

An Effective and Economic Strategy to Restore Acidified Freshwater Ecosystems with Steel Industrial Byproducts

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ABSTRACT

Blast furnace, converter and electric arc furnace (EAF) processes have produced iron and steel slag as byproducts. In terms of resource utilization, the EAF process making steel from scrap metals is superior to other steelmaking processes from iron ores or pig iron. Although all blast furnace slags can be completely recycled for use of steelmaking slag base and cement aggregate, parts of EAF slag ultimately end up in landfill sites. A laboratory-scale investigation was performed to develop novel applications of EAF slag in aquatic environments. To examine chemical properties of the EAF slag and the effects on organisms, strict experimental conditions were designed to elute the metal components of the slag using HCl based on JIS K 0058-1. Analysis of the chemical properties of the slag by ICP-AES and ICP-MS showed that the metal effluents from the slag were less than the concentrations defined by the environmental quality standards. Other analysis using a pH meter showed that the eluate in acidic freshwaters drastically changed their pH values from acidic to neutral. Regarding the effects of the slag on organisms, the eluate in acidic conditions notably induced proliferation of phytoplankton rather than cytotoxicity by improving the pH condition.

Keywords: acidification, electric arc furnace oxidizing slag, iron and steel slag, phytoplankton

INTRODUCTION

Iron and steel slags, which involve blast furnace slag and steelmaking slag including converter slag and electric arc furnace (EAF) slag, have been produced as steel industry by-products. All blast furnace slag (24,278,000 tons/year) can be recycled completely for the use of steelmaking slag base and cement as aggregates, while 317,000 tons/year of steel making slag (91,000 tons of converter slag and 226,000 tons of EAF slag) ultimately end up in landfill sites (Nippon Slag Association, 2007). In terms of resource utilization, EAF process of making steel from scrap metals is especially superior to other steel making processes from iron ores or pig iron. However, the social and industrial systems to recycle all of the by-products from EAF process are poorly established.

Applications of slag to depuratives and sand capping materials in coasts and lakes have been recently expected due to the limitation of final landfill sites and high costs of slag disposal. It is known that environmentally hazardous substances are enriched in each slag. The toxicity and biological impacts of the eluate from EAF slag on aquatic organisms remain poorly understood, whereas the physicochemical properties and the

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effects of converter slag on organisms have been often documented (Chlou *et al.*, 2006; Kang *et al.*, 2006; Xue *et al.*, 2006; Chaurand *et al.*, 2007; Miki *et al.*, 2010; Stimson *et al.*, 2010). The purpose of this study was to investigate the availability of EAF slag in aquatic environments through the assessments of both chemical properties of the EAF slag and their effects on organisms in aquatic environments. In this study, we present that EAF slag can function as a buffer agent and that its buffering action can result in proliferation of phytoplankton in acidified freshwater.

MATERIALS AND METHODS

EAF slag

Electric arc furnace normal steel oxidizing slag was provided from an iron and steel company and the EAF slag was used in this study (Table 1). After alkali fusion of the slag, chemical compositions of the oxides in the slag were calculated from the metallic components determined using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) as described previously (Yokoyama *et al.*, 2009). To assess several properties of the EAF slag in aquatic environments, a leaching test was performed to elute the metal components of the slag with HCl based on JIS K 0058-1 (Japanese Standards Association, 2005). Briefly, the slag was ground and sieved to select approximately 1 – 2 mm particles, which were the size of ground slag. Next, chemical components of the slag were eluted in distilled water adjusted to pH 6.0 with HCl (100 g slag/1L distilled water) for 6 hr. After the elution, the solution was filtrated with 0.45 µm pore filter to eliminate the slag particles.

The main chemical components of the filtrated eluate were analyzed by ICP-AES and ICP mass spectroscopy (ICP-MS). Total amounts of nitrogen were measured by alkaline potassium peroxydisulfate method and reflected light analysis. Briefly, all nitrogen compounds in the eluate were heated for 30 min at 120°C in alkaline potassium peroxydisulfate and changed to nitrate. The concentrations of nitrate were determined using a Reflectoquant based on reflected light analysis (RQ-flex, Merck, USA). Both the concentrations of the environmentally regulated elements including hexavalent chromium and the other minor elements of the eluate from the slag were analyzed by the external inspection institute.

Elution behavior from EAF slag at several pH values

Additional leaching tests were performed under different elution conditions. Chemical components of the slag were eluted in distilled water adjusted at pH 4.0 or pH 8.0 (100 g slag/1L distilled water) for 6 hr. After elution, the solution was filtrated with 0.45 µm pore filter. The main chemical components of a filtrated eluate were analyzed with ICP-AES.

Table 1 - Chemical composition of the slag used in this study.

	FeO	SiO ₂	CaO	Al ₂ O ₃	MgO	MnO	Cr ₂ O ₃	ZnO	NiO	CuO
mass%	35.1	19.2	20.8	15.2	4.1	5.1	0.43	0.071	0.028	0.025

Chemical properties of the eluate from EAF slag in freshwaters and sea water

A previous study revealed that the initial pH value of the eluate was about 9.5 just after the elution time of 6hr (Yokoyama *et al.*, 2009). Moreover, the pH value of the eluate was decreased by continuous elution over 6hr (Yokoyama *et al.*, 2009). In this study, the pH value of the filtrated eluate (pH 9.6) just after separating the slag particles from the eluate also changed and was finally stable at pH 7.5. The filtrated eluate, which was stable at pH 7.5, was used for the succeeding experiments.

Double distilled water (DDW) (pH 6.97), artificial pond water (APW; 0.1 mM each of NaCl, KCl, CaCl₂) (Tominaga *et al.*, 1991) (pH 6.17) and Van't Hoff artificial sea water (ASW; 462 mM of NaCl, 35.5 mM of MgCl₂, 9.39 mM of KCl, 99.8 mM of MgSO₄, 8.50 mM of CaCl₂ and 59.5 mM of NaHCO₃) (pH 8.50) were used to prepare each pH standard solutions adjusted with HCl or NaOH. These pH standard solutions are referred to as the pH-adjusted DDW, pH-adjusted APW and pH-adjusted ASW, respectively. Each pH standard solution in freshwater or sea water was mixed with the eluate from EAF slag (volume of pH standard solution : volume of the eluate = 1 : 1). In this study, DDW (pH 6.97) and 0.05 M Tris-HCl buffer (pH 7.20) were used as the negative and the positive control of buffering action, respectively. The pH value of the mixture was determined using a pH meter.

Algal strain

The origin of free-living alga, *Chlorella kessleri*, used in this study was the strain from the Institute of Applied Microbiology (IAM) culture collection at the University of Tokyo. Before the experiments, algae were maintained in the liquid CA medium as described by Nishihara *et al.* (1998).

Effects of the eluate from EAF slag on algae

To examine the effects of the eluate on algal growth, *C. kessleri* was cultured in a 1.5 mL Eppendorf tube. Each tube was filled with 1 mL of fresh CA medium adjusted to pH 5.0 containing the eluate from EAF slag (50%, v/v). Each culture was started at an initial density of 5.0×10^5 algal cells/mL. After 24hr, 48hr and 72hr of incubation under the light:dark (LD) conditions (12 hr light/12 hr dark) at ca. 3,000 lux of natural white fluorescent light at $23 \pm 2^\circ\text{C}$, the number of algae was quantified using a hemocytometer as described previously (Takahashi *et al.*, 2007). The pH value of each culture medium was determined using a pH meter.

The effects of the eluate on the morphology and population of algae were analyzed. Briefly, *C. kessleri* was cultured in fresh CA medium adjusted to pH 7.2 containing the eluate (70%, v/v). Each culture was started at an initial density of 1.0×10^4 algal cells/mL. After 1 week of incubation under the LD condition, algae treated with or without the eluate were collected and prepared for microscopic observation. From the digital data of algal microphotographs, each algal size as relative cell size was calculated from the pixel area of each alga using Image J software.

RESULTS AND DISCUSSION

Chemical properties of the eluate from EAF slag

The utilization of slag in aquatic environments has been restrained by several laws including the environmental quality standards (EQS) for soil pollution, Japanese Law Relating to the Prevention of Marine Pollution and Maritime Disaster and EQS for water pollution (EQS for human health). In this study, chemical properties including metal elution behaviors from the EAF slag and the effects of the slag on organisms in aquatic environments were investigated. The EAF slag is mainly composed of FeO , $2\text{CaO}\cdot\text{SiO}_2$, MgFeAlO_4 and $\text{FeO}\cdot\text{Al}_2\text{O}_3$ as described previously (Yokoyama *et al.*, 2009; Yokoyama *et al.*, 2010). The metal contents in the slag and the metal concentrations in the eluate are presented (Table 1, Table 2 and Fig. 1). Numbers of 4 – 6 and 8 – 11 of superscripts in Table 2 show EQS for conservation of the living environment, while No. 7 of the superscript is only categorized into EQS for human health. The results showed strong correlation between metal contents in the slag and the metal concentrations eluted (Fig. 2A). However, their correlations in Fe, Mn and Cr were weak, because elution efficiencies of Fe, Mn and Cr were extremely smaller than other metals (Fig. 2B). In addition to the leaching test at pH 6.0 based on JIS K 0058-1, the elution behaviors of metals from EAF slag at both lower pH and higher pH were also examined (Fig. 3). As a result of the leaching tests, concentrations eluted from the slag of metal and regulated substance including anionic components were approximately less at all of the elution conditions tested than the concentrations defined by EQS, except that the concentrations of Zn eluted at 6.0 and 8.0 were slightly over EQS for special life (Fig. 1B and Table 2). Although both elution behaviors of Ca and Mg changed dependently on pH, behaviors of other main and minor elements including elements regulated by EQS hardly changed (Fig. 3). Especially, the concentrations of Ni and Cu eluted from the slag were lower than 0.005 mg/L at all leaching conditions (Fig. 1B and Fig. 3). When the slag was exposed to the elution condition adjusted at pH 4.0, their concentrations of total Cr, Zn and Mn in the eluate were 0.024, 0.006 and 0.004 mg/L, respectively. After exposure of the slag to the elution condition adjusted at 8.0, the concentrations of total Cr, Zn and Mn in the eluate were undetectable, 0.012 and 0.003 mg/L, respectively. Moreover, both the total amounts of nitrogen and phosphorus inducing microbial pollution in aquatic environments were also less in the eluate than the concentrations defined by EQS (Table 2).

Table 2 - Environmental quality standards and concentrations of environmentally regulated elements and the minor elements of the elution components obtained from the leaching test at pH 6.0.

		Eluate of EAF slag (mg/L)	Environmental quality standards (mg/L)		
			Soil pollution	Marine pollution	Water pollution
Regulated substances	Total As	ND ¹ (RDL ² : 0.001)	0.01	0.1	0.01
	Total B	0.28	1		1 ³
	Total Be	ND (RDL: 0.0005)		2.5	
	Total Cd	ND (RDL: 0.0001)	0.01	0.1	0.01
	Chromium (VI)	ND (RDL: 0.005)	0.05	0.5	0.05
	Total Pb	ND (RDL: 0.0005)	0.01	0.1	0.01
	Hg	ND (RDL: 0.0001)	0.0005	0.005	0.0005
	Total Se	0.003	0.01	0.1	0.01
	Total V	0.01		1.5	
	Total Zn	0.014		2	0.03 ⁴ , 0.02 ⁵ , 0.01 ⁶
	F ⁻	0.5	0.8	15	0.8 ⁷
	Total CN	ND (RDL: 0.005)	ND	1	ND
Substances out of regulation	Total N	0.4			0.1-1 ⁸ 0.2-1 ⁹
	Total P	ND (RDL: 0.1)			0.005-1 ¹⁰ 0.02-0.09 ¹¹
	Cl ⁻	6			

1: Not detected.

2: Reportable detection limit.

3, 7: Standard value is not applied to coastal waters.

4: Habitable river or lake for an aquatic life.

5, 9, 11: Habitable coastal water for an aquatic life.

6: Habitable coastal water that needs conservation in particular for nidus and nursery ground.

8, 10: Habitable lake for an aquatic life.

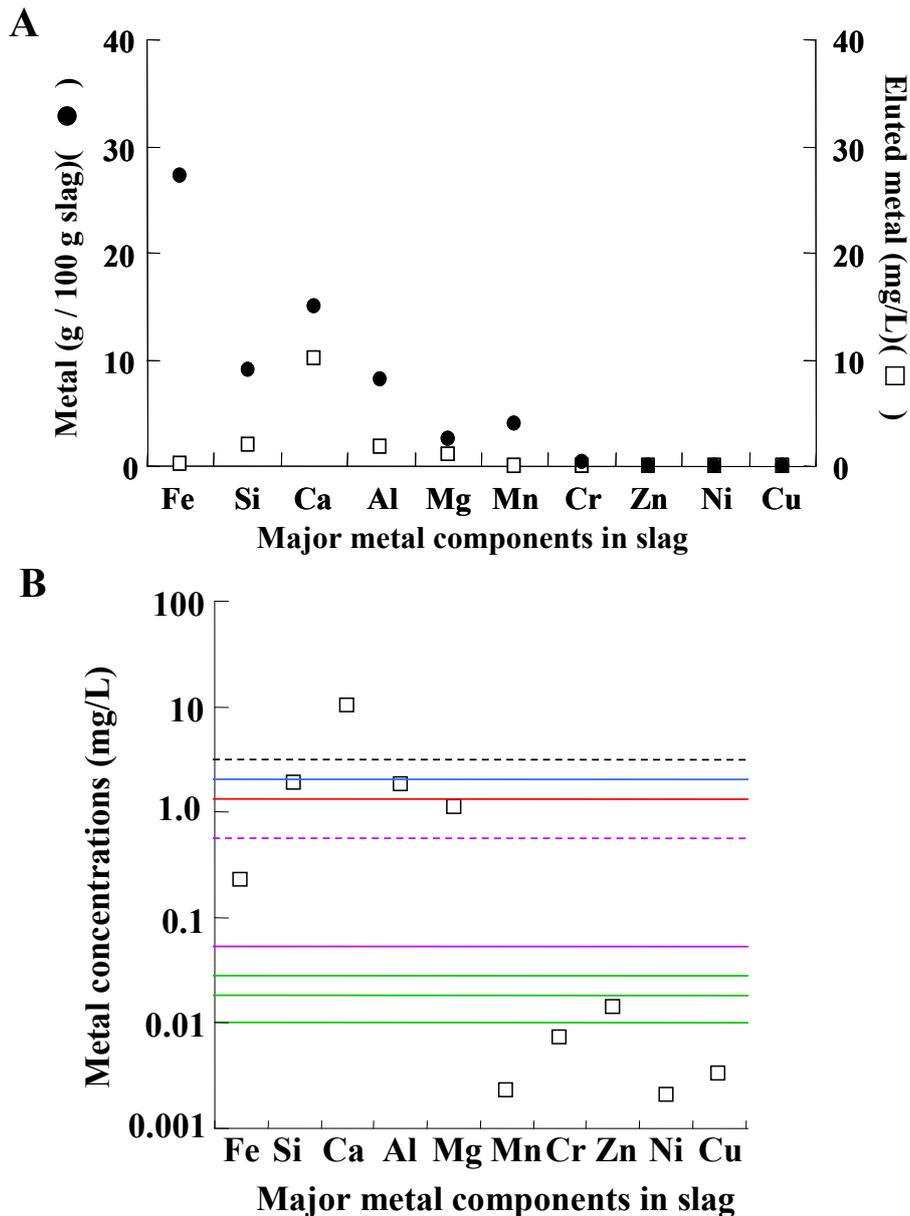


Fig. 1 - Major metal components in both the slag and the corresponding eluate resulting from the leaching test at pH 6.0.

(A) The dot graph shows the major metal components in the slag or the corresponding eluate. Total chromium was considered for Cr because of undetectable amounts of hexavalent chromium (see Table 2).

(B) The graph shows the concentrations of major metal components in eluate and values of EQS for several elements. The broken black line and solid blue and red lines represent the EQS of Cu (3 mg/L), total Cr and Zn (2 mg/L), and Ni (1.2 mg/L) for marine pollution, respectively. The three green lines represent the EQS of Zn (0.01, 0.02 and 0.03 mg/L) for water pollution (see No. 4 – 6 of superscripts in Table 2). Besides the EQS of total Cr, the broken purple line and the solid purple line represent the EQS of hexavalent chromium for marine pollution (0.5 mg/L) and for water pollution (0.05 mg/L) as informative data.

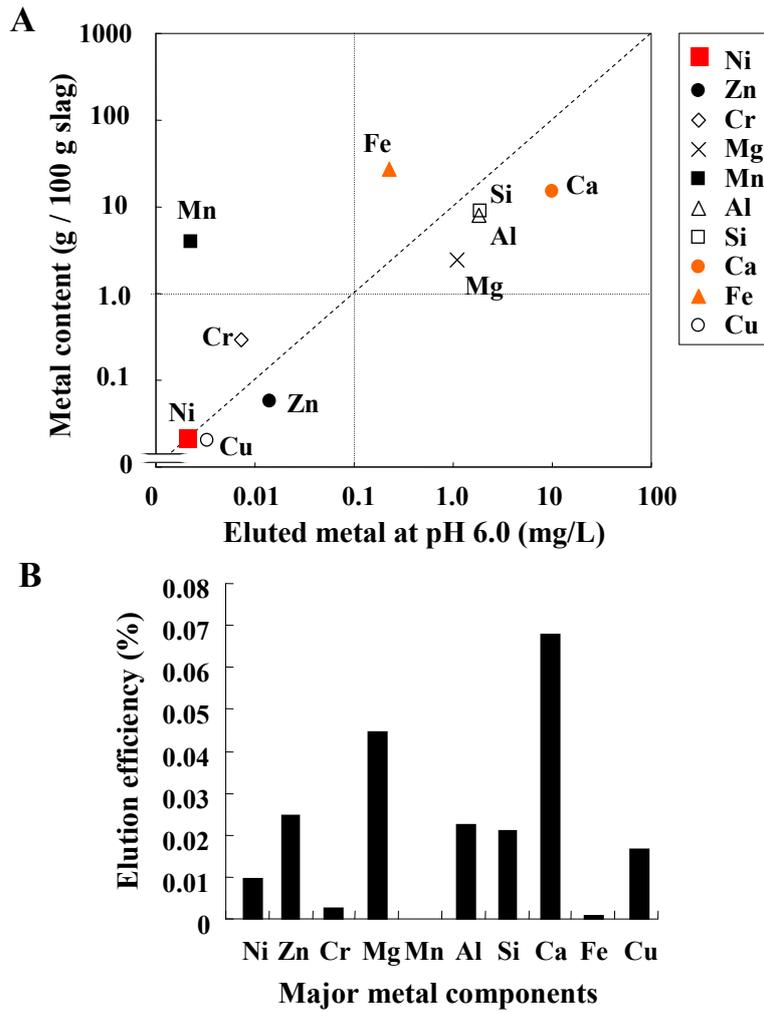


Fig. 2 - Elution behaviors of metals in the slag and the elution efficiencies of each metal. (A) The dot graph shows the relation between the metal contents in the slag and the concentrations eluted. Total chromium is considered for Cr because of the undetectable amounts of hexavalent chromium. (B) The bar graph shows the elution efficiency of each metal from the slag.

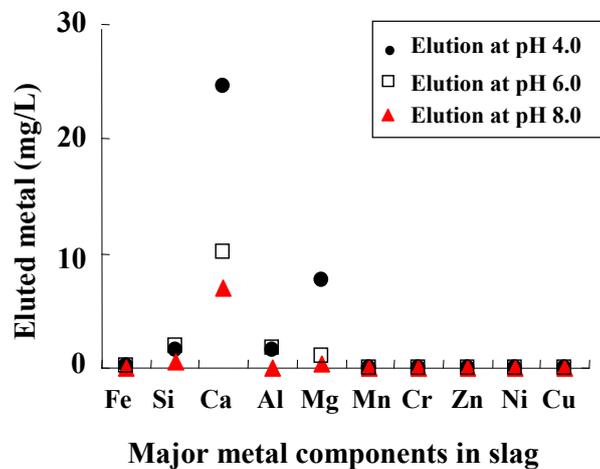
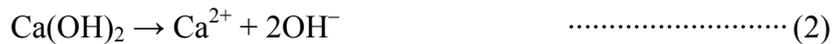


Fig. 3 - Elution behaviors of metals in the slag at different pH values.

After separating the eluate from the slag particles by filtration as described in the materials and methods section, the eluate stable at pH 7.5 was used in this study. Although precipitates including metal hydroxide were hardly visible in the eluate before and during this study, small amounts of metal components might precipitate after the pH change from 9.6 to 7.5. Generally, pH affects many aspects of cellular physiology including cell metabolism, enzymatic activities, and membrane channel functions. In addition to the chemical components of the eluate, the buffering action of the eluate was examined as one of the chemical properties in this study. By the addition of the eluate to pH-adjusted solutions, pH values of acidic pH-adjusted solutions drastically changed from acidic to neutral (Fig. 4A). An additional experiment with APW as a model freshwater-ecosystems revealed that the eluate could work as a buffer in acidified APW (Fig. 4B). On the other hand, the eluate hardly changed the pH values of alkaline pH-adjusted solutions as compared with 0.05 M Tris-HCl buffer (Fig. 4A). Calcium and Mg, which belonged to Group 2 elements and were included in the eluate (Fig. 1), were presumed to contribute to the pH variation. Aluminum as an amphoteric element might also contribute to that. The dissolution of Ca from the slag can be expressed as follows:



Magnesium in the eluate was assumed to be slightly present as MgO due to the lower solubility of Mg(OH)₂ than that of MgO. The chemical reactions of both Ca and Mg in acidic conditions can be expressed as follows:



Thus, these reactions of Ca and Mg could consume protons in acidic conditions, resulting in the pH variation from acidic to neutral. According to a previous study (Yokoyama *et al.*, 2009), the dissolution of Al eluted from the slag at pH 6.0 can be expressed as the following reaction:



Aluminum, which is the same as Group 2 elements in the eluate, is also involved in the following reactions to consume protons in the acidic condition:



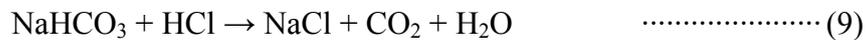
Thus, these components supplied from the eluate could contribute to the neutralization of acidified freshwater through chemical reactions including (3), (4), (6) and (7). On the other hand, the result obtained showed that the eluate did not work as a buffer in alkaline conditions (Fig. 4A). If unreacted Al(OH)₃ is present in the eluate, Al as the amphoteric element must consume hydroxide ions in alkaline conditions based on the

following reaction:

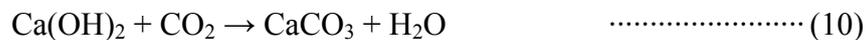


However, Al was almost already present as AlO_2^- ($[\text{Al(OH)}_4]^-$) because the solubility of Al(OH)_3 was very low. Thus, there were actually few molecules to consume hydroxide ions in the main components. From this reason, the relative potential to neutralize alkaline conditions was assumed to be weaker than that to neutralize acidic conditions, causing the eluate to function insufficiently as buffer in alkaline conditions. In this study, the concentrations of some anionic substances were also analyzed (Table 2). However, more comprehensive analysis is necessary to identify the other molecular structures of the conjugated anions contained in the eluate. Taken all together, even if the acidic environments dissolve the EAF slag, these components eluted from EAF slag can function as a buffer against excessive acidification in aquatic freshwater systems.

Additional tests with both the eluate and pH-adjusted ASW as a model sea water ecosystem were performed (Fig. 5). While the eluate in freshwater systems showed the drastic pH-change in acidic conditions (Fig. 4), the eluate in pH-adjusted ASW never worked as a buffer (Fig. 5A). Artificial sea water is more abundant in minerals including both alkaline and alkaline earth metals or their conjugated anions than freshwater such as DDW and APW. The high contents of their molecules generally vest seawater with the higher buffering capacity than freshwater. For this experiment, larger amounts of protons were needed to make the pH-adjusted ASW than pH-adjusted DDW (Fig. 5B). In acidic conditions, the chemical reaction of NaHCO_3 contained in ASW can be expressed as follows:



Because the amount of NaHCO_3 was much larger than elements from the eluate, the chemical equation (9) to produce CO_2 was assumed to proceed first. There are several reports about these reactions in freshwater between CO_2 and Ca(OH)_2 (Kawabata *et al.*, 1994; Sawamoto *et al.*, 1996; Monma, 1997). The reaction in freshwater between CO_2 and MgO has been reported (Botha & Strydom, 2001; Frost *et al.*, 2008). Thus, both Ca(OH)_2 and MgO work as CO_2 absorbents. Although some CO_2 produced may be released into the air, the other dissolved CO_2 is assumed to be related to the following reactions with both Ca and Mg from the eluate in acidified ASW:



Thus, both Ca(OH)_2 and MgO from the eluate in acidified ASW can not directly react with protons that hinder the increase in pH of the mixture, although acid soluble CaCO_3 slightly contributes to the resynthesis of carbonates. The reaction of CaCO_3 can be expressed as follows:



There are also several reports about the reaction between CO_2 and AlO_2^- in freshwater (Wang *et al.*, 2005; Begum *et al.*, 2012). The chemical reactions of AlO_2^- from the eluate in acidified ASW can also be expressed as follows:



Aluminate from the eluate in acidified ASW can not also react with protons. The practical production of CaCO_3 , MgCO_3 and $\text{Al}(\text{OH})_3$ was not analyzed in this study, because these elements from the eluate added in the experimental system were in trace amounts. For little buffering action of the eluate in acidified ASW, these carbonation reactions induced by the absorption of CO_2 were assumed to occur in acidified ASW. Therefore, if the amount of H^+ exceeds the buffer capacity of NaHCO_3 contained in ASW, the eluate in acidified ASW may insufficiently work as a buffer because their elements can not react with protons excessively added.

The pH of sea water is about 7.6 to 8.2 at present, showing that the experimental condition in this study was unrealistic. However, there are concerns that the increase of CO_2 from fossil fuel combustion may induce ocean acidification in the future (Doney,

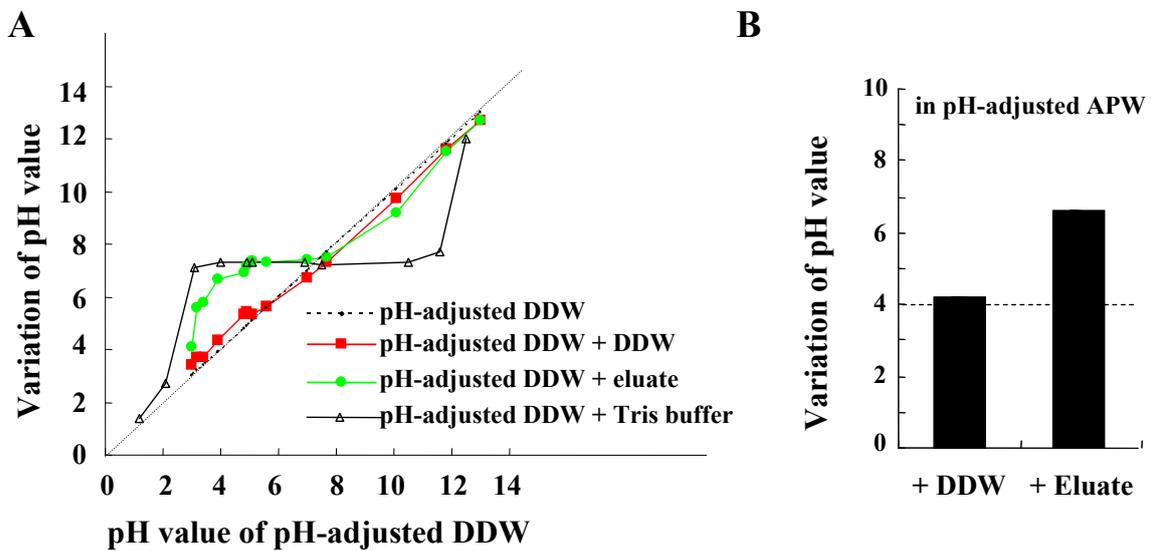


Fig. 4 - Buffer effect of the eluate from the slag in acidified freshwater environments. (A) The mixtures of pH-adjusted DDW and the eluate were used to examine the buffer effect of the eluate. Each sample with DDW or Tris-HCl buffer indicates the negative or the positive control sample of buffer action, respectively. The horizontal and the vertical axes show pH values of pH-adjusted DDW and the values of their mixtures, respectively. (B) In acid pH-adjusted APW, the eluate worked as a buffering solution. The broken line represents the initial pH in this experiment.

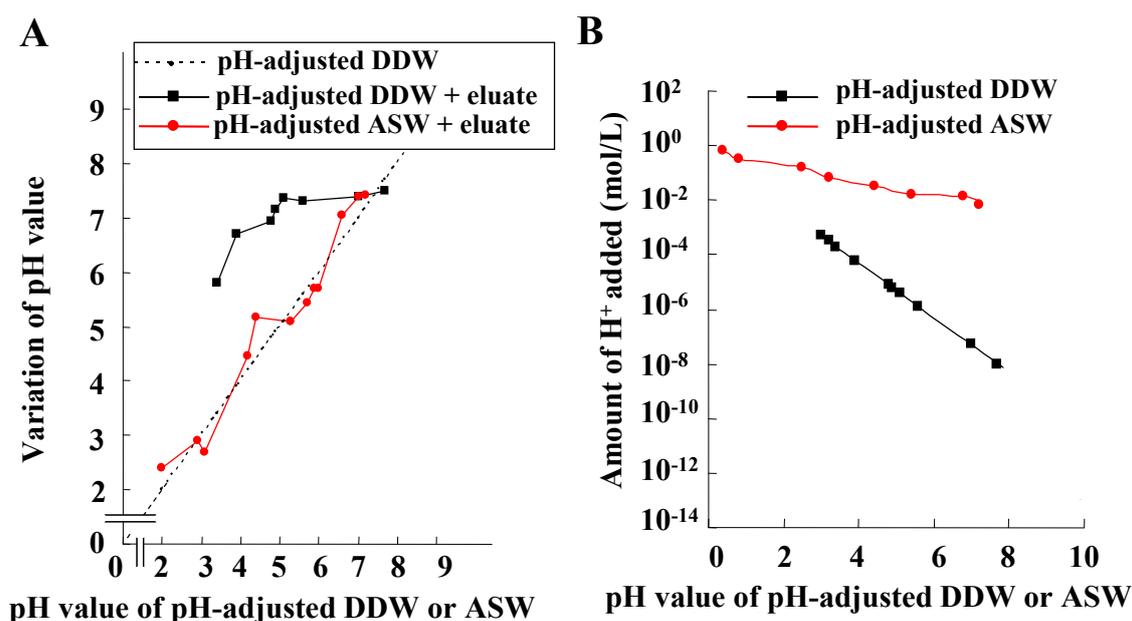


Fig. 5 - Buffer effect of the eluate from the slag in acidified sea water.

- (A) In this experiment, both pH-adjusted DDW and pH-adjusted ASW were prepared. The mixtures of each pH-adjusted solution and the eluate were used to examine the buffer effect of the eluate.
- (B) The graph shows the amount of protons added to make each pH-adjusted solution.

2006). From the data obtained in this study, it may be difficult to improve the acidified sea water with the eluate from the slag if pH in sea water changes from weak alkaline to neutral or acidic.

Effects of the eluate from EAF slag on algae in acidic environments

Chemical components and many physicochemical factors including light intensity and pH affect the metabolism and growth of algae (Gerashchenko *et al.*, 2002; Kawano *et al.*, 2005; Takahashi *et al.*, 2005). In this study, phytoplankton *Chlorella* was used as a bio-indicator to evaluate the effects of EAF slag in aquatic environments. *Chlorella kessleri* was cultured for several days in the conditioned medium containing the eluate (50%, v/v) at pH 5.0. The addition of the eluate to the culture medium neutralized the acidic condition (Fig. 6). After the pH improvement of the culture condition, higher algal growth in the presence of the eluate was induced compared to the control, suggesting that the eluate had no cytotoxicity either by lethality or growth inhibition. The morphological and population analyses on algae treated with the eluate were additionally performed (Fig. 7). *Chlorella* can be morphologically classified into a unicellular cell to 2 – 4 autospores. The inset photograph of Figure 7B shows algae in each stage of the cell cycle under the control condition. The morphological characters including algal size did not change between control and the treatment condition with the eluate (data not shown). From the population analysis, the eluate at the neutral condition neither induced any morphological change nor the population change of algae (Fig. 7). The data additionally supported that the eluate had no cytotoxicity.

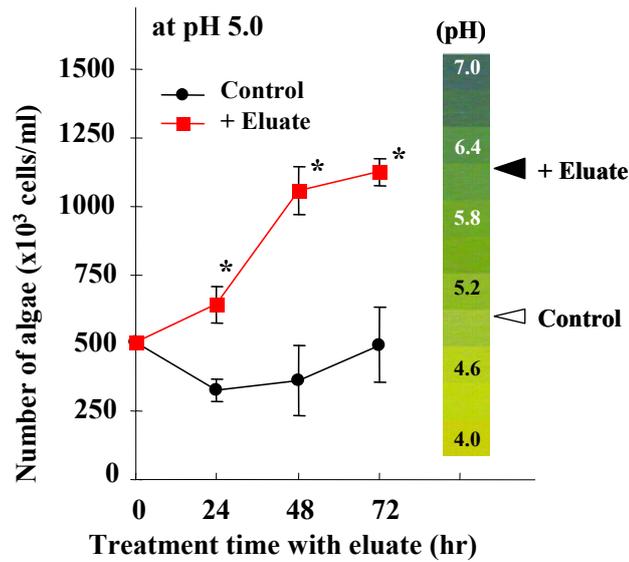


Fig. 6 - Effects of the eluate on algae in an acidic environment. Algal growth in an acidic environment was followed up for 72hr in the presence or absence of the eluate. The line graph shows the number of algae (\pm S. E.). * denotes a statistical difference of $P < 0.05$ vs. control by t -test. The inset color bar and arrowheads show pH values in control (DDW) and test sample treated with the eluate.

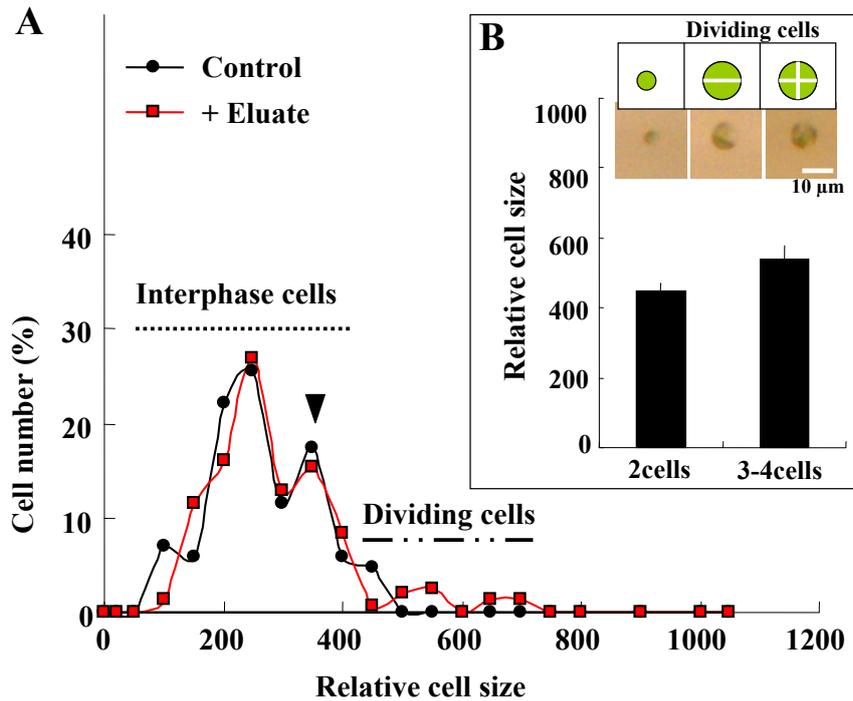


Fig. 7 - Morphological observation of algae treated with eluate from the slag. (A) The histograms show each algal size population after treatment with or without the eluate for 7 days. A relative cell size was measured as the pixel area using Image J software. Cells above 400 in relative cell size contained dividing cells in Fig. 7A. The arrowhead in Fig. 7A shows algae in growth stage just before cell division. (B) This data is a supportive data to show the sizes of dividing cells in Fig. 7A. The inset photographs show an interphase cell and dividing cells: Scale bar, 10 μ m.

An effective and economic strategy to restore acidified freshwater ecosystems with EAF slag

Acidification in aquatic environments has been caused by acidic precipitation containing SO_4^{2-} and NO_3^- ions. Sulfur oxide (SO_x) and nitroxide (NO_x), which are emitted into the atmosphere by fossil fuel combustion, are responsible for SO_4^{2-} and NO_3^- ions. Particularly, freshwater systems including ponds, lakes and rivers are the most sensitive to acidic precipitation because of the low buffering capacity (Hagar *et al.*, 2000). Acidification in freshwater systems affects their biota and results in decreases of fish population (Hagar *et al.*, 2000; Raddum *et al.*, 2003). In the future, large consumption of fossil fuel in recent rising nations may cause new aquatic acidification. As a conventional countermeasure against acidification in aquatic environments, extensive liming of lakes and rivers has been carried out. Electric arc furnace normal steel oxidizing slag is useful as a novel countermeasure to neutralize excessive aquatic acidification (Fig. 4). Additionally, this study presented that the eluate from the EAF slag possessing buffering action allowed phytoplankton to grow again in acidic environments (Fig. 6). Thus, acidified aquatic ecosystems can resolve the poor conditions of their biota by using EAF slag (Fig. 8).

Kamakita lake at Saitama Prefecture in Japan, as one of the model lakes, has been studied for the estimation of freshwater acidification (Ministry of the Environment, 1999). The water volume of Kamakita Lake is $3.0 \times 10^5 \text{ m}^3$. If the lake acidifies, 30,000

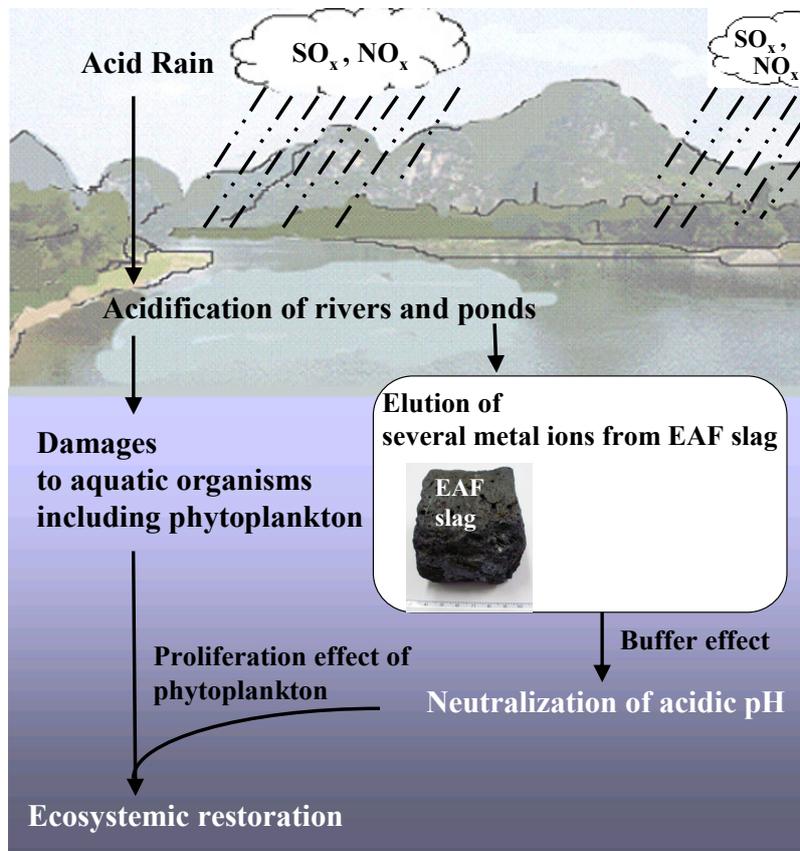


Fig. 8 - Strategy to restore acidified freshwater ecosystems with the slag.

tons of EAF slag less than the disposal quantities (Nippon Slag Association, 2007) may sufficiently restore the ecosystem of the acidified lake, assuming that the eluate made from the elution condition tested (100g slag/1L freshwater solvent) in this study is sufficient for the neutralization of acidified freshwater. Additional experiments are necessary to elucidate the permissive concentrations of chemical components derived from the slag.

CONCLUSIONS

In order to use EAF slag in aquatic environments, both chemical properties containing the elution behaviors of metals from the slag and the effects of the slag on phytoplankton were examined. When the slag was subjected to strict experimental conditions to elute metals in the slag, the elution of hazardous elements including hexavalent chromium were approximately less than the concentrations defined by EQS under all of the elution conditions tested in this study. The eluate as a chemical property could effectively act as a buffer agent in acidified freshwater environments. The eluate hardly exhibited toxicities on organisms including lethality or growth inhibition. From these chemical features and the effects on organisms, we propose the utilization of EAF slag as a useful and economic countermeasure to neutralize excessive aquatic acidification and restore ecosystems in freshwater systems.

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