

## Transfer mechanisms of contaminants in cement-based stabilized/solidified wastes

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### Abstract

Stabilization/solidification (S/S) processes are routinely used for the final treatment of hazardous wastes prior to land disposal. Cement-based binder systems with partial replacement of cement by pulverized fuel ash (PFA) are common. In order to predict the long-term leaching characteristics of S/S wastes, it is important to understand the leaching mechanism. This paper presents experimental results from a study that has investigated the leaching behaviour of contaminants from cement-based S/S waste forms. A novel radial leach test (RLT) has been used to study the migration of heavy metals. The results show that contaminants migrate from the inner core of the S/S waste during leaching to the sample surface and accumulate near the edge of the S/S waste. The degree of accumulation is related to the contaminant species and the Ca(OH)<sub>2</sub> content.

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### 1. Introduction

Stabilization/solidification (S/S) processes are routinely used for the final treatment of hazardous wastes to reduce contaminant leaching prior to land disposal. Among various types of S/S binders, cement-based systems are the mostly widely used, due to relatively low cost, wide availability and versatility [1–4].

Pulverized fuel ash (PFA), a by-product of coal-fired power generation, is often incorporated into cement-based S/S binder systems [5–7]. However, low-grade fly ash rejected from the ash classifying process has remained largely unused, due to high carbon content and large particle size. It has recently been shown that rejected fly ash can be used in S/S, as it gives comparable performance to mixes containing normal fine fly ash [8,9].

Although cement-based systems have proved to be effective, very little is known about the leaching mechanism associated with contaminants in S/S wastes and it is therefore difficult

to predict long-term leaching. A number of models have been developed to simulate leaching and assess the effects of different S/S treatments. Based on the assumption that transport of contaminants is determined by Fick's law, diffusion models [10–12] have commonly been used. These have also incorporated chemical dissolution and equilibrium processes for the leaching species [13–20]. In particular, a shrinking core model based on the neutralizing capacity of the cementitious matrix has been developed [21,22]. These models provide some indication and prediction of the leaching process. However, little consideration has been given to changes in contaminant concentrations that occur inside the S/S waste forms during leaching.

This paper reports on the leaching behaviour of heavy metal contaminants in cement-based PFA containing S/S wastes. A mass transfer mechanism has been identified that may explain the contaminant concentrations observed.

### 2. Experimental

#### 2.1. Materials

Synthetic heavy metal sludge was prepared by adding 6 M NaOH to a solution containing 0.1 M reagent grade lead nitrate, copper nitrate and zinc nitrate until the pH reached 9.00. Two

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Table 1  
Chemical compositions (wt.%) and physical properties of materials used in experiment

	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI	Fineness (m <sup>2</sup> /kg)	Density (kg/m <sup>3</sup> )
rFA	47.23	8.42	24.54	0.99	8.28	1.62	0.39	Nil	Nil	8.06	119.0	2.19
FGD	3.61	0.54	1.79	0.06	32.05	3.01	37.7	Nil	Nil	21.36	–	–
Cement	19.61	3.32	7.33	–	63.15	2.54	2.13	Nil	Nil	2.97	352.0	3.16
fFA	47.62	7.35	27.4	1.23	8.11	3.55	0.57	0.88	0.87	0.89	399.6	2.28

Total iron expressed as Fe<sub>2</sub>O<sub>3</sub>, nil, detection limited = 0.01% (w/w).

fly ashes were used in this study. These were a classified fly ash with an average particle sizes less than 45 μm (fine fly ash, fFA) and rejected fly ash (rFA) with a mean particle size greater than 45 μm. Both were low-calcium Class F type ashes and were generated as by-products from a major coal-fired power plant in Hong Kong (Castle Peak, China Light and Power).

Flue gas desulphurization sludge (FGD) generated as a by-product from air pollution control equipment was also obtained from a coal-fired power plant (Lamma Power Plant, Hong Kong Electric Co. Ltd.). This process uses lime to remove SO<sub>2</sub> and the resulting FGD sludge is mainly gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

A commercially available Portland cement (PC) equivalent to ASTM Type I and hydrated lime (Ca(OH)<sub>2</sub>) were also used in the S/S waste binder systems. The chemical and physical properties of the rFA, fFA, FGD, PC and the synthetic sludge are given in Tables 1 and 2.

## 2.2. Preparation of specimens

Four S/S binder mixes were prepared according to the mix proportions given in Table 3. The synthetic sludge was added to the solidifying reagents at sludge to reagent ratio of 0.4, and this resulted in water to solid ratio of 0.35. Distilled water was used instead of the synthetic heavy metal sludge in preparing blank samples. All samples were thoroughly mixed for 10 min at room temperature, cast into plastic vials (Ø 40 mm × 80 mm)

Table 2  
Chemical composition of the synthetic sludge used in the S/S wastes

Parameter	Value
Density (g/cm <sup>3</sup> )	1.064
Total solids (%)	7.83
pH	9.00
Heavy metals (mg/L)	
Pb	19.580
Zn	6.179
Cu	6.005

Table 3  
S/S waste binder proportions (w/w)

	rFA	fFA	Ca(OH) <sub>2</sub>	FGD	Cement
R	100	–	–	–	25
H	100	–	10	10	25
P	100	–	20	25	25
f	–	100	–	–	25

and compacted with a plastic rod until most of the entrapped air was removed. The samples were then placed in a fog tank at 25 °C and removed from the plastic vials after 56 days of curing.

## 2.3. Dynamic leach test (DLT)

Three S/S specimens per mix, cured for 56 days, were subject to the dynamic leach test [23]. The samples were suspended in a polyethylene beaker containing an extraction fluid volume to sample surface area ratio of 8. The toxicity characteristic leaching procedure (TCLP) no. 2 leachant (pH 2.88) was used as the extraction fluid and leaching tests were completed in an incubator at 20 °C. Table 4 shows the renewal schedule for the leachant. A portion of the leachate was withdrawn for analysis of metal concentrations using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after each leaching interval. The reported results are the extracted concentrations minus the background determined using blank samples.

## 2.4. Radial leach test (RLT)

In order to investigate the change of heavy metal concentration in the S/S samples during the leaching period, a modified DLT procedure was used, known as the radial leach test (RLT). In the RLT, cylindrical S/S wastes samples (one per mix) that had cured for 56 days, were cut into eight circular slices with a thickness of 8 mm, as shown in Fig. 1a. The parallel end faces of six of the cut slices were coated with a water resistant sealing wax to inhibit leaching. In order to ensure an effective seal between the wax and the edge of the sample, a ring of Araldite XD 4700/XD 4710 adhesive was applied as shown in Fig. 1b. The coated slices were then placed in plastic containers and subject to leaching following the same procedure used in the DLT. The last two remaining slices were not leached but were kept in the curing tank (100% humidity, 25 °C) as control samples.

Table 4  
Dynamic leach test—leachant renewal schedule

Leach interval <i>N</i>	Cumulative time <i>t<sub>n</sub></i> (h)	Interval duration <i>Dt<sub>n</sub></i> (h)
0	0	0
1	4	4
2	24	20
3	31	7
4	72	41
5	104	32
6	168	64

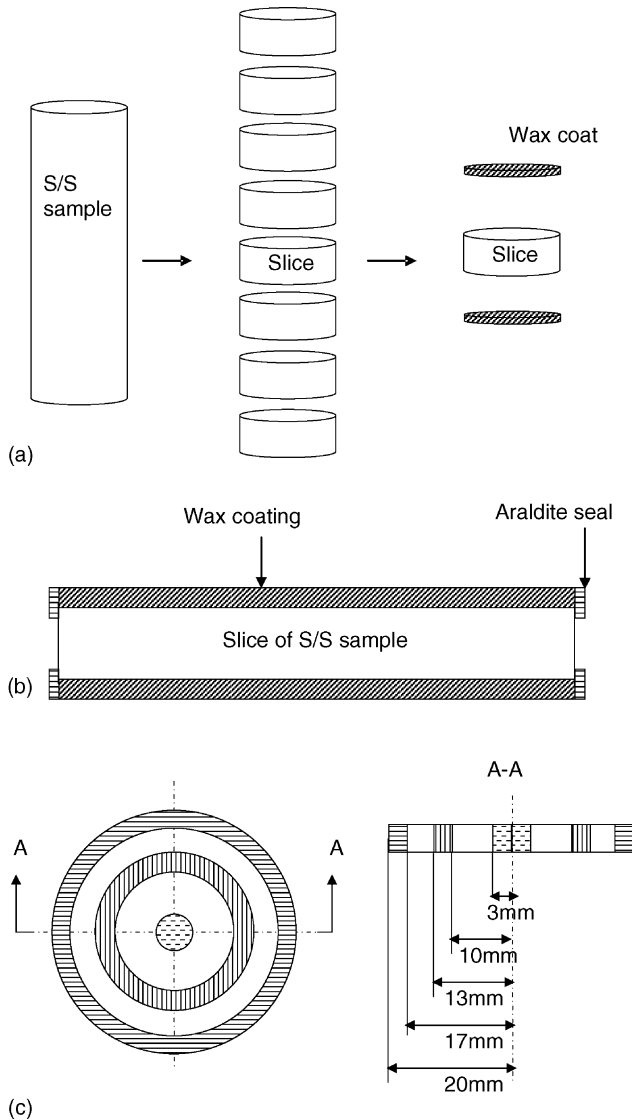


Fig. 1. (a–c) Preparation of samples in radial leaching test.

After each leachant renewal stage, one slice per mix was removed from the test and the wax coatings removed, prior to oven drying at 60 °C for 48 h in a vacuum oven. After the 2nd, 4–5th leaching intervals, the surface sections with radius of 17–20 mm were cut from the slices (Fig. 1c). These were digested following the method reported by Li et al. [24], and the total metal concentrations in the thin sections determined by ICP-AES.

After the last (6th) leachate renewal period, the sections with radius of 0–3, 10–13 and 17–20 mm were cut from the slices (Fig. 1c), and analysed for metal concentrations. Large quantities of calcium are removed from the sample during leaching. As a result the concentration of other heavy metal components will increase due to this effect. Therefore in order to correct the analysis data for this weight loss, the residual heavy metal concentration results were adjusted using the equation:

$$D_{cal} = D_h - (D_{Ca,i} - D_{Ca,d}) \times \frac{D_h}{(1000 - D_{Ca,d})}$$

where  $D_{cal}$  is the adjusted results,  $D_h$  the measured results,  $D_{Ca,i}$  the initial calcium concentration before leaching and  $D_{Ca,d}$  is the residual calcium concentration after leaching.

### 3. Results

#### 3.1. Dynamic leaching test (DLT)

The pH values measured after the 2nd, 4th, 5th and 6th leaching intervals in the DLT are shown in Fig. 2. For samples contained rFA (R, H and P), the pH generally increased with leaching time up to 104 h and then decreased. Sample P was found to give the highest pH value after each leach interval.

The cumulative leaching data for Ca, Pb and Zn after the 2nd, 4th, 5th and 6th leaching intervals are shown in Figs. 3–5, respectively, as a percentage of the total present in the samples.

Fig. 3 shows that the amount of Ca leached from all the samples increased with leaching time, and that the amount of Ca leached from sample P was the highest.

Fig. 4 shows that the amount of Pb leached from different samples. S/S mix P leached the highest levels and this was significantly higher than that from other samples. For samples R and H leached particularly low levels of Pb and these were lower than observed for mix f.

Zn leaching data is shown in Fig. 5. This exhibits very different behaviour. Higher amounts of Zn were leached from the

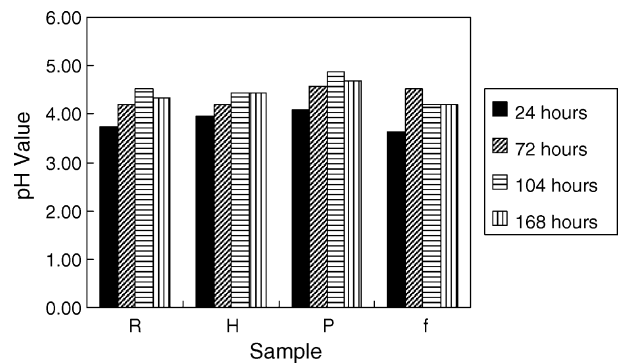


Fig. 2. pH values of leachate in the DLT.

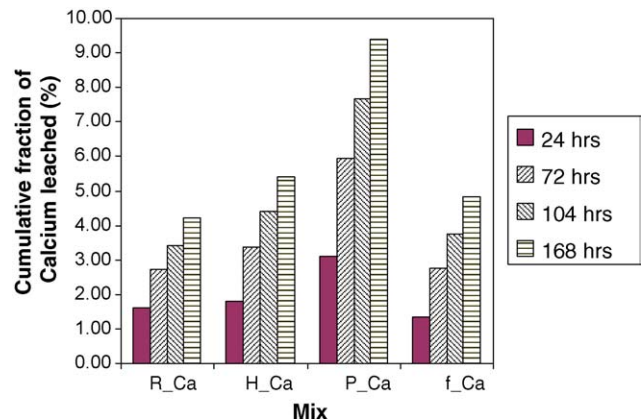


Fig. 3. Calcium content leached in the DLT.

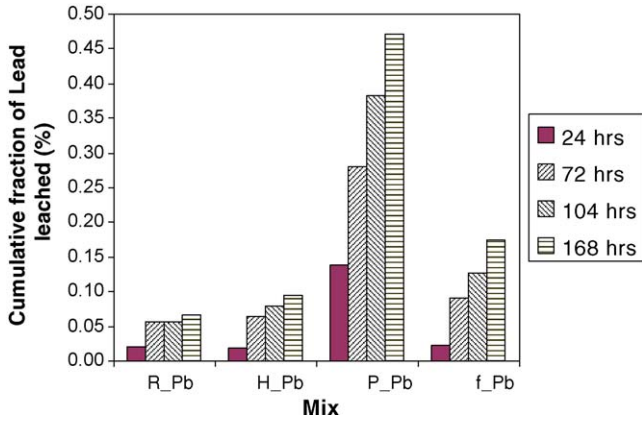


Fig. 4. Lead content leached in the DLT.

samples compared to Pb, apart from sample P, which leached the lowest levels.

There was minimal leaching of Cu from any of the samples as this was below the analytical detection limit in all leachates.

A thin soft shell layer was observed after the 5th RLT leaching period, which became loose after the 6th period and could be easily removed. This effect has previously been reported by Bishop and co-workers [21,22] and they attributed this to the results of dissolution of the S/S waste forms.

3.2. Radial leach test (RLT)

Figs. 6–9 show the percentages of residual metals remaining in the edges of samples after different leaching times in the RLT.

Fig. 6 shows that there is a clear decrease in Ca content in samples R, H and P that contain rFA. The percentage of Ca remaining in Sample P was the lowest after every leaching interval. The samples containing fFA showed the same initial fall in Ca content, but this then remained relatively constant during subsequent leaching. This may be related to the pozzolanic reaction that occurs between calcium hydroxide and fFA. It may also explain the reduced change in leachate pH observed after 72 h in the DLT.

Leaching of Pb, Zn and Cu showed distinctly different behaviour to Ca. Fig. 7 shows that the Pb content tends to

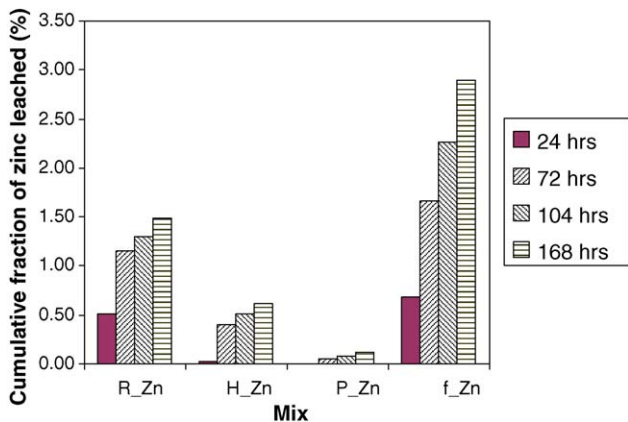


Fig. 5. Zinc content leached in the DLT.

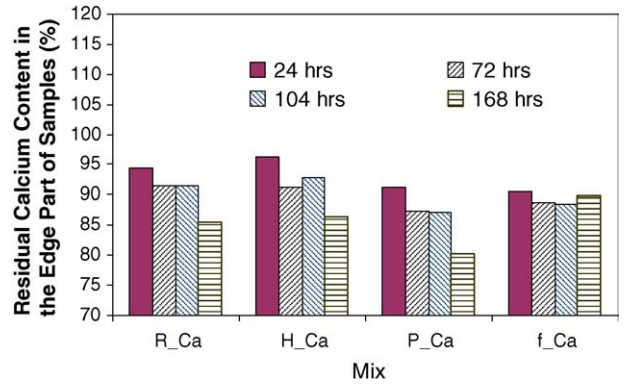


Fig. 6. Residual calcium content in the edge part of samples after radial leach test.

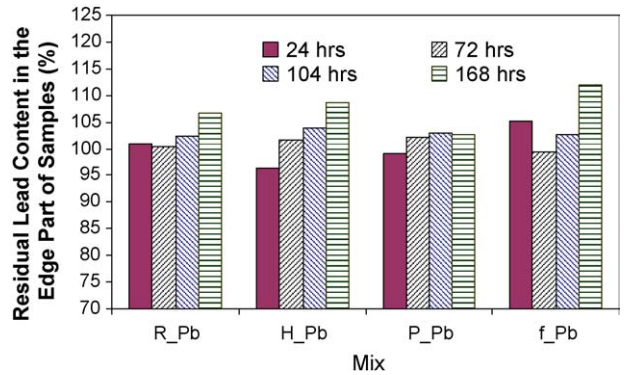


Fig. 7. Residual lead content in the edge part of samples after radial leach test.

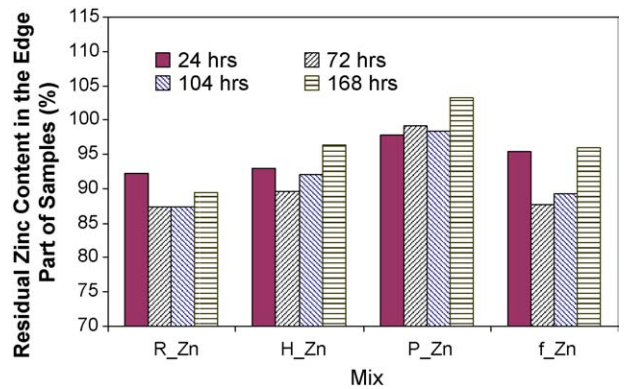


Fig. 8. Residual zinc content in the edge part of samples after radial leach test.

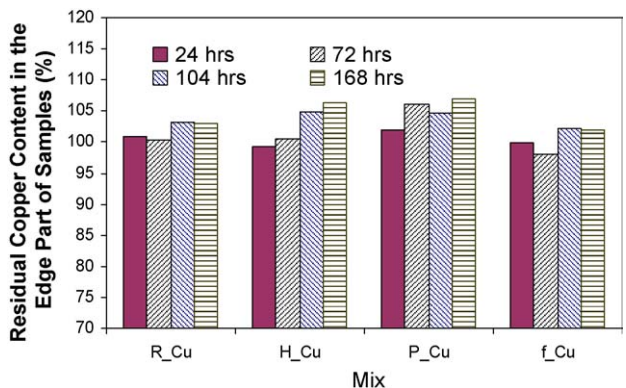


Fig. 9. Residual copper content in the edge part of samples after radial leach test.

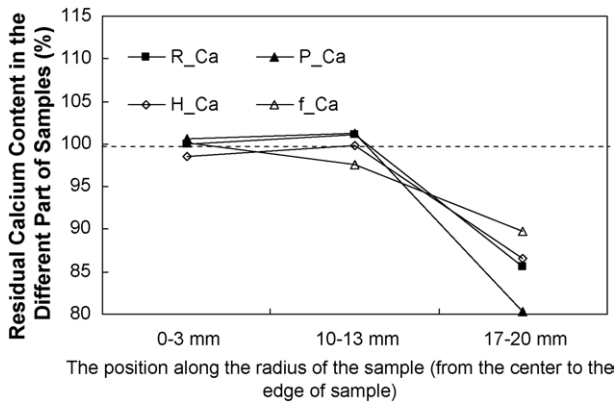


Fig. 10. Behaviour of calcium in the samples after radial leach test.

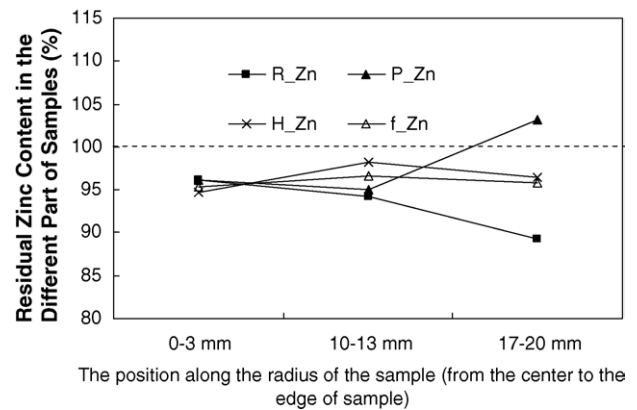


Fig. 12. Behaviour of zinc in the samples after radial leach test.

increase during leaching the edge region of the samples. The percentages of residual Zn decreases but then increased with time except for Sample P remained high and close to 100% as shown in Fig. 8. This sample displayed low leaching of Zn. There was little change in the Cu content in the edge part of the samples (Fig. 9), also as expected from the DLT leaching data.

### 3.3. Transfer of contaminants in the samples

The change of metal concentration across the cross-sections of samples after the 6th leaching interval is shown in Figs. 10–13.

Residual concentrations of Ca in the center (0–3 mm) and mid way between the center and the surface (10–13 mm) remain constant and close to 100% (Fig. 10). However, there was a sharp reduction in Ca in the edge region (17–20 mm).

The residual Pb concentrations in the center (0–3 mm) and middle (10–13 mm) of the samples were also similar and tended to be reduced. Unlike the Ca concentrations, the Pb concentration found at the edge of the sample (17–20 mm) was significantly increased apart from in sample P, which also showed high Pb leaching.

A similar trend to Pb was seen for Zn (Fig. 12) in sample P. However, for samples H and f, the residual concentrations of Zn in the three different positions were all about 95% of the initial unleached values. In sample R, the Zn concentration decreased from the center to the edge of the sample.

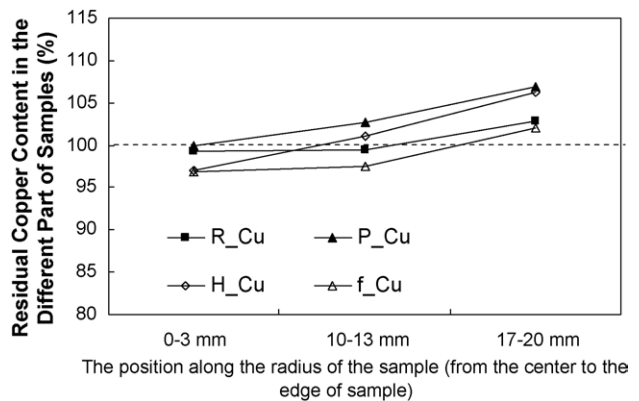


Fig. 13. Behaviour of copper in the samples after radial leach test.

The residual Cu concentrations in the center (0–3 mm) and middle (10–13 mm) of samples were close to, or higher than the initial unleached concentrations in the control samples and the residual Cu concentrations tended to be higher in the edge regions of the samples compared to the other positions analysed.

## 4. Discussion

The results in the RLT show that the Ca content at the edge of samples decreased with increasing leaching time. This is consistent with the results from the DLT. The results also show that Ca leaching occurs close to the sample surface. This implies that neutralization reactions between the acidic leachant and alkali content in the S/S samples also occur close to the solid–leachate interface and that only the leachant water can diffuse into the inside regions of the S/S samples.

Pb accumulated in the edge region of the samples although the concentration did not alter significantly from the center (0–3 mm) to the middle (10–13 mm) of the sample (Fig. 11). This suggests that Pb is transferred from the inner sample to the edge during the leaching process. However, the DLT data suggests that it is not removed from the solid phase into the liquid phase. This is believed to be due to the difference in pore solution pH in the S/S sample and the remaining leachant. Inside the S/S waste the pore solution pH is expected to be greater than 12 [25] resulting in significant Pb solubility [2]. As the Pb migrates into

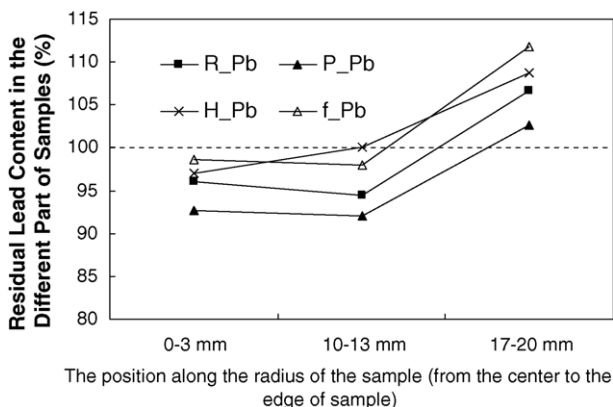


Fig. 11. Behaviour of lead in the samples after radial leach test.

the zone close to the sample surface the pH is reduced due to the interaction with the acidic leachant, and it is expected to precipitate. These precipitates may act as a self sealing mechanism, potentially reducing further Pb leaching.

This mechanism for the transfer of Pb also applies to Zn and Cu. However, although the amount of Zn in the sample edges increased with leaching time, the total amount of Zn was much lower than the initial values, except for sample P. This suggests that Zn could be easily leached from the sample and that a higher  $\text{Ca}(\text{OH})_2$  content was necessary to retard the leaching of Zn. This is supported by the data shown in Fig. 5, which shows high Zn leaching. The results for Cu (Figs. 9 and 13) suggest that it is effectively stabilized/solidified in the sample as very little was released through leaching.

The variation in heavy metal content and alkali content in the S/S waste sample after leaching has previously been described by the shrinking core leaching model [21,22]. In this model, it was assumed that the leaching of contaminants is controlled by the acidity in the leaching solution [21]. As the acid leachant penetrates into the S/S matrix, solubilized species are released into the leachant, or diffuse inward [22]. The inner core of the S/S matrix is assumed to remain unaltered [21,22].

Based on the results of this study, the following further development of the leaching mechanism (illustrated in Fig. 14) is suggested:

- The leaching of metal contaminants from the S/S waste forms in an acidic environment is dependent on the type of metal contaminants and the availability of alkalinity, especially from  $\text{Ca}(\text{OH})_2$ .
- Only water is expected to diffuse into the inner most part of the S/S matrix. The dissolved contaminants in the S/S waste matrix that diffuse towards the outside accumulate in a zone close to the sample surface. The width of this accumulation zone and the amount of heavy metal accumulated depends on the type of heavy metal and the availability of  $\text{Ca}(\text{OH})_2$  for neutralization. The amount of accumulated heavy metals in this zone can be higher than the initial concentration present in the core of the unleached S/S waste matrix.
- With increasing leaching time and continuous inward diffusion of leachant, the contaminants can become exhausted before the breakdown of the S/S matrix.

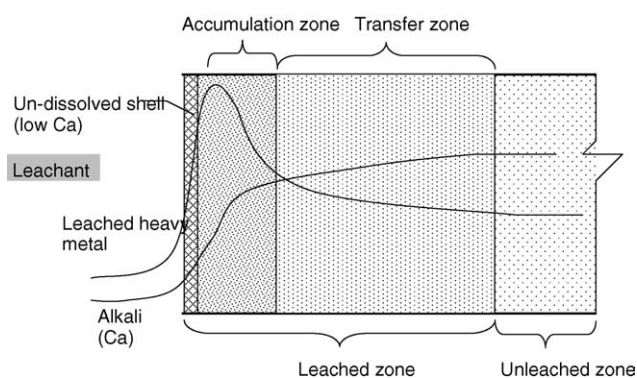


Fig. 14. Schematic showing the leaching mechanism of heavy metals from S/S waste forms.

## 5. Conclusions

- Acidic leachant diffuses into S/S waste samples where it reacts with  $\text{Ca}(\text{OH})_2$  and other alkaline materials.
- Leaching of heavy metals from the S/S waste depends on the type of metal contaminants and the availability of alkalinity.
- Dissolved heavy metals diffuse towards the outside of the sample and accumulate in a zone close to the sample surface where the pore water pH changes.
- Heavy metals leach from the accumulation zone into the leachate by chemical dissolution and diffusion. The leached surface region that extends into the S/S waste is porous and forms a shell that is weakly adhered to the remainder of the S/S waste.

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