Interactions of aqueous Cu^{2+}, Zn^{2+} and Pb^{2+} ions with crushed concrete fines

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Abstract

The crushing of reclaimed concrete-based demolition waste to produce recycled aggregate gives rise to a large volume of cement-rich fine material for which market development would be beneficial. It was envisaged that this fine fraction may prove to be an effective sorbent for aqueous heavy metal species by virtue of its ion exchangeable phases and high pH.

A batch sorption study confirmed that crushed concrete, in the particle size range 1–2 mm, successfully excluded Cu^{2+} (35 mg g^{-1}), Zn^{2+} (33 mg g^{-1}) and Pb^{2+} (37 mg g^{-1}) from aqueous media. Subsequent distilled water leaching of the metal-laden concrete particles indicated that 1.9, 0.9 and 0.2% of the bound metals, Cu^{2+}, Zn^{2+} and Pb^{2+}, respectively, were readily soluble. Scanning electron microscopy revealed that the removal of Cu^{2+} and Zn^{2+} arose from surface precipitation reactions, whereas, the principal mechanism of uptake of Pb^{2+} was found to be by diffusion into the cement matrix. The metal ion removal efficiency of crushed concrete fines is compared with those of other low cost sorbents and potential applications which may exploit this sorptive property are also discussed.
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Keywords: Recycling; Cement; Demolition waste; Heavy metal ions; Sorbent

1. Introduction

Environmental directives to preserve non-renewable resources and to divert waste consigned to landfill have encouraged aggregate recycling within the construction industry. The term 'aggregate' in this context relates to sand, gravel or crushed rock which is used in construction applications. It is estimated that approximately 20–30% of the 300 million tonnes of construction and demolition (C&D) waste generated in the USA is currently being recovered and recycled [1]. Accurate statistics regarding recycling are not available for every European Union (EU) member, although it is thought that between 175 and 300 million tonnes of C&D waste were generated in the EU each year during the late 1990s [1,2]. Most EU member countries have now established C&D recycling targets of between 50 and 90% [1].

The Netherlands and Denmark have already implemented exceptionally successful recycling programmes in which 95 and 90% of their respective C&D wastes are currently being recovered and reused [1]. Whereas, in the UK, the Environment Agency estimates that approximately 25 million tonnes of C&D waste were crushed and recycled during 1999 [3] and the government has set a target to reuse a minimum of 55 million tonnes of reclaimed aggregate per annum by 2006 [4].

The viability of aggregate recycling is determined by a number of parameters including; availability, engineering credentials, market forces and tax incentives. The potential applications of an abundant cost-effective supply of recycled aggregate are essentially limited by its physical and engineering characteristics [5]. Performance criteria such as; density, thermal expansion, absorption, soundness, strength and/or particle size distribution are subject to regulation depending on the prospective application. Crushing of reclaimed concrete-based demolition waste produces a large volume of fine matter (<5 mm) which is rich in hydrated cement phases,

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the coarser fraction being predominantly composed of primary aggregate. It is the coarse fraction which is of use in construction, whereas the low density, high absorption, inferior soundness and irregular size distribution of the fine fraction often preclude its use as aggregate, fill or sub-base material. Market development for this cement-rich fine fraction would provide a further incentive for aggregate recycling and mitigate the proportion of demolition waste destined for landfill.

The use of Portland and other alkaline cements for the treatment and conditioning of heavy metal-bearing liquid, sludge and particulate wastes is well established [6,7]. The mechanisms underlying immobilisation of heavy metal ions by cement matrices are summarised as: 'sorption' or ion exchange by the nanoporous hydration product, calcium silicate hydrate; precipitation of insoluble hydroxides and hydrated metal silicate salts; and lattice incorporation into crystalline components of the hydrated cement matrix. Conventional cement solidification and stabilisation are carried out by the intimate mixing of anhydrous cement, waste matter and water, with the possible incorporation of aggregate and other additives.

Heavy metal-bearing wastewater and sludges arise from a number of sources including; steelworks, tanneries, mining, plating, finishing and galvanising activities. The high cost of established water-treatment practices, such as adsorption onto activated carbon and ion exchange using resins, continues to stimulate research in the development of more economical sorbent materials, particularly those which are derived from other industrial waste products [8–11]. Accordingly, it is envisaged that mature cement paste matrices of the fine fraction of recovered concrete-based demolition waste may effect the removal of heavy metal species from aqueous waste streams. The research reported herein has been carried out to test this postulate and to determine the nature of the interactions of aqueous heavy metal species with the mature cement matrix.

The removal of Cu^{2+}, Zn^{2+} and Pb^{2+} from aqueous solutions by the 1–2 mm fraction of crushed concrete (hereafter, CCF) has been investigated in a batch sorption study. The crushed concrete was prepared in the laboratory rather than having been collected from a demolition site in order

that this initial investigation would be carried out on well-characterised, reproducible, uncontaminated material against which the performance of real C&D waste in future trials could be tested. Following batch sorption, the metal-bearing CCF granules were subjected to a distilled water leaching procedure to establish the persistence of binding and were examined by scanning electron microscopy and energy dispersive X-ray analysis to determine the nature of the CCF–metal ion interactions.

2. Experimental

2.1. Preparation of crushed concrete fines

A concrete block, $0.4\,m \times 0.4\,m \times 0.3\,m$, weighing approximately 125 kg, containing sea-dredged flint aggregate and ordinary Portland cement at a water:cement ratio of 0.4, was cast. One year after casting, the block was broken using a hammer and chisel and the concrete pieces were crushed in a jaw crusher and graded according to particle size. The 1–2 mm crushed concrete fraction (CCF) was stored in polythene bags in the laboratory at 21 °C for 2 years prior to the commencement of this investigation. The mixture composition and 28 day cube and core strengths are listed in Table 1.

2.2. Characterisation of crushed concrete fines

Four CCF sub-samples (of initial mass, M_i, 20.00 g) were digested in nitric acid at 80 °C and the dry-mass of the residual aggregate matter (M_r) was recorded. The cement paste-content of CCF was estimated from the following relationship:

$$\text{Cement paste-content} = \left(\frac{M_i - M_r}{M_i}\right) \times 100\% \qquad (1)$$

Cement paste-content data for both the original concrete block (which was estimated from the mix composition) and CCF are listed in Table 1.

Three grams of CCF were ground, sieved to 250 μm and characterised by differential thermal analysis using a Stanton Redcroft 673-4 Differential Thermal Analyser with cal-

Table 1
Mix proportions, strength data and cement paste-content for concrete and CCF

Constituent or property	Mass (kg)	Strength (MPa)	Cement-content (%)
Mix proportions of concrete block			
Cement	28.32	–	–
Water	11.37	–	–
5 mm aggregate	13.90	–	–
10 mm aggregate	44.22	–	–
20 mm aggregate	43.87	–	–
28-day compressive strength data for concrete block			
100 mm cube strength	–	65 MPa	–
75 mm × 75 mm core strength	–	53 MPa	–
Cement paste-content of concrete block (by mass)			~28
Cement paste-content of CCF (by mass)			50.1 (±0.4)

cined alumina reference material [12]. Twenty milligrams sub-samples were heated in air at a rate of $10\,°C\,min^{-1}$ to a maximum temperature of $800\,°C$.

2.3. Batch removal of Cu^{2+}, Zn^{2+} and Pb^{2+} from aqueous solutions

For simplicity, copper, zinc and lead ions in solution are referred to as divalent cations throughout this text. It should be noted that re-speciation is likely to have occurred to some extent via processes such as hydrolysis and interactions with leached constituents of CCF such as silicate and aluminate oxy-anions. Furthermore, it is probable that the speciation of each metal will have fluctuated throughout the duration of the investigation as a function of pH, redox potential and solution composition. Neither metal speciation nor redox potential was determined during this preliminary study, however, these parameters will be the subjects of further research.

The removal of Cu^{2+}, Zn^{2+} and Pb^{2+} from aqueous solutions by CCF was determined by single metal, sessile, batch sorption experiments. In each case, 2.5 g of CCF were added to $100\,cm^3$ of metal nitrate solution, at an approximate concentration of 1000 ppm, in a screw-capped polypropylene bottle which was maintained at $20\,°C$. The concentrations of Cu^{2+}, Zn^{2+} and Pb^{2+} in the initial metal nitrate solutions were 873 ± 29, 837 ± 17 and $1041 \pm 49\,mg\,dm^{-3}$, respectively. Contact times for specimens were 3, 6, 24, 48, 72 and 120 h, at which the supernatant liquors were recovered following centrifugation at 2000 rpm. Each experiment was carried out in triplicate. The recovered solutions were analysed for the relevant heavy metal, calcium, aluminium, sodium, potassium, magnesium and silicon. The concentrations of species in solution were determined by inductively coupled plasma analysis using a TJA Iris simultaneous ICP-OES. Appropriately acidified and diluted samples were analysed with reference to six-point calibration curves derived from matrix-matched standard solutions. The pH values of the supernatant liquors were measured using a Corning 140 pH meter.

An additional series of sessile batch experiments was also prepared, in triplicate, as outlined above, in which CCF samples remained in contact with metal nitrate solutions for a total of 60 days. The CCF samples were then recovered by sieving with a 0.5 mm mesh polypropylene sieve, washed once with $30\,cm^3$ distilled water to remove any loose precipitate and dried at $25\,°C$ to within 5% of their original mass. Triplicate sub-samples of the recovered CCF were then digested in concentrated nitric acid and the digest analysed for the relevant heavy metal. The proportions of metal species bound to CCF, present in solution and as loose precipitate and were then estimated via a mass balance for each metal.

2.4. Distilled water leaching of metal-bearing CCF

Recovered metal-bearing CCF specimens were subjected to a distilled water leaching procedure, conducted in accordance with DIN 38414 Part 4 [13]. The 24 h leaching protocol, in which the solid:solution ratio was $0.1\,g\,cm^{-3}$, was carried out in triplicate and repeated four consecutive times. The leachates were analysed for the relevant heavy metal and corresponding pH values were recorded.

2.5. Scanning electron microscopy

Electron micrographs of the surfaces of gold-coated CCF samples prior to and following 60 days immersion in metal nitrate solutions were obtained using a Jeol JSM-5310LV scanning electron microscope (at an accelerating voltage of 20 kV). Carbon-coated CCF surfaces and epoxy resin-impregnated CCF polished sections were examined by energy dispersive X-ray analysis (EDX) using an Oxford Instruments Isis 300 X-ray microanalysis system. Energy dispersive X-ray dot maps of calcium, silicon and the relevant heavy metals were acquired using characteristic $K\alpha$ X-ray lines for all elements other than lead for which $M_{\alpha 1}$ and M_β were used.

3. Results

3.1. Characterisation of CCF

It was imperative that the cement matrix of CCF selected for this investigation was sufficiently well-aged since immature cement pastes possess unrefined pore networks and contain appreciable proportions of residual anhydrous phases which would influence the nature of their interactions with heavy metal ions. Thus, the original concrete block was aged for one year prior to crushing, after which time the hydration processes of Portland cement are approximately 95% complete. A further 2 years elapsed before the CCF were employed in this investigation.

The differential thermal analysis curve of CCF typifies that of a mature cement paste (Fig. 1) [12]. Calcium silicate hydrate (CSH) and portlandite $(Ca(OH)_2)$ are formed during the hydration of alite and belite, and the hydrated calcium
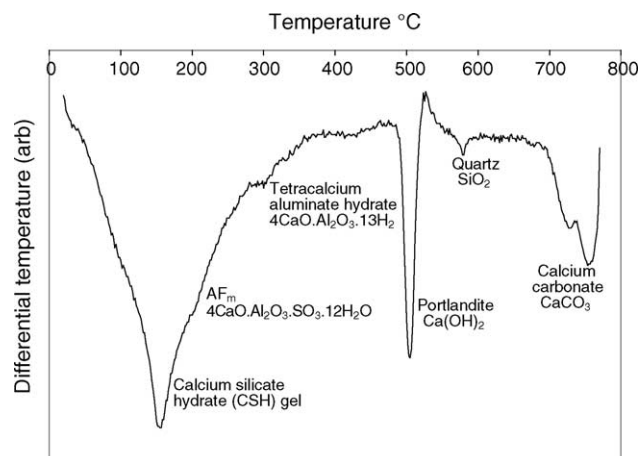

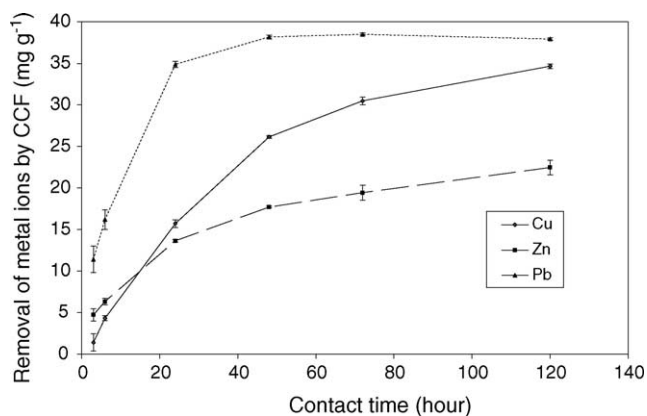Fig. 1. Differential thermal analysis curve for crushed concrete fines.

Fig. 2. Removal of metal ions from solution by crushed concrete fines.

Fig. 3. pH profiles of metal nitrate solutions in contact with crushed concrete fines.

(sulpho)aluminate phases (AF_m and tetracalcium aluminate hydrate) are the hydration products of aluminate and brownmillerite. Calcium carbonate arises from the atmospheric carbonation of calcium-bearing product phases, primarily portlandite and CSH. And the quartz signal is assigned to the presence of the aggregate. A more explicit account of cement hydration is given in [7].

The cement paste-content of the original concrete block was around 28% by mass, whereas that of CCF increased to approximately 50% (Table 1). This observation is consistent with reports in the literature pertaining to the enhanced cement paste-content of the fine fraction of crushed demolition waste [5].

3.2. Removal of metal ions by CCF

Fig. 2 shows the removal efficiencies for Cu^{2+}, Zn^{2+} and Pb^{2+} from aqueous solutions by CCF, and the corresponding pH profiles are shown in Fig. 3. The maximum extents of removal of Cu^{2+} and Zn^{2+}, recorded at 120 h, were 34.6 ± 0.3 and 22.5 ± 0.9 mg g^{-1}, respectively. The data indicate that equilibrium for the removal of Cu^{2+} and Zn^{2+} may not have been established by this time. Conversely, equilibrium removal of Pb^{2+} from solution, 37.9 ± 0.2 mg g^{-1}, was achieved within 48 h. During the course of the investigation a small quantity of loose floc was observed to have precipitated in the vicinity of the CCF particles. It is for this reason that the term 'removal' has been selected in favour of 'sorption' or 'uptake' in this instance. The comparatively rapid equilibration time for the removal of Pb^{2+} by CCF and pronounced concomitant rise in solution pH suggest that the mechanism of Pb^{2+}-removal differed from those of Cu^{2+} and Zn^{2+}.
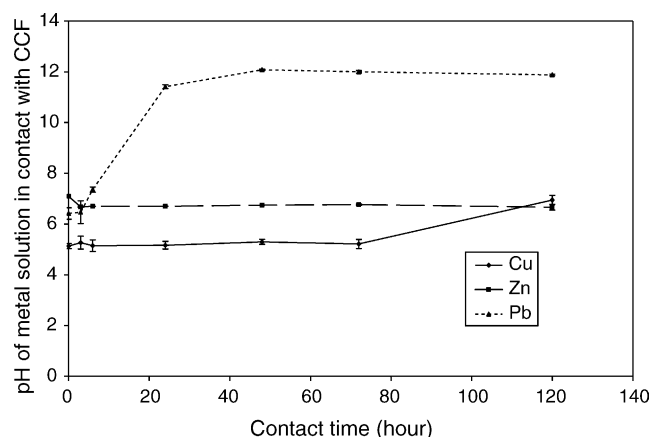
The dissolution profiles of Ca^{2+}, K^+, Na^+ and Mg^{2+} from the cement matrix during heavy metals-removal from solution (not shown) followed similar trends to those of the metal ion removal profiles shown in Fig. 2. Maximum Ca^{2+}-, K^+-, Na^+- and Mg^{2+}-release were found to be approximately 22, 0.55, 0.28 and 0.036 mg g^{-1}, respectively.

Ca^{2+}-release was primarily attributed to the dissolution of portlandite and CSH. Lines of regression for heavy metal-removal (mol g^{-1}) on corresponding Ca^{2+}-release (mol g^{-1}) for Cu^{2+}, Zn^{2+} and Pb^{2+} (not shown), gave correlation coefficients, R^2, of 0.98, 0.99 and 0.93, respectively, indicating that Ca^{2+}-release was proportional to heavy metal-removal. In mature cement alkali metal ions, Na^+ and K^+, primarily exist as hydrated species in the pore solution, and also in physical and chemical association with hydrated phases, particularly CSH [14]. Values of R^2 in the range 0.94–0.99 were obtained for linear regression plots of heavy metal-removal versus corresponding alkali metal release (not shown). The dissolution of silicon and aluminium were generally below the limits of detection, did not exceed 0.25 and 0.11 mg g^{-1}, respectively, and exhibited no particular trend during the course of the investigation.

The influence of prolonged contact between CCF and the heavy metal-bearing liquors on metals-removal and the dissolution of CCF-constituents was examined. The total exclusion of Cu^{2+} (35 mg g^{-1}), Zn^{2+} (33 mg g^{-1}) and Pb^{2+} (37 mg g^{-1}) from solution and the concurrent release of calcium, silicon and aluminium were obtained via analyses of the supernatant solutions after 60 days (Table 2). The uptake of Cu^{2+} (18 mg g^{-1}), Zn^{2+} (26 mg g^{-1}) and Pb^{2+} (33 mg g^{-1}) by binding to CCF after 60 days was determined by nitric

Table 2
Metal ion-removal and dissolution of constituents of CCF after 60 days

	Cu^{2+}	Zn^{2+}	Pb^{2+}
Metal ion-removal (mg g^{-1})	35 ($\pm$1)	33 ($\pm$1)	37 ($\pm$2)
Calcium dissolution (mg g^{-1})	28.1 ($\pm$0.3)	27.7 ($\pm$0.2)	15.7 ($\pm$0.7)
Aluminium dissolution (mg g^{-1})	0.036 ($\pm$0.004)	0.049 ($\pm$0.002)	0.112 ($\pm$0.004)
Silicon dissolution (mg g^{-1})	0.096 ($\pm$0.001)	0.014 ($\pm$0.04)	0.023 ($\pm$0.001)
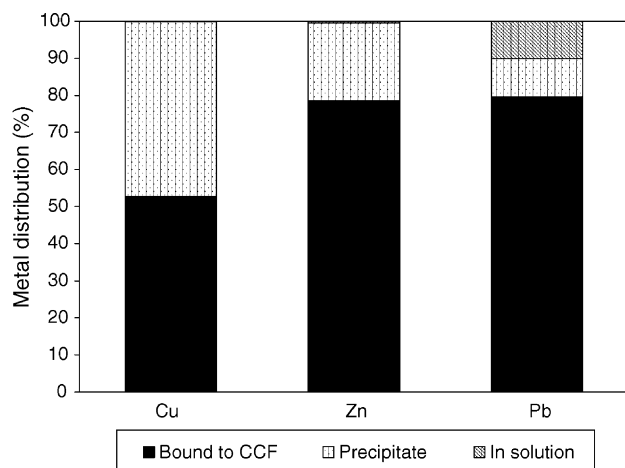
Fig. 4. The final partition of each metal after 60 days.

Fig. 5. Cumulative concentration of metal species in distilled water leachate.

acid digestion of the recovered CCF and the corresponding proportions of Cu^{2+}, Zn^{2+} and Pb^{2+} present in the loose floc precipitate were then estimated via a mass balance for each metal ion. The final partitioning of the metal species among that sorbed by CCF, that present as floc precipitate and that which remained in solution is depicted in Fig. 4.

Results indicate that Zn^{2+}-removal continued to increase from $\sim 22\,mg\,g^{-1}$ at 5 days to $\sim 33\,mg\,g^{-1}$ by 60 days, whereas no further exclusion of Cu^{2+} ($\sim 35\,mg\,g^{-1}$) or Pb^{2+} ($\sim 37\,mg\,g^{-1}$) from solution was observed during prolonged exposure to CCF (Fig. 2 and Table 2). In excess of 99% of Cu^{2+} present in the initial solution was removed during contact with CCF although only 53% of this was bound to CCF. Approximately 99% of Zn^{2+} and 90% of Pb^{2+} were excluded from solution, 79% of which, in each case, was bound to CCF (Fig. 4). The final pH values of the Cu^{2+}, Zn^{2+} and Pb^{2+} supernatant liquors were 11.3, 10.8 and 11.9, respectively.

Fig. 5 shows the cumulative concentrations of heavy metal ions leached from CCF during four consecutive distilled water leach tests and indicates that relatively little of the bound metal species was readily soluble. The proportions of heavy metals leached as percentages of those sorbed were: Cu^{2+}, 1.9%; Zn^{2+}, 0.9% and Pb^{2+}, 0.2%. The corresponding pH values of the leachate solutions were between 9 and 10.5 units.
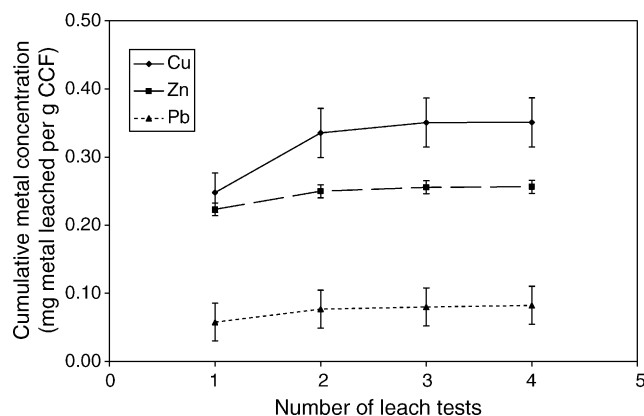
3.3. The fate of metal species bound to CCF

Secondary electron images of the surfaces of CCF prior to and following 60 days contact with Cu^{2+}, Zn^{2+} and Pb^{2+} solutions (hereafter, Cu–CCF, Zn–CCF and Pb–CCF, respectively) are shown in Fig. 6. The littered, irregular, fractured surface of CCF prior to immersion is depicted in Fig. 6(a). A corresponding energy dispersive X-ray (EDX) spectrum indicates the presence of calcium, aluminium, silicon, iron, magnesium, sulphur, sodium, potassium and trace quantities of titanium, manganese and chromium (Fig. 6(b)). These elements are typical constituents of Portland cement, however, it should be noted that hydrated cement paste is heterogeneous on a microscopic scale, and hence, constituent concentrations vary according to the proportions of phases present in a given locus.

Two distinct copper-bearing phases were observed to have formed on the surface of Cu–CCF: a copper-rich foliaceous mass (Fig. 6(c)) and rare, copper-bearing, calcium-rich, distorted polygons (Fig. 6(d)). EDX was used to determine the relative abundance of the major constituents of the metal-bearing structures formed on the CCF surfaces which are listed Table 3. The standard deviations for these data are comparatively high owing to

Table 3
Composition of metal-bearing structures on the surface of CCF

Structure	Relative elemental composition (moles per mole of Al)[a]			
	Al	Si	Ca	Metal (Cu, Zn, Pb, respectively)
Cu–CCF				
Foliaceous mass	1.0 (±0.8)	3 (±3)	3 (±1)	54 (±4)
Distorted polygon	1.0 (±0.5)	3 (±1)	156 (±9)	10 (±3)
Zn–CCF				
Cancelled network	1.0 (±0.4)	0.4 (±0.1)	0.5 (±0.1)	31 (±2)
Distorted polygon	1.0 (±0.6)	2 (±2)	84 (±13)	11 (±4)
Pb–CCF				
Reticular network	1.0 (±0.5)	4 (±2)	13 (±4)	3.2 (±0.9)
Distorted polygon	1.0 (±0.4)	3 (±2)	89 (±7)	6 (±1)

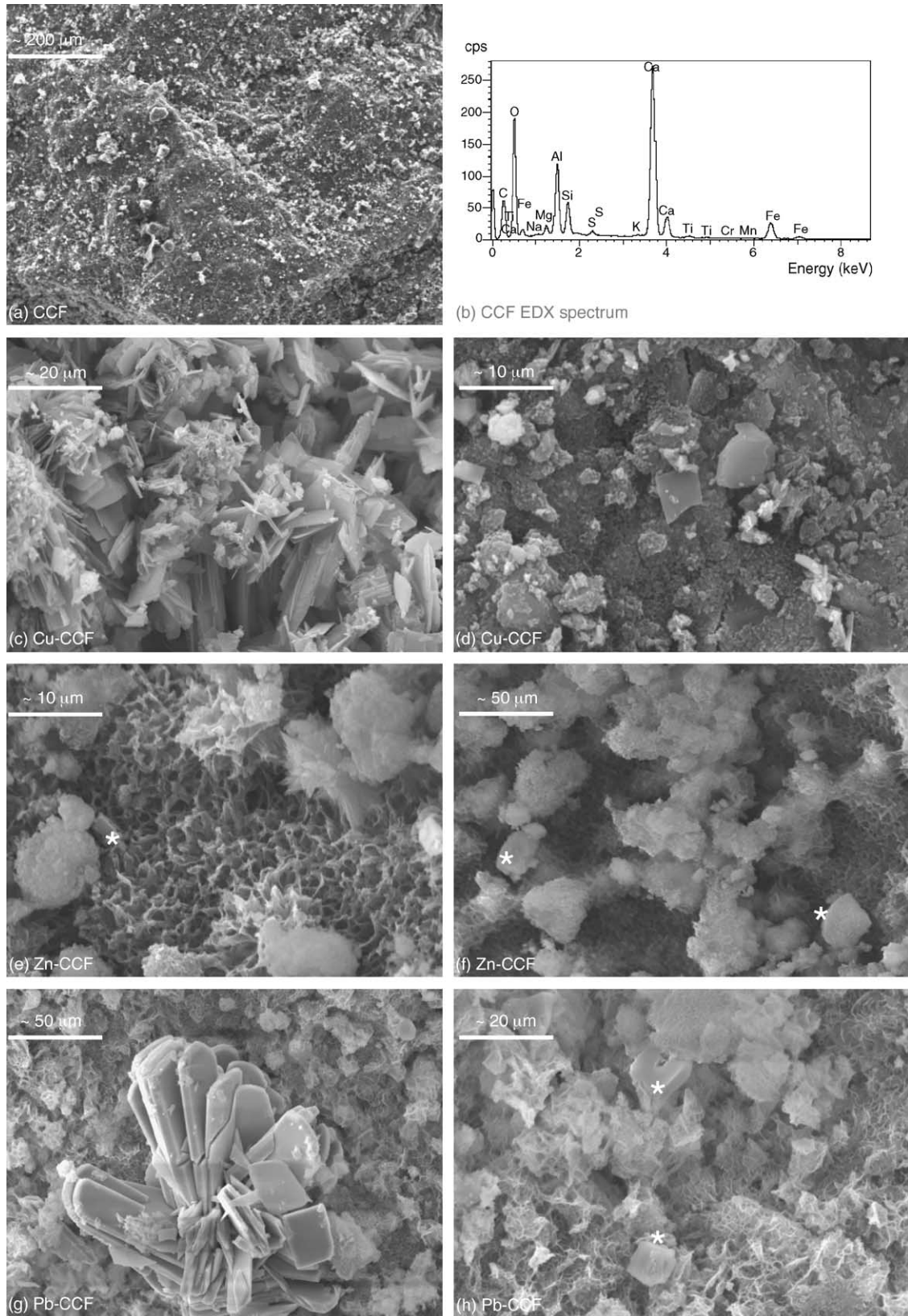[a] Composition data are normalized relative to the proportion of aluminium present.

Fig. 6. Electron micrographs depicting the surfaces of: (a) CCF; (c) copper-laden CCF showing a copper-rich, foliaceous deposit; (d) copper-laden CCF showing copper-bearing, calcium-rich, distorted polygons; (e) zinc-laden CCF showing a zinc-rich, cancellated network; (f) zinc-laden CCF showing zinc-bearing, calcium-rich, distorted polygons (denoted by asterisks); (g) lead-laden CCF showing a unique crystal cluster; (h) lead-laden CCF showing a lead-bearing calcium silicate network and lead-bearing, calcium-rich, distorted polygons (denoted by asterisks). An EDX spectrum of the CCF surface is shown in (b).
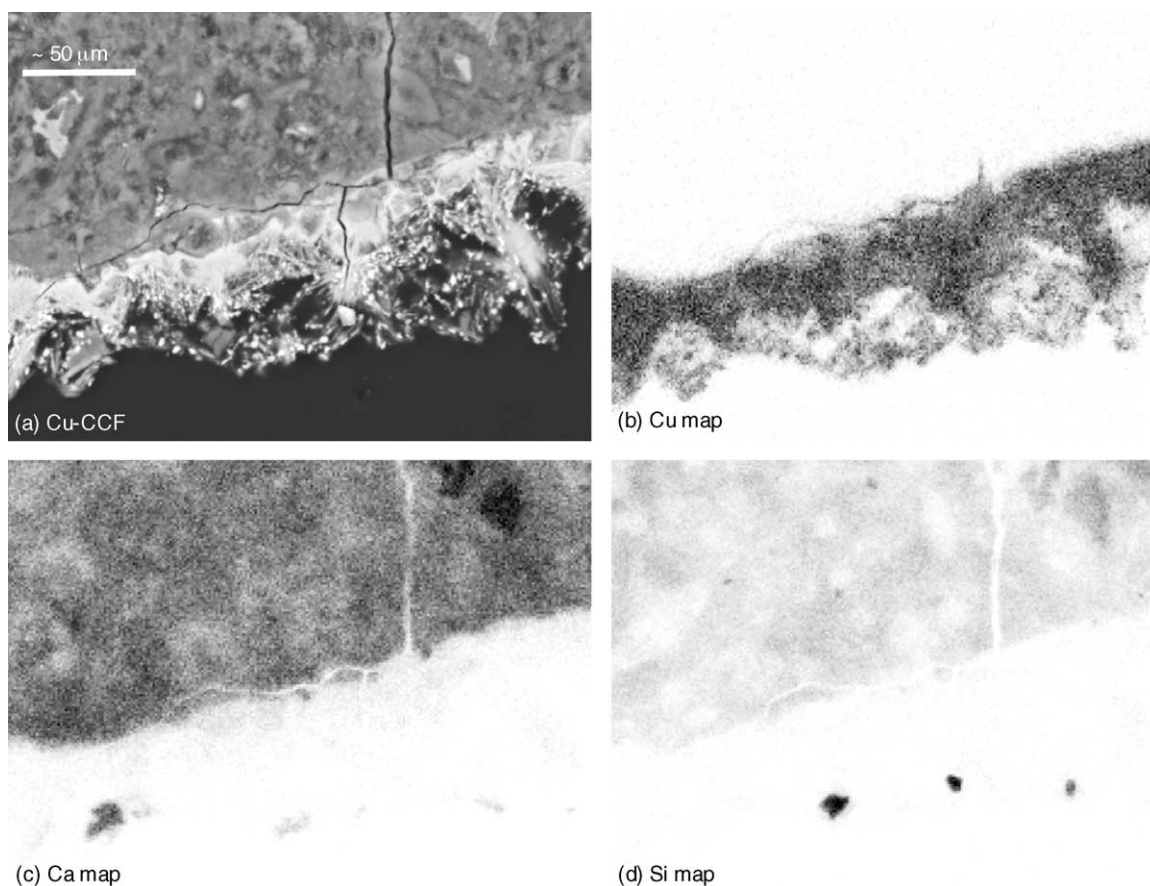
Fig. 7. (a) Electron micrograph of cross section of copper-laden CCF particle; and corresponding X-ray dot maps for (b) copper; (c) calcium; (d) silicon.

the intimacy of phases. A back-scattered electron image of a cross-section through the surface of a Cu–CCF particle is shown in Fig. 7(a). Corresponding Kα X-ray dot maps for copper, calcium and silicon are also shown in Fig. 7(b)–(d), respectively. The data indicate that the principal mechanism of uptake of copper by CCF was by precipitation of the foliated crystals onto the surface and that no appreciable diffusion of copper ions into the cement matrix had occurred.

Secondary electron images of Zn–CCF show a zinc-rich cancelled network and occasional, zinc-bearing, calcium-rich, distorted polygons (denoted by asterisks) over which a further diffuse deposit had formed (Figs. 6(e) and (f), and Table 3). In fact, three distinct zinc-bearing strata are indicated in the back scattered electron image and corresponding Zn Kα X-ray dot map of a cross-section through the surface of Zn–CCF (Fig. 8(a) and (b)). Hence, the mechanism of uptake of zinc by CCF was characterised by three stages: the initial deposition of a zinc-rich precipitate on the surface of CCF a few microns in depth, the formation of a second deposit of around $10 \, \mu m$ and a final superficial precipitate. It is likely that the different precipitation processes were mediated by pH and the concentration and speciation of zinc ions in solution.

Fig. 6(g) shows the secondary electron image of a unique crystal cluster on the surface of Pb–CCF; a thorough examination of the surface failed to reveal other items of similar morphology. The surface of Pb–CCF generally comprised a reticular, lead-bearing, calcium silicate network and rare, lead-bearing, calcium-rich, distorted polygons (denoted by asterisks) (Fig. 6(h) and Table 3). The morphology of the reticular, lead-bearing network closely resembles that of Type II CSH (one of four calcium silicate hydrate morphologies which are formed during cement hydration [15,16]). The back scattered electron image and corresponding characteristic X-ray dot map of Pb–CCF (Fig. 9(a) and (b), respectively) indicate that the removal of Pb^{2+} by CCF took place via diffusion into the cement matrix. It is likely that the underlying mechanism was isomorphic substitution by Pb^{2+} for Ca^{2+} in the calcium silicate hydrate phase. Similarly, substitution by Pb^{2+} for Ca^{2+} (ionic radii 1.17 and 1.00 Å, respectively [17]) in crystalline calcium silicate hydrates has been reported by other workers [18].

The rare, calcium-rich, heavy metal-bearing polygons observed on the surfaces of each of the recovered CCF specimens are likely to be re-precipitated portlandite crystals, distorted from their normal hexagonal morphology by the inclusion of Cu^{2+}, Zn^{2+} and Pb^{2+} ions.
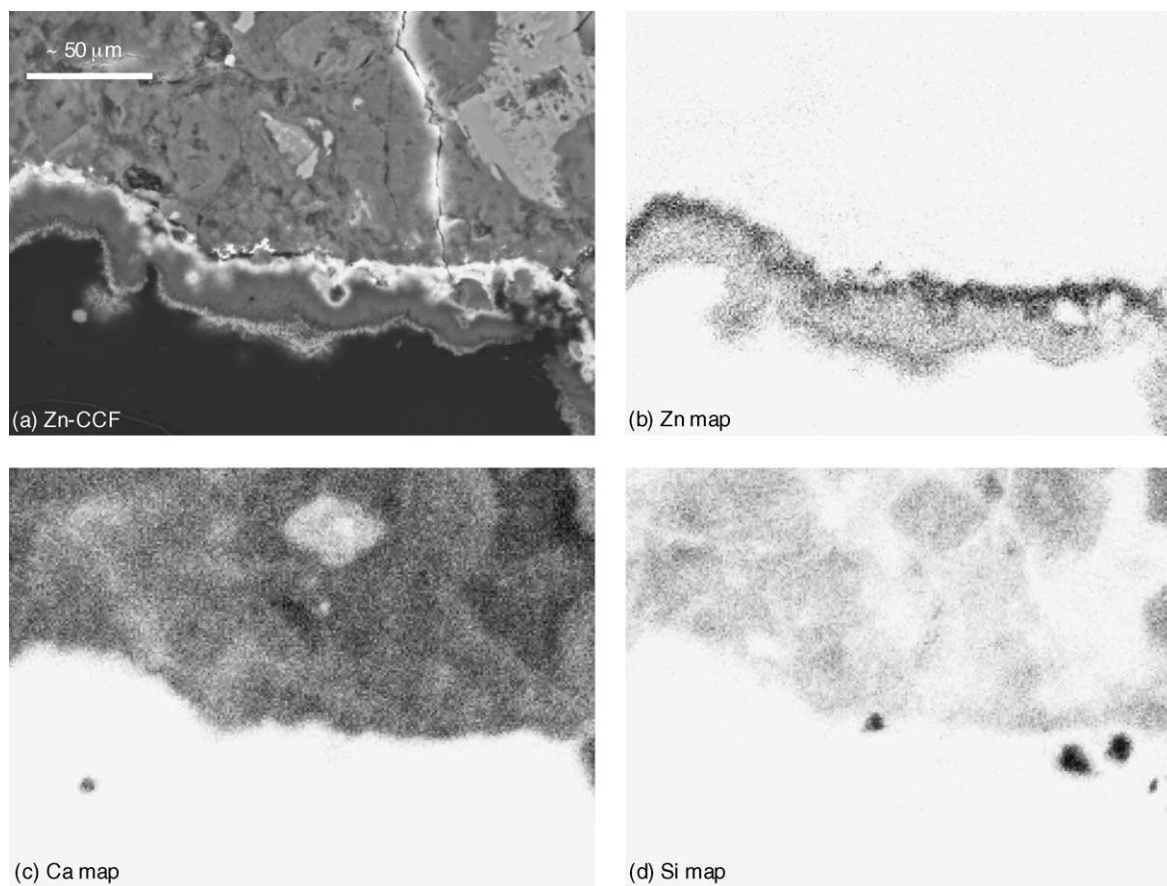
Fig. 8. (a) Electron micrograph of cross section of zinc-laden CCF particle; and corresponding X-ray dot maps for (b) zinc; (c) calcium; (d) silicon.

4. Discussion

4.1. Removal of metal ions by CCF

Crushed concrete fines have been shown to remove Cu^{2+} (35 mg g^{-1}), Zn^{2+} (33 mg g^{-1}) and Pb^{2+} (37 mg g^{-1}) from single metal nitrate solutions (Fig. 2, Table 2). The extents of metal ion-removal by CCF are compared with those of other waste-derived candidate sorbent materials in Table 4 [9,10,19–25]. The observed removal efficiencies for Cu^{2+} and Zn^{2+} were generally found to be superior to those of other waste-derived sorbents, whereas uptake of Pb^{2+} by CCF compared well with those of chitosan and sawdust, although was shown to be less extensive than those of modified rice husk, blast furnace sludge, sugar beet pulp and carbonised peanut husk.

Equilibration times for the removal of metal ions by CCF—generally observed to be greater than 48 h—are exceptionally long relative to those of many sorbent materials, which tend to fall within the range of a few minutes to a few

Table 4
A summary of batch sorption data for a range of waste-derived sorbents

| Sorbent	Concentration of sorbent (g dm^{-3})	Conditions	Time to equilibrium	Experimental sorption capacity (mg g^{-1})			Reference
				Cu^{2+}	Zn^{2+}	Pb^{2+}	
CCF	25	Sessile	120 h, >5 days, 48 h	35	33	37	
Carbonised peanut husk	Not specified	Agitated	2 h	–	13	114	[19]
Pinus sylvestris sawdust	1	Stirred	<20 min	–	–	9.78	[20]
Blast furnace sludge	50	Not specified	5 h	16.07	4.26	64.17	[21]
Modified rice husk	5	Agitated	120 min	29	–	108	[22]
Sugar beet pulp	2	Stirred	20–60 min	21	18	74	[10]
Chitosan	0.016	Sessile	6 h	20.92	11.66	12.61	[23]
Pelletised peanut hulls	6	Stirred	40 min	12	–	–	[9]
Olive mill residue	10	Stirred	2 h	13.5	–	–	[24]
S. cinnamoneum biomass	2	Agitated	15–30 min	–	21.3	57.7	[25]
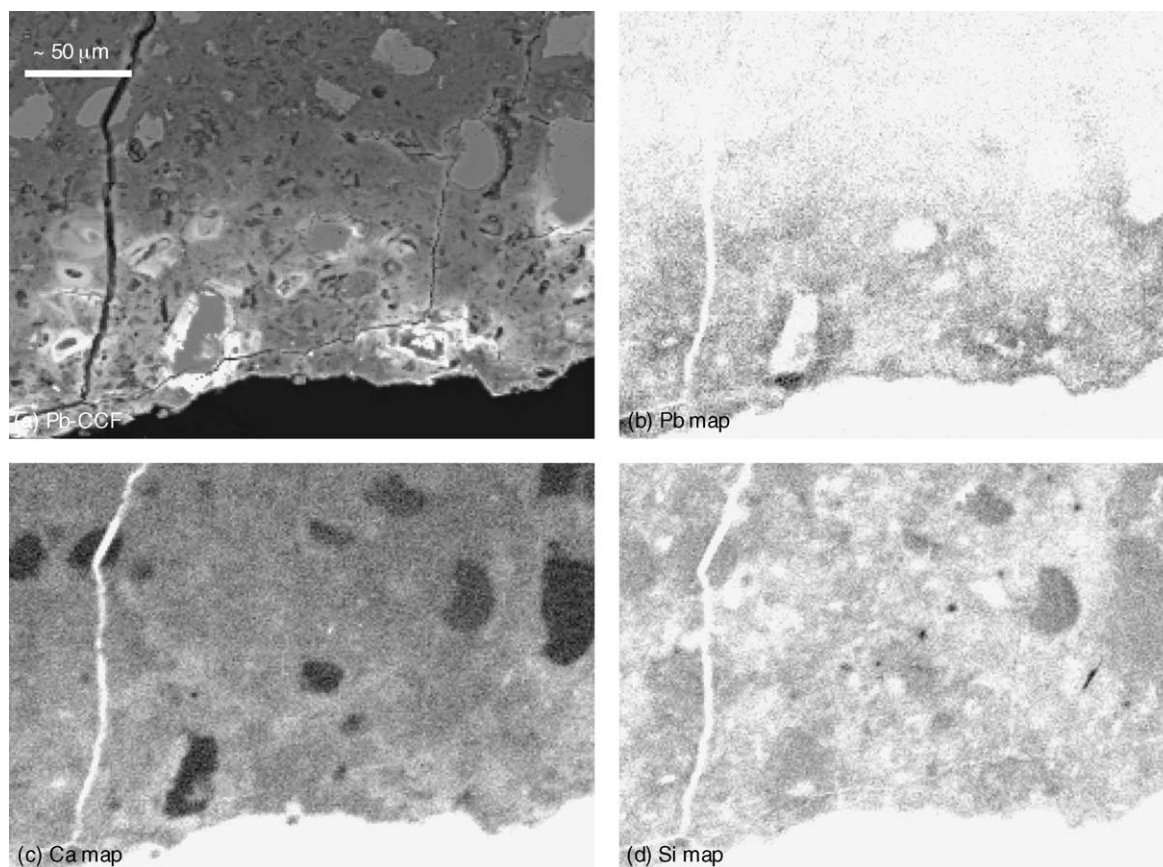
Fig. 9. (a) Electron micrograph of cross section of lead-laden CCF particle; and corresponding X-ray dot maps for (b) lead; (c) calcium; (d) silicon.

hours (Table 4). Efficiency is an important prerequisite of industrial sorption processes for wastewater treatment. This limits the application of sorbents with slow solute uptake rates and long equilibration times, for which inconveniently long residence times would be required.

4.2. Mechanism of removal of metal ions by CCF

Other research has indicated that the precipitation of hydroxides, hydrous oxides and solubility-limiting phases is one mechanism by which heavy metal ions are immobilised during conventional treatment of aqueous heavy metal-bearing waste using alkaline cements [6,7,14]. Precipitation in these systems generally occurs via multi-step processes involving initial pH-controlled formation of hydroxides and hydrous oxides followed by subsequent reaction with cement constituents such as calcium, aluminium and silicon. Similarly, electron microscopy has revealed that the uptake of Zn^{2+} by CCF occurred via the formation of three discretely precipitated layers on the surface of the cement matrix, which developed during the 60 days contact period. Conversely, the interaction between Cu^{2+} ions and CCF was characterised by the formation of a single foliated precipitate on the surface of the cement matrix within 120 h. Neither Zn^{2+} nor Cu^{2+} appeared to have penetrated the cement matrix to any appreciable extent.

CSH is a non-stoichiometric nanoporous layered structure of variable Ca/Si ratio which constitutes approximately 60% of the mature cement matrix and is reported to be the 'most active sorbing component of cement systems' [14]. Unlike the precipitation processes observed for Cu^{2+} and Zn^{2+}, the primary interaction of Pb^{2+} with CCF has been shown to be diffusion into the cement matrix, with isomorphic substitution of Pb^{2+} for Ca^{2+} in CSH as the postulated mechanism.

The proportional dissolution of Ca^{2+} during metals-removal indicated that nitrate counter ions present in the initial metal solutions were not significantly sorbed by CCF and that Ca^{2+} and other cations were released from the cement matrix such that the electrical neutrality of the solutions was maintained.

Distilled water leach tests indicated that less than 2% of the sorbed heavy metals were readily leachable. Hence, owing to the nature of the reactions of Cu^{2+}, Zn^{2+} and Pb^{2+} with CCF, and the persistence of binding, recycling of CCF for subsequent reuse as a sorbent would not be feasible.

4.3. Prospects

Despite favourable removal capacities for Cu^{2+}, Zn^{2+} and Pb^{2+} by CCF, the long equilibrium sorption times, floc formation, and high alkalinity of the final liquors observed during this investigation, are likely to preclude its use in many

conventional industrial wastewater treatment systems. In addition, the erratic supply and inconsistent composition of crushed concrete-based demolition waste are also likely to undermine its potential marketability as a sorbent for general wastewater benefaction [5].

One interesting and potentially more viable alternative for the re-use of the fine fraction of crushed concrete demolition waste may be its incorporation into chemically reactive barriers for in situ groundwater remediation [26–29]. Reactive barriers are engineered permeable zones placed within an aquifer which effect the extraction and containment of contaminants from polluted groundwater. The permeable barrier comprises a construction element containing a porous medium, such as sand, to which sorptive minerals, such as clays, limestone, zeolites and/or activated charcoal, have been added. As the contaminated plume passes through the barrier, contaminant species are retained by the mineral phase via sorption and precipitation processes.

The high heavy metal sorptive capacity and subsequent resistance to leaching may favour the use of the crushed concrete fine fraction as a component in reactive barriers wherein long equilibrium sorption times and the occurrence of precipitation processes would not necessarily be disadvantageous. Furthermore, the irregular supply of crushed demolition waste need not be problematic if an appropriate local or easily transportable source is identified during the design stage.

Similarly, the incorporation of waste concrete fines into multi-layered landfill encapsulation liners, between the low permeability clay and sub-soil strata, may afford additional defence against leaching [27]. Further laboratory-scale research to appraise the performance of reactive and defensive barriers which utilise crushed concrete waste in partial replacement of virgin minerals would provide an indication of the viability of this material in these roles.

5. Conclusions

The 1–2 mm crushed concrete fine fraction (CCF) has been shown to effect the removal of Cu^{2+} (35 mg g^{-1}), Zn^{2+} (33 mg g^{-1}) and Pb^{2+} (37 mg g^{-1}) from metal nitrate solutions. In addition to direct sorption onto the CCF particles a proportion of metal-bearing loose floc was also observed to have formed. Four consecutive distilled water leach tests indicated that less than 2% of the sorbed heavy metal was readily leachable.

Equilibrium times of approximately 120, >120 and 48 h were observed for the removal processes of Cu^{2+}, Zn^{2+} and Pb^{2+}, respectively. Cu^{2+} and Zn^{2+} ions were removed by surface precipitation, whereas the mechanism of interaction of Pb^{2+} with CCF was via diffusion into the cement matrix. Despite favourable removal capacities, the long equilibrium sorption times, floc formation and irregular supply of crushed concrete may prohibit its application in conventional wastewater treatment systems. Nonetheless the sorptive potential of

this material may be relevant to the design of reactive and defensive barriers for environmental protection.

Acknowledgements

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