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Suppression of Phosphate Liberation from Eutrophic Lake Sediment by Using Fly Ash and Ordinary Portland Cement

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In this study, the effect of suppression on phosphate liberation from eutrophic lake sediment by using fly ash and ordinary Portland cement (OPC) was investigated by small scale experiment. A system including sediment, lake water, and several kinds of capping materials was designed to clarify the suppression of phosphate liberation from sediment under the anaerobic condition. The suppression efficiencies of fly ash, OPC and glass bead used as control material were also determined, and these effects were discussed. The suppression efficiency of glass bead was 44.4%, and those of fly ash and OPC were 84.4%, 94.9%, respectively. The suppression by fly ash and OPC was mainly carried out by the adsorption effect, in addition to the covering effect. The suppression efficiency depended on the amounts of the material used, and about 90% of liberated phosphate was suppressed by fly ash of 10.0 Kg m^{-2}, and OPC of 6.0 Kg m^{-2}. The concentrations of heavy metals, such as mercury, cadmium, lead, copper, zinc, chromium, silver, arsenic and nickel, in fly ash and OPC were lower than those in the environmental materials. And it was considered that the concentrations of heavy metals in fly ash and OPC were too low to influence the ecosystem in natural water region.

Key Words: Fly ash; Ordinary Portland cement (OPC); Phosphate release; Eutrophic lake sediment; Suppression efficiency.

INTRODUCTION

Phosphorus (P) is an essential, often limiting, nutrient for growth of organisms in most ecosystems. However, excessive phosphorus may play an important

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role for the eutrophication in a closed water area, resulting in the bloom of aquatic plants, growth of algae and depletion of dissolved oxygen.[1] The supply of phosphorus from sediment is one of the main sources, and has an influence on the change of phosphorus concentration. The suppression of phosphorus liberation from sediment has been recognized as one of the important researches to control the eutrophication caused by the excessive phosphorus.[2]

Some earlier studies have shown that phosphate is adsorbed onto the surface of sediments in aerobic conditions. Conversely, in anaerobic conditions, the precipitated phosphate in sediment is dissolved and liberated into the overlying water.[3,4] In anaerobic condition, sulfate is deoxidized to sulfide ion by sulfate deoxidizing bacteria. On the interaction between hydrogen sulfide and liberation of phosphate from sediment under anaerobic state, Sugawara et al.[5] demonstrated that precipitated phosphorus (Fe-P, Al-P and Ca-P) is dissolved by the reaction with hydrogen sulfide, and the phosphate is released into overlying water as follows:

$$Fe(PO_4) \longrightarrow Fe_3(PO_4)_2 \tag{1}$$

$$SO_4^{2-} \longrightarrow S^{2-} \tag{2}$$

$$Fe_3(PO_4)_2 + 3S^{2-} \longrightarrow 3FeS + 2PO_4^{3-} \tag{3}$$

The precipitated phosphate of $Fe(PO_4)$ in sediment is deoxidized to $Fe_3(PO_4)_2$ at anaerobic state (Eq. 1) and also sulfate is deoxidized to sulfide ion by sulfate deoxidizing bacteria (Eq. 2). The generated sulfide ion reacts with $Fe_3(PO_4)_2$ and the phosphate ion is formed and liberated into water (Eq. 3).

In order to suppress the liberation of phosphate from sediment, many kinds of substances which adsorb phosphate or form insoluble compounds with phosphate have been investigated by several researchers.[6–10] Sodium aluminate,[6] gypsum,[7] lime[7–9] and slag[10] were studied, and these materials have suppressed a considerable amount of phosphate by adsorbing phosphate or producing an insoluble compound with phosphate.

The characteristics of adsorption of phosphate on the fly ash and ordinary Portland cement (OPC) were fundamentally studied in previous papers.[11] It was found that the efficiency of phosphate removal increased with increasing percent of CaO in the adsorbents. And, better removal was obtained at higher solute concentration, acidic pH and higher temperatures. The Frumkin isotherm was found to be the appropriate equation for modeling isotherms from the experimental adsorption data. And estimated adsorption capacity values of 32, 83 mg $PO_4{}^{3-}$/g adsorbent for fly ash, OPC respectively were obtained from breakthrough curves.

Accordingly, it is expected that fly ash and OPC adsorb phosphate dissolving in natural lake water, and that they suppress phosphate liberation from sediment even under anaerobic conditions. In this paper, the effect of suppression on phosphate liberation from sediment by using fly ash and OPC was investigated by small scale experiment. A system including sediment, lake water and several kinds of capping materials was designed to clarify the suppression of phosphate liberation from sediment under the anaerobic condition. The suppression efficiencies of fly ash, OPC, and glass bead were also determined, and these effects were discussed. The suppression mechanisms on phosphate liberation, such as covering effect and adsorption effect were proposed and discussed. And the influence of fly ash and OPC on ecosystem was studied on the grounds of the concentrations of heavy metals in them.

MATERIALS AND METHODS

Materials and Apparatus

Samples of fly ash and OPC were obtained from Nanhai Cement Factory of Foshan City, Guangdong Province, China, where they were also analysed by XRF and XRD. The chemical composition and physical properties of the materials are summarized in Table 1. The glass bead was used as a control material, which was obtained from the Department of Environmental Science and Technology, South China University of Technology, China, and the particle size was between 0.045 and 0.3 mm.

The used sediment and overlying water were obtained from the Taihu Lake, the fourth largest lake in China, which is located in Jiangsu Province,

Table 1: Chemical composition and physical characteristics of fly ash and OPC.

Chemical composition	Fly ash (%)	OPC[a] (%)
SiO_2	60.47	27.30
Al_2O_3	25.40	3.81
CaO	1.31	58.60
MgO	1.16	2.92
Fe_2O_3	2.92	1.60
MnO_2	0.11	0.73
TiO_2	0.90	0.10
K_2O	0.45	0.63
Na_2O	0.56	0.11
P_2O_5	0.25	0.31
SO_3	0.15	2.12
LOI at 1000°C	5.82	1.56
Particle size (mm)	0.045–0.3	0.045–0.3
Specific surface area (m^2/g)	0.86	0.95
Median diameter (mm)	0.10	0.08
Density (g/cm^3)	2.42	3.15
Porosity (%)	6.5	15.2

[a]Ordinary Portland cement.

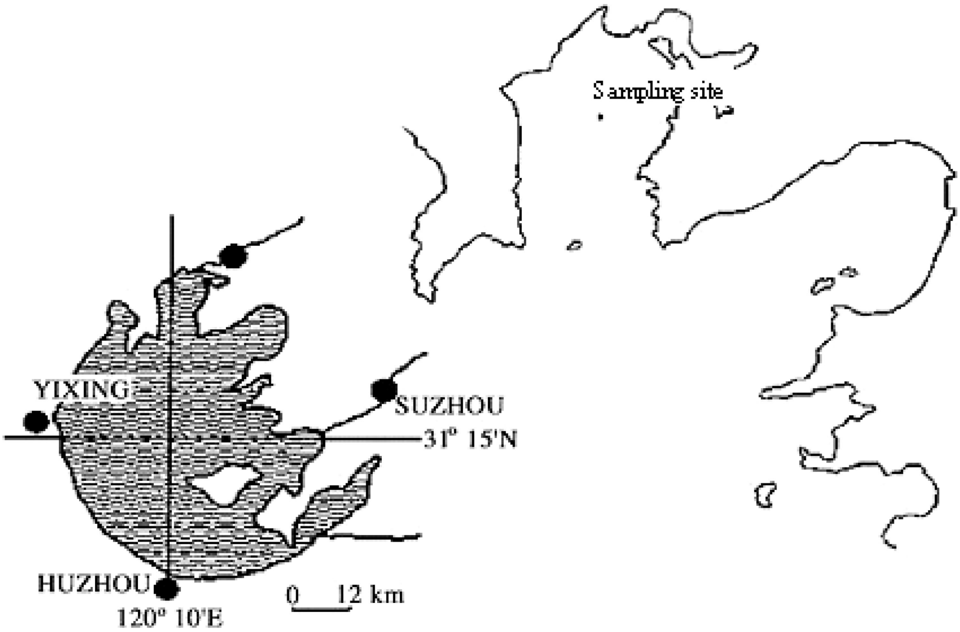

Figure 1: The sampling site of the used sediment and overlying water obtained from, Left: The sketch map of sampling in Taihu Lake. Right: Enlargement of Meiliang Bay at the northern part of the lake where sampling site located.

China, between 30°55′–31°34′N and 119°53′-120°37′E. The Taihu Lake is very shallow (area, 2338 Km^2; average depth, 2.1 m), with an approximate theoretical renewal time of 308 d.[12] Resulting from increasing industrial wastewater input, mostly from nearby cities, the eutrophication of the lake is accelerating. As a result, large cyanobacterial algal blooms are seriously affecting drinking water source and fishery industry.[13] The sampling time was at 14:00 on July 12, 2004. The sampling sites (31°29′10″N, 120°12′6″E) are shown in Figure 1.

The experiment on the liberation of phosphate from sediment was carried out in a plexiglass container, following Yamada et al.[10] The length, width and height of the container was 200, 200 and 600 mm, respectively. The apparatus presented in Figure 2 contained sediment, lake water and suppressing materials, such as fly ash, OPC and glass bead. Nitrogen was bubbled through a sintered glass ball to keep an anaerobic state in the container. All chemicals used were of analytical grade and deionized water was used for preparing solution.

Procedures

In the study of the suppression of phosphate liberation from sediment, two experiments were carried out as follows. A control experiment was carried out using both sediment and lake water in 2 containers, and suppression materials

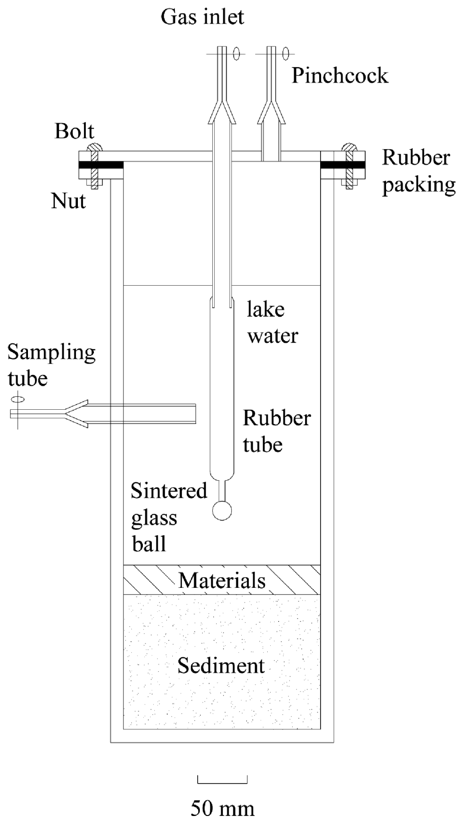

Figure 2: Schematic presentation of the experimental container.

were used in only one container. Glass bead, fly ash and OPC were used as suppression materials. The amount of sediment and lake water contained in each container was 5 Kg, 10 L, respectively. In order to study the effect of temperature, the particle size and the amount of the suppression material used on suppression efficiencies, the temperature, the particle size and the amount of the suppression material used were different in each group experiments (Figures 3, 5, 6, and 7). The concentration of several heavy metals, such as mercury, cadmium, lead, copper, zinc, chromium, silver, arsenic and nickel in fly ash and OPC were determined with atomic absorption spectrophotometer to study the influence of fly ash and OPC on the ecosystem. The duplicate experiments demonstrated the high repeatability of this experimental method and the experimental error could be controlled within 5–10%.

Analysis of Phosphate

The analysis of phosphate (as phosphorous) was done spectrophotometrically using the stannous chloride method described in Standard Methods.[14]

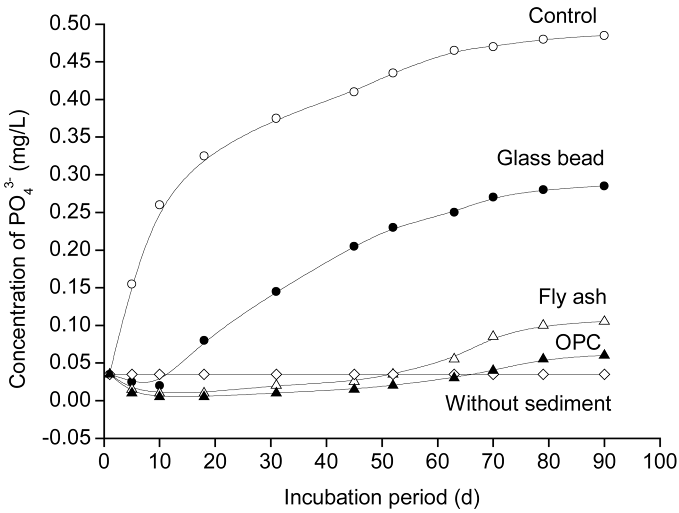

Figure 3: The changes of concentration of PO_4^{3-} in lake water during anaerobic incubation for 90 days. The temperature was 25°C, and the particle size of the material used was between 0.075 mm and 0.090 mm, and the amount of the material used was 6 Kg m^{-2}.

All the samples were analyzed in triplicate, and SD of all the results reported in this paper was in the range of ±2% to ±5%.

RESULTS AND DISSCUSSION

Suppression Effects by Fly Ash, OPC and Glass Bead

To compare the suppression effects on orthophosphate liberation by various materials, fly ash, OPC, and glass bead were investigated. As seen in Figure 3, the variations of phosphate in water were measured in the course of incubation period. The increase of the phosphate concentration in water was recognized during 10–90 days under the conditions of control and covered with glass bead on sediment, respectively. But the significant increases of the phosphate concentration were not recognized under the covering conditions of fly ash and OPC on sediment and lake water (without sediment), respectively. Therefore, it was considered that the increase of phosphate ion in lake water was mainly caused by the phosphate liberation from sediment and was not caused by the mineralization of organic phosphorus in lake water.

Comparing the concentration of orthophosphate in control with that in suppression experiment, the phosphate increased more rapidly in the former and remained at low level in the latter. Accordingly, it was clear that the liberation of phosphate was suppressed by glass bead, fly ash and OPC. The amount of orthophosphate released from sediment during the 90-day

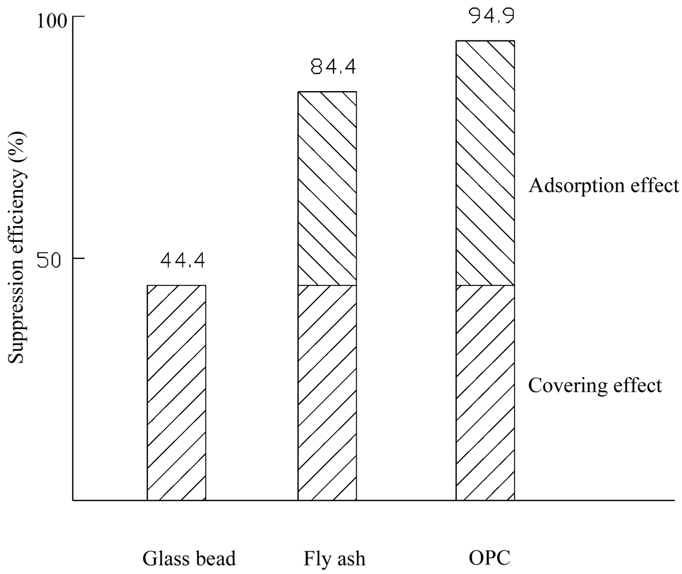

Figure 4: Suppression efficiency by various suppressing materials.

experimental period and the suppression efficiencies (ratio of the suppressed amount of phosphate to the released amount of phosphate in the control experiment) could be calculated from Figure 3. And the suppression efficiency of glass bead was 44.4%, and those of fly ash and OPC were 84.4%, 94.9%, respectively.

As described above, the suppression efficiency of glass bead covering on the surface of sediment was 44.4% in spite of no adsorption of phosphate. That is, this suppression effect was mainly carried out by covering the surface of sediment with materials (covering effect). The suppression efficiency of fly ash and OPC was 84.4%, 94.9%, respectively. That is, these effects were caused by not only covering effect but also adsorption of phosphate liberating from sediment (adsorption effect). Then it was considered that two effects were related to the suppression of phosphate liberation from sediment. This consideration was presented schematically in Figure 4. Fly ash and OPC had an effective suppression on the orthophosphate liberation, and the suppression was mainly carried out by both covering effect and adsorption effect.

Effect of Temperature

Hou et al.[15] observed that the liberation rate of phosphate from sediment varied with different environmental temperature. To study the temperature effect on phosphate liberation, a group of containers with different incubation temperature were prepared. And at each temperature, a container including only sediment and lake water as control was used.

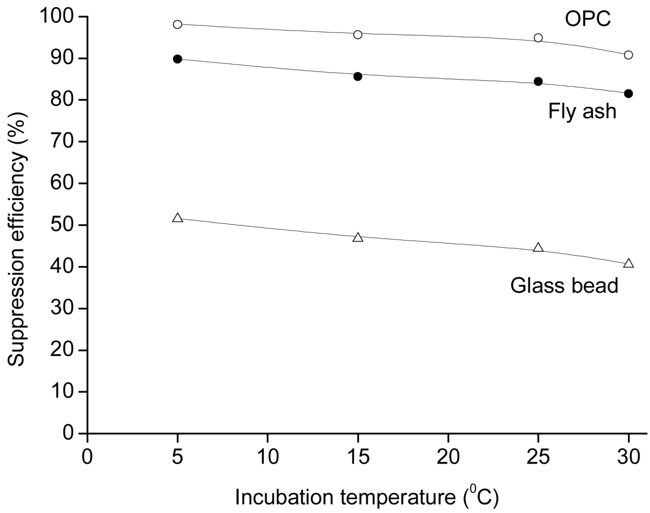

Figure 5: Effect of temperature on suppression efficiency. The particle size of the material used was between 0.075 mm and 0.090 mm, and the amount of the material used was 6 Kg m^{-2}.

Figure 5 illustrates the suppression efficiency of each material with different incubation temperature (from 5°C to 30°C). As described above, covering and adsorption effects were related to the suppression of phosphate liberation from sediment. Considering that fly ash and OPC would adsorb more phosphate at higher temperature, it was expected that the adsorption effect should increase with temperature increase. But the suppression efficiencies were observed to decrease slightly with temperature increase. This might be caused by the extra phosphate liberating from sediment at higher temperature. As Hou et al.[15] described in their study, phosphate liberated faster from sediment at higher temperature. Therefore, on the account of the adsorption effects of the suppression materials and the liberation of phosphate from sediment at different temperature, the suppression efficiencies decreased slightly with temperature increase in the capping experiment.

Effect of Particle Size

The suppression efficiency of each material with different particle size (from 0.045 mm to 0.3 mm) was shown in Figure 6. The suppression efficiencies of OPC and fly ash decreased slightly with the increase of particle size, and that of glass bead dropped drastically with the increase of particle size. There were several reasons for this phenomenon. For one thing, suppression efficiency of glass bead was caused mainly by covering effect, and this was closely related to the particle size. For another, the suppression efficiencies

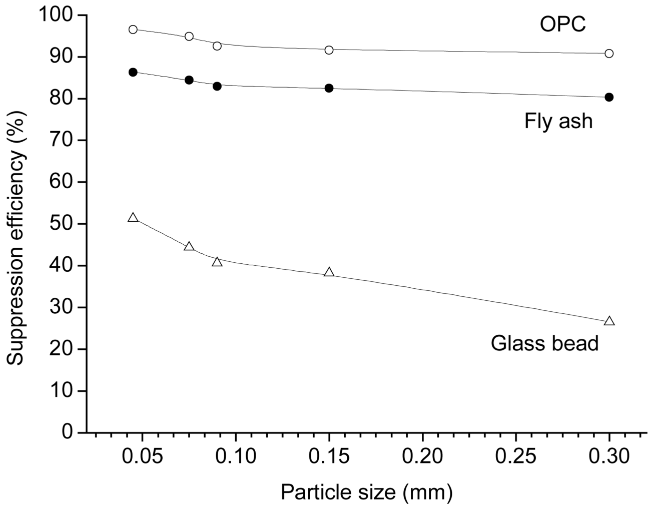

Figure 6: Effect of particle size on suppression efficiency. The temperature was 25°C, and the amount of the material used was 6 Kg m^{-2}.

of OPC and fly ash were also caused by adsorption effect. Agyei et al.[11] suggested that chemical adsorption is a more significant contributory phenomenon to the removal of phosphate by OPC and fly ash than physical adsorption. Physical adsorption is closely related to the specific area and particle size of the adsorbents. Thus in the case of the suppression of phosphate by glass bead, fly ash and OPC, the variations range of the suppression efficiencies with particle size were different.

Effect of the Amount of the Material Used

It is important to estimate how much fly ash and OPC are necessary for the suppression of phosphate liberation from sediment. A series of containers containing 2, 4, 6, 8, 10 Kg m^{-2} of fly ash or OPC with sediment and lake water, and a container including only sediment and lake water as control were used.

The relationship between the suppression efficiency and the amount of the material used was shown in Figure 7. The suppression efficiency depended on the amount of fly ash and OPC, which increased significantly with the amount of the material used from 2 to 10 Kg m^{-2}. From the present results, it was found that about 90.0% of orthophosphate liberation was suppressed by 6 kg m^{-2} of OPC or 10 Kg m^{-2} of fly ash. Yamada et al.[10] had successfully used slag to suppress phosphate liberation from sediment. And about 85% of orthophosphate liberation was suppressed by using 7.5 kg m^{-2} of slag. Compared with slag, OPC was more effective to suppress phosphate liberation from sediment.

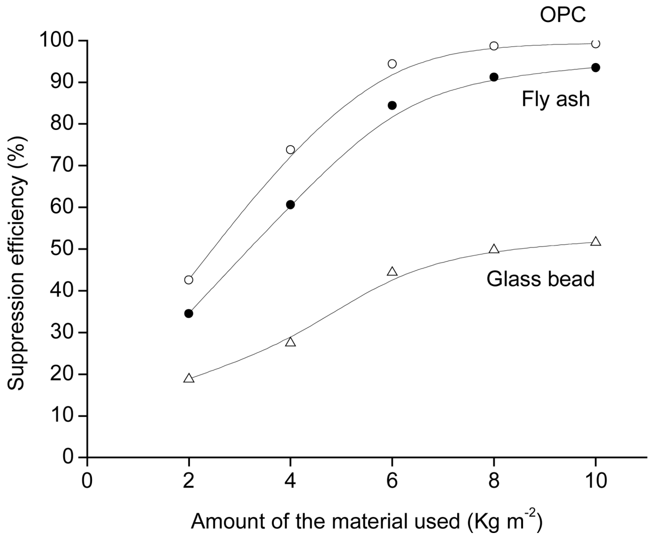

Figure 7: Effect of the amounts of the material used on suppression efficiency. The temperature was 25°C, and the particle size of the material used was between 0.075 mm and 0.090 mm.

Influence of Fly ash and OPC on Ecosystem

In the case of using fly ash and OPC for the suppression of orthophosphate liberation in water region, the influence of fly ash and OPC on the ecosystem must be researched. The concentrations of several heavy metals, such as mercury, cadmium, lead, copper, zinc, chromium, silver, arsenic, and nickel, in fly ash and OPC were determined with atomic absorption spectrophotometer, and the results were shown in Table 2. The background concentrations of mercury, cadmium, lead, copper, zinc and chromium, silver, arsenic, and nickel in the earth in the Taihu Lake region, China were 0.11, 0.27, 19.5, 18.9, 59.2, 79.3, 0.1, 9.4 and 15.7 ppm, respectively.[16]

The concentrations of mercury, cadmium and silver were much lower than the back ground values. And the concentrations of lead, copper, zinc, chromium, arsenic and nickel were low compared with the concentrations of those in the sediment of the Taihu Lake.[17] Therefore, the concentrations of

Table 2: Concentrations of several heavy metals in fly ash and OPC.

	Hg	Cd	Pb	Cu	Zn	Total-Cr	Ag	As	Ni
Fly ash (ppm)	<0.01	<0.02	2.6	0.5	5.5	22.3	<0.01	0.8	1.3
OPC[a] (ppm)	<0.01	<0.02	3.2	0.3	2.8	17.6	<0.01	0.5	1.3
Background (ppm)	0.11	0.27	19.5	18.9	59.2	79.3	0.1	9.4	15.7

[a]Ordinary Portland cement.

heavy metals in fly ash and OPC were lower than those in the environmental materials. Hereupon, it was considered that the concentrations of heavy metals in fly ash and OPC were too low to influence the ecosystem in natural water region. In the case of covering the surface of sediment by fly ash and OPC, the life of the bottom organisms may be affected. Hence, the influence of covering slag on biomass and the bottom dwelling organisms should be studied further.

CONCLUSIONS

The suppression efficiency of glass bead was 44.4%, and those of fly ash and OPC were 84.4%, 94.9%, respectively. The suppression by fly ash and OPC were mainly carried out by the adsorption effect, in addition to the covering effect. The suppression efficiency depended on the amount of the material used, and about 90% of liberated phosphate were suppressed by fly ash of 10.0 Kg m^{-2}, and OPC of 6.0 Kg m^{-2}. The concentrations of heavy metals, such as mercury, cadmium, lead, copper, zinc, chromium, silver, arsenic and nickel, in fly ash and OPC were lower than those in the environmental materials. And it was considered that the concentrations of heavy metals in fly ash and OPC were too low to influence the ecosystem in natural water region.

Fly ash and OPC have been used successfully for the suppression of phosphate liberation from eutrophic lake sediment. The relatively low cost and high capabilities of the fly ash and OPC make them potentially attractive materials for the suppression of phosphate liberation from sediment.

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