Leaching behavior and immobilization of heavy metals in solidified/stabilized products

Rachana Malviya, Rubina Chaudhary *

*Council for Scientific and Industrial Research, School of Energy and Environmental Studies, Devi Ahilya University,
Takshila Campus, Khandwa Road, Indore-17, M.P., India*

Abstract

Solidification/stabilization (S/S) of hazardous sludge from steel processing plant has been studied. Mechanical strength and leaching behavior test of solidified/stabilized product was performed. Mechanical strength decreases with increase in waste content. Pb, Zn, Cu, Fe and Mn could be considerably immobilized by the solidification/stabilization process. The elements least immobilized were Na, K, and Cl. Leaching of heavy metals in the S/S matrix can be considered as pH dependent and corresponding metal hydroxide solubility controlled process. Geochemical modeling was performed for the prediction of speciation. On the basis of test results, mobility and mechanism of leaching was assessed. Dominant leaching mechanism was surface wash off in the initial stages followed by diffusion for Pb, Zn, Cu, Fe and Mn. Diffusion coefficient was above 11.5 indicating low mobility in the cement matrix.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Stabilization/solidification; Diffusion leaching; Ordinary Portland cement; Diffusion coefficient

1. Introduction

Steel processing unit generates hazardous sludge, disposal of which, could pose serious environmental and ecological problems because it has a high content of mobile heavy metals. It is desirable to condition sludge before disposal, to immobilize the soluble constituent present. Solidification/stabilization (S/S) process converts heavy metals into less mobile form. This process is applicable to the type of waste, which are not amenable to physical, chemical or biological processing [1–5]. The broad objective of the S/S process is to contain waste contaminant and prevent or minimize the release of the contaminant into the environment [6].

Portland cement is the most commonly used binder for this process. High pH of this binder is effective in immobilizing many toxic metals, by precipitation and sorption reaction. In most cases, a solid is produced with sufficient strength to support itself and a landfill cover. A minimum unconfined compressive strength of 50 psi, has been proposed for this purpose [7,8].

The environmental compatibility and field application of the S/S product is based on the engineering properties and leaching characteristics [9,10].

In field, leaching of hazardous constituents from stabilized/solidified waste is a function of both the intrinsic properties of the waste form and hydrologic and geochemical properties of the site. The laboratory leaching data can simulate the behavior of waste forms under ideal, static or worst case field condition. Presently, leach test can be used to evaluate the effectiveness of stabilization/solidification process.

NEN 7345 [11], a semi dynamic leaching test, was used to characterize leaching behavior of waste material. In static monolithic leaching test, a monolith of regular geometry and known surface area is immersed in a definite volume of leachant solution. The leachant is replaced at regular intervals with fresh solution. This test is a rapid and inexpensive way to evaluate the leaching rate of species from cement-stabilized waste [12]. Leaching of contaminants from materials treated by S/S, can generally be described by the following leaching equation [13–16].

$$\frac{M_t}{M_0} = \frac{4D\mathrm{obs}^{t^{0.5}}}{\pi L^2} \tag{1}$$

* Corresponding author. Tel.: +91 731 2460309; fax: +91 731 2462397.
  E-mail address: rubina_chaudhary@yahoo.com (R. Chaudhary).

Table 1
Physico-chemical characteristics of raw sludge

Parameter	
Dry density (g/cm^3)	1.05
Bulk density (g/cm^3)	0.9488
Specific gravity (%)	1.48
Porosity (%)	24.09
Water holding capacity (%)	36
Moisture content (%)	10
pH	7.4

Table 3
Composition of solidified/stabilized specimen

Sample	W/B[a]	W/S[b]
A	0.0	0.36
B	0.16	0.41
C	0.5	0.45
D	1.0	0.50
E	2.0	0.55
F	4.0	0.62
G	5.0	0.66
H	6.0	0.65
I	7.0	0.64
J	8.0	0.69

[a] Dried waste/binder (w/w).
[b] Water/solid (w/w).

where M_t is the mass of leachable contaminant that has leached at time 't', M_0 the mass of leachable contaminant initially present in solid, Dobs the observed diffusivity, t the time of leaching in seconds, and L is the ratio of waste volume to surface area exposed to leaching.

It describes leaching of compounds that do not react, as well as compounds that are immobilized by sorption, precipitation and combination of reaction, in multi component system. The purpose of this study is to assess leaching behavior and effectiveness of solidification/stabilization process in terms of component immobilization.

2. Materials and methods

2.1. Waste and binder

Sludge was obtained from the wastewater treatment facility of a steel-processing unit. Sludge was collected from the sun drying bed of the effluent treatment plant. Ordinary Portland cement was procured from Vikram cements Pvt. Ltd. (M.P.). Physico-chemical characteristics of sludge are presented in Table 1 and heavy metals (Pb, Zn, Cu, Fe and Mn) content of sludge and ordinary Portland cement (OPC) are presented in Table 2. Total heavy metal content (T) represents overall content in mg/kg. Available heavy metal content (A) represents maximum leachable fraction of the component. The available fraction was tested by available leaching test – NEN 7341 [17]. Heavy metal analysis was carried out by atomic

absorption spectrophotometer (GBC Avanta, 13.1). Standard methods [18] were followed for the analysis of all the parameters. Sodium, potassium were analyzed using flame photometer (Amil). Sulphate analysis was done by turbidity nephalometer (systronic).

2.2. Solidified/stabilized samples

Solidified/stabilized samples were prepared by mixing different proportions of sludge with OPC and raw water. Compositions of samples are presented in Table 3. Prepared samples were cured for 28 days and were subjected to unconfined compressive strength testing and diffusion leaching test.

2.3. Unconfined compressive strength

For unconfined compressive strength (UCS) testing, the cubes of dimension 2 in. × 2 in. × 2 in. were prepared from the mixture containing different waste/binder (W/B) ratio. Mixture was inserted in the cubical mold, compacted and vibrated for about half an hour to remove all the entrapped air. The cube was unmolded after 24 h. The prepared specimens were cured under relative humidity of 90 ± 2% at 20 ± 1 °C for 28 days in incubator in triplicate. The testing was performed on universal testing machine (Enkay Machines)

3. Leach test

3.1. Diffusion leaching

NEN 7345 [11] is used to determine the leaching mechanism of heavy metals from solidified/stabilized products. It simulates the leaching of inorganic components from shaped and monolithic materials, as a function of time over 64 days. Monolith cubes of dimension 2 in. × 2 in. × 2 in. were hanged in the acidified leachant (pH 4). Volume of the leachant was four times the geometric area of the test specimen. Diffusion leaching test was carried out for eight successive steps of specified length 0.6, 1.0, 2.25, 4.0, 9.0, 16.0, 32.0, and 64.0 days. pH, conductivity, lead, zinc, copper, iron, manganese, chloride, sulphate, calcium, sodium, and potassium were determined for all eight extractions.

Table 2
Heavy metal content (mg/kg) of raw sludge and ordinary Portland cement

Metal	Sludge		Cement	
	T	A	T	A
Lead	4600	498	600	50
Zinc	10600	5098	615	4
Iron	41500	842	5259	60
Manganese	3750	1402	690	147
Copper	3000	270	67.92	BDL
Sulphate	65000	13781	2627	1783
Chloride	8893	6693	15632	5802
Sodium	491	386	400	219
Potassium	205	180	809	438

T: total heavy metal content in mg/kg; A: leached metal in available leaching test in mg/kg.

Cumulative measured leaching in mg/m^2 was calculated using the formula:

$$\varepsilon_n = E_i \times \frac{\sqrt{t_i}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \tag{2}$$

where ε_n is the calculated component leached for the nth period (mg/m^2), E_i the measured leaching of component in fraction i (mg/m^2), and t_i, t_{i-1} is the replenishment time of fraction i and $i-1$ (s).

Percentage depletion in relation to total availability was calculated using the formula:

$$\%D = \frac{U_{\text{dif},t}}{A} \times 100 \tag{3}$$

where $\%D$ is the percentage leached component in time t of the diffusion test [11] in relation to the available content in the monolith, $U_{\text{dif},t}$ the leached quantity of the component in time t of the diffusion test in mg/kg dry matter, and A is the quantity of the component available for leaching according to NEN 7341 [17] in mg/kg dry matter.

4. Geochemical modeling

The geochemical equilibrium model Visual MINTEQ Version 2.3 was used for speciation calculation. Authors had used Minteq geochemical models successfully for prediction of leaching species [19–21]. Input data were experimentally measured pH, Eh and concentrations of inorganic constituents of the leachates (Ca, Cr, Cu, Fe, K, Mn, Na, Pb, SO$_4$, and Zn). The available and diffusion leaching test data values were used for predicting speciation of different cations and anions in the leachate. Redox potential and the pH were not allowed to change in the simulations and solids were not allowed to precipitate. The temperature used was 25 °C. The thermodynamic database provided by the code was used.

5. Results

5.1. Unconfined compressive strength

For solidification/stabilization, sludge was mixed with OPC. The composition of each specimen and water required for spec-

Table 4
Average unconfined compressive strength after 28 days of curing

Sample	Strength (MPa)
A	22.93
B	10.63
C	10.04
D	4.82
E	2.54
F	0.55
G	0.30
H	0.19
I	0.14
J	0.18

imen preparation are presented in Table 3. For the same final weight of the mixture, the water consumption increases with increasing quantity of sludge. The average results of unconfined compressive strength after 28 days of curing are presented in Table 4. The basic criterion of screening was the attainment of 0.34 Mpa (50 psi) strength, which is recommended for the disposal in secured landfill. Samples A–F, with W/B 0.16–4.0, attained the required strength after 28 days of curing. The load taken by the sample F (W/B 4.0) was 0.55 Mpa. W/B ratio of 5.0–8.0 (G–J) with higher sludge content did not attain the criteria strength.

5.2. Diffusion leaching

The samples were subjected to diffusion leaching. After each interval of static leaching, the leachate pH and conductivity were measured (Table 5). The pH values at the end of each extraction were much higher than the initial pH (4.0) of the leachant [11]. Leaching concentrations are presented in Tables 6 and 7 and figures presents leaching trends.

6. Discussions

The alkaline nature of the S/S matrix could significantly change the initial pH of the leachant. The pH decreases with progressive extraction, the differences in pH values of various S/S matrixes at the same diffusion leaching extraction were also significant. The pH decreased with increase in W/B ratio. Through-

Table 5
pH and electrical conductivity (mS/cm) of leachate during diffusion test

Sample	1		2		3		4		5		6		7		8	
	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC	PH	EC	pH	EC	pH	EC
A	12.6	1.23	12.6	1.3	12.5	0.91	12.5	0.9	12.8	1.1	12.7	0.9	12.8	1.0	11.4	0.5
B	12.2	0.93	12.4	1.0	12.4	0.71	12.5	0.8	12.7	1.2	12.9	1.1	13.0	1.2	11.5	0.7
C	11.9	0.85	12.2	1.0	12.3	0.9	12.4	0.9	12.7	1.2	12.7	1.1	13.0	1.2	11.6	0.8
D	11.7	0.95	12.1	1.0	12.2	0.88	12.3	0.9	12.6	1.1	12.7	1.0	13.0	1.3	11.7	1.4
E	11.5	0.93	11.7	1.1	11.8	0.91	12.0	0.8	12.4	1.0	12.5	0.9	13.0	1.2	11.6	1.0
F	10.8	0.90	11.2	1.4	11.4	1.07	11.2	0.8	11.6	0.74	11.2	0.5	11.9	0.4	10.6	0.3
G	10.6	1.07	10.8	1.2	10.6	1.09	10.6	0.8	10.5	0.73	10.8	0.4	11.0	0.3	9.4	0.2
H	9.0	2.3	8.03	3.8	9.31	3.2	9.13	2.2	9.1	1.7	9.6	0.8	8.7	0.5	9.1	0.3
I	8.7	2.8	7.74	4.4	9.40	3.7	9.12	2.3	9.2	1.7	9.3	0.8	8.34	0.5	9.5	0.4
J	9.2	2.8	8.05	4.3	9.03	3.6	9.01	2.3	9.1	1.6	9.6	0.6	8.31	0.5	8.62	0.4

Table 6
Cumulative heavy metal leached and percentage depletion in relation to total availability

Sample	Pb		Zn		Fe		Mn		Cu	
	mg/m^2	%D	mg/m^2	%D	mg/m^2	%D	mg/m^2	%D	mg/m^2	%D
A	58.4	3.9	1.58	1.1	184.8	16.4	39.32	16.19	51.63	29.62
B	60.1	16.4	1.6	2.31	182	7.51	46.92	2.41	60.22	14.80
C	55.01	73.3	1.75	0.17	207.1	15.67	122.89	2.64	62.35	11.90
D	60	11.5	4.4	0.69	425.6	79.47	132.91	6.76	65.90	13.5
E	73	20.40	1.78	1.54	448.14	67.88	171.11	6.69	69.23	13.7
F	75.8	16.4	1.4	0.13	131.92	12.20	91.25	7.6	72.30	14.00
G	61	8.81	2	0.06	194.72	12.7	29.7	1.05	74.86	14.23
H	10.87	8.6	1.43	0.2	124.2	28.74	532.7	74.94	79.3	15.07
I	16	2.75	1.66	0.20	99	14.8	292.1	30.58	79.59	16.89
J	20.7	3.0	1.16	0.07	123.75	12.61	196.69	26.78	79.66	16.32

out the leaching test for S/S matrix A–F, pH was observed around 11. For the samples G–J, pH was 8–10. This pH difference alters the metal leachabilities of different matrix. pH of the system influences leaching, fixation and speciation of metals in the solidified/stabilized matrix [22,23]. From Table 6, it was observed that, the cumulative fraction of Pb leached from S/S samples H, I, and J (W/B ratio 6.0–8.0) was lower than the samples B and C (W/B 0.16 and 0.5). B and C contain lesser quantity of sludge than H, I, and J. Pb leaching seems to be controlled by the pH of the system. The final buffered pH of all the extraction of H, J, and I ranges between 8 and 9 (Table 5). In this pH range leaching of Pb is lowest (Table 6). Lead is amphoteric in nature and its theoretical lowest solubility point of occurs at pH 8.5 [24]. Leaching rate increases as the pH deviates from this pH range. Samples B and C were buffered at pH range ≥ 12, which resulted in a higher lead leaching. Similar, observations were reported by Brunner and Baccini [25]. Visual MINTEQ geochemical modeling was used for speciation predic-

Table 7
Average percentage of major species of heavy metals during diffusion leaching at pH range 11

Heavy metal	Percentage species
PbOH$^+$	2.796
Pb(OH)$_2$ (aq)	54.305
Pb(OH)$_3$$^-$	42.896
ZnOH$^+$	0.103
Zn(OH)$_2$ (aq)	79.676
Zn(OH)$_3$$^-$	19.902
Zn(OH)$_4$$^{-2}$	0.317
CuOH$^+$	0.217
Cu(OH)$_4$$^{-2}$	0.606
Cu(OH)$_3$$^-$	74.7
Cu(OH)$_2$ (aq)	24.476
Mn^{+2}	1.564
MnOH$^+$	1.895
Mn2(OH)$^{3+}$	96.471
MnSO$_4$ (aq)	0.064
Fe^{+2}	1.886
FeOH$^+$	36.213
Fe(OH)$_2$ (aq)	17.665
Fe(OH)$_3$$^-$	44.125
FeSO$_4$ (aq)	0.107

tion of dissolved species in solution, for lead dominating species were Pb^{2+}, PbOH$^+$, Pb(OH)$_2$, and Pb(OH)$_3$$^-$ (Table 7). At low pH condition, PbOH$^+$ is the dominant dissolved Pb(II) species, but with the increase of pH, Pb can form hydroxide precipitate. These hydroxide precipitates further reacts with hydrating cement phase, and are incorporated in hydrating calcium silicate hydrate.

It was also observed, that zinc showed excellent fixation in the Portland cement matrix. Only 0.1–2.3% zinc leached from the matrix through out the W/B range. Zinc forms hydroxides in the high pH conditions (>8) of cement system. Zinc hydroxide, a typical amphoteric functions both as an acid and a base. The hydroxy complexes Zn(OH)$_4$$^{2-}$ and Zn(OH)$_5$$^{3-}$ can be present in a strong alkaline solution. Their anionic properties preclude their adsorption onto the negative surface of the C–S–H, but they may form the zinc complex hydrated compound similar results are reported by Ecke et al. [26] and Todorvic et al. [27].

Considering the highly alkaline condition of S/S matrix, Cu, Fe, Mn exist as metal hydrated phases, metal hydroxides and calcium–metal compounds. Cu was predicted as Cu(OH)$_4$$^{2-}$, Cu(OH)$^{3-}$, Cu(OH)$_2$, these phases may react with calcium to form complex compounds in S/S matrix. Leachate modeling predicted two major phases of copper Cu(OH)$_2$ (aqueous) and CuOH$^+$.

It was observed, that manganese leaching increases with the increase in the quantity of sludge in the S/S samples (Table 6). It was better immobilized in the samples B–G, but no regular trend of fixation was observed. The fixation of manganese was independent of solidification recipe. The dominating species at this pH was Mn$_2$(OH)$_3$$^+$ followed by MnOH$^+$, and Mn^{2+} (Table 7). Similar trends were observed for iron. Iron can be precipitated as Fe(OH)$_2$ and can be incorporated in the hydration phases with Ca and Si.

Sodium, potassium, and chloride are weakly bound species of the matrix (Table 8). Leaching up to 99% for all three, support the statement. The chloride leaching in specimen A–C, with the W/B ratio 0–0.5 was 24–35%, which may be due to formation of monochloroaluminates of calcium [28]. The sulphate leached from 2.4–40%, through the W/B ratio range B–J. Sulphate leaching is due to formation of hydrated sulphate such as ettringite in the cement paste [14].

Table 8
Cumulative anion and cation leached and percentage depletion in relation to total availability

Sample	Na$^+$		K$^+$		Cl$^-$		SO4^{2-}		Ca^{2+}	
	mg/m^2	%D	mg/m^2	%D	mg/m^2	%D	mg/m^2	%D	mg/m^2	%D
A	639.0	72.0	3187.8	70	23247.2	24.5	38383.2	13.5	67978.68	0.32
B	908.0	26.8	3932.0	64.3	23873.7	30.4	13339.2	2.4	2174.12	0.032
C	1257.8	71.5	3028.5	87.4	30546.7	35	12849.6	9.9	3506.56	0.11
D	1147.6	71.5	2063.4	79.0	46426.2	89.98	14383.6	9.3	9475.89	0.23
E	1284.3	71.4	1695.6	79.0	130809.9	111.1	30910.5	16.1	53758.95	2.89
F	1455.0	64.0	1261.0	99.0	105028.6	74.0	39222.9	33.0	53748.32	3.46
G	1588.3	55.0	939.2	99.0	112567.2	95.0	38787.8	34.2	59322.25	5.28
H	969.4	66.0	1021.2	99.0	114587.2	99.0	42589.1	37	70740.51	4.40
I	2237.6	78.0	1047.8	99.0	115879.1	99.0	43658.2	39	64825.44	5.30
J	2211.0	89.0	778.8	99.0	116002.2	99.0	45325.2	40	58148.14	4.89

Most of the calcium was extracted with in the first three leaching fractions (Fig. 1). This may be due to the dissolution of calcium hydroxide (CH), nearly amorphous calcium silicate hydrate (C–S–H) and complex calcium metal compounds. Calcium hydroxide can dissolve at comparatively high pH condition during extraction. With the dissolution of calcium species, the matrix lost its buffering capacity. For heavy metals, their hydrated phases, and metal hydroxides precipitated on the surface of C–S–H or encapsulated could dissolve into solution. From these results, it seems that most of the heavy metals might exists as metal hydrated phases and metal hydroxides in the S/S waste matrix. The extraction of these metals with HNO$_3$ (pH 4.0) was related to the dissolution of C–H and C–S–H the hydrated phases in the S/S matrix.

The samples with higher binder content had lower depletion of most of the heavy metals from the S/S matrix. It should be pointed out that the main reason of heavy metals immobilized in the cement S/S matrix is due to alkaline nature and buffering capacity provided by calcium hydroxide and C–S–H. The leaching of metal contaminants in these matrixes can be considered as pH dependent metal hydroxide solubility controlled process.

7. Diffusion leaching

The leaching of ions from the solidified/stabilized matrix is diffusion controlled. Godbee provided an analytical solution for Fickian diffusion with simplifying assumption of zero concentration at the solid–liquid interface [29].

$$\frac{\sum a_n}{A_0} \frac{V}{S} = 2 \frac{D_e^{1/2}}{\pi} t_n^{1/2} \tag{4}$$

where a_n is the contaminant loss during leaching period, n (mg), A_0 the initial amount of contaminant in specimen (mg), V the volume of specimen (m^3), S the surface of specimen (m^2), t_n the time (s), and D_e is the effective diffusion coefficient (m^2/s)

From Eq. (4), D_e can be calculated from a slope of $\sum a_n/A_0$ versus $t_n^{1/2}$ according to the following relationship:

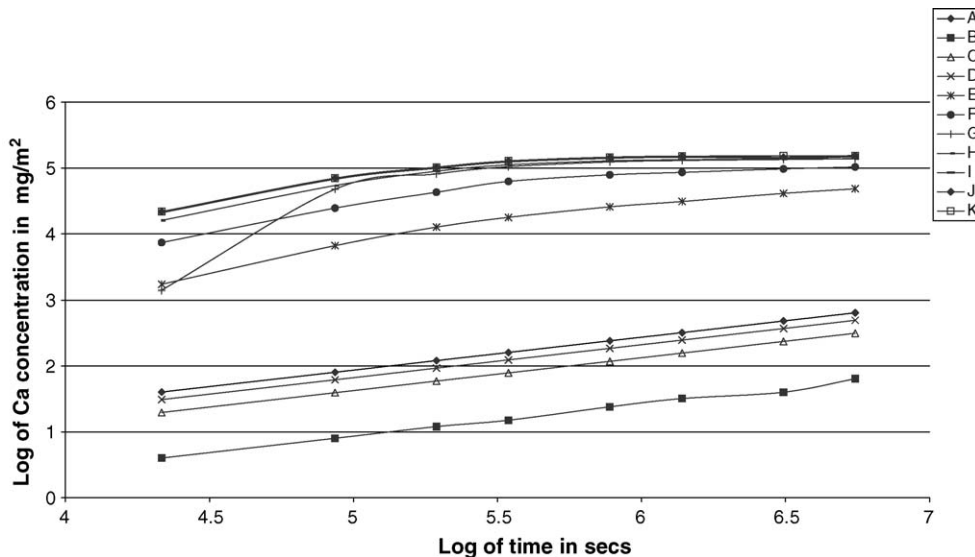$$D_e = \frac{\pi}{4} \left[\frac{V}{S} \right] \left[\frac{\sum a_n}{A_0/t_n^{1/2}} \right] \tag{5}$$

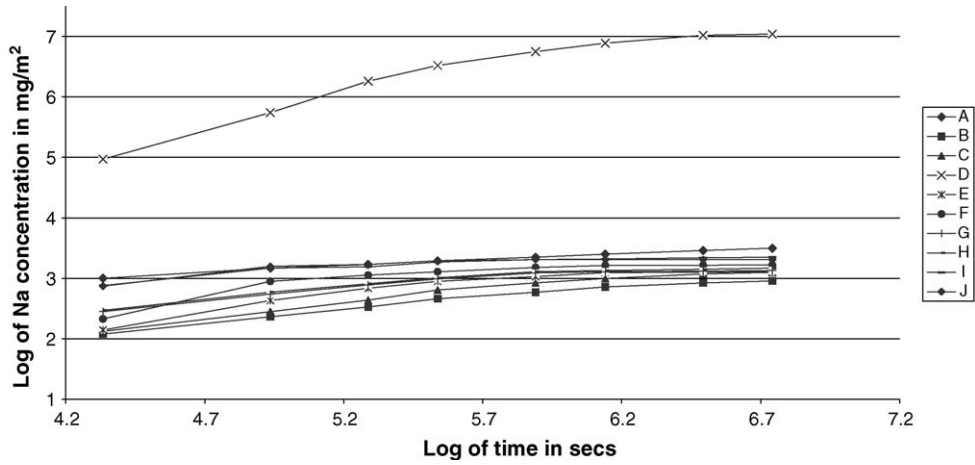Fig. 1. Cumulative calcium leached over 64 days from cement soldified/stabilized product.

Fig. 2. Cumulative sodium leached over 64 days from cement soldified/stabilized product.
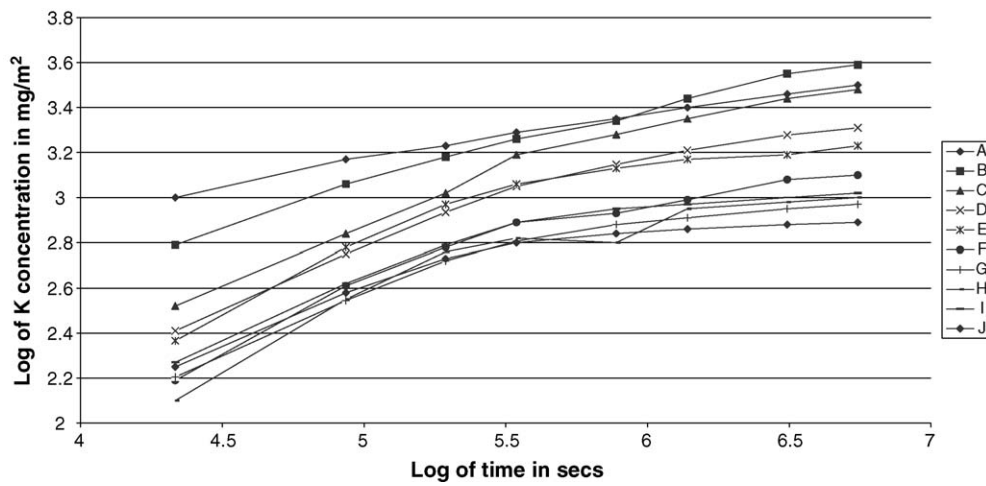

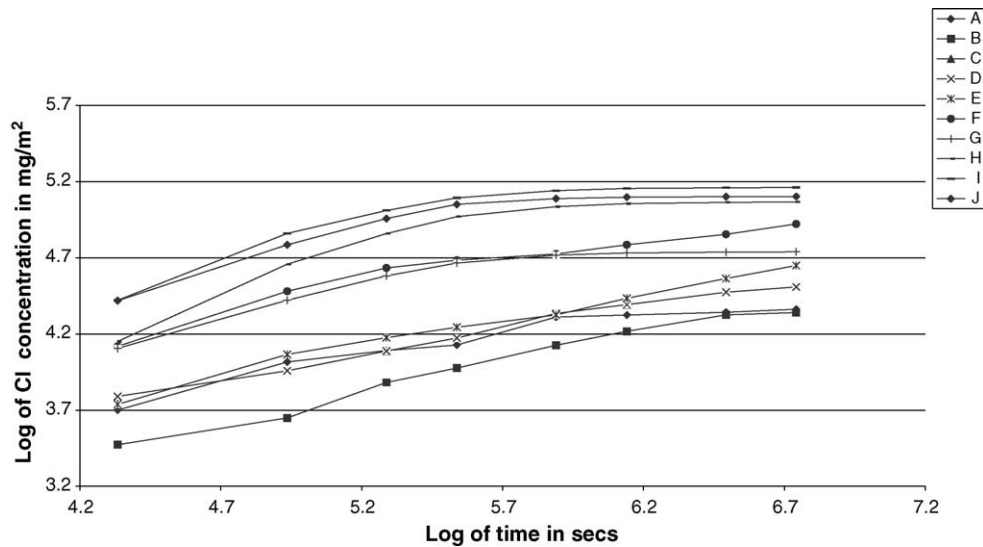Fig. 3. Cumulative potassium leached over 64 days from cement solidified/stabilized product.

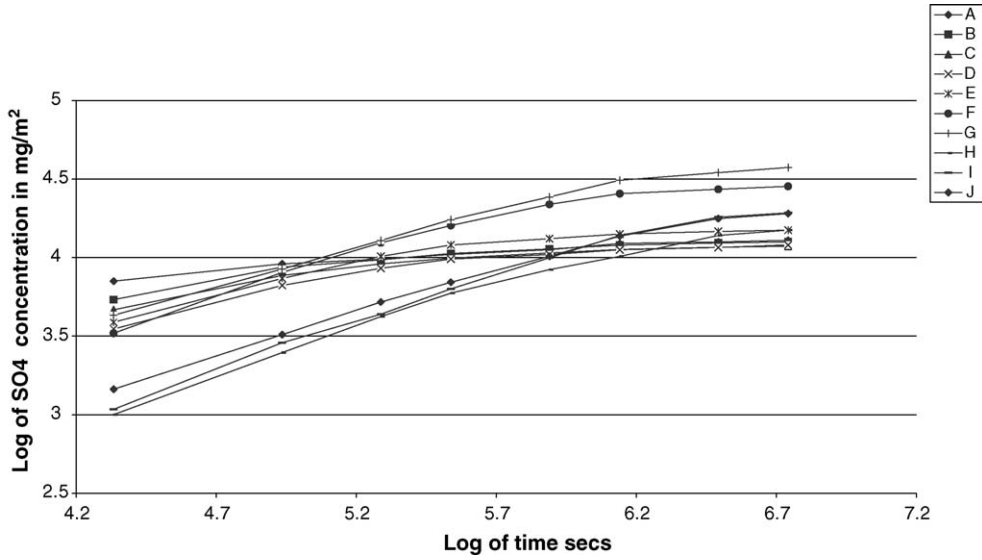Fig. 4. Cumulative chloride leached over 64 days from cement soldified/stabilized product.

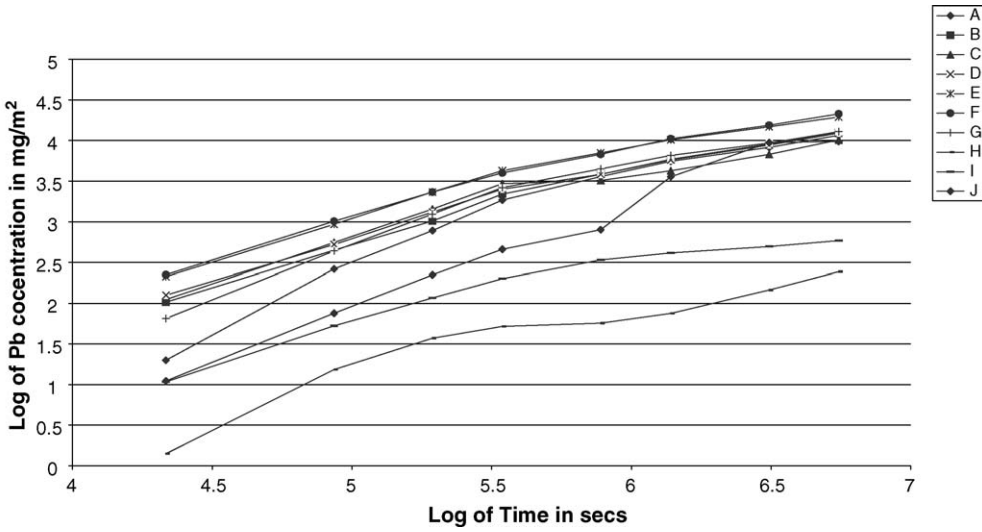Fig. 5. Cumulative sulphate leached over 64 days from cement soldified/stabilized product.

Fig. 6. Cumulative lead leached over 64 days from cement solidified/stabilized product.
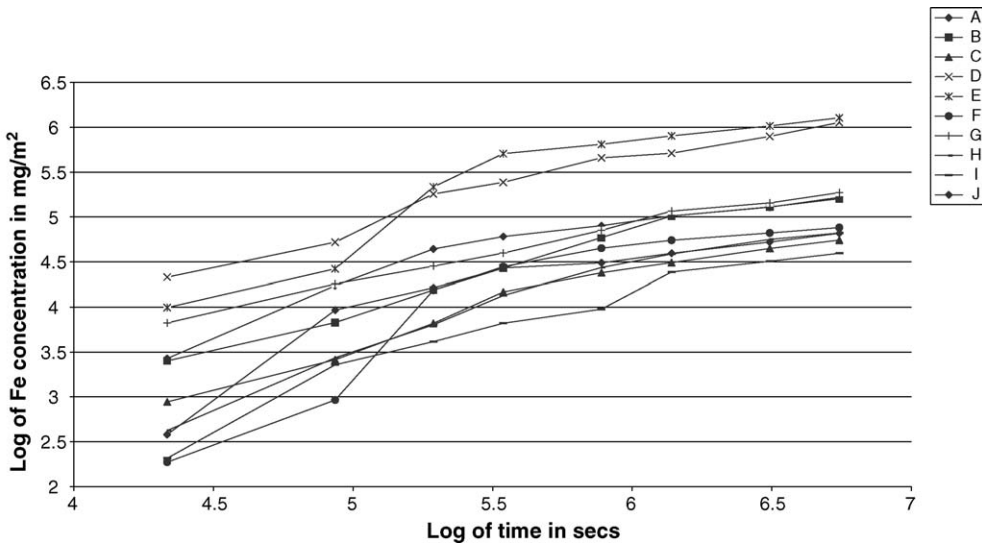

Fig. 7. Cumulative iron leached over 64 days from cement solidified/stabilized product.
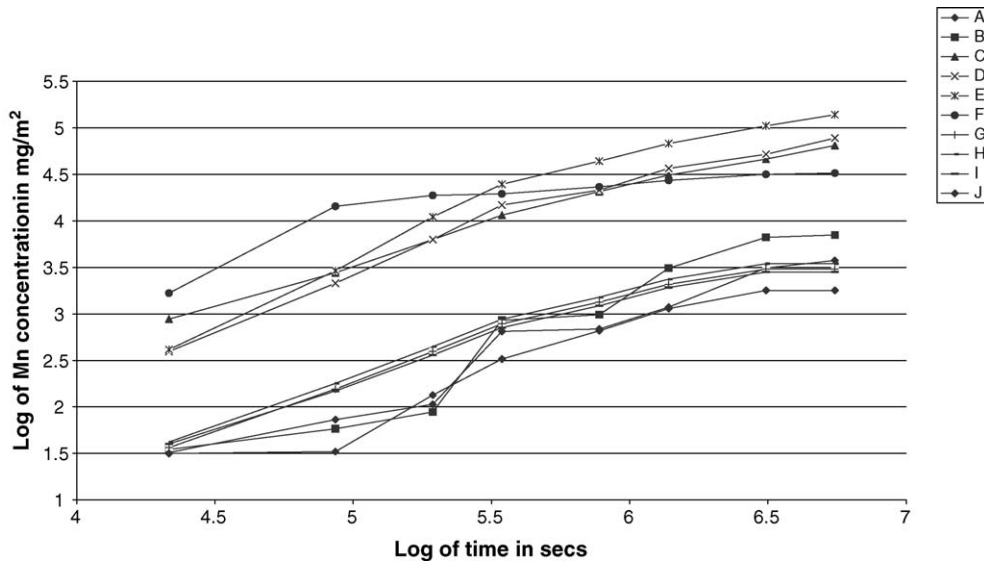
Fig. 8. Cumulative manganese leached over 64 days from cement solidified/stabilized product.

Test like NEN 7345(NEN 7345) characterizes detailed leaching mechanism and rate of release under mass-controlled leaching scenario.

8. Leaching mechanism and diffusion coefficient

For leaching mechanism assessment diffusion leaching test was performed. Leaching mechanism was determined from the slope of the linear regression through the eight data points (log of leached quantity versus log time). Following conditions are given for the different slope values (NEN 7345) [22].

Slope value	Leaching mechanism
Less than 0.35	Surface wash off
Between 0.35 and 0.65	Diffusion
Greater than 0.65	Dissolution

In order to interpret Figs. 1–10 and evaluate solidification process. The negative log of effective diffusivities in m²/s (ρD_e)

for each contaminant was calculated by linear regression of the cumulative fraction leached versus square root of time. The value of ρD_e indicates rates of leaching. The higher the ρD_e value, lower will be the mobility of the component, with constant availability. Constant availability is the concentration gradient, which is the deriving force for the diffusion (Table 9).

Low mobility	$\rho D_e > 12.5$
Average mobility	$11.0 < \rho D_e < 12.5$
High mobility	$\rho D_e < 11.0$

To measure the actual resistance provided by the matrix for the movement of elements. Na^+, K^+, were treated as inert components as these elements due to chemical properties show no interaction with the material and are expected to be weakly bound to the solids that comprise the matrix. The concentration of these elements in the elute fraction was well above three times the lower detection limit of the analytical process. These elements were used to assess the leaching mechanism. Comparing

Table 9
Diffusion coefficient (ρD_e) and dominant leaching mechanism for anions and cations

Sample	Na^+		K^+		Cl^-		$SO4^{2-}$		Ca^{++}	
	ρD_e	Mech.	ρD_e	Mech.	ρD_e	Mech.	ρD_e	Mech.	ρD_e	Mech.
A	11.6	DF[a]	10.9	DF	11.7	DF	12.23	DF	15.63	DS
B	11.7	DF	10.8	DF	11.5	DF	13.7	DF	14.93	DS
C	11.2	DF	10.8	DF	11.3	SW[b]	12.9	DF	13.62	DF
D	11.2	DS[c]	10.9	DF	11.2	DF	12.5	DF	13.45	DS
E	10.7	DF	10.6	DF	9.7	DF	12.0	DF	13.23	DF
F	10.9	DF	10.4	DF	10.7	DF	11.4	DF	12.90	DF
G	11.0	DF	10.4	DS	10.1	DF	11.4	DF	12.85	DF
H	10.9	DF	10.6	DS	10.3	DS	11.5	DF	12.65	DS
I	10.9	DF	10.6	DF	10.2	DF	11.0	DF	12.55	DS
J	10.9	DF	10.6	DS	10.4	DF	11.0	DF	12.45	DS

Mech.: mechanism of leaching.
[a] DF: diffusion.
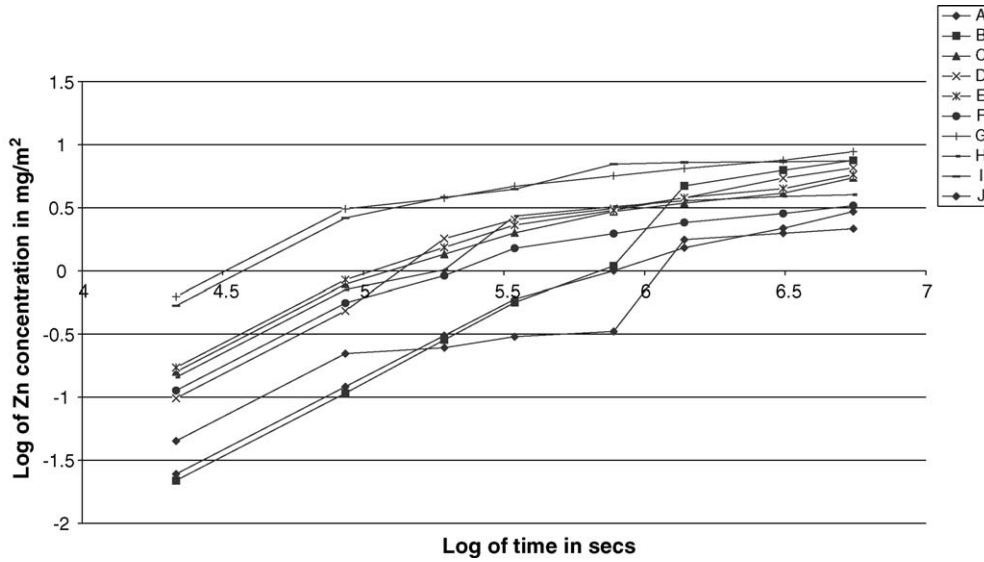[b] SW: surface wash off.
[c] DS: dissolution.

Fig. 9. Cumulative zinc leached over 64 days from cement solidified/stabilized product.
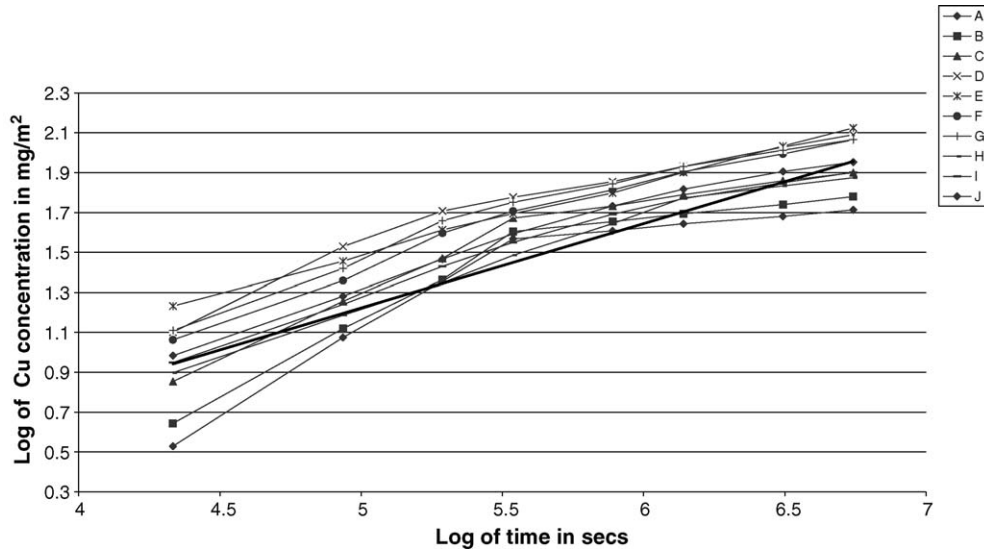

Fig. 10. Cumulative copper leached over 64 days from cement solidified/stabilized product.

Table 10
Diffusion coefficient (ρD_e) and dominant leaching mechanism for heavy metals

Sample	Pb		Zn		Fe		Mn		Cu	
	ρD_e	Mech.	ρD_e	Mech.	ρD_e	Mech.	ρD_e	Mech.	ρD_e	Mech.
A	13.3	DF[a]	13.3	DF	12.0	DF	11.6	DS[b]	13.0	SW
B	12.1	DF	13.7	DF	12.7	DF	13.7	DF	12.45	SW
C	11.2	DF	16.5	DS	12.5	DF	12.7	SW	12.2	SW
D	12.4	DF	14.8	SW[c]	10.7	DF	12.8	DF	12.15	SW
E	11.7	DF	14.0	SW	10.8	DS	12.8	DS	12.12	SW
F	12.0	DF	16.2	SW	12.3	DF	12.7	DF	12.0	DF
G	12.6	DF	16.9	DF	12.2	DF	14.4	DF	11.9	SW
H	14.6	DF	15.8	DF	11.5	DF	10.7	DF	11.84	DF
I	13.6	DF	16.4	DF	12.1	DF	11.5	DF	11.74	DF
J	13.5	DF	16.7	DF	12.2	DF	11.6	DF	11.79	DF

Mech.: mechanism of leaching.

[a] DF: diffusion.

[b] DS: dissolution.

[c] SW: surface wash off.

diffusion coefficient (ρD_e is the negative logarithm of effective diffusion coefficient for a specific component in m^2/s) for sodium, for sample A, ρD_e was 11.7, B = 11.6, E = 10.7, H = 10.9. For potassium the variation in the ρD_e value for samples B = 10.8, E = 10.6, and H = 10.4 (Table 10). This shows that increasing sludge increases the mobility of loosely bound inert components in solidified/stabilized matrix. The dominant leaching mechanism for sodium and potassium was initial surface wash off followed by diffusion (Table 8). Considering Figs. 2 and 3, it was observed that for almost all the ratio, Na$^+$ and K$^+$ leached maximum in the first three extractions that is in the first 2 days of leaching. Weakly bound Na$^+$, K$^+$ leached almost completely with respect to the fraction available for leaching (Table 9). Chloride is also weakly bound species in the cement matrix. The leaching was governed by surface washing in the initial stages, followed by diffusion (Table 10). The mobility of chloride ion in the matrix was in the high mobility range. From Fig. 4 it can be observed, that the concentration of the chloride for the entire W/B ratio was highest in the first or second extraction, which reflects its high mobility and weak binding with the matrix.

Sulphate leached with average mobility and its leaching mechanism is governed by surface wash off and diffusion (Fig. 5). The presence of sulphate is due to a surface washing of the hydrated sulphates formed in the cement paste hydration such as ettringite [10,29].

An initial resistance to diffusion was recognizable in the case of all heavy metals and that was probably due to an initial surface washing period [15]. For Pb, Fe, Cu and Mn, ρD_e above 11.5 was obtained, this indicate that the mobility of heavy metals is reduced in the cement matrix (Table 10). However with increasing sludge the mobility increases but that is in the average mobility range of $11.0 < \rho D_e < 12.5$. Values of ρD_e are also used as indicator of type of fixation. $11.0 < \rho D_e < 12.5$ indicates that heavy metals are stabilized by physical interaction with the hydration product of the cement. From Figs. 6–8, it can be seen that maximum leaching of Pb, Fe, and Mn was observed in the first three fraction, that is with in the time period of 0–2.25 day. For Zn (Table 10) ρD_e value is more than 13.0 indicating high level of immobilization. The release plot of Zn (Fig. 10) showed a increasing leaching till the fourth and fifth fraction of leaching. This delayed release pattern and ρD_e value indicate chemical fixation, which inhibits the release of metal from the matrix. Zinc–OPC interaction involve the formation of an impermeable layer of calcium zincate on the cement grain surfaces [30].

9. Conclusion

Cement was effective in immobilizing heavy metals (Pb, Zn, Fe Cu, and Mn) present in the steel processing plant sludge. Unconfined compressive strength decreses with increase in waste content. The leaching of metal contaminants in these matrixes can be considered as pH dependent metal hydroxide solubility controlled process. The dominant leaching mechanism was not diffusion controlled for all heavy metal species.

References

[1] J.R. Conner, Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand Reinhold, New York, 1990.

[2] Y.C. Yang, M.G. Shaaban, H.B. Mahmud, Chemical stabilization of scrap metal yard contaminated soil using ordinary Portland cement: strength and leachability aspects. Build. Environ., in press, corrected proof 2005.

[3] G. Qian, Y. Cao, P. Chui, J. Tay, Utilization of MSWI fly ash for stabilization/solidification of industrial waste sludge, J. Hazard. Mater. 129 (2006) 274–281.

[4] M.C. Ruiz, A. Irabien, Environmental behaviour of stabilised foundry sludge, J. Hazard. Mater. 109 (2004) 45–52.

[5] C.E. Halim, R. Amal, D. Beydoun, J.A. Scott, G. Low, Implications of the structure of cementitious wastes containing Pb(II), Cd(II), As(V), and Cr(VI) on the leaching of metals, Cement Concrete Res. 34 (2004) 1093–1102.

[6] E.F. Barth, C.C. Wiles, Technical and Regulatory Status of Stabilization/Solidification in the United States, Solidification and Stabilization of Hazardous Waste, Noyes Corporation, Park Ridge, NJ, USA, 1989.

[7] B. Batchelor, Leaching Models: Theory and Application Solidification/Stabilization Mechanism and Application, Gulf Cost Hazardous Substance Research Center, 1990, pp. 103–111.

[8] Nuclear Regulatory Commission, Branch technical position of waste form qualification, CONF-831174-61, Washington, DC, 1983.

[9] I. Hohberg, G.J. de Groot, A.M.H. Van der Veen, W. Wassing, Development of a leaching protocol for concrete, Waste Manage. 20 (2000) 177–184.

[10] S. Valls, E. Vasquez, Leaching properties of stabilized/solidified cement-admixtures- sewage-sludges systems, Waste Manage. 22 (2002) 37–42.

[11] NEN 7345, Leaching characteristics of soil and stony building and waste material, 1994.

[12] H.A. Vandersloot, D. Hoede, G.J. De Groot, G.J.L Van der Wegen, P. Quevauviller, Inter comparison of leaching test for stabilized Waste, Petten, The Netherlands, Document ECN-C-945-064 November, 1994.

[13] American Nuclear Society, Standard committee working group ANS-16.1, Measurement of leaching ability of solidified low – level radioactive wastes by short term test procedure, Standard ANSI/ANS-16.1-1986, Lagrange Park, IL, 1986.

[14] B. Batchelor, Leach models: theory and application, J. Hazard. Mater. 24 (1990) 255–266.

[15] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, England, 1975.

[16] D.S. Kosson, T.T. Kosson, H.A. Vander Sloot, Evaluation of Solidification/Stabilization Treatment Processes for Municipal Waste Combustion Residues, EPA/600/R-93/167, Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH, 1993.

[17] NEN 7341, Leaching characteristics of building material and solid waste material-leaching test- determination of leaching characteristics of inorganic components from granular and building materials, NNI Delft, The Netherlands, 1992.

[18] American Public Health Association, Standard Methods for the Estimation of Waters and Wastewaters, 16th ed., APHA, Washington, DC, 1989.

[19] R.N.J. Comans, J.A. Meima, P.A. Geelhoed, Reduction of contaminant leaching from MSWI bottom ash by addition of sorbing components, Waste Manage. 20 (2000) 125–133.

[20] A.-M. Fallman, Leaching of chromium and barium from steel slag in laboratory and field tests – a solubility controlled process? Waste Manage. 20 (2000) 149–154.

[21] B.S. Crannel, T. Eighmy, J.E. Krzanowski, J.D. Eusdem, E.L. Shaw, C.A. Francis, Heavy metal stabilization in municipal solid waste combustion bottom ash using soluble phosphate, Waste Manage. 20 (2000) 135–148.

[22] P.L. Cote, I. Denis, Application of dynamic leaching test to solidified hazardous wastes, in: L.P. Jackson, A.R. Rahlik, R.A. Conway (Eds.), Proceedings of 3rd Symposium ASTM STP on Hazardous Waste, American society for testing and materials, Philadelphia, 1984.

[23] H.A. Vandersloot, L. Heasman, P. Quevauiller, Harmonization of Leaching/Extraction Tests, Elsevier Science B.V., Amsterdam, 1997.

[24] J.A. Mundell, K.R. Hill, In place precipitation immobilization: technical and economic assessment at the A.Y. Mcdonald foundry site, Dubuque, Iowa, in: Proceedings of the Hazardous Wastes and Environmental Emergencies, Houston, TX, 1984, pp. 177–181.

[25] P.H. Brunner, P. Baccini, The Generation of Hazardous Waste by MSW-Incineration Calls for New Concept in Thermal Waste Treatment, Swiss Federal Institute for Water Resources, Dubendorf, Switzerland, 1988.

[26] H. Ecke, N. Menad, A. Lagerkvist, Treatment-oriented characterization of dry srubber residue from municipal solid waste incineration, J. Mater. Cycles Waste Manage. 4 (2002) 117–126.

[27] J. Todorvic, H. Ecke, A. Lagerkvist, Solidification with water as a treatment method for air pollution control residue, Waste Manage. 23 (2003) 621–629.

[28] N. Alba, Estabilitazcio/solidificacio de residus dincineracip de RSU en matrius de ciment. Valoracio ambiental doctoral thesis, 1989.

[29] H.W. Godbee, D.S. Joy, Assessment of the loss of radioactive isotopes from waste solids to environment. Part 1. Background and Theory," TM-4333, Oak Ridge National Laboratory, TN, 1994.

[30] C.D. Hills, C.J. Sollars, R. Perry, Ordinary Portland cement based solidification of toxic wastes: the role of OPC reviewed, Cement Concrete Res. 23 (1993) 196–212.