Determination of As, Sb and Se Speciation in Fly-Ash Leachates

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DETERMINATION OF As, Sb AND Se SPECIATION IN FLY-ASH LEACHATES

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Several studies have been carried out to determine the speciation of As and Se in fly ashes in order to understand the leaching behaviour of these elements and have reported widely varying results. Many of these studies make use of pH-selective hydride generation with sodium tetrahydroborate to determine the speciation of As. We found that these methods gave unreliable results for the speciation in fly-ash leachates. In this study the valency states of As, Sb and Se are determined by speciation methods which were specifically tested for fly-ash leachates. Coprecipitation with dibenzyldithiocarbamate appeared to be a good method to determine As(III) and Sb(III) in fly-ash leachates. It was possible to obtain the total leached amount of As and Sb by a one-step hydride generation method. Precipitation of Se(IV) on activated carbon appeared to be the most adequate of the methods tested in this study for Se. Only minor amounts of the more toxic and mobile oxyanions of As(III), Sb(III) and Se(VI) were leached from the five fly ashes investigated in this study.

KEY WORDS: Speciation, As, Se, Sb, fly ash, valency state, leaching

INTRODUCTION

Leaching of oxyanions from fly ash in landfills or after reuse in construction materials is of environmental concern[1]. As, Sb and Se can appear in the environment in a number of valency states, i.e. As as As(V), As(III), As(0) and As(-III); Sb as Sb(V), Sb(III), Sb(0), and Sb(-III); and Se as Se(VI), Se(IV), Se(0), and Se(-II). In oxic aqueous systems As, Sb and Se appear mostly as oxyanions[2]. The valency state is an important factor for the behaviour of the elements in the environment. For example, the toxicity of As(III)[3] and Sb(III)[4] is higher than that of their pentavalent species. In addition to other parameters, the valency state also determines the sorption behaviour and, hence, the mobility in the aquatic environment. Dependency on valency state has also been shown for the sorption of As(III) and As(V) on amorphous iron (hydr)oxide[5] and for the sorption of Se(IV) and Se(VI) on goethite[6] and amorphous iron (hydr)oxide[7,8].

This study was performed in the framework of a larger programme in which the leaching of oxyanions from fly ash is investigated. We have shown that leaching of As and Se from fly ash is sorption-controlled[9]. Therefore, it is important to know the

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valency state of the oxyanions during leaching. There have been a number of studies in which the speciation of As, Sb and Se in fly ashes has been determined. A review is given in Table 1.

Table 1 shows that there is a great discrepancy in the speciation results for both As and Se. This discrepancy may be attributed to the use of different fly ashes and leaching methods (leaching medium, leaching time, liquid/solid ratio, temperature and,

Table 1 Speciation of As, Sb and Se in fly ash and fly-ash leachates.

Ref.	Fly ash (FA)	Leaching method*	Speciation method	Speciation results	Percentage leached
10	oil ash	none, solid state speciation	EXAFS and XANES	mainly As(V)	–
11	coal FA > 3 y old	pH 3,7,11,50 g/l leaching over time	HG-AAS, SnCl$_2$ As(III)/As(T)	50% As(III) conc As(III) 749 µg/l	–
12	coal FA > 1 y old	pH 10.8, > 1 g/ml serial batch leaching	HPLC-GFAAS, DMAA, MMAA, As(V), As(III), rec 60%	only As(V), other species ND	1% As(T)
13	coal FA	in seawater, pH 8–10, 1–1000 g/l, leaching over time	HG-NAA, NaBH$_4$ Sb(III)/Sb(V) As(III)/As(V)	As(III) 40–70% Sb(III) 20–80% < 70 µg/l As(III)	0.05–18% As(T), 0.6–15% Sb(T)
14	coal FA kept under air	0.2 M NaOH, 40 g/l, several days	HG heterpoly blue NaBH$_4$, rec As(III) 60%	50% As(III) < 15 µg/l	–
15	coal FA oil FA	1 M Na citrate pH 5, 5–25 g/l, 16 h	HG-AAS, NaBH$_4$ As(III)/As(V) rec As(III) 96%	< 2% As(III) < 150 µg/l As(III)	80–90% As(T)
16	coal FA fresh	in seawater, pH 9.1–8.6, 20 g/l, analyzed instantaneously	HG-AAS NaBH$_4$ As(III)/As(T)	< 33% As(III) 45 µg/l As(III)	8–16% As(T)
17	coal FA fresh and old	pH 3–12, 20 g/l leaching over time	HG-AAS NaBH$_4$ As(III)/As(T)	As(III) < 22 µg/l (fresh fly ash) As(III) 350 µg/l	1–15% As(T)
18	FA SO$_2$- removed: 1) Ca-based 2) Na$_2$CO$_3$	0.5 M NaOH, 1 g/ml, 4 h	ion chromatography > 0.05 mg/l Se(IV)/Se(VI)	Se(T) 7–11 mg/kg 1) all Se(IV) 2) all Se(VI)	–
19	garbage incinerator residue e.g. FA	0.1 M HCl, Se(IV + VI) 3 M acid-70°C Se(IV + VI + 0), 2–4 g/l	HC-AAS Se(IV) Se(VI + IV) after 4 M HCl 110°C standard addition	no Se(0) Se(VI) < 3 µg/l	
12	1) coal FA 2) refuse FA > 1 y old	pH 10.8, > 1 g/ml serial batch leaching	fluorimetry Se(IV) DAN-extract, Se(VI + IV) after 120°C HCl	1) Se(VI) ND 2) Se(IV)/Se(VI) 0.19/0.05 µg/g	30% Se(T) 6% Se(T)

Continued

Table 1 Continued.

Ref.	Fly ash (FA)	Leaching method*	Speciation method	Speciation results	Bercentage leached
20	5 FA	Se(IV + VI + 0) in 70% HClO$_4$, Se(IV + VI) in water, 2 g/l	HG-AAS Se(IV) Se(VI + IV) after 12 M HCl	no Se(VI) ≈ 70% Se(IV) ≈ 30% Se(0)	70% Se(T)
113	1 coal FA	in seawater, pH 8–10, 1–1000 g/l, leaching over time	NAA Se(IV) reduction ascorbic acid Se(VI + IV) after 6 M HCl 100°C	all Se(IV)	10–70% Se(T)

*leaching medium, pH, solid/solution ratio, leaching time and temperature
EXAFS = Extended X-ray Adsorption Fine Structure, XANES = X-ray Absorption Near Edge Structure, HG = hydride generation, AAS = atomic adsorption spectroscopy, HPLC = High Performance Liquid Chromatography, GFAAS = Graphite Furnace-AAS, NAA = Neutron Activation Analysis, rec = recovery, ND = not detectable, DMAA = dimethylarsonic acid, MMAA= monomethylarsonic acid and DAN = 2,3 diaminonaphtalene.

consequently, in the amount leached). Another factor that can contribute to the discrepancy is the use of different methods for the determination of the speciation. For instance, Wadge and Hutton[12] and Hansen et al.[14] noted recovery problems for the determination of As(III). Furthermore, storage of the fly ash and of the leachate may alter the elemental speciation; for example, As(III) on the solid may be oxidized to As(V) during storage.[17]

The literature, summarized in Table 1, does not allow general conclusions to be drawn concerning the speciation of As, Se and Sb in fly ash. The intention of this study was to measure the speciation of As, Se and Sb in leachates of a number of distinctly different fly-ash samples, using methods which are validated for each of these three elements in the leachates. We also studied the influence of storage conditions of the fly ash and of the leachates on the measured speciation. As and Se leaching[9] and valency state[2] are strongly dependent on the pH. The pH can be imposed by the fly ash but also by external environmental conditions. Therefore, the fly ashes used in this study varied in their 'natural' pH values and were leached within a pH-range of pH 4 to 12.

METHODS

Fly ashes

The alkaline fly ash used in this study was obtained from the power plant *Stigsnæsværket* in Denmark. This material was also used in two earlier studies[9,21]. The acidic fly ash, the neutral fly ash and the fresh alkaline fly ash originated from the power plant *Amercentrale* in The Netherlands. The acidic fly ash was also used in an earlier study[9]. The neutral fly ash had already been used by Van der Sloot et al.[21]. The brown coal fly ash originated from a fluidized bed installation in Homberg, Germany. The fly ashes were chosen for their different pH (acidic, neutral and alkaline), storage time (varying between 30 days and 8 years) and storage conditions (air or N$_2$). Table 2 shows the

Table 2 Composition of the fly ashes.

	Acidic FA	Neutral FA	Alkaline FA	Alkaline (Fresh) FA	Brown coal FA
pH	4.24	8.9	11.9	12.1	11.5
Storage:	1 y, air	8 y, air	5 y, air	30 d, N_2	30 d, N_2
As	9.1 µg/g	55.8 µg/g	23.0 µg/g	25 µg/g	8.0 µg/g
Sb	3.44 µg/g	16.6 µg/g	3.6 µg/g	3.5 µg/g	1.3 µg/g
Se	3.7 µg/g	41.3 µg/g	7.9 µg/g	13.8 µg/g	14.7 µg/g
Si	31.8%	30.7%	26.2%	25.1%	6.25%
Al	9.9%	10.2%	12%	12.5%	3.28%
Fe	3.0%	3.1%	3.7%	3.16%	6.38%
Ca	0.2%	1.16%	2.2%	2.58%	31.3%
Mg	0.11%	0.5%	0.83%	0.61%	5.2%
S	0.08%	–	14%	0.15%	4.24%

'natural' pH, storage time and conditions and composition of the fly ashes as determined with ICP-AES and hydride generation (HG) -AAS.

Leaching

Suspensions of 96 g/l fly ash[9] in nanopure de-ionized water were prepared in acid-cleaned pyrex or teflon (PFA) vessels and leached at three different pH values of approx. 4, 7, and 12. Two of these pH values were set by adding acid or base; the third value was the 'natural' pH of the fly-ash suspension, which was obtained without any additions. The pH of the set values was kept constant within 0.2 pH unit by a pH-stat, that added 1 M NaOH or 1 M HCl when necessary. The solutions were continuously stirred at room temperature by a magnetic stirrer and after 24 h samples were taken and filtered through 0.45 µm membrane filters (Schleicher and Schüll, cellulose nitrate). During leaching the vessels were open to the atmosphere in order to enable O_2 and CO_2 to react with the fly ash, as would occur under 'natural' circumstances. The filtrate was acidified (pH < 2) with supra-pure HCl (Merck). Preliminary experiments indicated no significant changes in either total concentrations or valency state of As, Sb and Se in the leachates between 90 min and 24 h of leaching.

Testing of speciation methods

Several methods are available to determine the speciation of As, Se and Sb. We assume that no organic species of the oxyanions are present in fly ash because of the high temperatures at which coal combustion takes place. This is confirmed by the observations of Wadge and Hutton[12] who have been unable to detect organic species of As in fly ash leachates. Therefore, we have considered only methods for analysis of the non-volatile inorganic species of As, Se and Sb in solution. Hydride generation has generally been applied for this purpose (Table 1). In this study a hydride generation method, a coprecipitation method and a precipitation method have been tested and are described below.

Hydride generation method

The speciation method for As, Sb and Se of Hoede *et al.*[22], developed for seawater samples, was tested for fly-ash leachates. This method is based on a reaction of As, Se and Sb ions with sodium tetrahydroborate ($NaBH_4$) to form volatile hydrides. As(V) and Sb(V) species react only at low pH values (pH < 1) whereas the trivalent species also react at higher pH values (pH < 5)[23]. Volatile hydrides can only be formed from Se(IV) and, therefore, the speciation of Se can only be obtained after reducing Se(VI) to Se(IV) in a separate sample and measuring the total Se concentration[24].

To determine the speciation of As and Sb, the procedure was divided into two steps[22]

1. *Determination of As(III) and Sb(III)*   20–30 ml leachate solution was acidified with HCl to pH 2. 10% (w/v) $NaBH_4$ was added slowly to the leachate at 1 ml/min over a 3-min period to form the hydrides. Because of the instability of the $NaBH_4$ solution[22] this solution was aged for at least 0.5 h prior to its addition. The hydrides were continuously purged from the leachate by a carrier gas (N_2, 750 ml/min), followed by trapping of the water (–20°C), and subsequent collection of the hydrides on a carbon absorber. The carbon absorber was changed to proceed with step 2.

2. *Determination of As(V) and Sb(V)*   The solution was further acidified with concentrated HCl to obtain a concentration of 4 M HCl. Five ml of a mixture of 0.6 M potassium iodide/10% (w/v) ascorbic acid were also injected. Subsequently, $NaBH_4$ was added to the leachate for 20 min at a flow rate of 1 ml/min. After 10 min, another 5 ml of the 0.6 M potassium iodide/10% (w/v) ascorbic acid mixture was injected. The hydrides were collected on the fresh carbon absorber as described under step 1.

To determine Se(IV), the same procedure as in step 2 was followed except for the addition of the potassium iodide/ascorbic acid mixture.

Coprecipitation

Another method to determine As(III) and Sb(III) is the coprecipitation method of Van Elteren *et al.*[25]. This method is based on coprecipitation of As(III) and Sb(III) with dibenzyldithiocarbamate (DBDTC). DBDTC is known to react with a number of metals and metalloids[26]. The coprecipitation method has been developed for sea and surface waters[25]. However, in fly-ash leachates high concentrations of metals and metalloids are present and therefore a higher concentration of DBDTC is needed than in the original method.

After optimization for fly ash leachates, the final procedure was as follows:

1. *Determination of As(III) and Sb(III)*   30 ml leachate were acidified to pH 2 (HCl) and 1.5 ml 1% DBDTC (1 g in 100 ml methanol) was added. After 10 min the coprecipitate was collected on a 0.45 µm filter (Schleicher and Schüll, cellulose nitrate) and rinsed with 0.01 M HCl.

2. *Determination of As(V) and Sb(V)*   The As(V) and Sb(V) present in the filtrate were reduced to their trivalent species by reaction with 1 ml 20% (w/v) potassium iodide and 1 ml 25% (w/v) sodium thiosulphate for 20 min. Subsequently, the procedure for As(III) and Sb(III) was repeated.

It is also possible to determine Se(IV) in water by coprecipitation with DBDTC[27]. The difference with the above method is that the coprecipitate is collected on a 1 µm filter

immediately after adding the DBDTC; 100 mg of phenolphthalein may be added as a supplementary coprecipitant for stabilization of the Se(IV)-DBDTC complex.

Precipitation of Se(IV)

We also tested the method of Massee *et al.*[28] to determine Se(IV). In this method Se(IV) is reduced to Se(0) with ascorbic acid and adsorbed on activated carbon. After this method was optimized for fly ash leachates, the procedure was as follows.

1. *Determination of Se(IV)*   25 mg activated carbon and 2 ml ascorbic acid solution (10% w/v) were added to 30 ml fly ash leachate at pH < 2 (HCl). After 20 min the leachate was filtered through a 0.45 μm membrane filter (Schleicher and Schüll, cellulose nitrate) which was evenly covered with another 50 mg of activated carbon.

2. *Determination of total-Se*   Total Se was determined after reducing Se(VI) to Se(IV) in a separate sample: 20–30 ml fly ash leachate was acidified with concentrated HCl to obtain a concentration of 6 M HCl and was refluxed for 30 min. After reduction the above procedure for Se(IV) was applied except that 150 mg activated carbon and 3 ml ascorbic acid were added.

Radiotracers

Radiotracers were used to check the recovery of the speciation methods. Carrier-free ^{75}Se(IV), ^{75}Se(VI) and ^{125}Sb(V) were obtained from Amersham and ^{73}As(III) from Isotopen Dienst Benelux. ^{125}Sb(III) was obtained by reduction of ^{125}Sb(V) with ascorbic acid in 4 M HCl and ^{73}As(V) by oxidation of ^{73}As(III) with 25% H_2O_2 in 4 M HCl. The speciation of the radiotracers was checked by the speciation method of van Elteren *et al.*[25] and Massee *et al.*[28] in test solutions of 0.05 M $NaNO_3$, with and without added carrier.

The radiotracers were added individually to fly ash leachates and the speciation methods were carried out according to the procedures given above. The remaining radioactivity in the end product (on a filter or on a carbon absorber) was measured with a 3-inch NaI(Tl) well-type detector (LKB-wallac, 1282 Compugamma) relative to a standard containing 100% of the initially added radioactivity.

Recovery of the speciation methods

Table 3 shows the measured recoveries of different As, Sb and Se species. Clearly, the recoveries of both As(III) and As(V) using the hydride generation method are very low. Attempts to improve the recovery of As(III) in step 1 by changing the carrier gas flow rate or the amount of $NaBH_4$ were unsuccessful. Lowering leachate pH to values < 1 gave better recoveries. However, lowering pH did not only increase the recovery of As(III) in step 1, but also that of As(V), thus lowering the method's potential to measure the species separately. Quantitative recovery of both As(III) and As(V) can, however, be obtained by using step 2 direct.

A low recovery of As(III) has also been noted in similar studies with hydride generation of arsine (AsH_3) from fly ash leachates using sodium tetrahydroborate[12,14]. Only Silberman and Harris[15] found a recovery > 96% in 1 M sodium citrate leachates,

Table 3   Recovery of As, Sb and Se Species from fly-ash leachates.

	As(III)	As(V)	Sb(III)	Sb(V)	Se(IV)	Se(VI)
HG step 1	< 45%	< 5%	n.d.	n.d.	n.d.	n.d.
HG step 2	3 ± 1%	20 ± 6%	n.d.	n.d.	n.d.	n.d.
HG step 2 direct	**100 ± 2%**	**100 ± 4%**	**n.d.**	**100 ± 2%**	**< 5%**	**n.d.**
DBDTC coprecip. step 1	**95 ± 7%**	**0.3 ± 0.1%**	**91 ± 5%**	2 ± 1%	< 60%	n.d.
DBDTC coprecip. step 2	n.d.	90%	n.d.	< 1%	n.d.	n.d.
Precipitation on activated carbon, step 1	n.d.	n.d.	n.d.	n.d.	**100 ± 2%**	0.2 ± 0.2%
Precipitaton on activated carbon, step 2	n.d.	n.d.	n.d.	n.d.	**100 ± 1%**	**100 ± 4%**

HG = hydride generation; n.d. = not determined; methods used for final measurements are printed in bold.

although in one fly-ash leachate they also found a recovery of only 72%. An explanation for the low recovery may be the preferential reduction of transition metals and subsequent interaction of the metal precipitate with the arsine[29].

On the basis of the As results above and the fact that As(III) and Sb(III) show both a high recovery using the DBDTC coprecipitation method (see below), the hydride generation method was not further tested for Sb(III). Step 2 of this method was, however, tested for its recovery of Sb(V), which was 100 ± 2%. Although hydride generation appears to be not suitable for speciation measurements of As and Sb in fly-ash leachates, the direct use of step 2 can serve as a means to determine the total concentrations of As and Sb.

The recovery of Se(IV) from fly-ash leachate was < 5% when using the hydride generation method, even when helium was used as a carrier gas[24]. Hydride generation of Se(IV) is known for its inherent problems caused by the presence of oxygen[24] and, therefore, we did not attempt to further optimize this method.

The recovery of As(III) and Sb(III) from leachates of five fly ashes after coprecipitation with DBDTC was 95 ± 7% and 91 ± 5%, respectively. After reduction, the recovery from acidic fly-ash leachate was 90% for As(V) and < 1% for Sb(V). Probably the potassium iodide/sodium thiosulphate mixture is not strong enough to reduce Sb(V) to Sb(III). For Se(IV) the coprecipitation with DBDTC gave very low recoveries (< 60%). Therefore, this method is considered not suitable for the determination of Se(IV) and Sb(V) in fly-ash leachates.

Precipitation of Se(IV) from different fly-ash leachates on activated carbon using ascorbic acid gave recoveries of 100 ± 2%. The recovery of Se(VI) after reduction in 6 M HCl was 100 ± 4%.

Sample preservation

The speciation of As, Se and Sb in the samples may change during storage of the leachates. Turner[17] found that As(III) concentrations in filtered fly-ash leachates did not

alter for 33 d when frozen (dry ice) or kept at 4°C. Leachates with As(III) stored at 4°C in 0.1% (w/v) ascorbic acid were only stable for 48 h. De la Calle-Guntiñas et al.[30] found that Sb(III) in water did not oxidize when samples were stored at 0–4°C. When stored at 4°C in 1% (w/v) ascorbic acid, Sb(III) had decreased after 1 month and the solutions had turned yellow. Venghout and Agemian[31] found that Se(VI)/(IV) in water could be stored for 125 d at pH 1.5 in polyethylene containers at either 4°C or at room temperature.

We tested the storage of As(III/V), Sb(III/V) and Se(IV/VI) in acidic fly-ash leachates for 1 d in polyethylene containers, with and without ascorbic acid, and either at room temperature or at 4°C. We found that As(III) and Sb(III) were best preserved in 0.1% (w/v) ascorbic acid at 4°C. After 24 h, recoveries of 96% and 90%, respectively, were obtained, while without ascorbic acid these recoveries were 5% lower. As(V) and Sb(V) were not reduced in the presence of 0.1% (w/v) ascorbic acid. Apparently, sample storage in ascorbic acid only has a beneficial effect during short storage periods. We observed a lower recovery of Se(IV) (a loss of up to 30%) in ascorbic acid, probably as a result of the reduction of Se(IV) to Se(0). At 4°C and without addition of ascorbic acid, Se(IV) and Se(VI) could be preserved for 24 h (recoveries > 97%)

Final methods

After we leached the fly ashes, the acidified and filtered leachates were divided in four subsamples: one for As(III) and Sb(III) determination, one for total-As and total-Sb determination, one for Se(IV) determination and one for total-Se determination. All subsamples were preserved as described below. The analyses of As(III), Sb(III) and Se(IV) were performed within 1 day of sampling and the total concentrations were measured within 1 week.

Based on the testing and optimization of methods described in the previous section, the following approach was chosen for the determination of As, Sb and Se speciation in fly-ash leachates. As(III) and Sb(III) in the fly-ash leachates were determined using coprecipitation with DBDTC. We used step 2 of the hydride generation method for the determination of total-As and total-Sb concentrations. Se(IV) and total-Se were determined by the precipitation method with ascorbic acid. Leachate samples for Se(IV) determination were stored at 4°C and samples for As(III) and Sb(III) were preserved by addition of ascorbic acid (final concentration of 0.1%) and storage at 4°C.

The analyses of the filters and the carbon absorbers were performed with neutron activation analysis (NAA). The samples were packed in polyethylene containers. In order to correct for possible flux differences among the samples, iron flux monitors were applied. Irradiation of the As and Sb samples was carried out for 2 h at a neutron flux of 3×10^{11} cm^{-2}s^{-1} and of the Se samples for 6 h at a neutron flux of 4×10^{12} cm^{-2}s^{-1}. After approx. 3 days the As and Sb were counted for 2000 s on a Ge(Li) detector coupled to a multi-channel analyzer. After approx. 12 days the Se samples were counted for 4000 s on the same device. The cooling period of 3 or 12 days was selected on the basis of the background radiation of the samples and decay of the measured isotopes. More details are given in Van Elteren et al.[25], Van der Sloot et al.[24] and Saleh et al.[27]. Detection limits were approx. 1 and 0.5 µg/l for As and Sb, respectively, depending on the presence of Na which is largely responsible for the background in NAA. The detection limit for Se was approx. 2 µg/l.

All chemicals used were of analytical-reagent grade. The hydrochloric acid applied was suprapure (Merck). The activated carbon used as absorber and for the determination of Se was prepared according to Van der Sloot et al.[32], by carbonization of very pure PVC (polyvinylidene chloride) in a nitrogen atmosphere.

RESULTS AND DISCUSSION

In Table 4 the leaching results of As(III), As(V), Sb(III), Sb(V), Se(IV) and Se(VI) are presented for five fly ashes after 24 h of leaching. The percentages of these species in the leachates are presented in Figures 1, 2 and 3, respectively. In all fly-ash leachates, except for the fresh alkaline fly ash, the amounts of As(III) and Sb(III) are negligible. The highest amounts were found after leaching the fresh alkaline fly ash at acidic pH. Most of the Se leached from the coal fly ashes was Se(IV). There is a large variation in the Se(VI) concentrations because the differences between the concentrations of total-Se and Se(VI) were small relative to the analytical error. Se(VI) exceeded Se(IV) only in the low and neutral pH leachates of the acidic fly ash and in the leachates of the brown coal fly ash. Total-Se leached in these special cases was, however, lower than 50 µg/l. Also the relative amount leached was negligible (Figure 3). The highest concentration for all three oxyanions is leached from neutral fly ash in the order Se > As > Sb. The results shown in Figures 1–3 imply that Se is the most mobile of these oxyanions. Almost no As, Sb and Se were leached from brown coal ash.

As and Sb speciation

As(III) is expected to be leached better than As(V), because it is less strongly retained by geological materials[e.g. 5,33]. Therefore, if only a small percentage of As is leached as As(III), the relative amount of As(III) on the fly ash surface is likely to be small as well. Although little is known about the relative mobility of Sb(III) and Sb(V), the behaviour may be comparable with that of As[2].

Some authors[e.g. 34,35] have predicted that As in fresh fly ash is present as As(III). Those authors hypothesize that only oxides are formed during the burning of coal and that, theoretically, only As_2O_3 precipitates. These calculations, based on boiling and melting points, take into consideration that, during the burning of powder coal, temperatures can

Table 4 Speciation of As, Sb and Se in the leachate after 24 h at different pH-values. (µg/l, n = 2)

|	pH	As(III)	As(V)	Sb(III)	Sb(V)	Se(IV)	Se(VI)
Acidic	4.2	0.0 ± 0.2	1.0 ± 0.3	3.8 ± 4.6	3.7 ± 5.0	4.2 ± 3.4	5.8 ± 5.1
fly ash	7.2	0.0 ± 0.8	0.6 ± 1.2	4.7 ± 6.4	5.5 ± 6.7	16 ± 4	5.7 ± 5.5
	12.0	0.0 ± 0.2	365 ± 58	4.8 ± 5.6	40.4 ± 6.7	294 ± 16	3 ± 23
Neutral	4.0	0.0 ± 0.2	287 ± 6	6.4 ± 5.3	52.6 ± 6.7	394 ± 20	49 ± 31
fly ash	8.9	0.0 ± 0.3	133 ± 22	4.2 ± 5.0	82.0 ± 7.2	423 ± 22	662 ± 34
	12.0	0.0 ± 0.1	262 ± 24	0.6 ± 1.8	77.9 ± 4.7	2087 ± 107	197 ± 157
Alkaline	3.9	0.0 ± 0.2	557 ± 87	3.8 ± 4.7	15.1 ± 5.7	203 ± 11	18 ± 17
fly ash	7.0	0.0 ± 0.1	315 ± 23	2.7 ± 3.1	28.3 ± 5.0	234 ± 13	8 ± 19
	11.9	0.0 ± 0.4	5 ± 0	4.4 ± 5.2	7.6 ± 5.6	79 ± 6	11 ± 9
Fresh	4.1	17.6 ± 1.1	121 ± 23	3.0 ± 0.5	16.7 ± 12.2	588 ± 16	−2 ± 97
alkaline	7.4	11.1 ± 0.8	81 ± 35	3.2 ± 0.4	43.3 ± 15.9	481 ± 25	28 ± 28
fly ash	12.1	0.0 ± 0.0	1 ± 1	0.5 ± 0.0	1.0 ± 0.3	108 ± 3	49 ± 5
Brown	4.1	0.2 ± 0.4	0 ± 0.4	0.9 ± 0.5	0 ± 0.5	1.8 ± 0.0	21.0 ± 1.0
coal	7.2	0.1 ± 0.3	0 ± 0.3	1.1 ± 0.5	0 ± 0.5	2.2 ± 0.3	38.5 ± 1.3
fly ash	12.5	0.1 ± 0.2	0 ± 0.2	1.1 ± 0.6	0 ± 0.6	2.1 ± 0.1	19.8 ± 1.6
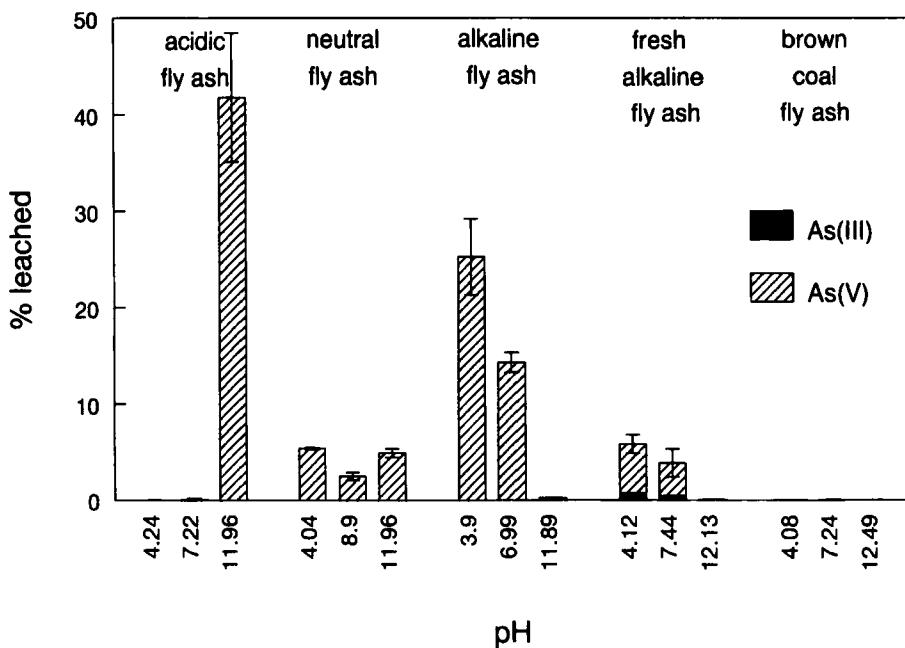
Figure 1 As(III) and As(V) leached from five different fly ash samples at acidic (pH ≈ 4), neutral (pH ≈ 7–9) and alkaline (pH ≈ 12) conditions. Percentages are relative to the total-As present in the ashes.
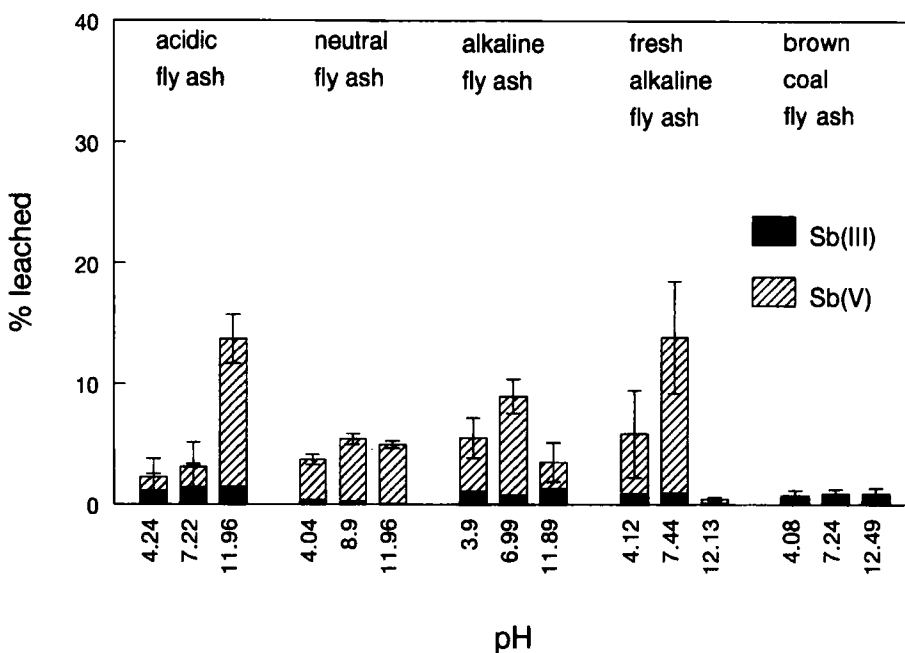
Figure 2 Sb(III) and Sb(V) leached from five different fly ash samples at acidic (pH ≈ 4), neutral (pH ≈ 7–9) and alkaline (pH ≈ 12) conditions. Percentages are relative to the total-Sb present in the ashes.
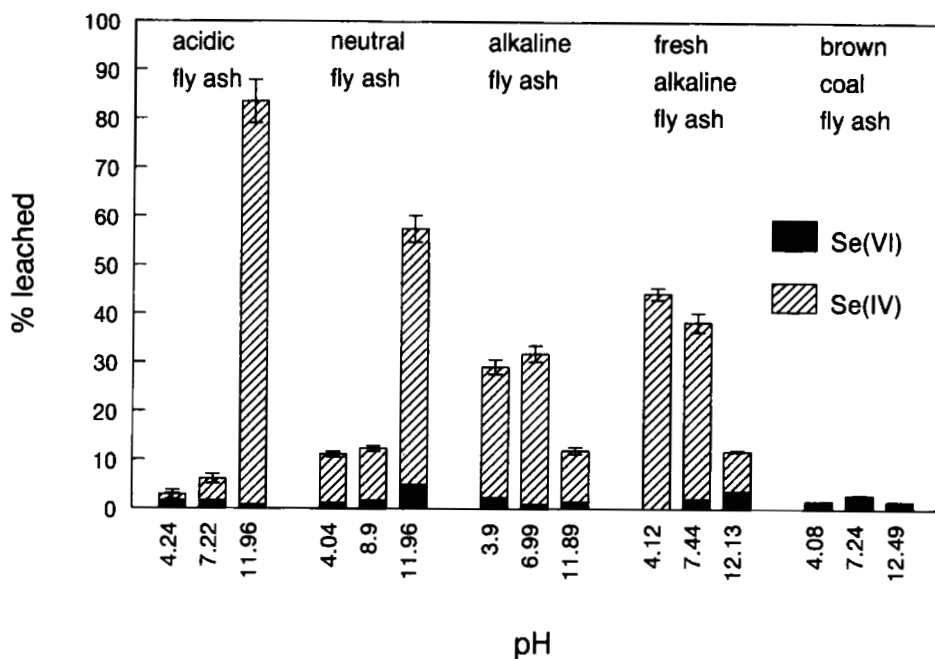
Figure 3 Se(VI) and Se(IV) leached from five different fly ash samples at acidic (pH $\approx$ 4), neutral (pH $\approx$ 7–9) and alkaline (pH $\approx$ 12) conditions. Percentages are relative to the total-Se present in the ashes.

rise to 1600°C and that the fly ash is precipitated on an electrostatic precipitator (ESP) at approx. 200°C[36]. However, considering these temperatures, metal arsenates can also precipitate[37]. The latter hypothesis is in agreement with the measurements of As in the gas stream before and after the ESP by Haynes *et al.*[38] and Meij[39], respectively. Both studies suggest that only small amounts of As_2O_3 are present on the solid surface. In addition to As, Haynes *et al.*[38] have measured also Sb and suggest the formation of metal antimonates.

Our results that As and Sb are leached mainly as As(V) and Sb(V) are consistent with the hypotheses of Haynes *et al.*[38] and Meij[39]. We have measured, however, minor amounts of As(III) and Sb(III) (Table 4) in the leachates of the fresh alkaline fly ash. These valency states were not measured in the other leachates. Possibly, minor amounts of As(III) and Sb(III) present in the fly ash are oxidized to the pentavalent states during storage. Turner[17] found high concentrations of As(III) only in leachate of a fresh fly ash. Therefore, the amount of As(III) and Sb(III) present in fly ash is likely to be small and is dependent on fly ash composition[39], age and storage conditions.

Se speciation

Thermodynamic calculations by Ericzon *et al.*[19] for the possible species precipitated on garbage incinerator residues indicate that in these systems (800–250°C) SeO_2 is the most stable species. However, according to these calculations, the formation of hexavalent Se remains possible.

We found that most of the Se in the fly-ash leachates was in the form of Se(IV). Selenate (Se(VI)) is less strongly retained on geological materials than selenite (Se(IV))[40] and is, therefore, expected to be more available for leaching. The small percentage of Se(VI) measured in the leachates suggests that a minor amount of hexavalent Se is present on the fly ash surface, in accordance with the calculations of Ericzon *et al.*[19] and the general findings summarized in Table 1.

Quin[20] and Ericzon *et al.*[19] applied extractions with strong acids to measure Se(0) in fly ash (Table 1). It is, however, likely that other mineral phases, e.g. iron oxides, dissolve from the fly ash matrix in these strong acids. Trace elements, such as Se, can be enclosed in those minerals.[41] Therefore, we believe that strong acid extractions cannot be used to obtain reliable measurements of Se(0) in fly ash.

In contrast with the other fly ashes, Se(VI) was the dominant species leached from the brown-coal fly ash. This difference in Se speciation may be related to the addition of calcium carbonate in the fluidized bed installation in which the brown coal was burned. Calcium carbonate is generally added to fluidized bed installations in order to bind SO_2[42]. This addition also explains the high Ca-content of this fly ash. Niss *et al.*[18] also found that only Se(VI) was leached from fly ash in cases where the combustion gas was treated with Na_2CO_3 to remove SO_2. The addition of carbonates during the burning process may, therefore, affect the speciation of Se on the fly ash.

CONCLUDING REMARKS

A review of the literature, summarized in Table 1, does not allow general conclusions to be drawn concerning the speciation of As, Sb and Se in fly ash.

In many studies a pH-selective hydride generation method with sodium tetrahydroborate was used to determine the speciation of As. We found that this method gives unreliable results for the speciation in fly-ash leachates, but that it can be used to obtain the total leached amount of As and Sb. DBDTC coprecipitation appears to be a good method to determine As(III) and Sb(III) in fly-ash leachates.

Precipitation on activated carbon was found to be a reliable method to quantitatively extract Se(IV) from fly-ash leachates. Se(VI) was determined by subtraction of Se(IV) from total-Se. Due to the low concentrations of Se(VI) the latter approach resulted, however, in a large analytical error.

The major oxyanionic species leached from fly ash are As(V), Sb(V) and Se(IV). Only minor amounts of the more toxic and mobile species As(III), Sb(III) and Se(VI) are leached. Fly ash composition, additions for flue-gas desulphurization and storage conditions may affect the speciation of leachable As, Sb and Se in fly ash.

References

1. C. L. Carlson and D. C. Adriano, *J. Environ. Qual.*, **22**, 227–247 (1993).
2. G. A. Cutter, *Marine Chem.*, **40**, 65-80 (1992).

3. Gesamp, (IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint group of experts on the scientific aspects of marine pollution) *Review of potentially harmful substances—arsenic, mercury and selenium*, Rept. Stud. GESAMP **28**, 1986.

4. E. Berman, *Toxic metals and their analysis,* Heyden, London, 1980.

5. M. L. Pierce and C. B. Moore, *Water Res.*, **16**, 1247–1253 (1982).

6. L. S. Balistrieri and T. T. Chao, *Soil. Sci. Soc. Am. J.*, **51**, 1145–1151 (1987).

7. K. M. Hayes, C. Papelins and J. O. Leckie, *J. Colloid Interface Sci.*, **125**, 717–726 (1987).

8. L. S. Balistrieri and T. T. Chao, *Geochim. Cosmochim. Acta*, **54**, 739–751 (1990).

9. E. E. van der Hoek, P. A. Bonouvrie and R. N. J. Comans, *Applied Geochem.*, **9**, 403–412 (1994).

10. J. E. Silk, L. D. Hansen, D. J. Eatough, M. W. Hill, N. F. Mangelson, F. W. Lytle and R. B. Greergor, *Physica B*, **158**, 247–248 (1989).

11. J. J. Alberts, M. J. Weber and D. W. Evans, *Environ. Technol. Lett.*, **9**, 63–70 (1988).

12. A. Wadge and M. Hutton, *Environ. Poll.*, **48**, 85–99 (1987).

13. H. A. van der Sloot, J. Wijkstra, C. A. van Stigt and D. Hoede, in: *Wastes in the Ocean* **4**, I. W. Duedall, D. R. Kester, P. K. Park, B. H. Ketchum, eds., J. Wiley, U.S. 1985, pp. 467–499.

14. L. D. Hansen, D. Silberman, G. L. Fisher and D. J. Eatough, *Environ. Sci. Technol.*, **18**, 181–196 (1984).

15. D. Silberman and W. E. Harris, *Intern. J. Environ. Anal. Chem.*, **17**, 73–83 (1984).

16. V. T. Breslin and I. W. Duedall, *Marine Chem.*, **13**, 341–355 (1983).

17. R. R. Turner, *Environ. Sci. Technol.*, **15**, 1062–1066 (1981).

18. N. D. Niss, J. F. Scharbron and T. H. Brown, *Environ. Sci. Technol.*, **27**, 827–829 (1993).

19. C. Ericzon, J. Petterson, M. Andersson and A. Olin, *Environ. Sci. Technol.*, **23**, 1524–1528 (1989).

20. T. A. Quin, *Chemical speciation of selenium in fly ash*, Ph.D Thesis, University of California Riverside, 1985.

21. H. A. van der Sloot. G. J. de Groot, D. Hoede and J. Wijkstra, *Mobility of trace elements derived from combustion residues and products containing these residues in soil and groundwater, Netherlands Energy Research Foundation*, ECN-C-91-059, Netherlands Energy Research Foundation, Petten, 1991.

22. D. Hoede, J. Wijkstra and H. A. van der Sloot, *Dissolved trace oxyanions and trace elements in suspended matter and sediments in indonesian waters. Datareport of the ECN participation in the snellius II expedition*, ECN-203, Netherlands Energy Research Foundation, Petten, 1987.

23. A. S. Braman, L. W. Justen and C. C., *Anal. Chem.*, **44**, 2195–2199 (1972).

24. H. A. van der Sloot, D. Hoede, Th. J. L. Klinkers and H. A. Das, *J. Radioanal. Chem.*, **71**, 463–478 (1982).

25. J. T. van Elteren, H. A. Das, C. L. de Ligny and J. Agterdenbos, *Anal. Chim. Acta*, **222**, 159–167 (1989).

26. H. R. Lindner, H. D. Seltner and B. Schreiber, *Anal. Chem.*, **50**, 896–899 (1978).

27. A. I. Saleh, J. R. W. Woittiez, G. D. Wals and H. A. Das, *J. Radioanal. Nucl. Chem.*, **140**, 357–363 (1990).

28. R. Massee, H. A. van der Sloot and H. A. Das, *J. Radioanal. Chem.*, **35**, 157–165 (1977).

29. B. Welz and M. Melcher, *Analyst*, **109**, 573–575 (1984).

30. M. B. De la Calle-Guntiñas, Y. Madrid and C. Cámara, *J. Anal. Chem.*, **334**, 27–29 (1992).

31. C. Venghout and H. Agemian, *Anal. Chim. Acta*, **113**, 237–245 (1980).

32. H. A. van der Sloot, D. Hoede, J. Zonderhuis and C. Meijer, *Preparation of pure active carbon*, ECN-80, Netherlands Energy Research Foundation, Petten, 1980.

33. R. R. Frost and R. A. Grivin, *Soil. Sci. Soc. Am. J.*, **41**, 53–57 (1977).

34. E. J. Wu and K. Y. Chen, *Chemical form and leachability of inorganic trace elements in coal fly ash*, EPRI-EA-5115, Electric Power Research Institute, Palo Alto, California, 1987.

35. D. F. S. Natusch and D. R. Taylor, *Environmental effects of western coal combustion, Part IV, Chemical and physical characteristics of coal fly ash*, U.S. Environmental Protection Agency Rept. EPA 600/3-80-094, 1980.

36. R. Helmuth, *Fly ash in cement and concrete*, Portland Cement Association, Skokie, Illinois, 1987.

37. R. C. Weast, M. J. Astle and W. H. Beyer, (eds.) *CRC Handbook of chemistry and physics*, 64th ed., CRC Press, Cleveland, Ohio, 1983.

38. B. Haynes, M. Neville, R. J. Quann and A. D. Sarofilm, *J. Coll. Interface Sci.*, **87**, 266–278 (1982).

39. R. Meij, in: *Environmental aspects of trace elements in coal*, D. J. Swaine and F. Goodarzi, eds., Kluwer Academic Publishers, Dordrecht, 1993, Ch. VI.

40. C. E. Cowan, J. M. Zachara and C. T. Resch, *Geochim. Cosmochim. Acta*, **54**, 2223–2234 (1990).

41. L. E. Eary, D. Rai, S. V. Mattigod and C. C. Ainsworth, *J. Environ. Qual.*, **19**, 202–214 (1990).

42. C. Tauber, *Spurenelementen in flugaschen: Kohle-Kraftwerk-Umwelt*, Verlag TÜV Reinland, 1987.