The incorporation of palm oil clinker (POC) in cement-based applications has been proven in recent studies. The aim of this work was to assess the heavy metal leaching behavior to ensure environmental safety of using POC in cement-based applications. The chemical composition, morphology, total organic carbon (TOC) and mineralogy were determined using XRF, FESEM, TOC analyzers and XRD to select appropriate chemical reagents for complete digestion. HNO₃, HF and HClO₄ were used for digestion of POC to measure heavy metal content using ICP-MS. The chemical reagents CH₃COOH, NH₂OH·HCl, H₂O₂+CH₃COONH₄ and HF+HNO₃+HCl were used for extraction of acid soluble, reducible, oxidizable and residual fractions of heavy metals in POC, respectively. The leaching toxicity of the POC was investigated by the USEPA 1311 TCLP method. The result showed the presence of Be, V, Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Ba and Pb with levels of 5.13, 11.02, 2.65, 1.93, 45.43, 11.84, 15.07, 0, 0, 81.97 and 1.76 mg/kg, respectively, in POC. The leaching value in mg/L of As (4.56), Cu (1.05), Be (0.89), Zn (0.51), Ba (0.26), Ni (0.17), V (0.15), Cr (0.001) and Se (0.001) is found well below the standard limit of risk. Risk assessment code (RAC) analysis confirms the safe incorporation of POC in cement-based applications.

Keywords: Cement-based applications; heavy metal; leaching toxicity; palm oil clinker; risk assessment code

Manfaat teknikal penggabungan Clinker Minyak Sawit (POC) dalam aplikasi berasaskan simen telah terbukti dalam kajian ini. Tujuan kerja ini adalah untuk menilai tingkah laku larut berat logam berat untuk memastikan keselamatan alam sekitar menggunakan POC dalam aplikasi berasaskan simen. Komposisi kimia, morfologi, jumlah karbon organik (TOC) dan mineralogy ditentukan menggunakan XRF, FESEM, penganalisis TOC dan XRD untuk memilih bahan uji kimia yang sesuai untuk pencernaan yang lengkap. HNO₃, HF dan HClO₄ digunakan untuk pencernaan POC untuk mengukur kandungan logam berat menggunakan ICP-MS. Bahan uji kimia CH₃COOH, NH₂OH·HCl, H₂O₂+CH₃COONH₄ dan HF+HNO₃+HCl digunakan untuk pengekstrakan asid larut, penurunan, pengoksidaan dan sisa pecahan logam berat masing-masing dalam POC. Ketoksisan lepasan POC telah dikaji menggunakan kaedah USEPA 1311 TCLP. Keputusan menunjukkan kehadiran Be, V, Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Ba dan Pb dengan tahap 5.13, 11.02, 2.65, 1.93, 45.43, 11.84, 15.07, 0, 0, 81.97 dan 1.76 mg/kg, masing-masing dalam POC. Nilai lepasan dalam mg/L As (4.56), Cu (1.05), Be (0.89), Zn (0.51), Ba (0.26), Ni (0.17), V (0.15), Cr (0.001) dan Se (0.001) didapati jauh daripada batasan piawaian risiko. Analisis kod penilaian risiko (RAC) mengesahkan keselamatan pematuhan POC dalam aplikasi berasaskan simen

Kata kunci: Aplikasi berasaskan simen; ketoksisan larut lesap; klinker minyak sawit; logam berat; penilaian kod risiko

Heavy Metals Leaching Behaviour Assessment of Palm Oil Clinker
(Penilaian Tingkah Laku Larut Lesap Logam Berat Klinker Minyak Sawit)

MOHAMMAD RAZAUL KARIM*, SUMIANI YUSOFF, HASHIM ABDUL RAZAK, Faisal I. CHOWDHURY & HOSSAIN ZABED

INTRODUCTION

The incorporation of palm oil clinker (POC) in cement-based applications are gaining more attention in recent years for sustainable use of this waste as well as to achieve a low carbon footprint in concrete production. At one hand, production of POC is increasing day by day due to uprisings demand of palm oil commodities; on the other hand, greenhouse gas (GHG) emission is also rapidly increasing, in which fast expansion of concrete industry is playing a major role (Awaluddin & Sulaiman et al. 2015; Commission 2013; Safiuuddin & Abdus Salam et al. 2011). POC is a waste material of palm oil mill which is dumped in open land that deteriorate the soil composition badly, contaminate the ground water and pollute environment (Ahmad et al. 2007; Kanadasan & Razak 2015, 2014a, 2014b). The technical feasibility of POC as supplementary cementitious material (Karim et al. 2017, 2016a) as well as aggregate in different type of concretes (Ibrahim & Razak 2016; Kanadasan & Abdul Razak 2015) are well proven in recent studies. One of the major concern of using POC in cement-based applications is the possibility of heavy metal content and its risk to leach out into the surrounding environment. Studies have shown that heavy metals are liable for serious health hazards, including alteration of DNA sequence (Azamana et al. 2015; Azrina et al. 2011; Grumiaux et al. 2015; Mani et al. 2007; Markad et al. 2015; Nayak et al. 2015). These metals can easily be transferred into ecosystem and food chain that can be hazardous to human health (Sahibin et al. 2008; Shaheen & Rinklebe 2015). Hence, heavy metal characterization and leaching toxicity assessment are an
urgent issue to ensure environmental and health safety before incorporation of POC in cement-based application. Although the actual reason behind the presence of heavy metals in POC has not yet been investigated thoroughly, it can be assume that the long term utilization of phosphate rock fertilizer for oil palm plantations increase zinc (Zn) and cadmium (Cd) content in soil (Azura et al. 2012) which in turn incorporate into POC. In addition, depending on geological condition of palm oil plantation area the nature of soil, rock (especially serpentinitic rock) and water also contain heavy metals such as magnesium (Mg), nickel (Ni), chromium (Cr), cobalt (Co) and manganese (Mn) (Aziz et al. 2015; Baharim et al. 2016; Yap 2012; Yunus et al. 2011). Due to soil erosion, heavy rainfall and overflowing flood carry these heavy metals to the plant soil. Moreover, the burning process might play a role to increase the heavy metals content in POC similar to the increase in oxides as a result of reduction of organic carbon (Karim et al. 2016). The chemical composition, morphology, mineralogy, organic carbon, heavy metal content were determined using XRF (Kanadasan & Abdul Razak 2015), FESEM (Karim et al. 2017), XRD (Karim et al. 2016), TOC analyzer (Karim et al. 2017) and ICP-MS (Singh & Kalamdhad 2013), respectively, in previous studies. Heavy metals mobility and bioavailability depend strongly on their chemical composition and mineralogical form (Li et al. 2011). The leach ability of heavy metals from POC depend on the bonding force of trace element in its matrix. The weak bonded metal fraction can easily leach out in water which can cause changes in pH level of soil (Singh & Kalamdhad 2013). The toxicity of heavy metals are expressed as a ratio of water-soluble fraction and total fraction of the content of metals (Pan et al. 2013; Singh & Kalamdhad 2013).

The present research is aimed to characterize the heavy metal content in POC and assess the potential risk of their presence in the POC for cement based applications. The leaching toxicity of the selected heavy metals i.e., As, Ba, Cu, Zn, V, Se, Be, Cr, Ni, Pb, Ag and Cd has also been investigated in this article. This study will be helpful for safe incorporation of POC in cement-based applications.

MATERIALS AND ITS CHARACTERISTICS

The POC was collected from Denkil, Kuala Lumpur, Malaysia which depicted in Figure 1. Samples were taken every alternative hour from the waste outlet of palm oil mill for a month. The collected POC is converted into small stones using a jaw crusher, then homogenized in rotary pan mixer. These small stones of POC were used for leaching toxicity assessment. The crushed POC stones were converted into palm oil clinker powder through grinding in a ball mill for 6 h with 150 RPM. The resulting homogenous material was used in this study for characterization.

The XRF (Model: AXions mAX) results (Table 1) show that POC powder is composed of inorganic oxides with a small fraction of organic carbon (3.35%). Previous studies also support the result of current research (Karim et al. 2017, 2016). Both FESEM micrographs and EDX spectra captured by Hitachi, SU8220 (Figure 2) show that As, Ba,
Cu, Zn, V, Se, Cr, Ni, Pb, Ag and Cd metals were present in POC powder. Particles of the powder were found irregular in shape and porous in nature due to unburned carbon (Karim et al. 2016).

The mineralogical composition as determined by using XRD of model Empyrean of Penalytical Co. (Figure 3) shows that quartz and cristobalite mineral of SiO₂ are found in the two theta range of 26.64° and 21.96° with intensity of 41442.21 and 9890.63 counts, respectively. The amorphisity hump at 2 theta range of 10° to 35° indicates glassy phase present in POC powder (Kanadasan & Abdul Razak 2015). The mineral eglestonite (Hg₉₆Cl₄₈O₃₂H₁₆), (K₆Na₄) Cl, lucite, halite (Na₄Cl₁₄), CrTaO₄ and lysite, elatossite (CuFeO₂), stbilite-Ca which may uptake from soil or water by palm oil plant. It is mentionworthy that the characteristics of POC powder is much controlled by the burning conditions, such as temperature, pressure and burning system (open or closed) as well as the material to be burnt (Haiying et al. 2010; Zhou et al. 2013).

HEAVY METAL DETECTION

The decomposition of POC is essential for accurate detection and measurement of heavy metal using the EPA 3052 method. The decomposition of POC depends on its characteristics as well as selection of chemical reagent for digestion. The EPA method allows variation in reagent. The chemical composition, mineralogy, morphology and TOC analysis confirm that the minerals of POC are stable and contain 3.35% of organic carbon. Parchloric acid (HClO₄) was used for the digestion of POC, because it contains organic carbon. The apparatus was washed carefully with acid and water for accurate results. One gram of POC sample was put into a vessel containing a mixture of 9 mL concentrated HNO₃ and 5 mL concentrated HF under a fume hood. Then, 5 mL of HClO₄ was added into it for decomposition of organic components. After adding the HClO₄ the color of digestion products becomes cream yellow. Thus the resultant mixture was run in a microwave digestor (Model: Multiwave PRO rotor 16 MF100) under p-rate of 0.80, temperature of 180°C and ramp of 100 for proper digestion. Mixture of hydrochloric acid (2 mL) and nitric acid (2 mL) was used in it for stabilization of Ag and Ba. The solid phase of POC sample almost disappeared into the solution. The digestive solution was then transferred to a volumetric flask and was diluted up to a volume of 100 mL with deionized water containing 3% of nitric acid. This solution was used for heavy metals analysis using ICP-MS (Model: Penalytical, 7500 series).

TABLE 1. Chemical composition of POC powder

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>61.29</td>
<td>5.89</td>
<td>4.31</td>
<td>3.20</td>
<td>3.16</td>
<td>10.79</td>
<td>3.12</td>
</tr>
</tbody>
</table>

HEAVY METAL DETECTION

The decomposition of POC is essential for accurate detection and measurement of heavy metal using the EPA 3052 method. The decomposition of POC depends on its
LEACHING BEHAVIOR ASSESSMENT

Leaching behavior of POC was investigated by applying TCLP of USEPA1311, 1992 (Lincoln et al. 2007; Sun et al. 2006). Five grams of POC with particle size less than 9.5 mm (solid sample: solution ratio = 1:20) was added to 100 mL acetic acid at pH of 4.93 ± 0.05 in a covered conical flask. This flask was agitated at 25ºC for 18 h in a control shaker by setting at 30±2 RPM. The extract was filtered into a 100 mL flask with a 0.45-µm pore size syringe filter, and then acidified by nitric acid to pH<2. The pH was determined on unfiltered aliquots of leachate using a polycarbonate tube for analysis of heavy metal using ICP-MS. TCLP analyses were performed three times in the sample and the outcomes was averaged and this value was considered as the leaching value of POC. The summary of test procedure and conditions has been presented in Table 2.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>USEPA 1311 TCLP, 1992</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test type</td>
<td>Batch</td>
</tr>
<tr>
<td>Solid to leachate ratio</td>
<td>1:20</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>4.93</td>
</tr>
<tr>
<td>Particle size</td>
<td>&lt; 9 mm</td>
</tr>
<tr>
<td>Sample mass/leachate volume</td>
<td>5 g/100 mL</td>
</tr>
<tr>
<td>Duration of agitation</td>
<td>18 h</td>
</tr>
<tr>
<td>Agitation system</td>
<td>Controlled shaker</td>
</tr>
<tr>
<td>Filtration</td>
<td>Syringe</td>
</tr>
<tr>
<td>Filter type</td>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>Filter pore size</td>
<td>0.45 µm</td>
</tr>
</tbody>
</table>

SPECIATION ANALYSIS

The chemical reagents used in speciation analysis were supplied by the Merck, Malaysia and a list is presented in Table 3. The four steps sequential chemical extractions were used for phase information (Wang et al. 2015) as shown in the same table. One gram of sample was added in Teflon beaker. This is a sequential method in which first step residue was used in the next step. Before used in the next step, the residue was washed with deionized water. The pH at second step was adjusted by 1N HNO₃. The beaker containing residual sample was heated up to dryness about 6 h on a heating plate. After that, 5 mL of nitric acid and 5 mL of water were added and the solution was filtered in a filter paper of medium porosity into a volumetric flask where the total volume of the solution was raised to 50 mL by adding distilled water (Pontes et al. 2010). The average of three samples was reported as the result in this experiment.

RESULTS AND DISCUSSION

HEAVY METAL LEVEL IN POC

The concentration of heavy metal depends on the geological condition of the area where palm oil tree was grown and burning condition in boiler of palm oil mill (Singh & Kalamdhad 2013). In the present study, the concentration level of the heavy metals in POC, as shown in Table 4, was found in the sequence of Ba > Cu > As > Zn > V > Se > Be > Cr > Ni > Pb > Ag > Cd. The results showed that the concentration of Ba is the highest (81.97 mg/kg) which is far greater than any other metal content in POC. This may be due to the high Ba based mineral content in soil.
value of 5 and 1 mg/L, respectively, of standard. The POC is produced as the burning of palm waste at a temperature range of 500-800°C. The oxide of As is vaporized easily at this temperature. This study ensure the presences of K₂O in POC. The gas phases K may react with arsenic and produce amorphous minerals at the time of cooling. This may be the possible causes of highest concentration Arsenic in POC. The concentration of Ni, Cu and Zn are much lower compared with standard values. These metals can easily be vaporized from palm oil waste during incineration; incomplete burning may be responsible for their presences in POC. The leaching values of the Cr, Ag, Cd and Pb are found near to zero. These may be vaporized at combustion temperature or redistributed in a stable mineral form which cannot be leached out from POC.

SPECIATION ANALYSIS

Leaching of heavy metals from waste material depends on its bonding energy in the matrix as well as leaching condition (Haiying et al. 2010; Singh & Lee 2015; Wu et al. 2015). The speciation analysis of POC provides an idea about the capability heavy metals in POC to leach in different environmental conditions. Speciation of different heavy metals from POC is presented in Figure 4. The acid soluble fraction of POC is found in the range of 0.0% to 9.27%. The weakly bonded metals of POC can be released and converted into free positive ions that can be consumed by different biological entity such as plants. The acid soluble fraction of heavy metals has greater mobility in nature because minerals or alloys containing As, Ni and Be metals are unstable in the presence of acid (Singh & Lee 2015). The significant mobility of the positive metal ions impose a greater risk of contamination of the ground water as well as surface water or soil composition.

The small amount of V, Se, Cu and As also be liberated from the POC matrix in acidic solution. The other metals were observed not to interact with an acidic solution. The higher leaching tendency of As, Ni and Be in acidic condition is the predominant factor in utilizing POC in concrete construction where acid rain is more likely.

From sequential extraction of heavy metals from POC, the reducible fractions of metals were found in the following order: Zn (21.73%) > V (16.80%) > Be (16.26%) > Se (11.50%) > Ba (9.06%) > Ni (8.81%) > As (7.81%) > Cu (4.49%) > Cr (1.10%) > Pb (0.15%). In addition, the oxidizable part of heavy metals in POC were present in following sequence: Cu (45.69%) > Se (37.25%) > Cr (24.68%) > Pb (23.0%) > Be (20.47%) > V (17.27%) > Ni (16.67%) > As (13.71%) > Zn (10.80%) > Ba (0.65%). The acid soluble fraction of heavy metals is less stable than the reducible and oxidizable fractions in POC matrix. Ag (0%) and Cd (0%) are totally absent in the acid soluble, reducible and oxidizable fraction. The residual parts in POC are mainly quartz minerals, which are stable in normal environmental condition. The residual parts in POC of Be, V, Cr, Ag, Cd, Ba, Ni, Cu, As, Se and Pb are 55.62%, 463.06%, 73.36%, 100%, 100%, 89.18%, 66.42%, 47.33%, 62.94%, 69.19%, 43.86% and 76.33%, respectively.

The major fraction of heavy metals is released in residual fraction indicating that heavy metals do not leach from solid matrix of POC in normal environmental condition (Pan et al. 2013; Wang et al. 2015). So, there is no potential threat to environment and health safety.

RISK ASSESSMENT CODE ANALYSIS

The solubility of POC depends on different bonding energy in solid matrix. If the hydration energy exceeds existing bonding strength of POC matrix, POC dissowed into the solution; otherwise, the metals of POC are deposited as residue at the bottom of the vessel (Li et al. 2011). The reactivity depends on the dissolving capability of metals in the medium. The bioavailability and potential leaching toxicity risk of POC for incorporation in concrete construction or disposal to landfills largely depends on the dissolving capacity of metals in a particular environmental condition (Pan et al. 2013; Wang et al. 2015). The Risk

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TABLE 4. Total concentration of different heavy metals in POC

<table>
<thead>
<tr>
<th>Elements</th>
<th>Be</th>
<th>V</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Se</th>
<th>Ag</th>
<th>Cd</th>
<th>Ba</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/kg)</td>
<td>5.13</td>
<td>11.02</td>
<td>2.65</td>
<td>1.93</td>
<td>45.43</td>
<td>11.84</td>
<td>15.07</td>
<td>6.5</td>
<td>0</td>
<td>0</td>
<td>81.97</td>
<td>1.76</td>
</tr>
</tbody>
</table>

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FIGURE 4. Speciation of targeted metals of POC
Assessment Code (RAC) of a particular heavy metal is the ratio of the acid soluble fraction to the total amount of the heavy metal in POC (Wang et al. 2015). The risk is categorized into five classes based on the value of RAC. The values of RAC obtained in the present study of Cr, Ag, Cd and Pb were 0.84%, 0%, 0% and 0.51%, respectively. The values of these metals are less than 1%, which is not harmful to environment. As can be seen from Figure 5, all the heavy metals Ba(1.09%), Ni(8.09%), Cu(4.62%), Be(7.63%), V(2.85%), Zn(4.53%), As(9.27%) and Se(7.38%) fall in the low risk class (Pan et al. 2013; Wang et al. 2015).

CONCLUSION

Heavy metal leaching behavior of POC and the corresponding environmental and health risk have been investigated in the present study according to the USEPA 1311 TCLP method standards. The following inferences may be drawn from the present study. Palm oil clinker (POC) consist of a mixture of inorganic oxides along with 3.35% organic carbon. While the major minerals composing POC are quartz and cristobalite, eglesonite (Hg_96Cl_48O_32H_16), K_Na_4Cl, leucite, Halite (Na_4Cl_14), CrTaO_4, lisyte, elattosite (CuFeO_2) and Stbilite-Ca minerals are also present in small scale. Heavy metals found in POC are Be, As, Ba, Cu, Zn, V, Se, Cr, Ni, Pb, Ag and Cd. The presence of Be, V, Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Ba and Pb with levels of 5.13, 11.02, 2.65, 1.93, 45.43, 11.84, 15.07, 0, 0, 81.97 and 1.76 mg/kg, respectively, is in POC. The leaching value in mg/L of As (4.56), Cu(1.05), Be (0.89), Zn(0.51), Ba(0.26), Ni (0.17), V(0.15), Cr(0.001) and Se (0.001) is found well below the standard limit of risk. Risk code analysis (RAC) confirms that the heavy metals of POC pose a low risk to the environment. The data reported in this study may be regarded as base values for the distributions of heavy metals in POC for Denkil region of Kuala Lumpur and may be used as reference for environmental leachiability of these heavy metals in that particular region.

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