

Arsenic leachability and speciation in fly ashes from coal fired power plants

S. Kambara*, M. Endo, S. Takata, K. Kumabe, H. Moritomi

Gifu University, Environmental and Renewable Energy Systems Division, Graduate School of Engineering, 1-1 Yanagido, Gifu, 501-1193, Japan

**Corresponding author: kambara@gifu-u.ac.jp*

Abstract

To determine dominant factors on arsenic leaching from the coal fly ash, arsenic leaching test under a constant pH was performed. Twelve fly ash samples were collected from two coal fired power plants (600 MWe) having different boiler types.

Arsenic in the raw coal was almost all associated with the fly ash in both power plants; however arsenic leaching fraction was strongly differed in boiler types. It found that the dominant factors of arsenic leaching were calcium contents in fly ashes and ash contents in raw coals.

1. Introduction

Major fractions of coal fly ash generated from pulverized coal combustion processes have been used as fill materials to reclaim land from the sea. Coal fly ash contains hazardous toxic elements such as arsenic, and often contains elevated concentrations of the toxic elements. An ash storage area is usually holding seawater and rainwater (called excess water), therefore some elements including arsenic in the fly ash are leach out the excess water. If arsenic concentration in the excess water exceeds the environmental limit (0.1 mg/L in Japan), the excess water can not be drained to the sea. This is a serious situation, because ash storage has to discontinue. In this concern, it is important to find leachability of arsenic from the fly ashes for various coal types.

Another interest is effect of the boiler types on the leachability, because the ash properties and arsenic partitioning may be changed by types of coal fired boilers. Some researchers investigated As partitioning and its mechanisms during coal combustion [1, 2]. It concluded that As in raw coal was released as vapor at high temperature during combustion, and generated gaseous arsenic oxide reacted with calcium oxide on fly ash. Consequently, $\text{Ca}_3(\text{AsO}_4)_2$ is formed on fly ash surface, which is the most thermodynamically stable calcium–arsenic compound under conditions of coal fired boilers [3]. Oxidation state of As (+3 and +5) is an important factor in controlling As leachability [4]: hence, As leachability may depend on combustion conditions.

In this paper, As leachability was investigated for various coal fly ashes collected from two different power plants. Effects of Ca and boiler types on As leachability were discussed.

2. Experimental section

2.1. Fly ash samples

Six fly ash samples were carefully collected from each coal fired power plants (Unit A and Unit B: 600 MWe). Fig. 1 depicts the process flow of the plants, ash collection locations, and typical gas temperatures between the boiler exit and the low temperature electrostatic precipitator (ESP). The unit B has a DeNO_x (SCR) system. To prevent contamination of samples, after enough time from coal switching, the ash sampling was began at each chamber (#1, #2, and #3).

Table 1 lists coal properties and ash composition. Coal F and G, and coal H and I are same coal between unit A and B.

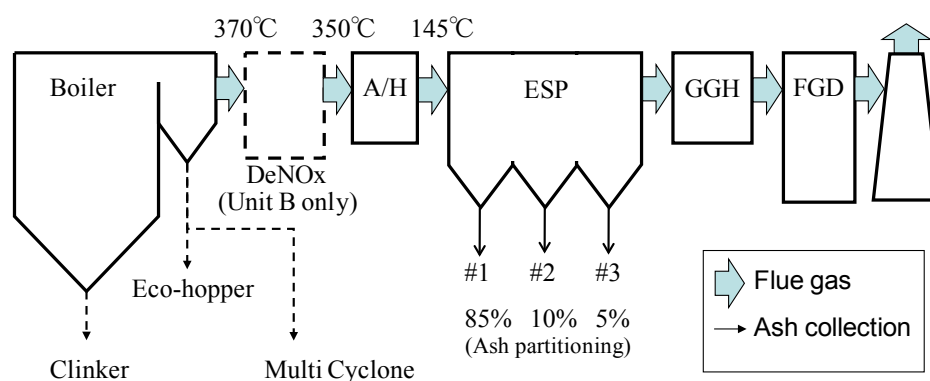


Fig. 1. Process flow of the coal fired power plants and ash collection points.

Table 1. Properties of raw coals and fly ashes collected from #1 chamber of ESPs.

Power station	Key	Raw coal (on dry basis)			Fly ashes (on dry basis)							
		C	Ash	As	As	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	SO ₃
		wt%	wt%	mg/kg	mg/kg	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Unit A	E	67.9	14.3	2.14	12.16	55.5	31.2	5.35	2.18	1.17	1.18	0.29
	F	71.5	13.3	0.84	3.16	67.0	26.2	2.26	0.68	0.26	0.60	0.24
	H	68.3	10.4	3.69	26.46	59.3	25.6	7.49	2.05	0.60	1.56	0.42
	O	69.6	9.7	1.45	15.65	75.7	17.2	2.79	0.97	0.47	0.94	0.00
	P	70.9	13.0	0.78	4.96	62.1	26.5	4.77	1.68	0.95	0.98	0.15
	R	76.5	9.5	0.88	8.23	62.6	28.7	3.86	0.93	0.45	0.69	0.00
Unit B	G	71.5	13.3	0.84	4.53	65.4	26.5	3.18	0.93	0.28	0.56	0.64
	I	68.3	10.4	3.69	39.22	59.0	26.0	7.25	2.09	0.65	1.50	0.51
	K	67.9	13.9	1.35	8.85	56.1	20.6	7.80	9.46	0.71	2.04	0.80
	L	73.1	10.3	0.87	9.46	58.1	21.4	6.40	8.24	0.83	1.86	0.84
	M	73.0	9.7	1.53	10.41	64.5	22.9	6.31	1.46	0.51	1.74	0.34
	Q	74.0	9.5	1.02	7.48	62.3	27.8	4.04	1.39	0.73	0.89	0.04

2.2. Leaching tests

To simulate pH of the excess water, a buffer solution adjusted pH = 10 was prepared as a leaching solvent. The ash sample (1.0 g) was added to the leaching solvent (10 mL), and it was shaken for 30 minute at 200 rpm. After shaking, the solid and the solvent were separated by filtration, and both arsenic concentration of the solid and the solvent was measured by ICP-AES.

3. Results and Discussion

3.1. Arsenic partitioning

In pulverized coal combustion processes, arsenic has classified as Group II elements which are not incorporated into the bottom ash. It is believed that volatilized arsenic during combustion is chemically condensed on fly ash at low temperature processes [2]. For twelve fly ash samples, percentage of As partitioning was ranged from 95–157% as calculated from data listed in Table 1, which represented the behavior of Group II elements.

To compare arsenic partitioning in the unit A and B, relation between modified arsenic concentration in the raw coals, $[As_0/Ash^{0.65}]$, and arsenic concentration in the fly ashes, As_{FA} , for the unit A and B is shown in Fig. 2. As_0 and Ash are As concentration and ash content in the raw coals, respectively. It found that As_{FA} can be accurately estimated by the parameter $[As_0/Ash^{0.65}]$, and arsenic partitioning was same behavior between the unit A and B.

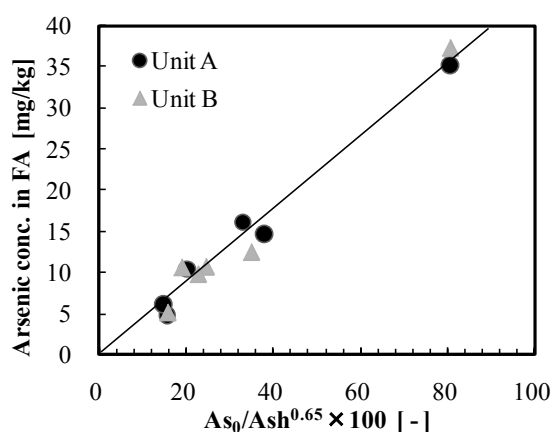


Fig. 2. Relation between modified As concentration in the raw coals and As concentration in the fly ashes for the unit A and B.

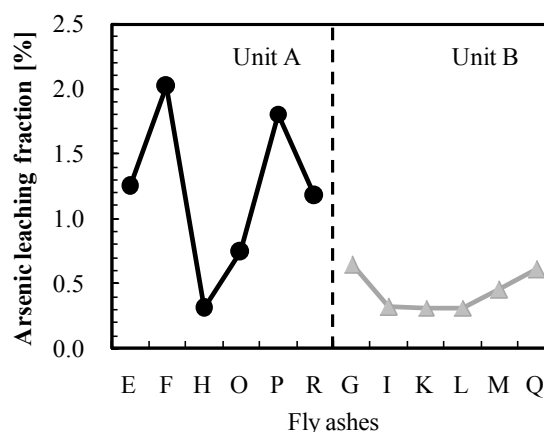


Fig. 3. Variation in As leaching fraction for various fly ash samples and for the unit A and B. (pH of the leaching solvent was fixed on 10.)

3.2. Arsenic leaching

Fig. 3 shows the arsenic leaching fraction, L_{As} , for the fly ash samples of the unit A and B. With the unit A, L_{As} was observed in the range of 0.3–3.0%, which was a wide range comparing that of the unit B. Particularly, L_{As} of fly ash F and G, although the both raw coals were same, significantly differed. It clarify that arsenic leaching is affected by boiler types.

3.3. Dominant factors on arsenic leaching

$Ca_3(AsO_4)_2$ is a stable compound formed during combustion, which is an insoluble material: it seems that fly ash types having high CaO/Ash ratios generate much $Ca_3(AsO_4)_2$, and have low As leaching fraction. Fig. 4 shows variation in L_{As} for all

fly ash samples as a function of $CaO/Ash \times 100$, where CaO is ash composition of the raw coal. L_{As} increased suddenly below $CaO/Ash = 50$ in both units. $CaO/Ash \times 100$ of coal F and G is 6.3: it is reasonable that both fly ashes have high L_{As} among the same unit. However, L_{As} of coal F (unit A) is much higher than that of coal G (the unit B). The reason for the difference may be the difference in CaO content of the fly ash between unit A and B.

Fig. 5 shows CaO% in the fly ashes of coal F and G. It found that the fly ash F from the unit A indicated low CaO% compared to the fly ash G. Therefore actual CaO/Ash ratio of the fly ash F was much lower than the appearance CaO/Ash ratio. It is supposed that high L_{As} of the fly ash in unit A is owing to the loss of calcium during combustion.

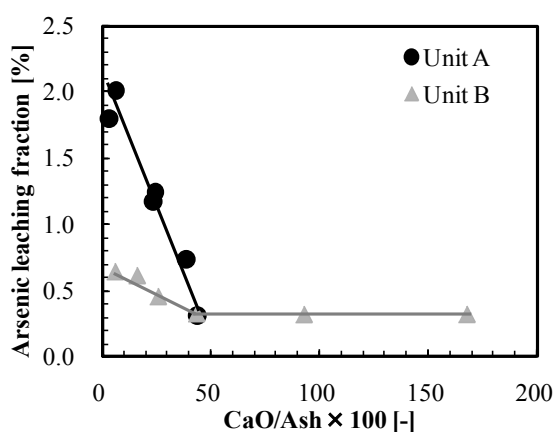


Fig. 4. Variation in L_{As} as a function of CaO/Ash ratios for the unit A and B.

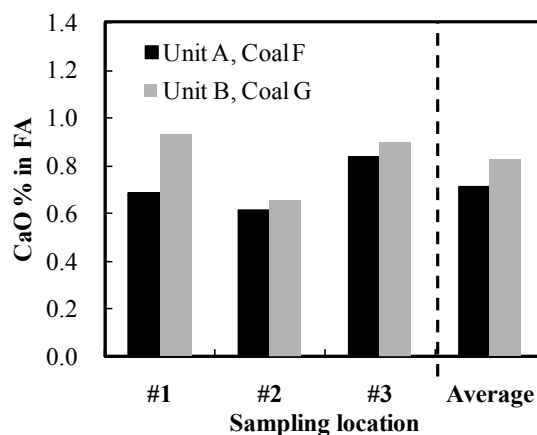


Fig. 5. Different in CaO% in the fly ashes between the unit A and B.

4. Conclusions

Arsenic partitioning in the unit A and unit B represented the same behavior. Most arsenic in the raw coal associated with the fly ash for various coal types. However, arsenic leaching fraction of the fly ashes in the buffer solution (pH = 10) was strongly affected by coal types and boiler types. It was found that arsenic content, calcium content, and ash content were the dominant factors controlling As leachability.

References

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