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Waste Materials in Construction: Putting Theory into Practice

Evaluation of treatment of gas cleaning residues from MSWI with chemical agents.

S. Mizutani*, H.A. van der Sloot**, S. Sakai*
* Environment Preservation Center, Kyoto University, Japan
** Soil & Waste Research, Netherlands Energy Research Foundation, Petten

Abstract

In Japan as in many other countries treatment of Municipal Solid Waste Incinerator (MSWI) fly ash is necessary to obtain a less hazardous material for landfilling (in the context of this paper MSWI fly ash consists of combined electrostatic precipitator ash and air pollution control residues). Ultimately, treatment may lead to potential use of materials. Different treatment processes based on the addition of chemical agents are currently in use or in development in Japan. In this paper, the leaching behaviour of untreated MSWI fly ash and chemically treated fly ash has been studied. The treatment processes involved are: treatment with a chelating agent, phosphate treatment, ferrite treatment.

In the characterization of the leaching behaviour of treated and untreated fly ash, which all fall in the category of granular materials, the Japanese leaching test (JLT-13), the Availability Test, a pH dependent leaching test, a redox property test, and the serial batch test under open condition and closed condition from L/S = 2 to 100 are performed. The tortuosity of the compacted materials was tested separately in diffusion tubes using Na-22-tracer.

The data obtained from the different tests are placed in perspective to derive conclusions on the environmental properties of the treated wastes under confined conditions and the management control measures that are needed to prevent undesired release of contaminants.

Samples

One untreated MSWI fly ash as commonly generated in Japan and three different chemically treated materials of the same residue have been studied. The treatment processes involved are: treatment with chelating agent, phosphate treatment, ferrite treatment. In the rest of the paper, the materials are coded as "original", "ch", "ph" and "fe" respectively.

The original fly ash is a mixture of fly ash and APC (air pollution control) residues from an electric precipitator in the stoker incinerator for municipal solid waste. The flue gas is treated with injection of dry $Ca(OH)_2$ into the gas stream, therefore the residue is highly alkaline material. This type of MSWI fly ash is very common in Japan. Chelating agents are very commonly applied treatment agents in Japan. It is based on complexation of heavy metals with an organic sulfide. Phosphate treatment is based on the formation of insoluble metal phosphates, such as $Pb_5(PO_4)_3Cl$,

Table 1 Contents of metals in samples

	pH[*1]	ANC[*2]	Contents (mg/kg)					
	—	meq/g	Cd	Pb	Cu	Zn	Na	K
original	12.6	4.44	74	1400	570	6000	29000	38000
ch	12.4	0.84	45	694	330	4220	30400	29100
ph	11.0	2.49	43	680	320	4120	25200	32100
fe	10.6	0.74	64	884	310	6300	26400	21700

*1 final pH contacting with 10 times volume distilled water.
*2 calculated from added HNO_3 up to pH 7 at Availability Test.

$Cd_3(PO_4)_2$. Ferrite process is a special treatment method. It is based on the formation of a crystalline form of Fe_2O_3. By adding $FeSO_4$ with water into the fly ash and subsequently adjusting the pH to 9.5 to 10.5 by addition of NaOH, the material is heated to about 60 - 70 °C. A crystalline phase of Fe_2O_3 is formed and some metals are included in the structure and thus stabilized. Contents of some metals and ANC (acid neutralizing capacity) of the samples are shown in Table 1.

Test Method

Exp. 1 JLT-13 (Japanese leaching test No. 13)[1)]

Weigh 50 g of samples and add 500 mL of distilled water into a polyethlene bottle to reach an L/S of 10. Then the bottle is closed with a cap and shaken horizontally for 6 hours. After shaking, the leachate is filtered over a glass fiber filter (1 um).

Exp. 2 pH dependent test

Weigh 25 g of sample and add 250 mL of distilled water into the polyethylene bottle to reach an L/S of 10. The liquid is stirred continuously while measuring the pH. Acid or base (reagent is HNO_3 or NaOH) are added in order to keep the pH at the preset pH value for 6 hours. After 6 hrs, pH and redox potential of the leachate is measured. The leachate is filtered over a membrane filter (0.45 um).

Exp. 3 Serial batch test under open condition and closed condition

open test;

Weigh 20 g of sample and add 40 mL of distilled water into a glass beaker (L/S =2). The liquid is stirred continuously for 23 hours. After 23 hrs, pH and redox potential of the leachate are measured. The leachate is filtered over a membrane filter (0.45 um). The residue on the filter was used as a sample for next step. To the residue, 160 mL of distilled water are added (L/S = 8, total L/S is now 10) to the beaker. It is stirred for 23 hrs. After stirring, the leachate is filtered over a membrane filter. These operations are repeated 5 times. Quantity of leachant was respectively 40 mL, 160 mL, 200 mL, 600 mL and 1000 mL to reach in individual steps L/S 2, 8, 10, 30, 50 respectively. Therefore the cumulative L/S values reached are 2, 10, 20, 50, 100.

closed test;

Weigh 20 g of sample and add 40 mL of distilled water into a plastic bottle which can be closed (L/S =2). Then N_2 gas is flushed in the head space of the bottle in order to purge the air. Other operations are performed in the same way as the open test. The first and second step are the same as in the recent CEN test[2)].

Exp. 4 Availability Test

This test was performed pursuant to NEN 7341[3)].

Exp. 5 Redox property test[4)]

Weigh 50 g of material and add 100 mL of distilled water in a bottle. Shake the bottle for 24 hours. After shaking, pH and Eh of the leachate are measured and compared to the Eh value of the distilled water, whose pH is adjusted to the same pH value as that of the leachate. When the Eh value of the leachate proves to be lower than that of the destilled water by more than 50 mV, then the material can be considered to exhibit reducing properties and the reducing capacity of the solid material needs to be determined. The reducing capacity is determined as follows: weigh 2 g of material in a plastic bottle and add 20 mL of 0.1 M Cerium (IV) sulfate. After shaking for 2 hours, the materials were titrated with 0.1 M Fe^{2+} - ferro sulfate. The reaction is:

$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$

The results are expressed in mMol O_2 per gram solid material.

Exp. 6 Diffusion tube test[5]

The diffusion tube is filled with untreated, wetted material to a length of 25 mm with a consistency similar to that of the labelled material. The Na-22-tracer labelled material is added up to a total length of 50 mm, and the second piston is put in position. The tube is stored in a saturated environment to avoid drying out during the experiment.

After one day, the combined segments are cut into slices and are transferred to pre-weighed counting tubes, dry at 85 °C, weigh, and count in a sodium iodide crystal connected to a two-channel analyzer. The mass of the slices and the total mass of the tube contents are used to calculate the axial length of each slice. The effective diffusion coefficient were calculated based on the mobility of the Na-22-tracer, sample weight and the moisture content. From the pDe of Na and its free mobility in water the tortuosity of the granular matrix is derived.

Results and discussions

Leaching concentration for JLT-13

The results of JLT-13 are shown in Table 2. As the final pH is high, Pb is leached from original fly ash in high concentration due to its amphoteric character (Japanese standard of Pb for waste disposal is 0.3 mg/L). All of the treated materials meet the requirements, because the release of the metals is controlled. However, it is a result of only one single batch test and other evaluations are needed to ensure that there are no long term environmental impacts.

Table 2 pH and metal concentration for JLT-13

(unit: mg/L except pH)

	pH	Cd	Pb	Cu	Zn
original	12.6	ND	7.44	0.04	2.54
ch	12.4	ND	0.01	ND	0.04
ph	11.0	ND	ND	ND	ND
fe	10.6	ND	ND	ND	ND

Availability of metals

Comparing the availability of the materials, we can see a significant difference between the three treated materials (Table 3), though there is almost no differences in JLT-13. For example, "ph" treatment decreases the availability of Pb significantly, though "ch" and "fe" material show little decreasing of the availability. For the other metals similar changes are observed. When availability is reduced, this implies that the metals are incorporated in insoluble mineral phases. The availability reflects a leaching potential and as such is an important factor for evaluating long term environmental impact.

Table 3 Release of metals in Availability Test

(unit: mg/kg)

	Cd	Pb	Cu	Zn
original	66	168	139	4490
ch	55	166	10	3500
ph	14	0	23	1590
fe	54	160	82	3520

pH and pe

pe of the leachates are plotted versus pH (Fig. 1). Here pe is a value of negative logalithm of electron activity and there is a relationship pe = $E_H/59.2$ (E_H means the standard hydrogen potential). For normal oxygenated water with pH adjusted to cover the range pH 4 - 13, there is an almost linear relation (slope is about 1) between pH and pe[6]. For leachates of fly ash or treated residues, there is a similar relation far from the level observed in oxygenated water. This points at strong reducing properties for all. The intercept of y-axis is indicative of the redox behaviour of the materials. As "ch" treated material has the smallest intercept value, we can see that chelating agent has a high reducing capacity. This is in agreement with the results of redox property test. The redox capacity values derived from redox property test are shown in Table 4. The lower value for ph and fe treatment relative to the original material may be due to some kinds of oxidation during the treatment process. On the contrary, chelating agent have reduced the original material in the treatment process.

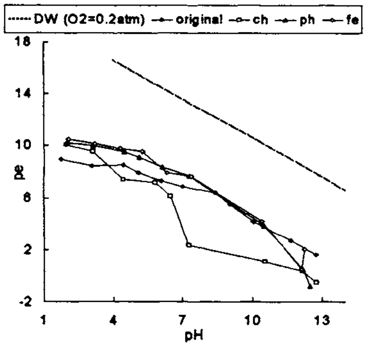

Fig.1 Relationships between pH and pe

Table 4 Redox capacity of samples (unit: mmol O_2/kg)

Sample	original	ch	ph	fe
redox capacity	387.8	448.8	235.0	188.1

Release of metals

Release of Cd, Pb, Cu, Zn versus pH from each materials are plotted (Fig. 2). As for cadmium, the leachability is reduced for all treatments. Particularly, the treatment

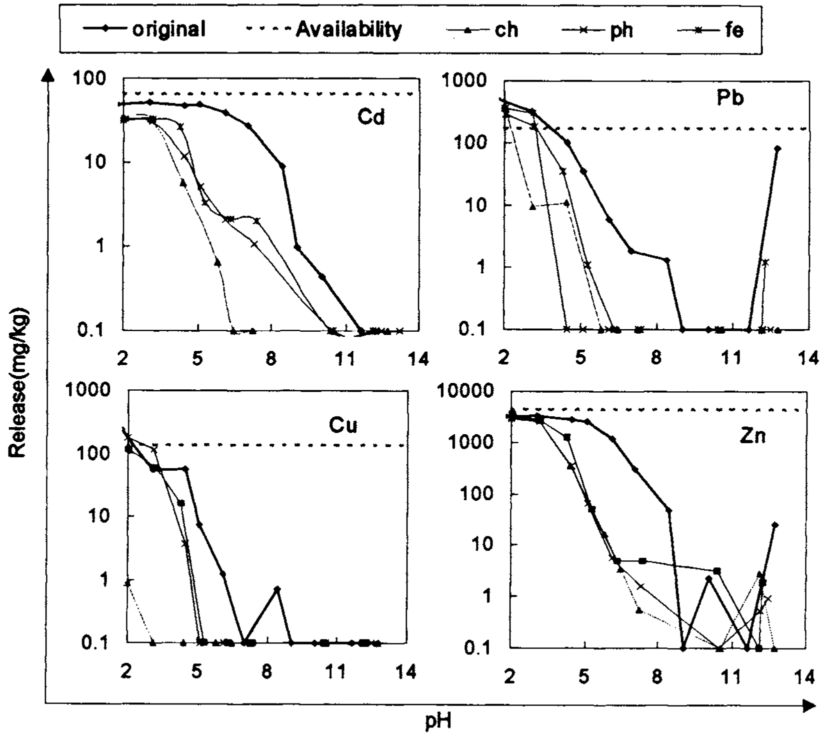

Fig.2 Metal release vs. pH of leachate

with chelating agent results in a significant reduction in release in the pH range 6 to 10 (> 500). For the two other treatments ph and fe the reduction is not as large, although still very significant. In the pH range below 4 the difference between the different treatment options is not as large (factor 2 to 10). As for lead, there are two pH domains to be discussed in relation to treatment effects: one is the behaviour of under alkaline conditions and the other is the behaviour under acidic conditions. In the neutral pH range leachability of Pb is small for all materials including the original material. All three treatments methods reduce Pb leachability significantly in the pH range 5 to 12. The "ph" reduces release even down to pH 4. In the acidic range below pH 4 the difference becomes less until at pH 2 the difference amounts to a factor of 2 - 3 only. As for copper, "ch" treated material has a strong effect over the entire pH range from 2 to 13. Although "ph" and "fe" materials show similar behaviour, there is a difference when both change in release and change of ANC (acid neutralising capacity) are taken into account. This aspect is discussed in the next section. As for zinc, there is small difference among three treated materials, though they are all lower than the untreated fly ash in the pH range 4 to 10.

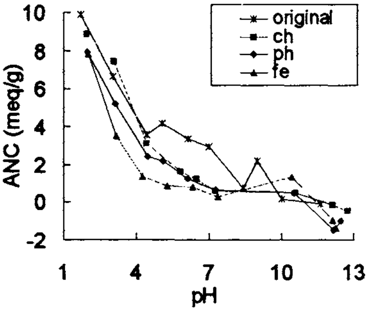

Fig. 3 ANC value vs. pH

ANC and release of metals

The ANC [meq/g] versus pH are plotted in Fig. 3. There is a significant difference between the four materials. In the neutral pH range 5 to 9, there is a significant difference between original fly ash and treated materials. It means that it is harder to decrease the leachate pH for original fly ash than treated materials. The sensitivity to externally imposed pH changes as reflected by the change of ANC in relation to pH is an important factor for evaluation of treatment methods.

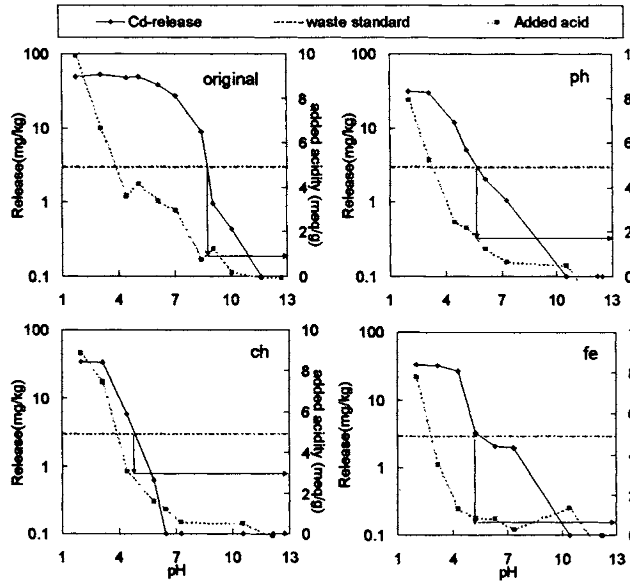

Fig. 4 Added acidity and release of Cd

In Fig. 4, the Cd release curve and added acidity curve versus final pH are plotted. Japanese standard for waste disposal for Cd (0.3 mg/L, it is equivalent to 3 mg/kg of release.) are also drawn as a dot-dash line in the same figure. However, the pH-release behaviour is not the only aspect to be addressed here. The amount of acid required to make a change in pH is crucial in the sensitivity analysis. The buffering capacity that reflects the resistance of the material to a change in pH due to acidification is higher for "ph" than for "fe". In Fig. 5 this is illustrated by the concentration change of Cd relative to the amount of acid required to make the change. A larger value indicates that less acid is needed to bring about a significant change in concentration. In the graph for "ph" and "fe" two maxima are observed; one at pH 7.5 - 8 and one at pH 4. In comparison with the untreated material the sensitivity for pH change has shifted from pH 8 to pH 4 for all treated materials. In the "ch" treated material, the peak at pH 8 is eliminated entirely. A pH of 4 will not be reached under landfill conditions easily provided there is no mixing with material containing degradable organic matter. Similarly, the role of changing the reducing conditions can be discussed. The information needed for such an evaluation is currently insufficient. However, as a general statement it is clear that oxidation of the sulfide treated materials must be avoided as significant changes in metal leachability can be expected upon oxidation. In a management option to be selected for disposing of the waste, this aspect must be addressed.

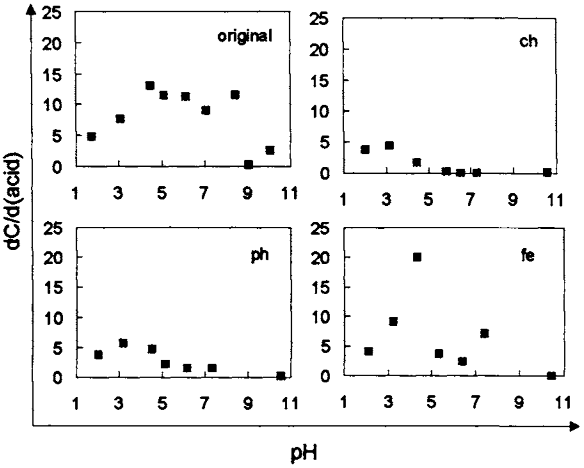

Fig. 5 pH vs. dC/d(acid) of Cd for 4 materials

pH change of leachate under open condition and closed condition

The pH change of the leachate versus L/S value of open and closed test are plotted (Fig. 6). There is a significant difference between open test and closed test. In open test, pH of the leachate decrease continuously. In the closed test the pH increases first and then decreases or remains at the same pH value. The final pH of the open test is always lower than that in the closed vessel for all samples by 1 to 2 units. It can be explained by CO_2 in the atmosphere[7] and it is an important to consider the effect of CO_2 during leaching test operations.

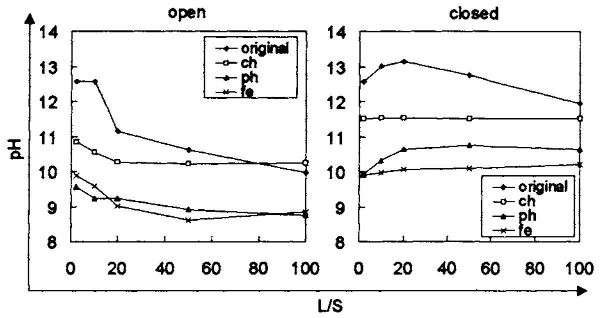

Fig. 6 Change of pH of the leachate

Redox potential of leachate under open condition and closed condition

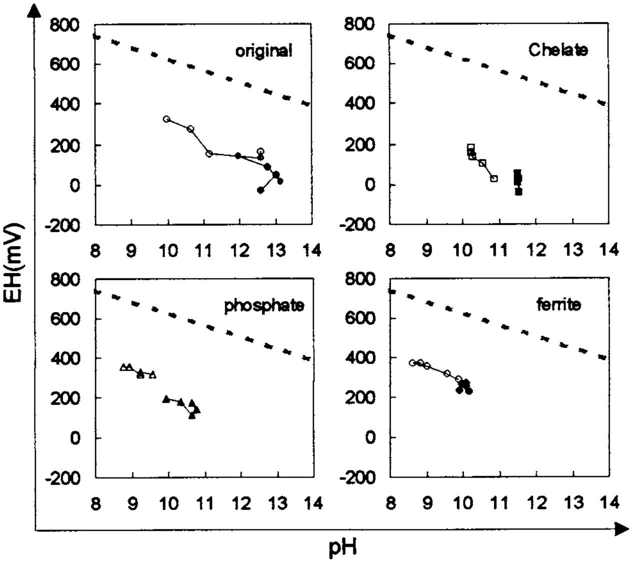

Fig.7 E_H vs. pH for serial batch test

The E_H (standard hydrogen potential) values are plotted versus pH in Fig 7. Solid marks (● ◆ ■ , etc.) mean closed tests' results, and open marks (○ ◇ □ , etc.) shows the open tests' results. As the ORP is a function of the pH, it is meaningless to compare the ORP values directly. In order to compare the ORP values in a meaningful way, the measured ORP values for the treated and untreated material must be compared relative to the dotted lines reflecting the ORP for oxidised conditions as a function of pH.In general, E_H values of the leachate in the open test are higher than the closed ones. This is a result of oxidation by O_2 in the air and exhalation of H_2 from the reaction of the material with alkaline water.

For original ash, the lowest points are the result of the closed test at L/S = 2. In the test the swelling of the closed bottle was obserbed. It may be the effect of the H_2 gas generation from the contacting with distilled water. This gas generation can be explained by following reaction:

$$2\,Al + 3\,H_2O + 8\,OH^- \text{--->} 2\,Al(OH)_4^- + 3\,H_2$$

The formation of hydrogen gas from original ash during the leaching test was confirmed by gas chromatography. The swelling of bottle was not observed for treated materials. The treated materials were mixed with water in treatment process at which state part of the H_2 may escape to the atmosphere, whereas, the leaching test is the first opportunity to contact with water for untreated fly ash. The large difference between the original fly ash in the open test and closed test is attributed to the degassing of H_2 from the open vessel. The "ch" treated materials are generally reducing and their leachate under open conditions are lower than the closed test results of other materials. Furthermore, for chelating material, E_H values increase at the same pH. It means the material is oxidized during the serial batch test. This is attributed to the higher reducing capacity of this material. On the contrary, the plots of ph and fe materials are almost pararell to the dotted line. It indicates these materials are neither oxidized nor reduced during the serial batch test.

Release of metals under open condition and closed condition

As for the metal concentration and release, almost Pb, Cd, Cu, Zn are not detected from treated materials. pH of the leachate is one of the most important factors. Therefore, only metal release from original ash are shown in the figures (Fig. 8). Pb, Zn and Cu in closed test leached out more than open test. Na and K leached out in highly concentration from all materials, and there is small differences between open and closed condition. The release of salts from original fly ash and treated materials is plotted in the figures (Fig. 9). Na and K from treated materials leached out more than original fly ash. It implies that with the additives Na and K are added. The salt release from untreated and treated materials is high. In evaluating environmental impact, it is important to focus on a broader range of elements than only heavy metals. Several studies have shown that also oxyanions can be important as they often show a maximum leachability at neutral pH[8].

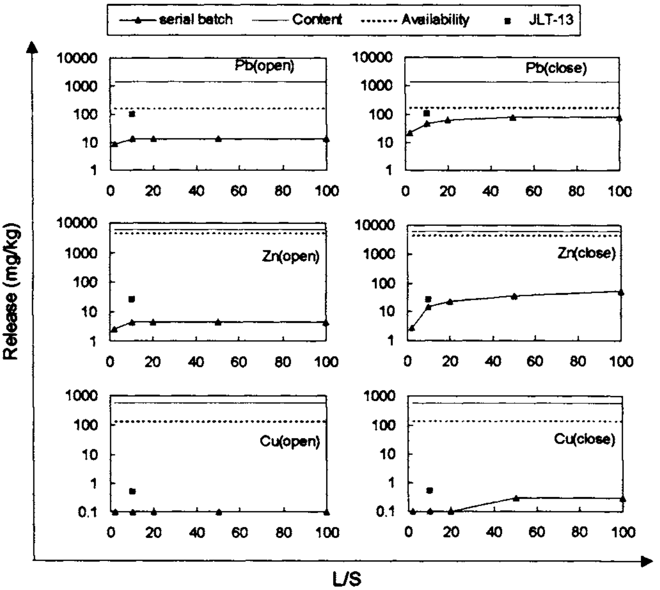

Fig.8 Metal release vs. L/S in the serial batch test

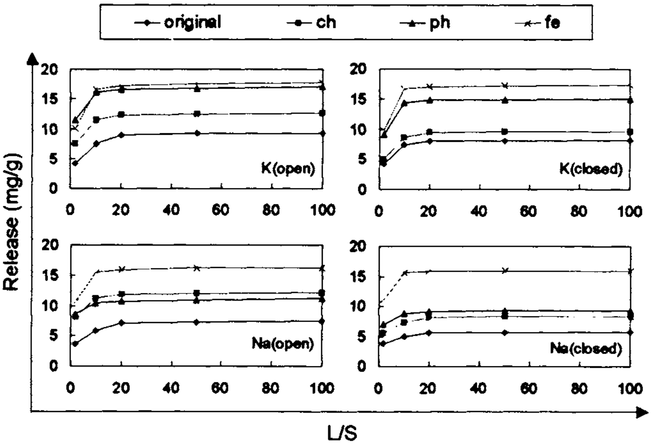

Fig. 9 K and Na release vs. L/S in the serial batch test

Effective diffusion coefficient and tortuosity of materials

In order to be able to quantify release under confined conditions, where diffusion may be the release controlling mechanism, it is important to determine if the treatment influences the physical behaviour of the material. This is done by measuring the tortuosity of the treated materials by carrying out diffusion tube tests with a constituent considered not to interact with the matrix (here Na is chosen). The pDe value for Na, which is an negative logarithm of an effective diffusion coefficient value, for each material are shown in the Table 5. The tortuosity is caluculated from D_0/De. D_0 is the free mobility of Na in water and the value is pD_0 = 8.88 at 22 °C9). All treatments show a pDe value larger than the untreated. This is attributed to the formation of a denser matrix in part caused by additional precipitate formed. This is consistent with the observation that "fe" treated material the effect most significant. As was shown in the batch extractions this positive physical effect does not necessarily mean a lower release as other factor come into play.

Table 5 pDe value and tortuosity of materials

material	original	ch	ph	fe
pDe	9.59	9.85	9.84	10.02
tortuosity	$10^{0.71}$	$10^{0.97}$	$10^{0.96}$	$10^{1.14}$

Conclusion

In order to evaluate the treatment of MSWI residues with chemical agents, the performance of three kinds of treated materials are compared with the behaviour of the untreated MSWI fly ash.

Each treated material shows good results for JLT-13 test, however the evlauation based on this single extraction test is too limited to assess the potential environmental impact of the materials in different disposal scenarios. The treatment using a chelating agent is based on complexation of metals with an organic sulfide and the treated material showed a very high reducing capacity and strong retention for metals over a wide pH range. The treatment with phosphate showed a significant decrease in availability, especially for lead, and a very low leachability over the entire pH range from 4 to 13. The treatment with ferrite showed an increased high physical retention as well as a good retention in the pH domain 5 - 12.

In order to evaluate the performance of the treatment by chemical agents, the changes in leaching behaviour of elements as a function of pH were compared with the buffering properties of the treated materials (Acid Neutralizing Capacity), that can be derived from the pH controlled leach test. Besides, the final ORP value of leachate are plotted versus pH of the leachate, the linear relationship are recognized for each material.

In order to know the effect of the air during the leaching test, the serial batch test under open conditon and closed condition are performed. There are clear differences between open test and closed test in view of pH and ORP. It is a result of carbonation and oxidation by respectively CO_2 and O_2 in the air. Furthermore, the H_2 generation from untreated ash explains the low ORP in a closed test.

In terms of waste management the following conclusions can be drawn:

- When materials are produced with very strong reducing properties either in-plant or afterwards through treatment, the management of the materials requires that measures are taken to ensure that the material will never be exposed to the atmosphere, as oxidation will ultimately lead to loss of retaining potential and could result in uncontrolled release.
- The generation of H_2 in treatment plants is potentially dangerous, if this aspect is not sufficiently recognised in the design and operation of such plants.
- Based on the information generated in the more elaborate tests, better predictions of

the behaviour of materials can be made. Particularly, in relation to quantifying the changes resulting from changes in exposure conditions (failure of lining, top cover or exposure to the atmosphere). This information can be used to better manage these wastes.

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