Fig. 12. Effect of agitating speed: Concn of total Cr after 180 min of aeration *vs.* Hz, at $C_0=1{,}000$ ppm, 25 °C, by No. 5C.

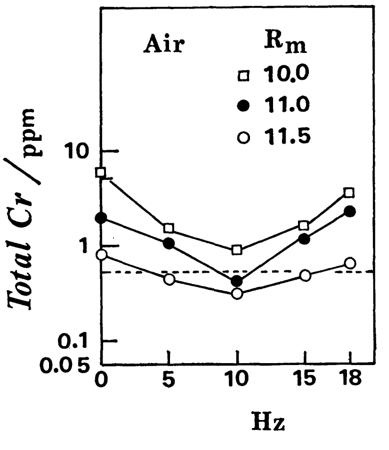

Fig. 13. Concn of total Cr with aeration *vs.* Hz, at $C_0=50$ ppm.

coagulated, by the vigorous mechanical agitation. The fragmentation may produce fine particles that pass through the No. 5C filter paper and detected as apparent Cd^{2+} concentration by atomic absorption measurements.

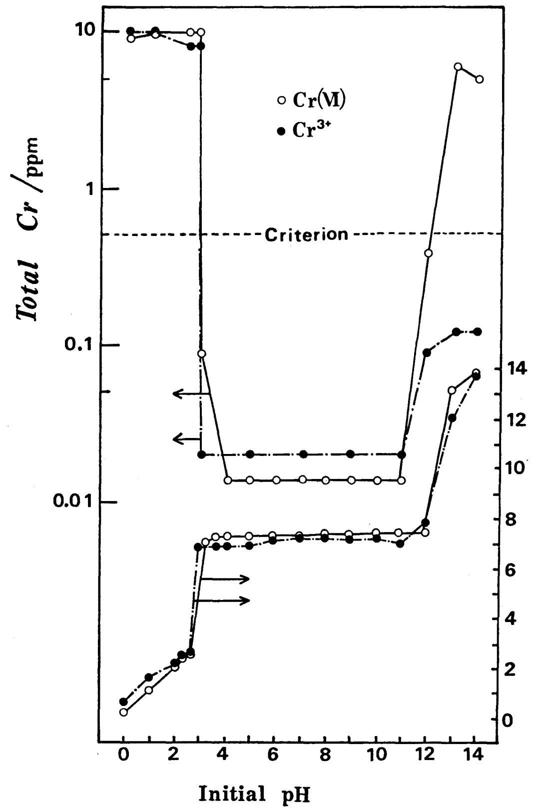

Fig. 14. Effect of pH: Concn of total Cr after 180 min of aeration *vs.* initial pH, at $C_0=25$ ppm, $R_m=25$, 25 °C, by No. 5C: Final pH *vs.* initial pH.

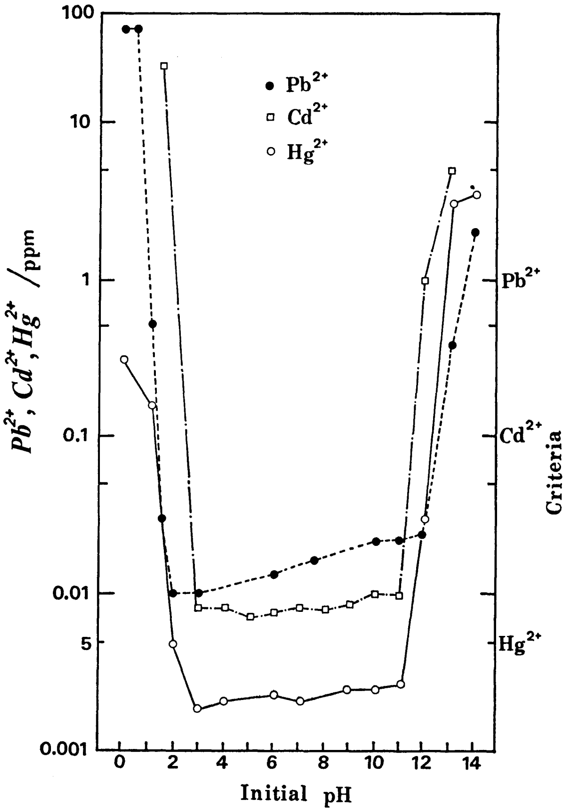

Fig. 15. Effect of pH: Concn of Pb^{2+}, Cd^{2+}, Hg^{2+} *vs.* initial pH at $C_0=25$ ppm, $R_m=25$, 25 °C, by No. 5C.

For the removal of Cr(VI), the effect of the agitating speed is shown in Fig. 12 with $C_0=1000$ ppm and Fig. 13 with $C_0=50$ ppm. In contrast to the Cd^{2+} removal, at $C_0=1000$ ppm the Cr(VI) removal was more affected by the aeration than at $C_0=50$ ppm. In the present, the reason for this is not so evident. Possibly, this may be due to the differences between metal sulfides and hydroxides in their mechanisms of flocculation.

Effect of pH. The results of removal with the wastewater having the initial pH from 0 to 14 are shown in Figs. 14 and 15. With a slightly acidic wastewater, the acid in the water may be neutralized by the strong alkaline base of the coagulant, *i.e.*, lime sulfurated solution. With alkaline water, it is neutralized by the acid of the blown gas (CO_2 in air or CO_2 gas) and by the protons liberated as stated in Eqs. 1 to 5. Figure 14 shows the removal of Cr^{3+} and Cr(VI) from simulated wastewater having pH's between 0 to 14. The final pH's are almost constant around pH=7.0, and the removal is satisfactory for the initial pH's between 3 and 11. Figure 15 shows the results of Pb^{2+}, Cd^{2+}, and Hg^{2+} removal from the wastewater of various initial pH's. The same pH range of removal is observed for these bivalent metals as that for Cr^{3+} and Cr(VI). For the other heavy metals Ni^{2+}, Zn^{2+}, and Cu^{2+}, approximately the same removal range of pH has been reported.[5]

Conclusion

The above experiments help to clarify the conditions of the CaS_x process for the removal of heavy metals from wastewater. The experimental findings are summarized as follows.

1) Almost stoichiometric amount of the coagulant is enough for the precipitation of heavy metals when their concentrations are more than about 100 ppm. When the concentrations are less than 100 ppm, several portions of coagulant are needed because of the colloidal properties of the precipitates.

2) The wastewater at wide temperature and pH range is expected to be treated far below the water quality standards for heavy metals in Japan.

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