

214 Arsenic Leachability and Speciation in Fly Ashes from Coal Fired Power Plants

Sri HARTUTI. Gifu University, 1-1 Yanagido, Gifu

Akihiro TAKEYAMA. Gifu University, 1-1 Yanagido, Gifu

Shinji KAMBARA. Gifu University, 1-1 Yanagido, Gifu

Abstract

The leaching characteristics of arsenic (As) in coal fly ash collected from two different coal fired power plants (Unit 1 and Unit 2) have been systematically investigated. To determine dominant factors on arsenic leaching from coal fly ash, speciation of arsenic during coal combustion was predicted from the perspective of thermodynamic equilibrium calculation and leaching tests under alkaline condition (pH = 10) at solid/liquid ratio of 1:10 was also performed. The results indicated that, arsenic leaching fractions in unit 1 was higher than that of unit 2, it was associated with the amount of reactive calcium oxide (CaO) containing in coal fly ash from unit 1 was lower than that from unit 2. As_2O_3 (gas) formed in the boiler reacts with CaO in the fly ash to form calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$. $\text{Ca}_3(\text{AsO}_4)_2$ is a stable compound formed during combustion, which is insoluble in water. Hence the coal fly ash from unit 2 having higher *CaO/Ash* ratios generate more $\text{Ca}_3(\text{AsO}_4)_2$ and have lower As leaching fraction than that from unit 1. *CaO/Ash* ratios was a promising index to prevent the emission of arsenic into ambient and reduce its leachability from fly ash.

Keywords: Coal fly ash, Arsenic, Leaching behavior

1 INTRODUCTION

Coal-based power generation produces large amounts of fly ash worldwide. Fly ash has been successfully used for many years in a wide range of applications. However, it is most commonly used as a high-performance substitute for portland cement and as a clinker addition in the manufacturing of portland cement. There are large amounts of fly ash either stored temporarily in stockpiles, disposed of in ash landfills. The phase transformations that mineral matter in coal undergoes during high temperature combustion may render the trace elements in the original coal matrix susceptible to leaching [1]. Some trace elements contained in fly ash are likely to be released from the storage/disposal site when ash comes in contact with water.

Arsenic (As), the most volatile and potentially toxic trace element in coal, is largely released into ambient as gas phase and/or associated with fine ash particulates during coal combustion [2-4]. Even for the fine ash which is captured in a power plant, the subsequent treatment through landfill results in the mobilization of As into aquifer systems, which consequently causes damage to either surface water or groundwater. In Japanese coal-fired power plant sites, the ash storage area usually holds seawater and rainwater (excess water); therefore, arsenic and some elements in the fly ash, are leached out into the excess water. If the arsenic concentration in the excess water exceeds the environmental limit (0.1 mg L^{-1} in Japan), the excess water cannot be drained into the sea. This situation is serious, because ash storage must be discontinued. Given these concerns, it is important to find leachability of arsenic

from the fly ashes for various coal types for the development of advanced control technology to reduce the negative impacts of this element on the environment.

The mode of occurrence of As in a raw coal have been summarized in some review papers [5]. In general, the majority of As in a coal exists as pyritic, organic and arsenate. Arsenic partitioning is dependent on many factors such as the initial concentration of As in a coal, combustion conditions (types of coal fired boilers) and ash properties [6, 7]. Arsenic 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 [8]. Oxidation state of As (+3 and +5) is an important factor in controlling As leachability [9]: hence, As leachability may depend on combustion conditions.

A large quantity of research works have been conducted on the behavior of As in coal combustion, but it is still far from complete with respect to the mechanisms of the partitioning of As during combustion and leaching from fly ash. In particular the effect of Ca Content/Ash Content on the leaching characteristics of arsenic in fly ash from pulverized coal combustion needs to be further clarified. In this work, As leachability for various coal fly ashes collected from two different coal fired power plants (Unit 1 and Unit 2: 600 MWe) was investigated and the effects of Ca and boiler types on As leachability were also discussed.

2 EXPERIMENTAL

2.1 Coal and fly ash properties

Six fly ash samples were carefully collected from each coal fired power plants (Unit 1 and Unit 2).

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). Only the unit 2 has a DeNOx (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). Approximately 85% of fly ash is collected in chamber 1, 10% in chamber 2 and 5% in chamber 3.

Table 1 lists coal properties and ash composition. Fly ash F and G, and fly ash H and I came from the same coal between unit 1 and 2 of coal fired power plants.

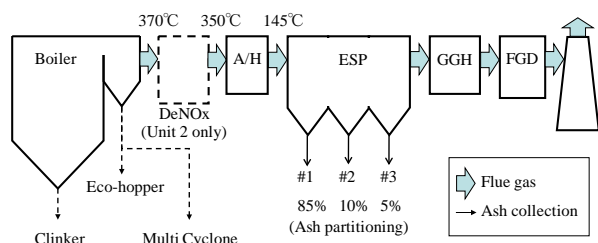


Fig. 1. Process flow of the coal fired power plants and ash collection points.

Table 1. Coal properties and ash composition for raw coals and fly ashes collected from #1 chamber of the ESP.

Power Staion	Key	Raw coal (on dry basis)			Fly ashes (on dry basis)							
		C wt%	Ash wt%	As mg/kg	As mg/kg	SiO ₂ wt%	Al ₂ O ₃ wt%	Fe ₂ O ₃ wt%	CaO wt%	Na ₂ O wt%	K ₂ O wt%	SO ₃ wt%
Unit 1	E	67.91	14.28	2.14	12.16	55.52	31.21	5.35	2.18	1.17	1.18	0.29
	F	71.52	13.29	0.84	3.16	66.96	26.19	2.26	0.68	0.26	0.60	0.24
	H	68.32	10.37	3.69	26.46	59.25	25.63	7.49	2.05	0.60	1.56	0.42
	O	69.59	9.66	1.45	15.65	75.69	17.17	2.79	0.97	0.47	0.94	0.00
	P	70.93	13.04	0.78	4.96	62.06	26.50	4.77	1.68	0.95	0.98	0.15
Unit 2	R	76.48	9.54	0.88	8.23	62.63	28.70	3.86	0.93	0.45	0.69	0.00
	G	71.52	13.29	0.84	4.53	65.45	26.48	3.18	0.93	0.28	0.56	0.64
	I	68.32	10.37	3.69	39.22	59.00	25.97	7.25	2.09	0.65	1.50	0.51
	K	67.92	13.86	1.35	8.85	56.14	20.57	7.80	9.46	0.71	2.04	0.80
	L	73.08	10.33	0.87	9.46	58.09	21.36	6.40	8.24	0.83	1.86	0.84
	M	72.99	9.70	1.53	10.41	64.52	22.90	6.31	1.46	0.51	1.74	0.34
	Q	74.02	9.54	1.02	7.48	62.32	27.76	4.04	1.39	0.73	0.89	0.04

2.2 Characterization of sample

Major elemental compositions of ash were quantified using Sequential X-ray Fluorescence Spectrometer (XRF-1800, Shimadzu).

The concentration of arsenic in fly ash was analyzed using HGICP-AES with the assistance of acid digestion. Sample digestion was carried out in a microwave oven (MDS 2000) fitted with an exhaust unit and a microprocessor to control the power and thermal program. Briefly, about 0.1 g ash sample was weighted and moved into PTFE bottle. An acid mixture capable of completely digesting ash sample were 2 ml of HNO₃ 65%, 4 ml of HF 50% and 5 ml of saturated

H₃BO₃. Boric acid was added after dissolution to neutralize the corrosive hydrofluoric. After cooling, the residue was dissolved and diluted to 50 mL using HCl 10% and KI 20%.

The concentration of arsenic in raw coal was analyzed using HGICP-AES with the assistance of wet destruction procedures using several concentrated acids. Prior to analysis coal sample was first grinded, about 0.5 g raw coal sample was weighted and moved into Erlenmeyer, involve heating (200°C), cooling and filtering procedures. Concentrated acids which is used were HNO₃ 60%, H₂SO₄ 60%, HCl 10%, HF 30 %, and another reagents which is used were KMnO₄ 2.5 % and FeCl₃ 5%.

2.3 Leaching tests

Leaching behavior of arsenic out of fly ash was quantified using leaching test. To simulate pH of the excess water, a buffer solution adjusted pH = 10 was prepared as a leaching solvent. In brief, the ash sample of 1 g was mixed with the leaching solvent (10 mL) and the slurry was shaken (200 rpm) for 30 minutes at room temperature. Filtration was performed to separate the fly ash using a filter (Advantec No.2). The concentration of arsenic in filtrate was measured by HGICP-AES.

2.4 Thermodynamic equilibrium calculation

The thermodynamic equilibrium software, FactSage 6.0, was employed to theoretically predict the speciation of arsenic during coal combustion. The elemental compositions of ash were used as calculation input. The databases used include ELEM, FACT and Fact53.

3 RESULTS AND DISCUSSION

3.1 Partitioning of arsenic

In coal combustion systems, the partitioning of arsenic between the vapor and solid phases is determined by the interaction of arsenic vapors with fly ash compounds under post-combustion conditions. Previous studies shown that trace elements can be classified into three broad groups according to their partitioning during coal combustion [10], arsenic has classified as Group II elements which are not incorporated into the bottom ash but it vaporized during combustion and chemically condensed onto particle surfaces in the flue gas stream during cooling process [11].

To compare arsenic partitioning in the unit 1 and 2, 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 1 and 2 was investigated. As_0 and Ash are As concentration [mg/kg-coal, db] and ash content [% , db] in the raw coals, respectively. As shown in Fig. 2, arsenic shows similar partitioning behavior between unit 1 and 2 of coal fired power plants. From the relationship obtained, arsenic concentration in fly ashes, As_{FA} , can be accurately estimated by the parameter $[As_0/Ash]^{0.65}$.

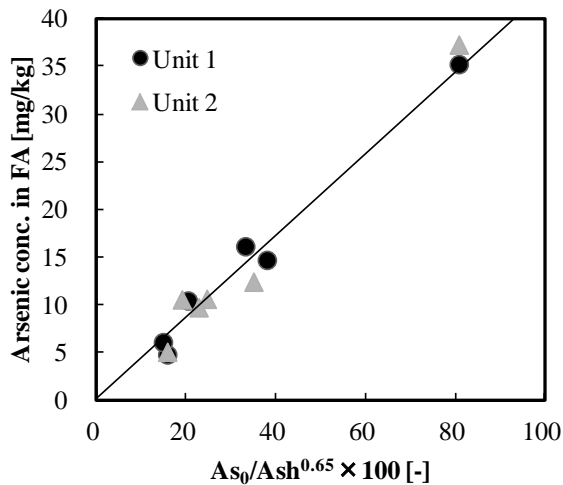


Fig. 2 Relation between modified As concentration in raw coals and As concentration in fly ashes for the unit 1 and 2.

3.2 Leaching fractions of arsenic

According to the above results, all of arsenic presents in raw coals for unit 1 and 2 are distributed to fly ash. The subsequent treatment of the resulting fly ash through landfilling will cause secondary pollution due to relative high concentration of arsenic in fly ash. Clarifying the leaching characteristics of arsenic in such fly ash generated from the coal combustion in coal fired power plants is highly significant.

To clarify the leaching characteristics of arsenic, the leaching test was conducted. Fig. 3 shows the leaching fraction of arsenic, L_{As} , in the fly ash collected from two coal fired power plants (Unit 1 and Unit 2).

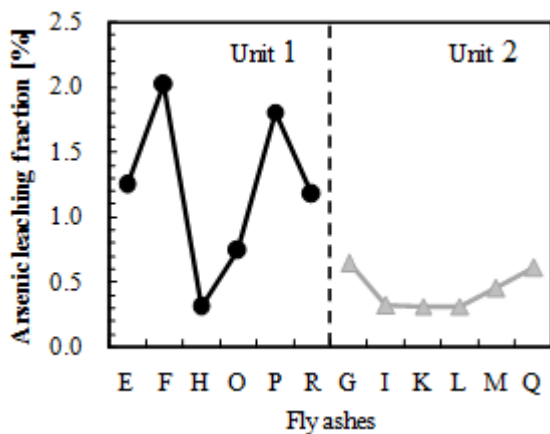


Fig. 3 Variation in As leaching fraction for various fly ash samples and for the unit 1 and 2.

Here the leaching fraction was defined as the percentage of total mass of arsenic in leachate to its mass in fly ash. Clearly, the L_{As} in the fly ash from combustion of coal in unit 1, range of 0.3–3.0%, is much higher than that coal in unit 2, range of 0.2–0.8%. Particularly, for the fly ash F and

G, which derived from the same coal between unit 1 and 2 of coal fired power plants, has different L_{As} value. L_{As} in fly ash F (2.1%) is quite higher than that in fly ash G (0.7%), indicating that the leaching of arsenic from fly ash is affected by boiler types.

3.3 Dominant factors on arsenic leaching

To better understand the dominant factor on arsenic leaching, the possible form of arsenic-bearing species during coal combustion and cooling process need to be clarified. Thermodynamic equilibrium calculation was conducted to predict the formation of arsenic-bearing species during coal combustion and cooling process. Arsenic trioxide (As_2O_3) was formed in as phase during combustion at high temperature. During the cooling through post-combustion processes, the flue gases cool and As_2O_3 formed in the boiler reacts with ash carried contains CaO in the flue gases to form stable compounds calcium arsenate $Ca_3(AsO_4)_2$. as shown in Fig. 4. It found that calcium was the most influential factor on arsenic transformation.

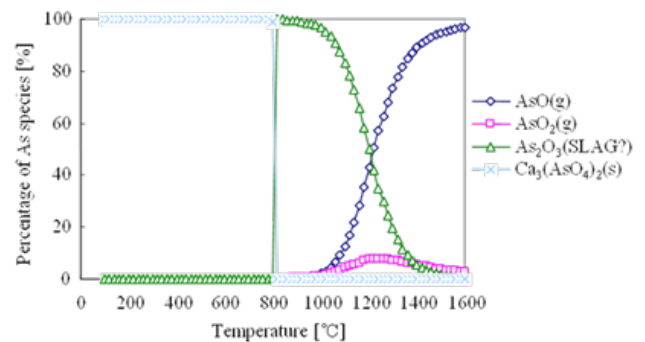


Fig. 4 Prediction of As functional forms during the cooling process of the power plants. Arsenic preferentially combines with calcium to form Ca-As compound.

Variation in L_{As} for all fly ash samples and CaO content in raw coal as a function of $CaO/Ash \times 100$, where CaO is ash composition in the raw coal, was investigated. As shown in Fig. 5, L_{As} in fly ash decreased with the increase of CaO/Ash ratios. L_{As} increased under the CaO/Ash of 50 in both units. $CaO/Ash \times 100$ of fly ash F and G is same, 6.28, shows that both fly ashes which derived from the same coal between unit 1 and 2 of coal fired power plants have high L_{As} value. However, L_{As} of fly ash F (2.1%) from unit 1 is much higher than that in fly ash G (0.7%) from unit 2. This trend can be explained by the difference of CaO content in fly ash between unit 1 and 2. To confirm such a hypothesis, CaO content in fly ash was also determined. As shown in Fig. 6, CaO content in fly ash F from unit 1 is lower than that in fly ash G from unit 2, and actual CaO content in fly ash F was much lower than the appearance of CaO/Ash ratio. It is supposed that high L_{As} of the fly ashes in unit 1 is owing to the loss of calcium during combustion. Abundant

of CaO/Ash ratio in fly ashes of unit 2 preferentially associates with arsenic to form stable compound, $Ca_3(AsO_4)_2$, and thus reduce the leaching of arsenic. This observation clearly indicates that CaO in coal is favorable for reducing the leachability of arsenic.

CaO is the most important factor both in arsenic vapor capture during coal combustion from pulverized coal fired power plants and prevention of its leaching from fly ash. Through controlling CaO/Ash ratio can efficiency inhibit the leaching of arsenic.

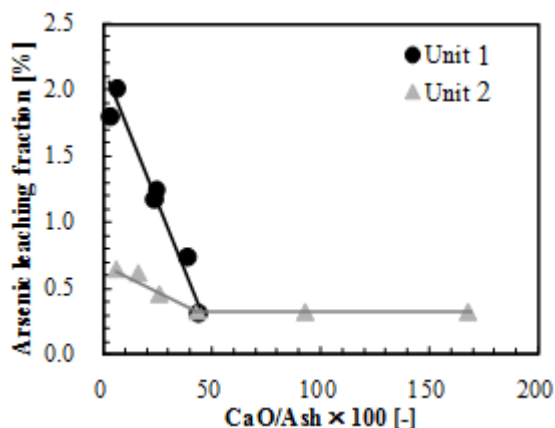


Fig. 5. Variation in LAs% as a function of CaO/Ash ratios for the unit 1 and 2.

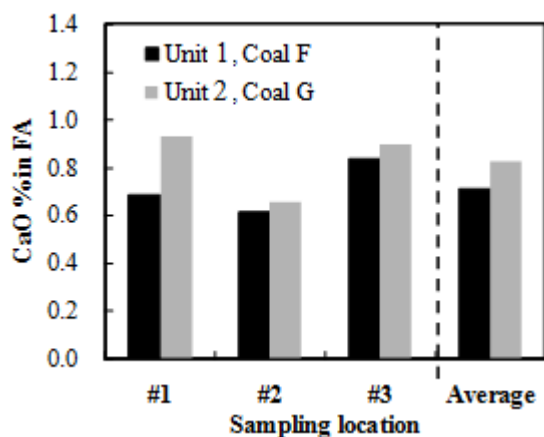


Fig. 6. Different in $CaO\%$ in fly ashes between unit 1 and 2. Note that coal F and G are the same coal as listed in Table 1.

4 CONCLUSION

The leaching characteristics of arsenic from fly ashes were examined to be clear effects of the difference in boiler types. The findings of this study are summarized as follows:

1. Arsenic partitioning in the unit 1 and unit 2 represented the same behavior. Arsenic vaporized during combustion and chemically condensed onto particle surfaces in the flue gas stream during cooling process.
2. Most arsenic in the raw coal associated with the fly ash for various coal types. However, leaching of arsenic

was different for each boiler.

3. CaO/Ash ratio in raw coal affects the retention of arsenic in fly ash through the chemical reactions of arsenic vapor with CaO . Unit 2 has higher CaO/Ash caused a significant reduction on the emission of arsenic, in comparison with unit 1.
4. Controlling CaO/Ash in raw coal is a promising method to shift the ash properties and in turn alters the leaching behavior of arsenic.

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