Study on the Removal of Inorganic and Organic Mercury in Waste Water by the Flotation Method

By

Shigeru MUKAI* and Yoshitaka NAKAHIRO*

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Abstract

The removal of inorganic and organic mercury in waste water by the flotation method was investigated as a part of the intensive studies of the water pollution control.

The removal of inorganic mercury was examined by the following two methods:

1) $Fe(OH)_3$ co-precipitation-flotation method,
2) $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method.

From the results obtained, it was recognized that inorganic mercury in waste water could be efficiently removed by the $Fe(OH)_3$ co-precipitation-flotation method with 80 mg/l cumulative addition of ferric ions in the pH about 9 after the third stage flotation using sodium oleate as a collector. By the first stage flotation, however, the removal of inorganic mercury in the waste water was inefficient. So, sodium sulphide was added to the waste water in order to precipitate completely the mercury. Thus, the precipitates of inorganic mercury produced with 40 mg/l ferric ions and 1 equivalent addition of sodium sulphide to the total amounts of mercury were completely removed at the pH 6.5—9.5 using sodium oleate in only the first stage flotation.

The removal of organic mercury in waste water was performed by the following methods. A substance which contains organic mercury was decomposed into inorganic mercury with gaseous chlorine, followed by the $Fe(OH)_3$ co-precipitation-flotation method and the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method. The decomposition of organic mercury into inorganic mercury was achieved readily by the oxidation reaction using Cl_2 gas. The optimum conditions of this reaction were found at pH below 1. The removal of excess chlorine in the flotation pulp is important for a successful flotation of the precipitates. The excess chlorine was eliminated by 8 g/l sodium thiosulphate or the aeration over 40 min. It was found that the mercury decomposed by Cl_2 gas was completely removed by the flotation method with an addition of 50—100 mg/l ferric ions and 1 equivalent of sodium sulphide to the total amounts of mercury at the pH 5.0—9.5.

This new method being applied, the removal of inorganic and organic mercury in the waste water was successful in a short time by only one stage flotation using sodium oleate, and mercury in the tailing solution was not detected.

1. Introduction

Such heavy metal ions as mercury, cadmium, lead, copper, zinc and arsenic etc. in waste water are known as harmful elements to the living environment.

* Department of Mineral Science and Technology

Especially among these heavy metals, inorganic and organic mercury compounds are the substances which show a remarkable poisoning effect, and have been polluting water. Accordingly, the removal of inorganic and organic mercury in waste water is one of the most urgent problems.

The authors have been studying the removal of such heavy metals as cadmium, copper and zinc in waste water by both the $Fe(OH)_3$ co-precipitation and flotation methods. The results obtained were very successful.

In this paper, the removal of inorganic and organic mercury in waste water by the $Fe(OH)_3$ co-precipitation-flotation and the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method was investigated as a part of an intensive study of water pollution control.

2. Removal of Inorganic Mercury in Waste Water by the $Fe(OH)_3$ Co-precipitation-Flotation Method

2.1. Co-precipitation Tests of Inorganic Mercury with Ferric Hydroxide.

In order to obtain the fundamental data prior to the flotation tests for the removal of inorganic mercury in waste water, the detailed conditions were examined on the co-precipitation of inorganic mercury with ferric hydroxide.

Mercuric chloride, which was chemically pure, was used as inorganic mercury

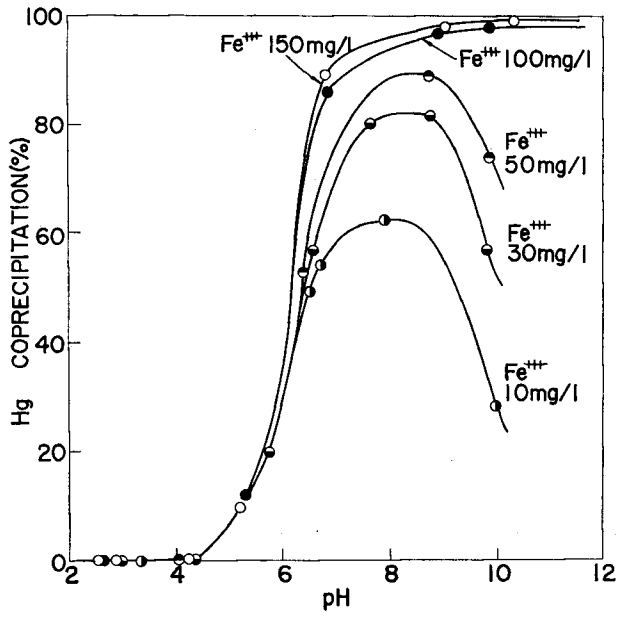

Fig. 1. Effect of pH on the co-precipitation of inorganic mercury with ferric hydroxide.

for these experiments. The mercuric chloride solution of concentration 100 mg/l as Hg^{++} was prepared. Ferric chloride which was chemically pure was used as the co-precipitant, and a ferric chloride solution of concentration 0.1—10 g/l as Fe^{+++} was prepared. The adjustment of pH was made with hydrochloric acid and sodium hydroxide.

In the first place, the effect of pH on the co-precipitation of inorganic merucy with ferric hydroxide was examined. The desired amounts of ferric ions were added to the mercuric chloride of Hg^{++} 1 mg/l. The mixture solution was quietly kept in thermostat at 25°C for 24 hours after pH adjustment to the desired value. Then, the mixture solution was centrifugally separated at 15,000 rev/min for 15 min by the ultra-centrifugal separator in order to eliminate the colloidal precipitates contained in the mixture solution. The mercury ion concentrations in supernatant liquid were measured by a Jarel-Ash atomic absorption mercury detector. The amounts of inorganic mercury co-precipitated with ferric hydroxide were determined from the difference between the initial and final mercury concentrations.

The results obtained are given in Fig. 1. As shown in Fig. 1, the co-precipitation of inorganic mercury was incomplete in the addition below Fe^{+++} 50 mg/l, and also decreased in the alkaline region above pH 9. By an increase above Fe^{+++} 100 mg/l, the co-precipitation of inorganic mercury showed about 98%. From these results, it was recognized that the effect of pH on the co-precipitation of inorganic mercury was considerable.

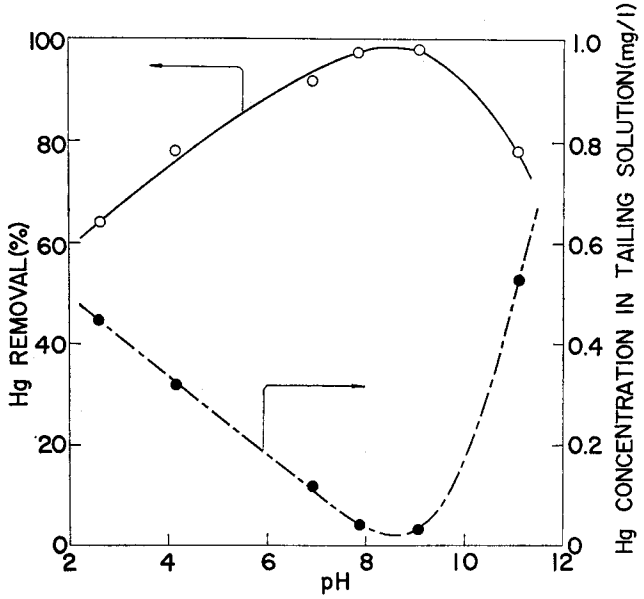

Fig. 2. Effect of pH on the removal of inorganic mercury by the $Fe(OH)_3$ co-precipitation-flotation method.

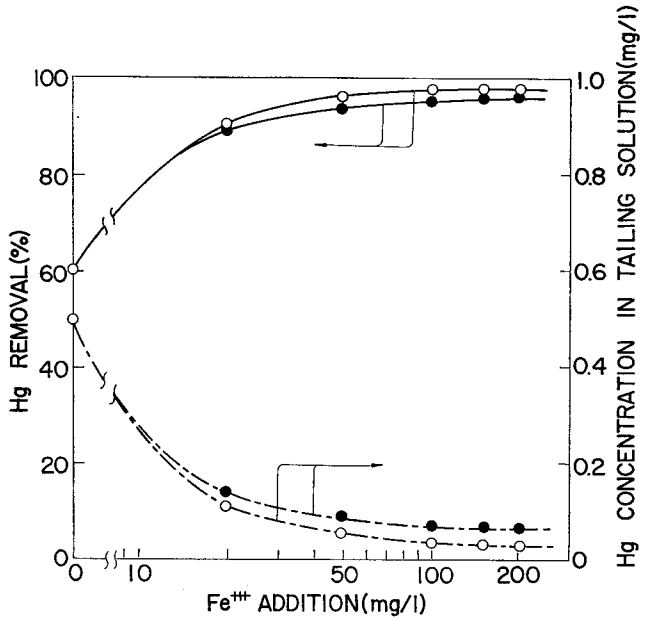

Fig. 3. Effect of the addition of ferric ions on the removal of inorganic mercury by the $Fe(OH)_3$ co-precipitation-flotation-method.
○ with settling for 24 hr after co-precipitation treatment.
● with no settling after co-precipitation treatment.

2.2. Removal of Inorganic Mercury in Waste Water by both the $Fe(OH)_3$ Co-precipitation and Flotation Methods.

A series of flotation tests was carried out in order to examine the applicabilities of the flotation method on the removal of inogranic mercury co-precipitated with ferric hydroxide.

In the first place, the effect of pH on the removal of inorganic mercury by the $Fe(OH)_3$ co-precipitation-flotation method was examined. The test solution containing Hg^{++} 1 mg/l was kept in thermostat at 25°C for 24 hours after co-precipitation with ferric salts and pH adjustment. The sodium oleate of 25 mg/l as a collector was added to the test solution and the pH was exactly adjusted again. The flotation tests were carried out for 5 minutes with the addition of pine oil 13 mg/l using the 500 g Kyoto University type flotation machine.

The results obtained are given in Fig. 2. As shown in Fig. 2, the removal of inorganic mercury was about 98% at pH 8—9, and the residual concentrations of mercury in the tailing solution were 0.03 mg/l. Thus, the removal of inorganic mercury in the waste water by only one stage flotation was incomplete. Also, the pH ranges for the removal of inorganic mercury by this method were narrow.

In the next place, the effect of the addition of ferric ions on the removal of

inorganic mercury by the $Fe(OH)_3$ co-precipitation-flotation method was examined. The flotation tests were carried out after the co-precipitation treatments of mercury in the solution with the various ferric ion concentrations. The flotation conditions were as follows: Hg^{++}, 1 mg/l; pH, 9.1 ± 0.1; sodium oleate, 25 mg/l; pine oil, 13 mg/l; flotation time, 5 min.

The results obtained are given in Fig. 3. As shown in Fig. 3, even if the settling of the solution was not carried out after the co-precipitation treatment, the removal of inorganic mercury was nearly equal to the amount in the case where the settling of the solution was carried out for 24 hours after the co-precipitation treatment. In both these cases, the removal of inorganic mercury showed constant values in the addition of above Fe^{+++} 100 mg/l.

As recognized from the above results, the complete removal of inorganic mercury in the waste water by only one stage flotation was very difficult, and a small quantity of inorganic mercury remained in the tailing solution after flotation. As provided by the law on the water pollution in Japan, provisions have been established that any inorganic mercury in waste water should not be detected. Accordingly, it is necessary to lower the mercury concentrations in the tailing solution to below the detection limit of mercury. Hence, there was a test to completely remove inorganic mercury in the tailing solution by the multistage flotation method.

The flowsheets and reagent conditions for the flotation tests are given in Fig. 4—7. The results obtained are shown in Fig. 8. As shown in Curve I of Fig. 8, the removal of inorganic mercury by one stage flotation was about 95%, and it was incomplete. On the other hand, the removal of inorganic mercury by a second

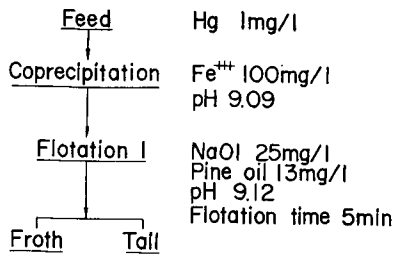

Fig. 4. Flow sheet of one stage flotation. (Curve I in Fig. 10)

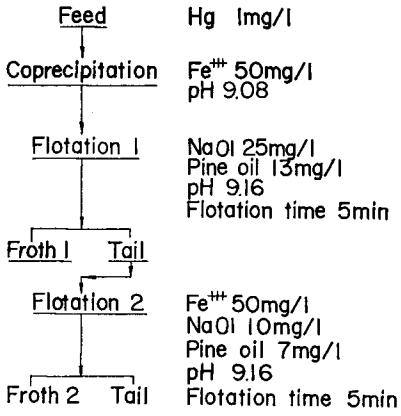

Fig. 5. Flow sheet of two stage flotation. (Curve II in Fig. 10)

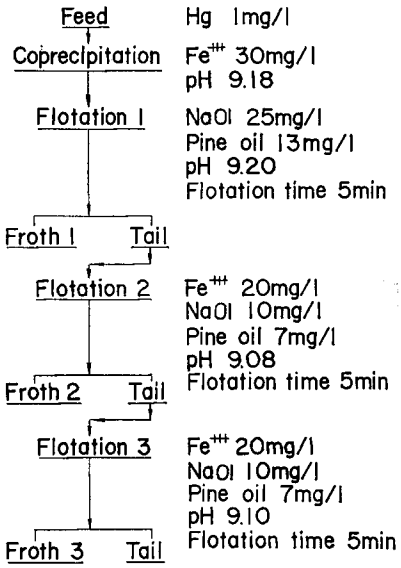

Fig. 6. Flow sheet of three stage flotation. (Curve III in Fig. 10)

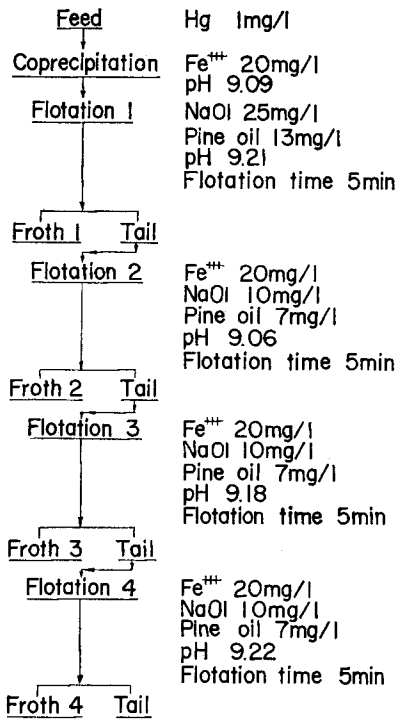

Fig. 7. Flow sheet of four stage flotation. (Curve IV in Fig. 10)

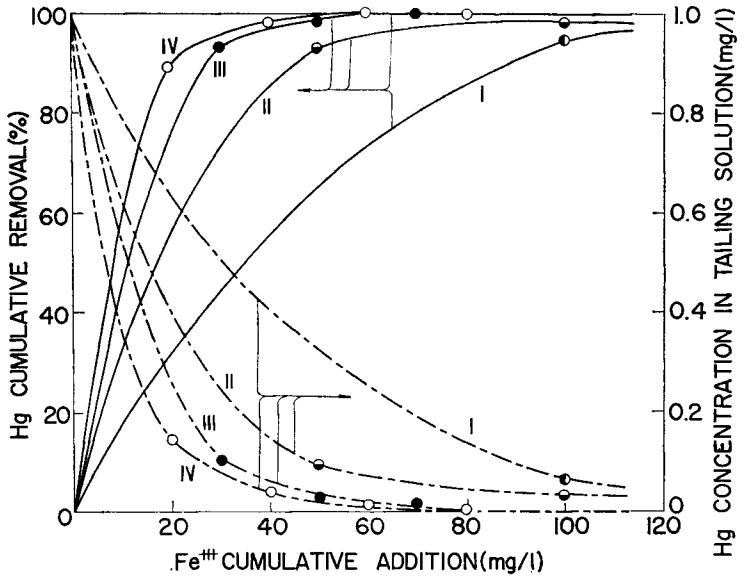

Fig. 8. Removal of inorganic mercury by the multistage flotation method.

stage flotation as shown in Curve II was increased to about 98%. As shown in Curve III and IV, the removal of inorganic mercury was complete by a third stage flotation with the cumulative addition of Fe^{+++} 80 mg/l.

From the above results, it was recognized that inorganic mercury in waste water could be completely removed by increasing the flotation stage.

3. Removal of Inorganic Mercury in Waste Water by both the Na_2S Precipitation and Flotation Methods

Sodium sulphide is regarded as the effective reagent for the removal of inorganic mercury in waste water because it reacts with mercuric ion to form very insoluble mercuric sulphide. So, a series of tests was carried out on the applicability for the remove of inorganic mercury in the waste water.

3.1. Precipitation Tests of Inorganic Mercury with Sodium Shulphide.

A series of tests for the precipitation of inorganic mercury with sodium sulphide was carried out in order to obtain the fundamental data. Sodium sulphide which was chemically pure was used, and sodium sulphide solution of concentration 120 mg/l as $Na_2S \cdot 9H_2O$ was prepared. The pH adjustment was made with hydrochloric acid and sodium hydroxide.

The precipitation tests of inorganic mercury with sodium sulphide were carried out with various concentrations of sodium sulphide under the fixed pH value of 9.40 ± 0.2. From the results previously examined on the effect of pH for the precipitation of inorganic mercury with sodium sulphide, it was confirmed that inorganic mercury was effectively precipitated at very wide pH ranges from a strong acid side to an alkaline side with 1 equivalent addition of sodium sulphide to the total amounts of mercury. Accordingly, the tests were carried out under the fixed pH value of 9.40 ± 0.2. In the first place, the desired amounts of sodium sulphide were added to the test solution containing Hg^{++} 1 mg/l. After precipitation with sodium sulphide and pH adjustment, the solution was centrifugally separated at 15,000 rev/min for 15 minutes in order to eliminate the colloidal precipitates containing the solution. The mercury concentrations in the supernatant liquid after centrifugal separation were measured by a Jarrel-Ash atomic absorption mercury detector. The amounts of mercury precipitated with sodium sulphide were determined from the difference between the initial and final mercury concentrations.

The results obtained are given in Fig. 9. As shown in Fig. 9, the precipitation of inorganic mercury with sodium sulphide increased remarkably with the increase of the addition of sodium sulphide. The precipitation of inorganic mercury was 95% with 1 equivalent addition of sodium sulphide to the total

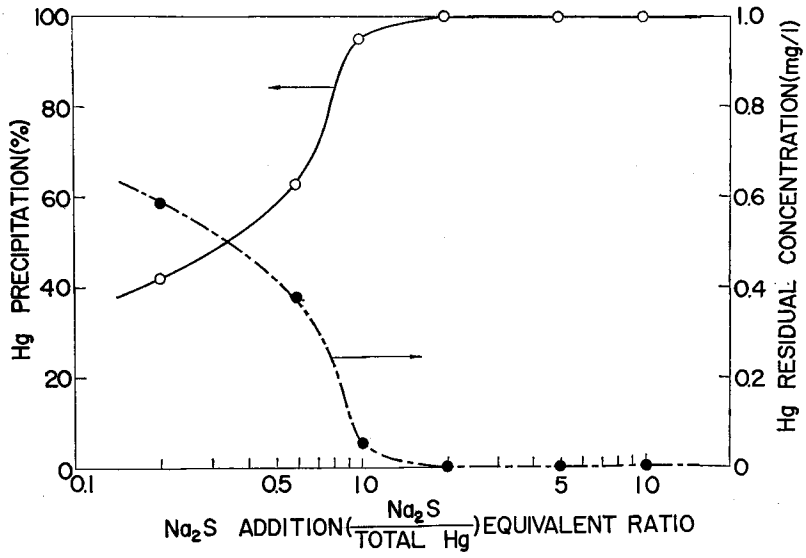

Fig. 9. Effect of the addition of sodium sulphide on the precipitation of inorganic mercury.

amounts of inorganic mercury and then was 100% with 2 equivalent additions of sodium sulphide.

3.2. Removal of Inorganic Merucry in Waste Water by both the Na_2S Precipitation and Flotation Methods.

On the basis of optimum conditions obtained from the above results, the removal of inorganic mercury precipitated with sodium sulphide by the flotation method was examined.

The desired amounts of sodium sulphide were added to the test solution containing Hg^{++} 1 mg/l, and then the pH was adjusted at about 9.1. After precipitation with sodium sulphide and pH adjustment, sodium oleate of 25 mg/l was immediately added to the solution. After the pH was exactly adjusted at 9.1 ± 0.1 again, the flotation tests were carried out with addition of pine oil 13 mg/l for 5 minutes.

The resuts obtained are given in Fig. 10. As shown in Fig. 10, the removal of inorganic mercury was only 60% with no addition of sodium sulphide. Sodium sulphide being added, however, the removal of inorganic mercury increased remarkably with the increase of the addition of sodium sulphide. Inorganic mercury was completely removed with 2 equivalent additions of sodium sulphide to the total amounts of mercury. Thus, it was recognized that the effect of sodium sulphide was considerable for the removal of inorganic mercury in the waste water.

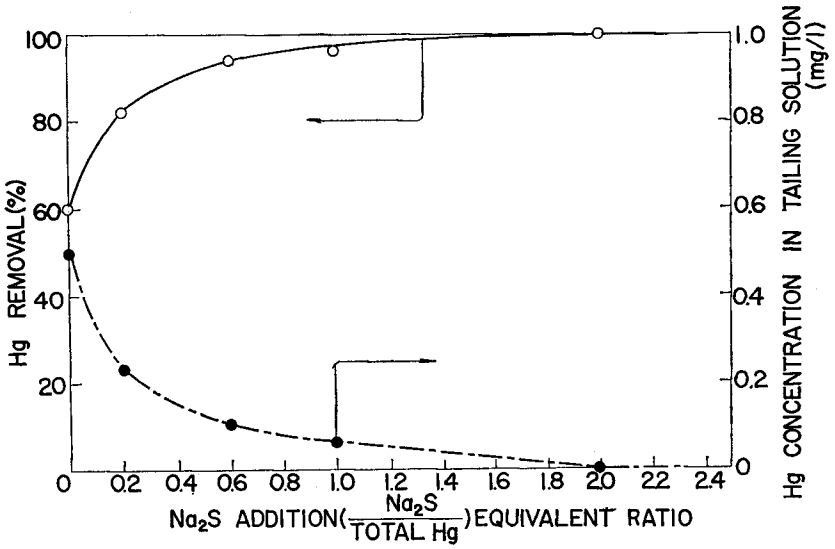

Fig. 10. Effect of the addition of sodium sulphide on the removal of inorganic mercury by the Na_2S precipitation-flotation method.

4. Removal of Inorganic Mercury in Waste Water by the $Fe(OH)_3$ Co-precipitation-Na_2S Precipitation-Flotation Method

4.1. $Fe(OH)_3$ Co-precipitation-Na_2S Precipitation Tests of Inorganic Mercury.

The effectiveness of sodium sulphide on the removal of inorganic mercury was found from the above results. Then, the removal of inorganic mercury co-precipitated with ferric hydroxide and precipitated with sodium sulphide by the flotation method using sodium oleate was examined.

The effect of the addition of sodium sulphide on the precipitation of inorganic mercury was examined in respect to the addition of Fe^{+++} 20 mg/l and 40 mg/l respectively.

The desired amounts of ferric ions were added to the test solution containing Hg^{++} 1 mg/l, and then the pH was adjusted at about 9.3. After co-precipitation with ferric hydroxide and pH adjustment, sodium sulphide was added to the solution and the pH was exactly adjusted at 9.3 ± 0.1 again. In order to eliminate the precipitates produced with ferric ions and sodium sulphide, the solution was centrifugally separated at 15,000 rev/min for 15 minutes. After centrifugal-separation, the mercury concentrations in the supernatant liquid were measured by an atomic absorption mercury detector.

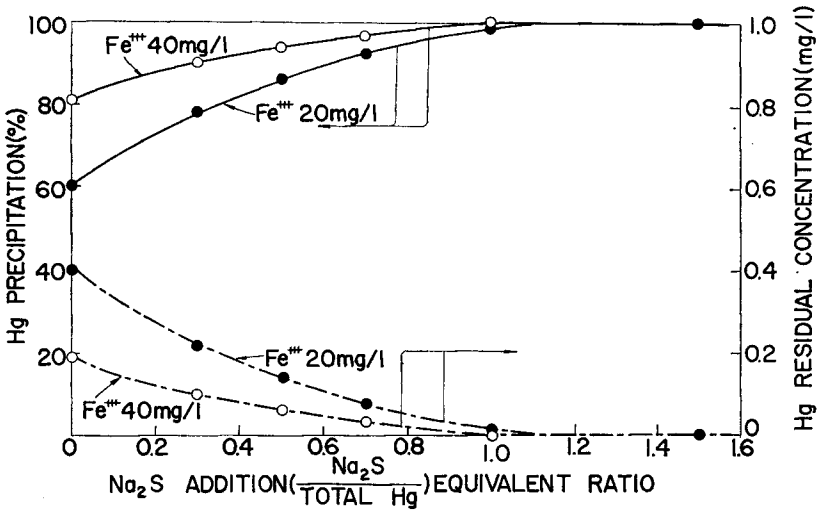

Fig. 11. Effect of the addition of sodium sulphide on the precipitation of inorganic mercury by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation method.

The results obtained are given in Fig. 11. As shown in Fig. 11, inorganic mercury was completely removed with 20 mg/l addition of ferric ions and 1.2 equivalent additions of sodium sulphide to the total amounts of mercury. Increasing the addition of ferric ions to 40 mg/l, the precipitation of inorganic mercury was complete with 1 equivalent addition of sodium sulphide.

From the results obtained, it was recognized that this method was more effective for the precipitation of inorganic mercury than the $Fe(OH)_3$ co-precipitation method or Na_2S precipitation method alone.

4.2. Removal of Inorganic Merucry in Waste Water by the $Fe(OH)_3$ Co-precipitation-Na_2S Precipitation-Flotation Method.

On the basis of results obtained from the above experiments, the flotation tests for the removal of inorganic mercury in the waste water by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method were carried out.

The effect of pH on the removal of inorganic mercury was examined. The flotation tests were carried out at various pH under the fixed conditions of Hg^{++} 1 mg/l, Fe^{+++} 40 mg/l and 1 equivalent addition of sodium sulphide.

The results obtained are given in Fig. 12. As shown in Fig. 12, this method being applied for the removal of inorganic mercury in the waste water, inorganic mercury was removed in the wide pH ranges of 6.5—9.5. And also the removal of inorganic mercury was successful in a short time by only one stage flotation using sodium oleate and mercury in the tailing solution was not detected.

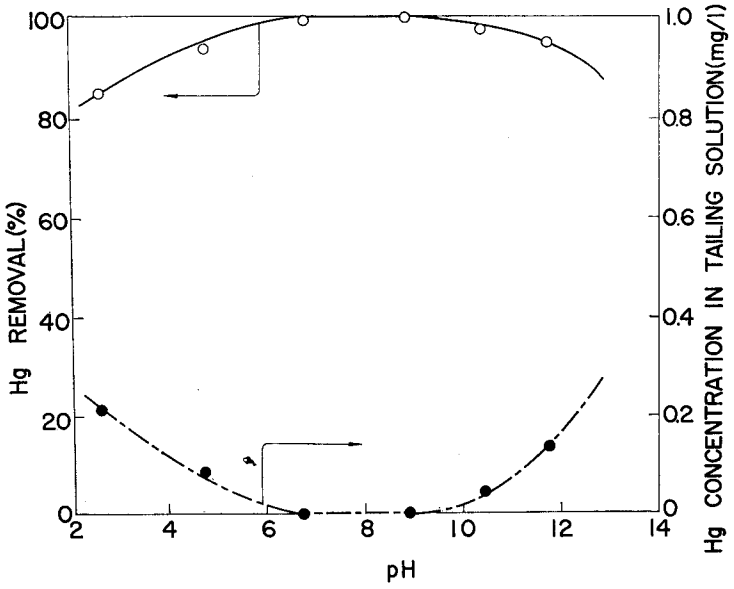

Fig. 12. Effect of pH on the removal of inorganic mercury by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method.

5. Removal of Organic Mercury in Waste Water by Flotation Method

Up to the now, the removal of inorganic mercury in waste water was examined. For the next step, methods for the removal of organic mercury in waste water were investigated. In these experiments, organic mercury was decomposed into inorganic mercury with gaseous chlorine, followed by a co-precipitation with ferric hydroxide. Then, the flotation of mercury co-precipitated with ferric hydroxide, or the flotation of mercury co-precipitated with ferric hydroxide and precipitated with sodium sulphide were also examined.

5.1. Decomposition of Methylmercury with Gaseous Chlorine.

On the decomposition of alkyl organic mercury with gaseous chlorine, the carbon number of the alkyl group is regarded as being related to the difficulty for the decomposition of alkyl organic mercury. In this study, methylmercury, very difficult to decompose by oxidation, was used.

Methylmercury chloride (CH_3HgCl) which was chemically pure was used as organic mercury in this experiment. The mehtylmercury cholride solution of concentration 100 mg/l as Hg was prepared.

In the first place, the effect of the treating time on the decomposition of methylmercury chloride by Cl_2 gas was examined. After the pH of methylmercury chlo-

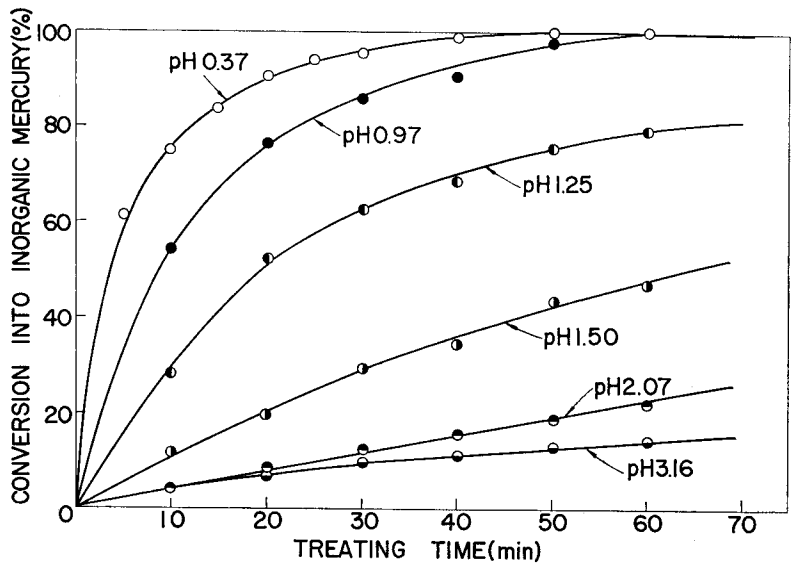

Fig. 13. Effect of pH as a function of treating time on the decomposition of methylmercury into inorganic mercury with Cl_2 gas.

ride solution containing Hg 1 mg/l was adjusted using hydrochloric acid or sodium hydroxide, gaseous chlorine was blown into the test solution for the desired time at Cl_2 gas flow of 500 ml/min. After treatment with Cl_2 gas, the concentrations of mercury decomposed with Cl_2 gas were measured by an atomic absorption mercury detector.

The results obtained are given in Fig. 13. As shown in Fig. 13, the decomposition of methylmercury into inorganic mercury with Cl_2 gas depended remarkably on the pH of methylmercury chloride solution. When the pH of methylmercury solution was below pH 1, the decomposition of methylmercury chloride into inorganic mercury was completed by oxidizing the solution with Cl_2 gas for about 60 minutes. At the pH above 1, the decomposition rate of methylmercury with Cl_2 gas became very slow with the increase of pH, and also the conversion into inorganic mercury decreased considerably.

5.2. Co-precipitation Tests of Methylmercury Treated by Cl_2 Gas with Ferric Hydroxide.

The solution of methylmercury, decomposed completely into inorganic mercury, was prepared for the co-precipitation tests. The conditions for the decomposition of methylmercury chloride with Cl_2 gas are as follows: Hg concentration in methylmercury chloride solution, 1 mg/l; pH, below 1; treating time of Cl_2 gas, 60 minutes; flow of Cl_2 gas, 500 ml/min. Then, after pH adjustment of the test solution,

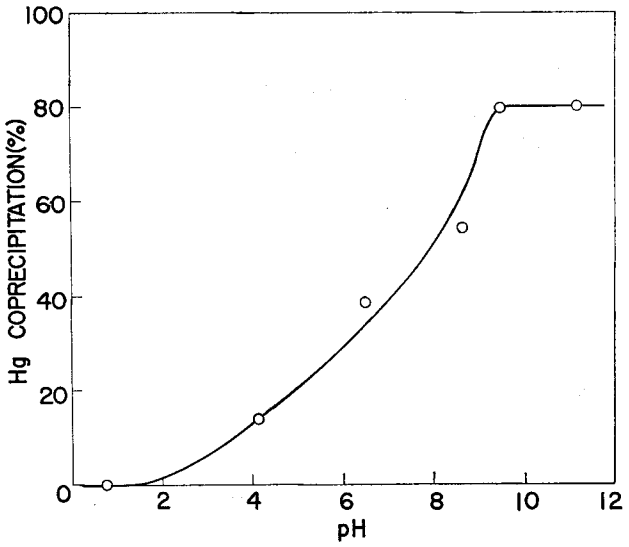

Fig. 14. Effect of pH on the co-precipitation of mercury decomposed with Cl_2 gas by ferric hydroxide.

ferric ions of 100 mg/l were added to the solution, and again the pH of the solution was exactly adjusted. At once, the solution was centrifugally separated at 15,000 rev/min by the ultra-centrifugal separator in order to eliminate the colloidal precipitates contained in the solution. After centrifugal separation, mercury concentrations in the supernatant liquid were measured by an atomic absorption mercury detector. The co-precipitation of mercury with ferric hydroxide after decomposition of methylmercury chloride into inorganic mercury with Cl_2 gas was determined from the difference between the initial and final mercury concentrations.

The results obtained are given in Fig. 14. As shown in Fig. 14, even if ferric ions of 100 mg/l were added, mercury co-precipitated with ferric hydroxide was no more than 80% at pH above 9.5. At the pH below 9.5, the co-precipitations of mercury decreased remarkably with the lowering of pH. From the results obtained, it was recognized that the co-precipitations of mercury with ferric hydroxide depended considerably on the pH of solution.

In the next place, the effect of Fe^{+++} addition on the co-precipitation of methylmercury decomposed into inorganic mercury with Cl_2 gas was examined. The co-precipitation tests were carried out under the fixed pH of 9.55 ± 0.05.

The results obtained are given in Fig. 15. As shown in Fig. 15, the co-precipitations of mercury increased remarkably with the increase of Fe^{+++} addition.

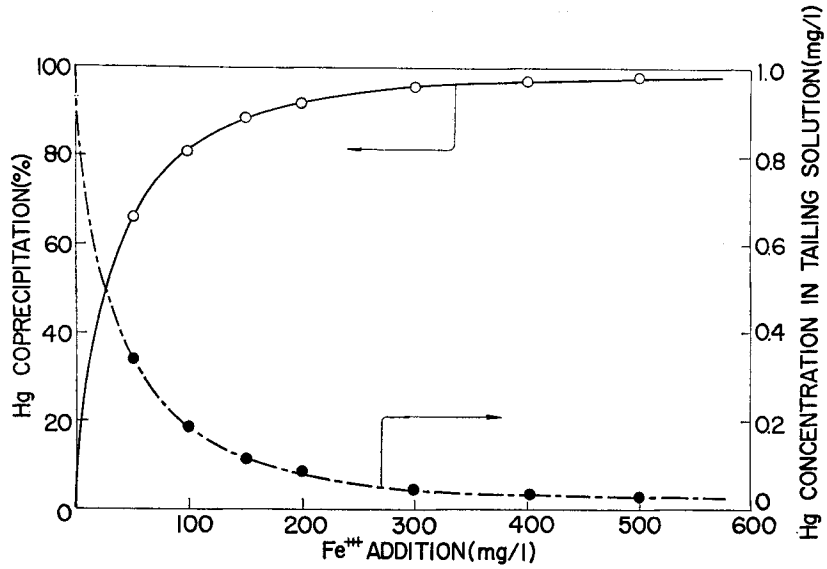

Fig. 15. Effect of the addition of ferric ions on the co-precipitation of mercury decomposed with Cl_2 gas.

When ferric ions of above 400 mg/l were added, the co-precipitation of mercury showed about 98%.

From the above results, it was recognized that the decomposition of organic mercury into inorganic mercury was achieved readily by the oxidation reaction using Cl_2 gas. The optimum conditions of this oxidation reaction were as follows: pH, below 1; treating time, about 1 hour. Also, mercury decomposed with Cl_2 gas could be efficiently co-precipitated with ferric ions of about 400 mg/l.

5.3. Removal of Methylmercury Decomposed with Cl_2 Gas by the $Fe(OH)_3$ Co-precipitation-Flotation Method.

On the basis of optimum conditions obtained from the decomposition tests of methylmercury with Cl_2 gas and the co-precipitation tests of mercury with ferric hydroxide, the flotation tests for the removal of methylmercury decomposed into inorganic mercury with Cl_2 gas were carried out.

In the first place, the effect of Fe^{+++} addition on the removal of mercury was examined by the $Fe(OH)_3$ co-precipitation-flotation method. After decomposition of methylmercury with Cl_2 gas and co-precipitation with ferric hydroxide, a series of flotation tests were carried out using the Kyoto University type of flotation machine under the fixed conditions as follows: total Hg, 1 mg/l; pH, 9.05 ± 0.02; sodium oleate, 50 mg/l; pine oil, 13 mg/l; flotation time, 5 minutes.

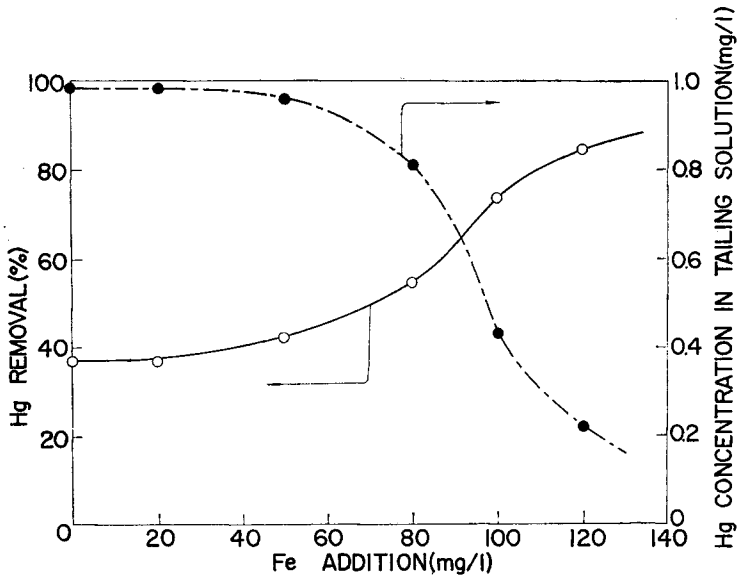

Fig. 16. Effect of the addition of ferric ions on the removal of mercury decomposed with Cl_2 gas by the $Fe(OH)_3$ co-precipitation-flotation method.

The results obtained are given in Fig. 16. As shown in Fig. 16, when ferric ions were not added, the removal of mercury by the addition of only sodium oleate was no more than about 38%. The removal of mercury by this method increased with the increase of Fe^{+++} addition, but it was only about 85% even if ferric ions were added above 120 mg/l.

From the above results, the flotation of mercury co-precipitated with ferric hydroxide was inefficient for the removal of mercury decomposed with Cl_2 gas. It was surmised that the difficulty of mercury removal was due to the presence of excess chlorine in the flotation pulp.

In order to eliminate the poisoning effect of excess chlorine in the flotation pulp, hereafter, sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) was used as a reducing agent.

The effect of the addition of sodium thiosulphate on the elimination of the poisoning effect of excess chlorine was examined. After decomposition of methylmercury into inorganic mercury with Cl_2 gas, the pH of solution was adjusted at about 9. Then, the desired amount of sodium thiosulphate was added to the solution. After co-precipitation with ferric hydroxide and pH re-adjustment, the flotation tests were carried out under the fixed conditions. The flotation conditions were as follows: total Hg, 1 mg/l; Fe^{+++} addition, 100 mg/l; pH, 9.05 ± 0.02; sodium oleate, 50 mg/l; pine oil, 13 mg/l; flotation time, 5 minutes.

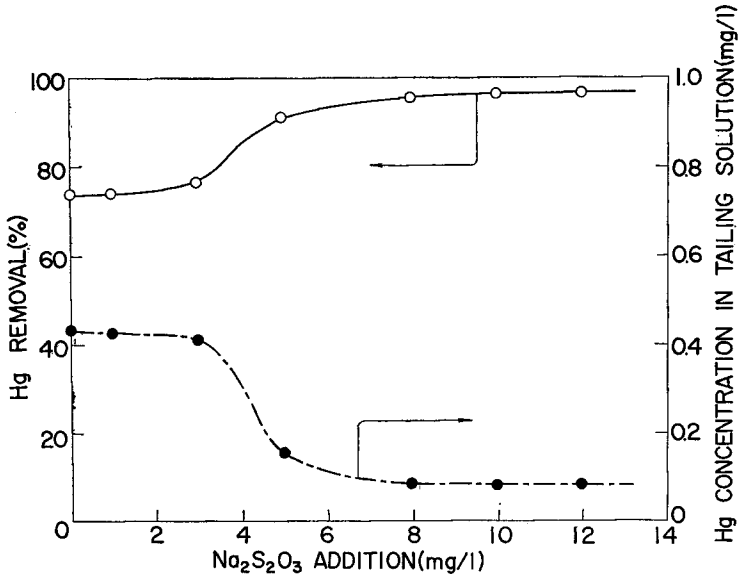

Fig. 17. Effect of the addition of sodium thiosulphate on the removal of mercury decomposed with Cl_2 gas by the $Fe(OH)_3$ co-precipitation-flotation method.

The results obtained are given in Fig. 17. As shown in Fig. 17, with no addition of sodium thiosulphate, the removal of mercury by flotation was very low and only about 74%. However, the removal of mercury by the flotation method increased remarkably to about 96% with the increase of addition of sodium thiosulphate. Thus, sodium thiosulphate was effective as a reagent removing the poisoning effect of excess chlorine.

Besides the above experiment, the effect of addition of sodium oleate was examined under the fixed conditions as follows: total Hg, 1 mg/l; $Na_2S_2O_3$, 8g/l; Fe^{+++}, 100 mg/l; pH, 9.05 ± 0.02; pine oil, 13 mg/l; flotation time, 5 minutes. From the results obtained, the removal of mercury showed the maximum values of about 96% in the addition of sodium oleate above 50 mg/l.

5.4. Removal of Methylmercury Decomposed with Cl_2 Gas by the $Fe(OH)_3$ Co-precipitation-Na_2S precipitation-Flotation Method.

Even if the poisoning effect of excess chlorine was eliminated with such a reducing agent as sodium thiosulphate, mercury decomposed with Cl_2 gas could not completely be removed by the flotation method. Since it was found with the removal of inorganic mercury in the waste water that the flotation of inorganic mercury co-precipitated with ferric hydroxide was improved greatly by sulphidizing

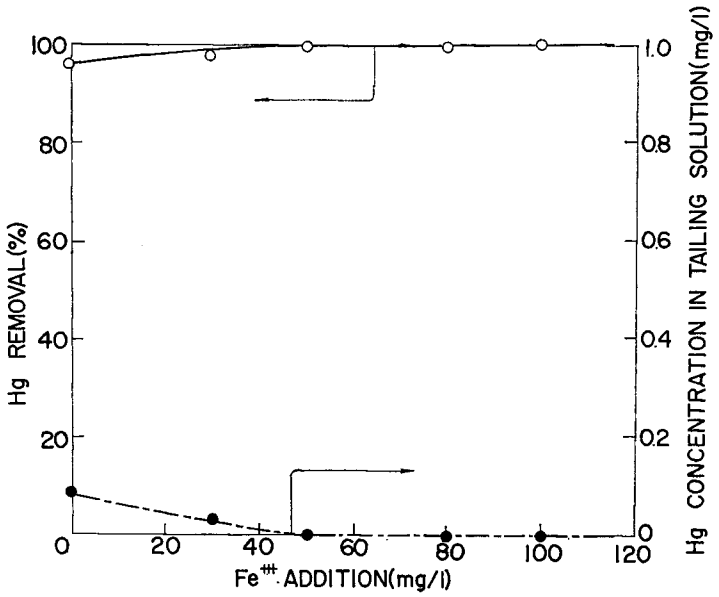

Fig. 18. Effect of the addition of ferric ions on the removal of mercury decomposed with Cl_2 gas by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method.

uncollected mercury with sodium sulphide, the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method was inverstigated also for the removal of organic mercury in the waste water.

In the first place, the effect of Fe^{+++} addition on the removal of mercury decomposed with Cl_2 gas by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method was examined.

After the methylmercury solution of total Hg 1 mg/l was treated with Cl_2 gas for 1 hour at the pH below 1, the pH of solution was adjusted at about 9.0. Then, sodium thiosulphate of 8 g/l was added to the solution in order to eliminate excess chlorine in the solution and the desired amounts of ferric ions were added to the solution. The pH of the solution was adjusted at about 9, again. Then, sodium sulphide of 1 equivalent to the total amounts of mercury and sodium oleate of 50 mg/l was added. After pH re-adjustment exactly at 9.05 ± 0.02, the flotation tests were carried out under the fixed conditions as follows: pine oil, 13 mg/l; flotation time, 5 minutes. With respect to the effect of Na_2S addition on the removal of mercury decomposed with Cl_2 gas by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method, it has been confirmed that the optimum addition of sodium sulphide is 1 equivalent to the total amounts of mercury.

The results obtained are given in Fig. 18. As shown in Fig. 18, with no addi-

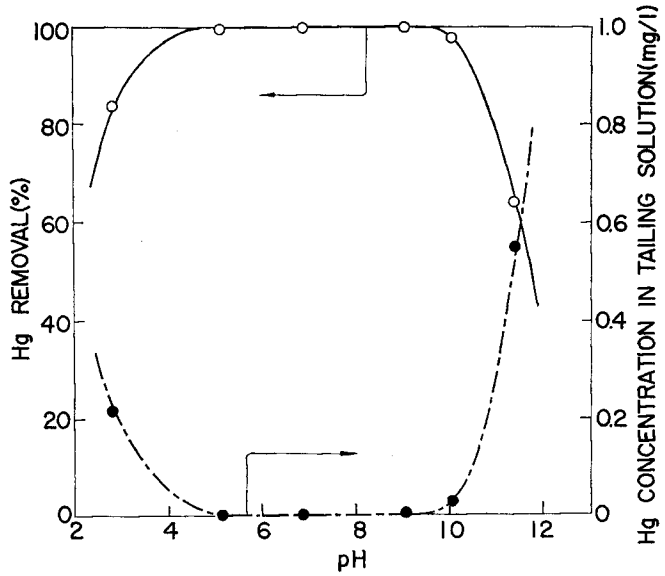

Fig. 19. Effect of pH on the removal of mercury decomposed with Cl_2 gas by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method.

tion of ferric ions, the removal of mercury was about 96% with 1 equivalent addition of sodium sulphide. Thus, mercury decomposed with Cl_2 gas could not completely be removed by the flotation method with the addition of only sodium sulphide. With the increase of Fe^{+++}, however, the removal of mercury increased remarkably and was completed with the addition of ferric ions 50 mg/l.

Further, the results examined on the effect of pH are as shown in Fig. 19. The experimental conditions are as follows: total Hg, 1 mg/l; $Na_2S_2O_3$, 8 g/l; Fe^{+++}, 50 mg/l; Na_2S, 1 equivalent to the total amounts of mercury; sodium oleate, 50 mg/l; pine oil, 13 mg/l; flotation time, 5 minutes.

As shown in Fig. 19, the flotation of co-precipitates of mercury produced with 50 mg/l ferric ions and 1 equivalent addition of sodium sulphide to the total amounts of mercury was effective at pH 5.0—9.5 using sodium oleate as a collector when excess chlorine was eliminated by 8 g/l sodium thiosulphate.

Though the flotation of mercury co-precipitated with ferric hydroxide could be improved greatly by the elimination of excess chlorine with sodium thiosulphate, much sodium thiosulphate was necessary to eliminate excess chlorine. So, the aeration method was examined to eliminate excess chlorine in the flotation pulp. After decomposition of methylmercury with Cl_2 gas, the test solution was aerated by blowing the air for the deisred time. Then, after $Fe(OH)_3$ co-precipitation and Na_2S precipitation, the flotation tests were carried out under the fixed conditions

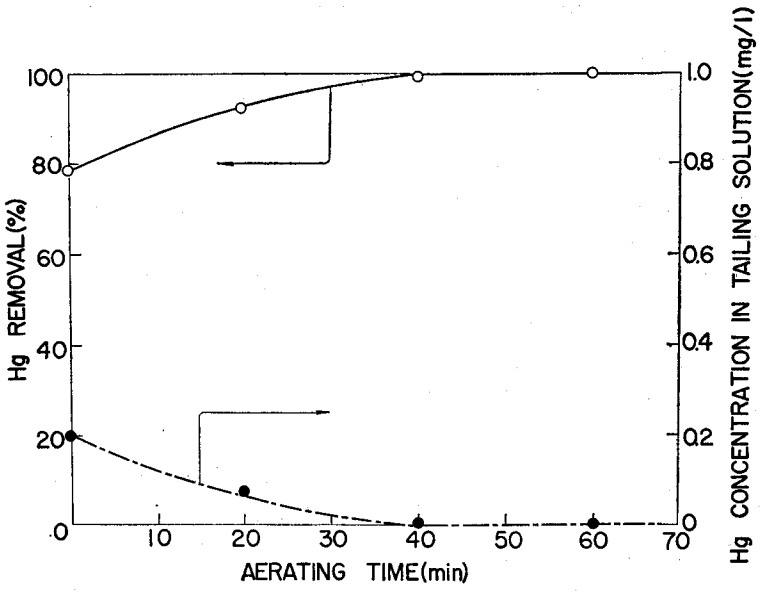

Fig. 20. Effect of the aeration in order to eliminate excess chlorine in the flotation pulp.

as follows: total Hg, 1 mg/l; Fe^{+++}, 100 mg/l; Na_2S, 1 equivalent; pH, 9.05 ± 0.02; sodium oleate, 50 mg/l; pine oil, 13 mg/l; flotation time, 5 minutes.

The results obtained are given in Fig. 20. As shown in Fig. 20, with no aeration, the removal of mercury by the flotation method was only about 78%. With the increase of aerating time, however, the removal of mercury increased remarkably and was completed by 40 minutes of aeration.

From the above results, even if sodium thiosulphate was not added to the solution, mercury decomposed with Cl_2 gas could be efficiently removed by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method when excess chlorine was eliminated by the aeration for 40 minutes.

6. Conclusions

In this study, the removal of inorganic and organic mercury in waste water was investigated as a part of the studies of water pollution control. A summary of the results obtained in this study is given as follows:

1) Inoraganic mercury could be completely removed by the $Fe(OH)_3$ co-precipitation-flotation method with 80 mg/l cumulative addition of ferric ions at the pH 9 after three stage flotation using sodium oleate.

2) The removal of inorganic mercury by the Na_2S precipitation-flotation

method was efficient with 2 equivalent additions of sodium sulphide to the total amounts of mercury.

3) The new method for the removal of inorganic mercury by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation methods was examined. From the results obtained, it was verified that inorganic mercury could be completely removed in the region of pH 6.5—9.5 with 40 mg/l addition of ferric ions and with 1 equivalent addition of sodium sulphide to the total amounts of mercury.

4) With respect to organic mercury, a solution containing methylmercury chloride was decomposed into inorganic mercury with gaseous chlorine, and then the solution was treated by the $Fe(OH)_3$ co-precipitation-flotation method and the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method. From the results obtained, it was recognized that the decomposition of organic mercury into inorganic mercury was achieved readily by the oxidation reaction using Cl_2 gas. The optimum conditions of this reaction were found at pH below 1.

5) Mercury decomposed with Cl_2 gas can be efficiently co-precipitated with ferric hydroxide. The required addition of ferric ions to the mercury solution will be in the order of 400 times at pH above 9.5.

6) The flotation of mercury co-precipitated with ferric hydroxide was inefficient for the removal of mercury decomposed with Cl_2 gas, because of the presence of excess chlorine.

7) Sodium thiosulphate was found to be a useful reagent in order to eliminate the poisoning effect of excess chlorine.

8) The flotation of mercury co-precipitated with ferric hydroxide can be improved greatly by sulphidizing uncollected mercury with sodium sulphide. Thus, the flotation of co-precipitates of mercury produced with 50 mg/l ferric ions and 1 equivalent addition of sodium sulphide to the total amounts of mercury was effective at pH 5.0—9.5, using sodium oleate as a collector when excess chlorine was eliminated by 8 g/l sodium thiosulphate.

9) Even if sodium thiosulphate is not added to the solution, mercury decomposed with Cl_2 gas can be efficiently removed by the $Fe(OH)_3$ co-precipitation-Na_2S precipitation-flotation method when excess chlorine was eliminated by aeration for 40 minutes.