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Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems

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Abstract

Batch leaching tests have been performed on fly ashes collected from four Australian power stations fuelled by chemically different coals. Two acidic and two alkaline fly ashes were subjected to long-term (144 h) leaching tests, and the behaviour of As, B, Mo and Se was investigated to obtain data on their potential for mobilisation during fly ash–water interactions. All four elements are mobile under different conditions and over different leaching times. The concentrations of these elements released in leaching solutions with initial pH values of 4, 7 and 10 were used to assess the influence of pH conditions on element mobility from the acidic and alkaline fly ashes. The most mobile of the four elements leached were Mo from alkaline fly ashes and B from acidic fly ashes. Arsenic concentration increased with time in leachate solutions from acidic and alkaline fly ashes; however, in solutions in contact with alkaline fly ashes the As concentration, after reaching a maximum, later decreased with time. Selenium mobility shows a similar pattern to that of As, with similar leaching concentrations. Boron has the highest relative mobility of all four elements. A process possibly responsible for the decrease in concentration of B, As and Se in alkaline leaching solutions is the formation of ettringite. Equilibrium between the solid phase (ash) and the leaching solution was not reached in any of the leaching experiments. The pH of the leaching solution is the key factor affecting the mobility of these trace elements in these fly ashes.

Keywords: Fly ash; Leaching; Trace elements; Australia

1. Introduction

Approximately 80% of the solid residue from pulverised fuel combustion is released as fly ash; the rest, consisting of larger particles and molten material, is mostly retained within the furnace as bottom ash. The properties of the fly ash depend on the physical and chemical properties of the coal source, the coal particle size, the burning process, and the type of ash collector. For ash in outdoor emplacements, where the long-term interaction of potentially toxic elements with surface water or groundwater systems may be a concern, it also depends on the degree of weathering [1,2] and the possible formation of secondary minerals [3]. The soluble salt content in fly ashes is closely related to the coal properties and the age of the fly ash [4], and also to the pH and other environmental conditions.

With destruction of the organic matter, the concentrations of trace elements in fly ash are higher than the equivalent concentrations in the source coal. Enrichment associated with combustion may concentrate elements by factors of 4–10 times [5], and enriched elements such as As, Se, Cd, Cr, Ni, Sb, Pb, Sn, Zn and B are most likely to be leached out of the solid phase [6,7]. Fly ash is also a very heterogeneous material, with variation both between particles and within particles [8]. The glass, in particular, can adsorb different elements in various concentrations and forms, including coatings of calcium and other sulphates as well as elements attached directly to the solid particles. Apart from Si, Al and Fe, fly ash may also be rich in potentially mobile major elements such as Ca, Mg, Na and K, and in minor elements, such as P and B. A number of metals and metalloids present as carbonates, oxides, hydroxides and sulphates, including Cd, As, Se, Pb, Ni, Cu, Cr, Co, Mo, Be, may also occur in lower but still significant concentrations.

The elements that are adsorbed on the particle surfaces are much more easily mobilised into solution during fly ash-water interaction. The leachability of these elements is closely related to the phases with which they are associated, as well as to the pH and other aspects of the leaching environment.

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Association with soluble phases will cause them to be leached at much higher rates. When fly ash interacts with water the principal processes affecting the leaching process are dissolution of primary solids and precipitation of secondary solids, as well as redox, sorption and hydrolysis reactions.

The amounts of trace elements released from fly ash into solution, and the rates of release, depend on three factors [9]: the total concentration of elements in the solid phases, the distribution of elements in the fly ash particles, and any incorporation of the elements into secondary solids. Minor elements present in soluble phases will be dissolved through congruent dissolution reactions. The alkaline-earth elements present on particle surfaces will be initially dissolved rapidly and pass into solution, but later, with increasing pH and element concentration, may re-precipitated to form secondary solids that are more stable during fly ash-water interaction. Reactive trace elements showing increasing concentration with leaching may also precipitate to form carbonate phases [10].

The mobilisation of trace elements from fly ashes is a very slow process, and equilibrium between solid and liquid phases may not be attained even after long leaching times [11–13]. Contaminated leachates from acidic fly ashes can pose the highest toxicity problem for aquatic environments [10]. Non-toxic soluble elements will dissolve first in water or weak acids [14], but long term leaching of toxic trace elements is associated with slow mobility of elements from glass, magnetite and related minerals [15]. Interaction of groundwater and surface water in fly ash emplacements will take a long time to remove mobile trace elements from the solid phase. Depending on the hydrogeochemical environment in which the ash is emplaced or used, this may give elevated concentrations over long periods of time, and create potential contamination of associated groundwater and surface water systems.

This paper presents results obtained from a series of batch leaching tests on two acidic and two alkaline fly ashes taken from different Australian power stations, based on exposure for up to 144 h to solutions with significantly different pH conditions (initial pH values of 4, 7 and 10). The overall object of the study was to evaluate more fully the role of pH and related environmental factors on the mobility of key elements from different types of ash materials, as a basis for comprehensive assessment of element behaviour under a range of groundwater conditions. The release mechanisms and the rates of mobilisation of As, B, Mo and Se, which represent the main potentially toxic elements with significant concentrations in the ashes or their leachates, were monitored as a basis for improved evaluation and prediction of ash behaviour in different natural environmental systems. This type of information is different from that produced by simple, standardised leaching tests, but is necessary for a more confident approach to ash management and environmental risk assessment for particular site conditions, and a basis for application of more sophisticated hydrogeochemical modelling techniques. The novelty of the paper lie in the application of long leaching time of 144 h and collection of leachates during other 12 periods to obtain detailed time-series of changes in chemical composition of leachate solutions. The second important novum is determination of pH and HCO_3 in leachates after leaching fly ash. The difference from standardised leaching tests is application of solutions with different pH, which is not very often performed.

2. Materials and methods

2.1. Materials

Four fly ashes, identified as FA15, FA16, FA21 and FA23, produced by pulverised coal combustion in different Australian power stations, were used for the batch leaching tests. The ashes were duplicates selected from a series of nine samples, covering a range of pulverised-fuel stations in New South Wales, Queensland and Western Australia, that had been comprehensively evaluated for a previous study based on column leaching experiments [16]. The ashes had been collected in a dry state from the power stations using either electrostatic precipitators or fabric filters, without any flue gas desulphurisation or other treatment, and were stored in airtight plastic containers until analysed. The samples for the present study were selected from the wider range evaluated in the previous work, based on their chemical properties and their behaviour in the column leaching tests, to provide two ashes expected to produce alkaline pH conditions and two ashes expected to produce acid pH conditions when exposed to water in emplacements and leaching experiments.

The leaching solutions used in the study were prepared by mixing appropriate amounts of 0.01 M HCl and 0.01 M NaOH with ultra pure Milli-Q-water, the latter being obtained by passing good quality tap water (electrical conductivity $<$ 200 μS/cm) through two systems of a mixed-bed ion exchanger, consisting of strong anion and cation resins mixed together. The Milli-Q-water obtained in this way had electrical conductivity values below 5 μS/cm, and concentrations of As $<$ 0.04, B $<$ 4, Mo $<$ 0.41 and Se $<$ 0.5 μg/L.

2.2. Chemical and mineralogical analyses

The proportions of major elements in the ashes were determined by X-ray fluorescence spectrometry using a Philips PW2400 spectrometer, supplemented by a C and S determination using a LECO CSN elemental analyser. Concentrations of trace elements in the ashes were determined by ICP-AES, ICP-MS and other techniques, as described more fully by Killingley et al. [16].

Other portions of the fly ash samples were finely powdered and subjected to X-ray diffraction (XRD) analysis using a Philips X'pert diffractometer system with Cu Kα radiation. Scans were run from 2 to 60° 2θ, with increments of 0.04° and a counting time of 2 s per step. The percentages of the different minerals in the fly ashes, and also the percentage of non-crystalline or glassy material in each case, were evaluated using the Rietveld-based Siroquant data processing system, following techniques described by Ward and French [17].

The pH developed by each fly ash from short-term contact with water was first evaluated. This pH value was obtained for each sample by averaging the pH of the leachate after the first flush by deionised water during separate column leaching tests [16], the pH developed after 15 min contact with Milli-Q-water during the batch leaching tests described below, and the pH obtained from several tests involving interaction of fly ash and Milli-Q water mixed in a 1:1 solid/liquid (S/L) ratio, measured daily over a one week period. Samples FA15 and FA23 represent acid-generating fly ashes, with pH values of 4.25 and 4.84, respectively obtained on exposure to water. FA16 and FA21 represent alkali-generating fly ashes, with pH values of 10.22 and 12.03.

Studies by Killingley et al. [16] suggest that the initial pH of the ash-water system depends on the balance between the concentration of alkaline-earth elements, Ca and Mg, in the ashes on the one hand and the proportion of potentially acid-generating SO_3 on the other. A wide range of variation in these percentages is represented in the sample suite, providing and opportunity to study ashes that generate low pH and ashes that generate high pH values in the same series of leaching experiments.

The particle size distributions of the fly ashes (Fig. 1), taken from the work of Killingley et al. [16], show bi-modal particle size distributions, with the main peak between 10 and 100 μm and a secondary peak between 0.1 and 1 μm. The particle size distribution is an important property of fly ash, with the smaller particles having greater surface areas. Size distribution is important during the interaction of the ash with different solutions, since it affects the mobilisation of any trace elements on the particle surfaces. Surface area data (Table 1) indicate that FA15 has a total area per unit mass three times larger than that of the other three fly ashes. On the basis of the surface area and size distribution, it appears that FA15 has particles that are more irregular in shape, compared with a more spherical shape for the particles in the other fly ashes.

X-ray diffraction studies (Table 2) show that the major crystalline solids in all four ashes are quartz and mullite, except for FA16, where the quartz content is very low. FA15 has the highest proportion of both quartz and mullite, and FA16 has the lowest. Iron oxides, in the form of magnetite, maghemite and hematite, are also important solid phases. FA23 contains the lowest proportion of iron oxide minerals. The remainder of the material, making up 55–85 wt% of the total, is represented by non-crystalline aluminosilicate glass [17].

Chemical analysis (Table 3) shows that SiO_2 is the dominant oxide, with appreciable Al_2O_3 in all of the fly ashes. Calcium and magnesium oxide concentrations are up to 3–4%, and sulphur in the form of SO_3 is well below 1%. The alkaline fly ashes (FA16 and FA21) have significantly higher concentrations of CaO, MgO, Na_2O and K_2O than the acid fly ashes (FA15 and FA23). Computations based on the XRD data [17] indicate that the glassy phase has an overall composition with about 50% SiO_2 and 10% Fe_2O_3 in two of the samples (FA15 and FA16) and 70% SiO_2 and 1–3% Fe_2O_3 in the other two (FA21 and FA23). The differences may reflect the mode of Fe occurrence in the original feed coals: FA15 and FA16 represent ashes derived from combustion of sub-bituminous coals and FA21 and FA23 ashes from bituminous coal sources. Perhaps more significantly with respect to leaching, the glass in the two alkaline fly ashes (FA16 and FA21) also appears to be significantly richer in CaO and MgO (totalling 6.9 and 6.4% of the glass, respectively) than the glass in the two acidic fly ashes, FA15 (3.8%) and FA23 (0.9%).

Both acidic fly ashes (FA15 and FA23) appear to have slightly higher concentrations of Mo, Pb and Se than the alkaline fly ashes. The other trace elements covered in this study, however, do not show any significant differences between the acid and alkali-generating groups. All of the fly ashes have relatively high concentrations of As, Co, Cr, Cu, Mo, Ni and Pb, compared with Cd and Se, which occur at much lower concentrations (Table 4).

2.3. Leaching experiments

Batch leaching tests were performed on all four fly ashes using three different solutions, to test the mobility and rate of release of particular elements from the ashes under a range of chemical conditions. The leaching solutions had pH values of 4, 7 and 10, made up in the laboratory prior to the leaching tests. Bulk solutions of pH 4, 7 and 10 were made in 3-l polyethylene bottles from ultra pure Milli-Q water, adjusted to acidic conditions (pH = 4) by adding 0.01 M HCl, and to alkaline conditions (pH = 10) by adding 0.01 M NaOH. The pH of the neutral (pH = 7) solution was adjusted slightly with 0.01 M NaOH, as the Milli-Q water had pH of 6.5–6.6. The pH of the initial leaching solutions was measured using an ORION

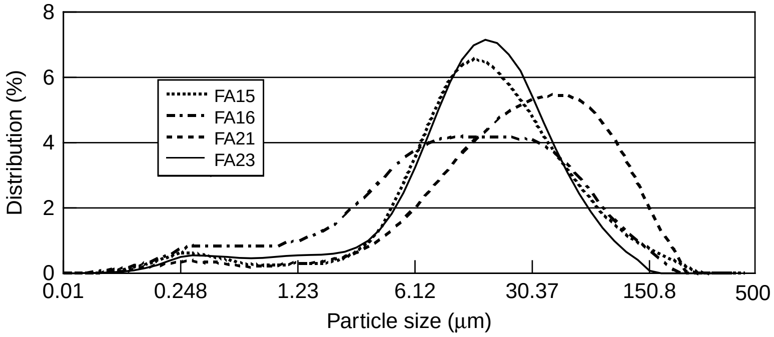

Fig. 1. Percentage distribution of particle size in four fly ashes.

Table 1
Selected physical properties of fly ash after Killingley et al. [16]

Fly ash no.	Particle density (g/mL)	Surface area (m^2/g)
FA15	2.07	9.65
FA16	2.22	3.16
FA21	1.91	1.72
FA23	1.96	0.91

Model 290A portable pH/concentration meter, calibrated against buffers of pH 4, 7 and 10. Cross-checking with two pH meters was used to validate the pH measurements for the solutions.

Fly ash samples of 39 g were weighted into acid-cleaned 140 ml polyurethane bottles, and 135 ml of pre-prepared solution was added, making the liquid/solid (L/S) ratio close to 3.5:1 ± 0.03 in all leaching tests. The concentrations of trace elements in the Milli-Q-water in duplicate pH solutions are less than 1 μg/L. These concentrations are well below the analytical data obtained from the leaching test and do not affect the values obtained from the leaching tests. The bottles containing the respective fly ashes and solutions were sealed and shaken in a horizontal shaker at 150 rpm at room temperature (22.5–23.5 °C). Thirteen different shaking periods were used: 15, 30 min, 1.5, 2, 3, 6, 12, 24, 48, 72, 96, 120 and 144 h.

After the required shaking time the solution in each bottle was extracted from the solid phase, and 60 ml of solution filtered through 0.45 μm Millipore cellulose acetate membrane filters. These solutions were immediately acidified, using 10 drops of analytical grade nitric acid, prior to major and trace element determinations. After acidification the containers were kept in a refrigerator at 4 °C, to prevent any additional chemical reactions. Another aliquot (approximately 60 ml) of each solution was filtered into a second container but not acidified, for determination of pH, electrical conductivity (EC) and HCO_3^- immediately after sample collection. The EC was measured using an ORION Model 135A conductivity meter calibrated against 0.001–0.1 M KCl standard solutions. The pH was measured using the same meters as were used to measure the pH of the initial solutions. The total alkalinity (alkalinity is the concentration of carbonate species of HCO_3^- and CO_3^{2-} in the solution) was calculated from the sum of CO_3^{2-} and HCO_3^-, determined by titration with 0.01 M HCl against methyl orange and bromcresol green indicators [18]. The alkalinity results are presented as the respective HCO_3^- concentrations.

Table 2
Mineralogy of fly ashes by X-ray diffraction and SIROQUANT

Minerals	FA15	FA16	FA21	FA23
Quartz	25.4	2.1	14.1	9.9
Mullite	24.2	11.9	15.5	15.7
Cristobalite	0.1	0.1	0.1	0.0
Magnetite	0.8	2.3	2.5	0.0
Maghemite	1.2	2.3	1.5	0.7
Hematite	0.9	1.4	0.0	0.0
Amorphous glass	47.3	80.0	66.3	73.7

Table 3
Chemical analyses of fly ash samples (%)

Element	FA15	FA16	FA21	FA23
SiO_2	52.3	48.8	64.9	66.0
TiO_2	3.7	2.4	1.4	1.3
Al_2O_3	19.2	27.8	17.0	27.6
Fe_2O_3	13.9	10.6	5.4	1.1
MgO	1.6	2.0	1.7	0.3
CaO	2.9	5.3	5.0	0.4
Na_2O	0.4	0.4	1.3	0.2
K_2O	1.4	1.1	2.9	2.9
P_2O_5	3.9	1.2	0.2	0.2
SO_3	0.6	0.3	0.2	0.1
Total	100.0	100.0	100.0	100.0

The acidified samples were analysed by ICP-AES Perkin Elmer Optima 3000 DV (major elements, Si Al, S) and ICP-MS Perkin Elmer Elan 6100 (trace elements).

3. Results and discussion

3.1. Leaching behaviour

Leached amounts of Ca, S, As, B, Mo and Se for all pH solutions are plotted versus concentration of the element in the original fly ash (Fig. 2). The correlation between leaching amounts of Ca, S and B versus its concentration in the solid phase show relatively week relationship, where points are just scattered, with all correlation coefficients (R^2) between 0.43 and 0.82. However, correlation coefficients for As, Mo and Se show that the amounts leached are not related to the concentrations of the respective elements in the fly ash.

The elements for which the highest proportions were removed from the fly ashes by the leaching solutions, as

Table 4
Concentration of trace elements in fly ash samples—mg/kg after Killingley et al. [16]

Element	FA15	FA 16	FA21	FA23
Al	127,000	147,000	108,000	134,000
As	11	22.30	6.58	12.4
B	11	56	89	25
Ba	3520	1190	653	393
Ca	9030	27,400	21,400	2630
Cd	1.34	0.52	0.25	0.404
Co	100	35	5.6	11
Cr	130	69.20	18	49.6
Cu	93.8	93	28.10	51.6
Fe	60,700	90,900	48,300	7070
K	4980	6660	14,600	22,000
Mg	4250	8870	6050	1710
Mn	225	1630	899	87.5
Mo	21	6.10	4.9	8.1
Na	1430	2390	5870	1090
Ni	242	52.90	10.5	41.2
P	7360	3760	648	719
Pb	80	49	48	59
S	1020	948	848	384
Se	3.01	2.26	2.48	5.15
Si	242,000	188,000	262,000	283,000
C	2.17	4.71	2.65	0.6

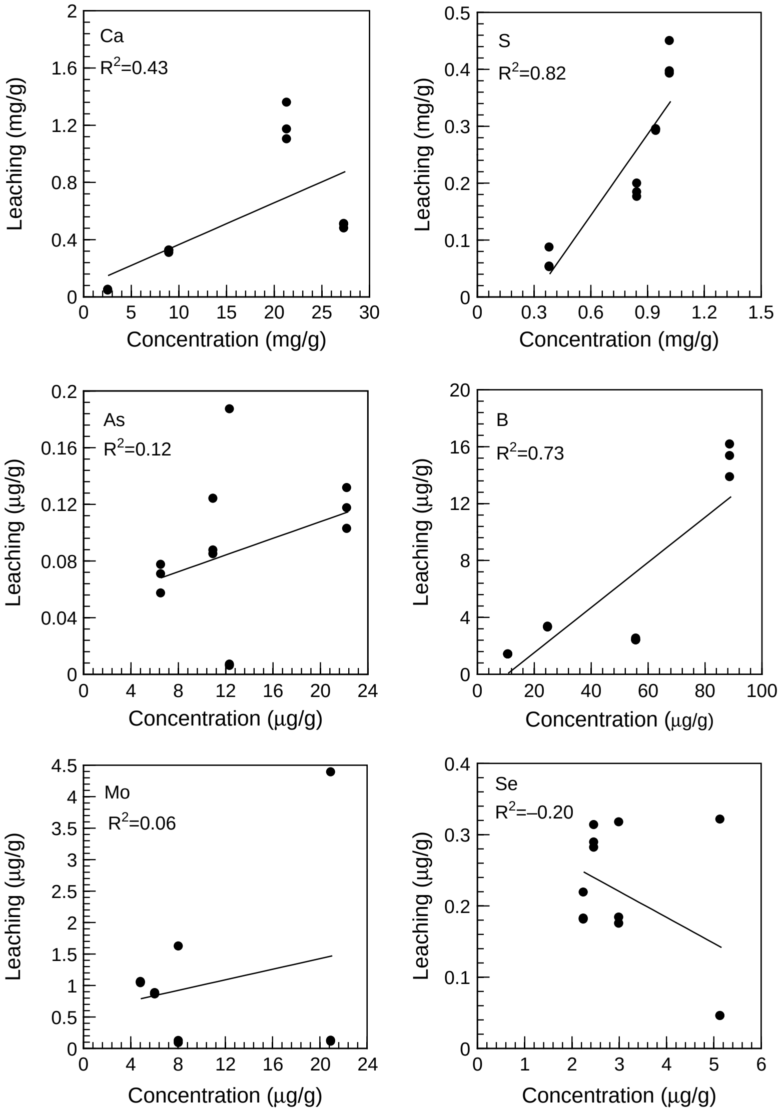

Fig. 2. Relationship between leaching amounts and concentration of elements in fly ashes.

a fraction of the total concentration in the original ash in each case, are: B (12–13%), Mo (0.5–21%) and Se (0.9–10%) from the acidic fly ashes and Mo (4–21%), B (4–18%) and Se (8–13%) from the alkaline fly ashes.

Sample FA15 has the highest surface area and FA23 the smallest (Table 1). However, there is no particular relationship between surface area and the amounts of As, B, Mo and Se leached from the samples studied.

Column leaching tests performed previously on the same fly ashes [16] showed that mobility of As decreased with increasing L/S ratio. Boron concentration in solutions leached from both alkaline fly ashes decreased very slowly, and B was still present in solution after 10 L/S ratios. The concentration of B decreased much more rapidly in solutions leached from acidic fly ashes. There was no clear concentration trend with respect to Mo and Se, however, for either acidic or alkaline ashes. Concentrations of both elements slowly decreased with increasing L/S ratio. Higher concentrations of Se were present in solutions leached from acidic fly ashes.

3.2. pH and HCO_3

In the present series of experiments, the pH of initially neutral and alkaline solutions in contact with acidic fly ashes decreased rapidly (after 15 min), and remained acidic over the rest of the test series. At the end of the test it was slightly higher than the original pH of the fly ashes (Fig. 3). The acidic solutions remained acidic for the whole period tested. For both alkaline fly ashes the pH values in all solutions increased after the initial 15 min, and during the test remained very similar to the original pH of the fly ashes. The concentration of bicarbonate in the leachate from both acidic fly ashes was low, and from starting concentration in leaching solutions of 0 mg/L (pH 4), 9 mg/L (pH 7) and 19 mg/L (pH 10) varied but remained in the range of 5–50 mg/L (Fig. 4). The low concentrations of HCO_3^- in both acidic fly ashes are explained simply by the fact that the dominant carbonate species were in the form of carbonic acid. There was thus not much carbonate to be dissolved, and also dissolution of the alkaline-earth oxides was slow to produce

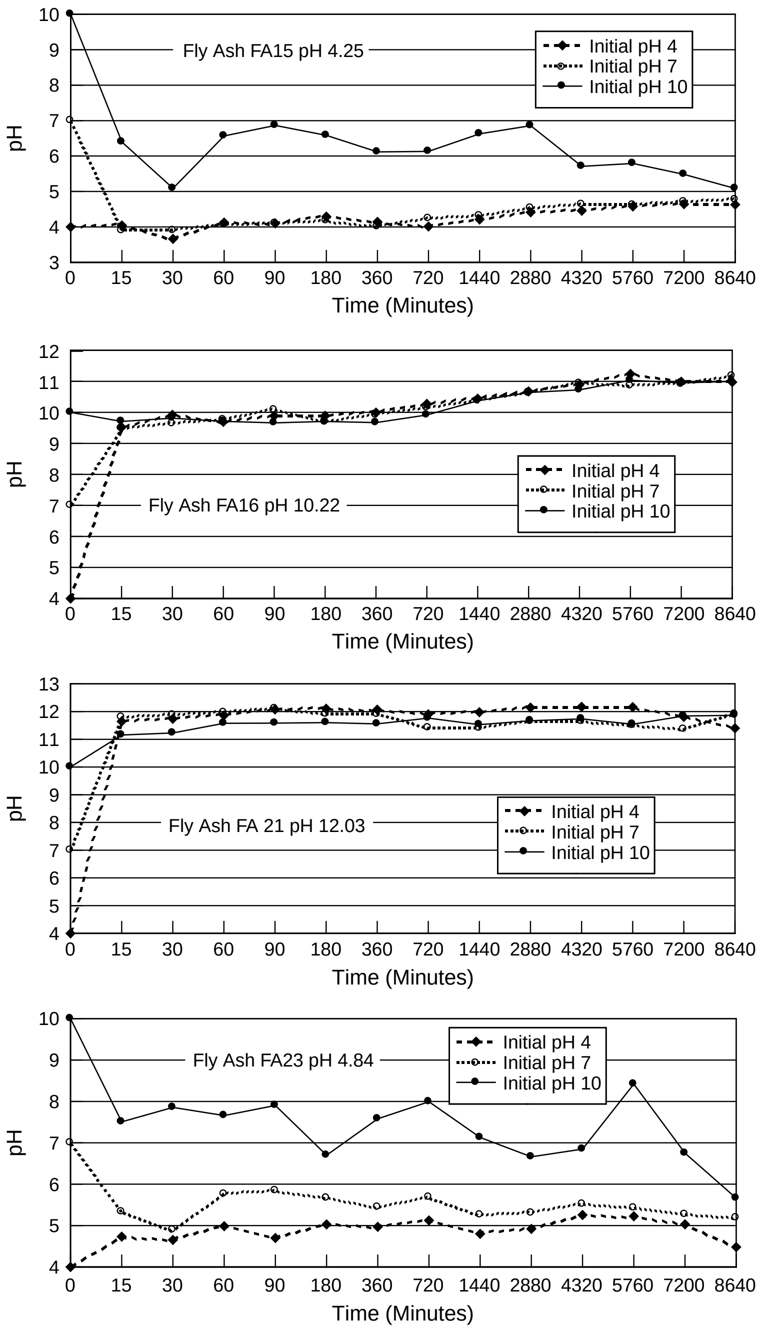

Fig. 3. Changes of pH values with time during leaching tests in contact with fly ashes.

bicarbonate. These two reactions could apparently not compensate for the solid phase acidity through OH^- and CO_3^{2-} production, and the H^+ released from the fly ash was therefore unable to be balanced by a neutralisation process. Even the solution with an initial pH of 10 could not maintain high pH and HCO_3^- levels through dissolution of CaO, as CaO and Ca concentrations are both very low. In both alkaline fly ashes HCO_3^- concentration increased significantly in all three leaching solutions. The highest concentration of 1000 mg/L is in the leachate from alkaline fly ash FA21 leached by a solution with initial pH of 10.

The decrease of HCO_3^- in FA16 at the end of the test is probably associated with precipitation of metal and/or calcium carbonates. Such precipitation would force further dissolution of CaO and/or $CaCO_3$ to replace the HCO_3^- used for carbonate precipitation. In alkaline fly ashes precipitation of $CaCO_3$ is apparently forcing incongruent dissolution of CaO to supply more Ca for the precipitation of $CaCO_3$, maintaining high pH values and high HCO_3^- level. Any decrease in HCO_3^- concentration is apparently associated with precipitation of $CaCO_3$ and other metal carbonates.

3.3. Arsenic

The As concentration in all fly ashes reached a maximum of 50 μg/L and showed a high degree of variability during

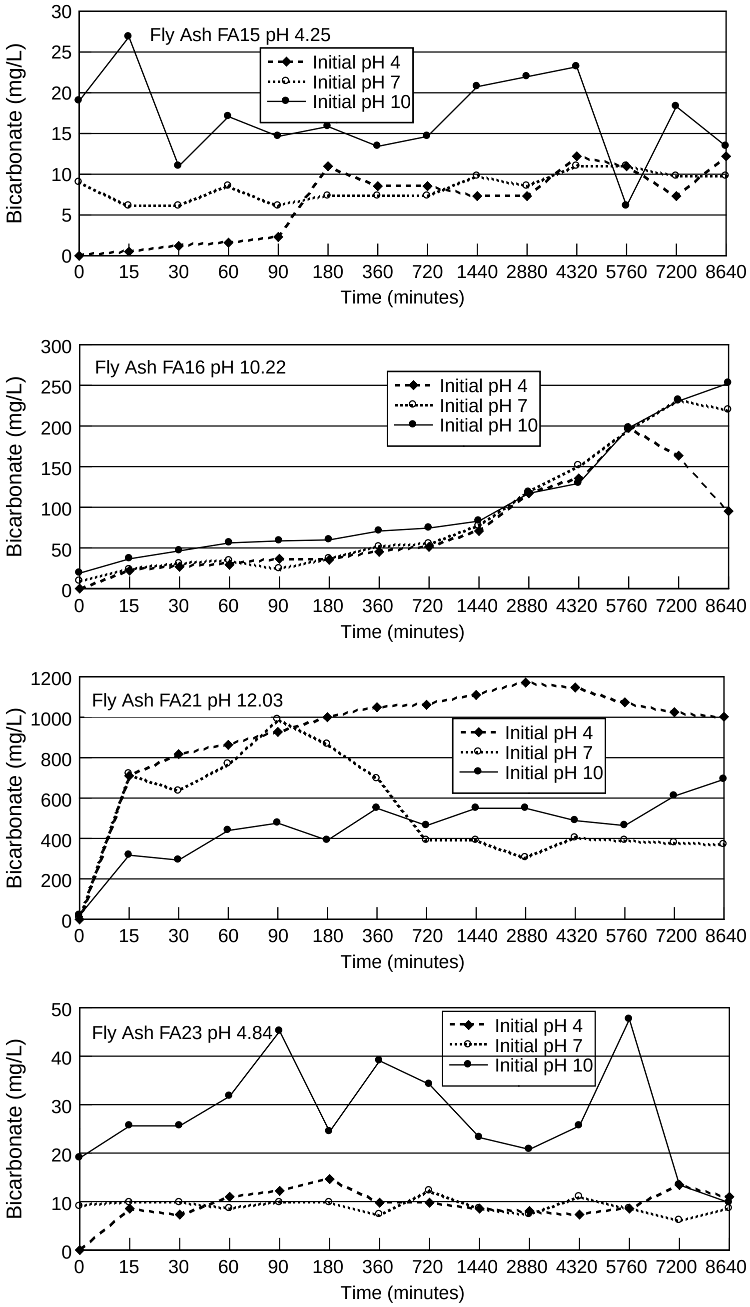

Fig. 4. Changes of HCO_3^- concentrations with time during leaching tests in contact with fly ashes.

the leaching tests (Fig. 5). The highest concentration of As from all four fly ashes was in leaching solutions where the initial pH was 10.

The study found a mobilisation pattern for As in acidic fly ashes similar to that observed by van der Hoek et al. [19]. In both acidic fly ashes (FA15 and FA23) the As concentration increased with increasing pH values, and in both alkaline fly ashes (FA16 and FA21) the As concentration also increased with increasing pH, but later in time the As concentration decreased. The latter observation is opposite to that reported by van der Hoek et al. [19], who found that, in alkaline fly ashes, the As concentration increased with decreasing pH. It was concluded [19] that different processes are responsible for controlling As partitioning and As concentrations in alkaline fly ashes and acidic fly ashes. It is thus possible that As in fly ash is present in significant amounts in the silicate matrix [15,20], and the rest is associated with iron rich glass phases, non-magnetic phases and non-silicates, or is accumulated on the surfaces of fine particles [21–25]. Because of As enrichment on the smaller particles, and also increased enrichment with increasing surface area [6,7,26], rapid mobilisation of As occurred in early phases of leaching (FA16), and later, where there was no available

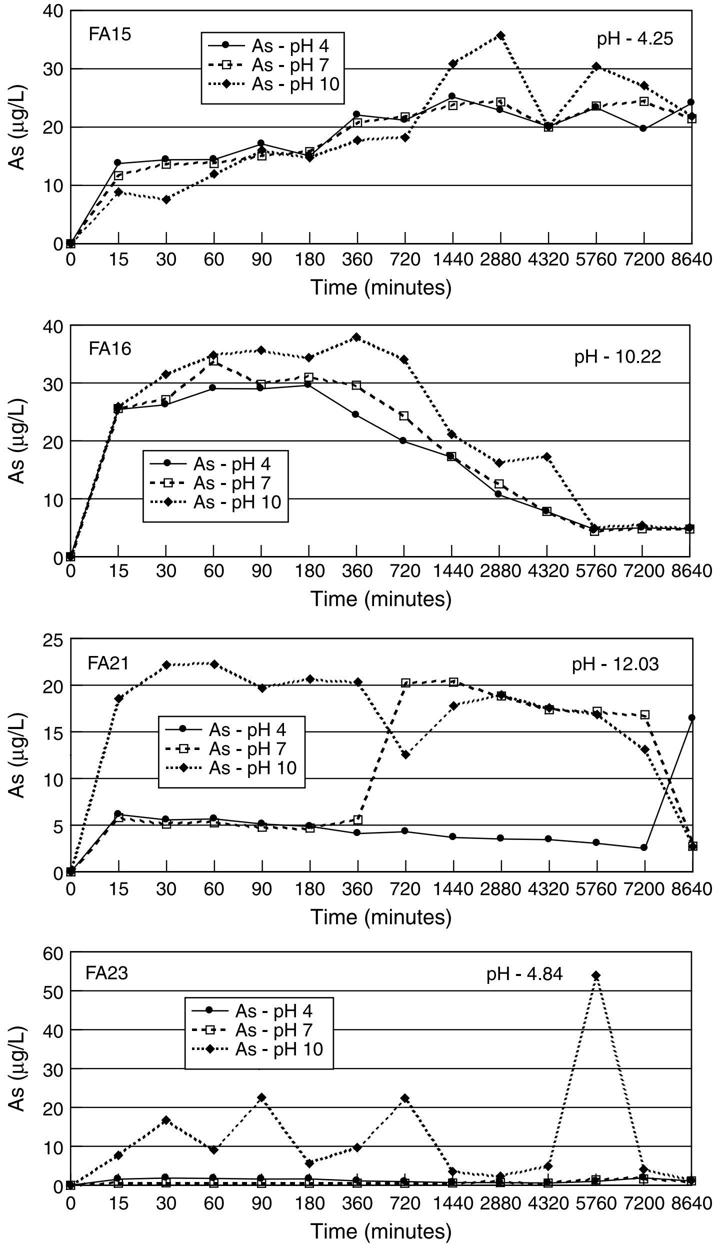

Fig. 5. Changes of As concentrations with time during leaching tests in contact with fly ashes.

As on the particle surfaces, the concentration decreased due to precipitation and/or sorption of As back into the solid phase.

Because pH controls As and its leachability, a low mobility is developed, where alkaline and neutral solutions are in contact with fly ash [25]. However, if the As is present as oxyanions, it is more soluble in alkaline solutions [27]. In alkaline fly ashes As solubility is low [28], but mobility is significantly higher than in acidic fly ashes [29], which is partly the case in the present study. Because the solubility of As(III) is nearly constant over a large pH range [30], solution of As(V) is probably responsible for the changes in As^{Tot} concentration, and solution of As(V) with acidity/alkalinity changes is a major factor controlling the solubility and mobilisation of As from fly ashes generally [31,32].

A similar situation may exist in the Australian fly ashes, as the solutions used were in equilibrium with atmospheric oxygen and any changes in As(V) concentration due to dissolution/precipitation and sorption would control the As^{Tot} concentration in the leachate under oxidising conditions. A plausible process for removal of As from FA16 would be one associated with precipitation of $Ca_3(AsO_4)_2$. As has been shown by Grisafe et al. [33], formation of insoluble $Ca_3(AsO_4)_2$ can lead to a decrease in the dissolved As concentration at high pH values if Ca is present. FA16 has the highest CaO content of all four fly ashes tested, and high concentrations of Ca occur in the leachate at a pH of around 12. If ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$) were to be formed in solutions under alkaline conditions, above a pH of 10.7 [34], substitution within the structure by arsenate is possible [34,35]. Formation of ettringite can significantly reduce the concentration of As in leaching solutions as leachability decreases [36].

The concentrations of As leached from all four samples appear to be independent of the concentration of As in the solid phase (raw fly ash) and the acidity/alkalinity of the fly ashes. All fly ashes show the highest mobility of As towards neutral pH values (Fig. 6). Acidic fly ashes in contact with solutions of pH 10 show increases in As concentration with increasing pH. For alkaline fly ashes the As concentration in solution increases with decreasing pH.

3.4. Boron

Of the four trace elements discussed B shows the highest concentration in the leaching solutions. Boron concentration reached more than 4000 μg/L in leaching solutions in contact with the most alkaline fly ash, and in other fly ashes is in range of hundreds of μg/L (Fig. 7). In most leachates B concentration increased with time.

Boron is very often associated with the smallest particles in the ash. It can accumulate on the surfaces of particles and in water-soluble fractions, and therefore has high leachability rates [21–23,37]. Other leaching tests show that B is highly leachable from fly ash, with 17–64% of the B in the ash being released in batch tests of ashes produced from several different North American coals [10,38,39].

Release of B to solution during the leaching process does not appear to be affected by its concentration in the solid phase for the ashes studied. Because boron is present in solution in anionic form, it is relatively soluble in the alkaline environment. Other studies, however, have shown that much greater leaching rates occur in acidic environments [37,38,40]. The rate of leaching has been shown to be independent of pH at nearly neutral values, and to decrease with further increases in pH [38]. Recent studies [25,28,41], have shown that the high solubility of B with alkaline pH values and very short contact times (15 min) is enough to release nearly all of the available boron from fly ash to water [38]. It is thus expected that this element will produce much higher concentrations in solution at higher pH ranges, and that more B will be released to solution from alkaline fly ashes. At higher pH values boron can co-precipitate with $CaCO_3$ [42,43]. However, our studies have

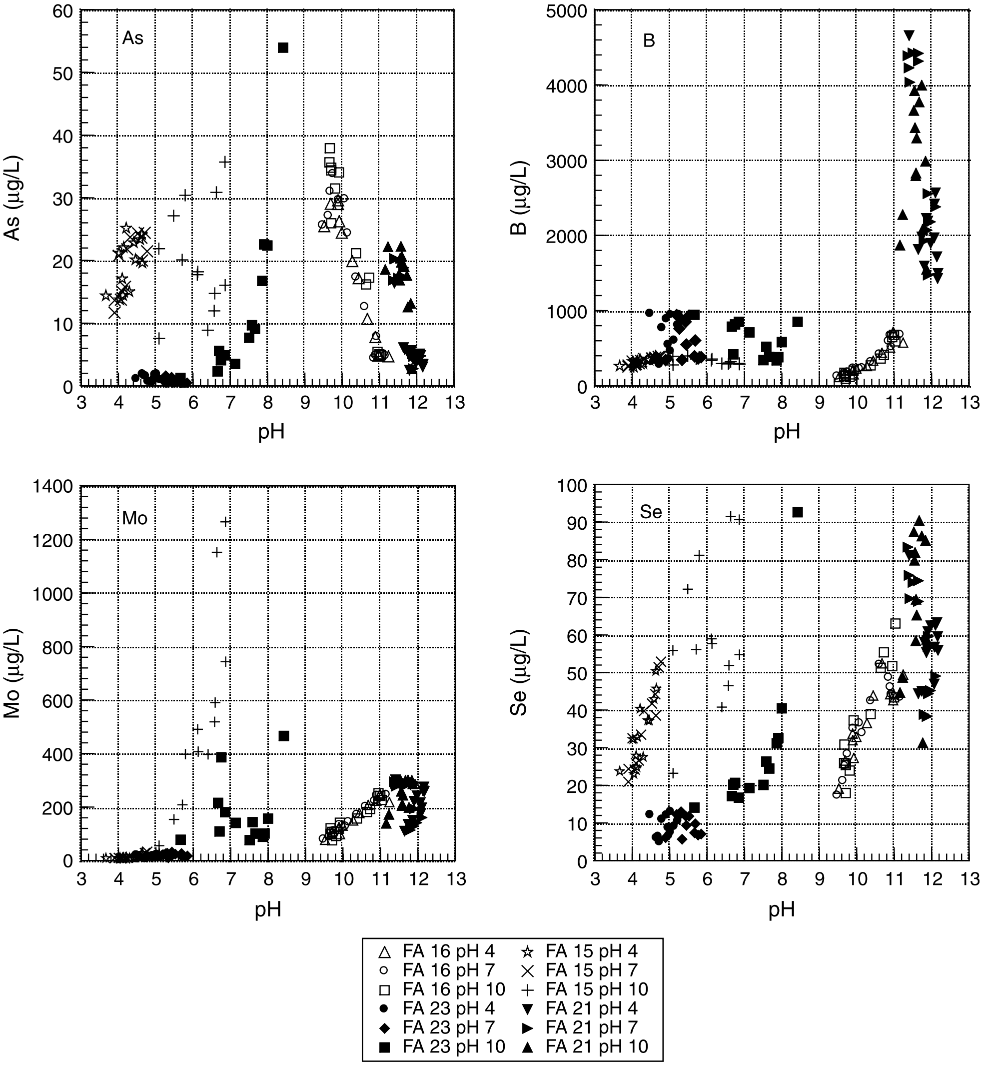

Fig. 6. Relationships between As, B, Mo and Se versus pH in fly ashes obtained during leaching tests.

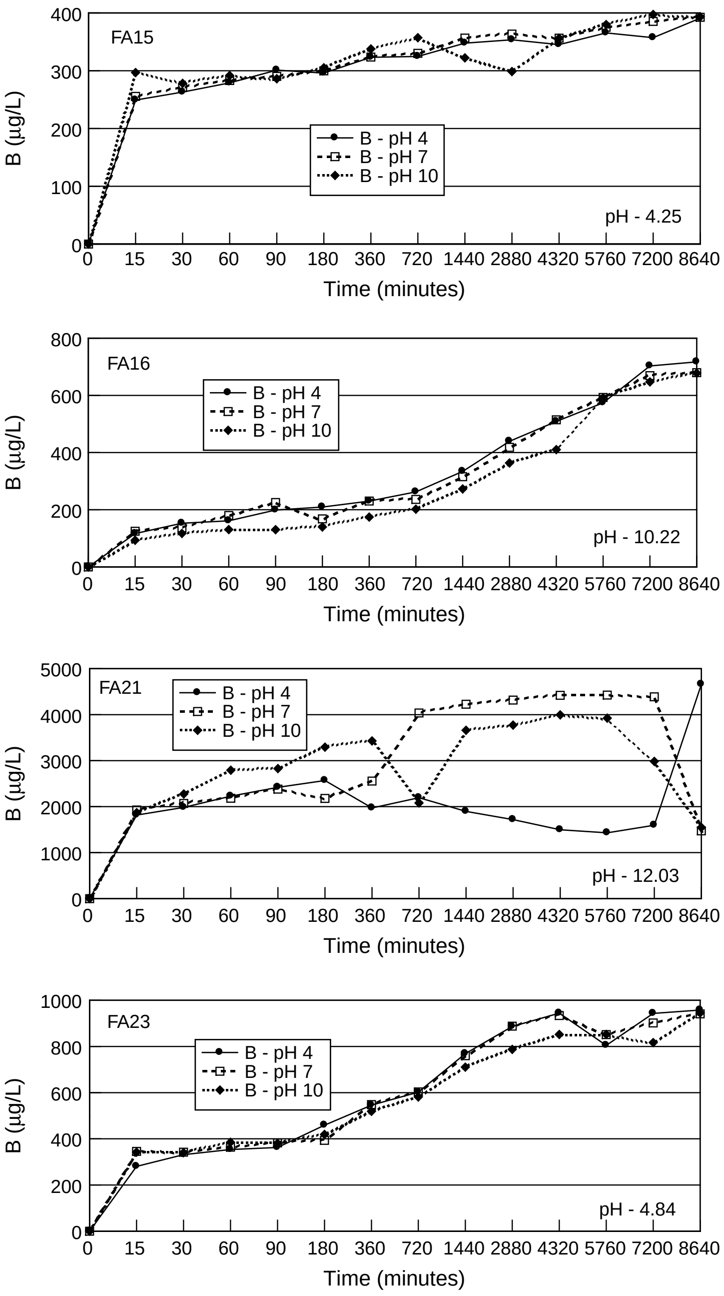

Fig. 7. Changes of B concentrations with time during leaching tests in contact with fly ashes.

shown that co-precipitation of B with calcium carbonate is unlikely to occur in these fly ashes.

Several papers have reported substitution of B in the ettringite structure in alkaline solutions during fly ash–water interaction [36]. Because solubility of B decreases when ettringite is formed [36,44–46] it is possible that decrease of B concentration in solutions leaching the most alkaline fly ash FA21 is due to the formation of ettringite. There is no simple relationship between concentration of B in the leachate solutions and the fly ash pH. The relationship between B and pH (Fig. 6) shows that the fly ash with the highest original pH released much more boron into solution than the other alkaline ash and both acidic ashes. Mobilisation of B from these fly ashes was only slightly pH dependent.

3.5. Molybdenum

Because Mo is concentrated on the small surface particles, and very often its concentration increases with decreasing particle size [7,21–23], the element has relatively high potential for mobility into solution.

Molybdenum is very mobile under alkaline conditions, and this was clearly the case in the present series of leaching tests. For both acidic fly ashes (FA15 and FA23) the Mo was mobile only when in contact with the solution of initial pH 10 (Fig. 8). For both alkaline fly ashes (FA16 and 21) the Mo concentration in solution progressively increased with time, reaching values around 250–300 µg/L at the end of the test for all three leaching solutions. Such a slow release of Mo from the alkaline fly ashes

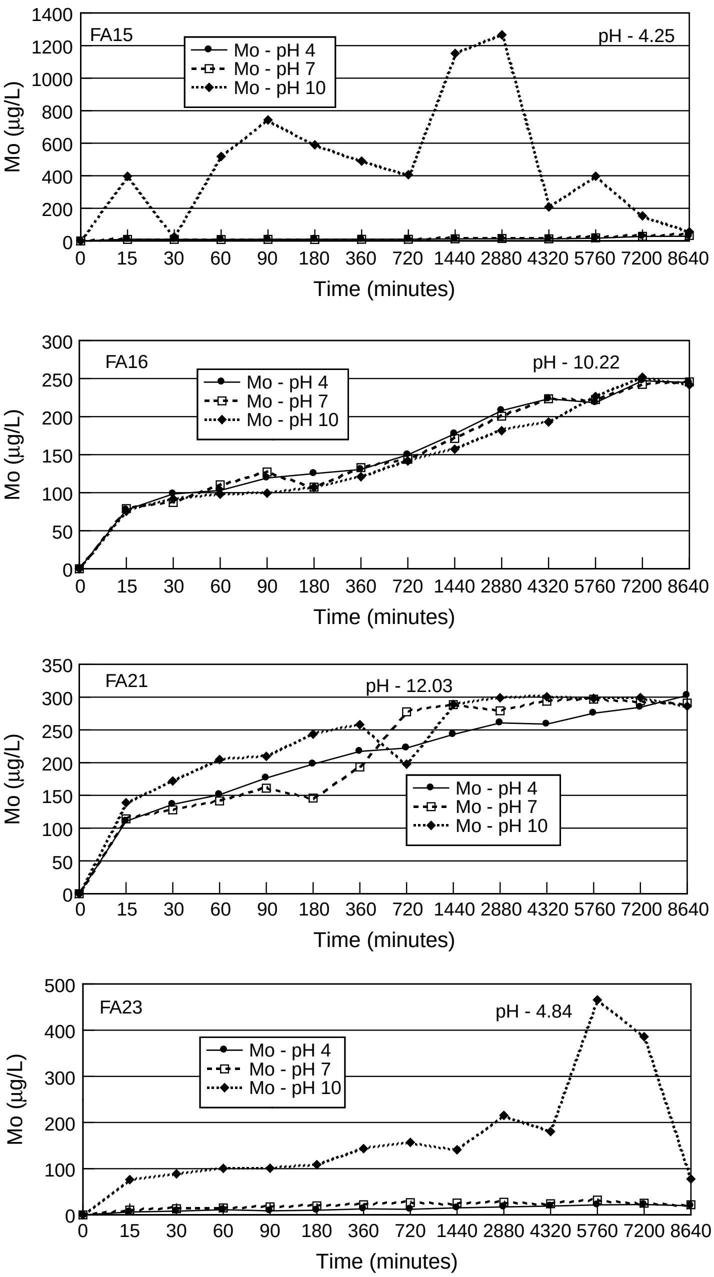

Fig. 8. Changes of Mo concentrations with time during leaching tests in contact with fly ashes.

can be attributed to the presence of Mo in the amorphous glass and not on the surfaces of the particles. The mobility of Mo was closely related to the pH of the solution. Higher rates of mobilisation and later concentration in solution corresponded with higher pH values. Removal of Mo from solution was probably associated with precipitation of MoO_3. Mobilisation of Mo from both acidic fly ashes shows that, with increasing pH, the concentration of Mo in solution also increases. This is when acidic fly ashes are in contact with alkaline leaching solutions of pH 10 (Fig. 6).

Mo concentration in leaching solutions is controlled by acidity and alkalinity, having higher solubility under alkaline pH conditions [25,28,41,47]. Under acidic conditions the solubility is significantly reduced, and Mo is sorbed on Fe- and Al-oxides [25]. Our leaching tests show that mobility is higher for acidic fly ashes in contact with alkaline solutions.

3.6. Selenium

Selenium is enriched on the fly ash surfaces [7], and is also present in fly ash in silicates and oxyanions [20,27]. Higher concentrations of Se in non-silicates are related to the element's presence in pyrite [32,48]. Se concentrations in leachates are controlled by the acidity and alkalinity of the leaching solution, and Se is one of the more mobile elements [48–50].

Our study showed that Se mobility has a similar trend to that of As in all four fly ashes (Fig. 9). In both acidic fly ashes,

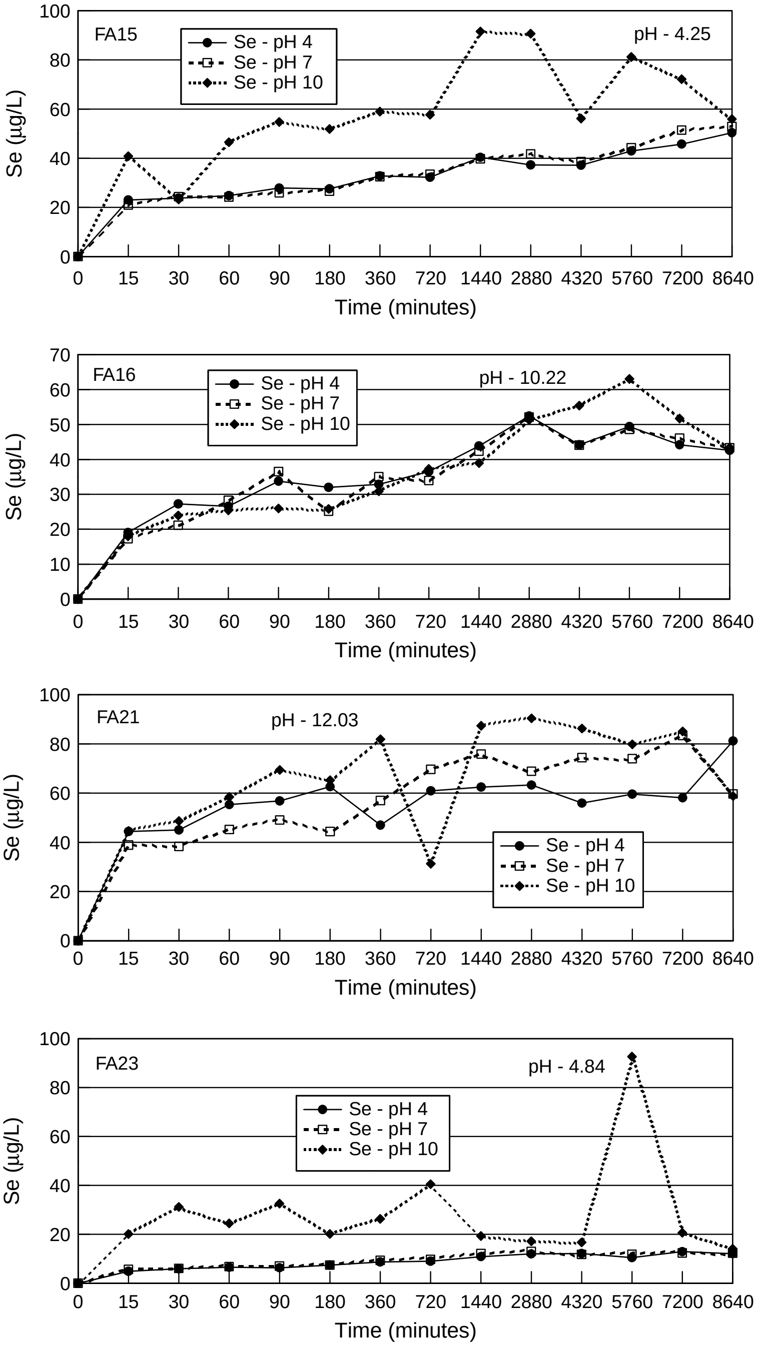

Fig. 9. Changes of Se concentrations with time during leaching tests in contact with fly ashes.

the Se in the solutions with an initial pH of 10 showed higher concentrations than the Se in the solutions of initial pH of 4 and 7 (Fig. 6). Such behaviour for Se is similar to that discussed by van der Hoek et al. [19], who concluded that highest concentrations of Se are leached into solutions having a pH opposite to the natural pH of the fly ash. No evidence for this was found, however, in either of the alkaline fly ashes studied. Leaching solutions in contact with alkaline ashes showed very similar concentrations for all pH solutions.

Selenium has a much lower concentration in the solid phase (raw ash) of all four samples, but the much higher Se concentrations in the leaching solutions show that the Se in the ashes has higher mobility levels than arsenic.

Our study has shown higher mobility of Se from solid phase in contact with alkaline solutions, and hence it is possible that Se is present in oxyanions that are highly soluble in alkaline solutions [27]. This process occurs when As availability is low during leaching, and Se is mobilised to solution faster than As [19].

Se concentration decreases in all alkaline solutions of initial pH of 10 in contact with fly ashes. A plausible explanation for this might be substitution of Se in the structure of ettringite [36].

4. Conclusions

The mobility of trace elements from fly ashes depends not only on the element concentration and mode of occurrence, but also on the chemical conditions associated with the leaching process. This in turn depends on the ash chemistry (acid or alkaline ash) as well as the pH of the leaching solutions used. The following more specific conclusions may be drawn from this study, for Australian ashes exposed to different leaching conditions:

1. The pH values of solutions developed during the leaching process appear to be related to the acidity and alkalinity of the original fly ashes.
2. The acidic fly ashes produced acidic to neutral leachates, with pH values independent of the pH of the solution to which they were initially exposed. However, both of the alkaline fly ashes produced alkaline leachates, all with pH values above 9.5, regardless of the pH of the initial solution used.
3. Increase of pH and HCO_3^- in both alkaline fly ashes is due to the dissolution of $CaCO_3$ and CaO with formation of bicarbonate around neutral and slightly alkaline pH's, and formation of carbonate in solutions at pH values above 10. Any decrease in HCO_3^- is related to precipitation of M-carbonates.
4. The release of trace elements from particular fly ashes is a slow and sometimes complex process, strongly dependent on the pH developed during interaction with the leaching solutions used. Equilibrium between solid phase and solution was not reached during any of the leaching experiments, despite an exposure of 144 h.
5. The highest As concentrations were in leaching solutions having an initial pH of 10. The concentration of As in the leachates was independent of the concentration of As in the fly ashes.
6. Boron has the highest concentration in the leachates of all the elements studied, except for Mo in FA16. The concentration of B in the leachates was closely related to the concentration of B in the fly ashes.
7. Mo concentrations were highest in originally alkaline leachate solutions in contact with acidic fly ashes; leachates in contact with alkaline fly ashes showed the same trend and concentrations with all three leaching solutions.
8. Higher Se concentrations were present in alkaline solutions in contact with fly ashes. Se concentration in leachates shows a similar trend to that of As. During the leaching tests the concentration of Se decreased in all alkaline solutions independently of the pH of the fly ash, possibly due to precipitation or re-adsorption processes.
9. Decrease of B, and oxyanions of As and Se, in leaching solutions in contact with alkaline fly ashes may be also attributed to precipitation of ettringite.

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