LEACHING BEHAVIOUR OF Cs-134 IMMOLISISED IN CEMENT-BIOCHAR MATRIX

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Graphical abstract

Abstract

The leaching behavior of cesium -134 (Cs-134) from cement mixed with 5%, 11% and 18% of biochar has been investigated accordance with the ANSI/ANS 16.1-2003 method. The leachate was collected and measured using gamma spectrometry after the leaching periods of 2 h, 7 h, 24 h, 14 days, 28 days, 43 days and 90 days. In order to evaluate the leaching behavior of Cs-134 from cement biochar matrix, the cumulative leach fraction, leaching rate, diffusion coefficient and leachability index for Cs-134 were calculated. The compressive strength of the specimen after 90 days of leaching test was also performed to evaluate its durability in the water. The results indicated that the addition of biochar affects the leaching behavior of Cs-134 from the cement matrix. The optimum amount of biochar required to obtain the lowest leachability and the highest compressive strength of Cs-134 was found to be at 11%. The leaching of Cs-134 from cement-biochar matrix was found less than 20%, in which the leaching behavior approximates that of a semi-infinite medium. The leachability indices of all specimens were above the recommend minimum value of 6, which suggest the leaching behavior of Cs-134 from cement-biochar matrix occurred in a very slow diffusion.

Keywords: Biochar, cement, cesium-134, leaching behavior

Abstrak


Kata kunci: Bioarang, simen, sesium-134, kelakuan larut resap

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1.0 INTRODUCTION

Cement is the best material for immobilisation of various types of low and intermediate level radioactive wastes. This method has been practiced for many years in many countries due to its low cost, durability, simple operational conditions and availability [1]. Most of low and intermediate level cemented radioactive wastes are stored and disposed of in near-surface disposal facility [2]. Thus, for the long-term durability of the cemented radioactive wastes in disposal facility it is crucial to prevent the migration and dispersion of radionuclides into the environment.

The most common type of cement used as a binding agent for radioactive waste is hydraulic cements i.e. Ordinary Portland Cement (OPC). This type of cement provides both physical and chemical contributions to immobilisation of radioactive waste [3]. However, cement has unfavorable characteristics as a binding agent i.e. high leachability of radionuclides, especially to cesium. The sorption of cesium in cement matrix is low and cesium also remains soluble in the high pH environment of cement [4]. Thus, there have been many studies conducted by researchers to improve the leaching properties of radionuclides in the cementitious material. It has been suggested that the leachability of radionuclides can be reduced by adding a proper amount of admixture such as bentonite, vermiculite, alumina, blast furnace slag, silica fume and ilmenite [5-7]. In this study, biochar was used as an admixture for cement immobilisation in cement. In general, biochar is a carbon-rich product of biomass pyrolysis that has a high degree of porosity and extensive surface area [8]. Recently, biochar received considerable attention because it has many potential in environmental applications and advantages [9]. Biochar made from various biomass materials are found to have the ability to remove heavy metals [10], organic pollutant [9] and radionuclides [11]. Therefore, this study aimed to evaluate the leachability of cesium-134 (Cs-134) immobilised in a cement-biochar matrix using the ANSI/ANS 16.1 leach test method [12]. Cesium was chosen because it exists as a crucial component of many waste streams [13] and Cs-134 was selected in this study due to its short half-life (2.1 years) compared to Cs-137 (30 years). The incremental leaching rate, cumulative leaches fraction, leaching rate, diffusion coefficient and leachability index for Cs-134 were determined using diffusion release models. Besides that, the characterization study for EFB biochar was also conducted.

2.0 METHODOLOGY

2.1 Preparation of Biochar

Empty fruit bunch (EFB) biochar was obtained from Universiti Putra Malaysia, Serdang Selangor, Malaysia. The biochar was produced from the pyrolysis of EFB at medium temperature (250 - 450°C). EFB biochar was ground and sieved by USA Standard Sieve No. 18 (corresponding to 1 mm) before used as an additive material for cement.

2.2 Characterisation of Biochar

C, H, N and S elemental analyses were performed with CHNS Analyser (Model CHNS-932, USA). Scanning electron microscopy (SEM) (Model FEI 400) equipped with energy dispersive X-ray analysis (EDX) was used to observe surface morphology and to determine the elemental composition of biochar. Crystalline minerals of biochar were identified by X-ray diffraction (XRD) (P Analitical Model PW3040/60 X’pert PRO). The chemical functional groups in biochar were determined using Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Model Spectrum 2000/L183).

2.3 Preparation of Specimens

The cement specimens used in this study was Ordinary Portland Cement (OPC) supplied by Lafarge Malaysia Berhad. It is local OPC manufactured according to British Standard BS EN 197-1:2000-CEM II/B-M 32.5. Cement-biochar based matrices were prepared by mixing the OPC with different amount of biochar (5%, 11% and 18%) (wt/wt) at water to cement (w/c) ratio of 0.5. About 2 g of CsCl solutions (8.8 x 10^6 Bq) were spiked into the cement biochar mixtures. The mixtures were mixed using laboratory cement mixer for about 10 min at room temperature (26 °C ± 1). The cement pastes were poured into the polyethylene cylinder moulds (10 cm diameter and 10 cm height) and vibrated to remove air bubbles. After a setting time of 24 h the specimens were removed from the moulds, inserted into plastic bags, sealed and allowed to cure for 28 days at room temperature.

2.4 Leaching Test

The main objective of leaching test of cemented radioactive waste is to assess its potential hazard to the environment [14]. The leaching test was performed according to the ANSI/ANS-16.1-2003 method [12]. The leachant was distilled water with a pH of 7.98 and the conductivity of 4.34 µs. All the specimens were leached in cylindrical polyethylene containers with a volume of leachant to the external geometric surface area of specimen (471.2 cm²) ratio of 10. The leachant was sampled and replaced after cumulative leach times of 2 h, 7 h, 24 h, 14 days, 28 days, 43 days and 90 days. The concentrations of Cs-134 in the leachates were analysed using gamma spectrometer.

The incremental leaching rate is the fraction leached per unit time (F/d). The incremental fraction leached rate (ILR) can be calculated by the following equation:

\[ \text{ILR} = \frac{\text{F}_d}{c} \]
\[ ILR = \frac{[A_n/A_0]}{[\Delta t]_n} \quad \text{(Eq. 1)} \]

where,

- \( A_n \) is the quantity of a nuclide released from the specimen during leaching interval \( n \) (Bq).
- \( A_0 \) is the total quantity of a given radionuclide in the specimen in the beginning of the first leaching interval (Bq).

\[ (\Delta t)_n = t_n - t_{n-1} \] is the duration of the \( n \)'th leaching interval (s)

For the cumulative fraction leached (CFL), it can be calculated as follows:

\[ \text{CFL} = \frac{\Sigma a_n}{A_0} \quad \text{(Eq. 2)} \]

where,

- \( \Sigma a_n \) is the cumulative quantity of a nuclide released from the specimen from the beginning of the first leaching interval to the end of leaching interval of concern (Bq). The percent release is calculated by multiplying CFL x 100.

It is assumed that if less than 20% of leachable species is leached from uniform, regularly shaped solid, its leaching behavior approximates that of a semi-infinite medium [12]. Thus, the effective diffusivity is calculated using the following equation:

\[ D = \pi \left( \frac{A_n/A_0}{(\Delta t)_n} \right)^2 \left( \frac{V}{S} \right)^2 T \quad \text{(Eq. 3)} \]

where,

- \( D \) is the effective diffusivity (cm²/s)
- \( V \) is the volume of specimen (cm³)
- \( S \) is the geometric surface area of the specimen as calculated from measured dimensions (cm²)
- \( T \) is the leaching time representing the mean time of the interval (s) and calculated as follows:

\[ T = \left[ t_n^{1/2} + t_{n-1}^{1/2} \right]^2 \quad \text{(Eq. 4)} \]

However, if more than 20% of leachable species, \( D \) can be calculated from a shape specific solution of the mass transport equations using tabular or graphical method as shown in ANSI/ANS-16.1-2003 [12]. Thus, \( D \) can be calculated using the following equation:

\[ D = G \frac{d^2}{t} \quad \text{(Eq. 5)} \]

where,

- \( G \) is a time factor for the cylinder, dimensionless that can be obtained from the table A.1 in ANSI/ANS-16.1-2003 [12]. To use this table, cumulative leached fraction and length-over-diameter (l/d) ratio are calculated to obtain the \( G \) value.

Once the effective diffusivity values are determined, the leachability index (L) can be calculated using this following equation:

\[ L = \frac{1}{n} \log \left( \frac{\beta}{D} \right) \quad \text{(Eq. 6)} \]

where,

- \( L \) is the leachability index (dimensionless)
- \( \beta \) is constant, 1 cm²/s
- \( n \) is leach interval
- \( D \) is effective diffusivity (cm²/s)

The leachability index is defined as the log of the reciprocal effective solid diffusion coefficient [15]. Based on NRC requirement, the leachability index as calculated in accordance with ANSI/ANS 16.1 should be greater than 6.0, which is considered satisfactory for an encapsulation process [16].

2.5 Compressive Strength

After 90 days of leach testing, the compressive strength test was conducted to the specimens. The compressive strength test was conducted according to ASTM C39 / C39M-05 [17]. For each formulation, three specimens were tested and the average values of compressive strength were reported. The compressive strength was measured using the ENERPAC compression tester (Model P-84/USA) with a maximum load of 1000 psi/700 bar. The criterion of mechanical strength for cement waste form more than 3.45 MPa (500 psi) was used to evaluate the waste form as recommended by the US Nuclear Regulatory Commission (NRC) Standard [16]. The comparison of the compressive strength was also made with the standard curing specimen (age of 28 days).

3.0 RESULT AND DISCUSSION

3.1 Properties of Biochar

Table 1 shows the result of elemental content of EFB biochar. It was found that carbon is the highest content in EFB biochar followed by nitrogen and hydrogen. Based on International Biochar Initiative (IBI) Standard (IBI-STD-01.1), this EFB biochar can be considered as a class 2 biochar (30 - 60% of carbon content) [18]. Generally, the hydrogen/carbon (H/C) ratio indicates the degree of carbonization [19] which is related to unburned of fuel material such as cellulose and lignin [20]. In this study, the H/C ratio of EFB biochar was 0.1 and can be considered low, which indicates that the biochar is highly carbonized. The H is primarily associated with the organic matter
in biomass [21] and the low value of H indicates that EFB biochar has low organic matter content.

Table 1 Elemental composition of EFB biochar

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>45.3 ±11.6</td>
</tr>
<tr>
<td>H</td>
<td>2.5 ± 0.22</td>
</tr>
<tr>
<td>N</td>
<td>3.01±1.32</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Figure 1 shows the SEM micrograph of biochar at 1000x and 500x magnification. As shown in Figure 1(a) and 1(b), the EFB biochar possesses well-defined pores structure and the smooth wall surfaces. This porous structure of biochar is beneficial for the removal of contaminants [22]. The result of EDAX (Figure 1(c)) showed that the amount silica in EFB biochar was about 2.4 %, which is considered low. Since the silica content was low and the carbon content was high it is believed that EFB biochar may has a low pozzolanic activity. XRD spectra of EFB peak are showed in Figure 2 and there are two diffracted peaks were observed. It could be said that EFB was amorphous material with little crystalline. The FTIR spectra of EFB biochar are shown in Figure 3. The spectra of EFB biochar display the bands containing O-H, C-H, C=O and C-O stretch. These functional groups can interact with cation to form surface complexes on biochars [10].
**Figure 2** XRD spectra of EFB biochar

**Figure 3** FT-IR spectrum of EFB biochar
3.2 Leaching Characteristics of Cs-134

The incremental leaching rates (ILR) obtained from Cs-134 immobilised in cement-biochar matrices are shown in Figure 4(a-c). As seen in Figure 4, it was found that the incremental leaching rates of Cs-134 from the cement-biochar matrices decrease with time. The incremental leaching rates of Cs-134 from the cement-biochar matrices with 5%, 11% and 18% biochar measured after 90 days were in the range of $4.8 \times 10^{-10} - 2.8 \times 10^{-7}$ cm/d, $5.8 \times 10^{-10} - 3.2 \times 10^{-7}$ cm/d and $4.6 \times 10^{-10} - 1.5 \times 10^{-7}$ cm/d, respectively. The variation in the leaching rates of the cement-biochar matrices may be related to their porosity. It seems that the leaching rates were influenced by the amount of biochar in the specimens. It is believed that the addition of biochar change the porosity of the cement matrix. However, based on the Figure 4, the specimen with 11% biochar content was the lowest among the three specimens. The incremental leaching rates for the three specimens in this study were ranked according to this following order: CBC 18% > CBC 5% > CBC 11%. Thus, the 11% of biochar should be selected as the admixture for cement because it showed a very low incremental release rate.

Figure 5 presents the cumulative fraction leached (CFL) of Cs-134 from the cement-biochar matrices with different amount of biochar. It was found that the CFL increases linearly with the square root of time in 90 days of leaching test. As shown in Figure 5, the specimen with 11% biochar showed much lower CFL compared to the specimen with 5% and 18% biochar. This finding suggests that the optimum value of biochar appears at 11%. The result also reveals that the released data indicates that about 1.6 - 2.2 \% of initial Cs-134 was released from the cement-biochar matrices after 90 days of leaching test. Since the leaching of Cs-134 was less than 20%, it seems that the leaching behavior of Cs-134 from cement-biochar matrix approximates that of a semi-infinite medium [12]. However, the mechanism that fully controls the leaching process can be determined by the slope of linear regression of the logarithm of CLF versus the logarithm of time [23]. Furthermore, the slope value of 0.35 indicates that the controlling leaching mechanism is surface wash-off, 0.35 - 0.65 is diffusion control and > 0.65 represents the dissolution mechanism [24]. Table 2 provides the slope of linear regression from the plot of the logarithm of CLF versus the logarithm of time for the cement-biochar matrices with 5%, 11% and 18% of biochar. From the data in Table 2, it is apparent that the slope values for the cement-biochar matrices with 5% and 11% biochar were less than 0.35 and thus indicate the surface wash off mechanism. Moreover, this surface wash-off mechanism is related to the release of soluble complexes on the surface of the specimen [25]. While, the slope value for the cement-biochar matrix with 18% biochar was 0.40, which demonstrate the diffusion mechanism. For the diffusion mechanism, the leaching process occurred through the pore space in the waste form.
Figure 5 Leachability of Cs-134 in cement-biochar matrix at different percentage of biochar

Table 2 The slope of linear regression from the plot of logarithm of CLF versus the logarithm of time and $R^2$ (correlation coefficient) for the specimen with 5%, 11% and 18% of biochar content

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBC5%</td>
<td>0.31</td>
<td>0.94</td>
</tr>
<tr>
<td>CBC11%</td>
<td>0.30</td>
<td>0.99</td>
</tr>
<tr>
<td>CBC18%</td>
<td>0.40</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Table 3 Average effective diffusivity (D) and leachability index (L) of Cs-134 from cement-biochar matrix and the comparison with other leaching studies

<table>
<thead>
<tr>
<th>Binder</th>
<th>Type of Waste</th>
<th>Admixture</th>
<th>Leaching Time (Day)</th>
<th>Volume/Surface Area (cm$^2$)</th>
<th>Average D (cm$^2$/s)</th>
<th>L$_i$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>Cs-134 solution</td>
<td>Biochar, 5%</td>
<td>90</td>
<td>10</td>
<td>$2.7 \times 10^{-12}$</td>
<td>12.1</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11%</td>
<td></td>
<td></td>
<td>$1.9 \times 10^{-12}$</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18%</td>
<td></td>
<td></td>
<td>$2.3 \times 10^{-12}$</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td>Borate radioactive resins (Cs-137)</td>
<td>Zeolite, 5%</td>
<td>42</td>
<td>12.7</td>
<td>$1.4 \times 10^9$</td>
<td>8.85</td>
<td>[29]</td>
</tr>
<tr>
<td>Cement</td>
<td>Cement solidified waste (Cs-137)</td>
<td>-</td>
<td>90</td>
<td>10</td>
<td>$1.2 \times 10^{-9}$ - $3.3 \times 10^{-9}$</td>
<td>8.55 - 9.02</td>
<td>[32]</td>
</tr>
<tr>
<td>Fly ash belite cement</td>
<td>Cs-134 solution</td>
<td>zeolite</td>
<td>90</td>
<td>10</td>
<td>$2.8 \times 10^9$</td>
<td>8.6</td>
<td>[33]</td>
</tr>
</tbody>
</table>

3.3 Compressive Strength

Figure 6 shows the compressive strength of the specimen after 90 days of leaching test versus the compressive strength of the standard curing specimen (28 days of age). Comparing with the standard curing specimen (28 days of age), the strength increases about 12% for the specimen with 5% of biochar and about 2.4% for specimen with 11% of biochar. Based on the result, the increase of the compressive strength after the specimen underwent the leaching test indicates that the further hydration
occurred when the specimen in contact with the water. It is believed that a part of water will penetrate into the structural cemented waste interlayer and leading to a decrease of the external porosity [28]. When the voids are filled with precipitated phases, the material strength could be increased by the segmentation of the porosity and by the different nature of the precipitated phases. However, the compressive strength was found decreased for the specimen with 18% of biochar. The decreased of the compressive strength may be related to the porous physical structure of biochar, which can absorb and retain water. Too much water in the specimen will increase the dissolution and leaching of CH in the water [28]. Therefore, it can increase the porosity of the cement matrix and lower the strength.

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The leaching behavior of Cs-134 from cement-biochar matrix was investigated. The experimental results have shown that the addition of biochar affects the leaching behavior of Cs-134 in the cement matrix. It could be stated that the addition of biochar to the cement has changed the porosity of the cement matrix in which the surface of cement matrix appears more heterogeneous. It is believed that porous structure of biochar plays a role in retained of Cs-134 in the cement-biochar matrix. However, the optimum value of biochar was apparently at 11% which showed the lowest leachability of Cs-134 and the highest compressive strength after 90 days of leaching test compared to 5% and 18% of biochar. The leaching of Cs-134 from the cement-biochar matrix was found less than 20% and suggests that the leaching behavior of Cs-134 from the cement-biochar matrix approximates that of a semi-infinite medium. Based on the data obtained from this study, it was found that the mechanism involved in the leaching of Cs-134 from the cement-biochar matrix was surface wash-off and diffusion mechanism. The leachability indexes of all cement-biochar matrices were above the recommended minimum of 6 that allowed their acceptance for disposal. Further work on the leachability of cesium in different types of leachant such as groundwater, rainwater and sea water need to be performed for fully assess the leaching behavior of cesium from the cement-biochar matrix in the disposal environment.

Figure 6 Compressive strength of the specimen after 90 days of leaching vs. the specimen at 28 days of age

4.0 CONCLUSION

The leaching behavior of Cs-134 from cement-biochar matrix was investigated. The experimental results have shown that the addition of biochar affects the leaching behavior of Cs-134 in the cement matrix. It could be stated that the addition of biochar to the cement has changed the porosity of the cement matrix in which the surface of cement matrix appears more heterogeneous. It is believed that porous structure of biochar plays a role in retained of Cs-134 in the cement-biochar matrix. However, the optimum value of biochar was apparently at 11% which showed the lowest leachability of Cs-134 and the highest compressive strength after 90 days of leaching test compared to 5% and 18% of biochar. The leaching of Cs-134 from the cement-biochar matrix was found less than 20% and suggests that the leaching behavior of Cs-134 from the cement-biochar matrix approximates that of a semi-infinite medium. Based on the data obtained from this study, it was found that the mechanism involved in the leaching of Cs-134 from the cement-biochar matrix was surface wash-off and diffusion mechanism. The leachability indexes of all cement-biochar matrices were above the recommended minimum of 6 that allowed their acceptance for disposal. Further work on the leachability of cesium in different types of leachant such as groundwater, rainwater and sea water need to be performed for fully assess the leaching behavior of cesium from the cement-biochar matrix in the disposal environment.

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