PERMEABLE REACTIVE BARRIER FOR ARSENIC REMOVAL FROM ARSENIC GROUNDWATER

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Abstract- Investigations were undertaken to study arsenic (As) removal from arsenic groundwater using fly ash (FA), bottom ash (BA), and bentonite clay (BC). Toxicity characteristic leaching procedure (TCLP) reveals that fly ash, bottom ash, and bentonite claycontained heavy metals such as Manganese (Mn), Copper (Cu), Zinc (Zn), Arsenic (As), and lead (Pb). Continuous column test with fly ash, bottom ash, and bentonite clay showed negligible heavy metal leach-out at neutral pH, except for Zn leached from bentonite clay.Column arsenic removal studies reveals order of arsenic removal using three ratios of reactive material mixturesas ratio of 60% BA, 20% FA, 20% BC mixtures> ratio of 80% BA, 10% FA, 10% BC mixtures> ratio of 100% BA. Removal of arsenic is attributed mainly to sorption due to negatively charged surface of fly ash, bottom ash, and bentonite clay.

Keywords- Arsenic Removal, Permeable Reactive Barrier, Coal Fly Ash, Coal Bottom Ash, Bentonite Clay.

I. INTRODUCTION

Today, coal is one of the world's primary source for power generation, accounting for about 36% of global electricity generation [1]. Use of coal in power plant generates fly ash, bottom ash, and flue gas desulfurization gypsum as main products. About 600-800 millions of coal ash is generated worldwide every year, of which, fly ash and bottom ash constitute about 65-95% and 5-35% respectively [2].Coal fly ash and bottom ash are extensively used in concrete, cement, structural fill, and road base/sub-base [3]. However, about 30% of coal ash produced in the world in currently reused [2], hence reuse of coal ash is a great challenge.

Worldwide, one billion people do not have access to safe water because of contamination of water by chemical and biological pollutants [4].One of the contaminated source is the naturally occurring chemical arsenic in groundwater, which affect millions of people in many countries worldwide, namely Bangladesh, Cambodia, China, Chile, Ghana, India, the Lao People's Democratic Republic, Mexico, Mongolia, Myanmar, Nepal, Pakistan, Taiwan, Thailand, USA, and Vietnam [4], [5]. Arsenic in groundwater in contaminated countries shows a very large range from 1 to 5000 µg/L [4]. Arsenic in groundwater affect agricultural food, human health, and social life.

Conventional arsenic treatment technologies include precipitative process, adsorption process, ion exchange process, and membrane filtration [6]. In case of contaminated groundwater, the most remediation technique is pump and treat[7], [8]. A low cost alternative technology is permeable reactive barrier (PRB) which is installed in path of contaminant plumes[7], [8]. Types of mechanisms, such as sorption and precipitation, take place within the reactive material zone, leading to the cleanup of contaminant plumes[7]. The selection of the most suitable reactive material is based on reactivity, permeability, environmental compatibility, stability, and cost [9], [10].

Recently, there has been growing interest in the utilization of coal fly ash and bottom ash as reactive material for the removal of heavy metals from wastewater[11]-[14]. Coal fly ash has been successfully used as reactive material of removal of iron, aluminum, cadmium, copper, manganese, zinc, nickel, and cobalt from acid mine drainage[11]andremoval of copper, manganese, lead, cadmium, and zinc from municipal solid waste leachate [12]. Coal bottom ash has also been successfully used as reactive material of removal of lead from aqueous solutions [13] andremoval of arsenic in drinking water [14].The high {SiO_2 + Al_2O_3 + Fe_2O_3} content and high calcium content make coal fly ash and bottom ash as attractive choice as a low cost reactive material. Accordingly, objective of this research was to determine the suitability of coal fly ash, coal bottom ash, and bentonite clay and their composition as alternative reactive materials for the removal of arsenic from arsenic groundwater entering in to the permeable reactive barrier. Physical and chemical characteristics of the fly ash, bottom ash, and bentonite clay were analyzed. Moreover, heavy metal leaching characteristics of the fly ash, bottom ash, and bentonite clay also analyzed. Column experiments were undertaken to assess the potential of fly ash, bottom ash, and bentonite clay for removal of arsenic from arsenic groundwater.

II. MATERIALS AND METHODS

Coal fly ash and bottom ash were obtained from the Mae Moh lignite coal fired thermal power plant of the

Electricity Generating Authority of Thailand (EGAT) located in Lampang, Thailand. Bentonite clay was obtained from Thai Nippon chemical industry located in SamutSakhon, Thailand.

2.1 Reactive Material Characterization
Physical properties such as pH, density, and acid neutralization capacity were analyzed using various analytical techniques.

2.2 Heavy Metal Leaching Tests
Toxicity Characteristics Leaching Procedure (TCLP):Heavy metals in the fly ash, bottom ash, and bentonite clay were characterized using TCLP, pH 2.88 as outlined in USEPA 1992.

Column leaching tests:Column tests for heavy metal leaching were conducted using up-flow percolation test as outlined by CEN/TS 14405 (CEN 2004).

Three columns made of polyvinyl chloride with empty volume of 2 liters (50 cm of length, 7 cm of internal diameter) were filled with a 45 cm layer of a reactive material (fly ash, bottom ash, and bentonite clay). Two layers of acid washed-sand, each of 2.5 cm with particle size of 2.0–2.4 mm were placed at the bottom and at the top end of column.

Leaching fluid (deionized water at neutral pH~6) was prepared and passed through the column in an up-flow rate of 60 ml/h using a peristaltic pump. Influent and effluent samples were collected and analyzed for heavy metal contents.

2.3 Column Arsenic Removal Tests
Column experiments were carried out in acrylic column having internal volume of 2 liters (50 cm height, 7 cm internal diameter) (Fig.1).

The column was fitted with 4 sampling ports located at 12.5, 25, 37.5, and 50 cm from the bottom inlet and capped with stainless steel ball valves. Column was filled with a 45 cm layer of mixed reactive materials in the middle, while two 2.5 cm sand layers were placed at the top and bottom ends of the column.

Mixtures in three ratios of fly ash, bottom ash, and bentonite clay were used in the column tests (designed mixtures 1-3; Table 1).

Synthetic arsenic groundwater with concentration of 3 mg/l as typical arsenic groundwater was prepared and pumped into the column in an up-flow mode at the fixed flow rate of 60 ml/h or 2 pore volumes per day using a peristaltic pump.

Experiment was conducted for 225 days and influent and effluent samples were analyzed for pH and arsenic concentrations.

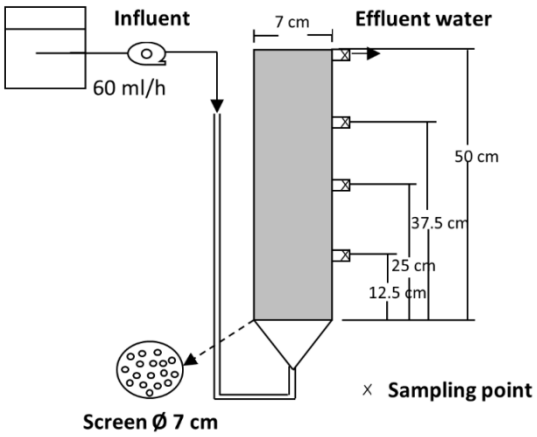


Fig. 1 Column experiment set up

Table 1 Proportion of reactive materials and main characteristics of the PRB

Mixture	BA:FA:BC[1]	Weight (g)	Porosity (%)	Residence Time (h)
1	100:0:0	1.72	0.436	13.998
2	80:10:10	1.88	0.436	13.998
3	60:20:20	2.10	0.384	12.331

[1] BA refers to bottom ash, FA refers to fly ash, and BC refers to bentonite clay

2.4 Analytical Methods
Reactive material characteristics were analyzed as procedure outlined in ASTM. pH was carried out by mixing of reactive material and deionized water at ratio of 1:20. Density was carried out by displacement method [15]. Acid neutralization capacity at pH 7 was estimated by titrimetric method [16].

Analyses of water samples were performed as per standard method of the examination of water and wastewater (APHA et al. 2005). pH was measured by pH meter (Mettler Toledo SG2). Heavy metal was conducted using inductively coupled plasma-optical emission spectrometer (ICP-OES) (Horiba, Ultima 2).

III. RESULTS AND DISCUSSION

3.1 Physical and Chemical Properties of Reactive Materials
The particle size, pH, density, and acid neutralization capacity at pH7 (ANC_7) of fly ash, bottom ash, and bentonite clay are presented in Table 2. The three reactive materials had strongly alkaline character, and the fly ash and bentonite clay also had high acid neutralization capacity.

Table 2 Physical properties of fly ash, bottom ash, and bentonite clay

Physical properties	FA	BA	BC
Particle size	fine	coarse	fine

pH	10.94	10.32	9.52
Density, g/cm^3	1.85	1.32	1.41
ANC_7, mmol H^+/g	0.8	0.3	1.2

The chemical composition of fly ash, bottom ash, and bentonite clay (factory data), as obtained from X-ray fluorescence spectrometry (XRF), is also presented in Table 3. As this data revels, the major constituents of three reactive materials were SiO_2, Al_2O_3, Fe_2O_3, and CaO.

Table 3 chemical composition of fly ash, bottom ash and bentonite clay

Chemical composition	Weight (%)		
	FA	BA	BC
SiO_2	31-40	29-47	56-60
Al_2O_3	16-21	14-26	16-18
Fe_2O_3	12-16	10-17	4-6
CaO	14-25	8-26	1.0-2.4
MgO	1.8-2.8	1.8-3.0	1.5-2.5
K_2O	2.3-3.1	1.8-3.1	1.5-2.5
Na_2O	0.8-1.1	0.5-1.3	0.4-1.0
TiO_2	0.3-0.4	0.3-0.5	0.2-0.5

3.2 Heavy Metal Leaching Tests

Toxicity Characteristics Leaching Procedure (TCLP): The purpose of this test is mainly to evaluate the leaching characteristics of heavy metals from the reactive materials under strong acidic condition.

The concentration of heavy metals in the leachate of the TCLP from fly ash, bottom ash, and bentonite clay is shown in Table 4. Their heavy metal concentrations in TCLP leachate were generally low, except for Mn

.

Table 4 Heavy metal contents in TCLP leachate

Heavy Metal	Leaching concentration from TCLP (mg/l)		
	FA	BA	BC
Mn	4.092	3.565	8.236
Cu	0.057	0.020	0.018
Zn	0.428	0.350	0.392
As	1.165	0.042	0.002
Pb	0.024	0.028	0.027

Column leaching tests: Fig. 2 presents the concentration of heavy metals in the effluent as a function of liquid/solid (L/kg) which is defined as the cumulative volume of effluent passing through a column containing a known mass of the reactive materials.

Data presented in Fig. 2 show that, with feed at neutral pH~6, the concentrations of all the heavy metals in the effluent leachate from fly ash, bottom ash, and bentonite clay generally remained constant and low, indicating negligible leaching at neutral pH~6, except for Zn leached from bentonite clay.

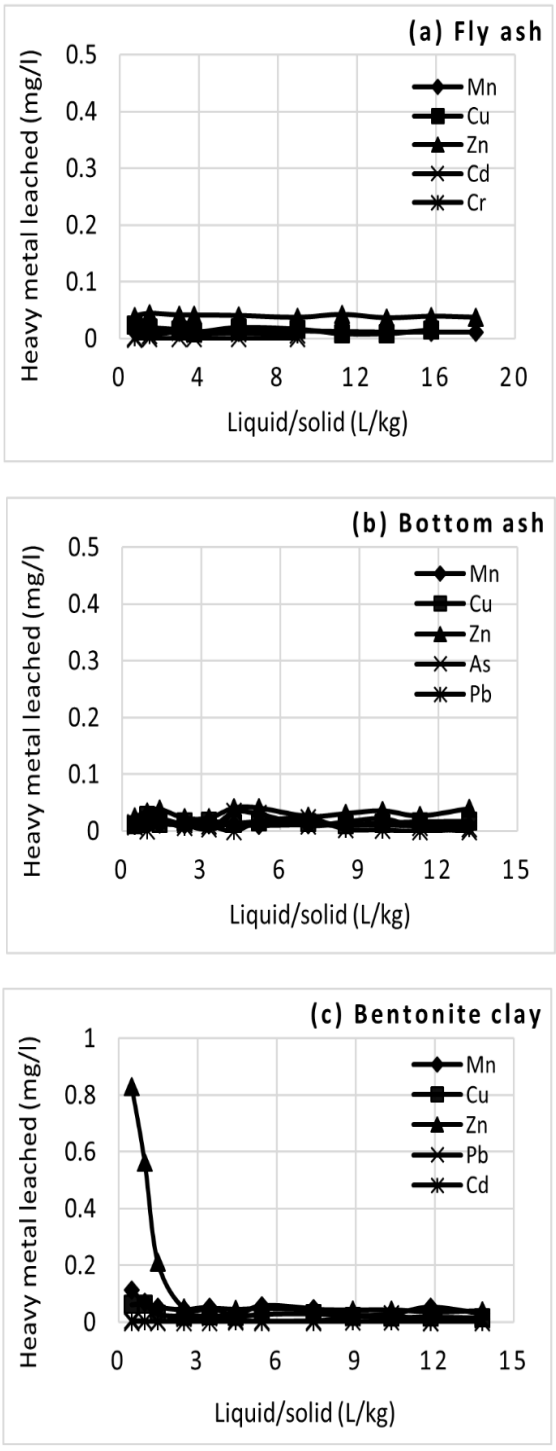


Fig. 2 Concentration of heavy metal leached from (a) fly ash, (b) bottom ash, and (c) bentonite clay in column test as a function of L/S ratio

3.3 Column Arsenic Removal Tests

Fig. 3 presents the results obtained from kinetic of arsenic removal from arsenic groundwater using three ratios of reactive material mixtures: "(I) ratio of 100% bottom ash, (II) ratio of 80% bottom ash, 10% fly ash, 10% bentonite clay mixtures, (III) ratio of 60% bottom ash, 20% fly ash, 20% bentonite clay mixtures" in 225 days of operation (450 pore volumes).

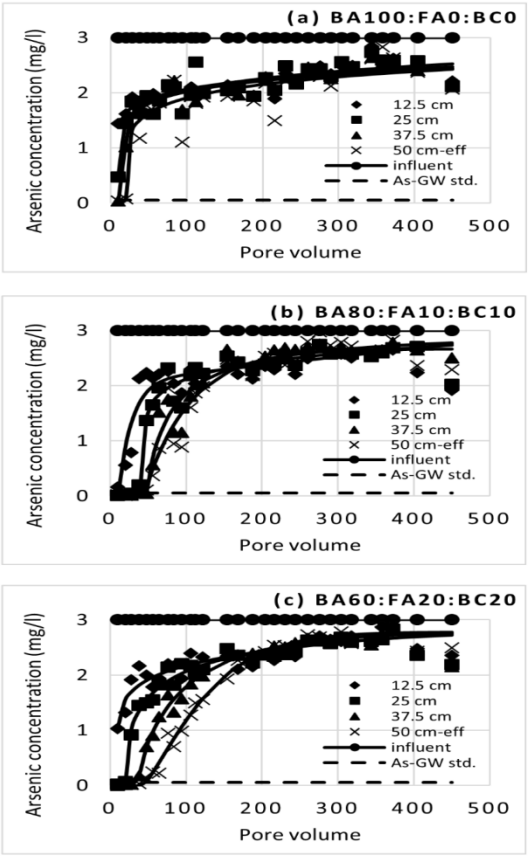


Fig. 3 Arsenic (As) removal as a function of pore volume treated using three ratios of reactive material mixtures

Fig. 3 brings out that arsenic concentrations in water treated at three ratios of reactive material mixtureswere lowest and remained constant at the initial stage of experiments (10-50 pore volumes), and then gradually increased with increase in pore volumes, reaching a steady state close to the initial arsenic concentration.

As a result, arsenic removal efficiency at the initial stage of experiments remained close to maximal due to reaction with fresh reactive materials, and arsenic removal efficiency at end stage of experiments decreased to low due to the decline of the reactive material surfaces caused by second mineral precipitates, re-dissolution of previously formed unstable precipitates, and leaching of arsenic from reactive materials[7], [11], [17].

The data in toxicity characteristic leaching procedure (TCLP) also reveals that present arsenic leachability is the highest for fly ash (16.690%), followed by bottom ash (3.835%), and bentonite clay (1.290%) in that order.

The breakthrough point, mass of arsenic sorbed, sorption capacity, percent arsenic removal, and pseudo-first order reaction rate constant of arsenic removal usingthree ratios of reactive material mixtures can be obtained from the characteristic 'S' shape (Fig. 3), as summarized in Table 5 and Table 6.

Table 5 Kinetic parameters for arsenic removal usingthree ratios of reactive material mixtures

Mixtures	Bed depth, (cm)	BT[1] point, (pv)	Mass of As sorbed, (mg)	Sorption capacity, (mg/g)	% As removal, (%)
BA100:	12.5	10	257.5	0.725	26.5
FA0:	25	10	268.2	0.377	27.5
BC0	37.5	10	299.5	0.281	30.8
	50	20	304.2	0.214	31.2
BA80:	12.5	10	232.9	0.576	23.9
FA10:	25	40	271.0	0.335	27.8
BC10	37.5	50	290.8	0.239	29.9
	50	50	326.7	0.201	33.6
BA60:	12.5	10	242.6	0.517	24.9
FA20:	25	20	251.2	0.267	25.8
BC20	37.5	30	289.4	0.205	29.7
	50	50	342.3	0.182	35.2

[1]BT refers to Breakthrough

Table 6pseudo-first order reaction rate constant (k_{obs}) of arsenic removal using three ratios of reactive material mixtures

Mixtures	k_{obs}, (h^{-1})
BA100:FA0:BC0	0.389–0.002
BA80:FA10:BC10	0.367–0.011
BA60:FA20:BC20	1.013–0.021

Effect of bed depth:Fig. 3 and Table 5 present the arsenic removal as s function of pore volume treated and the kinetic parameters of arsenic removal using three ratios of reactive material mixtures at different bed depth of 12.5, 25, 37.5, and 50 cm respectively. Fig. 3 reveals steepness of breakthrough or 'S' curve at initial bed depth for all the ratios of reactive material mixtures that the reaction front moves upwards much faster and therefore the efficiency of the reactive material system declines due to exhaustion of the reactive bed. Accordingly, Table 5 shows that breakthrough point of arsenic removal in all ratios of reactive material mixtures were the lowest at sampling port of 12.5 cm and the highest at

sampling port of 50 cm, suggesting that mass of arsenic removal and present arsenic removal gradually increased with increase in bed depth due to increase in sorbent doses which provided greater sorption sites and higher contact time[18], [19].

On the other hand, Table 5 reveals that sorption capacity of all ratios of reactive material mixtures decreased with increase in bed depth due to limitation of amount of sorbent available[20].

Effect of reactive material ratios:Table 5 brings out that percent arsenic removal at effluent was the highest for ratio of 60% bottom ash, 20% fly ash, 20% bentonite clay mixtures, while percent arsenic removal at effluent was the lowest for ratio of 100% bottom ash.And, Table 6 reveals that pseudo-first order reaction rate constant of arsenic removal also was the highest for ratio of 60% bottom ash, 20% fly ash, 20% bentonite clay mixtures.

This was because the increased proportion of fly ash and bentonite clay resulted in the increased number of sorption sites and more alkaline conditions due to its CaO contents (Table 3) which tend to highly precipitate as hydroxides.

Accordingly, pH of groundwater arsenic in the column test was 6.5. As the time progressed, the pH of bulk liquid increased and remained in the pH range of 8.0–9.5 at ratio of 100% bottom ash, and the pH range of 8.5–10.5 at ratio of 80% bottom ash, 10% fly ash, 10% bentonite clay mixtures, and at ratio of 60% bottom ash, 20% fly ash, 20% bentonite clay mixtures.

However, arsenic is the least likely to precipitate since its precipitation requires pH of 15.859 or above which is considered from the solubility product constant (K_{sp}) of the arsenic hydroxide (2.1×10^{-1}). This explains why percent arsenic removal is low (31-35%).

CONCLUSIONS

Arsenic removals from arsenic groundwater using fly ash, bottom ash, and bentonite clay were investigated. Following conclusions were drawn:

- The fly ash, bottom ash, and bentonite clay had strong alkaline character with pH value of 10.94, 10.32, and 9.52, respectively. Chemical composition of the fly ash, bottom ash, and bentonite clay indicated major presence of SiO_2, Al_2O_3, Fe_2O_3, and CaO.
- TCLP reveals that fly ash, bottom ash, and bentonite clay contained heavy metals such as Mn, Cu, Zn, As, and Pb. Continuous column test with fly ash, bottom ash, and bentonite clay showed negligible heavy metal leach-out at neutral pH, except for Zn leached from bentonite clay.
- Column arsenic removal studies reveals order of arsenic removal using three ratios of reactive material mixtures as ratio of 60% bottom ash, 20% fly ash, 20% bentonite clay mixtures > ratio of 80% bottom ash, 10% fly ash, 10% bentonite clay mixtures > ratio of 100% bottom ash. Removal of arsenic is attributed mainly to sorption due to negatively charged surface of fly ash, bottom ash, and bentonite clay.

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