International Workshop on Environment & Engineering 2014
November 19-20, 2014

215 The Leaching Characteristics of Trace Elements in Coal Fly Ash

Akihiro TAKEYAMA. Gifu University, 1-1 Yanagido, Gifu
Shinji KAMBARA. Gifu University, 1-1 Yanagido, Gifu
Sri HARTUTI. Gifu University, 1-1 Yanagido, Gifu
Farrah F HANUM. Gifu University, 1-1 Yanagido, Gifu

Abstract
The 1eaching characteristics of trace elements (As, B, and Se) in coal fly ash (CFA) were investigated. CFA samples were collected from a large scale power plant in Japan. It found that the leaching fractions of arsenic were low levels below 15% for six different CFA samples. On the other hand, the leaching fractions of boron and selenium were around 30% and around 50% for the CFA samples, respectively. Leaching test results were compared with solution equilibrium calculation to consider the leaching mechanisms: however, experimental results were significantly lower levels for any elements than the equilibrium calculation results. To elucidate the leaching mechanisms, the leaching rate were investigated by the expanded leaching tests for a long term. For arsenic, the leaching concentration was increased day by day, all amount of arsenic in CFA samples was completely leached in approximately 120 days. The leaching characteristics of boron and selenium was also investigated in the view of a long term leaching.

Keywords: coal fly ash, Arsenic, leaching rate, equilibrium calculation

1 INTRODUCTION

Coals contain harmful elements such as As, Se, and B. In the coal combustion process, for example pulverized coal fired power plants, trace elements are distributed to gas phase (flue gas), liquid phase (as desulfurization waste water), and solid phase (as fly ash collected by electric precipitator and gypsum formed in desulfurization). The trace elements existed in gas phase at low temperature are discharged to atmosphere [1]. However, the most amount of trace elements is distributed to the solid phase such as fly ash, which is recovered by electrostatic precipitators (ESPs).

The collected coal fly ashes (CFAs) by ESPs are usually effectively used as raw materials for cement production. The CFAs having large amount of unburned carbon are unsuitable as the raw materials for cement, which are scrapped as landfill materials at a near site of coal fired power stations. As another possibility to use large amount of CFAs, there is utilization as roadbed materials, which is desired to expand utilization of CFAs. However, roadbed materials are imposed severe regulations on leaching of harmful elements [2]. It is necessary to understand the leaching behavior for the utilization, however, the knowledge is insufficient.

In this work, leaching characteristics of arsenic, boron, and selenium in CFAs were investigated. Six different CFA samples were collected from a commercial power plant for the leaching experiments. Solution equilibrium calculation was employed to be clear the leaching mechanisms, and the calculation results were compared with the experimental results. Effects of leaching rate on the leaching behavior were discussed.

2 EXPERIMENTAL

2.1 Sample

Six different coal fly ashes (G, H, I, J, L, and N) were collected from a pulverized coal fired power plant. Table 1 shows the major chemical compositions that were measured by XRF. Trace elements (As, B, and Se) was measured by ICP-AES. It should be note that the concentration ranges of As, B, and Se have wide ranges in six CFA samples as shown in Table 1.

Table1 Chemical composition of FA

Fly ash		G	H	I	J	L	N
SiO_2	[%]	65.45	59.25	59.00	65.38	58.09	62.98
Al_2O_3		26.48	25.63	25.97	21.60	21.36	23.20
TiO_2		1.74	1.99	1.86	1.06	0.89	1.20
Fe_2O_3		3.18	7.49	7.25	7.14	6.40	5.33
CaO		0.93	2.05	2.09	1.43	8.24	2.59
MgO		0.54	0.79	0.86	0.52	1.07	1.16
Na_2O		0.28	0.60	0.65	0.43	0.83	1.36
K_2O		0.56	1.56	1.50	1.77	1.86	1.41
P_2O_5		0.07	0.18	0.17	0.16	0.27	0.19
MnO		0.11	–	0.10	–	–	–
V_2O_5		0.02	0.03	0.04	0.15	0.15	0.04
SO_3		0.64	0.42	0.51	0.38	0.84	0.54
As	[mg/kg]	4.53	35.01	43.94	14.92	11.71	23.68
B		44.2	269.7	326.6	244.2	536.1	527.2
Se		5.18	2.24	1.27	3.38	2.82	1.92

2.2 Leaching tests

The procedure of standardization leaching tests, No.13 Notification by the Japanese Environment Agency, were basically employed as leaching tests in this work. However, in this way, variation in pH of leachate during leaching tests strongly affects leaching concentration of elements. So a buffer solution (pH = 10) was used as a leaching solution, which can keep a constant pH around 10.

The ash sample weight of 50 g and 500 ml buffer solution were blended in a polyethylene bottle, after then, it was stirred for 6 hours at a shaking speed of 200 r.p.m. The solid-liquid sample was separated by a filtration using a membrane filter of 0.45 μm to obtain the filtrate. The concentrations of trace elements (As, B, and Se) in filtrate were carefully analyzed by ICP-AES.

Expanded leaching tests has carried out to elucidate effects of leaching time. For 120 day, the leaching tests were continued.

2.3 Solution equilibrium calculation

To consider solution equilibrium, thermochemical and database software "FactSage 6.0" (www.factsage.com) was used. It has optimized databases for solutions of metals, liquid, and solid, which can applied for equilibrium calculation in the liquid-solid system. In the equilibrium calculation, chemical composition as shown in Table 1 and liquid conditions (25 ºC, of 1 atm) were set on FactSage 6.0.

3 RESULTS AND DISCUSSION

3.1 Leaching characteristics

Fig.1 shows the leaching fraction of arsenic for 6 CFA samples. The fraction ranges were from 0% to 15%. It was considered that leaching fraction of arsenic was affected by an arsenic concentration in CFA and chemical compositions of CFA. In particular, calcium concentration in CFA was an important factor for leaching of arsenic. Sample L containing a large amount of Ca was As leaching fraction of 0%, on the other hand, sample G having a low concentration of Ca was As leaching fraction of 15%. It was considered that an insoluble material, $Ca_3(AsO_4)_2$, was formed in the solution in the case of sample G [3,4].

The leaching fraction of boron and selenium show in Fig.2 and Fig.3, respectively. They fractions were higher than that of arsenic. The fraction ranges were from 20% to 40% for boron, and were from 30% to 60% for selenium. It seemed that Ca contents in CFA was no relation to leaching behaviors for B and Se. Control factors for leaching of these elements was not found.

3.2 Comparison with equilibrium calculation results

To consider leaching mechanisms, solution equilibrium calculation was performed by FactSage 6.0. The calculation results show in Figures 1, 2, and 3 for As, B, and Se, respectively. Surprisingly, the leaching fractions of all elements were 100% for all samples as shown in figures. In the calculation, parameter survey also has carefully carried out, however, effects of temperatures of the solution and value of pH on the leaching fractions was negligible.

It found that the leaching fractions between experimental and equilibrium calculation were significantly differed for all elements. This discrepancy may be dependent on the leaching time, because the leaching time has been assumed an infinite in the equilibrium calculation.

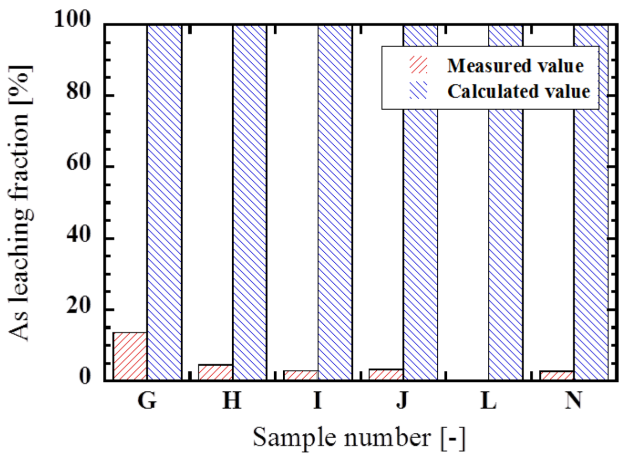

Fig.1 Leaching fractions of arsenic for 6 CFA samples: left bar is experimental result, and right bar is equilibrium calculation.

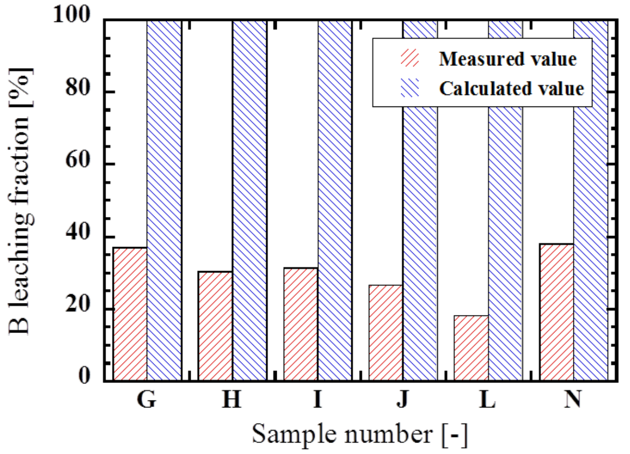

Fig.2 Leaching fractions of boron for 6 CFA samples: left bar is experimental result, and right bar is equilibrium calculation.

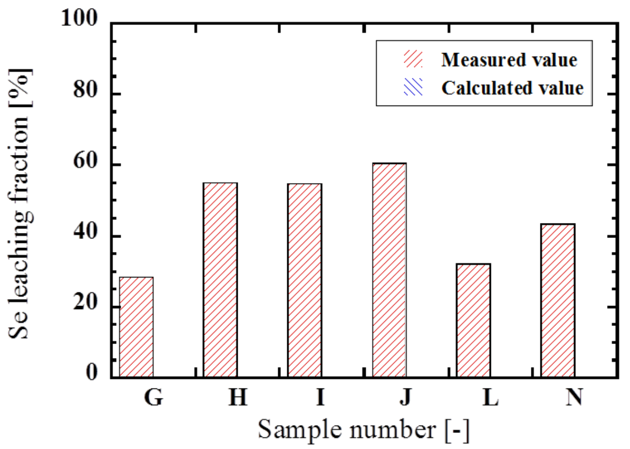

Fig.3 Leaching fractions of selenium for 6 CFA samples: left bar is experimental result, and right bar is equilibrium calculation.

3.3 Leaching characteristics for a long term

To investigate effect of the leaching time, the leaching tests for a long term were carried out. Fig. 4 shows leaching fractions of arsenic for 3 CFAs (H, I, and L) for 120 days. The concentration of arsenic in the leachate was measured every 30 days. As expected, the concentrations were increased with the leaching time for all samples.

The leaching fractions of sample H and I were much higher than that of the sample L for all terms. Most of arsenic in CFA was eluted at 120 days for the sample H and I. Even the sample I indicated 0% leaching fraction in Fig. 1, the leaching fraction was reached about 50%. It predicted that the leaching fraction of the sample L will be reached 100% in more long days. Therefore, the results of equilibrium calculations were give correct suggestions.

From the results shown in Fig. 4, it is clear that a leaching rate is an appropriate factor to evaluate leaching characteristics for various types of coal fly ash, and it is not leaching test results by standard procedures.

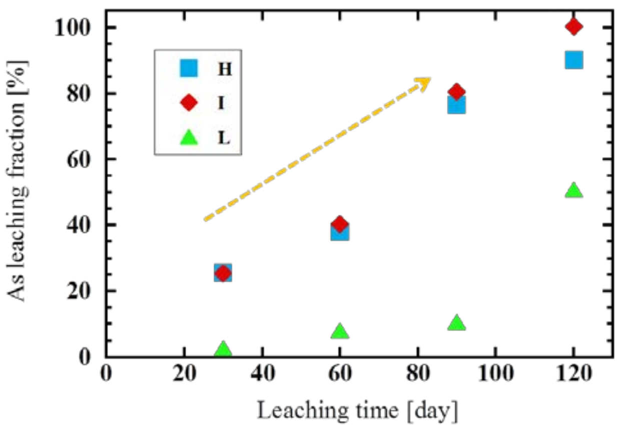

Fig.4 Effect of leaching time on As leaching fraction for 3 different coal fly ashes (H, I, and L)

3.4 Evaluation of leaching rates of arsenic

The behavior of leaching fractions shown in Fig. 4 was complex. It is difficult to express by a simple kinetic model such as first order reaction model. So a modified kinetic model was defined as follows:

$$X = 1 - \exp(-a \times t^{b}) \qquad (1)$$

where, X [−] is the leaching fraction of arsenic, and constant a and b were variables to express the complex behaviors of leaching fractions for a long term. The constant a and b are estimated by data fitting to equation (1). In the case of b = 1.0, equation (1) is correspond to the first order kinetic model. If b is smaller than 1.0, the leaching behavior indicates sigmoid curve.

Fig. 5 shows the results of data fitting, and constant a and b indicates in Table 2. It found that the behavior of leaching fractions was good agreement with the modified kinetic model by equation (1). For the sample L having the lowest leaching rate, constant a was low value and b was high value: that is, constant a indicates directly speed of the leaching, and constant b indicates a shape of the curve.

As mentioned above, the leaching fraction of arsenic related with Ca content in the CFA. Relation between constant a and Ca content was clear in Fig. 6. The leaching rate of arsenic was decreased with an increase of Ca content.

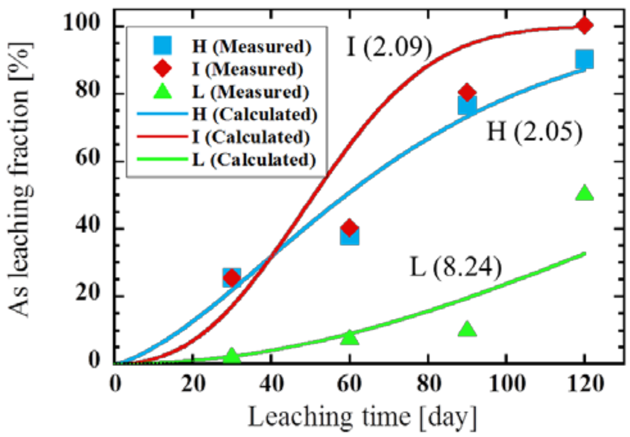

Fig.5 Fitting results by equation (1) for three different CFAs. The value in parentheses is CaO% in the CFA.

Table 2. List of constant a and b for 6 different CFAs.

	H	G	I	J	K	L
a	0.1049	0.2429	0.1627	0.2461	0.0043	0.1521
b	0.7073	0.3429	0.4164	0.2582	0.6696	0.2553

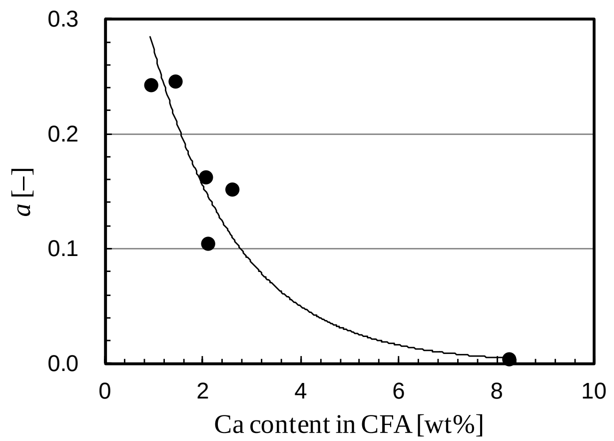

Fig.6 Relation between Calcium content in CFA and constant a obtained by data fitting based on equation (1).

3.5 Leaching behavior of boron and selenium

The leaching behavior of boron and selenium have been investigated, however, current results is for 16 days only. As shown in Figs. 7 and 8, the leaching concentrations for boron and selenium did not changed, which was predicted by the results of the leaching test for arsenic. More leaching test time is necessary to obtain the leaching rates.

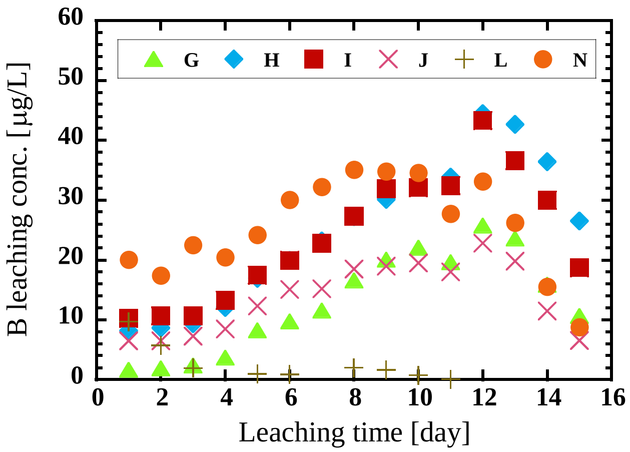

Fig.7 Variation in boron concentrations in the leachate for 16 days for 6 different CFAs.

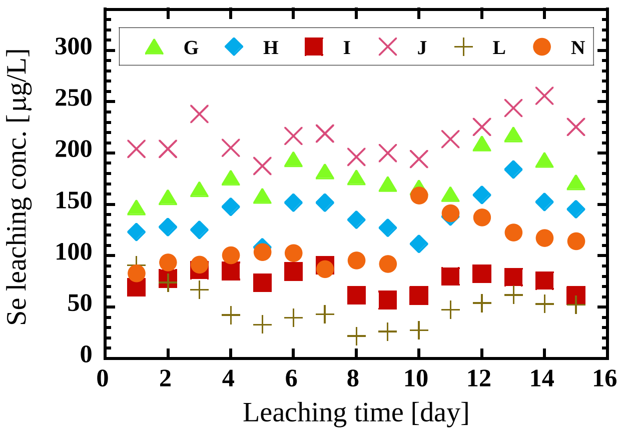

Fig.8 Variation in selenium concentrations in the leachate for 16 days for 6 different CFAs.

4 CONCLUSION

The 1eaching characteristics of arsenic, boron, and selenium from coal fly ash (CFA) were investigated for six different CFA samples that were collected from a large scale power plant in Japan. The results were summarized as follows:

(1) The leaching fractions of arsenic were low levels below 15%. It was affected by an arsenic concentration in CFA and calcium concentration in CFA.

(2) It found that the leaching fractions between experimental and equilibrium calculation were significantly differed for As, B, and Se. The leaching tests for a long term were required to reach solution equilibrium.

(3) Most of arsenic in CFA was eluted for 120 days. For the quantitative evaluation of leaching characteristics, leaching rate equation was defined using two variables. Constant *a* and *b* in the leaching rate of arsenic were determined for 6 CFAs. It found that constant *a* had good relationship with calcium content in CFAs.

REFERENCES

[1] Frandsen F., Dam-Johansen K., Rasmussen P. (1994): *Prog. Energy Combust. Sci.*, 20, pp. 115–138.

[2] Iwashita, A., Sakaguchi, Y., Nakajima, T., Tkeanashi, H., Ohki, A., Kambara, S. (2005): *Fuel*, 84, pp. 479-485.

[3] Yudovich, Ya. E., Ketris, M. P. (2005): *Int. J. Coal Geol*, 61, pp. 141-196.

[4] Zielinski, R.A., Foster, A. L., Meeker, G. P., Brownfield, I. K. (2007): *Fuel*, 86, pp. 560-572.