

# Reduction of Fluorine, Boron and Heavy Metals Leaching from Coal Ash by Adding Fixation Chemicals

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## ABSTRACT

In order to utilize coal fly ash (hereafter : coal ash ) discharged from coal boiler as a material for civil engineering usage such as snow melter or soil improver, we have to prevent leaching hazardous elements such as fluorine, boron and heavy metals from the coal ash because the leaching concentrations of some elements in the ash exceed the Japanese standards for environmental soil quality. Through the laboratory experiments and mill trials, we confirmed that the leaching concentrations of fluorine, boron and heavy metals were maintained below their environmental standards by mixing with fixation chemicals and curing for a short time.

## INTRODUCTION

In Nayoro mill, Oji Paperboard Company, the amount of coal ash discharged from a coal boiler was about of 4,0 00t/ year and the coal ash had been used to sell as a snow melter until February 2003 when Japanese Standards for environmental soil quality was enforced. Because the leaching concentrations of fluorine(F), boron(B) and some heavy metals such as arsenic(As) and selenium(Se) etc. from the coal ash exceeded their standards, Nayoro mill had to stop selling it as a snow melter and dispose it in own company management type landfill site. Therefore we started to investigate simple method for reduction of fluorine, boron and heavy metals leaching from the coal ash. The aim of this study is to establish it at the mill.

### Review of proposed methods

The following methods have been proposed for reduction in leaching of fluorine, boron and heavy metals from various kinds of ash.

#### Heat treatment

This is characterized separating volatile heavy metals by heat (1). Hexavalent chrome, mercury, cadmium and lead are easily volatilized by this method, and captured in a bag filter or an electrostatic precipitator, but treatment of the dust in which concentration of heavy metals is high becomes a problem. In addition, it is not economical because of a huge cost and long term for construction.

#### Washing/Extraction

This would be effective in the case of choosing appropriate chemicals and the proper extraction conditions (2). This method, however, includes many

steps such as washing/extraction, filtration and treatment of insolubilization of extracted elements. Therefore this method is suitable only for small scale, not for large scale.

#### Treatment of heat fusion

It is possible to fix fluorine, boron and heavy metals in ash by heating at high temperature more than 1,300 degrees Celsius. This method (3) is also effective for reducing the volume of ash and content of dioxin in it. Facility cost and running cost of this treatment, however, become high.

#### Cement solidification / insolubilization treatment

It is a treatment to let ash solidify by adding cement (4), however, lead, zinc, and chrome are easily dissolved as a hydration complex ion due to strong alkalinity of cement, which cause a strength loss of a solidified ash. In addition, mercury and arsenic are easily dissolved as thiocomplex ions.

#### About Japanese Standards for environmental soil quality

Because Japanese government was anxious about health of the people in the case of drinking the subsurface water which was supposed to be polluted by soil having hazardous substance, the government issued an *anti-soil pollution measure method* in May 2002, and decided the environmental standards for specific twenty five harmful chemicals and elements which have a possibility to influence human health in the case of existing in the soil. Furthermore, the environmental standards were changed to the regulation value in February in 2003. These standards have been applied to

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ashes when they are used as soil materials. Table 1 shows the environmental standards for specific elements related to coal ash (5).

Table 1 Environmental standard for specific elements

element	F	B	Cr(IV)	Se	Pb	As
Conc. of Leaching (mg/L)	0.8	1.0	0.05	0.01	0.01	0.01

### EXPERIMENTAL

#### Method for mixing coal ash and fixation chemicals

The coal ash used in this experiment was discharged from a stoker type boiler in Nayoro mill, Oji Paperboard Co., Ltd. As a fuel, DIP rejects and sludge other than coal are burned. A determined amount of coal ash from the mill was taken and put it in a plastic bag. At first fixed amounts of powder chemicals were added to the coal ash and mixed together by hands, and water or liquid chemical was added with spray and mixed them thoroughly by hands in order to be uniform. Hereinafter the coal ash was defined as untreated coal ash or as untreated coal ash if needed.

#### Measurement for leaching concentration

According to No.18th notified procedure by Japan Ministry of the Environment in 2003, a 50g (bone dry) of untreated coal ash or treated coal ash cured in a different period was taken to a 1L round shape poly bottle and 500mL distilled water was poured to it. The poly bottle was set in a shaking machine and shook it for six hours. After shaking, leaching liquor was taken out and centrifuged for 20 minutes in condition of 3,000 rounds per minute. The supernatant solution was taken and filtered by a 0.45  $\mu$  membrane filter.

#### Analysis of leaching elements

Fluorine ion was detected by DIONEX ion chromatography (ICS2000- type) using with a potassium hydroxide as for eluting agent. Boron and heavy metals were measured by ICP-OES method and CIROS120 type of RIGAKU was used for ICP emission spectroscopy device. In a case of high sensitivity measurement, a SPECTORO supersonic wave nebulizer was applied. Detection limit was more than three on S / N ratio.

#### Analysis of elements in coal ash

The analysis of content of elements in coal ash was done with PHILLIPS fluorescence X-rays (PW2404 - type).

#### Analysis of structure of compounds formed in coal ash

Analysis was done with a RIGAKU X-ray reflected Device (RINT2200- type).

#### Chemicals used for reduction of leaching

Calcium oxide and Aluminum sulfate solution (purity 52%) were prepared by one of mills in Oji paper Co., Ltd. Alumina cement was made in Asahi Glass Ceramic Co.,

Ltd., Portland cement and B-type blast furnace slag cement were made in Ube Mitsubishi Cement Co., Ltd. Other chemicals used in this experiment were the first grade chemical reagent.

#### Test samples used in laboratory experiment

All coal ash samples used for laboratory experiment were dry samples. Table 2 shows the origin of coal and boiler combustion conditions of each sample. These leaching concentrations of fluorine, boron, arsenic and selenium are shown in Table 3 and chemical compositions of each sample are listed in Table 4.

Table 2 Origin of coal and boiler combustion conditions

Sample	Origin of coal		Boiler combustion condition	
	Imported (%)	Domestic (%)	Steam generation (t/hr)	Temperature of EP (°C)
A	100	0	75-77	142-143
B	85	15	75	143-145
C	80	20	76-78	143-147

Table 3 Concentration of leaching of test samples

Standard	Concentration of leaching (mg/L)				pH
	F	B	Se	As	
Sample					
A	<b>5.2</b>	<b>2.5</b>	<b>0.06</b>	<b>0.02</b>	10.4
B	<b>5.6</b>	<b>1.7</b>	0.00	0.00	11.7
C	<b>2.7</b>	<b>3.7</b>	0.00	0.00	10.1

Numbers in Bold letters show over the standards  
pH means pH in liquor of leaching

Table 4 Chemical compositions of test samples

Sample	Chemical composition					
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O
A	57.9	24.1	5.1	3.6	1.3	1.5
B	48.0	25.7	9.0	5.6	1.9	1.2
C	44.0	27.3	13.1	5.3	1.3	0.67

## RESULTS AND DISCUSSION

### Leaching behavior of untreated coal ash

In addition to three coal ash samples listed in Table 2, fifteen coal samples from Nayoro mill were regularly collected to study leaching behavior in untreated coal ash. Figure 1 shows the relationship between pH in leaching and leaching concentration of fluorine and boron from these untreated coal ashes. There was a fairly good relation between them on both fluorine and boron, i.e., the higher pH increased the leaching concentration of

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fluorine, on the other hand, the lower pH increased the leaching concentration of boron. This indicated that the lower pH in leaching is effective for reduction of fluorine leaching, on the contrary, higher pH is preferable to reduce boron leaching.

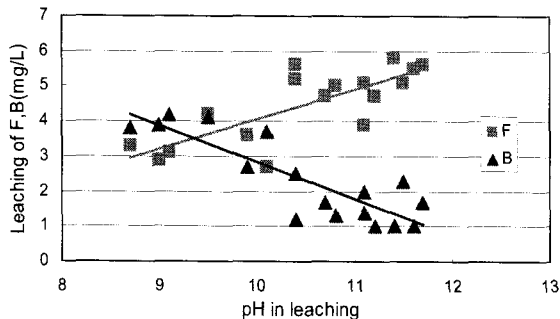


Fig.1 Relationship between pH in leaching vs. leaching concentration of F and B

### Reduction of F and B leachings by adding two kinds of chemicals to untreated coal ash

From the result mentioned above, it seems to difficult to reduce both fluorine and boron leachings simultaneously with one kind chemical, therefore we considered two kinds of chemicals composed by an acid chemical and an alkaline chemical would be needed for reduction of leaching of both. From economical and general usage points of view, calcium oxide (CaO) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were selected. With using these chemicals and untreated ash sample A, we started to investigate to reduce of both fluorine and boron leachings. Each chemical addition rate was determined 5% on untreated coal ash by considering pH in leaching. The curing period of time was varied from 4 hours to 6 days. The results are shown in Fig. 2.

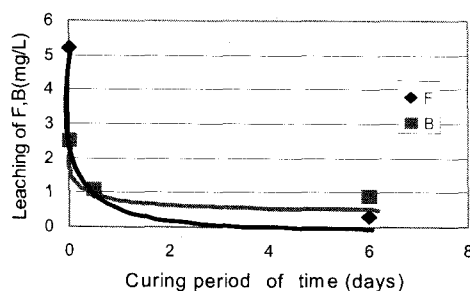


Fig 2 Effect of addition of CaO and H<sub>2</sub>SO<sub>4</sub>

By adding both CaO and H<sub>2</sub>SO<sub>4</sub>, the leaching concentration of fluorine was rapidly decreased from 5.2 mg/L (untreated coal ash) to 1.0mg/L within 4 hours and by 6 days it went down to 0.3mg/L that was clearly below the standard (0.8mg/L). This chemical formulation was also effective for reduction of boron leaching, however, the leaching concentration after 6days was still 0.9mg/L which was almost same as that of after 4 hours. From the result this formulation seemed not to be sufficient method to maintain below the standard

(1.0mg/L) under practical conditions. As to arsenic and selenium, their leaching concentrations in untreated ash were 0.02mg/L and 0.06mg/L respectively which exceeded those standards ( 0.01 mg/L each), however, an application of this method completely depressed them within 4 hours. Consequently, we focused to search a method to reduce both fluorine and boron leachings.

### Reduction of F and B leaching by adding three kinds of chemicals

It was reported that Ettringite formation with cement is effective for reduction of leaching of boron (6). In order to form Ettringite structure in the treated ash various kinds of cement (Portland cement, B-type blast furnace slag cement, (abbreviated: slag cement). and alumina cement (abbreviated: AC)) were added on CaO+H<sub>2</sub>SO<sub>4</sub> formulation. The cement addition rates were 5% on untreated ash sample A constantly. In this new formulation, CaO addition rate was reduced to 3% compared to 5% in CaO+H<sub>2</sub>SO<sub>4</sub> formulation because of strong alkalinity of added cement. The results are shown in Table 5.

Table 5 Reduction in leaching of F and B by chemical formulation consisted of CaO + H<sub>2</sub>SO<sub>4</sub> + various cement

Chemicals	Charge (%)	Cont. of moisture (%)	Standard pH	0.8mg/L						1.0mg/L		
				F						B		
				Curing period								
	4hr	1day	6days	4hr	1day	6days						
untreated	0	0	10.4	5.2				2.5				
water	0	25	9.8	4.5	4.4	3.2	2.0	1.5	1.0			
CaO/H <sub>2</sub> SO <sub>4</sub>	3/5	25	10.8	1.0		0.3	1.0		0.9			
CaO/H <sub>2</sub> SO <sub>4</sub> /PC	3/5/5	25	12.1	0.9	0.8	0.6	0.1	0.1	0.0			
CaO/H <sub>2</sub> SO <sub>4</sub> /SC	3/5/5	25	11.9	1.0	0.8	0.5	0.2	0.1	0.0			
CaO/H <sub>2</sub> SO <sub>4</sub> /AC	3/5/5	25	9.5	0.0	0.1	0.1	0.2	0.2	0.2			
CaO/Alum./SC	3/5/5	25	9.7	0.0		0.0	0.2		0.2			
CaO/Alum.	5/5	25	9.6	0.0		0.3	0.8		0.7			

PC=Portland cement, SC=B-type blast furnace slag cement, AC=alumina cement, Alum=Aluminum sulfate

Table 5 clearly shows the every formulation adding various kinds of cement on CaO+H<sub>2</sub>SO<sub>4</sub> formulation was effective to reduce the boron leaching to 0 mg/L (standard for B: 1.0mg/L) within 4 hours. The leaching of fluorine, however, turned worse than that of CaO+H<sub>2</sub>SO<sub>4</sub> formulation in case of adding Portland cement or slag cement on it. This phenomenon was interpreted that the leaching of fluorine is promoted by increase of pH in these chemical formulations. On the other hand, the pH in leaching of CaO+H<sub>2</sub>SO<sub>4</sub>+AC formulation was lower than that of CaO + H<sub>2</sub>SO<sub>4</sub> formulation, which is favorable to reduce the leaching of fluorine.

If leaching phenomenon were depended only on pH, the leaching of boron in CaO+H<sub>2</sub>SO<sub>4</sub>+AC formulation would be increased because the lower pH in leaching is favorable to increase the leaching of boron. But CaO+H<sub>2</sub>SO<sub>4</sub>+AC formulation was also effective for reducing boron leaching. This opposite result could be

explained by aluminum existed in AC. Based on this idea we examined new formulation consisted of CaO, aluminum sulfate (hereinafter: alum), and slag cement instead of CaO+H<sub>2</sub>SO<sub>4</sub>+AC formulation because sulfuric acid is corrosive and AC is expensive

As seen in Table 5, the pH in leaching and the reduction of fluorine and boron leaching of new formulation (CaO + alum + slag cement) were almost same as these of CaO+H<sub>2</sub>SO<sub>4</sub>+AC formulation.

In order to investigate the mechanism of reduction of leaching, the treated ash was analyzed by a XRD. From Figure 3 the XRD pattern of treated ash by the new formulation showed that the Ettringite structure was formed in the treated ash. The formation might be related to the reduction of boron and fluorine leaching.

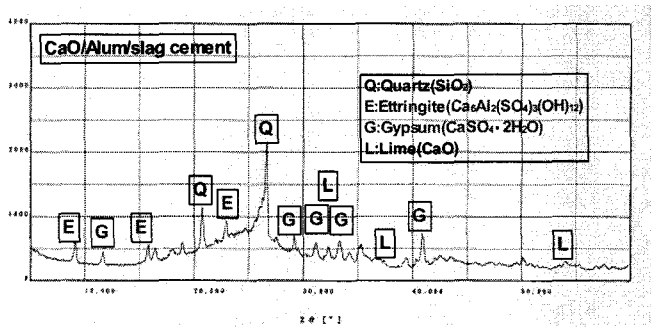


Fig 3 XRD patten of the Ettringite formed in coal ash treated by (CaO + alum + slag cement)

Since the chemical cost of new formulation was approximately equal to that of CaO + H<sub>2</sub>SO<sub>4</sub> + AC formulation and the reproducibility of fixation by this formulation was confirmed by another untreated ash B. (results were not shown here), we continued to investigate this fixation formulation consisted of CaO, alum and slag cement at laboratory tests and at mill trials.

#### Optimization of new fixation formulation (CaO +Alum + slag cement)

In order to use the coal ash treated by this formulation for snow melter, the less water content in treated ash is preferable for spraying snow melter uniformly. It means that the less alum addition is desirable because a state of alum is solution (8% as Al<sub>2</sub>O<sub>3</sub>). The reduction of alum addition rate, however, brings to increase of leaching pH, which is anticipated to promote the leaching of fluorine. The addition rates of alum were changed to find an optimum condition. The results are shown in figure 4.

Figure 4 shows increasing addition rate of alum decreased the leaching of fluorine and pH in leaching. In the range of more than 3% (o.d. ash) of alum addition rate, the leaching concentration of fluorine became lower than half of the standard (0.8mg/L), on the other hand, the dispersion characteristics of snow melter became worse because water content in treated ash was increased. As the leaching of boron, alum addition rate had no influence in the range of 2.5% to 5%. From these results,

alum addition rate of 3% seemed to be optimum.

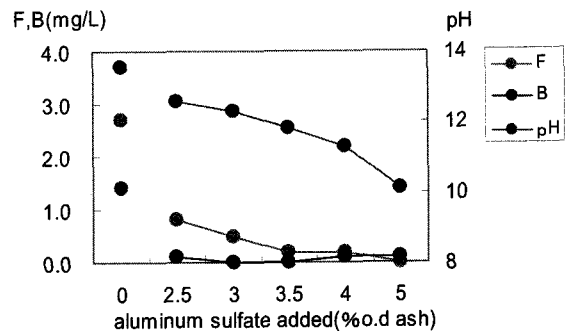


Fig.4 Influence of addition of alum on leaching of fluorine, boron and pH

With respect to optimization of CaO addition, the addition rate was varied from 2% to 5% and the results are shown in figure 5.

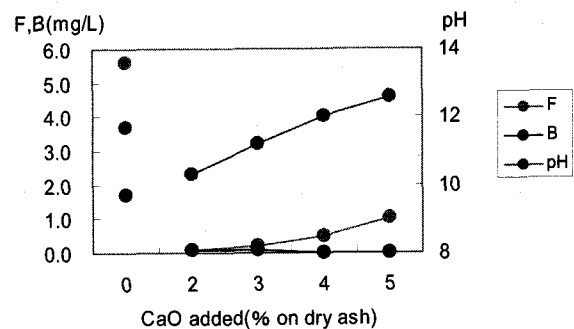


Fig.5 Influence of CaO addition on leaching of fluorine, boron and pH

The leaching concentration of fluorine was less than half of the standard (0.8mg/L) when CaO was added less than 4% (o.d. ash). By considering pH change of untreated ash, the addition rate of 3% is regarded as the most suitable for CaO.

#### Confirmation of the effect of new fixation formulation in Nayoro mill trials

##### Examination of formulation change in laboratory

The most suitable addition rate of Ca(OH)<sub>2</sub> in stead of CaO was studied because Ca(OH)<sub>2</sub> was more easily obtained than CaO in Nayoro mill. The addition rates of Ca(OH)<sub>2</sub> were varied from 1% to 5% on o.d. untreated ash C. The addition rates of alum and slag cement were constantly 3.5% and 3% (o.d.ash) respectively. The results are shown in table 6.

The optimum addition rate of Ca(OH)<sub>2</sub> was seemed to be of 3% or 4% (o.d. ash) from the results of leaching concentration of fluorine and boron. Taking into account of pH variation of untreated ash influenced by changes of boiler operation, we decided to perform a mill trial with Ca(OH)<sub>2</sub> addition rate of 4%.

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Table 6 Optimization of Ca(OH)<sub>2</sub> addition rate

Chemicals			Standard	0.8mg/L	1.0mg/L	
Addition rate(%)			Cont. of moisture (%)	pH	F B	
Ca(OH) <sub>2</sub>	Alum	Slag/cement			curing period(hours)	
					4	4
1	3.5	3	9.6	9.5	0.2	1.4
2	3.5	3	9.6	9.6	0.0	0.5
3	3.5	3	9.6	9.9	0.0	0.1
4	3.5	3	9.6	10.3	0.1	0.1
5	3.5	3	9.6	11.6	0.4	0.1

Mill trial using a paddle mixer

We designed and assembled a paddle mixer for mixing coal ash discharged from an electrostatic precipitator with fixation chemicals, i.e., Ca(OH)<sub>2</sub>, alum, and slag cement continuously. In order to improve mixing and transportation in the paddle mixer, the arrangement of paddle mixer was designed for dividing four parts, that is, forwarding, leveling, returning and forwarding. Since coal ash was periodically carried to the paddle mixer through a conveyer, small hopper was installed above the paddle mixer (Fig. 6) to send a certain amount (about 80%) of coal ash to the paddle mixer and to overflow the rest of ash. The mill trial was performed under the conditions shown in Table 7.

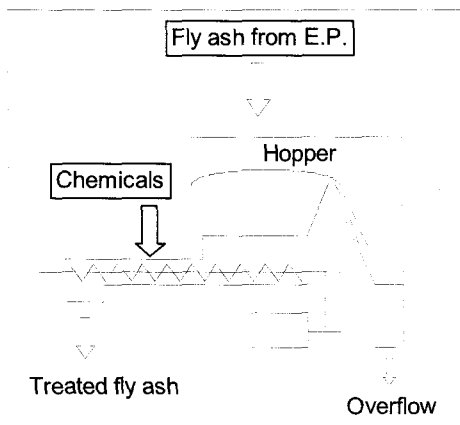


Fig.6 Flow sheet of ash treatment with paddle mixer

Table 7 Conditions of mill trial

condition of boiler	ash discharge (kg/hr)	steam generation (t/hr)	conc. of O <sub>2</sub> (%)	temp. of EP (°C)	
	630	70 ~ 72	5.0 ~ 6.2	139 ~ 141	
condition of mixing	ash treatment (kg/hr)	retention time (min.)	chemical addition rate (%)		
	492	9	Ca(OH) <sub>2</sub>	alum	slag cement
			4	3.5	3

The results of mill trial were shown in table 8. Though the concentrations of fluorine and boron leaching in untreated coal ash exceed their standards, they were almost completely reduced to zero level in the samples taken at 10 minutes after starting chemical addition and mixing. At the same time, the leaching of other heavy

metals was not observed. Furthermore, the depression on both fluorine and boron leaching had continued for 50 minutes during adding chemicals.

After 50 minutes when chemicals addition were stopped, the concentrations of both fluorine and boron leaching were almost same levels as the initial untreated ash. From these results obtained through laboratory tests and mill trials using a paddle mixer, we found out that this method was useful for reduction of both fluorine and boron leaching.

Table 8 Results of mill trial using a paddle mixer

		Standard(mg/L)		0.8	1.0	0.01	0.01
		Cont. of Moisture (%)	pH	F	B	As	Se
Untreated		0.3	11.1	3.9	1.4	0.00	0.00
Treated time (min.)	10	1	7.4	9.5	0.0	0.1	0.00
		2	7.4	9.6	0.0	0.1	0.00
	20	3	6.8	9.3	0.0	0.1	0.00
		4	6.8	9.4	0.0	0.1	0.00
	30	5	7.3	9.6	0.0	0.1	0.00
		6	7.3	9.6	0.1	0.1	0.00
	40	7	7.5	9.7	0.0	0.1	0.00
		8	7.3	9.7	0.1	0.1	0.00
	50	9	6.9	9.6	0.1	0.1	0.00
		10	6.8	9.7	0.1	0.1	0.00
Untreated		0.4	11.2	4.7	1.0	0.00	0.00

Confirmation of the result by several mill trials

In order to confirm the result obtained in the first mill trial, several mill trials had been done. These results were shown in Figure 7. Since the leaching of Selenium and Arsenic in a untreated ash rarely exceeded their standards, the leaching concentrations of fluorine and boron in both untreated and treated ashes were only shown in fig.7.

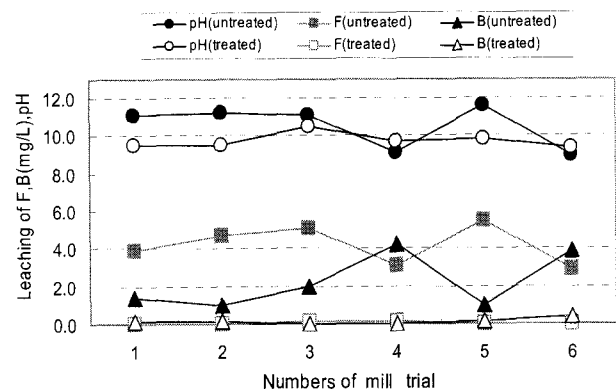


Fig.7 Trends of leaching concentrations of F and B and pH in both untreated and treated ashes.

The leaching concentrations of fluorine varied from 2.7mg/L to 5.8mg/L in untreated ashes, on the other hand, that of boron varied from 1.0mg/L to 4.2mg/L. Even though these concentrations of leaching varied in untreated ashes, the leaching concentrations of both of fluorine and boron in treated ashes were depressed to almost zero level by applied this fixation chemical

formulation. From these results, we were able to confirm our method in which fixation chemicals (CaO or Ca(OH)<sub>2</sub>+ alum + slag cement) are added to ash and mix them by a special paddle mixer is practical and reliable.

### CONCLUSIONS

1. It was found that the new chemical formulation consisted of calcium oxide (or calcium hydroxide), aluminum sulfate and B-type blast furnace slag cement is able to depress leaching fluorine, boron, selenium and arsenic from coal ash to the level below their standards.
2. Ettringite was formed when mixed with coal ash and this chemical formulation, which might be related to the reduction of fluorine and boron leaching.
3. This method composed by adding the fixation chemicals on coal ash and mixing together by a special paddle mixer shows practical and reliable method for reduction of leaching fluorine, boron, selenium and arsenic from coal ash through several mill trials.

### REFERENCES

- (1) Hanson, C., J. Pulp & Paper Sci., 22(9):346 (1996).
- (2) Jimno, T. and Kubo, H., Study on Boron non-Elutionized Processing of Coal Ash, Report from Oobayashi-gumi technology laboratory No.66:89 (2003)
- (3) Japanese patent (kougai) tokkai hei No. 9-271738
- (4) Sato, A. Nishimoto, S., Reduction in leaching of hazardous substances from coal ash by addition of solidification agent, Proceedings of STABILISATION/SOLIDIFICATION TREATMENT AND REMEDIATION Sym. (2005)
- (5) Japanese Environmental Department, Environmental Standard on the Contamination of Soil, Notice of the Environmental Dept. No 46(2001)
- (6) Solem-Tishmack, J.K et al., High-calcium coal combustion by-products: Engineering properties, Ettringite formation and potential application in solidification and stabilization of Selenium and Boron, Cement and Concrete research, 125(3) 658 (1995)