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Physicochemical Characterization of Singapore's Municipal Solid Waste Air Pollution Control Residues and its Stabilization by VKI Treatment

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Abstract

Vandkvalitets Institute (VKI) process is a treatment technology which employs the technique of extraction and chemical stabilization on waste, targeting an end pH of 7 to 10 using water, concentrated phosphoric acid (H_3PO_4) and carbon dioxide (CO_2) as the main stabilizing materials. Different parameters for the ash stabilization were investigated. Based on the acid neutralizing capacity (ANC) and pH-dependent leaching results of Singapore's air pollution control (APC) residues produced from a municipal solid waste (MSW) incineration plant, the main objective of this study was to examine the suitable end pH to be used to treat APC residues. After which, a two-step VKI treatment was carried out on APC residues, using CO_2 and H_3PO_4 dosing as the two main stabilizing items. ANC results showed that there was a steep drop in pH from 10 to 7 at approximately 20.40 equivalent/kg of acid addition, while pH-dependent leaching results indicated that the most ideal pH range for the suppression of most heavy metal release was between 7 and 10. Subsequently, pH 7 was then selected as the end pH for the VKI treatment process. Under optimum conditions of 0.2 g and 0.5 g of H_3PO_4/100 g of APC residues (equivalent to 2 and 5 kg H_3PO_4/ton of residues) with a CO_2 flow rate of 1500 cm^3/min, the treated APC residues had an end pH of around 7 after 100 and 80 minutes of treatment, respectively. Toxicity characteristic leaching procedure (TCLP) was used to evaluate the leaching of heavy metals (Cd, Cr, Cu, Pb, Zn) before and after treatment. The results showed that the leaching of Pb was significantly reduced after treatment, and was able to meet Singapore's acceptance criteria for landfill disposal. However, the leaching of Cd increased by two orders of magnitude after treatment, but was still below Singapore's acceptance criteria for landfill disposal.

Keywords Phosphoric acid; Carbon dioxide; Acid neutralizing capacity; Leaching; Air pollution control residues; Heavy metals

Abbreviations

ANC: Acid neutralizing capacity; APC: Air pollution control; IBA: Incineration bottom ash; IFA: Incineration fly ash; MSW: Municipal solid wastes; NEA: National Environment Agency; TCLP: Toxicity Characteristic Leaching Procedure; VKI: Vandkvalitets Institute

Introduction

The amount of municipal solid waste (MSW) disposed in Singapore has increased significantly over the years, from 1,260 ton/day in 1970 to 8,559 ton/day in 2016 [1]. Due to Singapore's limited land space, National Environment Agency (NEA)'s policy in waste management requires the incineration of all waste that cannot be recovered, reused or recycled [1]. Incineration reduces the total volume of MSW by up to 90% and is usually the preferred method to treat MSW in land scarce countries like Singapore [2]. However, incineration of MSW generates incineration bottom ash (IBA) and incineration fly ash (IFA) as end products which could lead to pollution. Although IBA is produced in larger quantities, it is considered non-hazardous, while IFA is classified as hazardous waste. Among the different types of IFA, air pollution control (APC) residues originating from flue gas cleaning, are the main environmental pollutants as they contain high levels of leachable heavy metals and soluble salts [3]. In addition, APC residues are also strongly alkaline due to their high content of excess lime. The high pH causes the leaching of some heavy metals, in particular, lead, which forms soluble lead complexes, e.g. $Pb_2(OH)_3Cl$ or $Pb_4(OH)_6SO_4$ under alkaline conditions [4,5]. Therefore, a proper and efficient treatment is required to ensure a safe disposal of APC residues from MSW incinerators.

Literature studies have shown that solidification and stabilization can be used to treat MSW IFA. They involve the application of chemical chelating agents [6,7] or soluble phosphate [8], followed by cement solidification to stabilize IFA, hence reducing the leachability of heavy metals into the environment [9]. Other studies advocated the use of extraction or washing to wash out heavy metals and excess soluble salts from MSW IFA followed by cement solidification to treat IFA [10-12]. To our awareness, little studies have been reported to evaluate the effect of both extraction and chemical stabilization methods in treating MSW APC residues in Singapore. Bournonville et al. studied the method of water extraction, followed by stabilization with phosphoric acid (H_3PO_4) to immobilize heavy metals in IFA [13]. The results showed that calcium phosphates formed can effectively trap heavy metals in a stable apatite mineral structure. In comparison, the Vandkvalitets Institute's (VKI) treatment method is a scalable process, which combines both extraction and chemical stabilization to treat wastes, using H_3PO_4 and carbon dioxide (CO_2) as additives to adjust the final pH to 7-10 [14,15]. Washing was first used to extract soluble salts out from the targeted waste. Afterwards, H_3PO_4 and/or CO_2 with water was introduced into the slurry and mixed for 1-1.5 hours, until the end pH was stabilized in the range of 7-10. Finally, the mixture that

consists of treated IFA and wastewater was filtered using a filter press and the wastewater was treated separately [14,15]. Figure 1 illustrates a schematic diagram of a two-step VKI treatment process. As both H_3PO_4 and CO_2 have a considerable buffering capacity, they have the potential to decrease the high pH of APC residues while preserving the alkalinity. This serves as a protection from any possible acidification in future [16].

Typically, variations in VKI treatment process include the one-step and two-step treatment, whereby one-step treatment excludes the filtration step after the initial extraction process, thus saving on water consumption [17]. In contrast to conventional treatments like stabilization and solidification, VKI treatment can greatly reduce the leaching of heavy metals, without increasing the mass and volume; and reducing the alkalinity of the treated IFA. Furthermore, VKI treatment is a possible green alternative as it could tap on industrial flue gas for CO_2 gas source.

This study aims to characterize the physicochemical properties, acid neutralizing capacity (ANC), and alkalinity of Singapore's APC residues from the MSW incineration plant. The treatment conditions of two-step VKI process were optimized, using pH, H_3PO_4 and CO_2 as the main parameters. The end pH for VKI treatment was determined by evaluating the ANC and pH-dependent leaching results of untreated APC residues. The effectiveness of VKI treatment was evaluated using the Toxicity Characteristic Leaching Procedure (TCLP) method, with Cd, Cr, Cu, Pb and Zn tested and compared to Singapore's acceptance criteria for landfill disposal. In addition, the feasibility of simplifying the two-step VKI process into a one-step VKI process under optimized conditions was explored as well.

Materials and Methods

Characterization of APC residues

The APC residues used in this study were collected from a MSW incineration plant in Singapore. Particle size distribution was determined by a laser particle size analyzer (LA-960 Horiba, Japan). The bulk density was determined by compacting the APC residues in a measuring cylinder. The moisture content was measured by drying the APC residues at 105°C for 24 hours. The loss on ignition (LOI) was determined by calcining the dried APC residues at 550°C for 2 hours.

BS EN 14429:2015 was adopted for evaluating the alkalinity and ANC of APC residues. 30 g of APC residues was mixed with 300 mL ultrapure water (18.2 MΩ.cm, Millipore Milli-Q, and USA) in 500 mL HDPE bottles to determine the natural pH of the leachate.

The bottles were placed in an overhead rotator (Heidolph, Germany) for 1 hour at 10 rpm, and pH measurements were taken every 12 hours over a 48 hour period. The pH was measured by Mettler-Toledo FiveEasy Plus pH meter. The experiments were then repeated in a similar manner with various HNO_3 concentrations in the range of 1.00-1.15 M for the determination of acid concentration required to reduce the pH to neutral levels.

For the ANC investigation, 100 and 135 mL ultrapure water were added to 15 g of APC residues, respectively in separate 250 mL beakers, covered with cling film and placed on a magnetic stirrer (IKA® RH basic 2, China) at 500 rpm.

Then, 5 M HNO_3 was added to the mixture every 30 minutes thereafter to induce a drop in pH, till a maximum liquid to solid (L/S) ratio not exceeding 10. Typically, 5 M HNO_3 was used so that the end

pH of the APC residues could be reduced further to acidic levels (at pH=2). ANC was then obtained in terms of the number of moles of HNO_3 equivalents per kg dry APC residues via Equation 1 below [2]:

$$ANC\left(\frac{eqv}{kg}\right) = \frac{Concentration\ of\ HNO_3\ \times\ Volume\ of\ HNO_3\ added}{Mass\ of\ APC}$$

(1)

pH-dependent leaching on APC residues

A pH-dependent leaching based on BS EN 14429: 2015 was carried out to evaluate the heavy metal leaching of untreated APC residues under different pH conditions. After leaching, the leachates were filtered with 0.45 μm nylon membrane using a vacuum pump. The leachates were acidified to pH <2 with concentrated HNO_3, and tested for Cd, Cr, Cu, Pb and Zn concentration with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) from PerkinElmer Optima 8300. The ICP-OES absorption wavelengths for Cd, Cr, Cu, Pb, and Zn were set at 228.802, 267.716, 327.393, 220.353 and 206.200 nm, respectively.

VKI treatment

In the two-step VKI process as shown in Figure 1, 100 g of APC residues were washed with 300 mL of ultrapure water corresponding to L/S ratio=3 L/kg for an hour to remove soluble salts. 250 rpm was optimized as the stirring speed due to the viscous nature of the slurry. After washing, the slurry was filtered through a 0.45 μm nylon membrane using a vacuum pump.

The filter cake obtained was further mixed with 300 mL of ultrapure water, and treated with concentrated H_3PO_4 (85%, Merck, Germany) and purified CO_2 (99.8%, Singapore Oxygen Air Liquide Pte Ltd, Singapore). The dosage range of H_3PO_4 investigated was between 0 to 90 g/kg of APC residues, while the CO_2 flow rate investigated was in the range of 1500 to 2500 cm³/min.

A flow meter (Gillian GilAir® Plus Air Sampling Pump) was used to monitor the flow rate of CO_2. The pH of the suspension was measured at an interval of 20 minutes until a final pH of 7 was attained. Afterwards, the suspension was filtered through a 0.45 μm nylon membrane filter. The treated filter cake was obtained, and the wastewater was treated separately which was not covered in this study.

In the one-step VKI process, 100 g of APC residues were washed with 300 mL of ultrapure water corresponding to L/S=3 L/kg. After one hour, without separating the washing water, optimized dosages of H_3PO_4 and CO_2 based on two-step VKI process were added to the slurry. The suspension was then filtered through a 0.45 μm nylon membrane to obtain the treated filter cake.
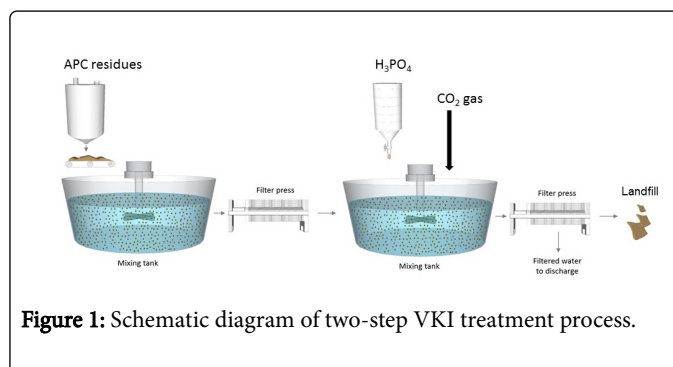

Figure 1: Schematic diagram of two-step VKI treatment process.

TCLP leaching

Toxicity characteristic leaching procedure (TCLP) based on US EPA SW-846 test method 1311 was used to evaluate the leaching behavior of heavy metals in untreated and VKI treated APC residues. Extraction fluid #2 (pH 2.88) was prepared using ultrapure water and glacial acetic acid (99.85%, Sigma-Aldrich, USA) [18]. After leaching, the leachates were filtered through 0.7 μm glass fiber filter using a vacuum pump. Triplicate leaching tests were done. All leachates were acidified to pH <2, and analyzed for Cd, Cr, Cu, Pb, and Zn using ICP-OES.

Results and Discussion

Physicochemical properties

It can be seen from Figure 2 that APC residues have a particle size distribution of 2 to 110 μm, with the most prevalent residue particle size by frequency being about 10 μm in diameter. The bulk density, moisture content and LOI results were consistent with literature data [2], and tabulated in Table 1.
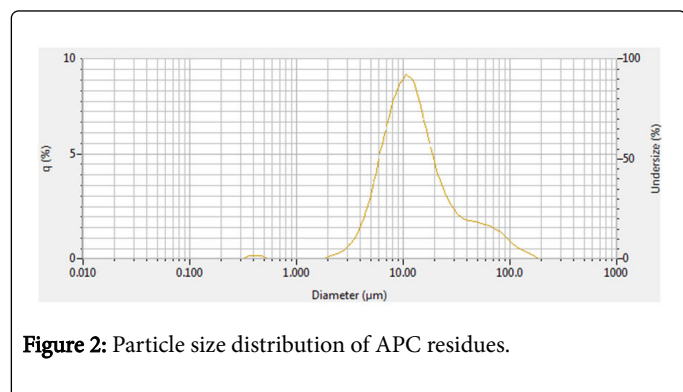

Figure 2: Particle size distribution of APC residues.

Parameters	Value
Bulk density (kg/m^3)	560
Moisture content (%)	1.71
LOI (%)	7.13

Table 1: Physicochemical characteristics of APC residues.

Figure 3(a) shows that APC residues had a very alkaline initial pH of about 12 when measured in ultrapure water. This is consistent with literature, which gives the range of 11.0-12.5 for APC residues [2]. APC residues are highly alkaline due to the presence of highly soluble hydrated calcium hydroxide and excess lime added during the flue gas cleaning stage. Figure 3(a) further indicates that it required about 30 hours for the APC residues to be completely neutralized by 1.10 M HNO$_3$ with pH dropping from pH 12 to 7.

In terms of ANC results, Figure 3(b) shows that there was a gradual decrease in pH from 12 to 11 when 19 eqv/kg of 5 M HNO$_3$ was added. However, there was a steep drop in pH from 10 to 7 after adding about 20.40 eqv/kg of 5 M HNO$_3$. Two prominent inflection points were also observed, at about 20.63 and 25.40 eqv/kg of acid addition. Comparing to similar studies from Chandler et al. and Zhang et al., it can be observed that the ANC of APC residues in this study was significantly higher [2]. One possible reason could be the variations in the initial pH of the APC residues, which in turn affected the amount of acid

required for neutralization. Another factor could be the difference in the incineration process and the chemical composition of the APC residues in different countries, possibly varied by the amount of lime or CaO being added. ANC reflects the amount of excess CaO present, which can indicate the operating conditions of the incineration plant process [2].
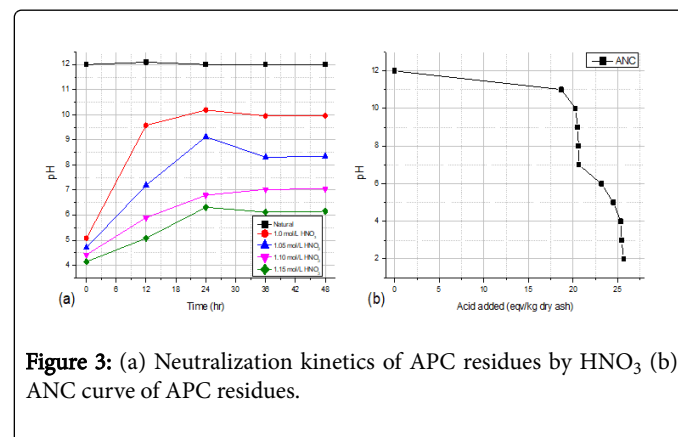

Figure 3: (a) Neutralization kinetics of APC residues by HNO$_3$ (b) ANC curve of APC residues.

pH-dependent leaching result

The leaching of Cd and Cu followed a typical cationic solubility pattern, namely the concentrations were significantly high under acidic conditions, and decreased gradually as the pH increased. Figure 4 shows that the leaching of Cd was the highest (6.41 mg/L) at pH 2, and it decreased steadily to 5.40 mg/L at pH 6. At pH 7 and above, Cd leaching dropped to 1.50 mg/L, and reached 0.03 mg/L at pH 9. Similar trend was reported in the literature [5,19,20] which indicated that the leaching of Cd increased under acidic conditions. Under alkaline conditions, the formation of possible insoluble Cd compounds, such as Cd(OH)$_2$ and CdCO$_3$, could have reduced the leaching of Cd significantly [19,20]. For Cu, the leaching was maintained at about 50 mg/L between pH 2-5, after which there was a significant drop to 3.18 mg/L at pH 6, and to below ICP-OES detection limit at pH 7 and above. A possible reason could be the production of tenorite (CuO) and Cu(OH)$_2$ at pH 5 and above [20,21]. Hence, Cd and Cu can be seen to show very limited solubility under basic pH conditions, due to the formation of highly insoluble compounds [22] that restrict their leaching into the environment.

Pb and Zn form amphoteric compounds, and thus leaching were high at both acidic and basic conditions, but demonstrated minimal leaching at neutral pH. Figure 4 shows that Pb leaching was high at both pH 2 (25.8 mg/L) and pH 12 (74.7 mg/L), and it remained below ICP-OES detection levels between pH 7-10. This could be caused by the formation of amphoteric oxides such as lead (II and IV) oxides that are readily soluble in acidic and alkaline solutions to produce the corresponding plumbite and plumbate soluble salts respectively [23]. It was reported by Jing et al. that the leaching behavior of Pb can be divided into three stages based on the leachate's pH [4]. At pH >12, a high leaching occurs as Pb forms soluble hydroxide anion complexes. Between pH 6 and 10, Pb leachability is low as a result of adsorption and precipitation. At pH <6, ANC is completely consumed and therefore free Pb ions leached out freely [4]. The leaching of Zn decreased from 567 mg/L at pH 2 to 0.26 mg/L at pH 8, possibly due to the precipitation of Zn(OH)$_2$ which reduced its solubility. Under alkaline conditions, Zn can form soluble zincate soluble complexes [24], which could explain the increase in leaching at pH 11 and above.

The leaching of Cr was relatively low compared to Cd, Cu, Pb and Zn. At pH 2, the release was 0.71 mg/L, and it dropped steadily to 0.003 mg/L at pH 5. Between pH 5 and 10, the concentration of Cr fluctuated, with some concentrations below the ICP-OES detection limit. At pH 11 and 12, Cr leaching increased gradually to 0.028 mg/L and 0.074 mg/L, respectively. Similar Cr leaching results were observed from earlier studies by Quina et al. and Zhang et al [5,20]. Generally, the leaching of Cr in alkaline solid wastes depends on the oxidation state of Cr with +3 and +6 being the two dominant oxidation states. Cr(VI) compounds are more soluble and toxic compared to Cr(III) compounds, hence Cr(VI) leaching could be predominant in APC residues [25].

From the pH-dependent leaching results in Figure 4, it can be observed that acidic pH levels promote the leachability of most heavy metals, with an increase in leaching potential observed with decreasing pH. On the other hand, the most ideal pH range for the suppression of most heavy metal releases seems to occur between 7 and 10, with pH 7 having low leachability of Cr, Cu and Pb but still relatively high leachability of Cd and Zn. From the ANC results discussed in Section 3.1, there was a steep drop in pH from 10 to 7 at approximately 20.5 eqv/kg of acid addition. Hence, in order to extract more heavy metals as well as to facilitate industrial scalability, the following VKI treatment process will target to achieve an end pH of 7 as one of the treatment parameters for the APC residues.
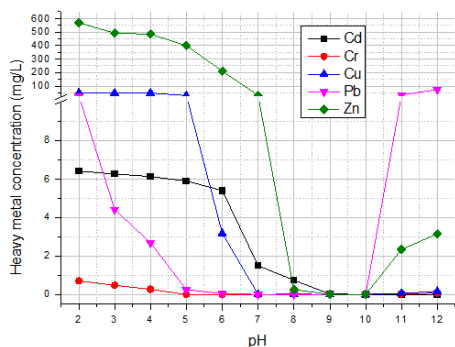

Figure 4: Effect of pH on heavy metal leaching of APC residues.

Effect of H_3PO_4 on VKI treatment

The effect of dosage of H_3PO_4 on the pH of APC residues is shown in Figure 5. The results indicated that the pH drop was not significant throughout the treatment process, even in cases where more H_3PO_4 was used. While the use of 2 g and 4 g of H_3PO_4 per 100 g of APC residues allowed for an overall drop in pH, the drop in pH was not substantial as the pH remained at 11.9 after 1 hour.

When a greater dosage of H_3PO_4 was used (e.g. 6 g and 9 g), the pH dropped initially to 11.9 and 12.0, respectively, but started to increase after 20 minutes. This can be explained from the alkalinity and ANC results from Section 3.1, where a concentration of approximately 1.10 M HNO_3 was needed to bring down the pH from 12 to 7. Converting the 9 g of H_3PO_4 added into ANC equivalent, it is approximately 0.918 mol/kg APC residues, which translated into a pH of approximately 11.8-12.0 based on Figure 3(b).

This means that excess H_3PO_4 may need to be added in order to break the buffering capacity of the APC residues and lower the pH. A parallel study from Eighmy et al. has also shown that 1.2 mol of H_3PO_4 per kg of APC residues only managed to reduce the pH slightly from 12.36-12.54 to 12.10-12.33 [8].
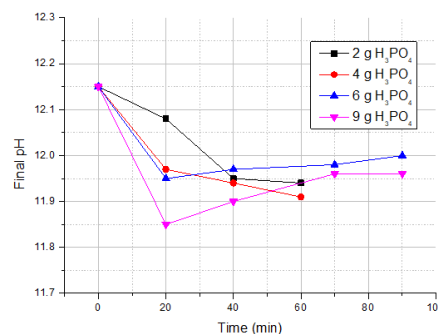

Figure 5: Effect of dosage of H_3PO_4 on final pH of the APC slurry, in the absence of CO_2. Experimental conditions: 2-9 g of H_3PO_4.

Economically, increasing the dosage of H_3PO_4 further is not practical in scale-up operations due to the high acid costs. Since H_3PO_4 alone could not bring down the high basal pH value of APC residues to 7 at an acceptable cost, CO_2 was introduced in the subsequent optimization experiments. When different dosages of H_3PO_4 (0-1.5 g) were used together with a constant CO_2 flow rate of 1500 cm³/min, the pH drop was more rapid as shown in Figure 6. Increasing the dosage of H_3PO_4 reduced the time needed for the end pH to reach approximately 7. For instance, it took less than 60 minutes for pH to reach 7 when 1.5 g of H_3PO_4 was used.
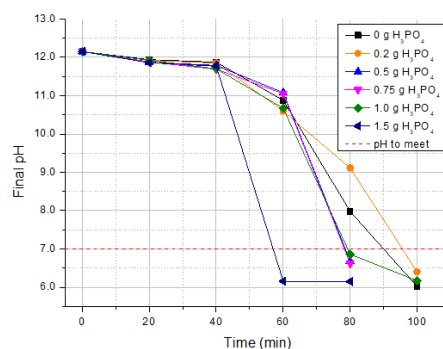

Figure 6: Effect of dosage of H_3PO_4 on the final pH of the slurry. Experimental conditions: 0-1.5 g of H_3PO_4 with 1500 cm³/min CO_2 flow rate.

Looking at the TCLP pH results of the APC residues from Figure 7(a) after VKI treatment, it can be observed that the final pH was between 6.8 and 7. Increasing the dosage of H_3PO_4 did not cause a pH decrease in the TCLP leachate. These results suggest that while using H_3PO_4 alone in VKI treatment may not be economical, a combination of H_3PO_4 and CO_2 allows the end pH of the slurry to reach 7, which meets the VKI treatment criteria. In addition, the pH remained neutral at around 7 after TCLP, without a drop in pH despite having an acidic

extraction leachant (pH 2.88 ± 0.05). This further proves that the buffering capacity of the APC residues was retained after VKI treatment.

In terms of the TCLP leaching of heavy metals before VKI treatment, Table 2 shows that only Pb failed Singapore's acceptance criteria for landfill disposal before VKI treatment for the sample of MSW APC residues [26]. After VKI treatment, the leaching of Pb decreased significantly by 3-5 orders of magnitude (Figure 7(b)). It appears that there is a sharp increase in Pb leaching as the mass of H_3PO_4 used increased from 0.5 to 0.75 g. The effect of pH on Pb leaching is ruled out in this case, as Figure 7(a) shows that there is no significant difference in the TCLP end pH (6.9-7) for all the different H_3PO_4 dosing treatment. Hence, there may be a possibility whereby a higher dosage of H_3PO_4 causes Pb to leach out from certain Pb minerals, despite having stabilized matrixes within this neutral pH range. Further studies, however, will need to be conducted in order to verify this observation. In view of these results, the maximum limit for H_3PO_4 dosage was capped at 0.5 g per 100 g of APC residues.
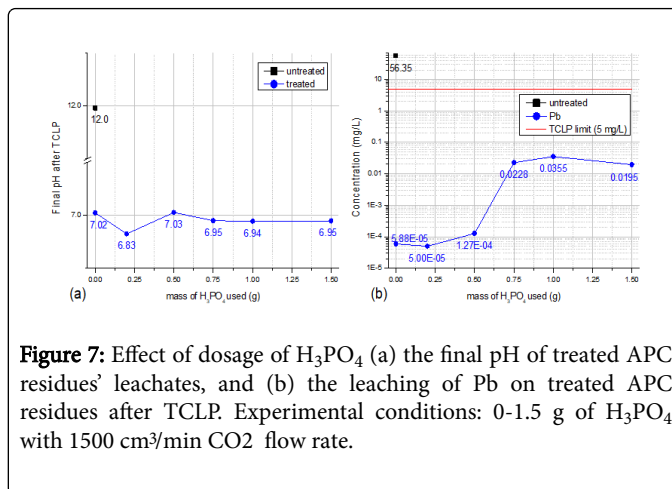

Figure 7: Effect of dosage of H_3PO_4 (a) the final pH of treated APC residues' leachates, and (b) the leaching of Pb on treated APC residues after TCLP. Experimental conditions: 0-1.5 g of H_3PO_4 with 1500 cm³/min CO2 flow rate.

Heavy metal (mg/L)	Untreated	0.2 g H_3PO_4			0.5 g H_3PO_4			TCLP limit (mg/L)
		1500 cm³/min CO_2	2000 cm³/min CO_2	2500 cm³/min CO_2	1500 cm³/min CO_2	2000 cm³/min CO_2	2500 cm³/min CO_2	
Cd	$3.24×10^{-4}$	0.0529	0.0312	0.0519	0.076	0.0712	0.0592	1
Cr	0.0465	0.0388	0.0273	0.0167	0.0543	0.0189	0.0199	5
Cu	0.0537	0.222	0.183	0.268	0.186	0.175	0.183	100
Pb	56.4	$5 × 10^{-5}$	0.014	0.0144	$1.27 × 10^{-4}$	0.0173	0.0182	5
Zn	4.52	18.8	12.2	16.2	8.24	8.83	10.9	100
End pH	12	6.83	6.71	6.84	7.03	6.88	6.73	NA

Table 2: TCLP leaching results on untreated and VKI treated APC residues. Experimental conditions: 0.2 g and 0.5 g of H_3PO_4 with 1500-2500 cm³/min CO_2 flow rate.

Effect of CO_2 on VKI treatment

Previous studies from Hjelmar and Birch in section 3.3 have shown that CO_2 dosing in VKI treatment has the ability to lower the end pH of the slurry, while maintaining the buffering capacity of the APC residues [14]. However, looking at Figure 6, CO_2 without H_3PO_4 dosing resulted in a longer time (100 min) for the end pH to reach 7, compared to other set-ups where both CO_2 and H_3PO_4 were used. In addition, the slurry generated was observed to be more viscous, which resulted in difficult slurry to handle and mix. These two points highlight the limited efficacy of CO_2 dosing alone, which may incur additional costs to future scale-up applications as longer time was needed.

Three CO_2 flow rates (1500 cm³/min, 2000 cm³/min and 2500 cm³/min) were further investigated, together with 0.2 g of H_3PO_4 to evaluate the CO_2 dosing effect on VKI treatment. It can be observed from Figure 8 that the drop in pH was faster when CO_2 was bubbled at a faster rate. CO_2 dissolves in water to form carbonic acid, and the carbonic acid further ionizes to form H^+, HCO_3^- and CO_2^-. This aids in lowering the pH of the slurry [27]. All three CO_2 flow rates were able to achieve an end pH of around 7 easily after VKI treatment.
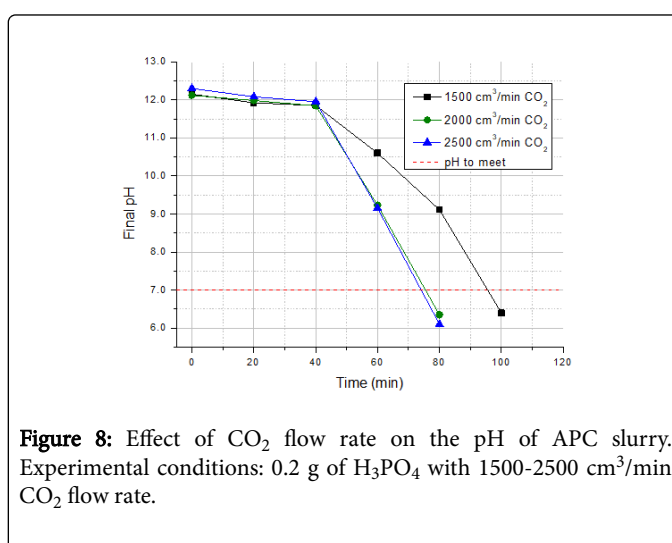

Figure 8: Effect of CO_2 flow rate on the pH of APC slurry. Experimental conditions: 0.2 g of H_3PO_4 with 1500-2500 cm³/min CO_2 flow rate.

TCLP leaching after VKI treatment

Table 2 shows the summary of the leaching of heavy metals before and after VKI treatment, using 0.2 and 0.5 g of H_3PO_4 per 100 g of APC residues, with 1500, 2000 and 2500 cm^3/min CO_2 dosing. Leaching of Cd increased by two orders of magnitude after VKI treatment, but remained below Singapore's acceptance criteria limit for landfill disposal. It seems that both H_3PO_4 and CO_2 dosing had no effect in reducing the leaching of Cd, which is different from Hjelmar and Birch and Hjelmar et al. [14,15] which indicated a slight decrease in Cd leaching after treatment. However, different leaching methods were carried out as TCLP was used in this study, compared with batch leaching tests from Hjelmar and Birch and Hjelmar et al. [14,15]. Another reason could be the pH, as pH-dependent leaching results indicated that Cd has a tendency to leach more under acidic than neutral pH conditions.

The effect of VKI treatment was not obvious on the leaching of Cr, although there was a slight decrease in the leaching when the CO_2 dosage increased to 2500 cm^3/min for both 0.2 g and 0.5 g H_3PO_4 set-ups. Pb leaching was reduced significantly to below ICP-OES detection limits when 1500 cm^3/min CO_2 dosing was used together with 0.2 g of H_3PO_4. Carbonate ions resulting from CO_2 interactions with water could bind with the lead (II) ions in the slurry to form stable and insoluble lead carbonates which provide chemical stabilization [27]. At the same time, some of the H_3PO_4 present neutralizes the excess lime that is typically found in the APC residues and forms apatite or apatite-resembling materials that are thermodynamically stable and possess good pH buffering capacities [16,28]. H_3PO_4 can also react with calcium carbonate (Equation 2), a by-product of the reaction between carbon dioxide and lime [29].

$$CaCO_3 + H_3PO_4 + H_2O \leftrightarrow CaHPO_4.2H_2O + CO_2 \qquad (2)$$

Calcium carbonate could react slowly with calcium phosphates, forming complex compounds such as calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ [28,30]. $Ca_{10}(PO_4)_6(OH)_2$ has been proposed as the fixation of several toxic divalent metal ions from aqueous solutions as it presents a high affinity with Pb [31].

However, when the CO_2 dosing rate increased to 2000-2500 cm^3/min, Pb leaching increased by two orders of magnitude to 0.014-0.0182 mg/L, but was still below Singapore's acceptance criteria for landfill disposal of 5 mg/L. The same trend was observed when 0.5 g of H_3PO_4 was used. While a higher flow rate of CO_2 can be applied for field applications to achieve faster kinetics, it compromises the leaching of Pb. This implies that a CO_2 flow rate of 1500 cm^3/min is sufficient for the treatment of APC residues.

Leaching of Cu and Zn increased slightly after VKI treatment. For both heavy metals, the degree of influence caused by H_3PO_4 in VKI treatment seems to be more dominant compared to CO_2. Both leaching patterns showed lower results when 0.5 g of H_3PO_4 was used, compared to 0.2 g. The effect of CO_2 dosing was not obvious in this case, as the leaching results varied among the three investigated flow rates.

Results of one-step VKI treatment

With the results obtained from the two-step VKI process, a one-step version of the VKI treatment was conducted using 0.5 g of H_3PO_4 with a CO_2 flow rate of 2500 cm^3/min. The time taken for the end pH to drop to 7 was slightly longer (90 min), compared to the two-step treatment which took 80 min. The suspension was also more viscous

compared to the two-step treatment, which hindered the filtering process. In terms of heavy metal leaching, Figure 9 shows that the leaching of Cd, Cr, Cu, Pb and Zn from the one-step treatment was not significantly different compared to two-step treatment. This could imply that soluble metal salts can be removed effectively through the combination of washing and stabilization process.
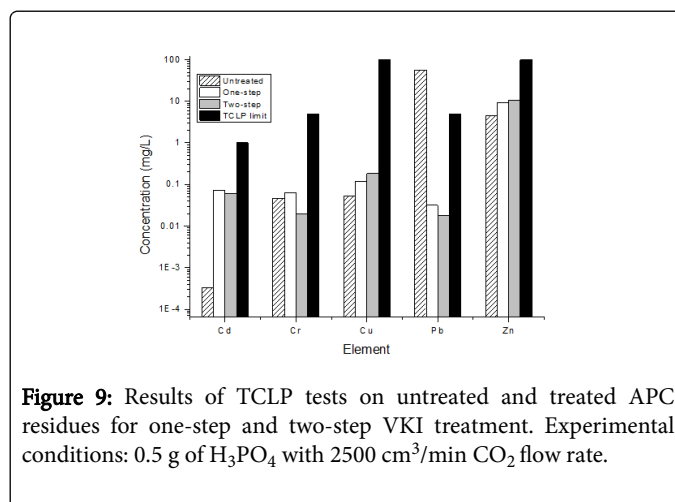
Figure 9: Results of TCLP tests on untreated and treated APC residues for one-step and two-step VKI treatment. Experimental conditions: 0.5 g of H_3PO_4 with 2500 cm^3/min CO_2 flow rate.

It can be seen clearly that the one-step VKI treated APC residues were able to meet Singapore's acceptance criteria for landfill disposal. The fact that a comparable level of quality of the treated APC residues was attained from both one-step and two-step treatment processes suggests that the one-stage treatment is a promising and viable modification that yields positive results.

Conclusion

This study provides a general perspective on the physiochemical properties on Singapore's APC residues produced from a MSW incineration plant, and the effect of VKI treatment on the leaching of heavy metals. The ANC studies have shown that the alkalinity and buffering capacity of APC residues were very high. From the pH-dependent leaching results, Cd, Cr, Cu, Pb, and Zn, had relatively low release between pH 7 and 10. For ease of industrial applicability, the end pH for VKI treatment was fixed at 7.

The two-step VKI process was optimized with H_3PO_4 and CO_2 as the two main parameters. Using H_3PO_4 alone was not able to achieve an end pH of 7 at a reasonable cost. Using CO_2 could bring the pH to 7, but the slurry became viscous which is not suitable for industrial application. Using both H_3PO_4 and CO_2 together proved to be successful in bringing the pH of the APC residues down to 7. The two-step VKI treatment on APC residues shows satisfactory stabilization with minimum leaching of heavy metals, and results for Pb leaching was significantly reduced. Subsequently, the development of the one-step VKI treatment was carried out using the optimized conditions from the two-step treatment. One-step VKI treatment was able to reduce the amount of water usage by 50%, due to the absence of the filtration process after initial washing. TCLP results of the treated APC residues from the one-step VKI treatment could achieve comparable metal leaching concentrations to the two-step process.

Acknowledgements

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