A result of batch test to select effective co-precipitator of zinc containing mine drainage treatment

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Abstract The Ministry of Environment of Japan revised the effluent standard of water pollution control law on December 2006 and the upper limit of zinc content in effluent from factories and business activity sites including metal mines has tightened from 5.0 mg/L to 2.0 mg/L in order to protect aquatic plants and animals. Application of new standard to mine effluents has extended to December 2011. In Japan 80 plants are treating drainage from suspended or abandoned mines and 23 plants of them treat drainage containing zinc and 6 of them may need process modification in order to meet the revised standard. The drainage of those 6 mines have common features that zinc content is relatively higher than iron content and removal of zinc by co-precipitation with iron hydro-oxide are not sufficient to meet the standard. In order to reduce zinc content by co-precipitation in those mines, various co-precipitator such as ferric iron sulfate, ferric iron chloride, bentonite, diatom, activated carbon, and zeolite are tested. The result of batch test using simulated drainage shows that ferric iron chloride and zeolite can remove zinc with additional cost less than 20% of current cost. Further batch test at a model mine site using real drainage shows that a process using ferric iron chloride shows better stability on zinc content after treatment than zeolite.

Key Words effluent standard, coagulant, co-precipitation

Introduction

The Japanese Ministry revised the effluent standard of water pollution control law in 2006 the upper limit of zinc content in Japan was built up 2.0 mg/L or less from 5.0 mg/L. The same law defines a 5-year provisional action for metal mines. The conventional standard of up to 5.0 mg/L provisionally applies to metal mines (including treatment of mine drainage) till December 10, 2011.

Zinc content is removed by the following two methods; "adsorption" for treatment of zinc ions by an adsorbent and "settlement process" for zinc coagulation as a hydroxide. However, in order to precipitate zinc as a hydroxide, however, it is necessary to increase pH of drainage to 9.0 or more. This can violate the effluent standard concerning pH in drainage. General mine drainage contains zinc, iron and other various metals. Therefore, zinc can be removed even if the value of pH is not increased to 9.0 or more by co-precipitation. Consequently, in order to remove zinc by settlement process in mine drainage that contains only zinc without iron, it is necessary to add iron to co-precipitate zinc with iron in a forced manner.

In this paper, a lower-cost treatment method for satisfying new regulations is formulated by the adsorption and settlement process in drainage containing only zinc without iron through a basic test using simulated drainage and an on-site test using real drainage.

Model Mine

A Model mine (it will be shown as E mine on this paper) was selected to use drainage containing only zinc in the test. The quality of drainage and treated water of the E mine is shown in Table 1. In winter, the Zn concentration of drainage tends to slightly high, resulting in a total concentration of zinc in the treated water exceeds 2.0 mg/L. A waste water treatment plant in the E mine charges slaked lime into drainage for neutralization. The quantity of waste water to be treated is 0.3 m^3/min on an annual mean basis, and the current treatment cost is 0.2 US$/$m^3$.

Basic Test

First, a cost-effective adsorbent is selected for the adsorption. Next, a cost-effective iron source is selected for the settlement process.

Adsorbent candidates, zeolite, bentonite, diatomite and activated carbon were selected by a

Table1 *The water quality of drainage and treated water of the E mine*

Quantity（m^3/min）	pH	Drainage		Treated water	Annual cost for treatment (US$)	Treatment cost per 1 m^3 （US$）
		Zn (mg/L)	Fe (mg/L)	Zn (mg/L)		
0.3	6.28	22	<0.10	2.28	35,000	0.2

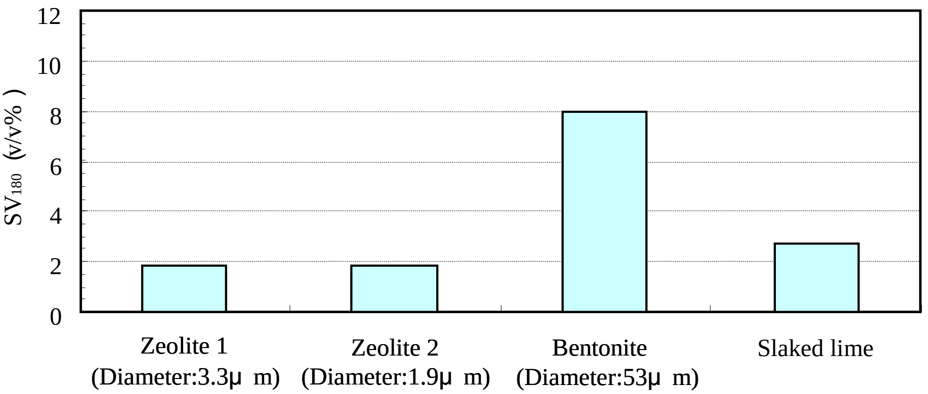
literature review. Then, a laboratory test was conducted to examine each of these adsorbents in simulated drainage. Items to be examined were adsorption capacity, properties of generated precipitates and cost efficiency. The adsorbents in equal proportions were added to artificial waste water simulated to drainage in the E mine. The concentrations of dissolved zinc in the water were determined and evaluated. As a result, zeolite and bentonite were found to eliminate more zinc than diatomite and activated carbon. Hence, diatomite and activated carbon were judged to be unsuitable in mine sites, and were excluded from countermeasures.

Next, the quantity of a precipitate generated when only slaked lime was charged for neutralization was compared with that when zeolite or bentonite was added to the drainage. With increased consolidation of the precipitate generated with the addition of zeolite, the quantity of the precipitate became smaller than that with only slaked lime for neutralization. On the other hand, with water absorbing and swelling properties of bentonite, the quantity was increased more than with the only slaked lime. As a result, it was determined that bentonite would be unsuitable for use in actual mines, and that zeolite was most advantageous as an adsorbent (Fig. 1).

Hence, a laboratory test was conducted to determine what amount of zeolite should be added to drainage to constantly meet the new standard. Results showed that 500 mg/L of zeolite was required to decrease the concentration of zinc in the E mine's drainage to 1.0 mg/L or less and that the cost for treatment was 2.2 times the current cost and exceeded a target value of 1.2 times. However, the test result revealed the effects of reducing dissolved zinc and generated precipitates. Consequently, a small amount of zeolite was added in a neutralization process in an on-site test described later in order to confirm these reduction effects.

Next, a laboratory test for iron chloride and iron sulfide was conducted to identify a more cost-effective chemical in iron sources. As a result, a difference between zinc removal effects of these two iron sources could not be confirmed (Fig. 2).

Hence, a laboratory test was conducted to determine what amount of ferric chloride should be added to drainage to constantly meet the new standard. The result showed that about 10 mg/L



SV_{180}: The quantity of a precipitate after 180min on neutralizing test

Figure 1 *The quantity of precipitate which is included zeolite, bentonite and slaked lime after neutralizing test*

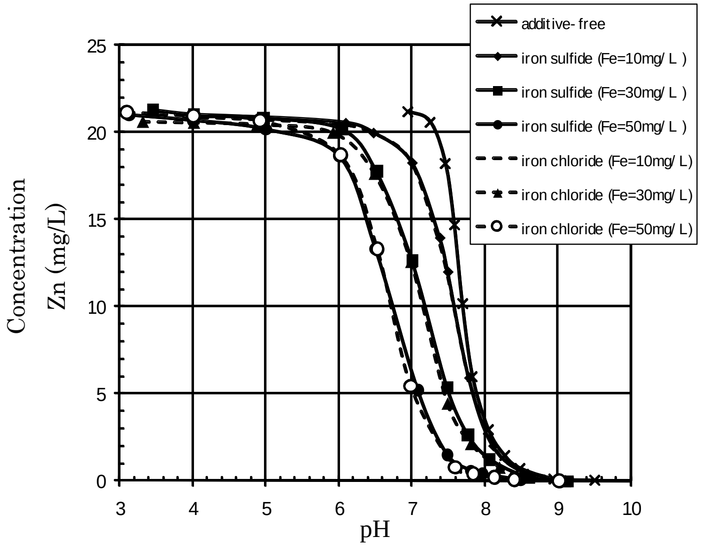


Figure 2 *The relationship of Concentration of Zn and pH for iron chloride and iron sulphide on Laboratory test*

of iron content was required to decrease the concentration of zinc in the E mine's drainage and that the cost for treatment of the waste water was 1.2 times the current cost.

These results from the basic test suggested the potential to limit the cost increase to 1.2 times or less by addition of ferric chloride and stable removal of zinc. Therefore, ferric chloride was adopted in the on-site test at the E mine was adopted.

On-site Test

An on-site test was conducted to determine the application of the results from the basic test. This test examined an additive amount of ferric chloride required to meet the new standard, measures against variations in flow rate of drainage, zinc reduction by zeolite and a rate of a cost increase against the current cost.

In the test, drainage flow rate was kept constant (assuming annual average of drainage in the E mine) to determine an additive amount of ferric chloride required to meet the new standard. Next, the flow rate was increased to evaluate an additive amount of ferric chloride required on an annual maximum flow rate in the mine. Furthermore, a small amount of zeolite was added in the neutralization process to confirm whether the concentration of zinc can be reduced more effectively.

The result of the on-site test showed that the concentration of zinc was successively decreased by ferric chloride and that an additive amount of ferric chloride required during ordinary drainage discharge was 6.0 mg/L on an iron basis. It was also found that the concentration of zinc could not be successively reduced with the increase of the additive amount during increased drainage discharge because suspended solids containing high-concentration zinc in treated water were discharged in large amounts. It was confirmed that the leakage of the suspended solids could be solved by the increase of a high-polymer coagulant (from 0.1 to 0.5 mg/L) used for the current treatment. The effect of decreasing the concentration of dissolved zinc by addition of zeolite widely varied. In some cases, the effect could not be confirmed. Hence, this substance was judged to be unsuitable in mine sites, and was excluded from countermeasures.

A confirmed effective method is that an additive amount of ferric chloride is fixed to 6.0 mg/L on an iron basis and an additive amount of a high-polymer coagulant is changed according to variations in flow. A cost for drainage treatment based on this method was up to 1.19 times as the current cost, or below 1.2 times of the target.

The results of the basic and on-site tests are summarized as follows: forced co-precipitation by ferric chloride is a method for meeting the new standard in a stable manner and at the lowest cost when the concentration of zinc is higher than that of iron, and the leakage of suspended solids containing high-concentration zinc during increased discharge can be solved by the increase of the high-polymer coagulant.

Conclusions

The basic and on-site tests were conducted for the E mine, where is low and it is difficult to achieve T-Zn<2.0 mg/L. As a result, it was found that the addition of iron chloride and the increase of the high-polymer coagulant reduced the concentration of zinc in treated water to 2.0 mg/L or less at the treatment cost 1.2 times below the current cost.