The Treatment of Hazardous Substances in Scrubbing Water

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The scrubbing waters of the combustion exhaust gases containing low concentrations of cyanide ion, formaldehyde, phosphate ion and fluoride ion were treated by the methods for concentrated liquid wastes. Such methods were applicable to the scrubbing waters which did not contain fluoride ions.

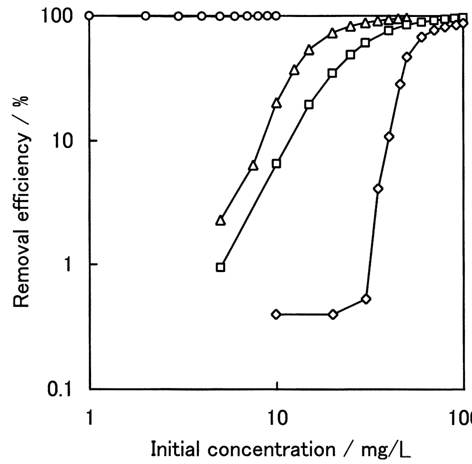

Fig. 1. Removal efficiency of hazardous substance in the scrubbing water.
(—○—, cyanide ion; —△—, phosphate ion as phosphorus; —□—, formaldehyde; —◇—, fluoride ion).

The liquid wastes containing various hazardous substances are generated at universities by experimental and research-related activities.[1] They are roughly classified into the two categories of inorganic and organic liquid wastes. Generally, organic liquid wastes are sprayed in a furnace and are thermally decomposed. The combustion exhaust gases are scrubbed by contacting with aqueous alkaline solutions. When the concentrations of hazardous substances have come down to those regulated by the law, the scrubbing waters must be treated secondarily. Although the adsorption column methods with chelate resin or active carbon are often used as the secondary treatment, running costs are expensive. The scrubbing waters contain approximately 2% salts as sodium chloride.[2] The guideline of discharge is less than 5% though there is no standard. The concentrations of hazardous substances are usually lower than 100 mg/L and are similar to the effluent standard levels. The hazardous substances concerned are mainly cyanide ion, formaldehyde, phosphate ion and fluoride ion. These substances are generated by thermal decompositions of liquid wastes containing acetonitrile, formalin, phosphate buffer and trifluoroacetic acid, respectively.[3] The following treatment methods[4–6] are already established for concentrated liquid wastes: the oxidation method for cyanide ion using sodium hypochlorite (method-A), the oxidation method for formaldehyde using hydrogen peroxide (method-B), the calcification method adding calcium chloride to precipitate phosphate ion as insoluble calcium phosphate (method-C) and similar calcification method for fluoride ion (method-D). If these methods become applicable to the scrubbing waters, they will be reasonable because of the economical running costs.

In this paper, the above-mentioned methods were applied to the scrubbing waters containing hazardous substances less than 100 mg/L. The relationships between initial concentrations (C_0) of various hazardous substances and removal efficiency (η) were examined. An example is shown in Fig. 1. The η value was obtained from the following equation: $\eta = 100\,(C_0-C)/C_0$, where the C value was the residual concentration of hazardous substance. The removal efficiency of hazardous substance was changed depending on the initial concentration of each substance. The residual concentration of cyanide ion was lower than 0.1 mg CN/L and was irrespective of the initial concentration. The removal efficiency was higher than 98.8% over the range of the initial concentration between 1 and 10 mg CN/L. In the case of phosphate ion, formaldehyde and fluoride ion, the removal efficiency increased gradually as the initial concentration increased. The method-B can be used for liquid waste containing high concentration of formaldehyde up to 2%. When liquid waste containing low concentration of formaldehyde is treated, it takes more than an hour to complete the decomposition reaction, because of a lack of the heat of the reaction.[7] Therefore, the stirring time was fixed for two hours. The precipitates produced by the method-C were mainly composed of calcium phosphate and contained small amounts of calcium carbonate because of the carbonate ion in the scrubbing water.[8] The removal efficiency by the method-D started to increase at 50 mg F/L. The sedimentation rates were more slowly than the case of phosphate ion, because of the minute precipitate of calcium fluoride. The solubility of fluoride ion as calcium fluoride was approximately 8 mg F/L.[9] The residual concentration of fluoride ion could be reduced to 8 mg F/L when the rate of crystallization was hastened by adding calcium fluoride as a core.[10]

The minimum limit of the treatment was defined as the minimum concentration at which the decomposition or the removal of hazardous substance was confirmed. The initial concentration of hazardous substance at the removal efficiency (η) of 10% was adopted as the minimum limit for the sake of convenience. The minimum limit was calculated by the regression derived from a linear plot of C_0 versus η at range close to the η value of 10%. The results obtained from the experiment on five kinds of scrubbing waters are shown in Table 1 with the effluent standard.[11] The effluent standard was the maximum concentration of substance discharged to the sewer. The concentration of formaldehyde is unregulated now. The minimum

Table 1. Minimum Limit of Treatment[a)]

Hazardous substance	Minimum limit mg L^{-1}	Effluent standard mg L^{-1}
Cyanide ion	< 1	1
Formaldehyde	12–20	—
Phosphate ion	8–14	16
Fluoride ion	39–59	15

a) The initial concentration at the removal efficiency of 10% was adopted as the minimum limit.

limit of the treatment changed according to the treatment conditions such as the amount of reagents, the pH value, the reaction time and so on. Since the minimum limits of cyanide ion and phosphate ion were lower than the effluent standards, the method-A and method-C seemed to be successfully applicable to the scrubbing water. The limit of formaldehyde was sufficiently lower. Then, the method-B seemed to be also applicable. On the other hand, the minimum limit of fluoride ion was higher than the effluent standard. When not devised along with promoting the crystallization by adding calcium fluoride as a core, the method-D could not be recommended. It was indicated that the method-D was a suitable method for the scrubbing water containing fluoride ion of 100 mg/L concentration or higher.

The scrubbing waters of the combustion exhaust gases containing low concentrations of cyanide ion, formaldehyde, phosphate ion and fluoride ion were treated by the methods for concentrated liquid wastes. The results from the separate treatment for each hazardous substance are described in this paper. It was confirmed the scrubbing water was treatable by the treatment method established for concentrated liquid waste, excluding fluoride ion. When these substances were intermingled in the scrubbing water, the oxidation method (method-A or method-B) should have priority over the calcification method, as was shown in the example of liquid waste.[12]

Experimental

The scrubbing water was sampled from the disposal plant in the Facility for Treatment of Liquid Waste, Hirosaki University. The pH value of the scrubbing water was between 9.3 and 10.2. The electroconductivity was between 14.8 and 44.6 mS/cm. The samples were prepared adding the standard solution of hazardous substances to five kinds of scrubbing waters. The standard solution (250 mg CN/L, 2500 mg HCHO/L, 2500 mg P/L or 2500 mg F/L) was added to 250 mL of the scrubbing water, and the sample was adjusted to the final concentration of 100 mg/L or lower. The treatment method for each hazardous substance was carried out and the residual concentration in the treated water was measured. The increase rate of the volume by the treatment was 3% or lower. The method-A was applied to the scrubbing water containing cyanide ion. It was adjusted at the pH value of 10.5 or higher and the ORP at 350 mV or higher using 12% sodium hypochlorite solution and was stirred for half an hour, and then it was changed at the pH of 8 or lower and the ORP of 600 mV or higher for an hour. The amount of sodium hypochlorite was controlled not by the theoretical amount but by the pH and the ORP. The method-B was applied to the scrubbing water containing formaldehyde. It was stirred for two hours at the pH of 11 to 12 using the twofold stoichiometry amounts of 3% hydrogen peroxide. The method-C was applied to the scrubbing water containing phosphate ion. It was stirred for half an hour at the pH of 10 to 11 using the twofold stoichiometry amounts of 10% calcium chloride solution. The method-D was applied to the scrubbing water containing fluoride ion. It was stirred for an hour at the pH of 6 to 7 using the fivefold stoichiometry amounts of 10% calcium chloride solution. The concentrations of cyanide ion, formaldehyde, phosphate ion and fluoride ion were measured according to the testing methods for industrial wastewater.[13]

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