Research Article

Heavy Metal Removal from Incineration Bottom Ash through Washing with Rainwater and Seawater

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Abstract

The use of incineration bottom ash (IBA) for practical applications requires overcoming the environmental impacts from its use. As IBA contains numerous potential pollutants, especially heavy metals, the use of IBA for practical applications would expose the surrounding environment to risks of heavy metal pollution. One possible, practical way to overcome the problem is pre-treat IBA through washing with naturally collected waters like rain and seawater. Repeated washing with fresh batches of rain or seawater each week over fifteen weeks could reduce heavy metal content by 6-7%. The final concentrations of heavy metals in the wash water were reduced to 27-57% of the initial concentration. However, the reductions varied greatly among the different heavy metals. Only half of the heavy metals analyzed showed a decreasing trend with increasing number of washings for both rain and seawater. Specifically, the final concentrations of all heavy metals in rain water were below the National Environment Agency's watercourse discharge limits, except for copper, while washing with seawater could reduce all heavy metals below the discharge limits. Antimony and arsenic concentrations did not show decreasing trend with increasing washings with both rain and seawater.

Keywords: Incineration bottom ash (IBA); Heavy metals; Leaching; Seawater; Rainwater

Introduction

Incineration bottom ash (IBA) is the major solid fraction from the combustion of solid wastes. IBA is a major form of solid waste that is currently disposed-off in landfills around the world, posing challenges to environmental health. In countries such as Singapore, land scarcity and public health concerns severely limit the amount of landfill space and locations available to dispose of over 580,000 tonnes of IBA every year [1]. Therefore, an alternative is to reuse IBA as secondary raw materials. It has been shown that IBA could be used as aggregates [2,3], road building materials [4,5], cement production [6-8], concrete production [9,10], glass and ceramic production [11] and in civil engineering applications such as embankments and landscaping [12] and land reclamation material [13,14]. Despite its numerous possible uses, only a small number of countries are currently actively utilizing IBA [15].

A primary concern is IBA's chemical stability in the environment, especially the potential leaching of heavy metals [16]. Numerous studies have shown that heavy metals could be mobilized from IBA and transported to its surrounding environment [5,17-19], increasing the availability of heavy metals to its immediate vicinity. As the toxicity of many heavy metals is high even at low concentrations [20-22], the risks of heavy metal pollution is the main quality criterion for IBA utilization [16].

Therefore, pre-treatment of IBA to reduce its heavy metal content would be a key process stage towards IBA utilization. Several studies on the washing of incineration ashes have focused on different washing methods and contaminants, but with generally similar conclusions.

Washing of IBA before utilization is necessary not only to reduce heavy metal content, but also to improve their mechanical properties [23].

Previous works on the washing of incineration fly ash showed that simple washing with water could reduce heavy metal content significantly [24,25]. This was despite the fact that fly ash had higher proportions of heavy metals than bottom ash [26]. Jiang [24] washed fly ash with distilled water at various liquid-to-solid ratios (L/S) ratios and found that chromium was removed the most (> 12%) among the heavy metals analyzed. The washed fly ash also had better stability than raw ash, due to the removal of network modifiers, including alkali metals and alkaline metal oxides such as Na, K, and Mg [24]. Thus, similar mechanisms for heavy metal removal could be present for IBA.

For bottom ash, Arickx et al. [27] used one extraction step with a 0.2 M ammonium citrate solution and three washing steps with distilled water. This process was found to decrease metal leaching to below the regulatory limits. Arickx et al. [27] used different concentrations of ammonium citrate to wash IBA, followed by one to three washings with DI water. They found that higher concentration of ammonium citrate could wash out more heavy metals. More heavy metals could also be removed with increased number of washings with ammonium citrate, but in both cases, subsequent leaching test showed high heavy metal concentrations, indicating that heavy metal removal by ammonium citrate washing alone was not effective. However, further washings of IBA with DI water after ammonium citrate washing was found to reduce leachate heavy metal concentrations subsequently [27-30]. Therefore, washing IBA with water was more effective than chemicals in reducing heavy metal leaching.

It was analyzed eight heavy metals in IBA and its leachates after one washing with water for six hours at L/S of 5. They found that heavy metal leaching was reduced by 80% after the single washing. Yang et al. [31] washed IBA with tap water under varying L/S ratios and different number of washings. Washing with reflux, i.e. recirculating the same

water to wash BA lead to increased amount of heavy metal dissolved in the wash water, reaching concentrations that exceeded the effluent standard limits. Using a higher initial L/S ratio or washing multiple times with fresh water could reduce heavy metal content in both IBA and the wash water. Their results indicated that repeated washing of IBA with fresh water was most effective in reducing heavy metals, significantly. Yang et al. [31] also found that the removal of ions, especially chloride, affected electrical conductivity, with high correlations between electrical conductivity and chloride content. Thus, a reduction in electrical conductivity of the wash water could indicate the effectiveness of the IBA washing efforts.

While washing of IBA had been proven to improve its properties, detailed investigation in the washing with natural waters such as rain or seawater had not been carried out. In order to assess the potential of IBA for full scale application, washing tests were carried out on IBA with collected rain water or seawater. Heavy metal concentrations in the wash waters were then analysed.

Experimental

Materials

IBA was collected at a local incineration plant in Singapore. Metal parts were separated from the ash at the plant after incineration. About one kilogram was removed and manually sorted to remove large pieces that are unsuitable for experimentation. The IBA sample was then further separated with a sieve size of 4.5 millimetres. The fraction passing through the 4.5 mm sieve was used for experimentation. Elemental analysis of this sieved IBA was performed with ICP–OES within one month using BS 1377-3: 1990 Methods of test for soils for civil engineering purposes (Part 3: Chemical and electro-chemical tests) (Table 1) by a commercial, government- accredited laboratory.

The heavy metal content analysis of the Singapore IBA is shown in Table 1. The levels of minerals and metals, particularly Cr, Cu, Pb and Zn, can be considered very low compared to literature values [29-31]. The relatively lower heavy metal content in Singapore IBA would suggest that heavy metal removal from IBA is relatively easier compared to other countries. IBA with different origins thus possesses different potential for heavy metal reduction and reuse.

Rainwater was collected from three rain events in August 2014 within Chemilink's premises. After each rain event, the rainwater was kept in a sealed container and kept at 4°C. A total of 5 liters of rainwater was collected from all three rain events, and this was deemed sufficient for the experiments and all three samples were homogenized by mixing them together before use. Seawater was collected along the north coast of Singapore in plastic bottles. The bottles were rinsed with the seawater several times before being filled at a depth of no more than one metre.

All glassware and plastic containers were washed thoroughly with DI water and oven-dried at 45°C before use. Conductivity and pH was measured with Sartorius Stedim professional meter pp-20, while heavy metal content was analyzed using ICP-OES, PerkinElmer, Optima 8000 (Tables 1 and 2).

Test Parameter	IBA (ppm)	Test Parameter	IBA (ppm)
Hg	14	Al	22000
Cd	<10	Au	<10
Ag	<10	B	<10
As	40	Be	<10
Cr	200	Sr	500
Cu	800	Bi	<10
Pb	300	Co	50
Zn	3200	Ga	70
Ni	90	In	<10
Se	<10	K	5100
Mn	700	Li	200
Ba	600	Na	6100
Fe	47000	Ca	187000
V	40	Sb	100
Sn	50	Mg	7900
Tl	<10	Mo	30

Table 1: Heavy metal contents of IBA sample.

	NEA-CWC	NEA-WC	Rainwater	Sea Water
pH	6.0 - 9.0	6.0-9.0	4.4	8.1
Cd	0.003	0.1	<0.022	<0.022
Ag	0.1	0.1	0.011	0.033
As	0.01	0.1	0.016	0.11
Cr	0.05	1	<0.012	<0.012
Cu	0.1	0.1	0.018	0.095
Pb	0.1	0.1	0.0042	0.033
Zn	0.5	1	0.089	0.338
Ni	0.1	1	<0.024	<0.024
Se	0.01	0.5	0.009	0.128
Mn	0.5	5	0.0049	0.0095
Ba	1	2	0.907	0.768
Fe	1	10	0.003	0.0014
Sb	-	-	0.006	0.088
Tl	-	-	<0.129	<0.129

Table 2: Heavy metal content of seawater and rainwater.

Method

The sieved IBA were placed in clear plastic containers with approximately 200 grams of IBA sample in each container. About 100 millilitres wash water (rainwater or seawater) were then measured with a measuring cylinder and then poured into each plastic container. The IBA was allowed to soak in the wash water for one week, after which the water was poured out while retaining IBA in the container.

The water (rainwater or seawater) that was used to wash IBA were filtered through 0.45 micrometer membrane filter before instrumental analysis. The heavy metals of concern in this study were Cd, Ag, As, Cr, Cu, Pb, Zn, Ni, Se, Mn, Ba, Sb, Tl and Fe.

The analyte relative concentrations were normalized dividing the measured concentration of the particular washing with the first detectable concentration.

$$RC_{m,i} = \frac{C_{m,i}}{C_{m,1stDC}}$$

where $RC_{m,i}$ is the normalized relative concentration. The final leachability for each element would be for $RC_{m,16}$, on the last wash. $C_{m,i}$ is the concentration of each metal in the wash water at the ith washing. Concentrations that were below the detection limit were given the value zero in the calculations. The final leachability was calculated by dividing the concentration in the final wash (16th washing) by Cm, 1stDC.

The removal percentage was defined as the proportion of heavy metal removed from IBA compared to the original amount of the same heavy metal present in IBA. It was calculated by dividing the total mass of the heavy metal in the fifteen wash waters with the total content using the values in Table 1, expressed as a percentage.

$$RP_m = \left(\frac{\sum_{i=1}^{15} C_{m,i} {}^x M_{water}}{C_{m,Table1} {}^x M_{IBA}} \right) x100\%$$

Results and Discussion

Comparing the washed water concentrations in Table 2 with the total metal content in Table 1, less than 1% of the total metal content of the solid MSW bottom ash was detected in the aqueous leachate and a corresponding difference in washed relative concentrations was observed.

Washing with rainwater

Comparing with WHO drinking water limits, only antimony exceeded the limits when washed with rainwater, and only chromium exceeded when washed with seawater. This could be due to the differences in the pH of the wash waters, which affected the complexation and speciation of the heavy metals, especially chromium (Tables 3 and 4).

All elements analysed were lower than the NEA watercourse discharge limits in the final wash (15th) except for Cu, in both cases, as seen in Tables 4 and 5. This may be caused by the high content of soluble copper compounds in IBA, which needs to be further studied. The leaching concentration of Cu continuously decreased with the number of washings, which means the copper compounds in IBA may be easily dissolved in water and leached out.

The final pH from washing with rainwater were slightly alkaline (7.7–8.4), with pH decreasing rapidly from 12 in the first washing to 7.7 on the 9th washing, and fluctuated above and below a pH value 8.0 in subsequent (10th to 16th) washings. In comparison to other studies, this pH was considered relatively low. The conductivity of the washed water also declined rapidly, from an initial value of 22.58 mS/cm to less than 1.8 mS/cm from the 9th washing onwards. These final values were quite low [32,33]. The series of washings with rainwater in Table 5 also simulated the situation of multi-raining events that can occur during IBA storage outdoors. Continuous washing with seawater simulated the situation where IBA is stored near the sea for civil engineering uses, as mentioned in the introduction.

Parameter	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th	15th	NEA-WC	WHO 2011
Conductivity (mS/cm)	23	22	8.977	3.7	4.8	25	4.7	2.3	1	1	2	2	1	2	2	-	-
pH	12	12	11.35	11	11	9.9	9.2	9.3	8	8	8	9	8	8	9	6.0 - 9.0	
Cd	0	0	0.006	0	<0.0003	<0.0003	0	0	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0	3
Ag	0	0	0.019	0	0	0	0	0	0	0	0	0	0	0	0	0	-
As	0	0	0.028	<0.008	0	0	0	0	0	0	0	0	0	0	0	0	10
Cr	0.1	0.2	0.167	0.1	0.3	0.3	0.3	0.2	0	0	0	0	0	0	0	1	0
Cu	1.5	2	0.891	0.3	0.6	0.3	0.4	0.3	0	0	0	0	0	0	0	0	2
Pb	<0.0041	<0.0041	<0.0041	0	0	0	0	0	0	0	0	0	0	0	0	0	10
Zn	0.1	0.1	0.02	0	0	0	0.1	0	0	0	0	0	0	0	0	1	-
Ni	0.1	0.1	0.036	0	0	0	0	0	0	0	0	0	0	0	0	1	0

Parameter	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th	15th	NEA-WC	WHO 2011
Se	0.1	0.1	0.069	0.1	0	0	0.1	0.1	0	0	0	0	0	0	0	1	40
Mn	0	0	0.003	0	<0.0001	<0.0001	0	0	0	0	0	0	0	0	0	5	-
Ba	2.0555	1.9	0.956	1.2	0.8	0.4	0.4	0.3	0	0	0	0	0	0	0	2	1
Fe	0	<0.0005	0.004	0	<0.0005	<0.0005	<0.0005	<0.0005	0	0	0	0	0	0	0	10	-
Sb	0	0	0.049	0	0	0.1	0.2	0.1	0	0	0	0	0	0	0	-	0
TL	0	0	0.016	0	0	0	<0.0073	0	<0.0073	<0.0073	<0.0073	<0.0073	<0.0073	<0.0073	<0.0073	-	-

Table 3: Results for IBA with rainwater in fifteen successive washings.

Parameter	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th	15th	NEA-WC	WHO 2011
Conductivity (mS/cm)	29.82	28.125	28.125	29.005	28.615	28.195	28.24	27.435	26.945	27.435	27.435	27.435	26.945	27.435	27.435	-	-
pH	11.81	11.55	11.545	11.46	11.36	11.27	10.99	10.925	11.065	10.960	10.96	10.55	10.755	10.64	10.895	6.0 - 9.0	
Cd	0.0024	0.0024	0.007	0.0065	0.0024	0.0024	0.0024	0.0045	-0.0116	-0.012	-0.023	-0.001	-0.020	-0.021	-0.028	0.1	3
Ag	0.041	0.0295	0.0525	0.028	0.044	0.044	0.047	0.043	0.0060	0.007	0.007	0.007	0.004	0.004	-0.005	0.1	-
As	0.0345	0.0205	0.0345	0.0325	0.03	0.023	0.03	0.016	0.0260	0.027	0.023	0.023	0.027	0.029	0.016	0.1	10
Cr	0.3185	0.25625	0.3065	0.34	0.374	0.3645	0.341	0.229	0.2194	0.211	0.206	0.174	0.186	0.185	0.160	1	0.05
Cu	1.913	0.92	0.636	0.447	0.266	0.199	0.17555	0.1227	0.1459	0.088	0.073	0.041	0.069	0.053	0.070	0.1	2
Pb	0.0048	0.0048	0.0048	0.0048	0.0048	0.0048	0.0048	0.0048	0.0121	0.013	0.007	0.014	0.002	0.002	0.000	0.1	10
Zn	0.0595	0.256	0.042	0.031	0.032	0.026	0.0285	0.0195	0.0230	0.022	0.019	0.018	0.020	0.008	0.015	1	-
Ni	0.0765	0.011	0.027	0.038	0.0735	0.0625	0.054	0.0205	0.0229	0.019	0.009	0.004	0.008	0.006	0.004	1	0.07
Se	0.1505	0.204	0.2225	0.141	0.05555	0.038	0.085	0.0805	0.0009	0.000	0.000	-0.001	0.002	0.003	-0.003	0.5	40
Mn	0.0001	0.0001	0.016	0.004	0.0001	0.0001	0.0001	0.02	0.0256	0.023	0.021	0.026	0.025	0.026	0.024	5	-
Ba	2.055	1.27005	1.135	1.0435	1.1765	0.7233	0.9033	0.6	0.8303	0.600	0.254	0.285	0.250	0.277	0.302	2	0.7
Fe	0.0029	0.0029	0.002	0.0029	0.0029	0.0029	0.0029	0.0029	0.0165	0.014	0.009	0.008	0.001	0.000	-0.006	10	-
Sb	0.0195	0.01	0.0285	0.0275	0.0095	0.007	0.009	0.0185	0.0250	0.026	0.018	0.029	0.021	0.023	0.013	-	0.02
TL	0.0395	0.017	0.0105	0.03	0.009	0.0175	0.0105	0.0435	0.0066	0.005	0.011	0.008	0.017	0.017	0.011	-	-

Table 4: Results for IBA with sea water in fifteen successive washings.

Table 5 shows the calculated values for the percentage removal and final leachabilities after fifteen washings for the fourteen heavy metals analyzed. Generally, washing with rainwater can remove heavy metals in IBA to a greater extent than seawater, with the highest removal for antimony from rainwater (29.4%). Barium was also significantly removed by both rain and seawater, at 16.4% and 19.5% respectively. However, none of the heavy metals had more than 30% of their content removed from IBA, but ten of the fourteen metals had leachabilities reduced to less than 50%. These results indicate that washing removed leachable forms of most heavy metals, even though majority of heavy metals remained in IBA.

In comparison with literature, final leachabilities were calculated to be 55.1% for Cu, while Cr and Cd reduced to undetectable levels by washing IBA with tap water with L/S ratio of 2 and with 4 washings [31]. Using water at L/S=5 for 6 hours, achieved 0.07% removal of Cu, 0.03% removal of Pb, 0.02% removal of Zn, with Cd and Ni below detectable limits. The differences were not due solely to different washing methods and medium, but also different IBA content. For example, in the case of Yang et al. [31] Pb was undetectable in the initial leaching results, but was found to have 0.22 – 1.37 mg/L in subsequent washing results (Table 5).

	Rainwater			Seawater		
Element	Total removed (mg)	% Removal	Final leachability	Total removed (ppm)	% Removal	Final leachability
Cd	0.24	N.A.	0.00%	0.3	N.A.	0.00%
Ag	2.125	N.A.	32.56%	3.636	N.A.	0.00%
As	2.805	7.49	66.67%	3.897	9.74	45.50%
Cr	19.42	9.75	8.00%	38.71	19.36	50.40%
Cu	69.935	8.78	1.83%	52.22	6.528	3.64%
Pb	1.31	0.46	75.00%	0.884	0.295	0.00%
Zn	10.15	0.33	39.51%	6.188	0.193	24.40%
Ni	3.595	4	1.69%	4.351	4.835	4.71%
Se	5.39	N.A.	4.88%	9.833	N.A.	0.00%
Mn	1.02	0.15	47.06%	2.102	0.3	148%
Ba	98.665	16.38	8.76%	117.05	19.51	14.70%
Fe	1.23	0.003	367%	0.706	0.0015	0.00%
Sb	14.01	29.38	156%	2.855	5.71	65.70%
Tl	1	N.A.	0.00%	2.517	N.A.	27.30%
Mean	-	7.45	57.80%	-	6.65	27.40%

Table 5: Percentage removal and final leachabilities of heavy metals in IBA.

There were three major trends that could be observed from the change in heavy metal concentrations in the rainwater with progressive washings. Figure 1 show that for half of the heavy metals analyzed, an overall decrease in relative concentrations to below a third of their first detectable concentration after 15 washings. Figure 1 shows a fluctuating, decreasing trend as relative concentrations could increase between washings, as these even heavy metals were exposed on the IBA solid surfaces with each wash.

Perhaps counterintuitively, half of the heavy metals analyzed did not decrease with increase in number of washings. Therefore, heavy metal reduction in IBA is not a simple linear process of decreasing concentrations with increase washing. Other parameters are required to be considered in addition to the attrition/dissolution removal mechanism.

Previous researchers had hypothesized that as the pH of IBA decreased, less soluble metal complex species, such as aluminium hydroxides with Cu and Pb were formed [34-36]. As the washed waters were filtered prior to the chemical analysis, mainly the free ion concentrations were measured in the ICP–OES analysis. The Pb and Cu ions complex readily with organic ligands, e.g. humic acids and only a small fraction of the total metal content is normally available as the free ion [37]. Although dissolved metal complexes with organic ligands or sorbent minerals would pass through a 0.45 micrometre membrane filter, the precipitated/undissolved fraction would not (Figure 1).
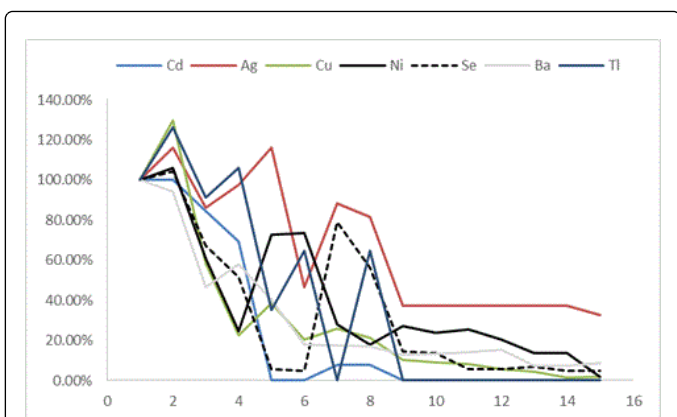
Figure 1: Staggered decreasing heavy metal concentrations with number of washings.

The next trend can be observed in Figure 2 for five heavy metals. The relative concentrations showed no apparent decreases from the initial concentrations after several washings, and final relative concentrations after 15 washings were all above 65%. This particular trend showed that some heavy metals were able to leach out in high concentrations even after repeated washings, and they did not reduce significantly even after 15 weeks of washing with rainwater. Some heavy metals in Figure 2 showed very high concentrations (> 900%) after the fifth washing, such as antimony and iron, while the others showed concentration fluctuations without significant decrease.

For example, arsenic relative concentrations were between 42 to 84% of the initial concentration, except for the 4th and 5th washings, where relative concentrations were below 20%. Arsenic also showed the lowest relative concentrations after 15 washings, at 66.7%, while iron showed the highest at 367%. Antimony showed a peak of 990% at the 7th washing, which gradually decreased in subsequent washings, while iron peaked at 1233% on the 11th washing.
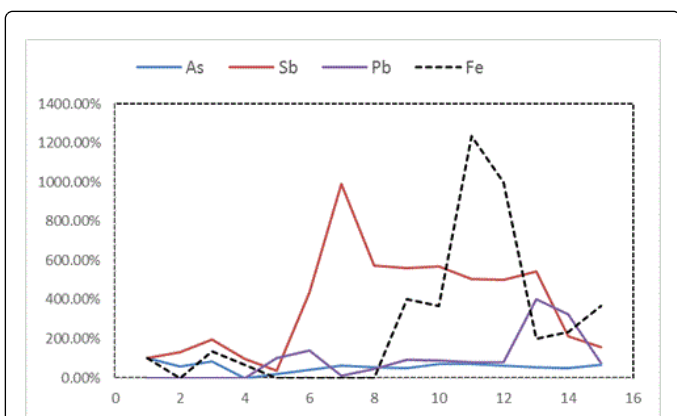
Figure 2: Fluctuating heavy metal concentrations with number of washings.

Kuo et al. [23] soaked IBA in deionized water with initial pH from 4.0 to 5.5, and measured the concentrations of Pb, Cu, and polycyclic aromatic hydrocarbons (PAHs) in a long-term (approximately 70 days) static-immersion experiment. The results showed that Pb and Cu exhibited short-term (approximately 10 to 15 days) leaching behaviour,

while PAHs exhibited long-term (more than 70 days) leaching behaviour. Therefore, the reductions in Pb and Cu from IBA washed with rainwater can be considered permanent, with no future increases in leachate concentrations expected, after having been washed for more than 105 days.

The trend of large increases, followed by gradual decrease for heavy metal relative concentrations is shown in Figure 3. Chromium, manganese and zinc showed a higher than 120% increase after the first washing, which subsequently reduced to below 39% after 15 washings. The increase in concentrations for these three heavy metals did not occur concurrently. Chromium showed two peaks at the second and fifth washing, with the largest increase of 465% on the fifth washing. In contrast, manganese and zinc showed the highest concentration at the 9th and 13th washings respectively, much later than chromium,
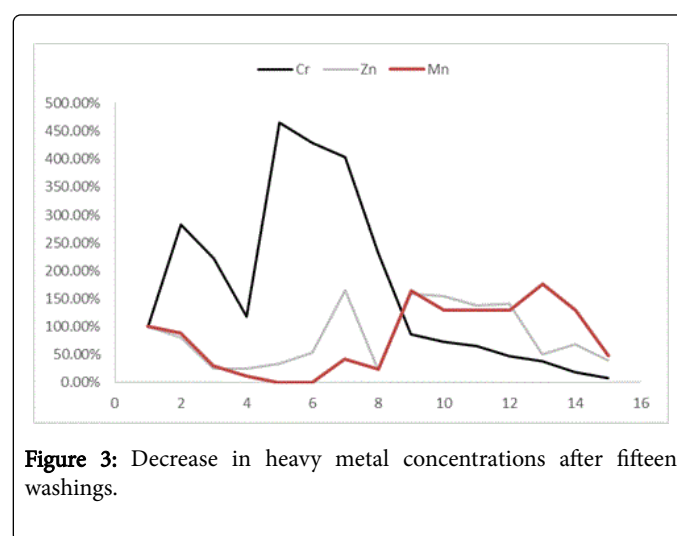

Figure 3: Decrease in heavy metal concentrations after fifteen washings.

Both cationic heavy metals and oxyanion metalloids can be found in the same trend. For example, selenium and copper both behaved similarly in Figure 1. Thus dissimilar leaching mechanisms cannot account for the different trends in concentrations observed. The removal of heavy metals was found to be dependent on pH which affects the surface charge of bottom ash, the degree of ionization, and the speciation of heavy metal [38].

Chemical speciation is a significant factor that governs the toxicity and mobility of heavy metals. Ash mineralogy could account for these differences, as IBA is known to be non-homogenous by nature [39,40]. Therefore, the non-homogeneity of heavy metal distribution within IBA is a plausible explanation for all three trends observed.

This particular characteristic of non-homogenous distribution of heavy metals within each batch IBA is well-known in literature. Shim et al. [40] used the Korea Standard Leaching Test for IBA with L/S ratio of 10, and found that the leachability of lead, nickel, copper and zinc was dependent on the solubility of the heavy-metal related compounds formed after incineration.

The results also showed that generally, heavy metal leaching from IBA did not reach stable levels within the first eight weeks of washings, as seen from their relative concentrations (Tables 3 and 4). Only about half of the heavy metals were reduced to stable levels after eight weeks of washings, for both rain and seawater. Other studies showed that the time required to reach equilibrium is mainly related to the maximum particle size of IBA assuming all other properties remain constant (e.g.,

observed diffusivity, liquid-solid ratio, fractional release at equilibrium) [27,41]. Generally, smaller particle sizes had shorter equilibrium times, with about 7 days needed for IBA maximum particle sizes of up to 5 mm. The amount of heavy metal leached from IBA also increased with decreasing particle size of IBA [41]. This was due to the increasing proportions of heavy metals such as Ti, Fe and Al with decreasing particle size [42]. However, the cation exchange capacity (CEC) increased due to increasing surface areas, with decreasing particle size. The rate and extent of adsorption were also found to be proportional to the specific surface area, or the particle size of IBA. The smaller the particle size of the bottom ash was, the greater the removal rate of heavy metals Cu and Ni [27]. Therefore, the concentrations of various heavy metals found in solution, like those observed in Figures 1 to 7, can be expected to vary with different IBA particle sizes and porosity in each sample.

Seawater washing

Washing of IBA with seawater produced significantly different trends from washing with rainwater, with four distinct trends compared with three for rainwater showed earlier.

Figure 4 show the trend of gradual decrease in relative concentrations of four heavy metals in successive washings. This was in contrast to washing with rainwater, where seven of the fourteen heavy metals analyzed were significantly reduced in concentrations.

Selenium showed spikes in concentration before decreasing to very low levels. This trend for selenium is similar to rainwater washing (Figure 1), where an increase in relative concentrations after the 6th washing was followed by gradual decrease to less than 8%. The trend for copper was also similar in both cases, where concentration decreases without major spikes, eventually reaching to a relative concentration below 4% for both rain and seawater washing (Figure 4).
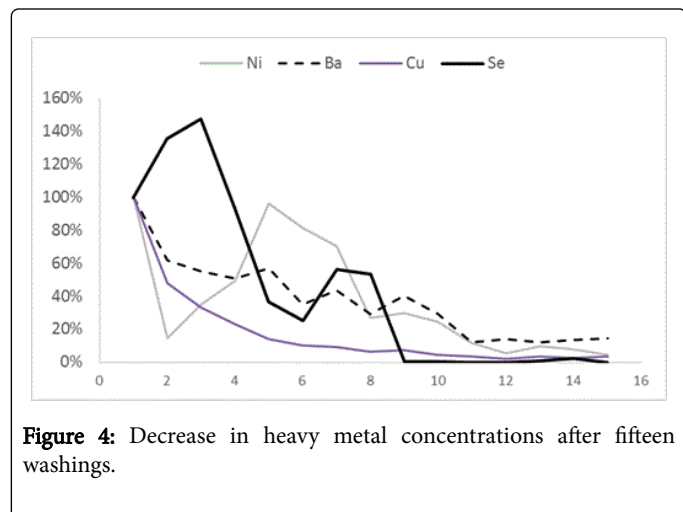
Figure 4: Decrease in heavy metal concentrations after fifteen washings.

Figure 5 shows large increased in relative concentrations after the first washing before abruptly decreasing to low concentration levels. Of the four heavy metals, only cadmium and selenium were reduced to below instrument detection limits before the 10th washing. The relatively quick reduction in cadmium concentration was consistent for both seawater and rainwater washings.

Zinc showed a sharp peak in the second washing, which decreased rapidly in subsequent washings.

The trend in Figure 6 showed no significant decreases in relative concentrations for five heavy metals after 15 washings.

Manganese was the highest after 15 washings at 147% its initial value, having increased concentrations sharply from undetectable levels from the 5th to 7th washings. This trend was similar to rainwater washing, where manganese showed a significant increase in concentrations from undetectable levels in the 4th to 6th washing. However, manganese concentrations were still significantly lower after 15 washings with rainwater than with seawater, 35% relative concentration for the former, compared with 147% with the latter, despite having similar initial concentrations.

The other four metals showed similar variations with final relative concentrations of between 27.3 to 69.8% after 15 washings. It is also noteworthy that the trend in Figure 6 is comparable with Figure 2, where heavy metal concentrations did not decrease significantly after repeated washings. Three heavy metals, antimony, manganese and arsenic were found to behave similarly for both rainwater and seawater washings. Therefore, the non-reduction in these three metals cannot be attributed the random variability in concentrations exhibited due to inhomogeneity.
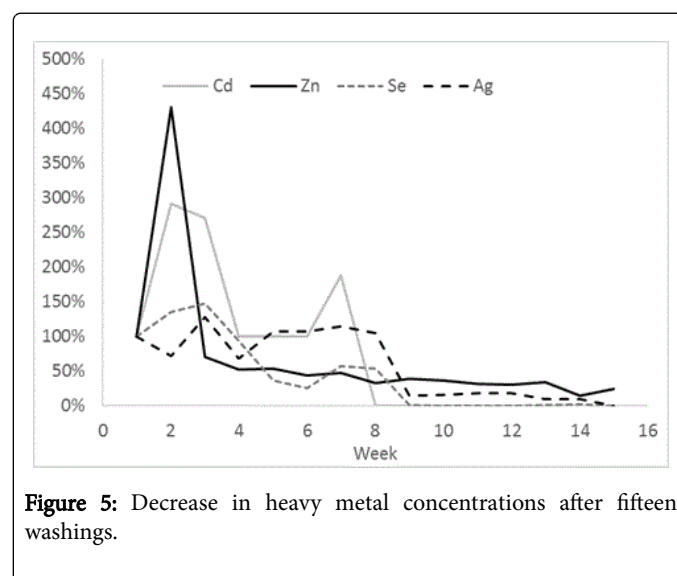
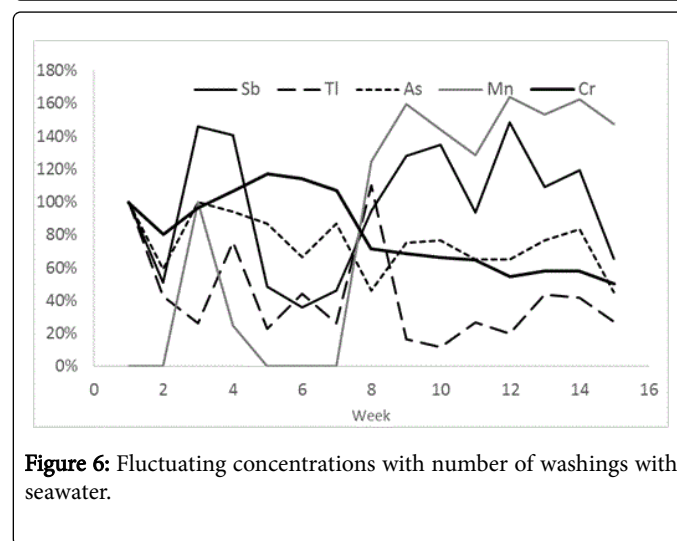**Figure 5:** Decrease in heavy metal concentrations after fifteen washings.

Figure 6: Fluctuating concentrations with number of washings with seawater.

Two heavy metals iron and lead, exhibited exceptional leaching behaviour with seawater. After the first 7 washings where concentrations were below detection limits, iron and lead concentrations became detectable from the 8th to the 13th washings, fluctuating between 113% and 6.5%. Both heavy metals fell below detectable levels again on the 14th washing onwards. This behaviour is not consistent with washings with rainwater, where iron and lead could not be reduced to below their initial concentrations even after 15 washings.

The surface charge of IBA in aqueous solution is a strong influence, affected mainly by pH and amount of ions present in the wash water. Seawater contained many pollutants such as organic matter, suspended solids and other heavy metals compared to rainwater (Table 2). It has been hypothesized that the presence of dissolved organics, especially fulvic acids, can increase the leaching of some heavy metals, such as Cu [27]. Therefore, the presence of these additional ions and pollutants could have reduced the effectiveness of seawater in the initial washings, compared to rainwater, in reducing heavy metal content in IBA. The higher pH of seawater also meant lower removal of cations as it is less able to neutralize the basicity of IBA. Lastly, the somewhat higher maximum relative concentrations, and more effective subsequent heavy metal removal, observed for rainwater could be due to its pH being lower than the point of zero charge of the IBA. This would give the IBA surface a net positive charge after soaking in rainwater for some time, which encourages cations to be released more readily than when soaking in a high pH solution, such as seawater.

In contrast, the hydrolyzation of metal cations, released from IBA, in forming precipitates would be more prevalent in seawater than rainwater. The metal hydroxides could be adsorbed onto metal oxide surfaces of IBA as metal hydroxides reduce the free energy of adsorption by removing the hydration sheath or rearranging this sheath [37]. This process of metal release into solution and re-adsorption with each washing could explain the fluctuations seen in Figure 6 and to a lesser extent in the other figures as well. The lack of homogeneity in the heavy metals distribution can explain the divergence in trends for many heavy metals observed in these results (Figure 7).
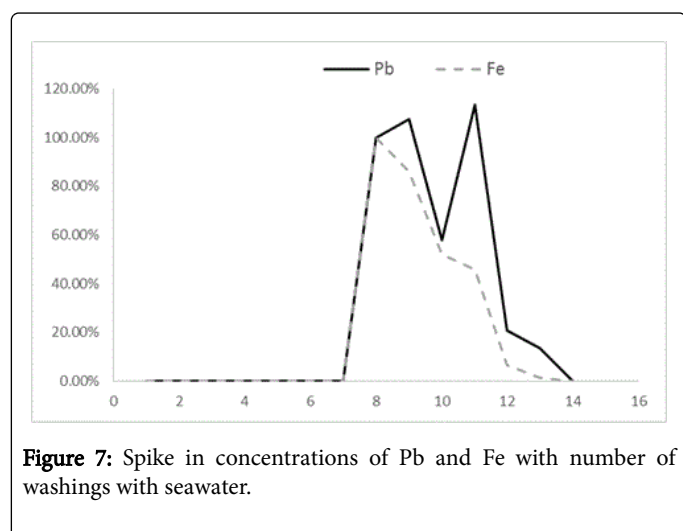

Figure 7: Spike in concentrations of Pb and Fe with number of washings with seawater.

Another explanation for the large fluctuations seen in the preceding figures could be due to the adsorption of the leached heavy metals. It was found by other researchers that the difference in adsorption capability among the various cations on IBA could be attributed to their hydration radius and energy. The smaller the radius of the hydrated metal ion was, the larger the hydration energy of the metal ion was. Furthermore, it is difficult for the some ions to enter the bottom ash pores and undergo cation exchange at available sites [41].

It was examined that the behaviour of lead in prepared solutions in an adsorption experiment with municipal solid waste incineration bottom ash. It was found that $Pb(OH)_4$ and a lead complex could be adsorbed onto the surface of Fe colloids on the bottom ash.

The competition of protons with metal ions for adsorptive sites can be used to explain metal adsorption. The adsorption strength of H+ at higher pH could be weakened, and the adsorption amount of metal ions could increase. The increasing OH- may form stable and insoluble precipitates with heavy metals, thus decreasing the leaching concentration. Shim et al. [40] attributed the removal of Cu and Ni by IBA to the content of silica, alumina, and iron oxide. These results agree with the high content of these elements in the IBA used in this research (Table 1). The mechanism of heavy metal removal could be similar to those proposed for fly ash, with calcium oxide, iron oxides, silica and alumina in IBA acting as adsorption surfaces [42,43].

Conclusion

Washing of IBA with natural waters fifteen times could reduce heavy metal leachabilities while removing heavy metal content by 6-7% on average of all fourteen heavy metals analysed. The final concentrations of heavy metals in the wash water were reduced to 27-57% of their first detectable concentration. However, the reductions varied greatly among the different heavy metals, and between rain and seawater wash.

Washing with seawater could reduce the final concentrations of all heavy metals in rain water below the National Environment Agency's watercourse discharge limits. Washing with rainwater could do so for all heavy metals except for copper. Heavy metal concentrations also exceeded WHO drinking water standards in both cases. Thus, only washing seawater can produce a final leachate that can be discharge without treatment.

For both rain and seawater washings, only half of the heavy metals analysed showed decreasing trends with increasing washings, while the variation in concentrations of the other heavy metals showed no clear trends. Three general trends in heavy metal concentration variation could be observed when IBA was washed with rain water while four trends were observed for seawater. Therefore, no specific variation in concentration trends could be attributed to any specific metal.

Acknowledgements

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