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The Removal of Heavy Metal, Phosphate, and COD Substances from Wastewater by the Lime Sulfurated Solution (Calcium Polysulfide) Process

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A new chemical precipitation process that had been developed for the removal of heavy metals was extended to the removal of phosphate and COD substances. For simulated wastewater contaminated with heavy metal, phosphate, and COD substances, removal experiments were undertaken in a batch, stirred vessel by using the lime sulfurated solution as a single coagulant. The coagulant, the main component of which is CaS_x, decomposes in water on contact with air or CO_2 gas, and liberates H_2S, CaS_2O_3, $CaCO_3$, $CaSO_4$, and solid sulfur particles. While heavy metals are precipitated as metal sulfides or hydroxides, phosphate is precipitated as calcium phosphate and COD substances are sorbed on the surfaces of the precipitates and they removed. The experimental findings are as follows: (1) The simulated wastewater contaminated simultaneously with phosphate and cadmium ions can be treated better than that contaminated only with the phosphate ion. Also, the CaS_x process is found to be more effective than the $Ca(OH)_2$ process for the removal of phosphate. (2) The removal percentages of COD substances ranged from 40% to 90% according to the sort of substance. The COD removal can be attained by the sorption of the substances mainly on the liberated solid sulfur particles, and partly on the calcium salts.

Wastewater issuing from communities and various industries is often contaminated simultaneously with many sorts of chemical species. Therefore, it is advantageous to develop a wastewater treatment process that can treat these contaminants by a single procedure. As the contaminants, phosphate and nitrogen compounds as well as heavy metals and COD substances have occasioned much public discussion. For the removal of nitrogen compounds, biological denitrification processes have recently been developed and have been playing very important role in the protection of the environment. As for the phosphate removal, however, there are only a few processes that can be practically applied. They are the precipitation processes of phosphate by injecting calcium hydroxide, aluminum sulfate, or iron salts into the wastewater.

In this paper, a new precipitation process is proposed for the removal of phosphate together with heavy metal and COD substances. This process has already been tested for the removal of heavy metals from simulated wastewater.[1,2] By utilizing the lime sulfurated solution as a single coagulant, the apparent reaction kinetics for the removal of heavy metals (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, and Cr(VI)) has been studied by us.[1] We have also discussed the conditions necessary for the precipitation of heavy metals at various initial concentrations from various examples of simulated wastewater with a variety of pH's and temperatures by injecting different amounts of the coagulant at several agitating speeds.[2] Sufficient removal below the water quality standards in our country has been ascertained for the heavy metals, which are precipitated as metal sulfides by the H_2S and CaS_2O_3 that are liberated on the decomposition of CaS_x by air or CO_2 gas, or as metal hydroxides by the strong alkaline base of the CaS_x solution. Accompanied by the decomposition of CaS_x in water, calcium ion and solid sulfur particles are also liberated. The phosphate ion in the wastewater can be expected to be precipitated as calcium phosphate by the calcium ion. Good removal may also be anticipated for the COD substances that may be sorbed on the solid sulfur particles and the other precipitates.

In the present study, experiments were carried out for the removal of phosphate, heavy metal, and some COD substances from the simulated wastewater. Discussion was also made for their removal percentages.

Experimental

Apparatus. The batch stirred vessel utilized in this experiment was the same as that used in the previous works.[1,2] The agitating speed of the impeller was fixed at 10 Hz. The vessel was immersed in a constant-temperature bath at 25 °C. Gas (air or CO_2) was blown into the vessel at a rate of 500 cm^3/min.

Method. For the phosphate contamination, distilled water containing potassium dihydrogenphosphate was used as simulated wastewater. As examples of COD contamination, water solutions of acetone, CMC (carboxymethylcellulose), and Methyl Violet were provided. After the start of a run by blowing in air or CO_2 gas, sample liquors were taken at predetermined time intervals. For the concentration determination with heavy metal, phosphate, and acetone, the liquors were filtered by means of No. 5C filter paper. The heavy metal concentration was determined by means of an atomic absorption spectrophotometer. The phosphate was detected according to JIS-K0102. The acetone was developed by a gas chromatograph (F. I. D.). For the measurement of the CMC concentration, a Stokes viscometer was applied to the liquor filtered by membranes of various pore sizes after the viscosity had been calibrated against the CMC concentration. In the case of Methyl Violet, the centrifugal separation of the precipitates in the liquor was executed at 4,000 G for 10 min, because Methyl Violet is a kind of dye and so, if filtered, it might be sorbed on the filter paper. The supernatant liquors were examined by means of a spectrophotometer in order to determine their concentrations of residual Methyl Violet.

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Results and Discussion

Removal of Phosphate. Figure 1 shows the removal of the phosphate ion, PO_4^{3-}, by means of the CaS_x process and the $Ca(OH)_2$ process. The ordinate indicates the residual PO_4^{3-} concentration after aeration for 180 min in order to decompose CaS_x in the case of the CaS_x process. The $Ca(OH)_2$ process does not need aeration. The abscissa implies the mole ratio of Ca^{2+} in the CaS_x or in the $Ca(OH)_2$ added per PO_4^{3-}.

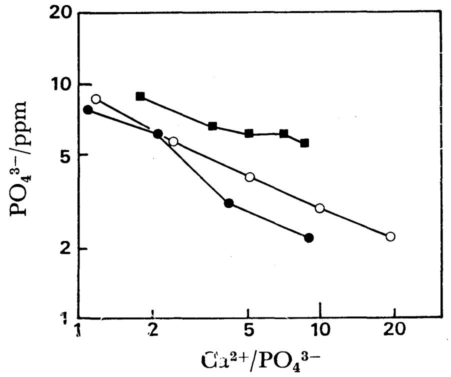

Fig. 1. Residua PO_4^{3-} concn against mole ratio of Ca^{2+} in CaS_x or in $Ca(OH)_2$. Initial concn of PO_4^{3-}=25 ppm, initial pH=6 and final pH=6.2. ■: PO_4^{3-} by $Ca(OH)_2$ process, ○: PO_4^{3-} by CaS_x process with aeration, ●: $PO_4^{3-}+Cd^{2+}$ by CaS_x process with aeration, initial concns are 25 ppm.

The initial concentrations of PO_4^{3-} and Cd^{2+} are both 25 ppm. For the simulated wastewater contaminated only with phosphate, the CaS_x process can treat PO_4^{3-} more effectively than the $Ca(OH)_2$ process for the same ratio of Ca^{2+}/PO_4^{3-}. This better removal of the CaS_x process can be thought to be due to the coprecipitation of calcium phosphate with the solid sulfur particles and calcium salts ($CaCO_3$ and $CaSO_4$) which are liberated from CaS_x. When the wastewater is contaminated simultaneously with PO_4^{3-} and Cd^{2+}, the removal is more effective. As a reason for this effective removal, the precipitation of PO_4^{3-} by Cd^{2+} may be considered. The residual Cd^{2+} concentration was determined to be 0.01 ppm, *i.e.*, far below the effluent standard of 0.1 ppm, for the treatment by the CaS_x process of the simulated wastewater contaminated simultaneously with Cd^{2+} and PO_4^{3-}.

Removal of COD Substances. The percentage of the removal of acetone whose initial cencentration was 1500 ppm was measured for the CaS_x process. The resulting removal percentage of the acetone is shown in Fig. 2 against the mass ratio of sulfur in the CaS_x added per acetone. A removal of more than 40% can be realized by the use of the CaS_x process. The peak of the removal percentage at a mass ratio of about 0.8 may be explained as follows. With the decrease in the quantity of the coagulant, the particle size of the solid sulfur liberated from CaS_x is reduced, as was found in a previous work.[2] The finer particles have a larger surface area in sum total, and so they can sorb more acetone. The removal percentages of acetone by the precipitated sulfur particles and calcium salts ($CaCO_3$(precipitated), $CaSO_4$) are also shown in Fig. 2, since the sulfur particles and the salts are components of the precipitates of the CaS_x process.[1,2] The precipitated sulfur particles used in the experiment of Fig. 2 were prepared by the decomposition of a CaS_x solution (1,000 ppm) with 0.1 M-HCl. The precipitates were filtered by No. 5C and washed with distilled water in order to dissolve the $CaCl_2$. The dried cake of the sulfur particles was assured to have a purity of more than 99.5% of sulfur. Figure 2 shows that the precipitated sulfur particles can sorb about 30% of acetone, while the removal percentages with $CaCO_3$ and $CaSO_4$ are, respectively, 10 and 5%. The CaS_x process can remove about 40% of the acetone, while the precipitated sulfur sorbs 30%. The colloidal sulfur particles generated by the CaS_x process may sorb more acetone by means of some force such as the attractive force by the surface charge,[7] though the mechanism is not evident at present.

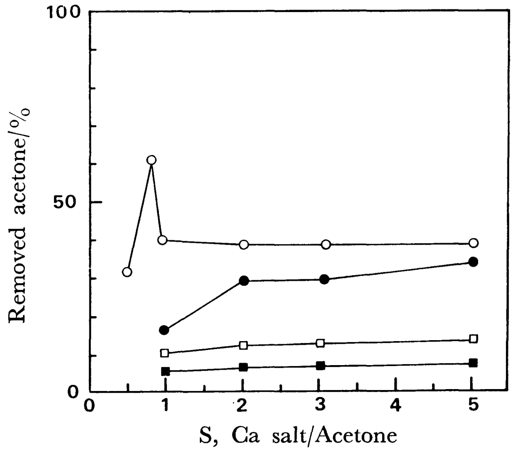

Fig. 2. Removal percentage of acetone against mass ratio of sulfur in CaS_x or of precipitated sulfur and of calcium salts, per acetone. Initial concn of acetone=1500 ppm.
○: By CaS_x process with aeration, ●: by precipitated sulfur, □: by precipitated $CaCO_3$, ■: by $CaSO_4$.

In Fig. 3, the residual concentrations of CMC are plotted against the pore size of the membrane filters used for the filtration of sample liquors. R is defined as the mass ratio of S in CaS_x per CMC. Without CaS_x injection, a part of the CMC, with so long a molecular length, was removed only by filtration with the membrane whose pore size was less than 0.5 μm. The initial concentration of CMC was 60 ppm. The residual concentration of CMC was about 12 ppm for the case of R=25 by aeration with a 0.45 μm membrane, as is shown in Fig. 3. The removal percentage for this case is about 75%. The apparent particle size of the precipitates (S, $CaCO_3$, and $CaSO_4$ with CMC) for the removal of CMC by the CaS_x process was measured by using membranes with various pore sizes like a standard sieve mesh. The apparent particle size distributions are shown in Fig. 4. These distributions are obtained by weighing the masses of the membranes and the cakes, after a processing time of 60 min using the CaS_x process. Aeration gives a little larger

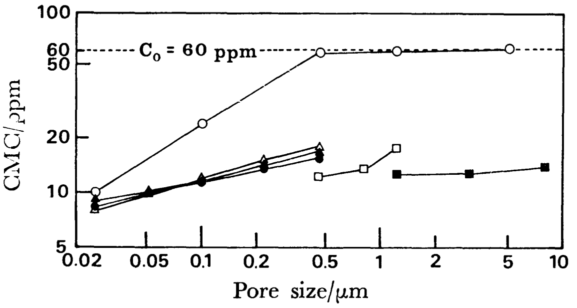

Fig. 3. Residual CMC concn against pore size of membrane. Initial concn of CMC=60 ppm.
○: Only by membrane filtration, ▲: *R*(mass ratio of S in CaS_x per CMC)=6.25 with aeration, ●: *R*=12.5 with aeration, □: *R*=25 with aeration, ■: *R*=50 with aeration, △: *R*=25 with CO_2 blowing.

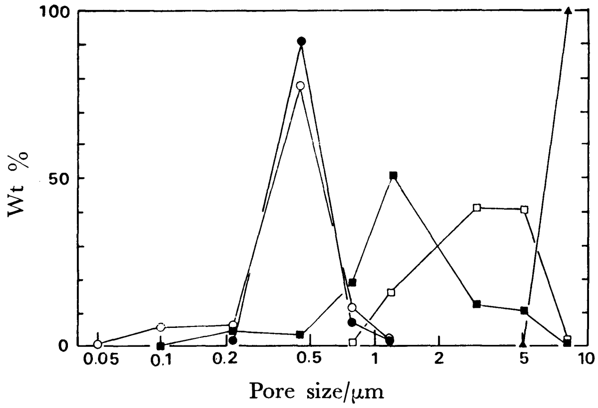

Fig. 4. Apparent particle size distributon of the precipitates formed on the removeal of CMC by CaS_x process.
○: *R*=6.25 with aeration, ●: *R*=12.5 with aeration, □: *R*=25 with aeration, ▲: *R*=50 with aeration, ■: *R*=25 with CO_2 blowing.

particle size than CO_2 blowing for the same *R* value of 25. The *R* value of more than 50 gives a particle size sufficient for the easy separation of the precipitates in the case of CMC processing by the CaS_x process. The particle size shown in Fig. 4 is rather finer than that observed for heavy-metal removal by the CaS_x process, as was reported in a previous paper.[2] This finer particle size may be due to the emulsifying characteristics of the CMC.

Figure 5 shows the removal of Methyl Violet. The initial concentration of 5 ppm was reduced within 0.1 ppm. The removal percentage is about 80% to 90%. The precipitates separated centrifugally were as violet in their color as if they had been dyed. On the other hand, a tentative experiment was carried out for the removal of Methyl Violet by the iron(III) hydroxide process. The removal percentage was only about 1%.

Figures 6 and 7 show photographs of the precipitates taken by means of an electron microscope when CaS_x decomposes in contact with air. Figure 6 shows the precipitates as cake caught on the fibril of No. 5C filter paper. A magnified photograph of the precipitates is shown in Fig. 7. Figures 8 and 9 (magnified) show precipitates obtained by the decomposition of CaS_x with CO_2 gas blowing. Figures 6 to 9 are cases when the substance is precipitated from the water which does not contain any contaminants but 1 cm^3 of the CaS_x solution per dm^3 of distilled water. Photographs of the precipitates when the water is contaminated with 25 ppm of Cd^{2+} and when the mole ratio of S in the CaS_x added per Cd^{2+} is equal to 25 are shown in Figs. 10 to 11 (magnified). While iron(III) hydroxide precipitates are known to be amorphous, the precipitates of the CaS_x process are found to be spheres, and so they have the advantage of easy filtration. Particle properties of the CdS precipitated from aqueous solution

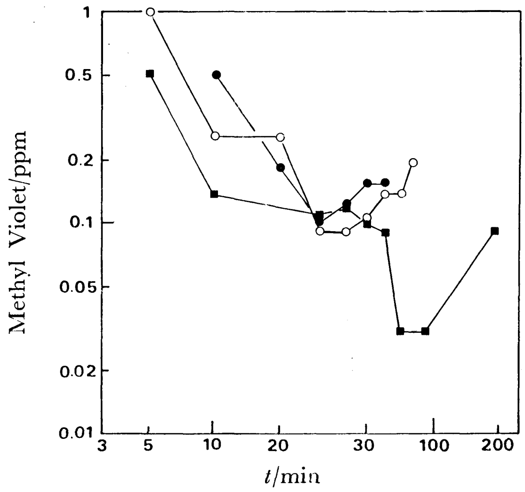

Fig. 5. Residual Methyl Violet concn against aeration time.
●: *R*(mass ratio of S in CaS_x per Methyl Violet)=25, ○: *R*=50, ■: *R*=125.

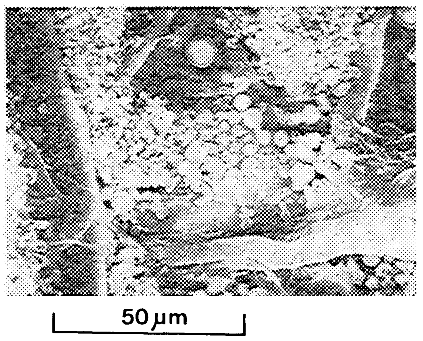

Fig. 6. Precipitates by decomposition of CaS_x with aeration.

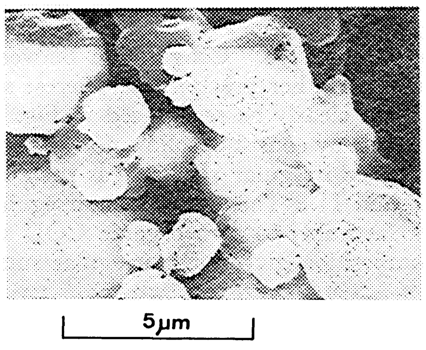

Fig. 7. Magnification of a part of Fig. 6.

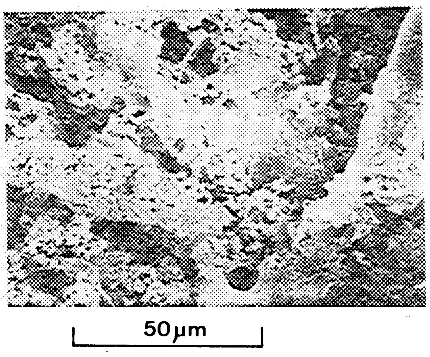

Fig. 8. Precipitates by decomposition of CaS_x with CO_2 blowing.

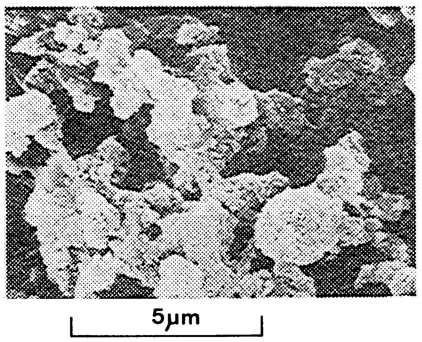

Fig. 9. Magnification of a part of Fig. 8.

of $Cd(NO_3)_2$ or $CdSO_4$ by adding $Na_2S_2O_3$ or H_2S have been studied recently by Hashimoto *et al.*[5] They have shown that the CdS particles are spherical in shape and that the diameter becomes the bigger for the higher concentration of Cd^{2+}. Since the solid sulfur particles formed in the CaS_x process are also spherical in shape as may be seen in Figs. 6 and 7, it is scarcely possible to distinguish CdS from solid sulfur in Figs. 10 and 11. The cubes in Fig. 10 are probably $CaCO_3$ as is shown in Ref. 6. Coagulation between $CaCO_3$ (cubes) and the other precipitates(spheres: solid sulfur and CdS) can clearly be recognized in Fig. 10. Most of the spheres may consist of solid sulfur particles, which have porous or irregular surfaces, as may be seen in Figs. 7, 9, and 11. These porous or irregular surfaces may work favorably to sorb organic COD substances. CO_2 decomposition gives more irregular surfaces than that by aeration. The reason for this is not evident, but the fact that the CO_2 blowing gives rise to the rapid decomposition of CaS_x[1] may be connected with this irregularity.

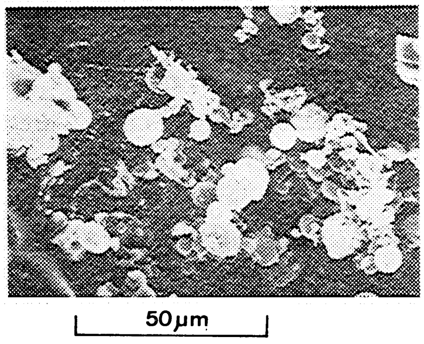

Fig. 10 Precipitates of Cd^{2+} processing by CaS_x process with blowing a gas which contains 97% of air and 3% of CO_2 gas. Initial concn of $Cd^{2+}=25$ ppm and mole ratio of S in CaS_x per $Cd^{2+}=25$.

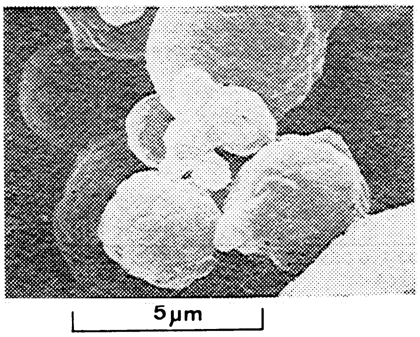

Fig. 11. Magnification of a part of Fig. 10.

The removal of heavy metals when the target material was simultaneously contaminated with COD substances was experimented within several cases. However, heavy-metal removal is not so severely affected by the simultaneous contamination with the COD substances used in the present experiments. This tendency may be explained by the fact that the COD substances were removed by the sorption on the solid sulfur particles and other precipitates, while the heavy metals were precipitated by reacting with H_2S and CaS_2O_3. The CMC might give finer particle sizes of the precipitates and so a lower removal percentage of heavy metals. However, so long as the No. 5C filter paper was employed for the separation of the precipitates, the heavy-metal removal was not affected by the COD contamination in the CaS_x process. It was shown by an auxiliary experiment that No. 5C filter paper had apparent pore sizes equivalent to membranes of between about 0.1 and 0.2 μm, and that the precipitates of the heavy metal sulfides or hydroxides were larger than these pore sizes. COD substances that form soluble-metal compounds, such as EDTA (ethylenediamine tetraacetic acid), citric acid, and tartaric acid, may affect the removal of heavy metals.[3]

An experiment was made at removing NH_3 in water by means of the CaS_x process. The initial NH_3 concentration of 25 ppm was reduced to 1 ppm after 60 min of aeration by the injection of CaS_x at an amount 25 times that of NH_3 in mole ratio. If the nitrogen compounds in the sewage are reduced as far as to free NH_3, a good removal can be realized by means of the CaS_x process. This good removal may be attributed mainly to the stripping of NH_3 from water to the exhaust-gas phase, as in the NH_3 stripping process,[4] or partly to the sorption of NH_3, though the reason for this is not evident, on the surfaces of the precipitates, for the odors of the exhaust gas and the sludge are that of NH_3 and the exhaust gas has a stronger odor than the sludge.

Conclusion

The CaS_x process is simple in its operation and makes it possible to remove various contaminants simultaneously. Thus, a good effect can be expected in waterpollution control. The CaS_x process can also be applied to the advanced treatment of sewage which usually contains COD/BOD substances, phosphate, ammonia, and a trace of heavy metals.

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