Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.771289

51 (2013) 7181–7193
November

Taylor & Francis
Taylor & Francis Group

Heavy metal removal from water by red mud and coal fly ash: an integrated adsorption–solidification/stabilization process

Julide Hizal[a,*], Esma Tutem[b], Kubilay Guclu[b], Mehmet Hugul[b], Sertac Ayhan[b]
Resat Apak[b], Fahriye Kilinckale[c]

[a]*Faculty of Engineering, Department of Chemical and Process Engineering, Yalova University, Yalova 77100, Turkey*
Tel. +90 226 8112658; Fax: +90 226 8112655; email: jyucesoy@yalova.edu.tr
[b]*Faculty of Engineering, Department of Chemistry, Istanbul University, Avcilar, Istanbul 34320, Turkey*
[c]*Faculty of Engineering, Department of Civil Engineering, Istanbul University, Avcilar, Istanbul 34320, Turkey*

Received 26 January 2013; Accepted 26 January 2013

ABSTRACT

The use of low-cost unconventional sorbents for the removal of heavy metals from aqueous solution has been extensively studied by the analytical chemistry research group of Istanbul University. The selectivity order of metal ion uptake was highest for Cu, medium for Pb and lowest for Cd, in accord with the order of insolubility of their corresponding metal hydroxides. The metal-loaded red muds and fly ashes were successfully solidified by adding cement, sand and water, producing both physically and chemically resistant durable concrete blocks as confirmed by chemical leaching and compressive strength tests. The metals were essentially held irreversibly, and would not leach out into carbonic acid or bicarbonate buffer and humic acid solutions. The metal-loaded solid wastes were solidified into an environmentally safe form by adding stabilization-solidification agents, thereby serving the doublefold aim of water treatment and solid waste disposal. Since lead (II) caused the major hardening and strengthening problems in the solidification-stabilization process, sodium aluminate or triethanolamine was added as a stabilization/promotion agent.

Keywords: Adsorption; Hazardous waste managment; Heavy metals; Solidification

1. Introduction

Environmental pollution, especially water pollution, has become a serious problem threatening our future. Cadmium (II), lead (II) and copper (II) are well-known toxic heavy metals which pose a serious threat to the fauna and flora of receiving water bodies when discharged into industrial wastewater. Various treatment technologies have been developed for the removal of these metals from water. Although processes such as ion exchange, electrodialysis, reverse osmosis, membrane filtration, sludge leaching, coagulation–flocculation and adsorption have frequently been used in wastewater treatment [1], adsorption is potentially the most applicable and lowest cost method [2]. Industrial wastes are the principal sources of heavy metal pollution mainly originating from electroplating and metal finishing operations, electronic circuit and battery production and steel and aluminium processes. Heavy

---

*Corresponding author.

metals accumulate in the organisms existing in soil, surface water, air and marine water; they are drifted everywhere with circulation and join the food chain [3].

A number of solid wastes such as bauxite waste red muds from aluminium production and fly ashes from coal-fired thermal power plants have been screened in this regard to serve as versatile and cost-effective sorbents for heavy metals [4,5] and radionuclides [6,7]. Red mud and fly ash have been widely used in heavy metal immobilization [8–10]. Fly ash can totally replace manufactured cement and make a concrete-like material. Fly ash-based geopolymer has been shown to be more durable than ordinary Portland cement when exposed to an aggressive environment. Both red mud and fly ash are known to have a high capacity for neutralizing acidic effluents. Both solid wastes are abundant in Turkey and show a high affinity for heavy metals, explaining why they were selected as metal sorbent in this study.

Solid contaminant barriers can provide efficient and relatively inexpensive means of containing mine wastes. Chemical-based barrier materials may provide performance improvements (such as lower hydraulic conductivity, improved resistance to degradation by contaminants, minimized diffusive transport of contaminants, etc.) over soil-based and cement-based materials, and include sodium silicate, colloidal silica and iron oxy-hydroxides as the suitable inorganic additives [11]. Owing to its pozzolanic and highly alkaline properties, fly ash from coal-fired power-generating stations has the potential to serve as a hydraulic and contaminant barrier [12]. Red mud has also been used for the same purpose [13]. Thus, this work involves a laboratory-scale investigation for the potential use of solid wastes as barrier materials to adsorb toxic heavy metals and radionuclides from water (a fixation or stabilization process) followed by solidification of the metal-loaded mass in a cement-based block totally resistant to atmospheric weathering and leaching conditions.

Minocha et al. [14], performed solidification studies using Portland cement, cement-fly ash, lime-fly ash and metal sludge containing Cr(III), Ni(II), Cd(II), Hg (II) nitrates. They investigated the effect of additive organic substances on compressive strength of the blocks, but leachability of heavy metal cations was not monitored. In another study, immobilization of As, Cd, Pb, Ni, Cr and Zn cations was provided by a cement-based solidification/stabilization process. Leaching behaviour tests were applied to mortar powder with respect to NEN 7,341 method and performed for 160 days. It was observed that Cr(III) and Ni(II) concentrations in leachate were rather low, and also, cement-based S/S process was more effective in immobilizing especially Cr and Ni cations. Other metal cations (As(III), Cd(II), Pb(II) and Zn(II)) were fixed in cement rotary kiln because of calcination and subsequent hydration during cement application [15]. Dermatas and Meng [16] immobilized Pb(II), Cr(III) and Cr(VI) by using {fly ash + quicklime} solidification method. The authors showed that in the presence of fly ash, the pH interval of immobilization of heavy metals was broadened, and reported that Pb(II) immobilization was also dramatically low at higher pH, because Pb(II) adsorption mechanism was dominant. It was mentioned that fly ash was a good S/S reagent provided that the minimum cement percentage was 40, using minimum 30% fly ash in cement [17,18]. Studies showed that, in cases where Ca materials (such as marble powder or lime) are used in mortar mixture, heavy metal immobilization increased and this manner is attributed to calcination of metals [19,20]. Gollmann et al.[21] worked on leaching behaviour of Pb (used as PbO_2) for different pHs and observed that Pb(II) immobilization was better at pH 8. The leached concentration of Pb was lower in solid mass having long curing time (28 days), because stabilization took place as a consequence of isomorphic substitution between the metal and some elements in cement matrix.

When adsorption is employed, there is an increasing trend toward substitution of pure adsorbents (e.g. activated carbon, alumina, and other hydrated oxides) with natural by-products, soil minerals or stabilized solid waste materials (e.g. bauxite waste red muds and fly ashes). These substances also serve as barrier material for passive wall technologies utilized around a heavy metal spill site or shallow-land burial facility of low-level radioactive wastes. Once these contaminants are stabilized within barrier walls, it is also desirable to fix them in an environmentally safe form by performing *in situ* stabilization/solidification by way of adding cement, and pozzolans if necessary, to obtain a durable concrete mass. The host matrix for metals and radionuclides, i.e. red muds, fly ashes and clay minerals may serve as inexpensive pozzolanic binders to be used along with cement for solidification.

The aim of this work is to design an integrated adsorption-solidification/stabilization process for fixing and immobilizing the three toxic heavy metals (Pb, Cd and Cu) and to develop unconventional cost-effective sorbents for irreversible fixation of these toxic heavy metal cations; the selected sorbents showed high capacities and fast retention kinetics for the so-called contaminants. The determination of conditions affecting stabilization/solidification of the loaded sorbents by adding pozzolans and cement was also aimed. Setting aids and promoters were added to mortars in order to improve the setting and hardening characteristics of the prepared paste formulations. Since cement-based solidified/stabilized wastes are vulnerable to physical and chemical degradation processes [22], durability and leachability of the final concrete blocks were tested. Finally, a reasonable unification of *in situ* physical/chemical treatment technologies, named as "integrated adsorption-solidification" technology, applicable to a spill/leakage site is proposed.

2. Materials and methods

2.1. Instrumentation

A cement mortar-mixing mechanical apparatus (capacity: 4.7 L, stainless steel, Kitchen Aid Inc.), a tamping-vibrating apparatus for tightening the mortar pastes before solidification (providing 60 free falls from a height of 15 mm at a vibration rate of 1 cps, Nejat Coşkuner Lab. & Med. Devices, Inc.), steel specimen moulds (of 400 vickers hardness, dimensions: $4{\times}4{\times}16\,cm^3$, three-compartment), ASTM Vicat needle apparatus (upper and lower diameters: 65 and 75 mm, respectively; metallic Vicat ring height: 4 cm; Nejat Coşkuner Lab. & Med. Devices, Inc.) for measuring the time taken for a cement to stiffen to a standard value after addition of water (i.e. commonly known as the set time) and compressive strength measurement apparatus (Akçansa Lab., Inc.) were used as appropriate for cement mortar testing. Measurement of pH was made with an E 512 pH-metre equipped with a glass electrode. Leach tests were conducted in sealed polyethylene containers of suitable size so as to contain the mortar moulds. Heavy metal ions in the leachates were quantitatively determined with the use of a Varian FS-220 model atomic absorption spectrometer (AAS).

2.2. Chemicals and Materials

Of the solid wastes used as heavy metal sorbents, the "red muds" were supplied from Etibank Seydişehir Aluminium Plant, emerging as the alkaline leaching wastes of bauxite in the Bayer process of alumina manufacture, and had the following chemical composition by weight: SiO_2: 16.9%, Al_2O_3: 17.6%, Fe_2O_3: 37.3%, TiO_2: 5.6%, Na_2O: 8.3%, CaO: 4.4%, loss on ignition: 7.2%. Red muds, being multicomponent systems, are composed of sodium aluminosilicates, kaolinite, chamosite, iron oxides (haematite) and hydroxides. Basically, Fe is in the form of haematite, Ti is in the form of Fe/Ti oxides and Al is in the form of aluminosilicates.

The second solid waste sorbent used in experiments "fly ash", recovered from the cyclones and electrostatic precipitators of Afşin-Elbistan Thermal Power Plant, had the following composition: SiO_2: 21.9%, Al_2O_3: 11.6%, Fe_2O_3: 2.4%, CaO: 42.5%, MgO: 1.3%, Na_2O: 1.0%, K_2O: 1.1%, SO_3: 13.6%, loss on ignition: 4.4%. Calcite, anhydrite, quartz, gibbs and haematite could be identified in the crystalline phase of water-washed fly ash by evaluating its X-ray diffractogram. Both sorbents were thoroughly washed with at least 10-fold mass of water until the washing pH was 7.5, dried, and used as such for heavy metal loading. The specific BET surface areas of water-washed red mud and fly ash were 14.2 and $10.2\,m^2\,g^{-1}$, respectively [23]. The characteristic particle size distribution (as particle diameters) X_{10}, X_{50} and X_{90} of red mud were 0.37, 1.57 and 56.88 μm, and of fly ash, 1.28, 37.7 and 158 μm, respectively [24].

The Portland cement supplied by Akçansa A.Ş. (PÇ-32.5) (SiO_2: 20.9%, Al_2O_3: 5.2%, Fe_2O_3: 3.3%, CaO: 63.5%, MgO: 1.2%, SO_3: 2.6%, loss on ignition: 2.2%) and TS EN 196 Rilem-Cembureau standard sand donated by Pınarhisar Set Çimento A.Ş. were used in the preparation of cement mortars.

The setting/hardening promoter or metal stabilizer compounds added to cement pastes were sodium aluminate, of technical purity, triethanol amine (TEA), calcium *tert*-phosphate and calcium chloride (all analytical reagent grade, from E. Merck). In the preparation of leach solutions, HNO_3, sodium bicarbonate (E. Merck), sodium humate(Aldrich) and distilled water were used.

2.3. Metal Loading and Adsorption Capacity Measurement

Batch sorption tests were carried out by agitating a suspension of 1 g sorbent in 50 mL metal nitrate solution for 8 h (equilibration period) at room temperature (25 ± 0.1°C) in stoppered flasks placed on a thermostatic water-bath/shaker. After centrifugation, the remaining metal concentration in the filtrate was determined by flame AAS and the equilibrium pH was measured by a pH-metre. The metal ion concentration retained in the sorbent phase (q_e, mg/g) was calculated by Eq. (1):

$$q_e = (C_o - C_e)\frac{V}{m} \tag{1}$$

where C_o and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (mg/L), V is the solution volume (L) and m is the mass of sorbent (g) [23]. For heavy metal loading to red mud and fly ash, C_o was chosen as 100 mmol/L (0.1 M). Batch sorption tests were carried out in accordance with the procedure explained by Apak et al. [23]. The equilibrium pHs of suspension including red mud-metal ion and fly ash-metal ion systems varied between 5.8 and

6.7. The metal-loaded sorbents were washed with water and dried before solidification experiments.

2.4. Initiation and Completion of Setting (Penetration Tests)

Blank (reference) or chemical aid-added cement (300 g) was mixed with 27% (by mass) of water (~81 g H_2O) for 3 min under continuous stirring until a plastic paste was obtained. The normal proportion of water for consistency was determined by placing the paste to the Vicat ring within 1 min at most and flattening its surface with a spatula. The setting times of the prepared mortars were measured by the Vicat needle penetration test in accordance with TS EN 196 standard. The display of the device was zeroed when the needle touched the glass plate. The time for initiation of setting was determined by letting the paste-immersed needle to stay at a distance of 3–5 mm to the glass plate. In order to find the time for completion of setting, the Vicat needle was immersed into the paste at different points every 15 min, and the required time was determined when the needle penetration depth was 1 mm at most.

2.5. Preparation of Samples for Mechanical Strength Tests

The mortars were prepared (as described below) so as to fit in the moulds.

(1) In parallel to the solid waste-added test mortars, a standard mortar paste in compliance with Turkish Standard (TS EN 196) was cast without any additives. The blank mortar formulation required the use of 1 part (450 g) cement, 3 parts (1,350 g) Rilem–Cembureau standard sand and ½ part (225 g) water;

(2) 1 part metal-loaded solid waste bearing or unloaded (free of solid waste) cement (450 g) + 3 parts Rilem–Cembureau standard sand (1,350 g) + 250 g water;

(3) 1 part metal-loaded solid waste bearing, setting-aid or promoter (sodium aluminate, calcium tert-phosphate, calcium chloride, or triethanolamine (TEA))−added cement (450 g)+ 3 parts Rilem–Cembureau standard sand (1,350 g) + 250 g water.

The ingredients of the above mixtures (i.e. 225 g (or 250 g) H_2O + 450 g cement (pertaining to blank or additive-bearing cement formulations) were transferred to a blender, operated for 30 s, and stepwise addition of standard sand (1,350 g) was made within 1 min while stirring. The blender was operated for an additional time of 15 s at high speed, stopped, paste resected by hand and kneaded within 15 s, and the blender was reoperated for one more min at high speed. Thus, within a total time of 3 min, the mortar was made ready for moulding. The steel moulds were lubricated from the interior with a thin grease, and placed into the tamping-vibrating apparatus for tightening the mortars. Initially, the first halves of the mould compartments were filled with the mortars, and 60 vibrations were made in a period of 60 s; after stopping of the apparatus, the second halves were added, and further 60 vibrations were made. The excess of the mortar pastes was removed with a trowel from the top of the moulds for flattening, and covered with glass plates (of which the interiors were lubricated). The moulds were left to stand in a room at 20°C temperature and 90% relative humidity. After 24 h of standing under the described conditions, formwork removal (demoulding) was accomplished. The 7–28-day hardened (in some cases, 56-day hardened) concrete blocks kept in distilled water at 20 ± 1°C were subjected to mechanical strength tests.

2.6. Optimization of the Ratio of Solid Waste or of Heavy Metal Load Added to Mortars

For solid waste-added formulations, partially substituting the cement mass, the waste percentage is given on the basis of cement weight. Solid wastes (red mud and fly ash) were added to cement at percentages (of cement weight): 10, 20, 30, 40, 50 and 60% (i.e. 45, 90, 135, 180, 225, 370 g), and the prepared mortars were subjected to mechanical strength tests to optimize the ratio of solid waste that can be added to cement to produce a stable and durable concrete mass. Once the reasonable solid waste ratio was determined, optimization of the ratio of heavy metal load to these solid wastes was made using mortars that contained 5, 10, 15, 20 and 30% red mud or fly ash, as confirmed by compressive strength tests of the final concrete blocks.

2.7. Determination of the Type and Quantity of Setting Aids and Promoters

Since the compressive strengths of Pb-loaded fly ash containing concrete samples were particularly low and their setting times were long, the addition of various chemical additives ($NaAlO_2$, calcium tert-phosphate, $CaCl_2$, and triethanolamine) to improve these properties was tested qualitatively and quantitatively. Sodium aluminate and TEA were added to 20% solid waste-added mortars (containing heavy metal load) at mass ratios of 0.5 and 0.05%, respectively, so as to improve their physical characteristics.

2.8. Leach Tests

For testing the heavy metal leachability from the concrete blocks originating from heavy metal-loaded solid waste-containing mortars, one acidic leachant (H_2CO_3 solution at pH = 4.1 or 10^{-3} M HNO_3 solution at pH = 3) and two alkaline leachants (4.2×10^{-3} M $NaHCO_3$ solution at pH = 8.3 and 0.5% humic acid (HL) solution at pH = 10.15) were used. The simulation of CO_2-injected groundwater conditions for imitating real contamination cases in the natural environment (i.e. soil and groundwater) was achieved by using carbonic acid and bicarbonate solutions as leachants. For this purpose, the 28-day (kept in distilled water) hardened blocks were contained in 400 mL leach solutions in covered glass tanks. The leach solutions were regenerated every 3 weeks, and pH as well as AAS-determined heavy metal ion contents of the leachates were periodically monitored.

All mortar of concrete block samples used in the leach tests contained 1,350 g standard sand + 250 mL water. The two processing blanks run for samples were: (i) without solid waste, containing 450 g cement and (ii) with solid waste, containing 360 g cement + 20% (of cement weight) waste sorbent (90 g). Metal-loaded solid waste-containing samples either had 0.5% promoter (e.g. 360 g cement + 81 g metal-loaded waste sorbent + 9 g $NaAlO_2$) or 0.05% promoter (e.g. 360 g cement + 89 g metal-loaded waste sorbent + 1 g triethanolamine).

3. Results and discussion

3.1. Adsorption Capacities and Experimental Metal Loads of Solid Waste Sorbents

Actual metal loads (under experimental conditions) and saturation capacities (Apak et al. 1998[23]) of solid waste sorbents added to mortars are given in Table 1. Linear equations for calculating the limiting pH (pH*) of metal ion precipitation (as hydroxides) were used to distinguish bulk/surface precipitation from chemical adsorption [25,26]. The equilibrium pHs of metal ion suspensions containing red mud and fly ash particles, the limiting pHs of metal ion solubility at the precipitation edge (pH*) for the working initial concentrations (pM_t) and the associated linear equations correlating pM_t to pH* are listed in Table 1. Comparing the working pH values with pH* in Table 1, it can be deduced that chemical adsorption and bulk/surface precipitation of the tested metal ions occurred simultaneously except of Cd(II) for which the prevalent mechanism seemed to be adsorption (as pH < pH*) for both red mud and fly ash suspensions. Generally, a metal hydroxide may precipitate and form at the surface of a hydrous oxide sorbent prior to its formation in bulk solution and thus contribute to the total apparent sorption. Comparison of the batch adsorption capacities calculated from Langmuir equation (Table 1) with the actual metal loads confirms that the sorbents were loaded with metals below their saturation capacities under the working conditions. The order of hydrolyzable metal cation retention (on a molar basis) by the selected solid waste sorbents were: Cu > Pb > Cd for fly ashes and Cu > Cd > Pb for red muds. Because of the high alkalinity and sulphate content of fly ash suspensions, the order of adsorption affinity changed (i.e. lead was adsorbed more than cadmium) probably due to surface precipitation of $PbSO_4$ on fly ash. The degree of insolubility of the metal hydroxides approximately followed the same order. In general, very high capacities have been achieved for metal sorption onto the selected unconventional solid waste sorbents, potentiating their utility in heavy metal removal from contaminated water.

3.2. Penetration Test Results

The effect of setting aids/promoters on setting time and water quantity to achieve normal thickness (consistency) of mortars is observed in Table 2. Red

Table 1
Metal loads and saturation capacities of solid waste sorbents (Q_R and Q_F are adsorbate concentrations on red mud and fly ash, respectively; M_t represents total molar concentration of dissolved metal species at the precipitation edge and pH* the critical pH of bulk metal ion precipitation as hydroxide)

Metal ion	Q_R (mg/g)	Q_F (mg/g)	Worked pH		pH*	$pM_t = b \times pH^* + a$
			Red mud	Fly ash		
Pb(II)	103 (166)[a]	103 (445)[a]	6.0	5.8	4.65	$pM_t = 2.00\ pH^* - 8.30$
Cd(II)	29 (66.8)[a]	81 (198)[a]	6.0	6.7	6.87	$pM_t = 2.84\ pH^* - 18.50$
Cu(II)	16 (75.2)[a]	35 (207)[a]	6.0	6.0	4.57	$pM_t = 2.00\ pH^* - 8.15$

[a] Second values in parantheses are saturation capacities (calculated in accordance with Langmuir adsorption modelling).

muds and fly ashes up to 20% of cement weight did not significantly affect the setting times of mortars compared to those without waste sorbents (prepared with respect to TS EN 196); however, both aluminate and TEA as setting aids strongly shortened the setting times (i.e. both the times for initiation and completion of setting). The presence of metal loads in the solid waste components of mortars prolonged both initiation and completion of setting, the strongest adverse influence being observed for lead(II) (Table 2). The tested setting aids/promoters were both effective in significantly reducing these setting times, TEA at a 10-fold lower concentration (by mass per volume) than aluminate. The positive effect of aluminate may be attributed to the formation of matrix-compatible $Pb(OH)_2$ instead of the matrix-disrupting $PbSO_4$ existing in fly ash [27]. It has been reported that TEA accelerates the hydration of $3CaO. Al_2O_3$ and $3CaO.Al_2O_3$–$CaSO_4. 2H_2O$ systems in cement, and possibly forms a complex with the hydrating silicate phase [28].

3.3. Optimizing Solid Waste Sorbent Ratio and the Resulting Mechanical Strength of Concrete Blocks

The compressive strength of concrete blocks as a function of solid waste ratio is seen in Fig. 1(a), showing that red muds and fly ashes can be incorporated in cement mortars up to 30% of the cement weight, and acceptable compressive strengths (close to that of the blank sample) can be achieved by 28-day hardening. The mechanical test results were generally satisfactory (i.e. compressive strengths of tested blocks above 80%

Table 2
The effect of setting aids/promoters on setting time and water quantity to achieve normal thickness (consistency) of mortars

Sample	Initial set (min)	Final set (min)	Required water for paste thickness (g)
Cement without additive (blank)	120	300	90
Cement + 0.05% TEA	53	105	90
Cement + 0.5% aluminate	50	90	104
Cement containing 20% red mud	75	180	110
Cement containing 20% fly ash	125	215	102
Cement containing 20% red mud + 0.5% aluminate	41	70	114
Cement containing 20% red mud + 0.05% TEA	24	54	100
Cement containing 20% fly ash + 0.5% aluminate	110	260	130
Cement containing 20% fly ash + 0.05% TEA	50	200	101.5
Pb(II)-loaded sorbent containing mortars			
Pb-loaded red mud	108	400	102
Pb-loaded Red mud + 0.5% aluminate	10	17	102
Pb-loaded red mud + 0.05% TEA	6	13	100
Pb-loaded fly ash	235	480	110
Pb-loaded fly ash + 0.5% aluminate	10	22	110
Pb-loaded fly ash + 0.05% TEA	7	19	103
Cu(II)-loaded sorbent containing mortars			
Cu-loaded red mud	100	232	100
Cu-loaded red mud + 0.5% aluminate	12	65	119
Cu-loaded red mud + 0.05% TEA	10	23	107
Cu-loaded fly ash	50	293	111
Cu-loaded fly ash + 0.5% aluminate	30	80	123
Cu-loaded fly ash + 0.05% TEA	26	55	112
Cd(II)-loaded sorbent containing mortars			
Cd-loaded red mud	120	265	90
Cd-loaded red mud + 0.5% aluminate	12	27	93
Cd-loaded red mud + 0.05% TEA	8	15	90
Cd-loaded fly ash	40	145	100
Cd-loaded fly ash + 0.5% aluminate	17	50	102
Cd-loaded fly ash + 0.05% TEA	11	45	101

of that of the blank) for cadmium-loaded sorbents up to 20% solid waste-added specimens. However, when heavy metal (Pb, Cu and Cd) cations were loaded to these waste sorbents, the acceptable ratio of solid waste incorporated in the mortar drops to 20% of cement weight, as 30% solid waste-bearing formulations could only reach $\sim$3–5 N/mm2 compressive resistance, unacceptable in CFS (chemical fixation and solidification) technology (Fig. 1(b)). Another noticeable observation was that a 28-day hardening period (in water) was insufficient for Cu-loaded formulations; however, after 56-day standing, these blocks approached the mechanical strength of the other metal-loaded solid waste formulations. Although there was no problem with Pb-loaded red mud, the curve for Pb-loaded fly ash was not included in Fig. 1(b), because in spite of the usage of various additives like $CaCl_2$, $CaCO_3$ and $Ca(OH)_2$, the setting times for Pb-loaded formulations (in 20% solid waste-incorporated mortars) could extend up to 10 days, remaining outside concrete standards. Possibly due to the matrix-disrupting effect of $PbSO_4$ forming with fly ash [27], mechanical strength criteria of Pb-loaded formulations enabled the incorporation of maximal 5% Pb-bearing solid waste in the mortars. Lead is known to cause problems in stabilization/solification of metal-bearing wastes [29], but Cd-containing or Cu-containing formulations produced mortars solidifying within 48 h to reach acceptable compressive strengths. Bishop claimed that Pb essentially (75%) remained in the silicate matrix due to the precipitation of lead hydroxide as silicate [30], and this event was interpreted by Bhatty by the chemical fixation of lead in the form of a double salt of calcium silicate hydrate [31]. Other investigators assumed that simple lead hydroxide could make isomorphic substitution in the silicate matrix without disrupting the basic structure.

3.4. The Effect of Type and Quantity of Setting Aid/Promoter

$NaAlO_2$, previously shown to be an effective promoter [27] for lead-bearing wastes, and TEA accelerating the hydration of cement calcium aluminates were separately added to the tested formulations in order to refine physical/chemical characteristics of metal-loaded mortars and hardened concrete blocks (Table 2). As a result of setting experiments, the amount of water required for normal thickness was chosen as either 225 or 250 mL, and 0.5% aluminate or 0.05% TEA was used as promoters to achieve the compressive strengths shown in Fig. 2 for 28-day hardened concrete blocks. With the exception of Pb-loaded red mud, all red mud-added mortars showed a decreasing trend for compressive strength with increasing amount of water, while the reverse (i.e. increasing strength with increasing water content) was true for fly ash-added mortars (Table 3, together with unreported preliminary experiments). An optimal combination of (3% $Ca_3(PO_4)_2$ + 1% $CaCl_2$) was previously shown to be effective for Pb-stabilization [27] in 20% Pb-loaded fly ash-incorporated mortars to reach the required mechanical strenghts, based on Pb-stabilizing effect of phosphates easily found in soils [32]. Data tabulated in Table 2 show that for 20% red mud-incorporated formulations without metal loading, the addition of promoters caused positive effects such as 61% and 70% reduction in the time of completion of setting (final set) with 0.5% $NaAlO_2$ and 0.05% TEA, respectively, whereas for fly ash-bearing formulations without metal loading, only the initiation of setting (initial set) could be accelerated to a limited extent. The real performance of the tested promoters was visible in improving the physical characteristics of metal-loaded solid waste-bearing mortars. Aluminate and TEA were the most effective set accelerators in

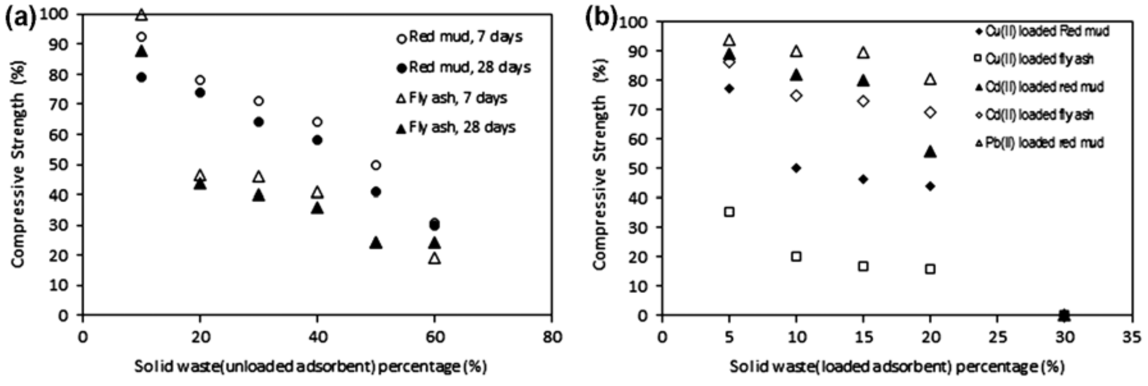

Fig. 1. (a) The compressive strengths of 7-day and 28-day hydrated/hardened concrete blocks as a function of unloaded solid waste content. (b) The compressive strengths of 28-day hydrated/hardened concrete blocks as a function of metal loaded solid waste content.

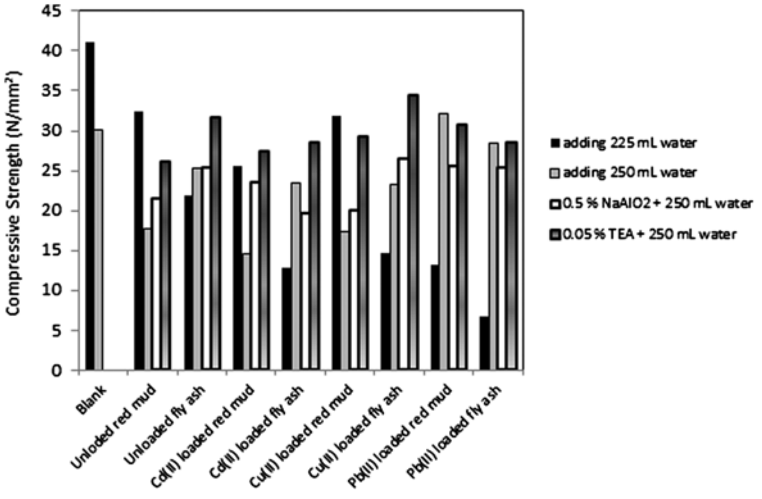

Fig. 2. The compressive strengths of 28-day hydrated/hardened concrete blocks containing 20% solid waste, either unloaded or loaded metal cations; the quantity of water added was either 225 or 250 mL.

Pb-loaded solid waste (at 20%)-bearing mortars: the addition of 0.5% $NaAlO_2$ or 0.05% TEA reduced the final set time of red mud-bearing mortars by 96% and 97%, respectively, while the corresponding reductions in fly ash-bearing mortars were 95% and 96%, respectively. Likewise, setting was accelerated in Cu (II)-loaded red mud and fly ash formulations at a percentage of 72–73% with aluminate and at 90–81% with TEA. In Cd-loaded formulations, the acceleration rates (%) using aluminate and TEA for final set were 90–94% for red mud- and 66–69% for fly ash-incorporated mortars (Table 2).

The compressive strengths of 28-day hardened concrete blocks prepared from metal-loaded solid waste-bearing mortars (recorded as arithmetic mean of four determinations for each sample) varied in a wide spectrum, generally remaining below blank (reference concrete block strength) values, but 0.5% $NaAlO_2$-added formulations showed significant improvements, and 0.05% TEA-added formulations even reached 90–120% of the blank strengths (Table 3). These results demonstrate that heavy metal-loaded solid wastes can be stabilized/solidified into environmentally disposable forms (i.e. concrete blocks) having sufficient mechanical resistance with the use of setting/hardening promoters at very low ratios.

3.5. Leach Test Results

Mortars with acceptable setting times were hardened into concrete blocks, and those found eligible in mechanical strength tests were subjected to chemical leaching tests using acidic and alkaline leachants. In all mortar formulations, the quantity of water was fixed at 250 mL, and the effect of promoters on metal leaching from final blocks was tested. The results obtained from the leaching test are depicted in Table 3. A background correction was made for metal ion concentrations of the leachates obtained from metal-loaded concretes by subtracting the values leached from solid waste formulations without added metal. The heavy metal concentrations leached into solution in the approximately 200-day follow-up period were generally very low, with the only exception of humic acid (HL) leach solutions (at alkaline pH) which showed slightly higher metal contents; Cu(II) was the most leached metal ion among others (Fig. 3). The higher leachability of copper(II) may be due to its strongest complex-forming ability (especially with phenolic –OH and –COOH groups of HL leachant) among the first-row transition metal ions of the periodic table, as described in Irwing-Williams order of complex formation. When the leachant was distilled water and not regenerated for concrete blocks prepared without promoters, only Cu(II) could be appreciably leached, and reached its maximal concentrations between the second and third months.

Confirming the reports of Brunner & Baccini pointing out to the pH-dependence of lead leachability and especially to the increased rate of Pb-leaching at $pH < 8$ [33], Pb concentrations passing into distilled water were found to be relatively low in this work, in accordance with the findings of other researchers [34]. Cartledge attributed the relatively high leachability of Pb to the precipitation of sparingly soluble Pb(II)-salts onto the surface of cement minerals and their redissolution into bulk solution [35]. It should be considered that pH is a major variable in investigating Pb leachability from concrete matrices in applications of CFS technology. For leachants not regenerated, all samples but the Pb-loaded fly ash sample caused a slight increase in solution pH (amounting to 0.5–1.0 pH unit) compared to that of the blank. In the first four weeks, metal (Pb, Cd and Cu) concentrations of the leachates remained below quantifiable levels (0.08 ppm), confirming metal stabilization in the tested matrices. Since lead immobilization in cement is hypothesized to arise from Pb-inclusion by an addition reaction in calcium silicate hydrates [31], $PbSO_4$ formation is detrimental to the stabilized/solidified matrix and hence to Pb stabilization applications of CFS technology. Possibly due to the formation of $PbSO_4$, the presence of fly ash was reported to be unfavourable toward lead fixation and to retard cement hydration [36], and this fact was confirmed with the findings of this work.

In experiments where the leachant solutions were regenerated every three weeks, higher concentrations of metals were observed to leach out from the tested matrices compared to cases of unregenerated leachants, possibly due to undersaturation of sparingly soluble matrix components in these pH-maintaining solutions enabling the continuation of the leaching process (thereby, shifting the solubility equilibria in favour of dissolution). The leachants reached their maximal metal-extracting power between the sixth and ninth weeks. The noticeable enhancement of metal (Pb, Cd and Cu) desorption/leaching from solid waste-bearing concretes in HL solutions may be attributed to metal-humate complexation with the aid of chelating phenolic -OH and -COOH functional groups of HL. On the other hand, metal leaching was negligible to H_2O, H_2CO_3, $NaHCO_3$ and 1 mM HNO_3 leachant solutions from 20% waste sorben-–bearing matrices without promoters, verifying the effectivity of metal fixation/stabilization (Fig. 3).

When Fig. 3 and Fig. 4 were compared as two groups, it was observed that metal leaching to pH 3.0 and pH 8.3 solutions slightly increased but still remained at a hundred thousandth (10^{-5}) level with the use of aluminate as promoter. Cu(II) leaching in presence of promoters was reduced to approximately 1/10 of that in their absence. Generally, all the tested metal ions leached out at a lower percentage from both red mud-bearing and fly ash-bearing masses into HL solutions, compared to the leachates of masses prepared without aluminate as promoter (Fig. 4). On the other hand, TEA as promoter was capable of protecting Cd but not Cu against leaching; (Cd(II) + TEA) combination produced about half of the metal leaching from the concrete mass prepared without TEA (Fig. 5), as opposed to the increased leaching of Cu with TEA for all leachants. (Pb(II) + TEA) combination produced about the same metal leaching into HL solution, but significantly lower leaching into the other leachants compared to those mortars prepared without TEA (Table 3).

To summarize the effect of promoters, TEA protects Cd while $NaAlO_2$ protects Pb and Cu against humate leaching. For mortars prepared with the use of promoters, H_2CO_3 was able to partly leach out Cd from all formulations and Pb from $NaAlO_2$-added formulations. Since Cd(II) and Pb(II) have amphoteric hydroxides [37] and their carbonates have solubility products close to those of the corresponding hydroxides, Cd and Pb could pass into the weakly acidic H_2CO_3 (or dilute HNO_3) leachate. On the other hand, Cu(II)—being the metal ion having the least soluble hydroxide—essentially did not pass to the weakly acidic leachate but passed to the leachates obtained from TEA-added mortars, in accordance with the Irwing-Williams order of complex formation (e.g. with the amine functional group of TEA having a known affinity toward copper). The Pb-protective effect of Na-aluminate was not seen with TEA in HL-leaching experiments, possibly because aluminate but not TEA was capable of forming the matrix-stabilizing double salts of calcium/aluminium and lead silicates and hydroxides, the definite compositions of which are currently unknown [22]. TEA is essentially a setting accelerator due to its positive effect on tricalcium aluminate hydration and to possible complex formation with the hydrating silicate phase [28], but its matrix-stabilizing effect against metal leaching has not been reported in the literature, and requires further investigations for full interpretation.

In cases when the leachants were not regenerated, the leachate pH was equilibrated between pH 8.0 and 9.5 within three weeks, and this had a stabilizing effect on Cd(II) and Pb(II) in the solified mass having minimal solubility of their hydroxides in the pH range of 7.5–10 [37]. The equilibrium pHs of the leachates irrespective of initial pH values were between 9.8 and 11.5 in this study due to long-term solid–liquid equilibria attained with alkaline constituents of the used solid wastes (Table 3). As opposed to theoretical expectations that amphoteric hydroxide-forming metal ions would leach out more at an alkaline equilibrium pH, hydroxide stabilization may have had a positive influence in our study on the long-term non-leachability of cadmium and lead. The overall results of leaching tests were favourable for metal ion fixation, in that during the 160-day follow-up period, the maximal leaching efficiencies of the tested metal ions (from masses without promoters) into pH 3, pH 8.3 and HL leachants were about 0.008%, whereas this value

Table 3

Compressive strengths and long-term metal ion leaching behaviour of unloaded and metal-loaded cement blocks

Cement Block	Added water (mL)	Compressive Strength (N/mm^2)	Metal ion concentration in H_2CO_3 or HNO_3 leach solution(in ppm) (pH = 4.1 or pH = 3)						Metal ion concentration in $NaHCO_3$ solution (in ppm) (pH = 8.3)						Metal ion concentration in humic acid solution (in ppm) (pH = 10.15)					
			7 days	19 days	69 days	92 days	126 days	168 days	7 days	19 days	69 days	92 days	126 days	168 days	7 days	19 days	69 days	92 days	126 days	168 days
Unloaded red mud	225	32.50	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Unloaded red mud	250	17.73	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Unloaded red mud + 0.5% $NaAlO_2$	250	21.55	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Unloaded red mud + 0.05% TEA	250	26.20	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Unloaded fly ash	225	21.80	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Unloaded fly ash	250	25.25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Unloaded fly ash + 0.5% $NaAlO_2$	250	25.42	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	—	–	–
Unloaded fly ash + 0.05% TEA	250	31.70	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cu^{2+} loaded red mud	225	31.85	–	–	–	—	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cu^{2+} loaded red mud	250	17.38	0.027	0	0.01	0	0.011	0.03	0.016	0.03	0.024	0	0.005	0	0.895	0.400	2.92	0.511	0.023	0.052
Cu^{2+} loaded red mud + 0.5% $NaAlO_2$	250	19.95	0.016	0	0	0	0	0	0.090	0	0.110	0.268	0	0	0	0.22	0	0	0	0
Cu^{2+} loaded red mud + 0.05% TEA	250	29.20	–	0.200	0.200	0.200	–	–	–	0.350	0	0	–	–	–	1.400	0.400	0.200	–	–
Cu^{2+} loaded fly ash	225	14.62	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cu^{2+}loaded fly ash	250	23.25	0.024	0	0.010	0.070	0.010	0.001	0.033	0.082	0.018	0.024	0.031	0.017	0.757	0.402	2.500	0.389	0.035	0.081
Cu^{2+} loaded fly ash + 0.5% $NaAlO_2$	250	26.52	0	0	0.042	0.016	0.362	0.378	0.138	0	0	0.026	0.100	0.350	0	0.269	0.166	0	0	0
Cu^{2+}loaded fly ash + 0.05% TEA	250	34.47	–	0.550	0.280	0.050	–	–	–	0.550	0.420	0	–	–	–	1.700	1.200	0.050	–	–
Cd^{2+} loaded red mud	225	25.60	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cd^{2+}loaded red mud	250	14.61	0.018	0.018	0	0.002	0.024	0.017	0.058	0	0	0	0.030	0.017	0.329	0.058	0.502	0.273	0.149	0.189
Cd^{2+}loaded red mud + 0.5% $NaAlO_2$	250	23.62	0	0	0.270	0	0.283	0	0.008	0	0.176	0.170	0.188	0	0.060	0.030	0.310	0	0	0
Cd^{2+}loaded red mud + 0.05% TEA	250	27.40	–	0.100	0.098	0	–	–	–	0	0	0	–	–	–	0.047	0	0.012	–	–
Cd^{2+}loaded fly ash	225	12.86	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cd^{2+}loaded fly ash	250	23.45	0.016	0	0	0	0.034	0.024	0.022	0	0	0	0.029	0.019	0.538	0.080	1.200	0.600	0.413	0.540
Cd^{2+}loaded fly ash + 0.5% $NaAlO_2$	250	19.72	0.020	0	0.124	0	0.086	0	0	0.070	0.184	0.348	0.016	0.090	0	0	0.054	0	0	0.002
Cd^{2+}loaded fly ash + 0.05% TEA	250	28.52	–	0	0	0.001	–	–	–	0	0.002	0.022	–	–	–	0.063	0.025	0.015	–	–
Pb^{2+}loaded red mud	225	13.18	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Pb^{2+}loaded red mud	250	32.15	0	0	0.072	0	0.150	0.060	0.050	0.050	0	0	0.230	0	0.240	0.500	2.260	0.290	0.070	0.350
Pb^{2+}loaded red mud + 0.5% $NaAlO_2$	250	25.57	0	0.113	0	0.042	0.026	0.160	0	0.170	0.460	0.032	0.237	0	0	0	0.320	0.080	0	0.023
Pb^{2+}loaded red mud + 0.05% TEA	250	30.77	–	0	0	0	–	–	–	0	0	0	–	–	–	0.230	0.260	0	–	–
Pb^{2+}loaded fly ash	225	6.78	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Pb^{2+}loaded fly ash	250	28.44	0	0	0	0	0.260	0	0	0.060	0	0	0.210	0	0	0	1.640	0.700	0	0
Pb^{2+} loaded fly ash + 0.5% $NaAlO_2$	250	25.37	0	0	0	0.198	0	0	0	0.170	0.260	0	0.264	0.024	0	0.100	0.160	0	0.088	0
Pb^{2+}loaded fly ash + 0.05% TEA	250	28.62	–	0	0	0	–	–	–	0	0	0.050	–	–	–	0.380	0	0	–	–

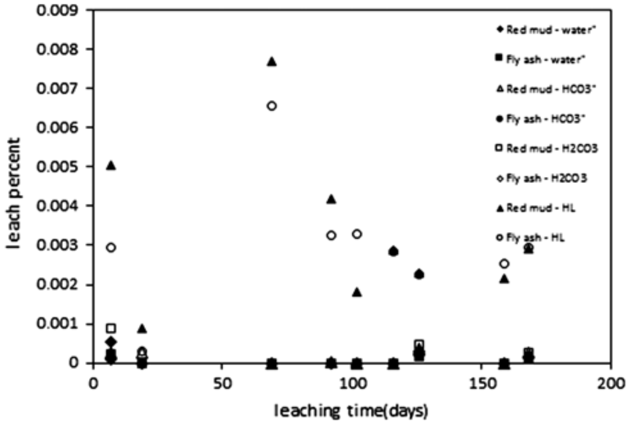

Fig. 3. The metal leach percentages of Cd (II)-loaded solid waste at 20% of cement weight bearing concrete blocks into H_2O, H_2CO_3, $NaHCO_3$ and HL leachants as a function of leaching time (without promoters).

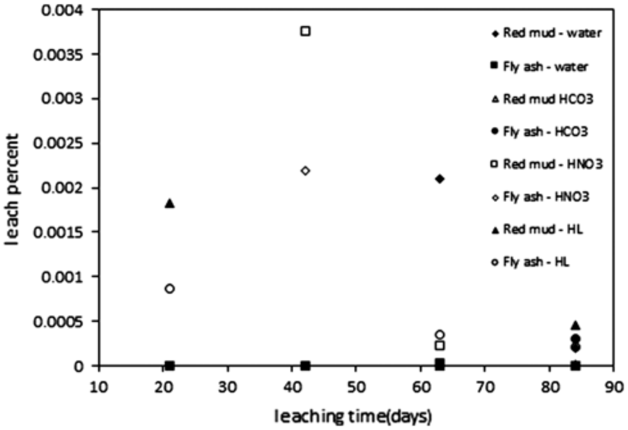

Fig. 5. The metal leach percentages of Cd (II)-loaded solid waste at 20% of cement weight bearing concrete blocks into H_2O, H_2CO_3, $NaHCO_3$ and HL leachants as a function of leaching time (with 0.05% TEA).

dropped to 0.004% from aluminate-incorporating masses, and to a few tens of ppm (10^{-5}) levels from Pb-containing and Cd-containing masses incorporating TEA. Turkish "Water Pollution Control Directory" states that the permissible lower limits of concentration ranges are given for the studied heavy metal ions as Cd(II): 3–10 ppb, Pb(II): 10–50 ppb and Cu(II): 20–200 ppb[38]. Inspection of data depicted in Table 3 reveals that all values were within the permissible ranges, rendering the proposed waste treatment technology as environmentally safe. As reflected in Fig. 2 and Table 3, the highest mechanical strength of the solidified blocks (especially in fly ash formulations) came from 0.05% TEA-incorporating pastes. These observations demonstrate that the proposed CFS technology is capable of stabilizing two distinct groups of wastes (i.e. heavy metals in contaminated water and solid waste materials) in a single solidified concrete mass having both chemical and mechanical resistance, safely disposable to natural environment.

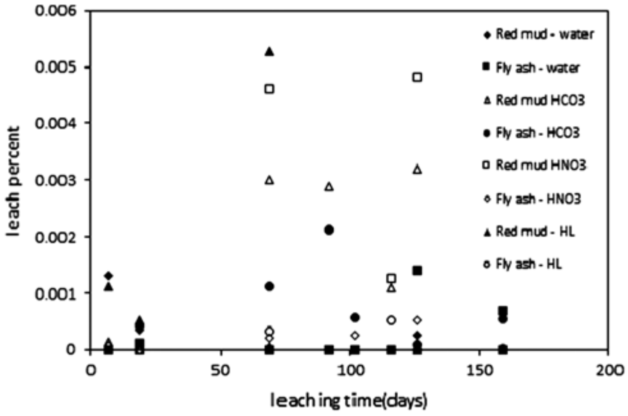

Fig. 4. The metal leach percentages of Cd (II)-loaded solid waste at 20% of cement weight bearing concrete blocks into H_2O, H_2CO_3, $NaHCO_3$ and HL leachants as a function of leaching time (with 0.5% $NaAlO_2$).

4. Conclusions

In investigating the possibility of usage of solid wastes as cost-effective sorbents in toxic heavy metal (Pb, Cd, and Cu) removal from contaminated water, red muds and especially fly ashes have been shown to exhibit a high capacity. The metal-loaded heterogeneous solid wastes comprising iron- and aluminium-oxides and silicates were successfully solidified by adding cement, sand and water, producing both physically and chemically resistant, durable concrete blocks. The setting and mechanical properties of concrete specimens obtained by optimal dosage of waste addition were satisfactory. The fixed heavy metals did not leach out appreciably into water over extended periods. The problem caused by the cumbersome metal, Pb, was solved with aluminate or TEA addition so as to improve the setting, hardening and mechanical strength of lead-bearing specimens. The tested solid wastes, red muds and fly ashes show the potential of being used as barrier material in the form of cost-effective grout for the prevention of expansion of a heavy metal contaminant plume. The presumed process is planned to be finished with *in situ* stabilization/solidification. However, an onsite demonstration has not been realized. Since the metal-loaded solid wastes could be solidified into an environmentally resistant form by adding stabilization-solidification agents and promoters, thereby serving the doublefold aim of water treatment and solid waste disposal, the finally emerging concrete blocks can be safely disposed of in the environment as possible landfill materials. This proposed process for metal-contaminated water treatment and solid waste disposal was, therefore, named as "integrated adsorption-solidification".

Acknowledgements

Various phases of this study were partially supported by TUBITAK, Turkish State Planning Organization (DPT) and Istanbul University Research Fund projects. A NATO/CCMS fellowship in the field of contaminated land and groundwater remediation enabled the presentation of some results of this work in international media. Author J. Hızal wishes to extend her gratitude to those organizations who contributed either to research equipment, materials or travel funds, and to all members of the Analytical Chemistry Team of Istanbul University, Faculty of Engineering, (who are the coauthors of international publications in the references list) for their collaboration.

References

[1] M. LaGrega, P.L. Buckingham, J.C. Evans, Hazardous Waste Management, McGraw-Hill Book Company, New York, NY, 1994.
[2] K. Shakir, A.F. Elkafrawy, H.F. Ghoneimy, S.G.E. Beheir, M. Refaat, Removal of Rhodamine B(a basic dye) and Thoron(an acidic dye) from Dilute Aqueous Solutions and Wastewater Simulants by Ion Flotation, Water Res. 44 (2010) 1449–1461.
[3] J.S. Chang, K.C. Yu, L.J. Tsai, S.T. Ho, Spatial disribution of heavy metals in bottom sediment of Yenshui River, Taiwan, Water sci. technol. 38 (1998) 159–167.
[4] V. Apak, E. Ünseren, Treatment of waste water and effluents with solid industrial wastes for the adsorptive removal of heavy metal contaminants, in: Y.A. Attia (Ed.), Proceedings Flocculation in Biotechnology and Separation Systems, Elsevier Sci. Publ., Amsterdam, 1987.
[5] R. Apak, E. Tütem, F. Kar, M. Hügül, Water treatment: I. The sorption of heavy metals onto metallurgical solid waste materials. II. The photooxidation of chlorinated hydrocarbons with H_2O_2. Report for TÜBİTAK (The Scientific and Technical Research Council of Turkey), 1993, Project No. KTÇAG-7.
[6] R. Apak, G. Atun, K. Güçlü, E. Tütem, G. Keskin, Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. I. Usage of bauxite wastes (red muds), J. Nucl. Sci. Technol. 32 (1995) 1008–1017.
[7] R. Apak, G. Atun, K. Güçlü, E. Tütem, Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. II. Usage of coal fly ash, J. Nucl. Sci. Technol. 33 (1996) 396–402.
[8] K. Bhattacharya, C. Venkobachar, Removal of cadmium (II) by low cost adsorbents, J. Environ. Eng. Div. 104 (1984) 110–112.
[9] K.K. Panday, V.N. Singh, Copper(II) removal from aqueous solutions by the fly ash, Water Res. 19 (1985) 869–873.
[10] K.P. Yadava, B.S. Tyagi, K.K. Panday, V.N. Singh, Fly ash for the treatment of Cd(II) rich effluents, Environ. Technol. Lett. 8 (1987) 225–234.
[11] R.H. Karol, Chemical Grouting, Marcel Dekker, New York, NY, 1990.
[12] M.B. Yeheyis, J.Q. Shang, E.K. Yanful, Feasibility of using coal fly ash for mine waste containment, J. Environ. Eng. 136 (2010) 682–690.
[13] K. Komnitsas, G. Bartzas, I. Paspaliaris, Efficiency of limestone and red mud barriers: laboratory column studies, Miner. Eng. 17 (2004) 183–194.
[14] A.K. Minocha, J. Neeraj, C.L. Verma, Effect of organic materials on the solidification of heavy metal sludge, Constr. Building Mater. 17 (2003) 77–81.
[15] J. Zhang, J. Liu, C. Li, Y. Lie, J. Li, Comparison of the fixation effects of heavy metals by cement rotary kiln co-processing and cement based solidification/stabilization, J. Hazard. Mater. 165 (2009) 1179–1185.
[16] D. Dermatas, X. Meng, Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils, Eng. Geol. 70 (2003) 377–394.
[17] Ü. Bulut, A. Özverdi, M. Erdem, Leaching behavior of pollutants in ferrochrome arc furnace dust and its stabilization/solidification using ferrous sulphate and portland cement, J. Hazard. Mater. 162 (2009) 893–898.
[18] M. Erdem, A. Özverdi, Environmental risk assessment and stabilization/solidification of zinc extraction residue: II. Stabilization/solidification, Hydrometallurgy 105 (2011) 270–276.
[19] T.S. Singh, K.K. Pant, Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials, J. Hazard. Mater. 131 (2006) 29–36.
[20] N. Jain, M. Garg, Effect of Cr(VI) on the hydration behaviour of marble dust blended cement: Solidification, leachability and XRD analyses, Constr. Building Mater. 22 (2008) 1851–1856.
[21] M.A.C. Gollmann, M.M. Silva, A.B. Masuero, J.H.Z. Santos, Stabilization and solidification of Pb in cements, J. Hazard. Mater. 179 (2010) 507–514.
[22] Q.Y. Chen, M. Tyrer, C.D. Hills, X.M. Yang, P. Carey, Immobilisation of heavy metal in cement-based solidification/stabilisation: A review, Waste Manage. 29 (2009) 390–403.
[23] R. Apak, E. Tütem, M. Hügül, J. Hizal, Heavy metal cation adsorption onto unconventional sorbents (red muds and fly ashes), Water Res. 32 (1998) 430–440.
[24] A. Kumar, S. Kumar, Development of paving blocks from synergistic use of red mud and fly ash using geopolymerization, Constr. Building Mater. 38 (2013) 865–871.
[25] R. Apak, J. Hizal, C. Ustaer, Correlation between the limiting ph of metal ion solubility and total metal concentration, J. Colloid Interface Sci. 211 (1999) 85–192.
[26] J. Hızal, R. Apak, W. Hoell, Modeling competitive adsorption of copper(ii), lead(ii) and cadmium(ii) by kaolinite-based clay mineral / humic acid system, Environ. Prog. Sustainable Energy 28 (2009) 493–506.
[27] F. Kilinçkale, S. Ayhan, R. Apak, Solidification-stabilization of heavy metal-loaded red muds and fly ashes, J. Chem. Technol. Biotechnol. 69 (1997) 240–246.
[28] V.S. Ramachandran, Hydration of cement – Role of triethanolamine, Cem. Concr. Res. 6 (1976) 623–632.
[29] J. Dragun, The fate of hazardous materials in soil, Hazard. Mater. Control 1 (1988) 41–65.
[30] P.L. Bishop, Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes, Hazard. Wastes Hazard. Mater. 5 (1988) 129–143.
[31] M.S.Y. Bhatty, Fixation of metallic ions in portland cement, Superfund'87–Proceedings of the 4th National Conference on Hazardous Wastes and Hazardous Materials (PCA & D serial No. 1834), Washington DC, 140–145.
[32] M.V. Ruby, A. Davis, A. Nicholson, In situ formation of lead phosphates in soils as a method to immobilize lead, Environ. Sci. Technol. 28 (1994) 646–654.
[33] P.H. Brunner and P. Baccini The Generation of Hazardous Waste by MSW-Incineration Calls for New Concepts in Thermal Waste Treatment, U.S. EPA, Cincinnati, 1988, 343–350.

[34] P.L. Cote, D.P. Hamilton, Evaluation of polutant release from solidified aqueous wastes using a dynamic leaching test, Hazard. Wastes Environ. Emergencies Conf., Houston, TX, (1984) 302–308

[35] F.K. Cartledge, L.G. Butler, D. Chalasani, H.C. Eaton, F.P. Frey, E. Herrera, M.E. Tittlebaum, S.L. Yang, Immobilization mechanism in solidification / stabilization of Cd and Pb salts using portland cement fixing of agent, Environ. Sci. Technol. 24 (1990) 867–873.

[36] G. Thevenin, J. Pera, Interactions between lead and different binders, Cem. Concr. Res. 29 (1999) 1605–1610.

[37] P.L. Cote, T.R. Bridle, Long-term leaching scenarios for cement-based waste forms, Waste Manage. Res. 5 (1987) 55–56.

[38] Water pollution control directory of the ministry of environment, Turkey, published in the Official Newspaper Issue No: 25687 dated 31 Dec., 2004.