

Fine Ash Leaching in Tailings Dams – An Impact on the Underlying Aquifers?

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Abstract

Fine ash is a by-product generated during coal combustion and gasification at power stations around the world. The majority of fine ash is stored on tailings dams over decades where it is influenced by weathering processes. In the presence of water, weathering causes dissolution of fine ash components which may be transported along preferred pathways through the tailings dam or re-precipitate. This study aimed to investigate the leaching behavior of fine ash and to evaluate the impact of long-term leaching on the underlying aquifers. Fresh and weathered fine ash samples were collected from different depths of a tailings dam in Mpumalanga, South Africa. A kinetic leaching test was conducted to analyse the leachate composition, calculate the release rate of major ions and trace elements of environmental concern and to compare the leachate composition with the groundwater chemistry. Leaching results showed that the release rates of elements including Ca, B, Ba and Al decreased with depth and age of the fine ash while it increased for V, Mo, Cu, Mn, Si, Li, Cr and SO₄. A constant release rate was measured for Se, Fe, Na, Mg, K, NO₃ and Zn. The main components of the fine ash leachate (SO₄, Ca, Na, Cl, Mg and K) were found to influence the water composition of the underlying aquifers. Downstream of the tailings dam, the water type of the shallow aquifer changed from Ca/Mg/SO₄/Cl/NO₃ to NaSO₄/Cl with a significant increase in Na, K and decrease in Ca and Mg over time. A reverse trend in water type alteration was observed in the deeper aquifer. This confirmed that the leachate plume moved laterally and vertically from the shallower to the deeper aquifer and that the underlying clay strata were insufficient in retaining the leachate from the tailings dam.

Key words: fine ash, leaching, tailings dam, aquifer

Introduction

South Africa is heavily dependent on its coal production to generate low cost electricity by coal-fired power stations to meet the growing energy demand. During coal combustion, high quantities of by-products are generated including fly, bottom and gasification ash (Mahlaba *et al.* 2011). South Africa produces approximately 30 Mt of fly ash annually, making it the fourth largest fly ash producer in the world (Furter 2011). For disposal purposes, the combustion by-products are mixed and screened into a particle size range between 0.01 µm and 250 µm and above 250 µm, forming fine and coarse ash respectively (Mahlaba *et al.* 2011). Approximately 5% of the generated fine and coarse ash is recycled; the remainder is disposed separately on tailings dams either hydraulically or via conveyor belts (Gitari *et al.* 2009).

The chemical composition of fine ash is influenced by the coal constituents, the materials added during combustion, the combustion process itself and on the pollution control technology applied (Neupane and Donahoe 2013). Major fine ash components include SiO₂, Al₂O₃, Fe₂O₃ and CaO (Gitari 2006; Mahlaba *et al.* 2012). Minor oxides are MgO, Na₂O, K₂O, P₂O₅, TiO₂, MnO and SO₃ (Mahlaba *et al.* 2012). A wide variety of trace elements may occur in fine ash which differs depending on the coal composition (Akynemi *et al.* 2012). In addition, the high specific surface area and small particle size of fine ash favours the accumulation of trace elements and results in a high chemical reactivity (Gitari 2006).

The disposal of fine ash on tailings dams over decades poses a potential threat to the environment if heavy metals leach into the surrounding area due to weathering. Weathering processes occur in physical, chemical and biological forms and are influenced by temperature changes, precipitation and

pressure within the tailings dam (Selby 1993). Chemical weathering processes include dissolution and precipitation of minerals, cation exchange, reduction and oxidation as well as hydration and hydrolysis which may alter the composition of fine ash over time (Price 2009). Ingressing CO₂ from the atmosphere and the infiltration of rain water are the main causes for changes in pore water pH, which control the mobility of several elements and consequently the leachate composition of fine ash (Gitari *et al.* 2009).

The leaching capacity of fine ash and the extend of environmental pollution depends on the chemical composition of the ash, and the type of disposal, wet or dry, which may enhance or reduce the leaching of toxic elements into the environment. The literature has been controversial about the effects of fine ash disposal on the environment. Research conducted on the leaching potential of fine ash by Mahlaba *et al.* (2011) and Matjie *et al.* (2005) indicated that no significant leaching of toxic elements took place from fine ash tailings dams into the environment. Carlson and Adriano (1993) conversely observed that fine ash which was disposed in form of saline slurry in drying ponds showed enhanced leaching of toxic elements into the environment. Jones (1995) found that elements such as B, Cd, Cr, Co, Se and As leached from fine ash dams which are harmful to fauna and flora, even at low concentrations. In addition, leaching tests conducted on fine ash produced by Sasol and Eskom often revealed major soluble ions such as Ca²⁺, Na⁺, SO₄²⁻, K⁺ and Cl⁻ (Gitari *et al.* 2009; Matjie *et al.* 2005). These ions can be problematic to the environment as their concentration in solution cannot be controlled (Matjie *et al.* 2005).

The purpose of this article is to describe the leaching chemistry of fresh and weathered fine ash and to assess the influence of fine ash leaching on the underlying shallow and deeper aquifer. Each tailings dam is a unique system due to its heterogeneity in chemical composition and layering of alternating grain sizes. Therefore, this research aimed to add to the understanding of fine ash leaching through a tailings dam profile to predict the impact of long-term ash storage on the environment.

Materials and Methods

Twenty-four weathered fine ash samples were collected from the terraces of a tailings dam and one fresh ash sample was collected from the surface of a tailings dam in Mpumalanga, South Africa. Three samples were collected per terrace, dried, well mixed and thereafter combined to one composite sample. X-ray fluorescence (XRF) was utilized to determine the chemical composition for each sample. Each composite sample was split with a riffle splitter to a sample size of 1 kg for kinetic leaching. In total, eight composite samples and one replicate were leached over a test period of 21 weeks by using humidity cells.

The humidity cells were constructed according to option B described in the ASTM D5744-13 (2013) guideline with several alterations. The cell height was changed to 12.5 cm and the outer and inner diameter was altered to 19.9 cm and 19.45 cm respectively due to the dimensions of the PVC pipe available. The filter medium was composed of 2 mm thick polyester felt positioned on top of the perforated plate. An inlet was added at the upper part of the humidity cell for the inflow of moist and dry air according to Price (2009). A drainage outlet was constructed at the bottom side of the humidity cell (fig. 1). The humidity cell test procedure was conducted according to the ASTM D5744-13 (2013) guideline.

Inductive coupled plasma/optical emission spectrometry (ICP/OES) with the aid of a Perkin Elmer Optima 3000 DV ICP system was applied to analyse the chemistry of the obtained leachate. For each humidity cell sample, the pore volume (V_p) was calculated with the following equation:

$$V_p = \frac{\text{weight of saturated sample} - \text{weight of dry sample}}{\rho_w}, \text{ where } \rho_w \text{ is the density of water: } \rho_w = 1.01 \frac{\text{g}}{\text{cm}^3}.$$

The leachate chemistry results were normalised against the exchanged pore volume (EPV) of each fine ash sample and compared to the sample depth of the tailings dam. In addition, the leachate chemistry of the fine ash was compared to the groundwater chemistry of five boreholes obtained during 25 years of monitoring in the vicinity of a fine ash tailings dam. The boreholes were located downstream of the groundwater flow direction and included two shallow (BH1S, BH2S) and one deep aquifer intersecting boreholes (BH1).

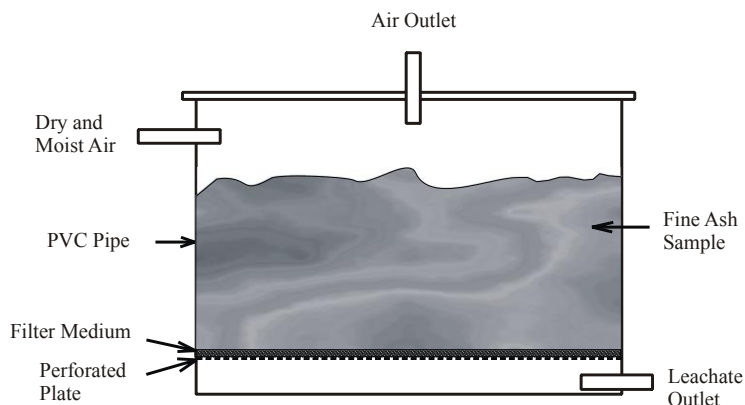


Figure 1 Humidity cell design with alterations (modified from Price 2009).

Results and Discussion

Chemical Composition of Fine Ash

An XRF analysis of the fresh and weathered fine ash samples indicated that the chemical composition contained major oxides SiO₂, Al₂O₃, CaO, Fe₂O₃, and minor oxides MgO, TiO₂, Na₂O, K₂O, P₂O₅ as well as MnO. A broad spectrum of trace elements were detected in both fresh and weathered fine ash which varied in concentration due to the alternating composition of the coal source. XRF-results indicated that the fresh fine ash was on average more enriched in trace elements As, Br, Co, Cr, Nb, Pb, Rb, V and Y. Most of these trace elements occurred as oxyanions and were therefore more readily leached from the negatively charged fine ash particle surface at a high pH (9.4). Consequently, weathered fine ash was more depleted in trace elements, as they were rinsed off from the particle surfaces during leaching.

Leachate Composition

The average concentrations of readily soluble components detected in the fine ash leachate after 21 weeks of induced weathering are indicated in Table 1. Sulfate, Ca, Na, Cl, Mg and K were highly soluble in fresh and weathered fine ash. This was mainly caused by the interaction of fine ash with brine during disposal that formed soluble salts on the particle surface. These salts were readily dissolved during leaching.

Table 1 Average concentrations and standard deviation (±) of readily soluble fine ash components after kinetic leaching over 21 weeks.

Soluble components	Concentration (kg/t)
SO ₄	2.67 ± 1.13
Ca	0.74 ± 0.26
Na	0.56 ± 0.53
Cl	0.41 ± 0.47
Mg	0.10 ± 0.08
K	0.09 ± 0.04
B	0.027 ± 0.009
NO ₃	0.022 ± 0.019
Si	0.007 ± 0.003
Li	0.004 ± 0.003
Al	0.003 ± 0.001
Cr	0.002 ± 0.001

Leaching Profiles of Major and Minor Elements

The average release rates of major (Si, Al, Fe, Ca and M-alkalinity) and minor (Mg, Na, K, Mn, NO₃ and SO₄) fine ash components as well as trace elements were compared to the depth of the tailings dam (fig. 2). It was found that most elements were released at a higher average rate from the fresh fine ash compared to weathered fine ash. This was caused by elements being concentrated on the relatively big surface area of the fine ash particles during cooling after combustion. Elements which did not show an increased release rate in fresh fine ash compared to weathered fine ash included K, Fe and Mo. This suggests that a large amount of these elements was locked in the ash matrix and was rather gradually released during weathering of the fine ash particles. Potassium is particularly known to be absorbed into the fine ash particle during amorphous clay formation, leading to a relative constant concentration in the leachate.

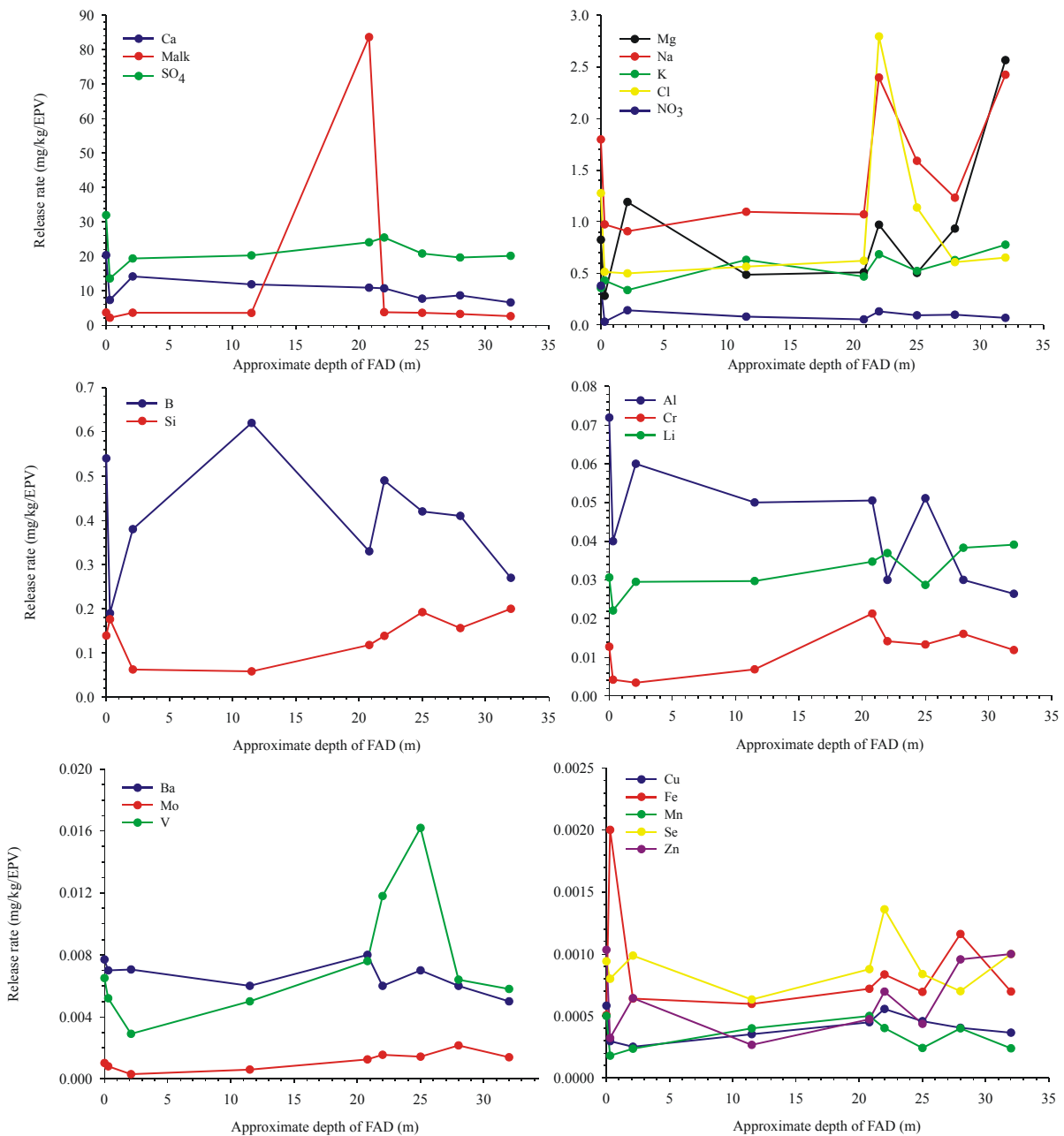


Figure 2 Leaching rate profiles of major and minor components and trace elements in fine ash normalised to exchanged pore volume (EPV).

At a depth of circa 0.3 m from the top of the tailings dam, the release rate of Ca, Mg, SO₄, NO₃, B, Al, Li, Se, Mn and Zn was substantially lower, whereas Fe and Si had an increased release rate (fig. 2). It is suggested that the low release rates were influenced by the precipitation of less soluble secondary mineral phases in the presence of atmospheric CO₂ and water reducing the release rates at shallow depth. The high release rate of Fe was attributed to the elevated Fe concentration in the fine ash collected at 0.3 m depth which was a result of the addition of Fe-rich catalysts during the combustion process.

At approximately 2.1 m depth, the release rate of Ca, Mg, NO₃, Al, Se and Zn was elevated compared to other major, minor and trace elements (fig. 2). This could be a result of ingressing atmospheric CO₂ at shallow depth forming carbonic acid which in turn dissolves carbonate minerals and glass particles. The formation of carbonic acid also led to higher concentrations of HCO₃⁻, Ca²⁺, Mg²⁺, NO₃⁻ and associated trace elements Al, Se, and Zn ions in solution. During evapotranspiration near the surface, these ions then precipitated as carbonate and sulphate minerals as well as amorphous clay if oversaturated. Gitari *et al.* (2009) also noted that enhanced weathering took place at the upper layer of a tailings dam where carbonates formed in the presence of atmospheric CO₂ and water.

Except for the leaching rates varying at shallow depth, three general trends of release rates with increasing depth were observed in the unsaturated zone of the tailings dam:

- Elements which had a decreasing release rate with depth (Ca, B, Al and Ba);
- Elements which had an increase in release rate with depth (V, Mo, Cu, Mn, Si, Li, Cr and SO₄);and
- Elements which had a constant release rate throughout the depth of the tailings dam (Se, Fe, MAIk, Na, Mg, K, Cl, NO₃ and Zn).

The declining release rates of Ca, Al, B and Ba suggests that these elements are progressively leached over time and lower concentrations are therefore available to be leached from the deeper and older fine ash samples. In addition, during prolonged weathering, Ca and Al continuously precipitate to form an amorphous crust on the fine ash particles which alters into crystalline clays which are less soluble (Janssen-Jurkovicová *et al.* 1994). Barium and B could co-precipitate with amorphous clay and other secondary mineral phases which could decrease their solubility with depth and age of the tailings dam.

An increase in release rate observed with depth of most trace elements could be explained by their concentrations increasing relative to the other elements in the leachate solution which were more likely to precipitate or adsorb onto mineral surfaces in an alkaline environment. Oxyanions such as V, Mo, Cr (VI) and SO₄ are expected to be leached and transported from upper to lower fine ash layers as they are more soluble under alkaline conditions due to the increased negative charge of the fine ash particles (Jones 1995). An increase in the Si release rate with depth represents the gradual dissolution of primary silicate minerals present in the fine ash (Brubaker *et al.* 2013).

Elements which had a constant release rate throughout the unsaturated zone of the tailings dam suggested that their dissolution and precipitation had reached an apparent steady state in the system. The solubility of these elements was most probably controlled by the dissolution rate of major mineral phases containing these elements.

An elevated release rate of all major, minor and trace elements of interest was observed in the saturated zone at 22 m and 25 m. This could be a result of percolating rain water mobilising highly soluble elements over time. These elements may be transported through the tailings dam to lower layers where they accumulate and become supersaturated. A higher moisture content (57%) and lower pH (9.2), measured in the deeper layers towards the middle of the tailings dam, enhance the dissolution of soluble salts and the precipitation of less soluble hydroxide and carbonate minerals facilitated by a long interaction time between the pore water and ash.

Implications of Leaching on the Groundwater Chemistry

Long-term monitoring of boreholes downstream of the tailings dam over 25 years showed changes in groundwater over time. The shallow aquifer (BH1S) altered from a Ca/Mg/SO₄/Cl/NO₃ water type to a

NaSO₄/Cl water type over time (fig. 3). This was caused by increasing concentrations of Na, K and Cl and decreasing concentrations of Ca and Mg. Calcium and Mg were precipitated as oxides and/or exchanged with other ions in the rock matrix and were hence attenuated in the plume migration process. The low alkaline pH in the pore water also promoted the release of Na, K and Cl from the host rock due to a lower CEC.

An opposite trend in the water type alteration was observed in the deeper aquifer (BH1). The water type of the deeper aquifer changed from a NaSO₄/Cl to a Ca/Mg/SO₄/Cl/NO₃ water type (fig. 3). This indicates that movement of the fine ash leachate plume occurred from the upper to the deeper aquifer containing the most readily soluble ions Ca²⁺, Mg²⁺ as well as Na⁺, SO₄²⁻, Cl⁻ and NO₃⁻ observed from fine ash leaching and the addition of brine during hydraulic fine ash disposal. The initial analysed NaSO₄/Cl water type may have either originated from the local geology of alternating shale, sandstone and mudrock or from the addition of brine over many years of ash slurry deposition in the vicinity prior to the monitoring program or a combination of the two.

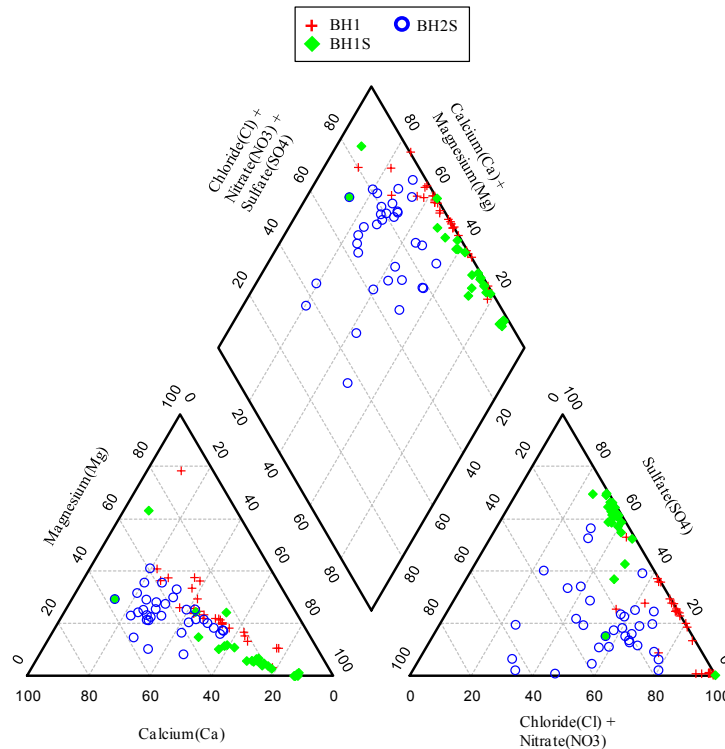


Figure 3 Piper diagram indicating the groundwater chemistry of boreholes downstream of a tailings dam.

In addition to monitoring boreholes BH1 and BH1S, the adjacent shallow borehole BH2S was also affected by the downward migration of the fine ash leachate plume. Its water type altered from a CaMg-bicarbonate to a Ca/Mg/SO₄/Cl/NO₃ water type. Over time, the Ca and Mg concentrations decreased in the groundwater, while the concentrations of K, Cl and NO₃ increased due to leaching from dissolved salts in the fine ash tailings dam and possibly ion exchange in the host rock. The CaMg-bicarbonate water type could either be the natural water type derived from carbonaceous shales or more likely formed by percolating mine water from the ash disposal site. Similar results were also found in a study conducted by Spadoni *et al.* (2014) on the impact coal ash disposal has on the water quality. The groundwater was often found to be high in bicarbonate as a result of the addition of treated industrial water on the disposal site. Calcium and Mg decreased slowly in the groundwater because of processes involving cation-exchange, redox reactions and sorption/precipitation.

Borehole BH2S was monitored prior to most other boreholes and contained higher concentrations of Si and heavy metals (B, Fe, Mn, Cu, Cr, V and Zn) between 1990 and 2000, compared to that of other boreholes monitored from 2000 to 2014. This indicates a fast release of readily soluble elements from the surface of the fine ash particles during the early stage of fine ash leaching. Over time, the leached

concentrations declined in the groundwater due to a slow release from less reactive primary and secondary minerals.

Aluminium, Mn, Si and Fe concentrations were very high in the shallow aquifer compared to the deeper aquifer during earlier years of monitoring. These initial high concentrations however declined rapidly to low and stable concentrations in the groundwater due to sorption onto particles of the host rock matrix as well as precipitation as (oxy)hydroxides. These processes most likely attenuated the metal transport in the leachate plume. A rapid decline in Al and Mn concentration and a lower but constant Fe concentration were also observed in the deeper aquifer because of further sorption and hydrolysis processes. The concentration of Mn and Fe remained relatively constant but high in solution when compared to the other detected metals in the groundwater. These elevated Mn and Fe concentrations were caused by their high solubility during fine ash leaching and possible further dissolution of Fe (oxy)hydroxides in the presence of a low groundwater pH. The B concentration increased during a period of 14 years in the groundwater of both shallow and deeper aquifers due to continuous leaching of B from the tailings dam. Boron occurs as an oxyanion which is not very likely to be adsorbed by clay and fine ash particles at a high pH as result of their high negative charge. Electrostatic repulsion between BO_3^{3-} ions and fine ash particles as well as minerals in the host rock enhances the leaching of B and increases its concentration in the groundwater over the years.

In general, most trace element concentrations in the shallow and deeper aquifers were high during the early onset of monitoring and then declined drastically to concentrations below the detection limit. This shows that most of the heavy metals detected were controlled by sorption and co-precipitation with oxides and hydroxides. Trace elements Li and Cr were found to rapidly leach from fresh and weathered fine ash at relatively high concentrations, but had too low concentrations to be detected in the groundwater. This suggests that these elements were mostly absorbed in the tailings dam. Barium, B, Cu, V and Zn were found in the groundwater indicating that fine ash was not able to store these trace elements under alkaline conditions, partly due to their oxyanionic properties.

Conclusions

Kinetic leaching indicated that the major and minor fine ash components, SiO_2 , Al_2O_3 , CaO , MgO , Na_2O and K_2O were leached at the highest rate from fresh and weathered fine ash and hence dominated the leachate chemistry. Overall, the highest release rates of most fine ash components were observed in fresh fine ash and in the saturated zone of the tailings dam. Three different trends of fine ash leaching were identified in the unsaturated zone of a tailings dam profile:

- Elements which had a decreasing release rate with depth (Ca, B, Al and Ba);
- Elements which had an increasing release rate with depth (V, Mo, Cu, Mn, Si, Li, Cr and SO_4); and
- Elements which had a constant release rate throughout the tailings dam profile (Se, Fe, MAlk, Na, Mg, K, Cl, NO_3 and Zn).

Elements which were released at high rates were found to dominate the groundwater type in the shallow and deeper lying aquifers in the vicinity of the tailings dam. As a result, the chemical composition of the groundwater surrounding the tailings dam was dominated by a Ca/Mg/ SO_4 /Cl/ NO_3 water type. Major and minor elements and trace elements Ca, Mg, SO_4 , K, Cl, Al, Si, Fe, Ba, B, Mn, Cu, V and Zn were found to leach into the groundwater and could pose a potential threat of groundwater pollution.

However, weathering processes such as secondary mineral precipitation, sorption of elements to negatively charged fine ash particle surfaces under alkaline pH as well as ion exchange were able to attenuate the leaching process of readily soluble elements. The formation of less soluble secondary mineral phases including amorphous clay, carbonates and Fe and Mn oxides co-precipitated a substantial amount of heavy metals. Furthermore, a low hydraulic conductivity of fine ash, the compacted and hardened surface of the tailings dam as well as the alkaline system lead to the storage of most heavy metals and toxic trace elements associated with fine ash leaching.

Each fine ash disposal site should be closely monitored as the leachate chemistry and leaching behavior is site specific. Leaching should be prevented and minimised by lining tailings dams with an impermeable layer prior to construction. A vegetation or clay cover after closure could also reduce the infiltration of precipitation and hence the leaching of fine ash.

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