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## Evaluation of leaching characteristics and environmental compatibility of solidified/stabilized industrial waste

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**Abstract** An attempt was made to judge the environmental compatibility, the governing leaching mechanism, and mobility patterns in a waste–cement solidified/stabilized matrix after 21 days of curing. The mixed sludge from a steel pickling facility was stabilized by ordinary Portland cement. Iron was the major leachable metal, along with Pb, Zn, and Mn. To characterize the leaching behavior, the mobility and mechanism of leaching were determined by diffusion leaching tests. In the solidified/stabilized matrix, the mobility of all the elements studied was reduced, and average to low mobility was observed. Values for the negative log of the effective diffusion coefficient of more than 12.5 were obtained for the metals. The dominant leaching mechanisms were surface wash off in the initial stage, followed by diffusion. The environmental performance of the solidified/stabilized product when considered in terms of mass leached over 64 days was found to be satisfactory for consideration for the safe disposal and reuse of waste.

**Key words** Solidification/stabilization · Ordinary Portland cement · Leaching · Diffusion · Diffusion coefficient

### Introduction

The performance of solidification/stabilization (S/S) of mixed sludge with ordinary Portland cement (OPC) was assessed by leach testing, a standard tool to estimate the potential release of hazardous constituents from the S/S matrix. The leaching of ions from the S/S matrix is diffusion controlled. Godbee provided an analytical solution for

Fickian diffusion with the simplifying assumption of zero concentration at the solid–liquid interface:<sup>1</sup>

$$\left[ \frac{\Sigma a_n}{A_o} \right] \left[ \frac{V}{S} \right] = 2 \left[ \frac{D_e}{\pi} \right]^{1/2} t_n^{1/2} \quad (1)$$

Where,  $a_n$  is the contaminant loss during the leaching period (mg),  $A_o$  is the initial amount of contaminant in the specimen (mg),  $V$  is the volume of the specimen ( $m^3$ ),  $S$  is the surface area of the specimen ( $m^2$ ),  $t_n$  is time (s), and  $D_e$  is the effective diffusion coefficient ( $m^2/s$ ). From Eq. 1,  $D_e$  can be calculated from the slope of  $\Sigma a_n/A_o$  versus  $t_n^{1/2}$ , according to the following relationship:

$$D = \frac{\pi}{4} \left[ \frac{V}{S} \right] \left[ \frac{\Sigma a_n}{A_o} \right]_{t_n^{1/2}} \quad (2)$$

Tests such as the Dutch tank leaching test (NEN 7345)<sup>2</sup> characterize the detailed leaching mechanism and the rate of release under mass-controlled leaching conditions. In this study, the conventionally preferred binder OPC was used to solidify/stabilize pickling plant sludge. The magnitude and mechanism of release of contaminants from the S/S matrix was studied after 21 days of curing and an attempt was made to assess the environmental compatibility.

### Materials and methods

As raw materials, the steel processing industry uses low carbon steel in rolled coils and hydrochloric acid for steel pickling, along with small quantities of commercial chemicals like Cool Cut 70, Gictane, Pyrobond, Pyroclean, Pyrotube, and Metax. The acid surface treatment of steel coils generates pickling effluent rich in heavy metals. The pickling effluent is treated in an effluent treatment plant and heavy metals are precipitated as lime sludge. A grab/composite sample of sludge was collected from the sludge drying bed of a commercial effluent treatment plant.

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**Table 1.** Solidified/stabilized specimen composition

Specimen	W/B	W/S	UCS (MPa)
OPC	0.0 <sup>a</sup>	0.36	19.20
C <sub>1</sub>	0.16	0.41	10.63
C <sub>2</sub>	0.5	0.45	8.41
C <sub>3</sub>	1.0	0.50	4.46
C <sub>4</sub>	2.0	0.55	2.35
C <sub>5</sub>	4.0	0.62	0.39
C <sub>6</sub>	5.0	0.66	0.26
C <sub>7</sub>	6.0	0.65	0.13

W/B, ratio of dried waste weight to binder weight; W/S, ratio of water to solids; OPC, ordinary Portland cement

<sup>a</sup>The sludge content was zero

**Table 2.** Details of analytical processes used

Parameter	Instrument	Detection limit (mg/l)
pH	Orion 720 A+	–
Lead	GBC Avanta 13.1AAS	0.05
Zinc	GBC Avanta 13.1AAS	0.005
Iron	GBC Avanta 13.1AAS	0.02
Manganese	GBC Avanta 13.1AAS	0.01
Sulphate	Systronic	1.0
	Nephalo-turbidity meter	
Chloride	Argentometric titration	0.15
Sodium	Flame photometer	0.1
Potassium	Flame photometer	0.1

### Solidified/stabilized specimens

The specimens were prepared by mixing different quantities of sludge, cement, and raw water (Table 1). The mixture was compacted, vibrated, and molded in a cubical mold of dimensions 5 × 5 × 5 cm. The cubes were unmolded after 24 h and specimens were cured for 21 days under a relative humidity of 90% ± 1% at 20° ± 1°C in an incubator.

### Leach test

NEN 7345, the Dutch tank leaching test, was used to determine the leaching characteristics of toxic components in solid monolithic materials. The S/S monolith cubes, as prepared above, were immersed in distilled water acidified with 1-M HNO<sub>3</sub> to pH 4 at a liquid/solid ratio of 4 in terms of volume. The leaching vessel was a closed polypropylene plastic container. The leachant solution was replaced after a contact period of 0.25, 1.0, 2.25, 4.0, 9.0, 16.0, 36.0, and 64.0 days. The potential leachability was assessed by the available leaching test.<sup>3</sup>

The parameters were analyzed using the standard methods<sup>4</sup> as given in Table 2. Lead, zinc, and sulphate were studied because of environmental concerns. Iron and manganese were studied because of the very high concentration of these metals in the sludge and to monitor any possible hazard because of leaching. Sodium, potassium, and chloride were studied to assess the mobility and governing

**Table 3.** Physicochemical characteristics and heavy metal content of sludge

Parameter	Value
Dry density (g/cm <sup>3</sup> )	1.1
Bulk density (g/cm <sup>3</sup> )	0.96
Specific gravity (g/cm <sup>3</sup> )	1.52
Porosity (%)	24.25
Water holding capacity (%)	36
Moisture content (%)	20
pH	7.4
Cl (mg/kg)	8900 ± 267
Na (mg/kg)	500 ± 25
K (mg/kg)	200 ± 6
SO <sub>4</sub> (mg/kg)	65100 ± 1966
Pb (mg/kg)	4700 ± 155
Zn (mg/kg)	10700 ± 214
Fe (mg/kg)	41600 ± 1289
Mn (mg/kg)	3800 ± 114

leaching mechanism. According to NEN 7345, sodium, potassium, and chloride do not show any chemical or physical interaction with the cement matrix, and are free to move. This provides an idea of the actual, minimal resistance provided by the matrix structure to movement in the matrix. If for two out of three inert components, leaching is governed by diffusion, then it is assumed that leaching is diffusion controlled for other components also. The value of the negative log of the effective diffusion coefficient ( $pDe$ ) describes the mobility of the mobile contaminants in the cement matrix.

### Results and discussion

The raw sludge was fine, with a porosity of 24.25% and a pH of 7.4. The water holding capacity of the sludge was 36%, an indication of the moisture retained by the sludge.<sup>5</sup> Investigation of the water holding capacity involves comparison of the weight of dried sludge (at 103°C for 2 h) and saturated sludge. Because of the high iron content, the color of the sludge was reddish brown. The physicochemical characteristics of raw sludge and concentrations of heavy metals are presented in Table 3.

The S/S specimens with higher sludge content needed more water to achieve the required consistency of the mixture. The water/solid ratio thus increased with increasing waste/binder ratio. It was found that higher water/solid ratios reduce the strength of the specimen as a result of the higher water content and lower binder percentage (Table 1).<sup>6</sup>

The addition of cement to the solidified waste increased the leachate pH (Table 4). All extractions were buffered at alkaline pH for all waste/cement ratios. The pH of all extractions for specimens C<sub>4</sub>–C<sub>7</sub> was alkaline in the pH range of 8–9; this is because of the relatively low cement content. The pH of all other ratios was higher, being in the range of 11–13. The movement of ionic species from monolith to leachant was indicated by the increases in the conductivity of the leachant (Table 4).

**Table 4.** pH and conductivity (mS/cm) of the leachates over 64 days

Days	OPC		C <sub>1</sub>		C <sub>2</sub>		C <sub>3</sub>		C <sub>4</sub>		C <sub>5</sub>		C <sub>6</sub>		C <sub>7</sub>	
	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC
0.25	11.60	0.70	11.00	0.42	10.80	0.13	10.40	0.34	9.70	0.33	8.50	0.39	8.20	0.66	8.20	1.83
1.0	11.80	0.79	11.70	0.77	11.40	0.76	11.30	0.36	10.40	1.76	8.80	1.77	8.40	0.76	8.40	1.87
2.25	11.70	0.85	11.60	0.98	11.60	1.13	11.40	1.16	10.70	1.87	9.20	1.81	8.80	1.77	8.60	1.84
4.0	12.46	0.77	12.42	1.04	12.59	1.19	12.37	1.17	11.63	1.55	8.23	1.96	8.67	1.81	7.80	1.67
9.0	12.54	0.96	12.59	1.36	12.43	1.71	12.12	1.42	11.99	1.90	9.29	2.10	8.49	1.96	8.07	2.10
16.0	12.45	1.03	12.63	1.37	12.63	1.50	12.49	1.56	12.40	1.70	10.60	1.02	9.90	2.10	9.47	0.95
36.0	12.15	1.14	11.75	1.48	12.29	1.62	12.59	1.99	12.40	2.20	11.66	0.85	10.73	1.02	10.68	0.54
64.0	12.39	1.15	12.34	1.00	12.13	1.00	12.61	2.20	12.80	1.99	11.93	0.64	10.87	1.50	10.70	1.69

EC, electrical conductivity

**Table 5.** Quantity leached per unit mass in the diffusion test over 64 days ( $U_{\text{dif},64}$ ) in mg/kg and percentage depletion (%  $D$ ) in relation to total availability of cations–anions

	Na		K		Cl		SO <sub>4</sub>		Ca	
	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$
OPC	70.0	18.29	122.0	15.10	200.0	10.36	2360.0	10.36	642.8	71.42
C <sub>1</sub>	74.0	24.95	233.1	39.60	271.2	13.20	240.1	1.00	63.9	6.91
C <sub>2</sub>	93.0	23.10	32.8	8.62	5257.0	64.77	7098.0	40.44	314.6	23.08
C <sub>3</sub>	1353.5	>100	498.2	>100	11571.0	>100	117.2	0.70	494.4	48.11
C <sub>4</sub>	179.5	79.29	987.1	>100	19571.0	>100	6549.4	41.03	6764.6	>100
C <sub>5</sub>	514.7	>100	1213.0	>100	19005.0	>100	762.2	6.80	8004.2	>100
C <sub>6</sub>	680.5	>100	1218.0	>100	22251.0	>100	924.5	8.26	10265.4	>100
C <sub>7</sub>	740.0	>100	1289.0	>100	24250.5	>100	1012.0	6.81	8489.9	>100

See Appendix for the calculation method for  $U_{\text{dif},64}$  and % $D$ 

The quantity leached per unit mass in the diffusion test over 64 days and the percentage depletion in relation to the total available fraction are presented in Tables 5, 6. The availability data is given in Table 7. The quantity leached and the percentage depletion increases as the sludge content of the specimen increases. For the diffusion test, the data for the release of contaminants from pure OPC is given to so that its contribution can be monitored. For samples C<sub>1</sub>–C<sub>7</sub>, lead was found to deplete only in the range of 0.1%–19.51%. This low depletion results from the higher pH of the cement matrix. Lead leaching seems to be controlled by the pH. Consider specimen C<sub>4</sub>: the pH ranged from 9.70 to 12.83 (average pH of 11.50) for all eight extractions, and the cumulative lead leached was 2.14 mg/kg – for C<sub>5</sub> and C<sub>6</sub>, the pH range was 8.50–11.93 and 8.20–10.87 (average pH 9.77 and 9.25) and the lead leached was 3.25 and 1.80 mg/kg, respectively. Despite the increasing amounts of sludge and the high availability of lead in specimens C<sub>4</sub>–C<sub>6</sub>, the leaching of lead was low in C<sub>6</sub> compared to C<sub>5</sub> and C<sub>4</sub>; this is because, in the pH range of 8.0–10.0, the leaching of lead is lowest. The leaching rate of lead increases as the pH decreases or increases beyond this pH range. Similar observations were reported by Brunner and Baccini.<sup>7</sup> Lead fixation in the cement matrix is through an addition reaction, forming a nonstoichiometric metallic calcium silicate.<sup>8</sup> This is further supported by the observation that the lead dissolution rate exactly follows the silicon dissolution rate.<sup>9</sup> The higher rates of calcium leaching with

increased sludge content indicate that the metal leached in the form of nonstoichiometric calcium–metal complexes (Table 5). For zinc, the quantity leached over 64 days ranged from 0.003 to 0.27 mg/kg, with the percentage depletion being 0.01%–0.32%. This high degree of fixation is attributed to the tricalcium component of Portland cement.<sup>8</sup> Zinc possesses amphoteric properties and its solubility is lowest at pH range of 9–11.<sup>10</sup> Cohen and Petrie<sup>11</sup> stated that immobilization of Zn in cement-stabilized waste is not the result of physical changes, but of chemical stabilization. During the hydration process, the formation of Ca(OH)<sub>2</sub> results in a highly alkaline environment in which the solubility of Zn species is reduced. The studies of Ecke et al.<sup>12</sup> and Todorovic et al.<sup>13</sup> support this statement and attribute the low leachability of Zn in the pH range 9–11 to the predominance of Zn(OH)<sub>2</sub>.

The calcium content increases in the leachate from C<sub>1</sub>–C<sub>7</sub> (Table 5) and this is attributed to the fact that as the sludge content of the mix increases, precipitation of metals as carbonate and hydroxide species increases, creating a continuously increasing demand for Ca<sup>++</sup> in the matrix. This increase in demand is satisfied by the unhydrated cement fraction. This again accelerates the hydration of tricalcium silicate, resulting in high decalcification in the cement matrix and the release of calcium.

Iron and manganese show excellent fixation in the cement matrices: The percentage depletion was in the range 0.01%–12.31% and 0.08%–26.82%, respectively. The curing

**Table 6.** Quantity leached per unit mass in the diffusion test over 64 days ( $U_{\text{dif},64}$ ) in mg/kg and percentage depletion (% $D$ ) in relation to total availability of heavy metals

	Pb		Zn		Fe		Mn	
	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$	$U_{\text{dif},64}$	% $D$
OPC	3.99	17.63	0.1	5.55	0.10	0.13	0.10	0.94
C <sub>1</sub>	0.01	0.11	0.004	0.17	0.01	0.01	0.12	0.08
C <sub>2</sub>	0.10	0.28	0.003	0.01	0.30	0.24	0.23	0.15
C <sub>3</sub>	0.11	0.37	0.04	0.11	0.10	0.08	2.10	1.17
C <sub>4</sub>	2.14	5.43	0.13	0.32	13.83	12.21	17.06	26.82
C <sub>5</sub>	3.25	5.08	0.16	0.08	13.70	11.68	14.00	7.20
C <sub>6</sub>	1.80	3.11	0.17	0.07	24.15	12.31	4.47	1.07
C <sub>7</sub>	4.0	19.51	0.27	0.13	14.16	6.92	13.60	6.67

See Appendix for the calculation method for  $U_{\text{dif},64}$  and % $D$

**Table 7.** Total availability in mg/kg (NEN 7341)

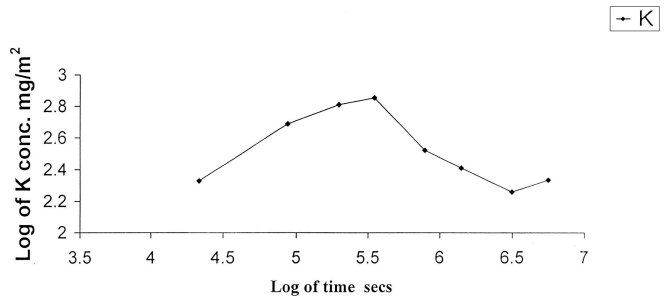
	Na	K	Cl	SO <sub>4</sub>	Ca	Pb	Zn	Fe	Mn
OPC	382.60	807.8	1928.8	22774.9	900.0	22.6	1.8	74.4	10.63
C <sub>1</sub>	296.60	588.52	2053.44	23993.5	925.0	8.5	2.3	74.2	143.3
C <sub>2</sub>	402.53	380.17	8115.57	17555.04	1362.7	34.5	19.2	122.9	156.5
C <sub>3</sub>	409.70	386.93	9475.4	16696.8	1027.5	29.6	36.4	125.8	179.3
C <sub>4</sub>	226.38	290.1	11298.62	15959.79	1129.5	39.4	40.7	113.2	63.6
C <sub>5</sub>	234.50	234.5	15481.00	11194.94	1085.7	64.0	204.7	117.2	194.2
C <sub>6</sub>	392.23	138.44	12563.14	11190.31	842.0	57.7	256.1	196.1	415.3
C <sub>7</sub>	204.59	122.75	12774.8	14853.9	943.0	20.5	202.6	204.6	204.6

time of 21 days was thus sufficient for immobilization of the heavy metals. Considering the percentage depletion data, sample C<sub>4</sub> was identified as being suitable for further use.

#### Diffusion coefficient and leaching mechanism

To assess the dominant leaching mechanism the NEN 7345 leaching test was performed after 21 days of curing. This curing period was selected from the results of a previous study.<sup>6</sup> It was concluded that this was the optimum curing period in terms of strength and potential contaminant leaching. Samples cured for 21 days were used to ascertain the dominant leaching mechanism and characteristics of the contaminants in the S/S matrix.

Figure 1 shows the log of the concentration of leached potassium for C<sub>2</sub> versus the log of time. The slopes of the linear regression lines through eight extraction data points were determined. For analysis, each set of observations was divided into four parts: the start (data points 1–3), the middle (data points 3–6), the end (data points 5–8), and the total (data points 2–7); the slope of the regression line for each part was calculated and the following conclusions were drawn. If the slope was greater than 0.65, the mechanism of leaching was dissolution (DS). If the regression coefficient was less than 0.35, then the mechanism was surface wash off (SW). The mechanism of leaching is diffusion (DF) controlled when the value of the slope is between these two values. The leaching mechanisms are given in Tables 8 and 9.

**Fig. 1.** Log of the concentration of leached potassium versus the log of time

To interpret Figs. 2, 3 and to evaluate the solidification procedure, the negative log of effective diffusivities in m<sup>2</sup>/s ( $pD_e$ ) for each contaminant was calculated by linear regression of the cumulative fraction leached of each contaminant on the square root of time. The value of  $pD_e$  indicates rates of leaching. The higher the  $pD_e$  value, the lower the speed of the component concerned with constant availability [i.e., the concentration gradient that is the driving force for the diffusion (NEN 7345<sup>2</sup>)].

For  $pD_e > 12.5$ , the component has low mobility; for  $11.0 < pD_e < 12.5$ , the component has average mobility; and for  $pD_e < 11.0$ , the component has high mobility.

For establishing the leaching mechanism and the mobility of ions in the cement matrix, three inert components, Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup>, were selected. Inert components show no

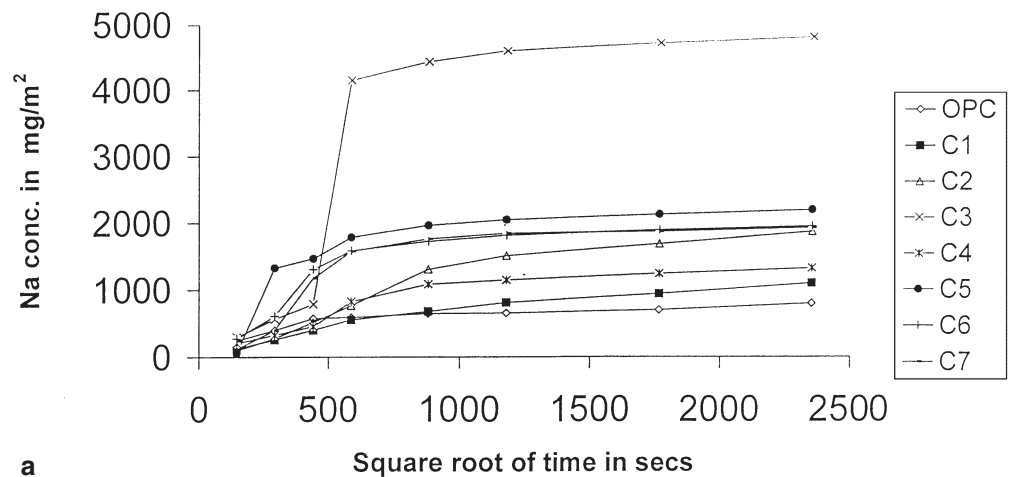
**Table 8.** Negative log of diffusion coefficient ( $\rho D_e$ ) and dominant leaching mechanism for cations and anions

	Na		K		Cl		SO <sub>4</sub>		Ca	
	$\rho D_e$	Mech	$\rho D_e$	Mech	$\rho D_e$	Mech	$\rho D_e$	Mech	$\rho D_e$	Mech
OPC	11.5	DF, DS	11.2	SW	11.0	DF, DS	11.0	SW, DF	16.07	SW, DF
C <sub>1</sub>	11.68	SW, DF	11.3	SW, DF	11.21	SW, DF	11.18	SW, DF	17.04	DF, DF
C <sub>2</sub>	11.7	SW, DF	11.16	SW, DF	11.51	SW, DF	11.28	SW, DF	16.21	SW, DF
C <sub>3</sub>	10	SW, DF	10.27	SW, DF	11.5	SW, DF	14.2	SW, DF	15.49	SW, DF
C <sub>4</sub>	10.7	SW, DF	10.55	SW, DF	10.01	SW, DF	13.27	SW, DF	13.57	SW, DF
C <sub>5</sub>	9.8	SW, DF	10.96	SW, DF	10.32	DW, DF	12.8	SW, DF	13.42	SW, DS
C <sub>6</sub>	12.25	SW, DF	9.89	SW, DF	9.79	DF, DS	12.25	DF	12.91	SW, DF
C <sub>7</sub>	12.5	DS	10	SW, DF	10.22	DF	12.35	DF	12.84	SW, DF

Mech, leaching mechanism; DF, diffusion; DS, dissolution; SW, surface wash off

**Table 9.** Negative log of diffusion coefficient ( $\rho D_e$ ) and dominant leaching mechanism for heavy metals

	Pb		Zn		Fe		Mn	
	$\rho D_e$	Mech	$\rho D_e$	Mech	$\rho D_e$	Mech	$\rho D_e$	Mech
OPC	12.7	SW, DF	11.99	SW, DF	13.09	SW	14.24	DS, DF
C <sub>1</sub>	15.3	SW, DF	16.06	SW, DF	15.12	SW, DF	17.38	DS, DF
C <sub>2</sub>	15.59	SW, DF	19.96	SW, DF	15.62	SW, DF	15.96	SW, DS
C <sub>3</sub>	15.34	SW	16.32	DF	15.32	SW, DF	12.82	SW, DF
C <sub>4</sub>	12.7	DF	13.46	SW, DF	12.32	SW, DS	12.58	SW, DS
C <sub>5</sub>	13.08	DF	16.62	SW, DF	12.27	SW	12.78	SW, DF
C <sub>6</sub>	13.30	DF	16.6	DF	12.31	SW, DS	14.24	SW, DF
C <sub>7</sub>	11.92	SW	16.11	SW	10.84	DF, SW	12.10	SW, DF

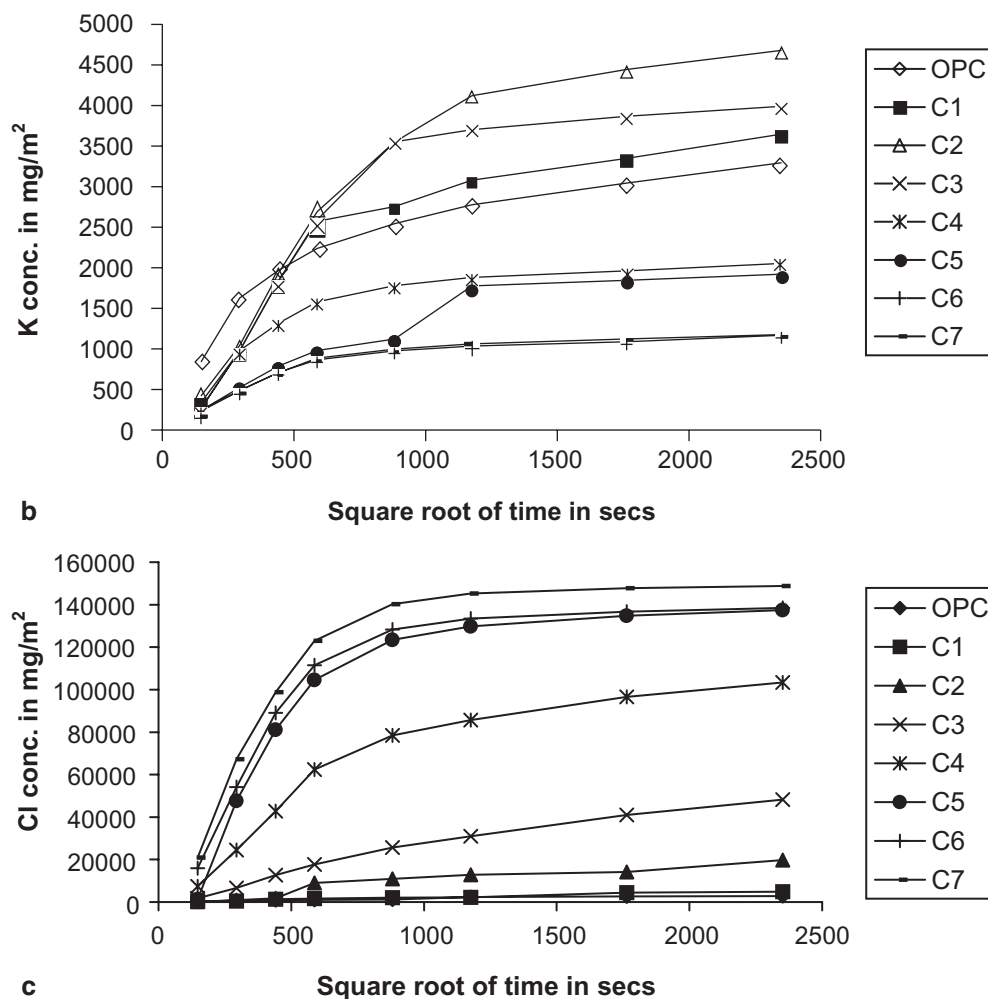
**Fig. 2a–e.** The leaching of various ions per unit surface area over a period of 64 days. **a**, sodium; **b**, potassium; **c**, chloride; **d**, sulphate; **e**, calcium. *OPC*, ordinary Portland cement; *C<sub>1</sub>–C<sub>7</sub>*, specimen composition as defined in Table 1

physical or chemical interaction with the cement matrix. Their leaching mechanism and mobility pattern represent the actual resistance presented by the cement matrix against the movement of ions.

Table 5 indicates that, Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup> leached out almost completely with about >100% depletion in the matrix (C<sub>3</sub>–C<sub>7</sub>). “>100%” indicates that in diffusion leaching, the

constituent has leached more than the potentially leachable fraction estimated by leaching availability. The mechanisms and mobility for Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup> are presented in Table 8; for the inert components, surface wash off followed by diffusion was the dominant leaching mechanism, and the mobility increases from average to high (12.5 to 10.0), as the cement content in the mix decreases for the specimens

Fig. 2a–e. Continued



OPC, C<sub>1</sub>–C<sub>7</sub>. The higher the cement content, the lower the mobility of ions in the matrix. Figure 2a–c shows leaching of Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>−</sup> per unit surface area over 64 days. It was observed that the leaching increases up to extraction three and four, i.e., the maximum amount of ion is leached in first three extractions and after that no significant leaching was observed. A similar pattern was observed for sulphate (Fig. 2d).

Calcium ion leaching was governed by surface wash off in the initial stages, followed by diffusion in almost all cases. The mobility was observed to be low in the sample of OPC. For the specimens C<sub>1</sub>–C<sub>7</sub>, the mobility of calcium ions increases as we move from specimens with higher cement content toward those of lower cement content; the specimens with lower cement content result in higher releases of calcium ions in comparison to the total amount available for leaching. Figure 2e shows that there is a regular increase in the calcium leached through eight extractions, indicating that a constant concentration gradient is maintained in the matrix. This gradient is caused by the decalcification of cement grains; decalcification is initiated by the consumption of Ca(OH)<sub>2</sub> by the heavy metal species.

Comparing the negative log of the effective diffusion coefficient for lead for specimens C<sub>1</sub>–C<sub>3</sub> with C<sub>4</sub>–C<sub>7</sub> (Table

9), it can be seen that as the cement content in the mix decreases from C<sub>1</sub> to C<sub>7</sub>, the mobility of lead ions increases, shifting from the low to average mobility range (15.3–11.9). Similar results are reported by Veronika and Vandecasteele<sup>14</sup>, and the leaching of lead was governed by diffusion phenomena. In almost all specimens, lead was found to leach more in the first four extractions, i.e., in the first four days of the experiment Fig. 3a.

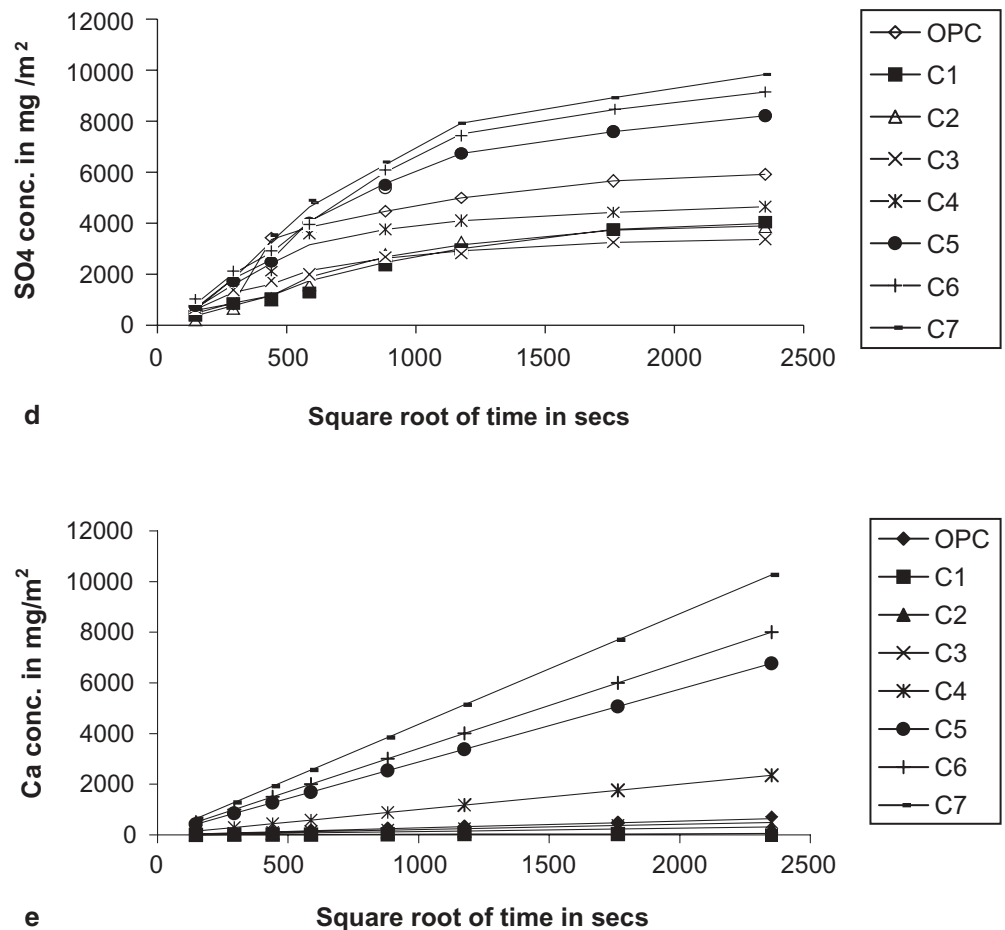
All mixes were successful in reducing the mobility of zinc, (for the range C<sub>1</sub>–C<sub>7</sub>, the negative log of diffusion coefficient was in the range 16.06–16.6) (Fig. 3b). The governing leaching mechanism was surface wash off in the initial stages followed by diffusion. The initial surface washing is indicated by the increasing leaching up to the fifth extraction in all samples.

Iron and manganese leaching was diffusion controlled Fig. 3c,d. The mobility of both the ions was reduced in samples with higher cement ratios.

The values of the negative log of diffusion coefficients for the elements studied indicated low mobility, i.e.,  $\rho D_e > 12.5$ . This shows that heavy metals are stabilized by chemical interaction with the hydration products of the cement.



Fig. 2a–e. Continued



### Environmental performance of the solidified/stabilized product

The diffusion test has two limits ( $U_1$  and  $U_2$ ) that enable the environmental impact of the materials to be classified.  $U_1$  and  $U_2$  are two categorizations of a material depending on the concentration of the elements present. The total metal released in all the extractions for lead and zinc (Fig. 3a,b) is lower than the given lower  $U_1$  limit from NEN 7345 (Table 10). These low concentrations make such samples after 21 days of curing suitable for application on land and as a potential building material.

### Conclusions

- The leaching of metal ions is probably in the form of non-stoichiometric calcium complexes. Confirmation can be obtained by speciation modeling and microstructure studies.
- The mobility of ions is reduced in the cement matrix and the leaching is governed by surface wash off followed by diffusion for almost all waste/binder ratios.

**Table 10.** Limits from the diffusion test NEN 7345

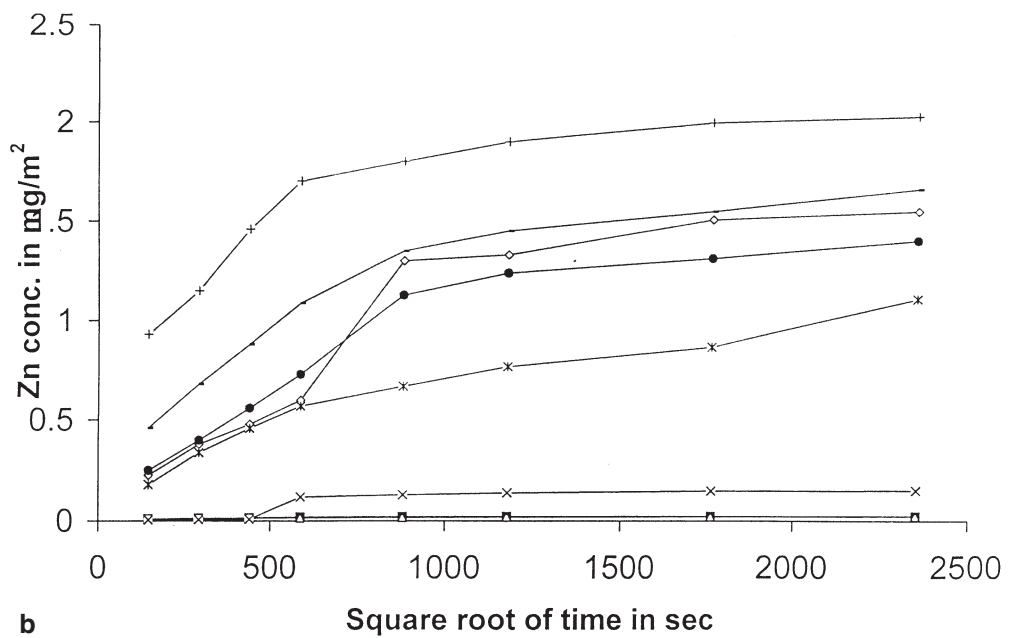
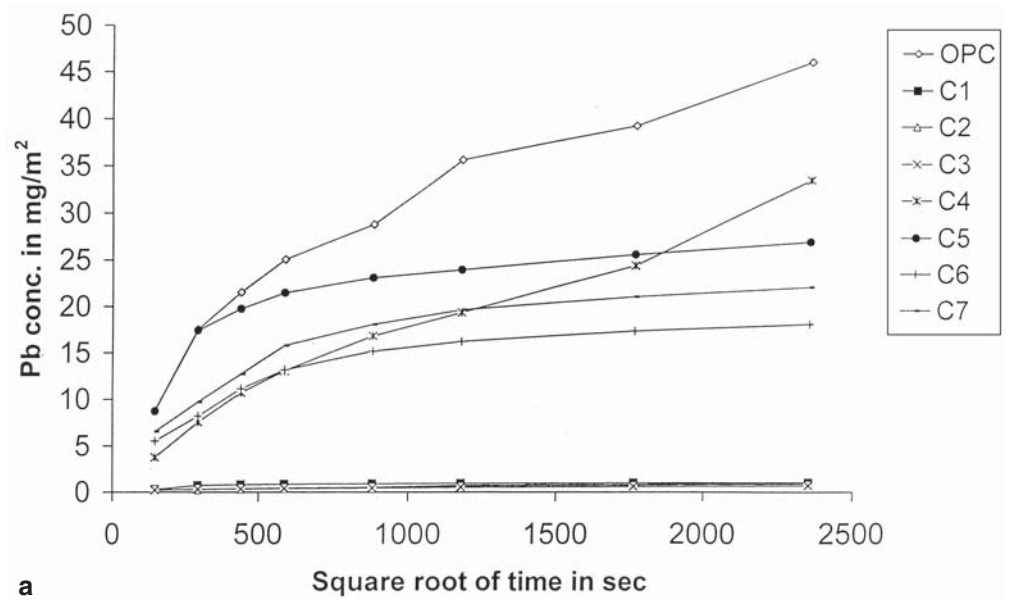
Contaminant	Limits (mg/m <sup>2</sup> )	
	$U_1$ (Lower limit)	$U_2$ (Higher limit)
Pb	100	800
Zn	200	1500
Cl	20000	150000
SO <sub>4</sub>	25000	200000

$U_1$ ,  $U_2$ ; limits in the diffusion test, used for assessing environmental impact

- The leached concentrations of all the metals of environmental concern were lower than the given  $U_1$  limit of NEN 7345.

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**Fig. 3a–d.** The leaching of various heavy metals per unit surface area over a period of 64 days. **a**, lead; **b**, zinc; **c**, iron; **d**, manganese



#### Appendix: calculation methods for $U_{\text{dif},64}$ and %D in Tables 5, 6

$$U_{\text{dif},64} = \frac{2 \cdot A \cdot \rho \cdot U_{\text{bes}} \cdot \sqrt{D_e \cdot t}}{\pi \cdot m}$$

$$\%D = \frac{U_{\text{dif},t}}{U_{\text{bes}}} \times 100\%$$

where:

$U_{\text{dif},64}$  = quantity of a component leached out in the diffusion test in time  $t$  in mg/kg dry matter

$U_{\text{bes}}$  = quantity of component available for leaching according to NEN 7341 in mg/kg dry matter

$D_e$  = effective diffusion coefficient of the component in m<sup>2</sup>/s

$t$  = time of the leaching in s

$A$  = area of the test piece in m<sup>2</sup>

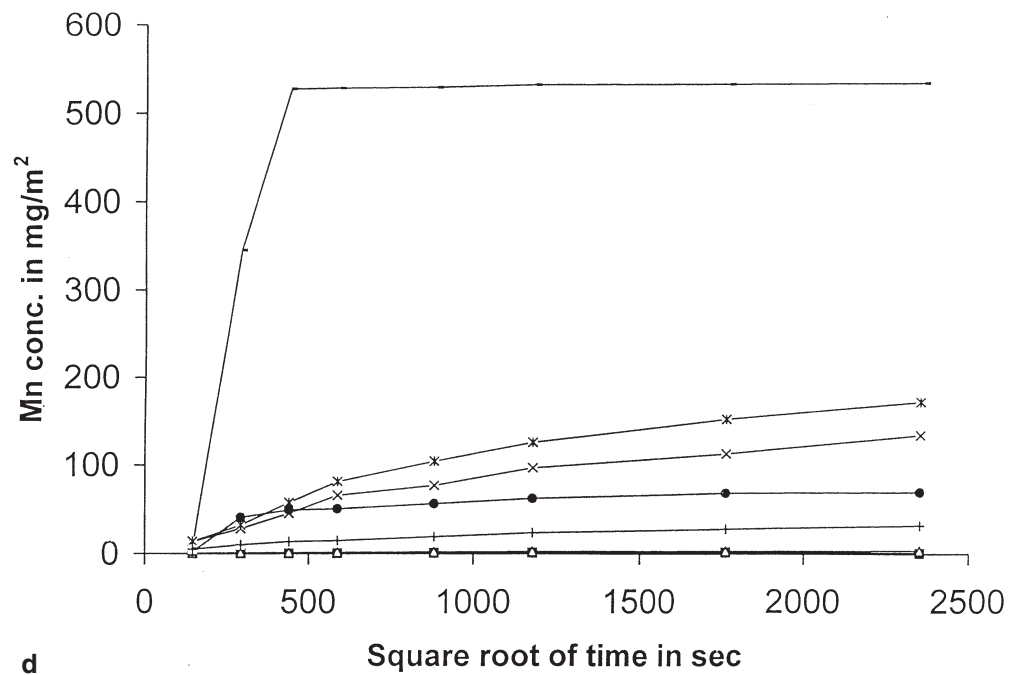
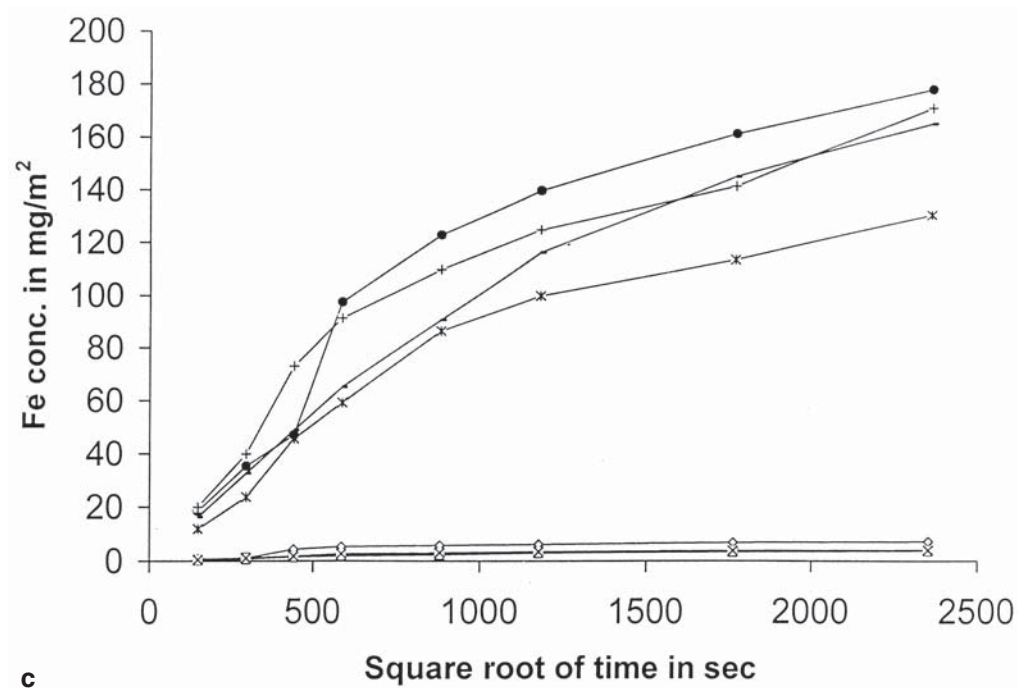
$\rho$  = volume mass of the test piece in kg dry matter per m<sup>3</sup>

$m$  = mass of the test piece in kg dry matter

%D = percentage depletion



Fig. 3a-d. Continued



## References

- Godbee HW, Joy DS (1994) Assessment of the loss of radioactive isotopes from waste solids to the environment. Part 1: Background and theory. TM-4333, Oak Ridge National Laboratory, TN
- NEN 7345 (1994) Leaching characteristics of soil and stony building and waste materials-leaching tests-Determination of the leaching of inorganic components from building and monolithic waste materials with diffusion tests. NNI, Delft, The Netherlands
- NEN 7341(1992) 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
- American Public Health Association, APHA (1989) American Public Health Association, standard methods for the estimation of waters and waste waters, 16th edn. APHA, Washington, DC
- Chopra SL, Kanwar JS (1986) Analytical agricultural chemistry. Kalyani, New Delhi
- Malviya R, Chaudhary R (2004) Study of treatment effectiveness of solidification/stabilization process for waste bearing heavy metals. J Mater Cycles Waste Manag 6:147-153
- Brunner PH, Baccini P (1988) The generation of hazardous waste by MSW-incineration calls for a new concept in thermal waste treatment. Swiss federal Institute for Water Resources, Dubendorf, Switzerland
- Bhatty MSY (1987) Fixation of metallic ions in Portland cement. Superfund 1987, pp 140-145

9. Bishop PL (1988) Leaching of inorganic hazardous constituent from stabilized/solidified hazardous wastes. *Hazard Waste Hazard Mater* 5(2):129–143
10. Cote PL, Denis I (1984) Application of dynamic leaching test to solidified hazardous wastes. In: Jackson LP, Rahlik AR, Conway RA (eds) *Proceedings of the third symposium ASTM STP on hazardous waste*. American Society for Testing and Materials, Philadelphia
11. Cohen B, Petrie JG (1997) Containment of chromium and zinc in ferrochromium flue dusts by cement-based solidification. *Canadian Metall Q*36:251–260
12. Ecke H, Menad N, Lagerkvist A (2002) Treatment-oriented characterization of dry scrubber residue from municipal solid waste incineration. *J Mater Cycles Waste Manag* 4:117–126
13. Todorvic J, Ecke H, Lagerkvist A (2003) Solidification with water as a treatment method for air pollution control residue. *Waste Manag* 23:621–629
14. Veronika D, Vandecasteele C (1996) An evaluation of the solidification/stabilization of industrial arsenic-containing waste using extraction and semi-dynamic leaching. *Waste Manag* 16:625–631