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Journal of Hazardous Materials 38 (1994) 65–74

JOURNAL OF HAZARDOUS MATERIALS

A long-term leachability study of solidified wastes by the multiple toxicity characteristic leaching procedure

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Received 12 January 1993; accepted in revised form 30 January 1994

Abstract

Solidification is a common practice for the treatment of wastes containing heavy metals before they can be disposed of in a landfill. In order to evaluate the suitability of the solidified waste for landfilling, the multiple toxicity characteristic leaching procedure (MTCLP) was introduced to study the long-term leachability of solidified wastes. To this end, an untreated and two cement-based solidified mercury-containing wastes were evaluated by the MTCLP to simulate the long-term leaching behavior of heavy metal contaminants of these wastes in an improperly designed sanitary landfill. The multiple toxicity characteristic leaching procedure is designed by combining the multiple extraction procedure and the toxicity characteristic leaching procedure, which are being used by the US EPA. This paper presents and discusses the experimental procedures of the MTCLP as well as the results of the chemical analysis of leachates obtained from the MTCLP of these wastes.

1. Introduction

The toxicity characteristic leaching procedure (TCLP) (published in US Federal Register [1]) is currently adopted by the US EPA to determine the leaching toxicity of wastes. It means that a waste exhibits the characteristic of toxicity if the concentration of any regulated contaminants in its TCLP leachate is greater than the regulatory threshold. However, the TCLP is a batch leaching procedure, it may underestimate the potential hazards of those wastes of high alkalinity. This is due to the TCLP acetate buffer leaching solution which may not properly account for the leaching of

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SSDI 0304-3894(94)00034-E

heavy metals from wastes in a high alkalinity environment. Thus, the multiple toxicity characteristic leaching procedure (MTCLP) is developed by combining the multiple extraction procedure (MEP) and the TCLP to study the long-term leachability of the wastes of high alkalinity. The MEP is designed by US EPA to simulate the leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill. In this study, the experimental method of the MTCLP was introduced. Furthermore, a mercury-containing waste (brine purification mud, K071) and two types of its cement-based solidified monoliths were evaluated by the MTCLP to study their long-term leachabilities.

2. Development of MTCLP

The MTCLP is a combination of the MEP and the TCLP. It is designed in this study to compensate the drawback of TCLP, which may not reveal the long-term leachability of heavy metals in a waste of high alkalinity. The MEP was introduced in method 1320, SW-846, US EPA [2]. According to method 1320, the objective of the MEP is to simulate the leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill. The repetitive extractions reveal the highest concentration of each constituent that is likely to leach in a natural environment.

The experimental procedure of the MEP can be summarized as follows: First, the testing waste sample is extracted by the extraction procedure (EP) which is also introduced by the US EPA in method 1310, SW-846 [2]. Then, the remaining solid portion of the testing sample is reextracted nine times by using a synthetic acid rain extraction fluid. The synthetic acid rain is prepared by adding the 60/40 wt% of concentrated sulfuric acid and nitric acid to distilled deionized water until the pH is 3.0. If the concentration of the concerned constituent increases from the 7th or 8th extraction to the 9th, the extraction procedure should be repeated until these concentrations decrease.

The EP was adopted by US EPA to identify wastes, which exhibit a hazard due to their potential to leach significant concentrations of concerned toxic constituents. However, in the US Federal Register published on March 29, 1990, the waste generators have been asked to determine the toxic characteristic of their wastes by using TCLP instead of using EP [1]. The large quantity of generators have 6 months to comply with the new regulation, whereas the small quantity generators have 12 months to comply. Since the EP is no longer valid under current regulation, the MEP that uses the EP as its first extraction procedure may also not be appropriate to be used any more. Thus, the MTCLP is developed following the MEP procedure by replacing the EP with TCLP. The main difference between the MEP and the MTCLP is that, for the first extraction sequence, the MEP uses the EP but the MTCLP uses the TCLP. Thus, the MTCLP should be able to simulate the long-term leachability

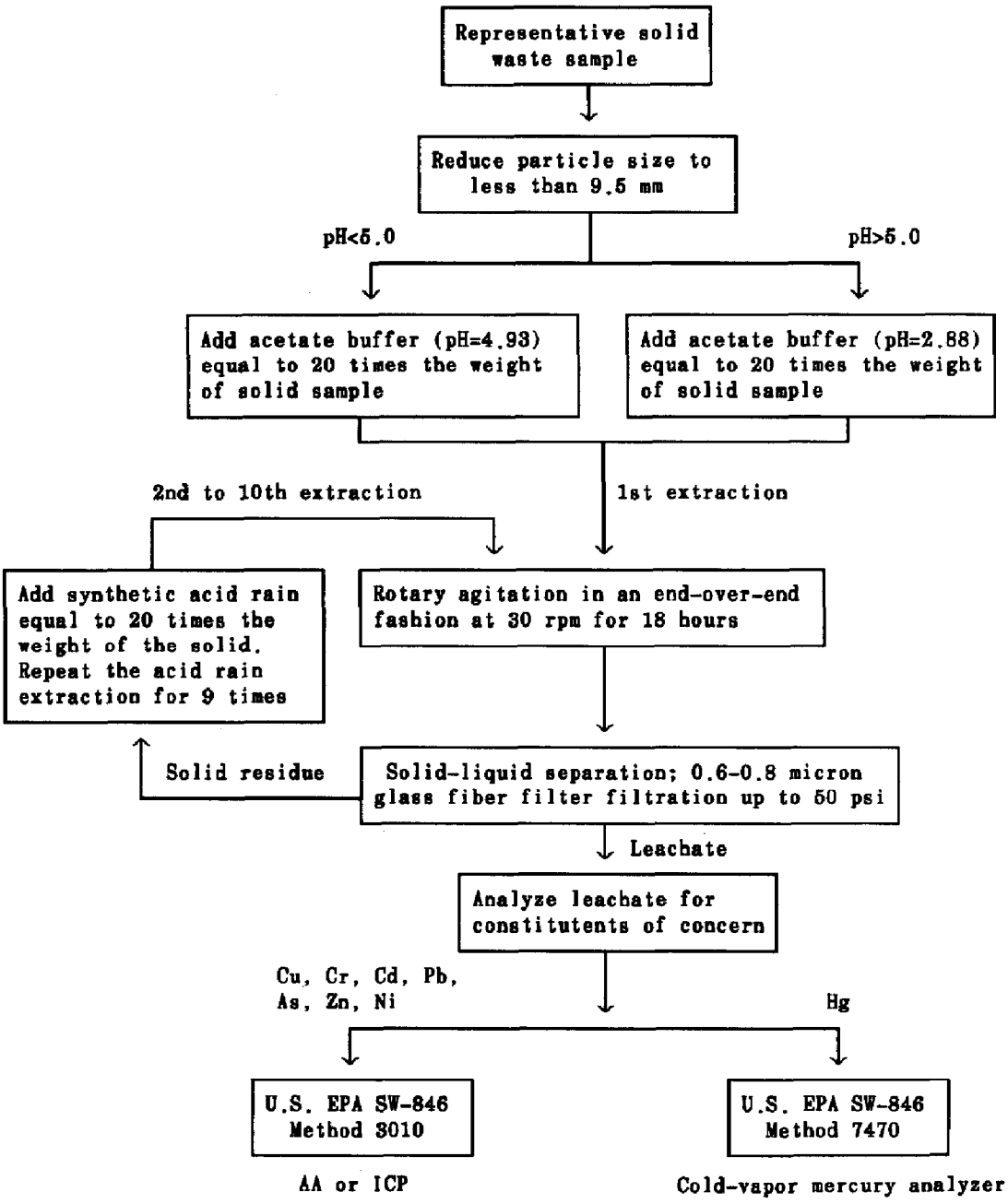

Fig. 1. MTCLP flowchart for inorganic waste.

for a waste undergone repetitive precipitation of acid rain on an improperly designed sanitary landfill. This is the design concept of the MEP and the MTCLP. The flowsheet of the multiple toxicity characteristic leaching procedure is presented in Fig. 1.

3. Comparisons of MEP and MTCLP

Since the main differences between the MEP and MTCLP are their first extraction sequence (i.e., the MEP using the EP; the MTCLP using the TCLP) and their subsequent extraction technique (i.e., the MEP is the same as the EP; the MTCLP is the same as the TCLP), the comparisons of MEP and MTCLP can be characterized by the differences between the EP and TCLP. The differences between the EP and the TCLP can be found elsewhere [3].

The main objective of the replacement of the EP by the TCLP is to accurately simulate the mobilities of pollutants from wastes, especially organic pollutants. Other objectives are to improve the reproducibility of the test results as well as to reduce the conducting cost of the test [4].

The comparisons of the MEP and the MTCLP are presented below. The MTCLP is more suitable for organic constituents than the MEP since the former uses a zero-headspace vessel for volatiles. The MTCLP is more accurate than that of the MEP since it adopts a specific extraction vessel, filter type and agitation method. The MTCLP is simpler than that of the MEP since it uses a shorter extraction time, filter of a larger opening, and needs no pH adjustments during the extraction. Also, the MTCLP will leach out more pollutants than that of the MEP since it uses a finer particle size (i.e., equal to or less than 9.5 mm).

4. Experimental

Based on the experimental procedures stated in Fig. 1, three materials were evaluated by the MTCLP method. Sample no. 1 is the mercury-containing brine purification mud, which is classified by the US EPA as K071 waste. Sample nos. 2 and 3 are the cement-based solidified monoliths of sample no. 1 with different admixtures. A representative solid waste of 100 g of sample nos. 1, 2, and 3 was used, respectively, for the MTCLP tests in this study.

First, the representative sample (except sample no. 1) was ground to a particle size of less than 9.5 mm. Second, the pH value of ground sample was determined. Based on this pH value, a proper extraction fluid was chosen for the leaching test. In this study, the extraction fluid of pH = 2.88 was adopted for all of the three samples. Third, the representative sample with the selected extraction fluid (20 times of the weight of solid sample) were put into an end-over-end rotary agitation device. This device was then operated at 30 rpm for 18 h to extract the pollutants from the solid sample into the extraction fluid. Fourth, the leachate was separated from the solid residue by filtration with a 0.6–0.8 μ glass fiber filter by gradually applying a pressure up to 50 psi. The collected extraction fluid was kept for further chemical analysis. Fifth, the solid residue was further extracted with a synthetic acid rain (sulfuric acid/nitric acid = 60/40 by weight, pH = 3.0) following the TCLP method. Sixth, the fifth step was repeated for another 8 times.

According to the experimental procedures described above, each solid sample was subjected to 10 extractions. The first extraction was conducted by using the TCLP

method, and the subsequent nine extractions were also conducted by tbe TCLP method except that the extraction fluid was replaced by a synthetic acid rain. Thus, 10 leachates were obtained for each solid sample under the MTCLP test in this study. These leachates were kept for determining the concentration levels of concerned pollutants. In this study, the pollutants of concern are Cu, Cr, Cd, Pb, Zn, Ni, and Hg. The concentrations of Cu, Cr, Cd, Pb, Zn, and Ni were determined by using an inductively coupled plasma atomic emission spectroscopy (ICP), whereas the concentration of Hg was determined by the cold vapor mercury analyzer.

5. Results and discussion

The total concentrations of Cu, Cr, Cd, Pb, Zn, Ni and Hg as well as the pH values of sample no. 1 to sample no. 3 were analyzed and tabulated in Tables 1–3, respectively. These tables show that sample no. 1 has the highest concentrations of the concerned pollutants, but the lowest pH values comparing other samples. This is due to the fact that sample nos. 2 and 3 are the monoliths solidified by a cement-based technique.

According to the procedures given in Fig. 1, sample nos. 1–3 were extracted 10 times by the MTCLP method. After each extraction, the leachates of these samples were collected to analyze the concentrations of Cu, Cr, Cd, Pb, Zn, Ni and Hg as well as the final pH values. These analytical results were also tabulated in the Tables 1–3.

Among the pollutants of concern (i.e., Cu, Cr, Cd, Pb, Zn, Ni and Hg), only Cd, Cr, Pb, and Hg are regulated by the US EPA. The regulatory thresholds for Cd, Cr, Pb, and Hg are 1.0 mg/l, 5.0 mg/l, 5.0 mg/l and 0.2 mg/l, respectively [1]. As mentioned

Table 1
Total metal concentrations and MTCLP analytical results of sample no. 1

Sequence of extraction	Analytical results							
	Ni (ppm)	Cu (ppm)	Cr (ppm)	Cd (ppm)	Pb (ppm)	Zn (ppm)	Hg	Final pH
0th (total concen.)	89.6	108.6	40.2	11.5	202.3	192.5	174.4 (ppm)	9.90
1st (TCLP)	0.28	< 0.1	< 0.2	< 0.05	< 0.3	0.12	810 (ppb)	7.05
2nd (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.07	21.90 (ppb)	7.85
3rd (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.06	8.95 (ppb)	7.37
4th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.06	11.30 (ppb)	7.15
5th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.07	9.74 (ppb)	7.10
6th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.06	12.60 (ppb)	7.00
7th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.08	10.60 (ppb)	7.25
8th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.12	6.51 (ppb)	6.65
9th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.17	27.90 (ppb)	6.77
10th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.09	1.51 (ppb)	7.08

Table 2
Total metal concentrations and MTCLP analytical results of sample no. 2

Sequence of extraction	Analytical results							
	Ni (ppm)	Cu (ppm)	Cr (ppm)	Cd (ppm)	Pb (ppm)	Zn (ppm)	Hg	Final pH
0th (total concen.)	12.5	72.8	19.3	1.5	58.9	99.9	39.0 (ppm)	11.80
1st (TCLP)	0.51	< 0.1	< 0.2	< 0.05	0.51	0.07	1.46 (ppb)	9.34
2nd (acid rain)	0.16	< 0.1	< 0.2	< 0.05	< 0.3	< 0.05	< 0.5 (ppb)	10.11
3rd (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	< 0.05	1.68 (ppb)	9.20
4th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.05	< 0.5 (ppb)	9.20
5th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.13	0.62 (ppb)	3.10
6th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	< 0.05	0.53 (ppb)	8.50
7th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.10	1.85 (ppb)	3.15
8th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.12	< 0.5 (ppb)	3.21
9th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.14	< 0.5 (ppb)	3.65
10th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.18	< 0.5 (ppb)	7.91

Table 3
Total metal concentrations and MTCLP analytical results of sample no. 3

Sequence of extraction	Analytical results							
	Ni (ppm)	Cu (ppm)	Cr (ppm)	Cd (ppm)	Pb (ppm)	Zn (ppm)	Hg	Final pH
0th (total concen.)	26.2	43.3	21.2	1.7	55.8	71.4	53.9 (ppm)	11.60
1st (TCLP)	0.42	0.10	0.20	0.11	0.34	0.11	< 0.5 (ppb)	10.95
2nd (acid rain)	0.21	< 0.1	< 0.2	< 0.05	< 0.3	0.05	< 0.5 (ppb)	11.20
3rd (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.06	< 0.5 (ppb)	10.50
4th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.06	< 0.5 (ppb)	10.80
5th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.09	< 0.5 (ppb)	10.40
6th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	< 0.05	< 0.5 (ppb)	10.50
7th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.11	< 0.5 (ppb)	8.85
8th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.13	< 0.5 (ppb)	10.10
9th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.17	< 0.5 (ppb)	9.65
10th (acid rain)	< 0.1	< 0.1	< 0.2	< 0.05	< 0.3	0.18	< 0.5 (ppb)	9.81

above, the first extraction of the MTCLP is the same as the TCLP extraction. By comparing these regulatory thresholds with the analytical results of the first extraction, which tabulated in Tables 1–3, it shows that only the Hg concentration of sample no. 1 (i.e., 0.81 mg/l) is greater than the regulatory threshold. It means that sample no. 1 is indeed a hazardous waste, whereas the other samples can be considered as

non-hazardous. This also indicates that the solidification technique employed in this study is capable of reducing the leachability of mercury.

From Tables 1–3, the analytical results of the second through the tenth extractions (i.e., synthetic acid rain extraction) reveal that there are no significant amounts of Ni, Cu, Cr, Cd, Pb, and Zn leached out of these samples. Thus, based on the results of MTCLP test, it can be concluded that the pollutants of Ni, Cu, Cd, Pb, and Zn of these samples will not present any severe hazards to the environment.

As discussed previously, mercury is the only contaminant that would cause environmental problems for these samples studied. Thus, the leachability of mercury of these samples should receive more attention in this study. Based on the data shown in Tables 1–3, the mercury concentrations of MTCLP leachates of sample no. 1–3 were plotted and compared in Fig. 2. It is clear that the MTCLP leachates of sample no. 1 have the highest mercury contents. This is because sample no. 1 is the untreated waste, whereas sample nos. 2 and 3 are solidified monoliths. However, it cannot be concluded that the solidification treatment is effective because this may also be due to the total Hg concentrations of these solidified samples are less than that of the untreated sample.

To understand the actual solidification effectiveness, the weight percent of Hg leached and the cumulative weight percent of Hg leached by each MTCLP extraction

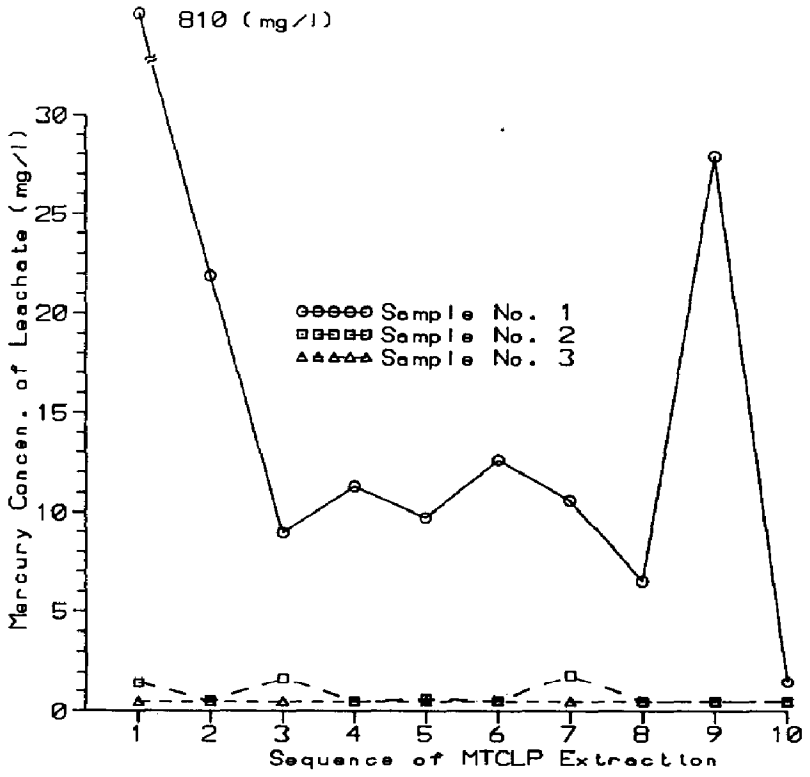

Fig. 2. Mercury concentration of MTCLP leachates for sample nos. 1–3.

Table 4
Mercury leached of each MTCLP extraction for testing samples

Sequence of extraction	Mercury leached of sample no. 1			Mercury leached of sample no. 2			Mercury leached of sample no. 3		
	Weight (mg)	wt%	Cumulative wt%	Weight (mg)	wt%	Cumulative wt%	Weight (mg)	wt%	Cumulative wt%
0th (total conc.)	17.4	0.00	0.00	3.9	0.00	0.00	5.39	0.00	0.00
1st (TCLP)	1.620	9.31	9.31	0.003	0.08	0.08	0.001	0.02	0.02
2nd (acid rain)	0.044	0.25	9.56	0.001	0.03	0.11	0.001	0.02	0.04
3th (acid rain)	0.018	0.10	9.66	0.003	0.08	0.09	0.001	0.02	0.06
4th (acid rain)	0.023	0.13	9.76	0.001	0.03	0.22	0.001	0.02	0.08
5th (acid rain)	0.019	0.11	9.90	0.001	0.03	0.25	0.001	0.02	0.10
6th (acid rain)	0.025	0.14	10.04	0.001	0.03	0.28	0.001	0.02	0.12
7th (acid rain)	0.021	0.12	10.16	0.004	0.01	0.39	0.001	0.02	0.14
8th (acid rain)	0.013	0.07	10.23	0.001	0.03	0.42	0.001	0.02	0.16
9th (acid rain)	0.056	0.32	10.55	0.001	0.03	0.45	0.001	0.02	0.18
10th (acid rain)	0.003	0.02	10.57	0.001	0.03	0.48	0.001	0.02	0.20

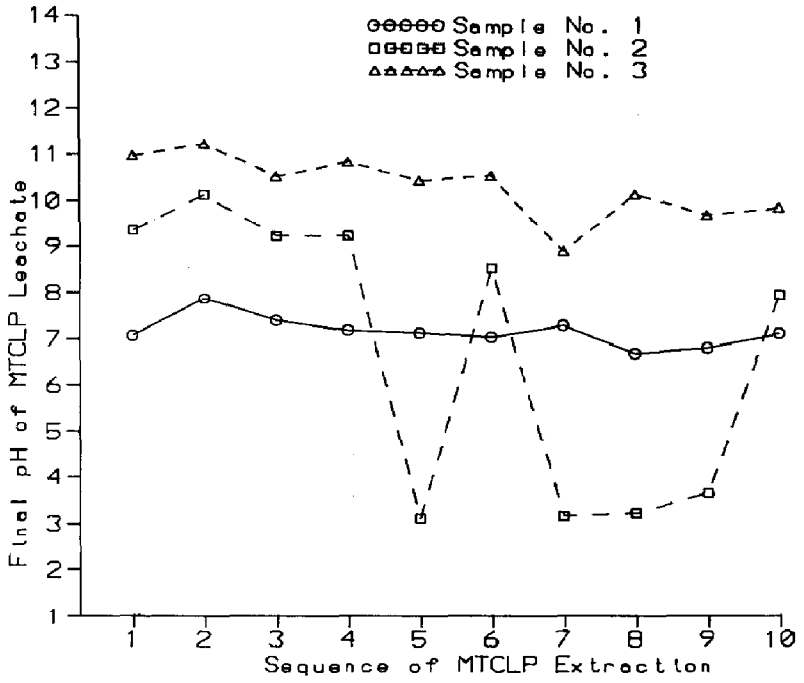

Fig. 3. Final pH of MTCLP leachates of sample nos. 1–3.

for each sample were calculated and tabulated in Table 4. Table 4 shows that, after 10 extractions, a total of 10.57 wt% of mercury would be leached out of the untreated sample no. 1, whereas it would be less than 0.5 wt% for any of other samples. Thus, it can be concluded that the solidification technique employed in this study can effectively reduce the potential hazards caused by the leaching of mercury.

Since the pH value of the leachate will reflect the leachabilities of metal pollutants, the final pH values for all MTCLP leachates were listed in Tables 1–3. Fig. 3 illustrates the relationships of the final pH value of each MTCLP leachate against the sequence of MTCLP extraction. This figure shows that the final pH values for 10 MTCLP leachates are almost in the neutral region for sample no. 1. For sample no. 3, its final pH values of 10 MTCLP leachates are all in the alkaline region. This can be explained by the lower pH value of sample no. 1 comparing to sample no. 3. However, for sample no. 2, the final pH values of its MTCLP leachates randomly vary from alkaline to acid regions. The reasoning for the fluctuation of the final pH values is not clear. Further investigations in this regard is needed.

6. Conclusions

By combining the multiple extraction procedure (MEP) and the toxicity characteristic leaching procedure (TCLP), the multiple toxicity characteristic leaching

procedure (MTCLP) was developed in this study to investigate the long-term leachabilities of wastes. From the comparisons of the MEP and the MTCLP, the MTCLP has following merits: (1) It is suitable for organic pollutants. (2) It is more accurate and simpler than that of the MEP. Thus, the MTCLP can be used to replace the MEP to simulate the leaching of a waste subjected to repetitive precipitation of acid rain on an improperly designed sanitary landfill.

The MTCLP results show that, among the metal pollutants of concern (i.e., Cu, Cr, Cd, Pb, Zn, Ni and Hg), the mercury is the only pollutant that would cause the environmental problems for these waste samples. The MTCLP results also reveal that, after 10 extractions, the total mercury can be leached from the untreated mercury-containing waste would be 10.57% by weight, whereas less than 0.5% by weight for solidified specimens. Thus, it can be concluded that the mercury-containing waste studied can be effectively solidified by the present cement-based technique, which has greatly improved the long-term stability of the solidified monoliths.

Acknowledgments

This work was funded by the EPA of Republic of China (ROC) under Project No. EPA-80-E3H1-09-23. The authors would also like to express their appreciation to Mr. W. S. Yang and Misses S. L. Fan and R. C. Liu of Energy and Resources Laboratories, ITRI for the experimental assistance.

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