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High Quality Treatment of Waste Water Containing Heavy Metals and Recovery or Recycling of Heavy Metals by Use of Hydrogen Sulfide Gas Sensor

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Abstract: Most of the existing treatment process of waste water containing heavy metals is based on separation of the metals as their hydroxide generated by adding alkali such as lime. This process allows easy reactivity and high stability. But unfortunately, as it produces volumes of sludge including not only metal hydroxides but also much crystalline water and other salts, the product is hardly to be brought back to the metal mine so as to be converted into the original metal. Meanwhile, the sulfide process presented in this paper allows the residual metal concentration in the treated water to decrease to a lower level than that by the hydration process. Besides, the sulfide process has advantages as such that the volume of generated sludge is small and the refining at the refinery is comparatively easy. Despite the above fact, this technology has not yet been widely accepted. We attribute this problem to the following reasons.

1) It is difficult to control the amount of sulfide to be added.
2) Precipitate is too fine to cohere, which easily results in colloid. Polymer coagulant is not effective.
3) There is a risk to generate poisonous hydrogen sulfide gas, which is corrosive and has offensive odor.

As 1) above, as a result of our intensive study for last two years, we have found that there is a fixed relationship between the reaction of metal ion with sulfide ion and hydrogen sulfide gas generated during the reaction process. When the sulfide process is practiced by adding sulfiding agent in the waste water containing heavy metal, the reaction specified in the formula (2) does not occur in the reaction tank as long as the metal ion remains even under acid atmosphere and meanwhile only formula (1) occurs. After metal ion in the liquid is completely converted into metal sulfide precipitate, hydrogen sulfide gas starts to generate.

$M^{++} + S^{--} \rightarrow MS$ (1)

$2H^{+} + S^{--} \rightarrow H_2S$ (2)

Here M shows metal ion. It is assumed to be bivalent

Based on these findings, we have developed a process to feed the sulfiding agent by use of a hydrogen sulfide gas censor. As a result of actual treatment of waste water with heavy metal by this system, it has proved to bring on a rem

arkable result without any offensive odor or generation of colloid.

Keywords: waste water containing heavy metals, recovery , recycling, hydrogen sulfide gas sensor

1. Introduction

Human beings has made progress and prospered by using metals. But it is difficult to say that we have been using them effectively because some of them are just thrown away without recycling use. Metal resource is limited. Except some, the mining life of many metals is under 50 years. Metal is an element essentially having a property to be easily recycled. But the ratio of metal actually reused is low. As to the source of recycling, most metals are recycled from scrap and rarely from waste water sludge. Despite the warning that the resources are running up and the dumping ground is becoming scarce, people continue to throw away into the ground most of the sludge with

valuable metals from waste water without recycling use.

Today the prevailing treatment process for waste water containing heavy metals is to precipitate the metal hydroxide by adding alkali materials such as lime and then to separate it between the solid and the liquid. It is easy to control the reaction by pH. Also this process is safe and stable. However the process produces volumes of sludge as well as crystalline water and miscellaneous salt. This makes it difficult to bring the sludge back to the refiner as a source for valuable metals and to recycle the contained metals through dry refining process. Therefore, as a matter of fact, without changing the water treatment process itself, it is difficult to carry out the recycling of metals from waste water with heavy metals.

Through the study on a variety of alternatives effective technically as well as economically, we have come to notice the sulfide process. The sulfide process, comparing with the hydroxide process, has substantial advantages such as to enable us to lower the residual metal ion density, to reduce the sludge generation and to provide comparatively easy refining at the refinery. On the other hand, as stated in the summary above, it is true that this process has a serious disadvantage. So we have devoted our study to overcoming the disadvantage. We started our study with a development of feeding method of sulfiding agent. Through the research on the interdependence among the volume of metal ion and sulfide ion and sulfide gas generated towards the end of reaction, we have found that there is a kind of fixed relationship between the reaction speed of sulfide material in the water containing metal ion and the volume of generated sulfide gas. To say this relationship in other words; when we precipitate the sulfide material by adding sulfiding agent in the waste water with heavy metal ion, as long as the metal ion remains in the reaction tank, formula (1) precedes formula (2) even though pH value is low. Here the sulfide gas does not occur. Only after the density of metal ion becomes low enough in the course of the precipitation of metal sulfide, the sulfide gas appears.

Based on this finding, we have developed a feed control system of sulfiding agent. We have already confirmed that the feed control system enables us to control the precipitating process of sulfide materials precisely, economically and stably.

2. Experimental Procedures

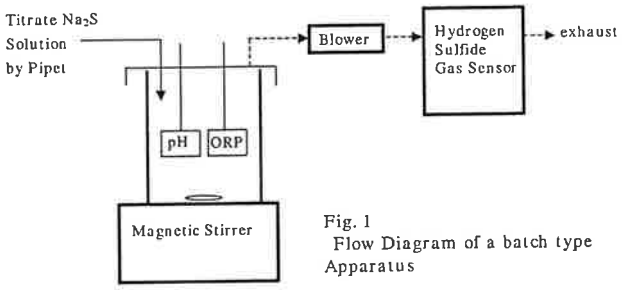

Fig. 1
Flow Diagram of a batch type Apparatus

Fig. 1 shows its flow sheet

For a preliminary, we carried out a test by a batch type equipment.

We prepared as standard reagent three different test water, with copper sulfate, lead nitrate and nickel sulfate, each concocted to contain 200 mg of metal in one liter of water. Each 100 milli-liter of test water was kept in the beaker of 200 milli-liter and there pH was controlled by adding sulfate acid or sodium hydroxide. After that, the beakers were covered with lids. Then we titrated sodium sulfate aqueus solution (2000mg/L as S^{--}) into the beaker by use of a pipet. During the process, the gas staying around the upper part of beaker was introduced to the hydrogen sulfide monitor at the speed of 0.5 liter/min.

For the inspection of pH, ORP and concentration of hydrogen sulfide gas, we used the hydrogen sulfide gas monitor. Meanwhile we inspected metal ion concentratioin, for Cu and Pb by an ion electrode and for Ni by an absorption spectrophotometry.

Figure 2 shows the flow sheet of middle sized continuous typed test equipment.

The capacities of reaction tank, coagulation tank and precipitation tank are 2 liter, 1 liter and 6 liter respectively. We used the same test water as used for the batch system, keeping the water for one hour in the reaction tank, and the absorption speed of gas into the sulfide gas monitor at 0.5L/min. We repeated our

experiment in the way that once the density of hydrogen sulfide monitor reached prefixed value, we stopped the supply of the sulfiding agent and when the density became sufficiently low, restarted the supply.

3. Result and Discussion

Figure 3 shows the test result with water containing Pb as a representative of the batch type experiment. The concentration of Pb ion, originally showing 200 mg/L in the treated water at point A decreases gradually as sulfiding agent is added and comes down to 0.6mg/L at the equivalence point of B.

The content of S^{--} in the treated water is 0mg/L at this moment and hydrogen sulfide is 0 ppm. As the supply of sulfiding agent increases, the hydrogen sulfide gas starts to occur. The point is designated as point C. The density of remaining Pb is 0.13mg/L and S^{--} is 6.50mg/L at point C. As the supply of sulfiding agent toward point D further increases, Pb density in the treated water still remains at 0 mg/L while S^{--} becomes 6.51mg as a result of slight increase of 0.01mg/L. The concentration of hydrogen sulfide at this moment is 240ppm. Figure 3 shows that small addition of sulfiding agent toward the end of reaction process causes a rapid increase of hydrogen sulfide. When we found the characteristic, we presumed that we might be able to apply such characteristic to the sulfiding agent control for continuous treatment process; that is, once concentration of hydrogen sulfide reaches certain level, it works to stop the adding of sulfiding agent and restarts the adding after the generation of hydrogen sulfide comes to a stop.

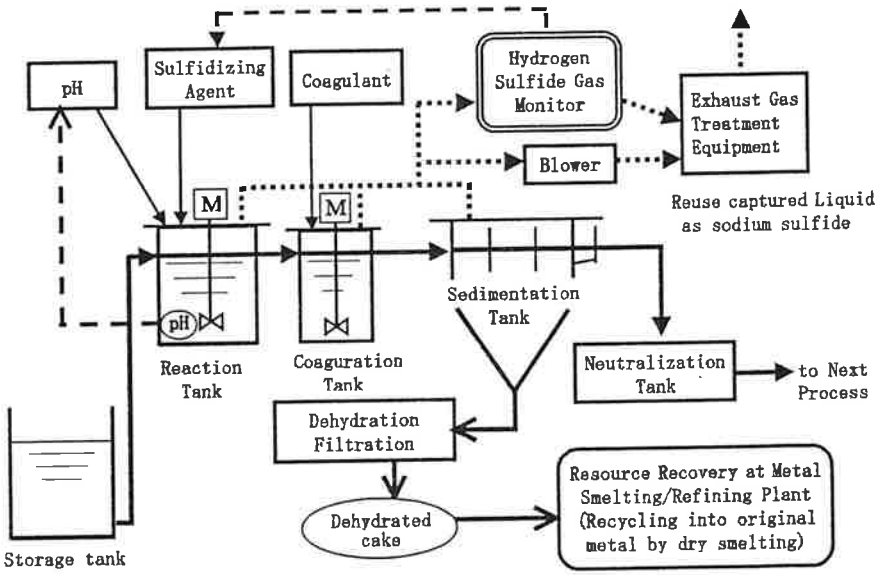

Fig.2 Flow Diagram of SS Process

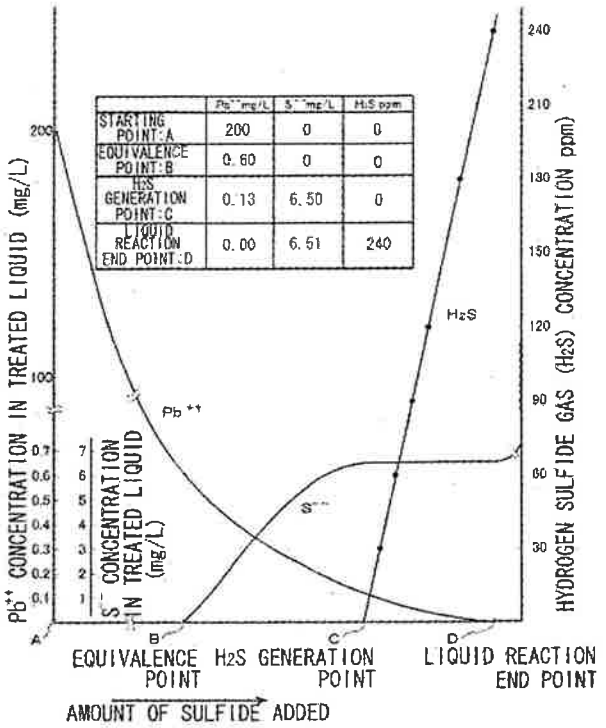

Fig.3 The test result with water containing Pb

Figure 4 and 5 show the result of actual test carried out by use of a middle sized continuous treatment equipment and the same waste water used for the batch system. If treating the density of hydrogen sulfide between 180 to 240 ppm, the system can treat the waste water with Cu and Pb efficiently to the level where no residual metal is found. Besides during the treatment we have not detected any offensive odor or generation of colloid.

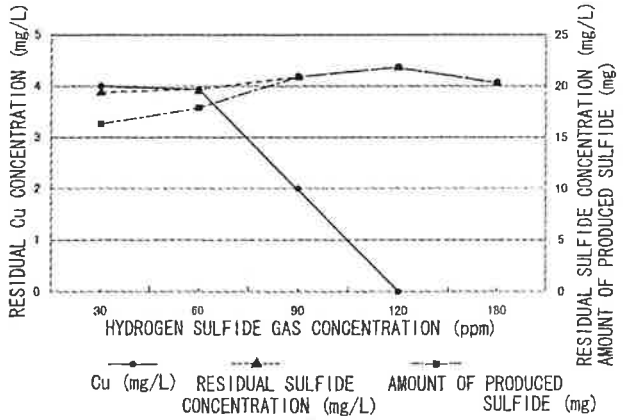

Fig.4 Relationship between hydrogen sulfide concentration and residual Cu concentration, residual sulfide concentration and amount of produced sulfide
(pH-1.6, 200mg/L Cu)

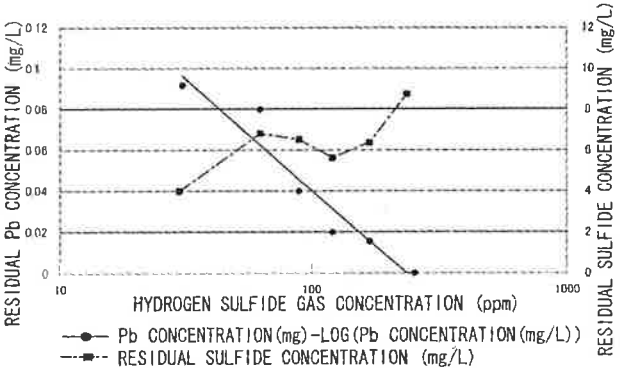

Fig.5 Relationship between hydrogen sulfide gas concentration and residual Pb concentration (continuous test, pH-3.5)

4.Test Result on Industry Scale

We have carried out the treatment of waste water discharged from nonelectreolytic plating by using two units of batch typed reaction tank with 2 cubic meters. Table 1 shows the result. The water content of the cake after dehydration was some 40% but it came down to some 20% after discharging the heat for one month. The volume of generated sludge is one third of that of conventional process. The dehydrated cake could be

Table 1 : The result of treatment with actual waste water.

Batch No.	Waste water			Removal ratio of Ni	※1 [%]	※2 [%]
	untreated	treated				
	Ni mg/L	pH	Ni mg/L	[%]		
1	5,000	7.0	-	-	42	32
2	5,000	7.5	-	-		
3	5,000	7.0	1.4	99.97		
4	5,000	7.5	4.3	99.91	43	36
5	5,000	6.5	1.5	99.97		
6	5,000	6.5	2.1	99.96		

※1 : Water content in dehydrated cake

※2 : Ni content of dried cake

Ni content is a quantity contained in the solid body after drying .This value is expected to further improve because the further technology of cleaning sludge will enable us to remove more impurities.

reused at the refinery as a metal source. We have already operated this system for 9 months without any trouble.

5.Conclusion

The addition control technology of hydrogen sulfide by a gas sensor has enabled us to add the sulfiding agent in quite precise and stable way. To this day we have confirmed the effectiveness of this process through the continued test with waste water prepared by using standard reagent. Besides we experimented with actual waste water from lead-acid battery plants or from chemical plants containing Cu, Ni, Pb, Zn, Se, As, Mn and Fe and found that all such result is good. We also applied this process to a treatment of waste water of nonelectrolytic nickel plating plant (initial nickel content 5,000 to 8,000 mg/L) on the industrial scale. The result is such that the removing ratio of nickel is 99.9%, generated volume of dehydrated cake is some one third of the conventional method, water content is under 40% and nickel content in the cake is some 35%. Since the cake can be refined and reused as nickel ore, it helps to reduce the running cost of the process itself. For reference, the dehydrated cake produced by the conventional hydroxide process is only dumped away as industrial waste even paying some treatment cost because it cannot be reused. An industrial waste treatment company, already employing this system, has a plan to establish a new recycling center which can recover metals other than nickel by expanding their capacity.