Acid neutralizing capacity (ANC) and leaching test scheme for short and long term behaviour of granular waste

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Abstract

Japanese standard leaching test (JLT-13), pH dependent test and availability test were performed for municipal solid waste incineration fly ash and electric furnace dust. pH dependent test showed that the leaching quantity was controlled by a final pH of the leachate. In order to predict the final pH of the waste after landfill, ANC (acid neutralizing capacity) of the waste titrated in the availability test were plotted versus initial pH. The final pH were predicted by comparing the ANC with contacting acidity. Leaching test scheme for short and long term assessment, composed of two steps serial batch test, were proposed and performed. The first step is JLT-13 to know initial leaching behaviour. The second step is a batch test (carbonic acid, L/S = 90, 6 hours) to know long term leaching behaviour. Those tests showed short term and long term pH and the leaching concentration at the pH.

Key words: acid neutralizing capacity (ANC), granular wastes, leaching test, availability test, pH dependent test, carbonic acid, serial batch test, municipal solid waste incineration fly ash, electric furnace dust

1. Background and objectives

The leaching behaviour of heavy metal from some granular waste, such as municipal solid waste incineration residues and their chemical treated materials, contaminated soils, coal fly ash, electric furnace dust and saw dust of preservative treated wood, have to be checked before landfill in order to prevent environmental pollution. There are many types of leaching test to predict environmental load of disposal of granular waste materials. Many countries adopt a single batch test method such as JLT-13 (Japan), DIN 38414 (Germany), TCLP (U.S.A.), and so on. Recently, pH dependent test are proposed [van der Sloot et al., 1997] in order to research leaching behaviour of materials under various pH condition in the environment.

In this study, JLT-13, availability test, pH dependent test are performed for municipal solid waste incineration fly ash (MSWI FA) and electric furnace dust (EF dust) and metal leaching behaviour of the wastes in the various pH condition are studied. Then, ANC (acid neutralizing capacity) of the wastes are calculated based on availability test and long term pH change is predicted. Finally, two steps serial batch test are performed, which is a combination of a single batch test using distilled water for short term behaviour and a single batch test using carbonic acid for long term behaviour.

2. Leaching test

2.1 Materials

Three kinds of municipal solid waste incineration fly ash and two kinds of electric furnace dust from electric steel-making industry were used. The pH and metal contents are shown in Table 1. Acid gas treatment method are also shown in the same table. In the leaching test, EF dust-A was ground under 5 mm of diameter and the other materials used directly.

Table 1 Materials for experiments

Materials	Gas treatment	pH	Metal contents (mg/kg)			
			Cd	Pb	Cu	Zn
MSWI FA-A	Dry	12.2	76	1920	408	5470
MSWI FA-B	Dry	12.4	74	1400	570	6000
MSWI FA-C	Wet	10.0	125	4980	1060	15100
EF dust-A	Wet	7.4	156	16500	2450	142000
EF dust-B	Dry	13.0	75	4900	808	159000

2.2 Method

<u>JLT-13</u>

Weigh 5 g of samples and add 50 mL of distilled water into a 100 mL of polyethylene 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 membrane filter (1.0 μm). Although original JLT-13 uses a glass fiber filter (1.0 μm), a membrane filter is used in this study in order to remove residues from the filter to use next step (2 steps serial batch test).

<u>pH dependent test</u>

Weigh 20 g of samples and add 200 mL of distilled water into a glass beaker to reach an L/S of 10. The liquid is stirred continuously while measuring the pH. Acid or base (reagent is 1N HNO_3, 6N HNO_3 or 2N NaOH) are added in order to keep the pH at the preset pH value (pH 4, 7, 10, 13) for 6 hours. After 6 hrs, pH of the leachate is measured. The leachate is filtered over a membrane filter (0.45 µm).

Availability test

This test was performed pursuant to the Availability test in the Netherlands [Draft NEN 7341, 1992]. Weigh 8 g of samples and add 400 mL of distilled water into a glass beaker (L/S = 50). The liquid is stirred continuously while measuring the pH. Acid (1N HNO_3) was added in order to keep the pH 7 for 3 hours. The leachate is filtered over a membrane filter (0.45 µm). This is called as "leachate No. 1". Remove the residues on the filter into the glass beaker and add 400 mL of distilled water again (L/S = 50, total L/S = 100). The liquid is stirred continuously while measuring the pH. Acid (1N HNO_3) was added in order to keep the pH 4 for 3 hours. The leachate is filtered over a membrane filter (0.45 µm). This is called as "leachate No. 2". Metal concentration in the both leachate are determined by ICP spectrometry (SEIKO SPS-1500VR) separately. Leaching quantity were described in leached quantity of metals (mg) from 1 kg of waste (mg/kg). Furthermore, Acid Neutralizing Capacity (ANC) of the waste were calculated from the quantity of added HNO_3. The ANC calculated from the acidity to keep pH 7 for 3 hours were called "ANC7", the ANC calculated from the acidity to keep pH 4 for 3 hours were called "ANC4".

Two steps serial batch test with carbonic acid

Two steps serial batch test were performed in order to predict short term and long term leaching behaviour of the wastes. In the first step, JLT-13 were performed. Then, remove the residues from the filter into a polyethylene bottle and add 450 mL of carbonic acid (L/S = 90, total L/S = 100) and closed. The bottle was shaken for 6 hours. After shaken, pH of the leachate are measured and the leachate is filtered over a membrane filter (1.0 µm). The scheme of the experiment are shown in Fig. 1. L/S is made reference to the availability test (total L/S = 100). Carbonic acid is made by injecting CO_2 gas to the distilled water at the velocity of 600 mL/min for 60 minutes and the pH was 4.0. The concentration of the CO_2 is 21.6 mmol/L by equilibrium (partial pressure of CO_2 is 1 atm, 25 oC, dissociation constant of the carbonic ion are $pK_1 = 6.35$, $pK_2 = 10.33$). Under the condition of L/S = 90, the acidity provided from this leachant to 1 g of the waste is 3.74 meq/g (2nd dissociation) or 1.87meq/g (1st dissociation) (L/S = 90). This is almost same level of acidity of the leachant of TCLP [Duranceau, 1987], which is a standard leaching test in the United States, 1.995 meq/g (99.75mmol/L of CH_3COOH, L/S = 20). This scheme is made reference to the serial batch test in the Netherlands [Draft NEN 7343, 1992] and European standard test "CEN test" [CEN TC 292 Working Group 2, 1994].

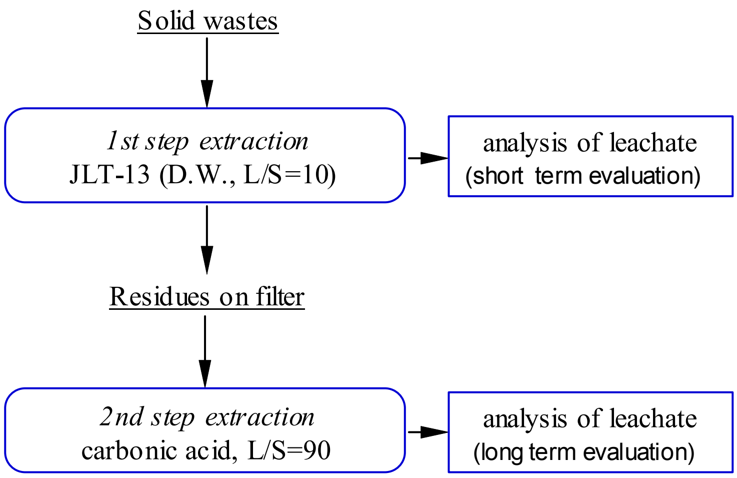

Fig. 1 2 steps serial batch test scheme

3. Results and discussion

3.1 Results of JLT-13

The results of JLT-13 are shown in Table 2. The leaching concentration of Pb from MSWI FA-A and MSWI FA-B was over Japanese standard for landfill (0.3 mg/L), and adequate treatment is required before final disposal. Neither Cd nor Pb from MSWI FA-C was over the standard and it is not a hazardous waste. Cd and Pb from EF dust-A and Pb from EF dust-B show high leaching and they are required to adequate treatment of stabilization of the metals.

Table2 pH and leaching concentration for JLT-13 (unit:mg/L)

Materials	pH	Cd	Pb	Cu	Zn
MSWI FA-A	12.2	0.01	17.5	0.09	4.41
MSWI FA-B	12.4	ND	8.3	ND	3.54
MSWI FA-C	10.0	0.05	0.19	ND	0.01
EF dust-A	7.4	2.7	2.7	0.19	74
EF dust-B	13.0	0.01	105	0.12	4.5
Criteria in Japan	--	0.3*1	0.3*1	(3)*2	(5)*2

*1 Japanese standard for landfill
*2 Japanese standard for drainage

3.2 Release of pH dependent test and availability test

Leaching behaviour of Pb and Cd under the various pH of the MSWI fly ash are shown in Fig. 2(a), and that of EF dust are shown in Fig. 2(b). Results of availability test are shown in Table 3. All three pH dependent curves of Pb and Cd from MSWI fly ash are very similar. That is, metal leaching behaviour of these three ashes are similar when the pH is the same. Although only Fly ash-C is non-hazardous wastes based on JLT-13, when pH is changed, leaching of metals is expected to be high. Furthermore among three MSWI fly ashes availability, that is leaching potential, of Fly ash-C are the highest for all metals. From these facts, leaching behaviour in changing pH or leaching potential in the worst case is not judged by JLT-13.

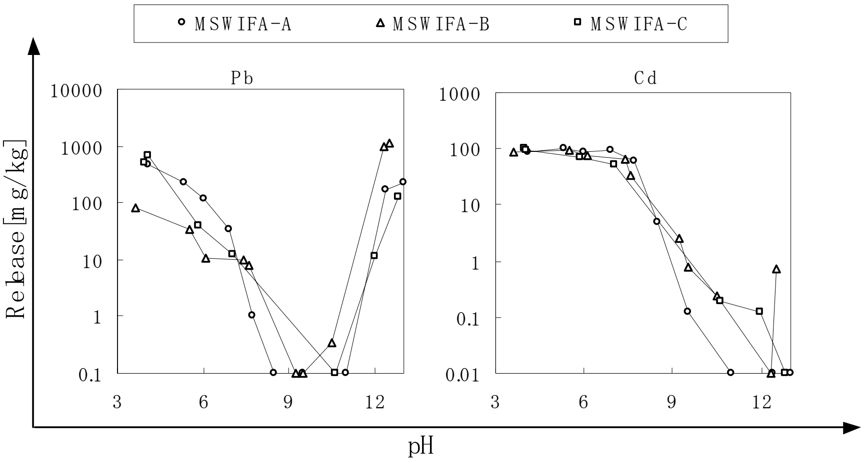

Fig.2(a) Pb and Cd leaching from MSWI fly ash

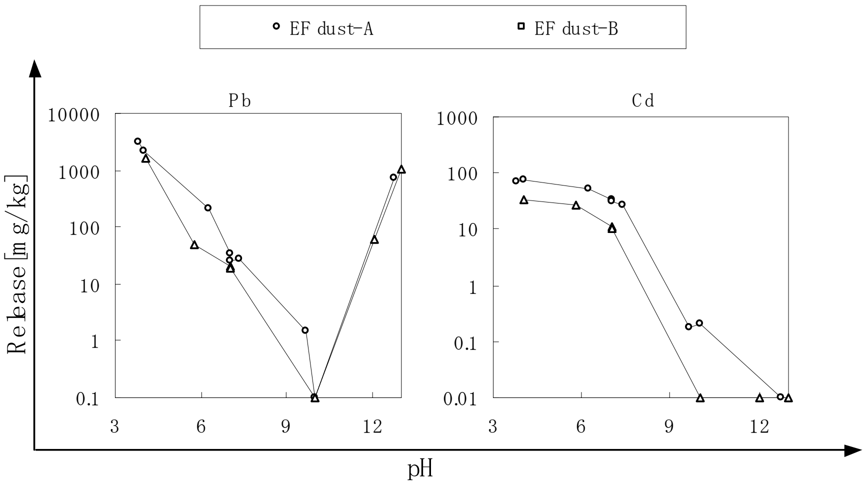

Fig.2(b) Pb and Cd leaching from electric furnace dust

Pb leaching curves of both EF dusts overlies each other. Release of Cd from Ef dusts were different, but the figure of the curves were very similar like translation. That is, the concentration is different but leaching pattern versus pH is similar for all materials. Leaching potential of Cd and Cu from EF dust is not so higher than that of fly ash. The metal leaching concentration of JLT-13 are not related to availability.

Table 3 Results of availability test

Specimen	ANC (meq/g)		Release (mg/kg)			
	ANC7	ANC4	Cd	Pb	Cu	Zn
MSWI FA-A	9.46	10.48	72	356	135	4250
MSWI FA-B	4.44	6.94	66	168	139	4490
MSWI FA-C	0.49	2.79	124	533	541	10200
EF dust-A	0.045	0.886	84	11300	185	20600
EF dust-B	3.81	7.54	47	2220	88	45200

3.3 ANC of solid wastes and long term pH change

In order to evaluate leachability of waste, we should research the following two questions:

-How do metals leach in the various pH?

-How does pH of the waste change?

pH dependent test are useful for knowing leaching behaviour in changing pH and availability test is useful to know maximum leachability in the worst case. These leaching tests give some answers about the first questions. However, in order to know potential leachability after final disposal, not only information about behaviour pH changed but also information how pH of the waste is changed is important. Final pH is controlled by ANC of the waste and contacted acidity. ANC7 and ANC4 are different for all materials, as shown in Table 3. The maximum value of ANC4 is 10.5 meq/g and minimum value is 0.89 meq/g; there are more than ten times. Due to the differences, final pH of the waste is expected showing various values in contacting with acidic fluent in the environment.

ANC7 and ANC4 of the wastes were plotted versus initial pH (pH of JLT-13) (Fig. 3). The fact plot is high means that pH of the waste does not decrease easily in contacting with acid. Because ANC of MSWI FA-C and EF dust-A are smaller than MSWI FA-A and MSWI FA-B, pH of MSWI FA-C and EF dust-A will decrease in the environment earlier. Although initial pH of MSWI FA-A and MSWI FA-B are higher than 12, pH of Fly ash-B decrease easier, because its ANC is smaller. ANC of the waste of which initial pH is high tends to be large generally. However, initial pH value is not enough to estimate the value of ANC. For example, initial pH of MSWI FA-A is lower than EF dust-B but ANC of FA-A is larger. The distance between ANC7 and ANC4 means buffering capacity that the waste pH decrease from pH 7 to pH 4. It is reflected chemical composition of the waste and different for all materials. Comparing EF dust-B with FA-B, we expects the former pH decrease to 7 earlier but the latter decrease to 4 earlier.

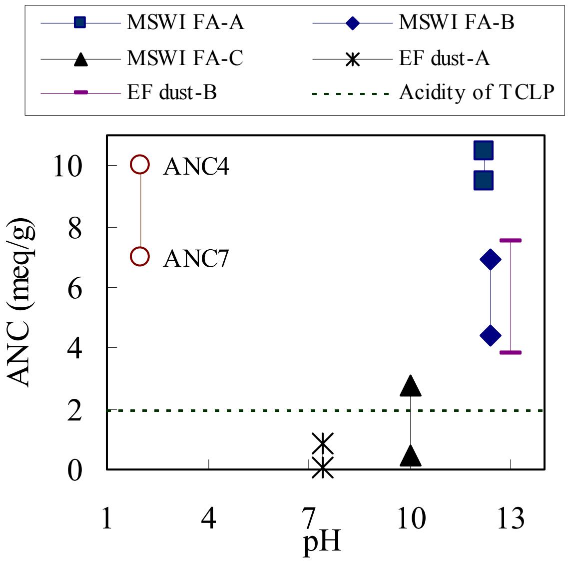

Fig.3 Initial pH and ANC of wastes

The fact ANC of the waste are different means that long term pH value of the waste is different for each waste, when the waste contact with the same acidity. Acidity of the leachant of TCLP (2 meq/g) was also drawn with dotted line in the Fig. 3. When this acidity contacts with the waste in the environment, pH of EF dust-A, of which ANC4 is lower than the line, decrease lower than 4. Final pH of MSWI FA-C falls on between 4 - 7. On the other hand, pH of MSWI FA-A, MSWI FA-B and EF dust-B is higher than 7. Prediction of final pH is important to know which pH range we should evaluate, and studying ANC for many kinds of waste is necessary.

3.4 Results of 2 steps serial batch test with carbonic acid

The results of 2 steps serial batch test and pH dependent curves are shown in Fig. 4. Final pH were plotted on X-axis, metal release ([leaching concentration] x [L/S]) were plotted on Y-axis. The results of JLT-13 (1st step) were plotted in square and results of carbonic acid leaching test (2nd step) were plotted in triangle, versus pH of the leachate. An open square and a open triangle mean the value is under detection limit. Standard for landfill of Pb and Cd (0.3mg/L) and standard for drainage of Zn and Cu (3 g/L, 5 mg/L respectively) are translated to release by multiplying of L/S (10). These values, 3 mg/kg (Pb and Cd), 30 mg/kg (Zn), 50 mg/kg (Cu) respectively, were also drawn with dotted line. Zn and Cu from MSWI FA-A were not analyzed.

Release of JLT-13 was controlled by the final pH of the leachate, because all plots were almost on the pH dependent curve. When pH of the waste (or leachate) is changed, the leaching concentration will be changed. Because distilled water reflects waste characteristic, we can see pH and leaching behaviour in short term. Therefore, JLT-13 or distilled water leaching test is useful to know short term behaviour. As to Pb leaching, acidic extraction is not realistic and may lead to dangerous evaluation because release under alkaline condition is high.

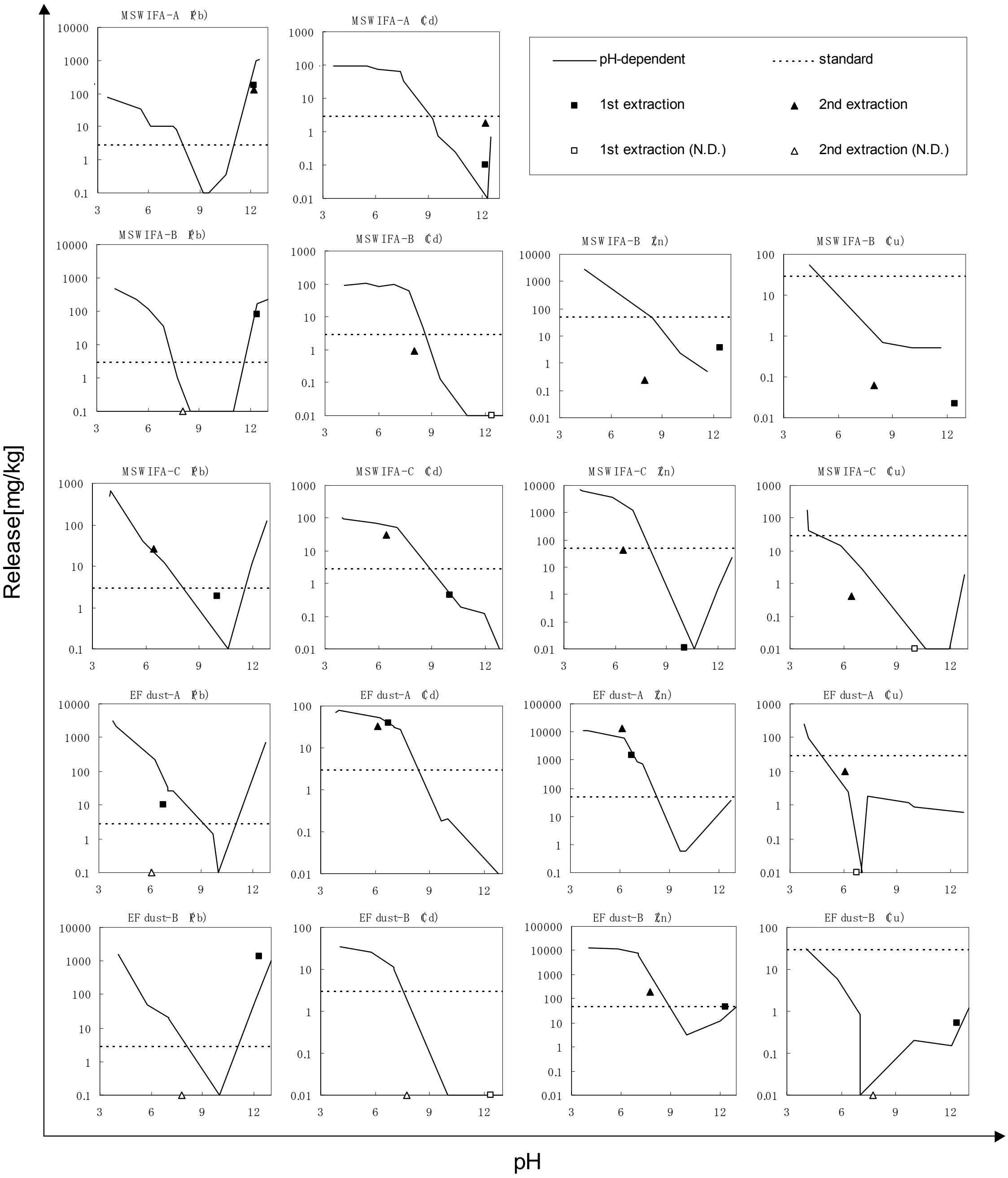

Fig.4 pH dependent curve and release of 2 steps serial batch test

From results of carbonic acid batch test, we can see various final pH of the waste. Release of metals was also controlled by the final pH generally. ANC of MSWI FA-A is very large and pH is not changed so much. It is important to see leaching behaviour under alkali condition for such a strong alkaline wastes like this ash even in the long term. Using strong acid and keeping pH low to these wastes is not realistic. Furthermore, it may lead to underestimate of leaching concentration in amphoteric metals such as Pb and Zn or oxy-anion such as As and Se even though in long term behaviour because they leached out higher under alkali condition or neutral condition [Mizutani et al., 1997, van der Sloot et al., 1991]. The reason why Cd release increase even though the final pH is almost same value is due to the evaluation based on release. Both leaching concentration (1st step and 2nd step) is as low as the detection limit value, so calculated release show the 9 times of the others due to difference of L/S (10 and 90). It is one of the problem of evaluation method based on release. Initial pH of MSWI FA-B was high and Pb was leached out high. However, it is expected that pH and Pb release decrease with the time. Release of Cd and Cu will increase and these metals are important in long term. The reason why release of Zn decreased, even though pH decrease, is not clarified. Neither Pb nor Cd leached out from MSWI FA-C in JLT-13 and it classified as non-hazardous waste. However, pH decrease and higher leaching of Pb and Cd are suggested in long term and the potential hazard of this material is large. pH of the leachate of EF dust-A in 1st step and 2nd step is not changed clearly, however, Pb release decreased and Cu release increased. Pb decrease is relation to detection limit of analysis and the leaching concentration is seen low due to large L/S (L/S = 90). On the contrary, increase of Cu release is due to increase of solubility of copper, which can be seen from pH dependent curve. ANC of EF dust-B and MSWI FA-B are similar and their leaching behaviour is also similar. Focusing on pH changing range, we should pay attention to Cd leaching behaviour, because Pb tends to decrease but Cd tend to increase.

Consequently, two steps serial batch test scheme, combination of batch test with distilled water and batch test with acidic leachant enables us to see and evaluate not only short term leaching behaviour but long term leaching behaviour. However, the leaching condition such as leachant or L/S should be discussed more.

In this study, carbonic acid is used as a leachant of acidic leaching test. The disadvantages using carbonic acid as a leachant is pointed as follows:

1. It is pointed that extraction by carbonic acid is not realistic and Zn release from cemented municipal solid waste incineration fly ash is accelerated by CO_2 [van der Sloot et al., 1994].
2. Because carbonic acid is a weak acid, pH of the leachant is higher than 4. pH 4 is the lower limit of the realistic fluid in the environment and it may lead to under estimate of metal leaching.
3. Because lead carbonate ($PbCO_3$) is insoluble to the water (the solubility is 1.1 – 1.7 mg/L at 20 oC), leaching test with carbonic acid may lead to underestimate of Pb leaching. Indeed the standard leaching test in Switzerland, TVA, of which leachant is carbonic acid, is pointed that it may lead to underestimate of some materials compared with other acidic test [van der Sloot et al., 1991].

However, there are many advantages using carbonic acid as a leachant as follows:

1. The pH of the leachant is realistic in spite of high acidity.
   For example, if we make HNO_3 leachant with 2 meq/g of acidity, the leachant shows pH 1.7 (in the case of L/S =10). It is too low for realistic fluid.
2. It is a realistic acidic leachant after landfill and the neutralizing effects of CO_2 in the air is large [Mizutani et al., 1999].
3. We can prepare pH 4 carbonic acid easily by injecting CO_2 gas into distilled water under the atmosphere.
4. Special equipment such as pH controller is not needed.

Therefore, it is useful to use carbonic acid as a leachant for evaluation of long term behaviour, although the discussion about carbonation of metals in the environment is necessary.

4. Conclusions and requirements

JLT-13, availability test, pH dependent test were performed to 3 kinds of MSWI fly ash and 2 kinds of EF dust and pH of the leachate, metal leaching behaviour and ANC of the waste were studied. Furthermore, the scheme of two steps serial batch test, which is JLT-13 (distilled water and L/S = 10) as a first step to see short term behaviour and batch test with carbonic acid (CO_2 saturated water) and L/S = 90 as a second step to see long term behaviour were tried. The results from this study are followings:

- pH dependent curves were very similar for all materials. Release of JLT-13 exist almost on the curves, and the fact the release is controlled by the pH of the leachate is clarified. When pH is changed in contacting with acidic fluid, high concentration of leaching is expected. Therefore only JLT-13 is not enough to know hazardous/ non-hazardous of waste in the long term.
- ANC of the wastes was focused on as an index of pH change of the waste in the environment. The waste of which initial pH is high tended to show high ANC, but some wastes does not show the same tendency. Plotting ANC of the waste versus pH of JLT-13 is useful to predict pH decrease.
- Two steps serial batch test scheme to know short term and long term leaching behaviour of the waste were tried. That scheme is a combination of JLT-13 (distilled water, L/S = 10) and carbonic acid extraction (L/S =90). Due to the differences of ANC, pH of the leachate in the 2nd step is different for each wastes, and this method is possibly predict long term leaching behaviour.
- Discussion about influences of CO_2 on neutralizing of waste, influences of carbonation of metals on mobility of the metals are required as for using carbonic acid (CO_2 saturated water) as a leachant.

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