

Variations in Element Mobility from Fly Ashes Stored in Different Environments

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ABSTRACT

The leaching characteristics of acid and alkaline PF ashes emplaced below water level for up to around 25 years, and also in dry emplacement installations, has been evaluated by batch testing, using solutions of different initial pH, different liquid:solid ratios and different leaching times. The results were compared to the leaching characteristics of fresh dry fly ash from the relevant power stations, as a basis for predicting the long-term behaviour of coal ash in different types of emplacements.

The fresh dry fly ashes had natural pH values in water ranging from around 4.5 (acid ash) to 12.0 (alkaline ash), with all ashes exhibiting a strong buffering capacity. Ashes from the same power stations stored in water had more neutral pH values than the equivalent fresh dry materials, ranging from 6 to 7 for the acid ashes and 7.5 to 8.5 for the alkaline ashes, depending on test conditions. Dry-stored ashes showed characteristics that were much more similar to the original material. Ashes stored under water for long periods of time and ashes from the same source recently deposited in water both had similar pH characteristics. The water-stored ashes showed a greater variation in pH with different leaching reagents, suggesting a reduction in buffering capacity with the immersion process.

While loss of some mobile elements may take place on contact with water, the different pH values developed in the water-stored ashes, compared to the equivalent fresh ashes, appear to be responsible for changes in mobility of some of the major and minor elements present. These changes suggest that laboratory testing of fresh dry ash alone, especially at its natural pH level, does not necessarily provide guidance on element mobility from the same ashes after they have been stored under water in the short or long term. Ashes stored under dry conditions (above water table) tend to show leaching characteristics closer to those of the fresh dry ash, although changes in pH and mobility may still occur in near-surface samples due to rainfall and other exposure effects.

INTRODUCTION

Approximately 13.5 Mt of coal ash is currently produced in Australia per year. Although a growing proportion is used in areas such as cement and concrete production or for other beneficial purposes, the major portion of this material continues to be emplaced in ponds or on dry disposal sites¹. The ash from Australian coal-fired power stations ranges considerably in chemical composition and mineralogy²⁻³, depending on the mineral matter in the feed coal and the combustion conditions in the power plant. Overall concentrations of environmentally-significant trace elements in these ashes are generally relatively low, compared for example to Chinese or European coal ashes³⁻⁵, but even so responsible ash management requires the potential for release of these elements from the stored ash to be evaluated, and the impacts predicted if possible on the prevailing hydrogeological system.

The trace elements in fly ash may occur as part of the crystalline phases (e.g. magnetite), within the aluminosilicate glass, or as coatings deposited on the surfaces of the individual particles by condensation of elements released from the coal into the furnace gases. Because of their mode of occurrence and chemical form, the elements deposited on the particle surfaces probably have the greatest potential for mobilisation when the ash interacts with water, such as in an ash dam or at a dry disposal site, as well as when the ash is used as a soil amendment, a structural fill or a mine backfilling material.

A critical factor in the mobility of particular elements in emplaced ashes is the pH developed within the relevant ash–water system. Ashes with high proportions of Ca and Mg, for example, in relation to those of adsorbed sulfate ions, may develop a very alkaline pH (11–12) on contact with water⁶. Ashes that do not have significant concentrations of Ca or Mg in relation to the sulfate content, however, typically develop acid pH values (around 4–5)⁷. Fly ash, especially ash with an alkaline pH, also has a relatively strong buffering capacity, and tends to retain its natural pH value to a significant extent even if placed in a contrasting pH environment⁸.

Experimental studies on Australian ashes, combined with the application of hydrogeochemical modelling, has shown that the mobility of many elements from coal ash, including elements of environmental significance, depends significantly on the pH of the ash-water system⁸⁻¹⁰. The purpose of the present study is to evaluate the extent to which the pH of ash-water systems may change over time, due to factors such as immersion in water associated with pond-based storage activities, and the possible relation between those pH changes and the mobility of particular trace elements in the different ash materials.

SAMPLING AND EXPERIMENTAL PROGRAM

Fresh fly ashes (ASTM Class F), and in some cases also bottom ashes, were sampled from several different Australian PF power stations, including ashes with acid and alkaline pH characteristics. Samples were also taken of ashes from the relevant stations recently deposited in storage ponds, using a boat and a clam-shell sampler, and of ashes from the subsurface in previously filled parts of the same ponds, up to 25 years old, using either hand auger or vibro-corer equipment. The ash from a depth of up to 10 m at a dry disposal site was also sampled, for comparison to fresh ash from the same power station.

The ash samples from the ponds were air-dried, and together with the fresh dry ashes and the ashes from the dry disposal site were subjected to chemical analysis for major and trace elements using ICP-AES, ICP-MS and related techniques. Although a number of samples were taken from each hole at the pond sites, only those representing the oldest ash recovered from each hole are reported in the present paper. The air-dried ashes from the relevant intervals in each hole, as well as the air-dried pond sediment, air-dried ashes from the dry disposal site, and the fresh dry ashes sampled at each station, were also subjected to a comprehensive program of chemical and mineralogical analysis. The pond waters, where available, were analysed for their major and trace element components.

A program of batch leaching tests was carried out on each of the air-dried ash samples. The tests were conducted using solutions with initial pH values of 4, 7 and 10, to evaluate the response of the ashes to different chemical conditions. Testing was carried out at room temperature, using liquid:solid ratios of 3.5:1 and 20:1, with shaking times of 1, 3 and 7 days. The leachate from each test was recovered, filtered, and analysed using ICP-OES and ICP-MS techniques. To provide a simple basis for comparison, only the results of the 7-day tests, carried out at a liquid:solid ratio of 3.5:1, are discussed in the present paper. Focus for the present paper is on five elements, B, Al, Cd, Mo and V, to illustrate some of the variations involved.

RESULTS

Water-stored Acid Ash

Figure 1 shows the contrast between the pH and the mobility of selected elements under the test conditions for six samples from a location where ash with a low proportion of Ca and Mg has been emplaced in a fresh water ash pond. The samples in each plot, left to right, represent fresh fly ash, fresh bottom ash, the ash from the bottom of the current pond and three ash samples of increasing age recovered from depths of up to 3 m in the oldest part (up to 25 years) of the pond fill.

The pH of the fresh fly ash under the test conditions varied from 4.4 when the ash was placed in a pH=4 solution to 4.6 when placed in a solution of initial pH=10. This small variation shows the relatively strong buffering capacity of

the fresh dry ash material. The bottom ash, having a different chemical composition, has a pH that ranges from 7.8 to 8.0 under the same test conditions. The ash deposited in water, whether for only a short period of time (the pond sediment sample) or for up to 25 years (the core samples), made up of fly ash with only a small proportion of admixed bottom ash, has pH values between 5.6 and 6.7, reflecting a loss of acid-forming material (probably adsorbed SO_4^{2-}) with the immersion process. The individual water-stored ash samples also show a greater variation than the fresh ash with initial the pH of the leaching solutions, indicating a lesser degree of buffering capacity.

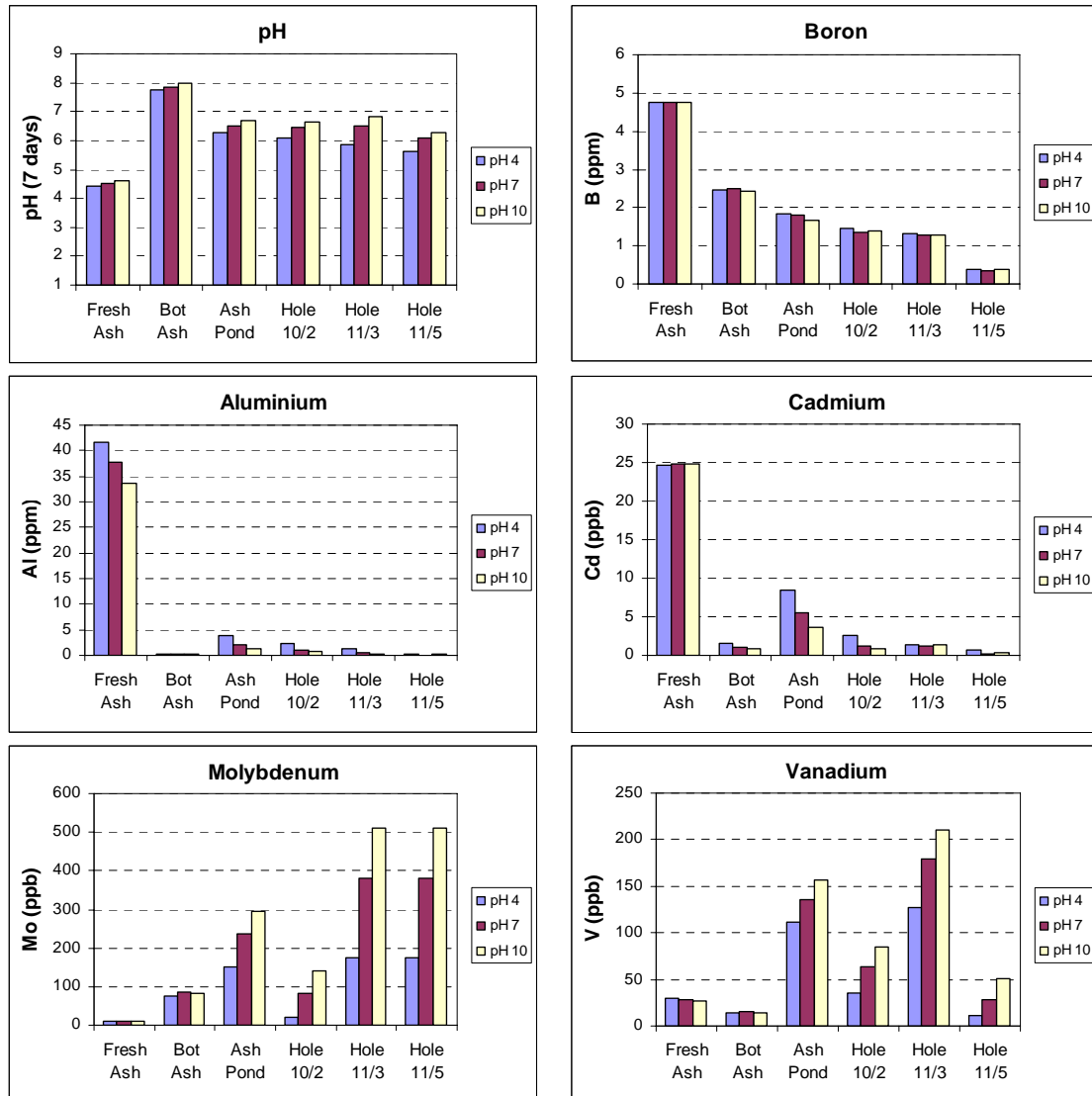


Figure 1: Leachate pH and concentration in the leachate of selected elements from laboratory testing of fresh and water-stored acid ash samples. Leaching time = 7 days; liquid:solids ratio = 3.5:1.

The mobility of some elements, such as boron, seems to decrease steadily from the stored ashes over time. Since the source of the coal for the power station has not changed over the period in question, this may indicate a progressive loss of potentially mobile B from the ash with storage, or possibly a reduction in mobility at the increased pH associated with the stored ash

materials. Hydrogeochemical modelling of boron species from Australian ashes ⁹ suggests that B released as boric acid (H_3BO_3 or $B(OH)_3$) would be very soluble up to a pH of around 7.5. This covers the pH range associated with both the fresh and stored acid ash samples, and hence suggests that the changes in B mobility associated with the stored acid ash represent loss with storage rather than reduced mobility under changed pH conditions. Overall concentrations of B (and also of other elements) in the ash are much higher than the concentrations released into solution, obscuring the small changes that might indicate any loss from the ash with time.

Several other elements, such as Al and Cd, show much lower levels of mobility from the stored ashes than from the fresh fly ash, while still other elements, such as Mo and V, show higher levels of mobility from the stored ashes than from the fresh dry fly ash sample. Because of the constant source of coal supply associated with the power station, it is suggested that at least some of this variation in mobility is due to the changes in pH of the ash-water system associated with the water immersion.

Hydrogeochemical studies ⁸⁻⁹ show that cations such as Al^{3+} and Cd^{2+} tend to be more mobile at low pH values, whereas elements that form oxy-anions, such as Mo and V, are more mobile under neutral to alkaline pH conditions. This is consistent with the higher levels of mobility shown by Al and Cd, especially from the older ashes, in tests at initial pH=4 than in tests at initial pH=10, and with the higher levels of mobility shown by Mo and V in tests with initial pH=10 compared to tests at initial pH=4. The mobility of B, by contrast, does not vary significantly with the initial pH of the leaching test solutions, possibly confirming that pH changes are unlikely to be involved.

Water-stored Alkaline Ash

Summaries of the pH and the concentrations of the same elements in the leachates from the alkaline ash samples are given in Figure 2. The fresh alkaline fly ash had a pH under the test conditions of 11.7 to 11.8, with only a very small difference between the pH in the acid (pH = 4) and alkaline (pH = 7) solutions used. The leachates from the bottom ash had lower pH levels (8.7-9.1). Most of the water-stored alkaline ashes had leachate pH values, depending on the initial solution, that ranged from 8.0 to 8.7. The oldest ash sampled (Hole 1) produced leachates with still lower pH values of 7.4 (initial pH=4) to 7.8 (initial pH=10). These results suggest that, as with the acid ash, the strong buffering capacity of the alkaline fly ash is reduced to some extent by the subaqueous storage process.

The concentration of B in the leachates from the fresh alkaline fly ash was 1.5 to 1.7 ppm, with lower values still from the bottom ash sample. In contrast to the acid ash described above, the leachates from the stored alkaline ashes had B concentrations that were higher than those from the fresh dry ash sample, with values from 3.1 to 5.2 ppm. Although relatively high below pH=7.5, the modelled solubility of $B(OH)_3$ decreases at higher pH levels ⁹. While other forms of B may become more soluble, $B(OH)_3$ would be expected to have very low solubility at pH values above 10.5. This may possibly explain

the low mobility of B from the fresh alkaline fly ash compared to the equivalent water-stored materials.

Much lower concentrations of Al were found in the leachate from the stored alkaline ash samples than from the fresh fly ash material. Together with the high Al concentrations in the leachates from the fresh acid ash (discussed above), this is probably an expression of the amphoteric behaviour of Al in solution, with high solubility at very low and very high pH levels but low solubility over the middle part of the pH range.

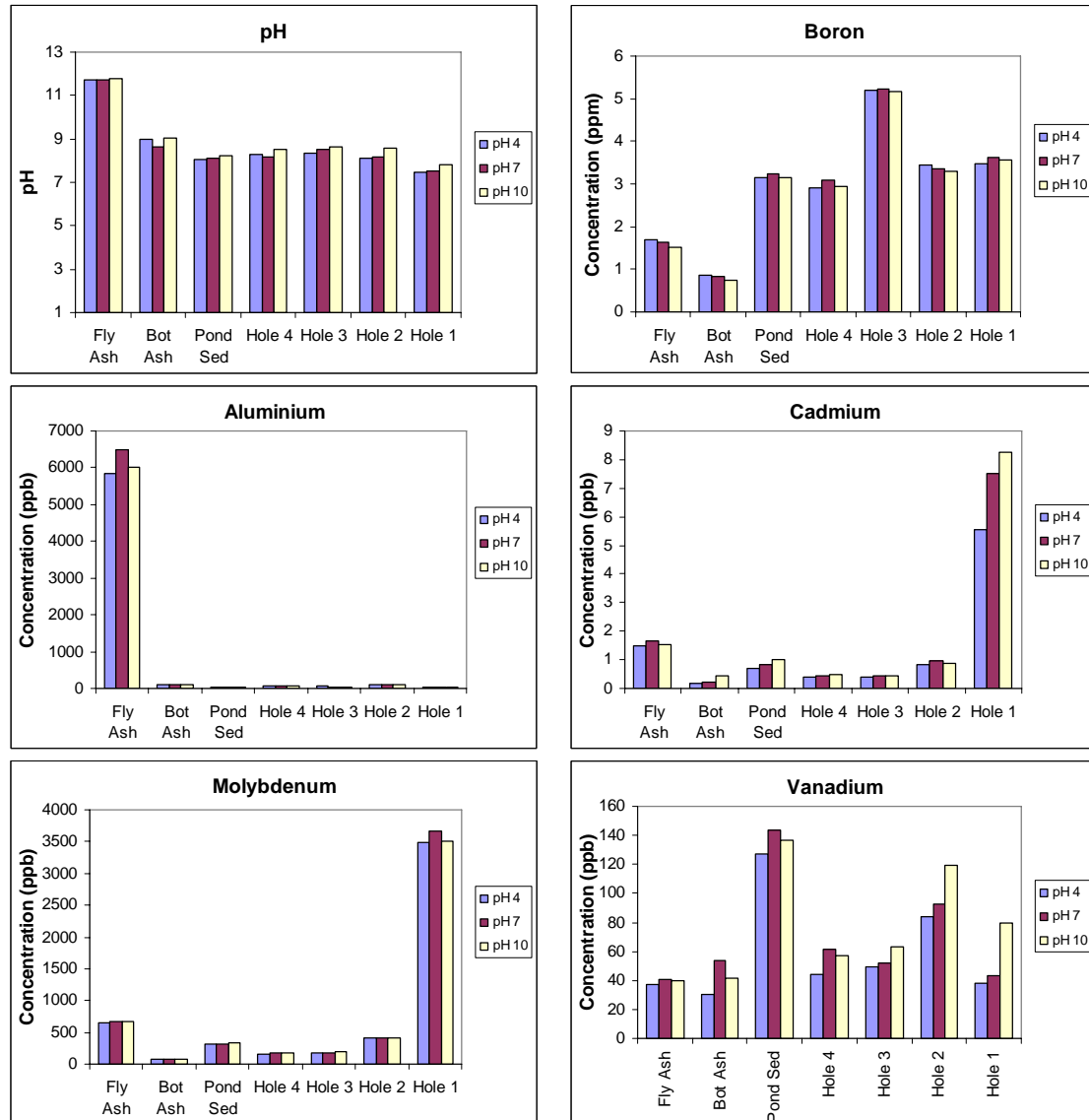


Figure 2: Leachate pH and concentration in the leachate of selected elements from laboratory testing of fresh and water-stored alkaline ash samples. Leaching time = 7 days; liquid:solids ratio = 3.5:1.

The mobility of Cd from the fresh ashes and most of the stored ashes was relatively low (<1 ppb). This is also consistent with the very low Cd concentration (again around 1 ppb) noted in the pond water at the storage site. However, Cd was found to be slightly more mobile (up to 8 ppb under

the experimental conditions) from the longest-stored alkaline ash sample. The oldest ash sample also had the lowest pH value of those tested (7.4 to 7.8), but the contrast with the other stored ashes (pH 8.0 to 8.6) does not appear to be sufficiently large to explain the change in Cd mobility levels. It is also notable that Cd was more mobile from this sample when tested with an alkaline (initial pH=10) rather than an acid reagent (initial pH=4). The ash from the oldest ash had a similar total Cd concentration to the other stored ashes, and the reason for the higher Cd mobility is not clear at the present time.

Although difficult to discern from Figure 2 due to the scale involved, Mo has slightly lower concentrations (160-420 ppb) in the leachates from the stored alkaline ashes than from the fresh alkaline fly ash sample (650-665 ppb). This may reflect decreased Mo mobility at the lower pH levels of the stored ash materials. The leachates from the oldest stored ash (Hole 1), however, have unusually high Mo concentrations. The total Mo concentration in this ash sample was also unusually high compared to the other ashes from the area, including other samples from the same hole, for reasons that are not yet apparent, and this may explain the higher Mo concentrations in the leachates from that particular ash sample.

Similar to slightly higher levels of V mobility were observed in the stored alkaline ashes compared the fresh fly ash sample. Total V in the pond sediment sample was a little higher than in the other ashes, and this may explain the higher level of V mobility observed in the leachate from that particular ash. In some cases V was slightly more mobile when tested in an alkaline (pH=10) solution, but in the majority of samples the initial pH of the leaching solution did not seem to affect the mobility characteristics.

Acid Ash Stored in a Dry Disposal Area

Figure 3 shows the pH and mobility of the same elements from a series of samples at increasing depths (down to around 10 m) recovered from an acid ash emplaced over time at a dry disposal site. Data from two fresh fly ash samples taken from the relevant power station several years apart are included in the plots, along data from with a bottom ash sample.

In contrast to the changes associated with storage under water, the pH characteristics of the dry-stored ash samples are similar to those of the relevant fresh ash samples. The pH of the stored ash increases slightly with depth, from around 5.3 (initial pH = 7) at the surface to around 6.6 in the lowermost samples studied. The buffering capacity, indicated by the difference in pH between the tests at initial pH values of 4 and 10, also seems to be fairly stable, except for development of a high pH value in the bottom-most sample (depth 5) when treated with a pH=10 solution.

Boron mobility from the fresh fly ash in this instance is slightly higher when tested with acid and slightly lower when tested with an alkaline reagent, possibly consistent with the modelled behaviour of boric acid as discussed above. Mobility of B from the stored ash is generally lower than from the fresh

material for tests in neutral and alkaline solutions, but is markedly higher from the stored ash when the ash is leached in an acid medium.

Aluminium mobility is high (up to 1,000 ppb) from the fresh ash and near-surface stored ashes in acid solutions and lower but still significant (around 200 ppb) from the same ashes when treated with an initial pH=7 solution. This probably reflects the pH of the ash-leachate system in each case. Al mobility is lower from the deeper ash samples, probably due to the still higher pH levels. It increases in some samples (e.g. the bottom ash) when tested with an initial pH=10 solution, probably reflecting the amphoteric behaviour of Al in aqueous solution generally.

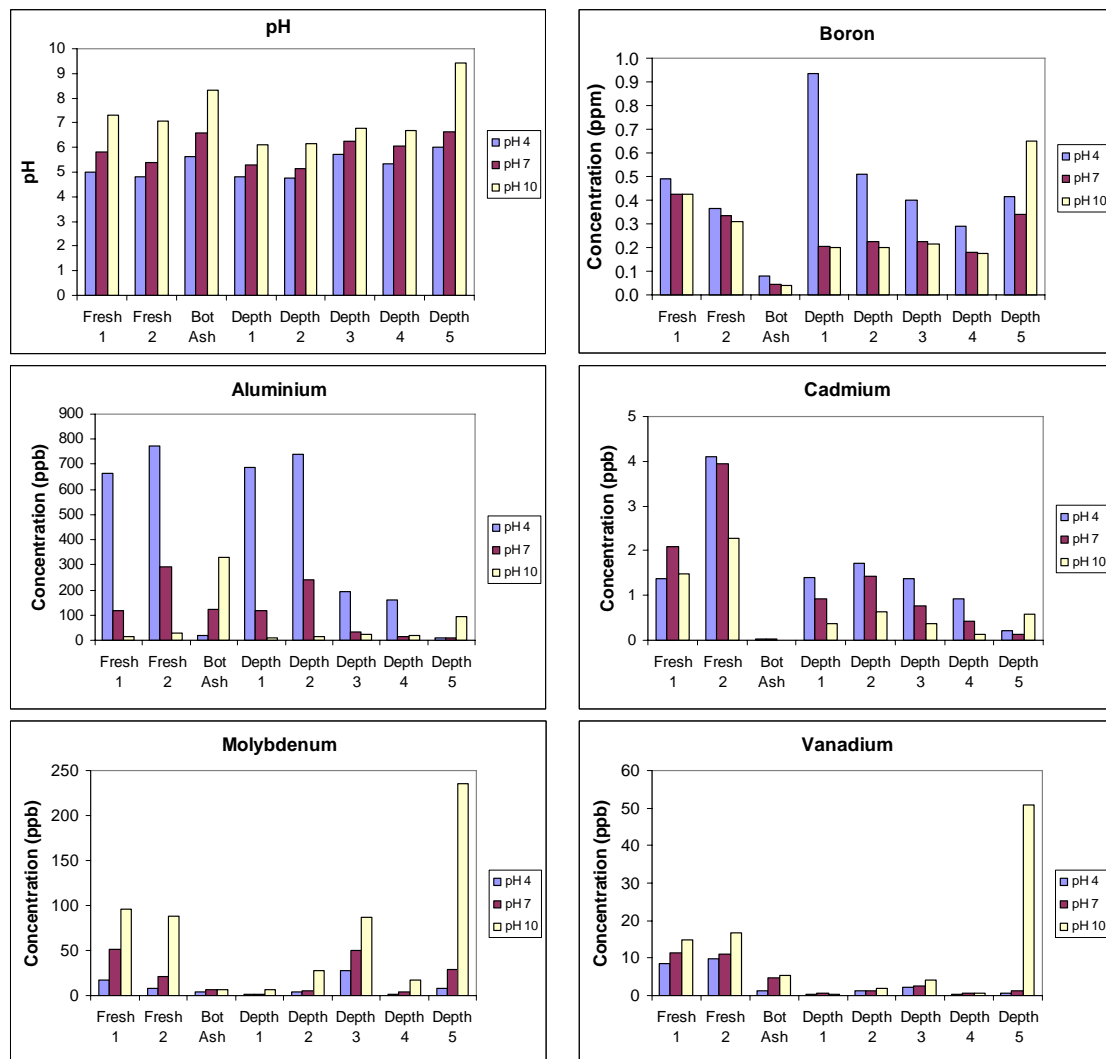


Figure 3: Leachate pH and concentration in the leachate of selected elements from laboratory testing of fresh and dry-stored acid ash samples. Leaching time = 7 days; liquid:solids ratio = 3.5:1.

The mobility of Cd from both the fresh and stored ashes is overall very low (<5 ppb). It is lower from the stored ashes, especially those from the deeper parts of the deposit, than from the fresh fly ash material. As with Al, the mobility of

Cd is also slightly higher from the acid treated samples and lower from those tested with the alkaline (pH=10) solution.

Unlike the acid ash stored under water, the mobility of Mo and V from the dry-stored acid ashes appears to be lower than from the fresh fly ash material. Mobilities of these elements are, however, higher from each sample when tested in an initially alkaline (pH=10) solution, and lower when the respective ashes are tested with an initially acid (pH=4) solution. Although the ashes are from different sources, the pH levels in the dry-stored acid ash samples appear to be lower than those in the water-stored acid ash materials, thus providing a possible explanation for the lower Mo and V mobilities associated with the dry storage emplacement.

CONCLUSIONS

This study has indicated that the mobility of many elements from ashes stored under water, even for relatively short periods of time, may be significantly different to the mobility of the same elements from equivalent fresh dry ash samples. In some cases, for example with Al and Cd from acid ashes and with Al from alkaline ashes, the mobility from the water-stored ashes is indicated to be less than that of the same element from the fresh ash materials. In other cases, such as with Mo and V from the acid ash, and possibly with B from the alkaline ash, the mobility from the water-stored materials may be higher than from the equivalent fresh dry ash components.

These differences in element behaviour appear to be largely associated with changes in the pH of the ash water system. For the water-stored acid ash, elements mobilised in cation form, such as Al^{3+} and Cd^{2+} , become less mobile as the pH moves to more neutral values after immersion, and thus become increasingly immobile with longer storage times. Possibly due to mobilisation as boric acid, but more likely due to progressive loss from the ash with time, B also appears to be less mobile from the water-stored than from the fresh acid ash sample. Elements expected to be mobilised as oxy-anions, however, such as Mo and V, appear to become more mobile from the acid ash with water storage, due to increased solubility at more neutral pH levels.

These contrasts appear to be less evident for a different acid ash emplaced under dry storage conditions. The pH and buffering capacity of the ash in this case appears to have remained essentially constant with storage, as does the mobility of the elements considered in this paper. Al, B and to a lesser extent Cd, however, were somewhat more mobile when the stored ashes were subjected to leaching by an acid (pH=4) solution, and Mo and V showed greater mobility from some ash samples when treated with an alkaline (pH=10) leaching reagent. Such observations further confirm the role of pH as a significant factor in controlling both cation and oxy-anion mobility.

A significant move towards neutrality (i.e. a decrease in pH) and a decrease in buffering capacity were noted for the alkaline ash with water storage. Although Al was also mobile at the high pH of the dry alkaline fly ash, due to the amphoteric nature of that element, Al mobility was much lower from the lower-

pH water-stored alkaline ash samples. Boron mobility, on the other hand, was slightly higher, possibly due to increases in boric acid solubility at decreasing pH levels. With the exception of one sample for which the results are still being investigated, the mobilities of Mo and Cd from the water-stored alkaline ash samples were slightly lower than from the equivalent fresh ash material. In contrast to Mo, however, the mobility of V was slightly higher from the water-stored alkaline ashes than from the fresh ash sample.

The overall results of the study suggest that the different pH values developed in the water-stored ashes, compared to the equivalent fresh ashes, are at least partly responsible for changes in mobility of the different elements studied. An implication of this observation is that laboratory testing of fresh dry ash alone may not necessarily provide guidance on element mobility from the same ash after storage under water in either the short or long term. This appears to apply especially to acid ashes, but is also relevant for some elements at least (e.g. Al, B) in alkaline ash materials.

Ash (in this case acid ash) that is stored under dry conditions (above water table) appears to show leaching characteristics closer to those of original the fresh dry material, and thus laboratory testing of fresh dry ash may still be a useful guide to longer-term leaching behaviour. Changes in pH and element mobility may nevertheless still occur in near-surface parts of dry deposits, due to rainfall and other exposure effects, and these could be further investigated by laboratory tests of appropriately treated ash samples.

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