ROLE OF CALCIUM COMPOUNDS ON REDUCTION OF ARSENIC AND SELENIUM DURING FLUIDIZED BED COAL COMBUSTION

F. Jiao*, L. Zhang**, N. Yamada*, A. Sato* and Y. Ninomiya*

E-mail: ninomiya@isc.chubu.ac.jp (Corresponding author: Prof. Yoshihiko Ninomiya)
*Department of Applied Chemistry, Chubu University, Kasugai, Aichi 487-8501, Japan
**Department of Chemical Engineering, Monash University, PO Box 36, Clayton Campus, Victoria 3800, Australia

Abstract

Effect of calcium-bearing compounds in fly ash on the retention of Arsenic (As) and Selenium (Se) has been examined by conducting the combustion of two Australian coals without and with the addition of calcium hydroxide ($Ca(OH)_2$) at 860^oC in a lab-scale fluidized bed reactor. Apart from calcium hydroxide, another two additives, $CaSO_4$ and Fe_2O_3, have also selected and tested. Speciation of As and Se during fly ash leaching test were also predicted from the perspective of thermodynamic equilibrium. The results indicate that, increasing Ca/S molar ratio in coal is favorable for the retention of As and Se through possible gas-solid reactions of As and Se vapors with free calcium (CaO) in fly ash. This reaction was retarded by SO_2 in flue gas via preferential calcium sulfation. Leaching test of the resulting fly ash suggested that the leaching behavior of As and Se is largely dependent on the final pH of the leachate. Increasing Ca/S caused the shift of acidic fly ash into basic fly ash, thereby leading to a reduction of the leaching extent of As and Se. Ca concentration in leachate at alkaline condition also can reduce As leaching. Regarding the effect of different additives on the reduction of As leaching from fly ash, a descending sequence of $Ca(OH)_2 > CaSO_4 > Fe_2O_3$ was observed.

Introduction

Arsenic (As) and selenium (Se) are two of the most volatile and potentially toxic metals in coal. They are largely released into ambient as gas phase and/or associated with fine ash particulates during coal combustion [1-3]. Even for the fine ash which are captured in a power plant, the subsequent treatment through landfilling results in the mobilization of As and Se into aquifer systems, which consequently causes damage to either surface water or groundwater. In light of this, it is of importance to clarify the partitioning of As and Se during coal combustion as well as their leaching behavior from fly ash for the development of advanced control technology to reduce the negative impacts of these two metals on the environment.

The mode of occurrence of As and Se in a raw coal have been summarized in some review papers [4, 5]. In general, the majority of As in a coal exists as pyritic, organic and arsenate while the dominant forms of Se are sulfidic and organic. Regardless of their species in coal, As and Se are preferentially vaporized as element and/or oxide during coal combustion, which subsequently condense on existing particle surface via physical and chemical reactions in post-combustion regions, or escape into atmosphere directly. This partitioning is dependent on many factors such as the initial concentration of As and Se in a coal, combustion conditions and ash properties. Fine ash particulates with the diameter less than 10 μm show high capture ability of As and Se, due to its high specific surface area [6, 7]. Moreover, ash chemical composition affects the behavior of As and Se during combustion,

especially for Ca in fly ash. It has been evident that calcium hydroxide ($Ca(OH)_2$) has a high efficiency for the capture of As and Se at a moderate temperature of around 600^oC in comparison to other minerals such as kaolinite, alumina and silica [8, 9]. On the other hand, calcium-bearing minerals including calcium oxide, di-calcium silicate and mono-calcium silicate also show different capture ability to As and Se vapors at the temperature range of $600-1000^oC$ in both air and nitrogen atmosphere [10]. These processes are attributed to the dominant mechanism of irreversible chemical reaction rather than physical adsorption [11]. In light of this, using Ca-bearing compounds as additives to coal is one of the possible and practicable methods to in-situ capture As and Se vapors, and in turn reduce their emission into ambient. This definitely needs to be further confirmed by experimental method.

The leaching of As and Se from fly ash during landfill can cause potential hazard on aquifer systems and soil, which is thus of environmental concern. A large quantity of research works have indicated that the leaching behaviors of As and Se are strongly dependent on the pH of the leachate [12-14]. The addition of Ca-bearing compound to coal are expected to shift the ash property from acidic to alkaline, which in turn potentially influences the leachability of As and Se during fly ash landfilling.

Although many works have been conducted on the behavior of As and Se in coal combustion, it is still far from complete with respect to the mechanisms of the partitioning of As and Se during combustion and leaching from fly ash. In particular the effect of the addition of Ca-additives needs to be further clarified. In this work, the combustion of two Australian coals was carried out at 860^oC in a lab-scale fluidized bed reactor. The effects of Ca additives on the fate of As and Se during coal combustion and their leaching characteristic in fly ash were investigated.

2. Experimental

2.1 Coal properties

Two Australian bituminous coals, A1 and A2 mined from different seams in the same coal mine, were chosen for the combustion experiments. The coal samples were air-dried and sieved to 106-300 μm prior to use. As shown in table 1, two coal samples demonstrate similar properties in proximate analysis and ultimate analysis. About 0.5% sulfur was detected in two coal samples. With respect to chemical composition of two ash samples prepared at 815^oC in muffle furnace, the concentration of iron, calcium and sulfur in coal A2 were slightly higher than that of coal A1.

Table 1. Properties of tested coals.

	Proximate analysis, air-dried, wt%				Ultimate analysis, daf, wt%				
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O*	N	S
A1	6.0	9.7	28.7	55.6	76.4	3.8	17.6	1.69	0.5
A2	6.8	8.6	28.9	55.7	74.8	4.2	18.7	1.69	0.58

	Ash composition, wt%									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	SO_3
A1	56.1	34.4	3.9	0.52	0.29	0.56	0.2	1.59	0.59	0.41
A2	56.5	24.5	6.4	2.6	1.01	0.39	0.37	1.06	0.36	2.05

*: by difference.

2.2 Combustion conditions

Combustion experiments were carried out in a lab-scale fluidized bed combustor as shown in Fig.1. The fluidized bed reactor was made of a quartz tube with a length of 1000 mm and an inner diameter of 85mm. The furnace temperature was kept at 860^oC, consistent with the typical combustion temperature employed in industrial fluidized bed boiler. Coal sample at a

feeding rate of around 0.5g/min was fed through a piezo feeder into the combustion zone, which was also entrained by 2L/min secondary gas through an injector installed at the top of the reactor. The primary gas of 6L/min was introduced from the bottom for coal combustion and bed material fluidization (quartz sand with a diameter of 300 – 500 μm). The resulting ash was entrained by flue gas out of the reactor and subsequently separated by two cyclones. The tail gas composition including O_2, CO_2, SO_2, N_2 and CO was analyzed real-time and continuously by a gas analyzer. The ash collected from two cyclones was mixed together (termed as fly ash hereafter) and stored in fridge prior to analysis. Bed material was also collected once the reactor was cooled down to room temperature.
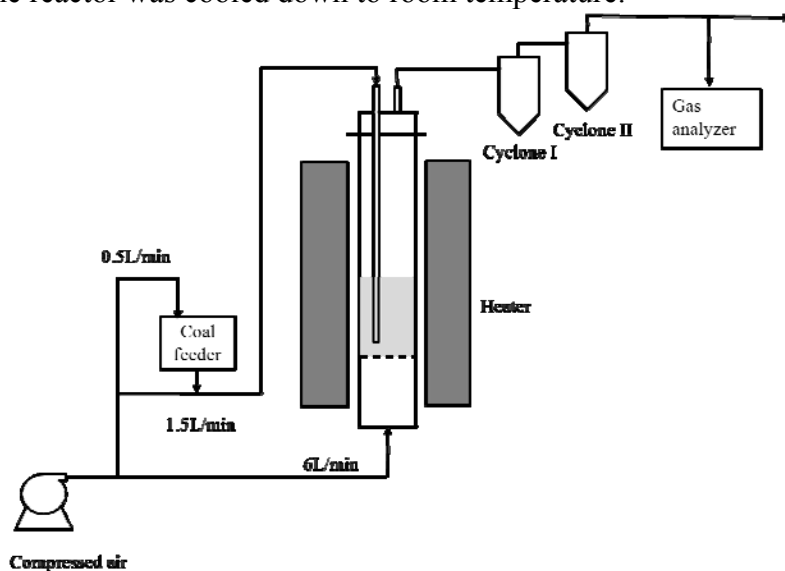
Figure 1. Schematic of fluidized bed reactor.

Apart from raw coal sample, the combustion experiments of coal A1 mixed with different amount of $Ca(OH)_2$ (analytical reagent, purity>98%) for matching the Ca/S (mol/mol) of 0, 1, 3, 5 and 10 was conducted to evaluate the effect of $Ca(OH)_2$ on the behavior of As and Se during combustion and their leaching in fly ash. Here, the ratio of Ca/S was defined as

$$Ca/S \ (mol/mol) = \frac{Ca \ in \ additives}{S \ in \ coal} \tag{1}$$

On the other hand, in order to compare the effects of different additives on As leaching two other additives $CaSO_4$ and Fe_2O_3 (analytical reagent, purity>98%) were also employed for coal A2 with a Ca (Fe)/S molar ratio of 3.

2.3 Leaching test
Leaching behavior of As and Se out of fly ash was quantified using leaching test according to Japanese Industrial Standard, JISK0102-61.2 for As and JISK0102-67.2 for Se. In brief, the fly ash was mixed with deionized water at a liquid to solid ratio of 10 and stirred for 6 h at room temperature. Filtration was performed to separate the fly ash. The concentration of As and Se in filtrate was measured by hydride generation ICP-AES.

2.4 Characterization of sample
Major elemental compositions of ash were quantified using XRF, Rigaku 2100. Crystalline structures in ashes were determined by X-ray Diffraction Spectrometer (XRD), Rigaku RINT,

using Cu_α edge at a voltage of 40 kV and a current of 40 mA. The concentration of As and Se in fly ash and bed material were quantified using ICP-AES with the assistance of acid digestion. EDX mapping were examined using scanning electron microscopy (SEM, JSM-6510) coupled with energy dispersive X-ray spectroscopy (EDX) under a working distance of 10 mm and a working voltage of 15 kV.

Computer-controlled scanning electron microscopy (CCSEM) analysis was carried out to characterize mineral species. Around 3000 individual particles were analyzed for each sample under three magnifications covering a particle size range of 0.5~211.0 μm. The modes of occurrence of the elements of interest were determined with the use of a variety of classification categories [15]. In comparison to XRD analysis, the amorphous phases in a fly ash sample can be analyzed by this method.

2.5 Thermodynamic prediction
The thermodynamic equilibrium software, FactSage 6.1, was employed to theoretically predict the distribution of As and Se (solid and ion) in water solution under different pH. The elemental compositions of ash were used as calculation input. The databases used include ELEM, FACT, Fact53 and EXAM.

3. Results and Discussion
3.1 Coal combustion
To monitor the coal combustion performance in fluidized bed reactor, flue gas composition was analyzed online by a gas analyzer. As shown in Fig.2, the lines of all gas concentration as a function of experimental time are almost flat, suggestive of a stable combustion of coal in the period when ash sampling was conducted. The O_2 concentration in flue gas remained at around 11% to obtain a carbon conversion of >90%. CO concentration in flue gas was about 15 ppm while the concentration of SO_2 and NO was 180 ppm and 300 ppm, respectively.
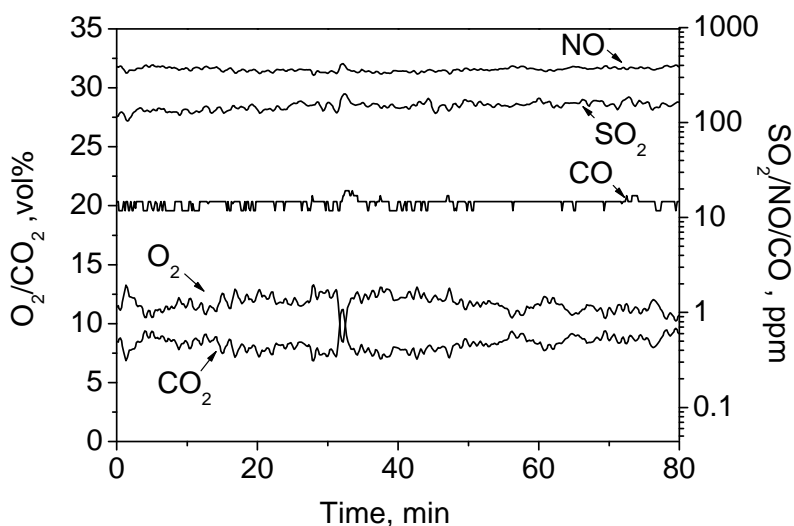

Figure 2. Flue gas composition during the combustion of coal A1.

3.2 As and Se in coal
EDX mapping was employed to describe the distribution of As and Se in the raw coals. A typical morphology of coal A1 was shown in the upper panel in Fig.3. Two bright particles marked A and B refer to inherent minerals while the organic carbon-rich particle was shown in gray. EDX analysis suggests that particle A is dominant in Fe and S, possible Fe_2S according to their atom ratio. Whereas Si and Al are the two major elements in particle B,

they seem to be combined as clay minerals such as kaolinite, which is the predominant crystalline phase in raw coal as suggested by XRD analysis. EDX mapping results in the bottom panels of Fig.3 show higher intense signal of both As and Se at the corresponding position of minerals than that in other region. This observation reflects that these two metals primarily associated with minerals in raw coal. On the other hand, the signal in particle A is more intense in comparison to that in particle B, indicating a preferential combination of As and Se with Fe/S. This results are consistent with previous studies, in which the As and Se are found to be primarily associated with pyrites/sulfides [5, 16, 17], where they substitute for sulfur in the pyrite structure [16, 18]. The As and Se dispersed in clay mineral is likely due to the association with silicates. This fraction was estimated to account for up to around 15-30% in bituminous coal [19, 20].


At%	A	B
O	4.7	20.5
Si	1	49.2
Al	0.2	18.8
Fe	30.5	1.4
S	63.4	0.2
Ca	0.2	4.7
Na	-	5.2
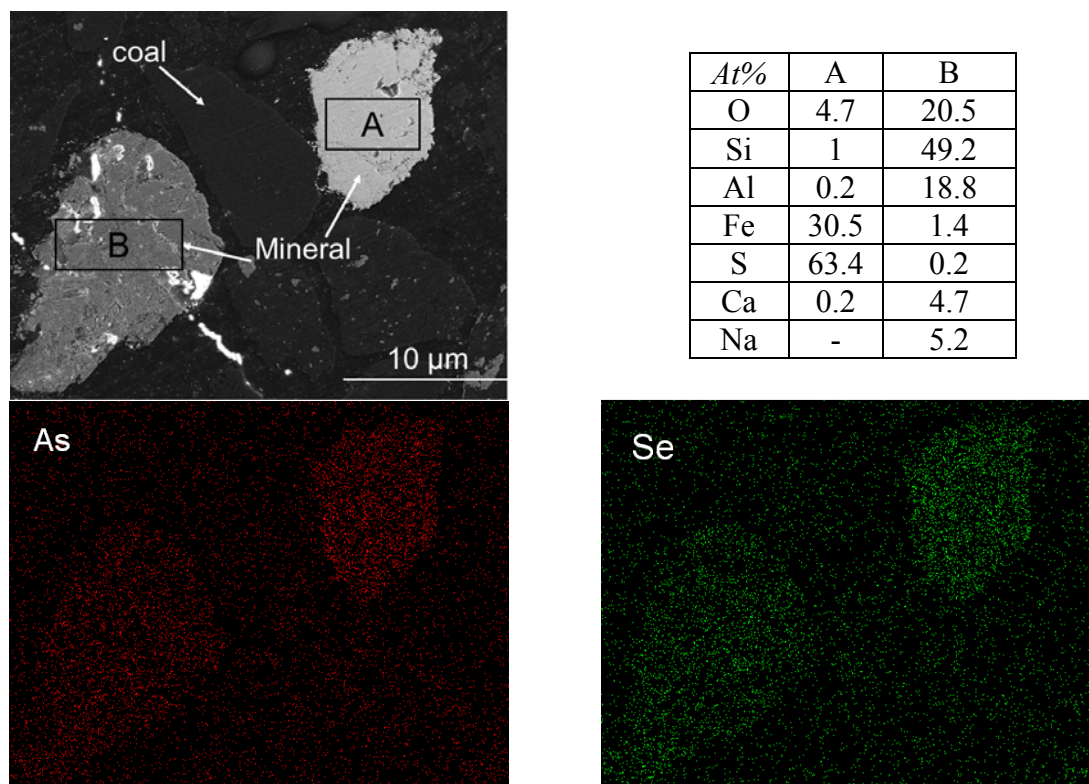
Figure 3. SEM picture and EDX mapping of As and Se in coal A1.

3.3 Retention rate of As and Se during combustion

Fig.4 illustrates the retention rate of As and Se as a function of Ca/S molar ratio during coal combustion. Here, the retention rate, reflecting the As and Se capture capacity by fly ash, was defined as the amount of As and Se in fly ash and bed material during the combustion of one gram coal. As can be seen, irrespective of the Ca/S ratio, the retention of As in bed material is larger than that in fly ash, whereas Se poses a converse tendency that its retention in bed material is very minor and even negligible in comparison to that in its fly ash. It suggests a higher vaporization propensity of Se than that of As under the same combustion conditions, which was consistent with the prediction of thermodynamic equilibrium calculation using FactSage.

As shown in Fig.4, increase in Ca/S from 0 (combustion of raw coal) to 10, the overall retention of As (bed material plus fly ash) increased from 0.029 to 0.078 mg/g-coal. Similarity, under the identical conditions the retention of Se increased from 0.00052 to 0.0018

mg/g-coal. It is a clearly sign that increase in Ca content in coal is favorable for improving the capture capacity of fly ash to As and Se vapors and hence reduces their emission into ambient.
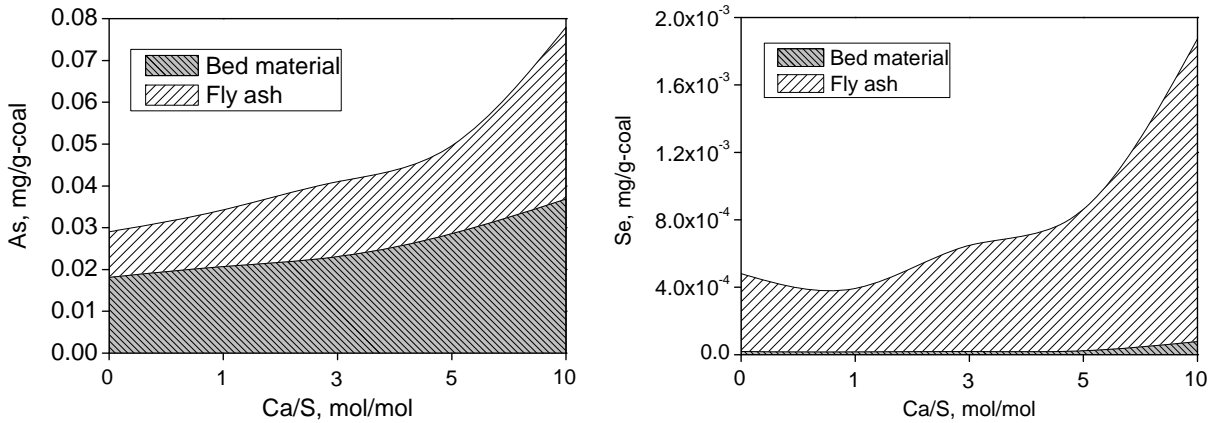

Figure 4. The retention of As and Se during combustion.

At%	A	B
O	27.1	33.1
Al	29.6	2.7
Si	40.6	5.5
S	0.7	9.3
Ca	1.4	48.5
Fe	0.6	1.0
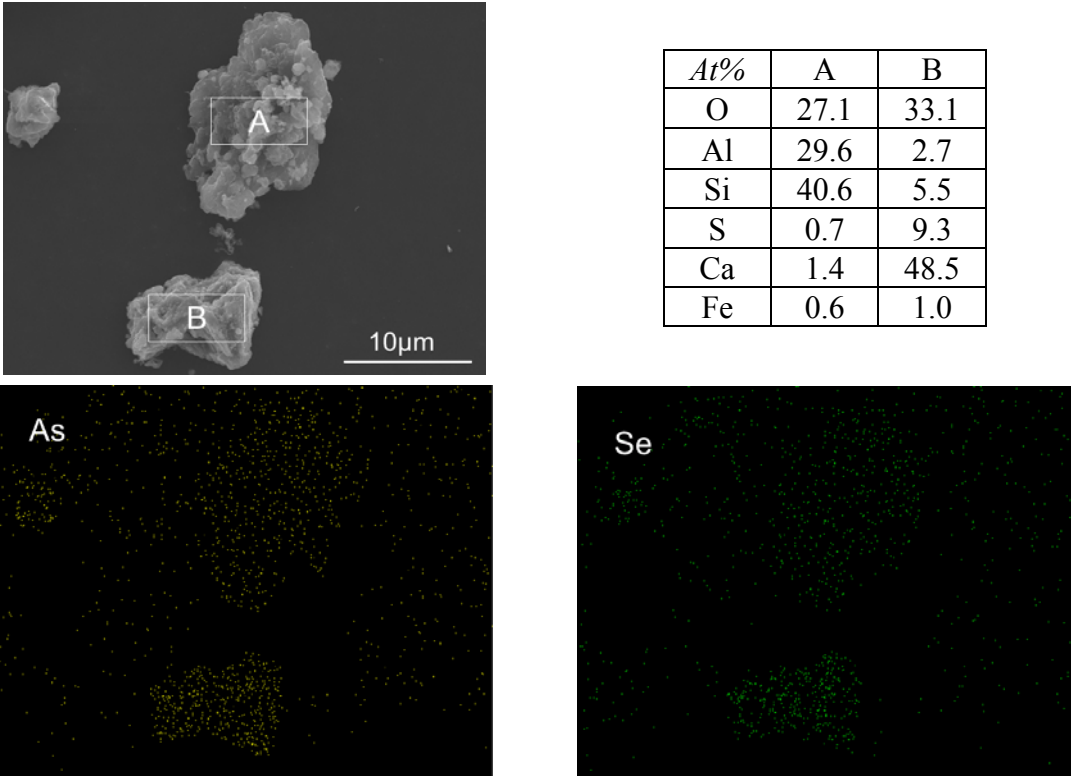
Figure 5. SEM picture and EDX mapping of As and Se in fly ash collected from coal combustion with Ca/S =1.
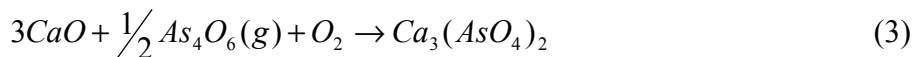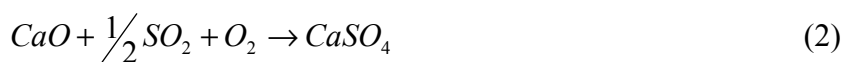
Fig.5 demonstrates the EDX mapping of fly ash particle, in which two particles marked A and B with quite different chemical composition are shown. As can be seen, As and Se are enriched in the particle B, in which Ca content is around 48% according to EDX analysis. In contrast, their abundance in particle A, dominated by Si and Al, is lower through the comparison of the characteristic signal, suggesting a chemical reactions of these two metals with Ca triggered during coal combustion. Regardless of the species of As and Se in coal, under coal combustion flame conditions they would be rapidly vaporized and readily oxidized

to $As_2O_3(g)$ and $SeO_2(g)$, which were subsequently subjected to the interaction with calcium compounds in fly ash to form stable compounds in post-combustion zone.
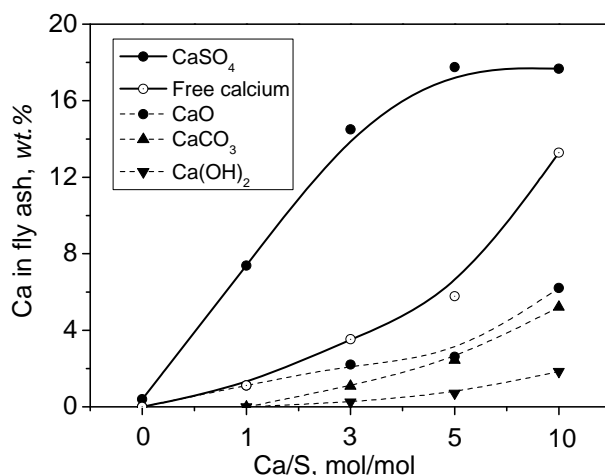
Figure 6. Quantitative analysis of Ca-compounds in fly ash.
Free calcium, $wt\% = CaO, wt\% + CaCO_3, wt\% + Ca(OH)_2, wt\%$

Fig. 6 shows the partitioning of major Ca-bearing compounds in fly ash collected from coal combustion with different Ca/S. These results are obtained from the quantitative analysis of their XRD charts. As can be seen, $CaSO_4$ was the solely detectable crystalline species in fly ash on the combustion of raw coal, due to the sulfation via reaction (2). With the increase in Ca/S ratio, apart from $CaSO_4$, CaO, $CaCO_3$ and minor fraction of $Ca(OH)_2$ were detected and their proportion was stably increased. The compounds including $Ca(OH)_2$ and $CaCO_3$ likely formed through the reaction of CaO with steam and CO_2 respectively during ash collection stage. Accordingly, the free calcium (CaO) at high temperature can be defined as the total amounts of CaO, $CaCO_3$ and $Ca(OH)_2$. As the Ca/S of 5, $CaSO_4$ fraction shows an initial increase and however was leveled off with the Ca/S further increasing from 5 onwards. It reflects that SO_2 was nearly entirely captured by CaO under the condition of Ca/S=5 during coal combustion, which was supported by the near zero SO_2 emission monitored using gas analyzer. Free calcium in fly ash shows a sustained growth with the increase of Ca/S. Through comparing Fig.4 and Fig.6, a similar variation trend between As/Se and free calcium in fly ash was observed, indicative of a profound influence of CaO rather than $CaSO_4$ on the capture of As/Se vapors. Otherwise the retention of As and Se should be constant as the Ca/S larger than 5. The reactions between CaO and gaseous As_4O_6/SeO_2 can be depicted using the following equations (3) and (4) [21].

$$CaO + \frac{1}{2}SO_2 + O_2 \rightarrow CaSO_4 \qquad (2)$$

$$3CaO + \frac{1}{2}As_4O_6(g) + O_2 \rightarrow Ca_3(AsO_4)_2 \qquad (3)$$

$$CaO + SeO_2(g) \rightarrow CaSeO_3 \qquad (4)$$

In terms of the above mechanisms, it is undoubted that the competition between reaction (2) and reactions (3) and (4) affects the capture of CaO in fly ash on the As/Se vapors. Although $Ca_3(AsO_4)_2$, once formed, is a stable compound at the temperature up to 1400°C [8], its formation rate is slower than that of the sulfation of CaO under the same conditions over a temperature range of 600-1000°C [10]. Consequently, $CaSO_4$ are preferentially formed and in turn lead to extensive pore plugging/blocking of the active site of CaO and rendered the

reaction with gaseous As. With respect to Se, it has been found that when the temperature is below 740°C the reaction rate of Se with CaO is bigger than S, but dropped sharply above this temperature due to the decomposition of CaSeO$_3$ at higher temperatures [22]. In case the effects of SO$_2$ was compensated by the addition of enough CaO, the retention of As and Se would be improved obviously. This presumption was evidenced by the experimental observation that the retention of As and Se shows a rapid raise as the Ca/S shift from 5 to 10 as shown in Fig.4.

3.4 Leaching behavior of As and Se in fly ash

According to above results, the retention of As and Se in fly ash during coal combustion was improved via adding the additive of Ca(OH)$_2$. The subsequent treatment of the resulting fly ash through landfilling will cause secondary pollution due to the high concentration of As and Se and their mobility. Clarifying the leach behavior of As and Se in fly ash generated from the combustion of coal with Ca(OH)$_2$ additive becomes very important.
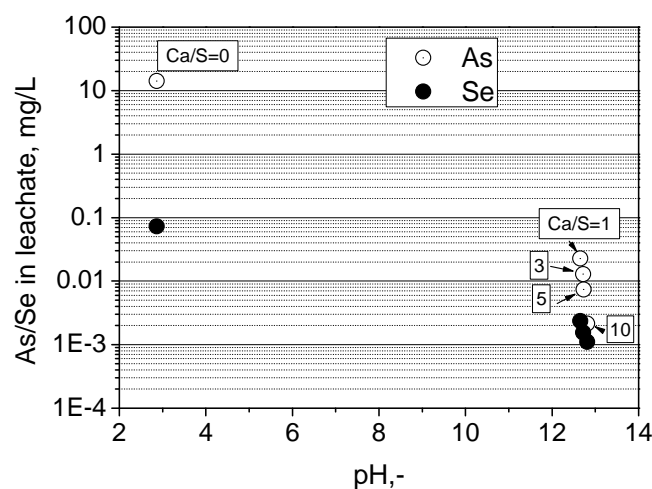

Figure 7. As and Se concentration in leachate as a function of pH.

Fig.7 shows the leaching of As and Se from fly ash as a function of the final pH value of the leachate. As can been seen, the leachablilty of both As and Se is largely dependent on the pH of leachate at a wide pH range. Arsenic concentration of 14.2 mg/L with the pH value of 2.86 (Ca/S=0) decreased to 0.023 mg/L with the pH of 12.63 (Ca/S=1) while selenium concentration decreased from 0.073 to 0.0024 mg/L. However, at high pH range the decrease of As leaching is independent on pH as shown by experimental data (Ca/S of 1-10) in Fig.7, indicating the influence of other factors on the As leaching, which will be discussed later.

The thermodynamic equilibrium prediction of As and Se distribution in solution was demonstrated in Fig .8. Clearly, it can be observed that the variation trend of As concentration against the pH of leachate was consistent with the experimental results. Regarding the concentration of As in solution, the As in solution determined experimentally are far lower than that from prediction. For instance, at the pH value of 2.86, the As concentration of 14.2 mg/L was achieved, compared to about 22 mg/L as predicted. A plausible explanation is the kinetic control during leaching test due to a short leaching duration tested here.
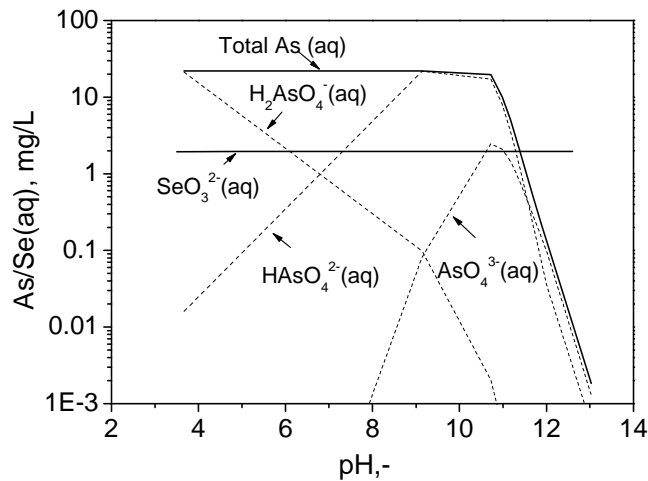
Figure 8. The prediction of As species distribution in solution.

The prediction of As species in solution shift with pH value is also shown in Fig.8 with dot line. Three types of As species, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}, in turn appeared along with the increase of pH value, which is consistent with the fact that the arsenic acid possesses three acidity constants of 2.26, 6.76 and 11.29, respectively. As the pH value above 11, AsO_4^{3-} was the dominating species, which can form less-soluble compounds or precipitates with Ca [13]. The prediction for selenium shows the sole species of SeO_3^{2-} in solution over the wide range of pH from 3 to 13. This results are difference from the experimental observation that the leaching of Se decreased drastically at high pH value (see Fig.7), indicating the negligible effect of reaction between SeO_3^{2-} and Ca^{2+} in solution. The leaching behavior of Se is likely attributed to the surface reaction of the hydrated mineral phase, for instance ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), formed in water under alkaline condition, can trap oxyanionic species including selenite [14].
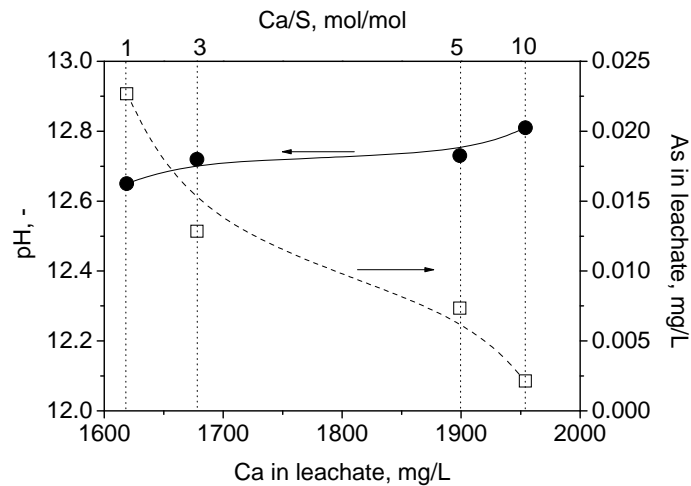

Figure 9. Relationship among Ca leaching, As leaching and pH under alkaline condition.

As mentioned before, apart from the effect of pH, arsenic leaching should be affected by other factors under the condition of Ca/S of 1-10. Fig.9 demonstrates a relationship among Ca leaching, As leaching and pH of leachate. It indicates that the largely decrease of As leaching under alkaline condition was linked with the increase of Ca in leachate. Such an observation is in agreement with other reports [13]. The increase of Ca with Ca/S of 1-10 in this experiment can be attributed to the higher content of free calcium in fly ash since the $Ca(OH)_2$, derived from the reaction of free CaO with water, possesses a higher solubility during leaching test than other species such as $CaSO_4$ and $CaCO_3$ [23].
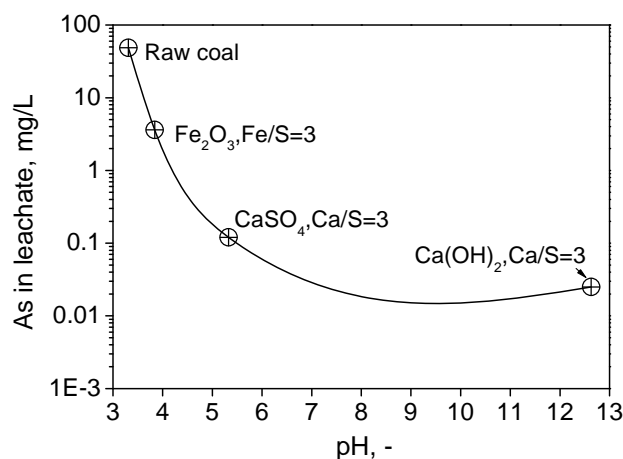
Figure 10. Comparison of different additives on the leaching of As.

To examine the role of different additives on the leaching behavior of As, apart from $Ca(OH)_2$, another two additives $CaSO_4$ and Fe_2O_3 were also added to coal A2 with the ratio of Ca(Fe)/S of 3. Regardless the type of additives, the leaching of As decreased obviously compared to that of raw coal fly ash, as shown in Fig.10. Regarding the role of Fe_2O_3, the final pH values was observed as about 3.8, indicative of an acidic characteristic of the resulting fly ash under this condition. However, no solid phase of As compounds could be formed in solution, as predicted by FactSage. This phenomenon can be explained by the sorption of As on iron oxide/hydroxide in solution, which has been suggested as a possible process controlling the leaching of As from acid fly ash [24]. On the other hand, in contrast, the addition of $Ca(OH)_2$ with Ca/S of 3 results in the highest pH of leachate among three additives and therefore caused the lowest As leaching, followed by an ascending sequence of $CaSO_4$ and Fe_2O_3, indicating the more profound impact of Ca compounds especially for free CaO in fly ash on the leaching of As.
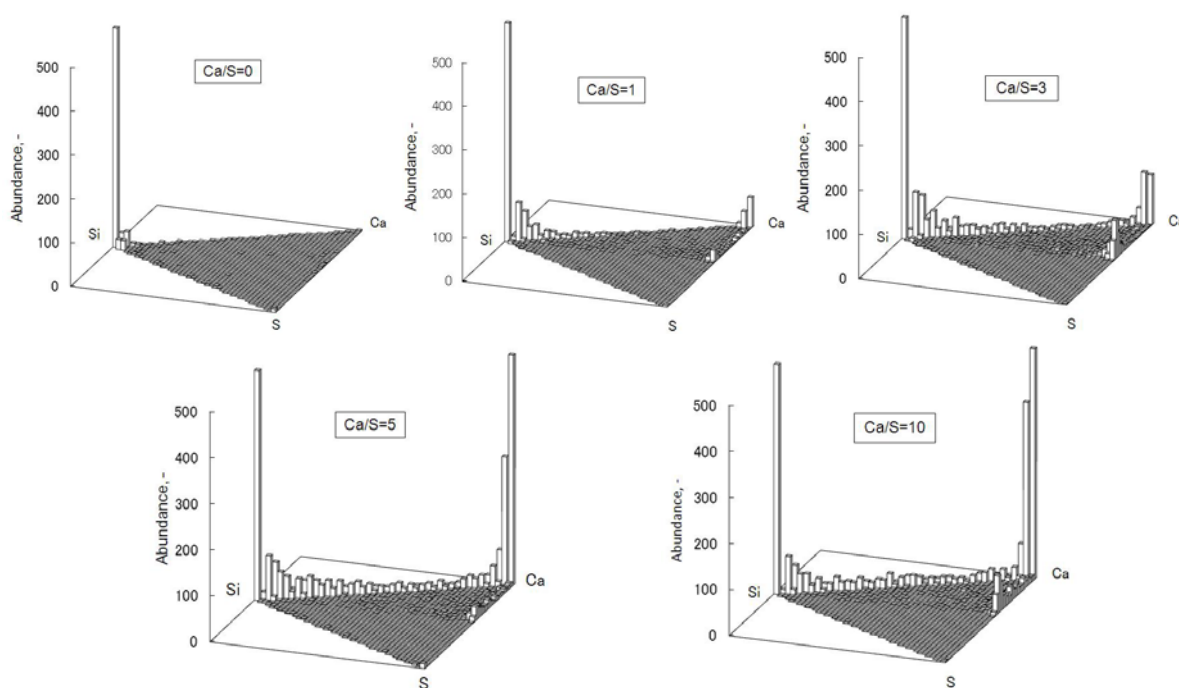
Figure 11. Ternary diagram for Ca-Si-S associate in fly ash collected from the combustion of coal with addition of $Ca(OH)_2$.

In addition to XRD measurement, CCSEM characterization of individual ash particles also proved the variation of free CaO in fly ash with and without the addition of $Ca(OH)_2$. As indicated in Fig.11, in the fly ash derived from raw coal combustion, Ca was mainly associated with sulfur and Si, less of free Ca was observed in the close to Ca corner. These are different from that observed for ash derived from coal combustion with addition of $Ca(OH)_2$. Apart from abundant Ca-S-Si association, a larger quantity of free Ca in the Ca corner was formed and its abundance was increased continuously with increase of Ca/S, which caused the fly ash properties to be shifted from acidic into basic and inhibited the mobilisation of As and Se through the formation of insoluble precipitates.

4. Conclusions

The effect of calcium additive on the retention of As and Se during fluidized bed coal combustion and their leach behavior in fly ash was experimental investigated. The following conclusions are obtained:

1. Adding $Ca(OH)_2$ during coal combustion facilitated the retention of As and Se in solid ash due to the possible gas-solid reactions with free calcium. This reaction was retarded by a competitive reaction of CaO with SO_2.

2. The leaching of As and Se from the fly ash was reduced with $Ca(OH)_2$ addition during coal combustion. Apart from the effect of pH, Ca concentration in leachate under alkaline condition also can reduce As leaching.

3. The reduction of As leaching from fly ash with adding different additives was observed as a descending sequence of $Ca(OH)_2 > CaSO_4 > Fe_2O_3$.

References

[1] Jankowshi, J., Ward, C. R., French, D., Groves, S., "Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems", *Fuel* 85: 243-256 (2006)

[2] Saikia, N., Kato, S., Kojima, T., "Composition and leaching behaviours of combustion residues", *Fuel* 85: 264-271(2006)

[3] López-Antón, M. A., Díaz-Somoano, M., Fierro, J. L. G., Martínez-Tarazona, M. R., "Retention of arsenic and selenium compounds present in coal combustion and gasification flue gases using activated carbon", *Fuel Proc. Technol.* 88: 799-805 (2007)

[4] Yudovich, Ya. E., Ketris, M. P., "Arsenic in coal: A review", *Int. J. Coal Geol.* 61: 141-196 (2005)

[5] Yudovich,Ya. E., Ketris, M. P., "Selenium in coal: A review", *Int. J. Coal Geol.* 67: 112-126 (2006)

[6] Zielinski, R.A., Foster, A. L., Meeker, G. P., Brownfield, I. K., "Mode of occurrence of arsenic in feed coal and its derivative fly ash, Black Warrior Basin, Alabama", *Fuel* 86: 560-572 (2007)

[7] Xu, M., Yan, R., Zheng, C., Qiao, Y., Han, J., Sheng, C., "Status of trace element emission in a coal combustion process: a review", *Fuel Proc. Technol.* 85: 215-237 (2003)

[8] Mahuli, S., Agnihotri, R., Chauk, S., Ghosh-Dastidar, A., Fan, L.-S., "Mechanism of arsenic sorption by hydrated lime", *Environ. Sci. Technol.* 31: 3226-3231 (1997)

[9] Ghosh-Dastidar, A., Mahuli, S., Agnihotri, R., Fan, L.-S., "Selenium capture using sorbent powers: Mechanism of sorption by hydrated lime", *Environ. Sci. Technol.* 30: 447-452

(1996)

[10] Sterling, R. O., Helble, J. J., "Reaction of arsenic vapor species with fly ash compounds: kinetics and speciation of the reaction with calcium silicates" *Chemosphere* 51: 1111-1119 (2003).

[11] Li, Y., Tong, H., Zhou, Y., Li, Y., Xu, X., "Simultaneous removal of SO_2 and trace As_2O_3 from flue gas: mechanism, kinetics study, and effect of main gases on arsenic capture", *Environ. Sci. Technol.* 41: 2894-2900 (2007)

[12] Jegadeesan, G., Al-Abed, S. R., Pinto, P., "Influence of trace metal distribution on its leachability from coal fly ash", *Fuel* 87: 1887-1893 (2008)

[13] Wang, T., Wang, J., Tang, Y., Shi, H., Ladwig, K., "Leaching characteristic of arsenic and selenium from coal fly ash: Role of calcium", *Energy Fuels* 23: 2959-2966 (2009)

[14] Iwashita, A., Sakaguchi, Y., Nakajima, T., Takanashi, H., Ohki, A., Kambara, S., "Leaching characteristics of boron and selenium for various coal fly ash", *Fuel* 84: 479-485 (2005)

[15] Zhang, L., Jiao, F., Binner, E., Bhattacharya, S.,Ninomiya, Y., Li, C-Z., " Experimental investigation of the combustion of bituminous coal in air and O2/CO2 mixtures:2. Variation of the transformation behaviour of mineral matter with bulk gas composition", *Fuel* 90: 1361-1369 (2011)

[16] Huggins, F. E., Huffman, G. P., "Modes of occureence of trace elements in coal from XAFS spectroscopy", *Int. J. Coal Geol.* 32: 31-53 (1996)

[17] Shah, P., Strezov, V. Stevanov, C., Nelson, P. F., "Speciation of arsenic and selenium in coal combustion products", *Energy Fuels* 21:506-512 (2007)

[18] Huggins, F. E., Shah, P., Zhao, J., Lu, F., Huffman, G. P., "Nondestructive determination of trace element speciation in coal and ash by XAFS spectroscopy", *Energy Fuels* 7: 482-489 (1993)

[19] Senior, C. L., Lignell, D. O., Sarofim, A. F., Mehta, A., "Modeling arsenic partitioning in coal- fired power plant", *Combustion and Flame* 147: 209-221 (2006)

[20] Zhang, Y., Liu, G., Chou, C-L., Wang, L., Kang, Y., "Sequential solvent extraction for the modes of occurrence of selenium in coals of different ranks from the Huaibei coalfield, China", *Geochemical Transactions*, doi: 10.1186/1467-4866-8-14 (2007)

[21] Shah, P., Strezov, V., Prince, K., Nelson, P. F., "Speciation of As, Cr, Se and Hg under coal fired power station conditions", *Fuel* 87: 1859-1869 (2008)

[22] Li, Y., Tong, H., Zhou, Y., Wang, S., Xu, X., "Simultaneous removal of SO_2 and trace SeO_2 from flue gas: Effect of SO_2 on selenium capture and kinetics study", *Environ. Sci. Technol.* 40: 7919-7924 (2006)

[23] Khodadoust, A. P., Naithani, P., Theis, T. T.,Murarka, I. P., " Leaching characteristics of arsenic from aged alkaline coal fly ash using colum and sequential batch leaching", *Ind. Eng. Chem. Res.* 50: 2204-2213 (2011)

[24] Vanderhoek, E., Comans, R. J., "Modeling arsenic and selenium leaching from acidic fly ash by sorption on iron(hydr)oxide in the fly ash matrix", *Environ. Sci. Technol.* 30: 517-5234 (1996)