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Kinetic Studies on the Lime Sulfurated Solution (Calcium Polysulfide) Process for Removal of Heavy Metals from Wastewater

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A new process has been developed for wastewater purification, utilizing "Lime Sulfurated Solution" as a coagulant. Calcium polysulfide, the main component of this solution, decomposes in water on contact with a gas (atmospheric air or CO_2 gas) and reacts with heavy metals. The heavy metals are removed as practically insoluble precipitates. The kinetics of this process were studied in a batch stirred tank vessel to obtain the fundamental data needed for development of a commercial continuous process. The findings are as follows: (1) Processing of bivalent metals Hg^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, and Cu^{2+} are completed in a few minutes to achieve the water quality standards in Japan. (2) Cr^{3+} is flocculated as $Cr(OH)_3$ by the strong alkaline base of CaS_x solution. It takes about 60 minutes for the precipitation with CO_2 blowing, and 30 min with aeration. Cr(VI) is quickly reduced to Cr^{3+} and removed as $Cr(OH)_3$. (3) A simulated wastewater simultaneously contaminated with 6 kinds of heavy metals can be brought well within the standards within 20 min of processing time.

The development of a new process for removal of heavy metals from industrial wastewater is essential for the protection of the environment. A variety of processes have already been proposed and some have been put into practice. For example, ion exchange, reverse osmosis, chemical precipitation, and others have been developed. Among these, the chemical precipitation process is now the most practical and the least expensive.[5] This process can be further divided into the "Hydroxide process" and the "Sulfide process." In the former, heavy metals are precipitated as metal hydroxides. In the ferrite process, which is one kind of hydroxide process, heavy metals are removed by being occluded in the ferrite crystals. Thus, the sludge from this process is less soluble than that from the other hydroxide processes. In the latter process, the heavy metal ions are removed as metal sulfides. A typical example of coagulant is sodium sulfide. The precipitated metal sulfides of a sodium sulfide process, however, are often colloidal and do not grow large enough to allow easy filtration. Consequently, the sodium sulfide process is inevitably followed by the injection of another coagulant (iron(III) chloride or sulfate) for coprecipitation of these colloidal metal sulfides. The sulfide process has the advantage of removing mercury more effectively than the other process, because HgS has the very low solubility products of 10^{-52}.

In the present study, a new sulfide process has been developed, utilizing "Lime Sulfurated Solution" as a single coagulant. The main component of this solution is calcium polysulfide, whose chemical formula is CaS_x, $x=4.7-5.4$.[6] Hereafter, lime sulfurated solution will be briefly written as CaS_x solution. This solution is well known as an insecticide or a disinfectant in agriculture.[1] When used as an insecticide, CaS_x solution decomposes slowly in contact with atmospheric air and produces calcium thiosulfate, hydrogen sulfide, and solid sulfur.[7] For the purification of wastewater contaminated with heavy metals, CaS_x solution decomposes rapidly by blowing a decomposing gas (air or CO_2 gas); heavy metals react with calcium thiosulfate or hydrogen sulfide and are precipitated as metal sulfides or hydroxides. However, the kinetics of these reactions have not been well studied. Thus, some experiments in a batch stirred tank reactor with air or CO_2 blowing were conducted aimed at the removal of heavy metals in order to gain the fundamental kinetic data needed for the design of a commercial continuous process.

Experimental

Apparatus. A batch stirred tank reactor of 2 dm^3 in volume was constructed, as illustrated in Fig. 1, to study the kinetics for the removal of heavy metals from wastewater by CaS_x. The decomposing gas (air or CO_2; flow rate, 500 cm^3/min) is blown in and dispersed into bubbles. The revolution of the impeller was 10 Hz. These revolution and gas flow rates were ascertained to be sufficient for the finest dispersion of the gas bubbles. The excess hydrogen sulfide was caught by the adsorber A, which was packed with appropriate adsorbing pellets. The pH and the temperature in the reactor were measured with a pH meter and a thermometer T.

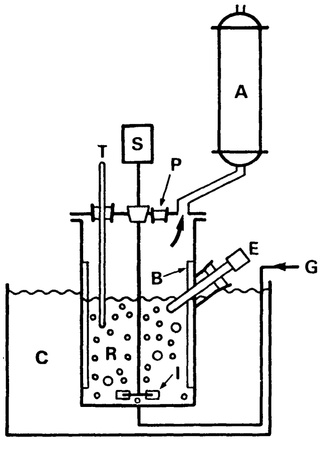

Fig. 1. Experimental apparatus. A: H_2S adsorber, B: baffle plate, C: constant temperature bath, E: glass electrode for pH measurement, G: pipe for gas aspiration, I: turbine impeller, P: plug for CaS_x injection, R: batch reactor, S: stirrer, T: thermometer.

Method. Water contaminated with 6 kinds of heavy metal ions: Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+}, was used as simulated wastewater in this experiment. Cr(VI) was also provided for the removal test by dissolving crystals of potassium dichromate. 2 dm^3 of the simulated wastewater was first placed in a constant temperature bath of 25 °C. The brown-colored CaS_x solution was injected into the reactor, and the blowing of the decomposing gas was immediately started. The sample liquors of 20 cm^3 were taken at the predetermined time intervals and filtered through No. 5C filter paper. The concentration of heavy metals in the filtrates was analyzed by an atomic absorption spectrophotometer according to JIS-K0102.[2] Sample liquors were concentrated by extraction with chloroform solution of dithizone, if high sensibilities were required. The initial pH of the simulated wastewater was set at 5.0. The simulated wastewaters were prepared in two ways. One set contained only one chemical species from among 6 heavy metals to investigate the behavior of each metal. The other was simultaneously contaminated with 6 kinds of heavy metals to determine the practical application requirements.

Results

Heavy metal concentrations in the treated water are compared with the water quality standards (criteria) in Japan. The batch processing time to clear the criteria is also checked to obtain the required residence time (or reactor volume) of a continuous process.

Typical examples of the heavy metal concentrations in the filtrate are plotted against the processing time in Figs. 2 to 5. As for the removal of mercury (Fig. 2), the severe criterion (5 ppb) is clearly covered by this CaS_x process; pure H_2S gas blowing and the Na_2S process can not cope with this criterion. The S^{2-} ion which may dissolve HgS can be eliminated by the decomposition of CaS_x with air or CO_2 gas in the case of the CaS_x process. Calcium salts and solid sulfur are also liberated from CaS_x and they work as flocculating aids to precipitate the metal sulfide (HgS). This flocculating ability was ascertained by an auxiliary experiment, in which precipitation of HgS from colloidal HgS solution was observed by adding a solution that had contained only air-decomposed CaS_x. R_m in the figures indicates the mole ratio of sulfur in CaS_x or Na_2S to heavy metal. For quantities of Na_2S injected larger than $R_m=25$, the processing results in a less effective removal of Hg^{2+}. A limited duration (10 s) blowing of H_2S gas does not give any better removal than the $R_m=2$ injection of Na_2S.

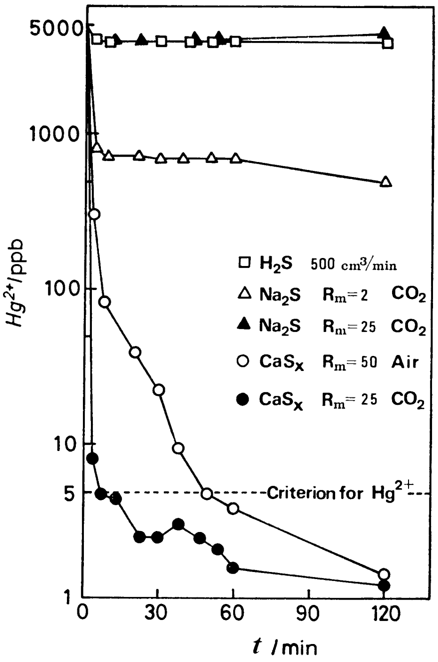

Fig. 2. Removal of Hg^{2+}, initial concentration of Hg^{2+} =5 ppm.

For the conditions of $R_m=25$ and the initial metal concentration of 25 ppm, the other metals were tested. For Cd^{2+} and Zn^{2+} (Fig. 3), CO_2 gas blowing can reduce the processing time compared with the aeration.

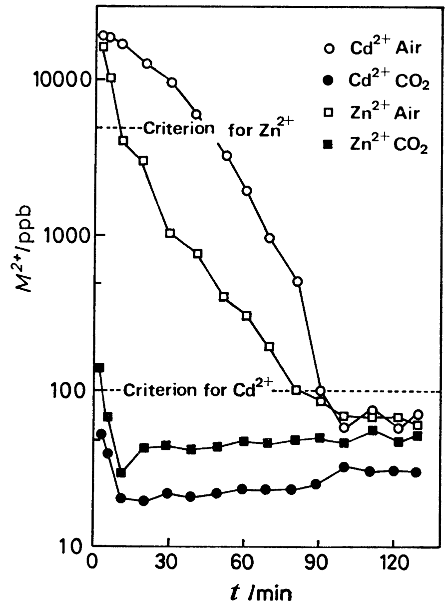

Fig. 3. Removal of Cd^{2+} or Zn^{2+}.

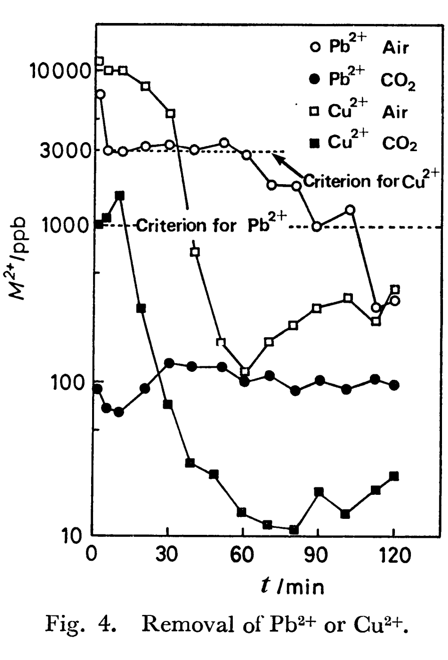

Fig. 4. Removal of Pb^{2+} or Cu^{2+}.

The same tendency is found for Pb^{2+} and Cu^{2+} (Fig. 4). For Cr^{3+} and Cr(VI), the aeration is desirable to shorten the processing time, as illustrated in Fig. 5.

Removal of heavy metals from the simulated wastewater simultaneously contaminated with 6 kinds of heavy metals is shown in Figs. 6 and 7. Long processing time is required for the aeration. CO_2 gas blowing, however, can reduce the processing time to within 30 min.

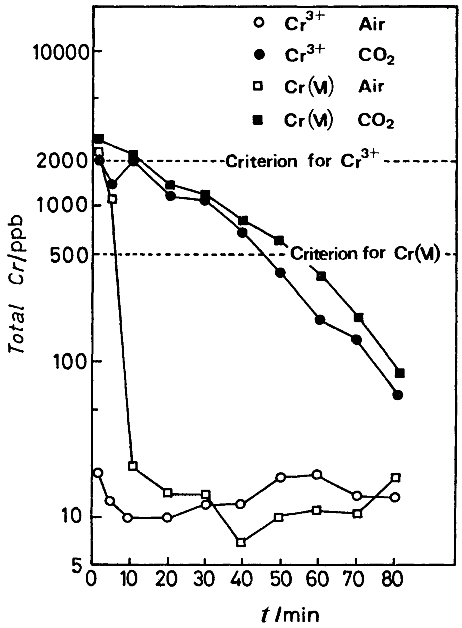

Fig. 5. Removal of Cr^{3+} or Cr(VI).

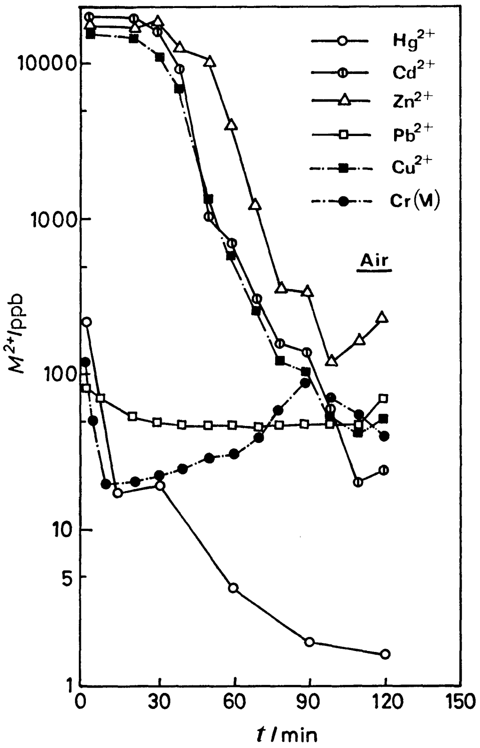

Fig. 6. Simultaneous removal of heavy metals with aeration.

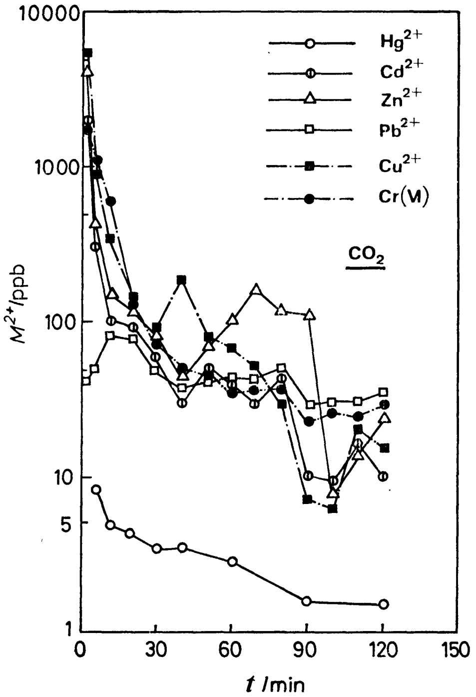

Fig. 7. Simultaneous removal of heavy metals with CO_2 blowing.

Discussion

Apparent kinetic data have been obtained, but it is unsettled question whether the processing time is needed for the decomposition of CaS$_x$ or for the flocculation of the precipitates. The reactions for the decomposition of CaS$_x$ by air or CO_2 and for the precipitation of heavy metals need to be discussed.

The changes in color of the precipitates (or suspended solids) and of the liquid phase were observed while CaS$_x$ was decomposed by air or CO_2, with and without heavy metals. Without any charging of metal ions, the water in the reactor become light brown after the injection of CaS$_x$, because the CaS$_x$ solution has a reddish brown color.

After the aeration, white particles (solid sulfur) which were liberated from CaS$_x$ could be recognized as a suspension or scum, while the liquid phase was still brown. 60 min after the start of aeration, the brown color had gradually disappeared. When the heavy metal ions were in the water, the color of the suspended particles of metal sulfide was gradually predominating over the color of the sulfur particles. Yellow suspended particles (CdS) could vividly be seen in the water containing Cd^{2+}. Similarly, white (ZnS) for Zn^{2+}, dark gray (PbS) for Pb^{2+}, brown (CuS) for Cu^{2+}, and black particles (HgS) for Hg^{2+} were observed.

Upon blowing CO_2, on the other hand, the brown color of CaS$_x$ solution instantaneously disappeared and white sulfur particles were produced. With the presence of heavy metal ions, the color of the suspended metal sulfide, which was different for each heavy metal, was observed immediately (within 1 s) after the start of CO_2 blowing. Thus the decomposition of CaS$_x$ and the precipitation of bivalent metal ions by aeration was found to be considerably slower than that

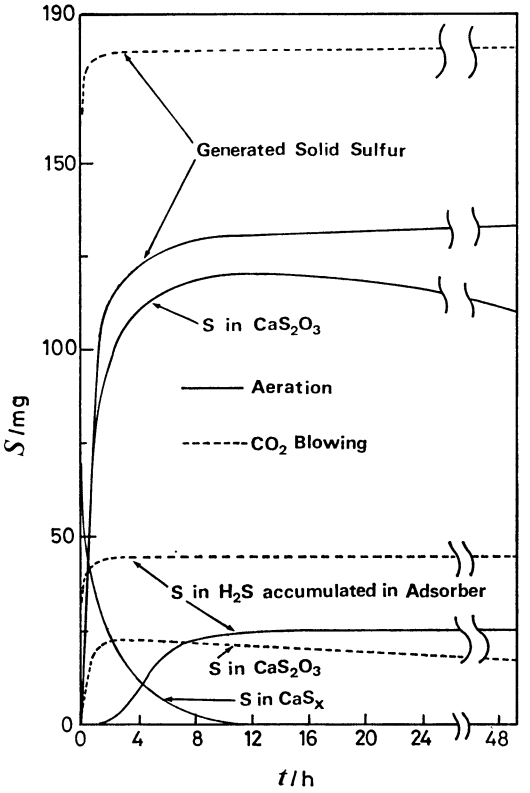

Fig. 8. Decomposition of CaS_x in a flask by aeration or CO_2 blowing; 1 cm^3 of CaS_x solution was added per 1 dm^3 of water.

by CO_2 blowing.

For more detailed research about the reaction kinetics for the decomposition of CaS_x, an auxiliary experiment was undertaken to determine quantitatively how the amounts of generated chemicals vary with time when CaS_x was decomposed in water without heavy metals. The decomposition of CaS_x by air or CO_2 was performed in a flask with a blowing pipe. The substances obtained after the decomposition were chemically analyzed[3,4] as shown in Fig. 8. Hydrogen sulfide, calcium thiosulfate, and solid sulfur (as suspended particles) were clearly recognized. Figure 8 indicates that CO_2 blowing gives rise to a more rapid decomposition of CaS_x than does aeration. This is consistent with the observations of color changes.

From another experiment for the decomposition of CaS_x with pure oxygen gas, it was found that hydrogen sulfide was not evolved by O_2.

The principal reactions of the decomposition of CaS_x by CO_2 and O_2 can be represented as Eqs. 1 and 2, following the above information:

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

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

Equations 1 and 2 imply that the decomposition of CaS_x by CO_2 generates a larger quantity of sulfur than that by O_2 or air. This agreed with the result of Fig. 8. Some H_2S, though only a small amount, was detected for the aerated case in Fig. 8. This H_2S was generated due to the decomposition by trace CO_2 in air, according to Eq. 2. For the wastewater containing heavy metal ions, the precipitating reactions can be written as

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

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

The rate of reaction for Eq. 3 was measured experimentally by a batch test. The test showed that formation of CdS precipitate was observed immediately after the injection of Cd^{2+} into the calcium thiosulfate solution. Equation 3 was found to proceed as quickly as the reaction with Eq. 4.

These processes, from Eq. 1 to 4, are known as the heterogeneous gas-liquid reaction with the formation of precipitates. An analytical treatment by a mathematical model is difficult. In the present study, the apparent kinetics are discussed experimentally.

An interesting result was the color change with the processing of Zn^{2+}. As the solid precipitates (ZnS, S, $CaSO_4$, and $CaCO_3$) are all white and CaS_x is brown, the time needed for the decomposition of CaS_x can be observed as the color change in the solution. With aeration, complete decomposition of CaS_x was observed at about 60 minutes of processing. The time when the steep decrease in the concentration of Zn^{2+} ended agreed exactly with the time when the brown color of injected CaS_x had disappeared (see Fig. 3). For removal of heavy metal ions by aeration, Eq. 1 is thought to be rate-controlling step. This slow decomposition was partly supported by pH measurements, for CaS_x which might dissolve heavy metal ions was thought to be stable in the alkaline side until the base of CaS_x solution was neutralized by the trace of CO_2 in air. The initial pH (pH=5) become rapidly alkaline (about pH=11 in this experimental condition with the simulated wastewater contaminated with a heavy metal) on the injection of CaS_x solution, which has a strong alkaline base. After aeration, the pH gradually returned to neutral (pH=7). With CO_2 blowing, the pH returned rapidly to the slightly acidic side (pH=6). These speeds of pH change may have a relation to the neutralizing speeds of alkaline base of CaS_x solution by CO_2 gas (in air or pure CO_2) and, therefore, partly relate to the rate of decomposition of CaS_x. In applying this CaS_x process to wastewater treatment, the treated water has pH values ranging from 6 to 7, and so can pass the water quality criteria for pH range without injecting any other alkaline reagents. Thus, a more economical treatment is expected than the usual chemical precipitation processes.

For the removal of Cr^{3+}, since the sulfide of Cr^{3+} is unstable in water, Cr^{3+} is not precipitated as Cr_2S_3, but easily removed as $Cr(OH)_3$ by the strong alkaline nature of CaS_x solution. The reduction of Cr(VI) (dichromate) to Cr^{3+} ion is easily attained by H_2S or CaS_2O_3 according to either pair of Eqs. 5 and 6 or 5 and 7.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O, \qquad (5)$$

$$2CrO_4^{2-} + 3H_2S + 10H^+ \longrightarrow 2Cr^{3+} + 3S + 8H_2O, \qquad (6)$$

$$2CrO_4^{2-} + 3S_2O_3^{2-} + 10H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 3S + 5H_2O. \qquad (7)$$

The reduction sheme from Cr(VI) to Cr^{3+} through CrO_4^{2-} was also confirmed by the observation of the color change in the solution. The color of the solution was initially brown (dichromate), and changed to yellow (chromate) on injection of CaS_x and further to light green ($Cr(OH)_3$). With the aeration, these changes were observed within 10 min. For the CO_2 blowing, however, the changes ended in a few seconds, and a fine floc of $Cr(OH)_3$ which partly passed through the No. 5C filter paper was generated. As shown in Fig. 5, the aeration is more effectively than CO_2 gas blowing, for the faster precipitation of Cr^{3+} and Cr(VI). For the precipitation of Cr^{3+}, the slow change in pH with aeration is thought to be favorable to the flocculation of $Cr(OH)_3$ particles. Rapid decomposition of CaS_x with CO_2 blowing may give to the fast formation of a fine floc of $Cr(OH)_3$ by the alkaline base which has been coordinated to CaS_x and freed by the decomposition. The processing rate of Cr^{3+} may be determined by the step of flocculation of the hydroxide floc. For the aeration, the difference between the curves of Cr^{3+} and Cr(VI) in Fig. 5 shows the time required for the reduction of Cr(VI) to Cr^{3+} according to Eqs. 5, 6, and 7. Figure 7 also indicates that chromium can be precipitated faster in the simultaneous removal than in the removal for the case when the water was contaminated only with chromium. This effect is thought to be due to the coprecipitation of $Cr(OH)_3$ with the other sulfides.

Minimum values are observed in the detected concentrations in Figs. 2 to 7. Thus, in the continuous CaS_x process, the mean residence time of the reactor used for the treatment should be so designed as to be equal to the time when the minimum values in the concentrations are attained in batch tests.

Conclusion

From the preceding experiments and discussion, the kinetics of the CaS_x process can be summarized as follows.

(1) CaS_x is decomposed slowly by aeration and rapidly by CO_2 gas blowing, and produces H_2S, $CaCO_3$, $CaSO_4$, and solid sulfur particles. Bivalent heavy metals are precipitated as metal sulfides. The precipitating rate is determined by the step of CaS_x decomposition. Cr^{3+} can also be precipitated as a metal hydroxide more rapidly with aeration than with CO_2 blowing. The precipitating rate of the hydroxide is determined by the step of the flocculation. Cr(VI) is easily precipitated as $Cr(OH)_3$ after rapid reduction from Cr(VI) to Cr^{3+} by H_2S or CaS_2O_3. The solid sulfur and calcium salts work effectively to coprecipitate the metal sulfides and the hydroxide.

(2) The water treated by a single coagulant, CaS_x, can pass the water quality standards in Japan for 6 kinds of heavy metals, within 60 min of processing time. Based on these batch kinetic data, development of a continuous purification process is thought to be easily possible.

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