

Research Article

Simultaneous Recovery of Boron and Other Major Elements from a Coal Fly Ash by pH Control

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Abstract

Coal fly ashes, which contain various hazardous elements, may be disposed of or reused. The existence of the hazardous elements in coal fly ashes can pose environmental problems. Therefore, it is desirable to remove these elements before reusing coal fly ash. In this study, the simultaneous recovery of boron and other major elements from a coal fly ash was investigated. The amounts of boron and other major elements in solution were measured after leaching using pure water and HCl of several different concentrations with leach times of 6 h at a liquid/solid ratio of 10. Pure water leached boron and calcium. Dilute HCl leached aluminum, boron, calcium, iron, and magnesium. The amount of all elements almost reached a maximum when the final pH of leachate was approximately 1. The boron and other elements were co-precipitated when the pH of these leachates was adjusted to 12. Aluminum, magnesium, and iron were removed completely by the precipitation while boron and calcium were removed at the ratios of 30-40% and 60-75%, respectively. Residual boron was removed using glucomannan semi-gel at a pH of approximately 12. Approximately 70% of the boron that leached from the coal fly ash was finally removed by co-precipitation and adsorption with glucomannan semi-gel.

INTRODUCTION

Coal fly ash is a waste material produced at coal-fired plants. Nowadays, great amounts of the ash are required to be recycled. Coal fly ashes contain various hazardous elements in traces but the large amounts of the ash have a great effect on ecosystem. The hazardous elements may cause environmental problems by leaching into environmental waters when the ashes are disposed or reused. Boron, arsenic, and molybdenum contained in coal ashes are easily leached [1,2]. Boron is chemically classified as a semi-metal; however, it is considered a rare metal as it has great value as a functional material. On the other hand, boron may be toxic to animals, plants and humans [3-7]. Therefore, these fly ashes are pre-treated to prevent contamination of various hazardous elements into water environments before reusing the ashes. Several leaching methods are proposed [8]. Deionized water has been used in the leaching of coal fly ash. Recently acid solution such as dilute HCl and H₂SO₄ are used as leaching solvents to obtain a large fraction of elements from fly ashes [1, 8-14]. These acidic solutions leached not only boron but also other elements, such as calcium, iron, magnesium, and aluminum. It is important for the reuse of coal fly ashes to determine the

amount of each element that can be leached from the coal ash and to recover selectively these elements from the leachates. Accordingly, a technique for effective recovery of metals containing boron is required. It is also desired to be a simple and low-cost.

Authors reported that dissolved boron was recovered selectively using glucomannan semi-gel at pH \geq 11 [15]. The higher pH condition was one of important factors for effective boron removal.

The effects of the pH control on leaching amounts of elements from a coal fly ash and on effective recovery of boron and other major elements from the leachate were investigated in this study.

MATERIALS AND METHODS**Materials**

A coal fly ash was obtained from the Kyushu Electric Power Co., Inc., Fukuoka, Japan. PROPOL ISLB[®] was produced from konjac glucomannan at Shimizu Chemical Co., Hiroshima, Japan. This is a "semi-gel", which is gelled only at the surface when placed in water and is insoluble.

Determination of boron and other elements

Boron concentrations were measured by the azometin H method [16]. Other elemental concentrations were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin-Elmer Optima 5300 DV) after pretreatment with 0.1 N HNO₃ at the Center of Advanced Instrumental Analysis, Kyushu University, Fukuoka, Japan.

Flow for recovery of boron and other elements from coal fly ash

A summary of the overall fractionation scheme for the elements released from a coal fly ash is illustrated in (Figure 1).

Leaching of boron and other elements from coal fly ash

Leachates were produced by shaking the 50 g of coal fly ash and solvent in a liquid to solid ratio (L/S) of 10 for 6 h at room temperature. Pure water and dilute HCl were used as leaching solvents. The dilute HCl was prepared at 0.1, 0.25, 0.5, and 1.0 N concentrations.

Analysis of elements in leachates

The leachates obtained in the above section were centrifuged at 800 *xg* for 10 min. The supernatants were filtered through a membrane of 0.1 μm pore size. The pH of the filtrate was measured and then adjusted to the same pH (12) as the leachate using pure water by using 1N NaOH. One hour later, the leachates were again centrifuged at 800 *xg* for 10 min. The supernatant and precipitate were obtained. The concentration of elements in the supernatants was measured after treatment with 0.5% HNO₃. The precipitates were dissolved using 0.5% HNO₃ and the elemental concentrations measured.

Adsorption of dissolved boron with glucomannan semi-gel

A total of 15 g of the semi-gel powder was added to 300 mL of the supernatant obtained in the above section (Figure 1). The mixture was incubated at 20°C for 4 h on an orbital shaker at 120 rpm. After incubation, the mixture was centrifuged at 800 *xg* for 10 min. The boron concentrations in the supernatant were determined. Boron adsorbed by the semi-gel was calculated by comparing the concentration of the final to the initial concentrations. All experiments were conducted at least in triplicate.

RESULTS AND DISCUSSION

Effect of pH on leaching of elements from coal fly ash

The major elements and their amounts in the leachates from coal fly ash by pure water or dilute HCl of various concentrations are shown in Table 1. Boron and calcium were slightly soluble in the leachates when using pure water, but other elements were not detected. Dilute HCl tended to increase the amount of the elements leached in the following order: Ca > Al > Fe > Mg > B. In the leachates produced using 0.25 N HCl, these elements approached a maximum value. The leachate produced in pure water reached a pH of approximately 12. Leachates at concentrations of 0.1, 0.25, 0.5 and 1.0 N HCl reached a final pH of 3.5, 1.1, 0.6 and 0.2, respectively. The amount of elements leached

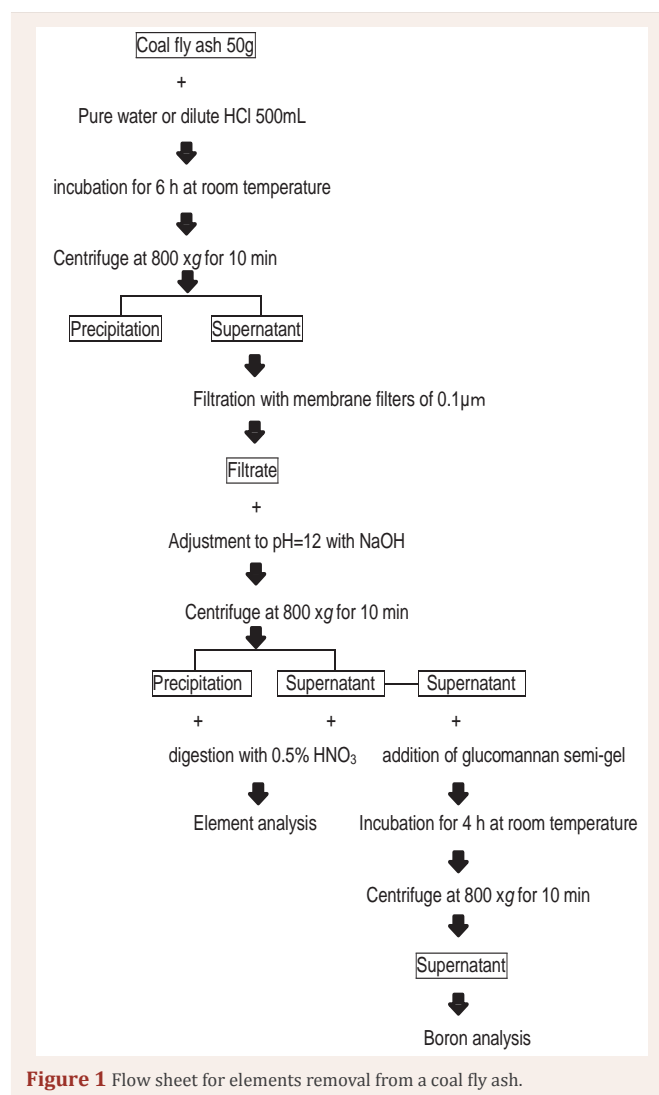


Figure 1 Flow sheet for elements removal from a coal fly ash.

increased with decreasing final pH of the leachate and almost reached a maximum when pH of leachate was approximately 1 (Table 1).

Boron exists in two phases in coal fly ash: the leachable and mineralogical bound phase. It has been shown that a large fraction of boron is leached from coal fly ash under low pH conditions [1, 8-12,17]. The pH has an important role in the distribution between the fly ash and liquid phase [18]. Most of the boron is likely to be distributed at the ash surface. Therefore, boron in coal fly ash is removed efficiently using dilute HCl. It is reported that the boron level in fly ash was as high as 1900 ppm, and approximately 50% was leachable into water [11]. Many types of coal from various countries are used in coal fired power plants. Thus, the properties of coals and their ashes are quite varied; however, an essential factor for effective leaching of the elements from coal fly ashes is control of the final pH of leaching solution.

Recovery of elements from leachates by co-precipitation with pH control

According to the fractionation scheme illustrated in (Figure

Table 1: Chemical composition of leachates from coal fly ash using pure water and dilute HCl of several concentrations and mass balances of elements in the supernatants and the precipitate after adjusting the leachates to pH=12.

leaching solvent [-]	elements [-]	final pH [-]	leachate [mg]*	surpernatant [mg]	precipitation [mg]	recovery [%]	precipitation /leachate [%]
pure water	Al	11.8	ND	-	-	-	-
	B		1.7	-	-	-	-
	Ca		178	-	-	-	-
	Fe		ND	-	-	-	-
	Mg		ND	-	-	-	-
HCl 0.1N	Al	3.5	48	ND	53	110	110
	B		7.6	5	2.4	98	31
	Ca		957	688	208	94	22
	Fe		ND	ND	ND	-	-
	Mg		49	ND	74	152	152
HCl 0.25N	Al	1.1	210	0.2	198	95	94
	B		8.8	4.6	3.8	96	44
	Ca		1146	382	666	92	58
	Fe		132	ND	139	105	105
	Mg		87	ND	104	120	120
HCl 0.5N	Al	0.6	209	ND	209	100	100
	B		8.2	5.5	3	104	37
	Ca		1176	166	902	91	77
	Fe		98	ND	135	137	137
	Mg		21	ND	86	408	408
HCl 1.0N	Al	0.2	244	ND	222	91	91
	B		7.8	6.2	3.4	122	43
	Ca		1196	113	893	84	75
	Fe		125	ND	145	116	116
	Mg		28	ND	84	297	297

*: amounts leached from 50g of a coal fly ash

1), the major elements in leachates produced using pure water and dilute HCl were fractionated. The mass balance of these elements was calculated from the sum of their amounts in the supernatant and precipitate after adjustment to a pH of 12 (Table 1). Total recovery ratios of all of these elements except for magnesium ranged from 80 to 120%. The recovery ratios are able to be evaluated with the high reliability. Except for boron and calcium, almost all of elements in these leachates were recovered as a precipitation. Generally, dissolved metals form metal hydroxides and are precipitated when adjusted to a high pH. Metal-rich solutions such as the leachate from coal fly ash cause the precipitation of metal hydroxides under higher pH conditions. On the other hand, aluminum and boron are dissolved as $\text{Al}(\text{OH})_4^-$ and $\text{B}(\text{OH})_4^-$ at a pH greater than 10, respectively. Therefore, they should not precipitate in theory. However, they were concentrated in the precipitates (Table 1). Aluminum was not precipitated with boron at a pH of 12 when only boron and aluminum co-exist [15]. Table 1 shows that aluminum and boron co-precipitated with calcium, iron and magnesium hydroxides when leachates by dilute HCl were adjusted to a pH of 12. Dissolved metals incorporate boron into their hydroxides under higher pH condition [1, 21]. Boron is precipitated mainly in the form of magnesium borate that is converted to the boracite mineral $[\text{Mg}_3\text{Cl}(\text{B}_7\text{O}_{13})]$ [22,23]. The formation of positive borate-ion pairs may cause coordinative bonds with negatively charged

magnesium hydroxide [18]. Therefore magnesium hydroxide results in the co-precipitation of boron and its removal from solution [18]. Boron is also formed both $\text{CaB}(\text{OH})_4^+$ and $\text{B}(\text{OH})_4^-$ in the presence of calcium [24]. The former will be precipitated by ion-pair formation and the latter will remain dissolved.

The magnesium was not detected in the supernatant, but done in the precipitation with 1.2 to 4-fold excess of the leachate amount (Table 1). A possible explanation for this result is that a calcium matrix effects on ICP-AES analysis [25-27]. The calcium/magnesium ratio is more than 10-fold (Table 1). The presence of more than a 10-fold excess of calcium to magnesium interferes in magnesium analysis with ICP-AES. The solubility of $\text{Mg}(\text{OH})_2$ is very low in comparison with $\text{Ca}(\text{OH})_2$. Therefore, the mass balance of magnesium may lack in accuracy, but magnesium must have been concentrated in the precipitation.

Generally, leachates from coal fly ashes have been disposed after dilution or controlling to neutral pH value. However, boron and other elements in the leachates were recovered as precipitation under $\text{pH} \geq 12$ condition (Table 1). The combination of the leaching of elements from coal fly ash by dilute HCl and controlling of the leachates to $\text{pH} \geq 12$ is useful for the effective removal of boron and other major elements from coal fly ashes. The pH control of the leachates is one of most important processes in the simultaneous recovery of boron and other elements from coal fly ash leachates.

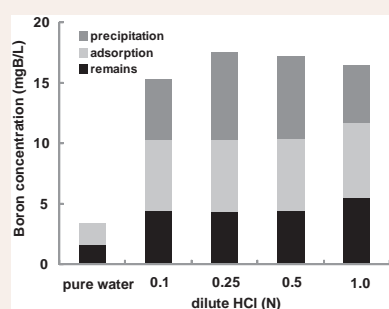


Figure 2 Boron removal by precipitation and adsorption using glucomannan semi-gel at pH=12 from leachates of a coal fly ash by pure water and dilute HCl of several concentrations.

Recovery of boron from leachates using glucomannan semi-gel

The major elements were almost all recovered except for boron and calcium by precipitation when the leachates were increased to a pH of 12 (Table 1). In a previous paper, authors reported that glucomannan semi-gel had a high capacity for $B(OH)_4^-$ removal at the same pH condition as above [15]. Therefore, this semi-gel was used to recover boron from the supernatant after precipitation process at pH=12 under the same pH conditions. Results are summarized in (Figure 2). About 40% of the dissolved boron was removed by adsorption to the semi-gel. The diol groups in the semi-gel form complexes with $B(OH)_4^-$ under high pH conditions [15]. The dissolved boron forms $B(OH)_4^-$ and $CaB(OH)_4^+$ in the presence of calcium at high pH conditions. Therefore boron species not removed by the semi-gel will be mainly the form of $CaB(OH)_4^+$.

CONCLUSION

Leaching from coal fly ashes by dilute HCl, controlling of the leachates up to a pH of 12, and adsorption using glucomannan semi-gel under the same pH conditions were performed successively for the effective removal of boron and other major elements. The amount of boron and major elements leached approached a maximum value when the final pH of the leachates was approximately 1. The major elements in the leachates were aluminum, boron, calcium, iron, and magnesium. These elements were precipitated by the formation of metal hydroxides when the pH of the leachates was increased to approximately 12. Dissolved aluminum and boron were co-precipitated by ion-pair formation with calcium and magnesium under their pH condition.

The combination of leaching with dilute HCl, controlling of the leachates up to a pH of approximately 12 and adsorption of the dissolved boron by glucomannan semi-gel led to the removal of approximately 70% of the boron and almost all of the major metals. The methodology may provide a new technique for the effective removal of boron and major elements from coal fly ash.

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