Leaching Procedures and Leaching Behaviors of Heavy Metals in Cement-solidified Fly Ashes

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1. Introduction

In 1998 about 6.8 million tons of fly ash was generated in Japan, 75% of which was reused, the residual 25% was disposed and buried as waste. It is known that there is a small/trace amount of heavy metals in fly ash. Will secondary pollution occur due to the release of heavy metals from buried fly ashes and fly ash products? It is thus necessary to correctly evaluate the leachability of heavy metals in them. In this study a review of present laboratory leaching and extraction procedures were made and, based on which a pH controlled shaking extraction test was proposed and applied to fly ash cement mortars and solidified fly ashes.

2. A Review of Present Laboratory Leaching and Extraction Procedures

Many leaching methods have been developed to estimate the leach rate and leaching mechanisms of wastes, such as the French X31-210, German DEV S4, Dutch NEN 7345, USA's TCLP, Swiss TVA, British repetitive shaker test and so on. They can be briefly classified into static and dynamic types. The former is a serial batch leaching system, such as the methods of exchanging leachant periodically, percolation and recycling leachant in a closed system; the latter is actually an accelerated leaching procedure by stirring or shaking specimens in a closed or open system without renewal of leachant. Generally, water (distilled, ion exchanged or pure) is used as leachant and the leaching/extraction process is conducted under a pH-free condition. Among the various procedures it is difficult to say which is the best one and can be universally applied because every procedure, which has been developed in respective to particular waste or for different purpose, has its own merits and disadvantages. Another commonly arguable topic is the relation between laboratory leaching/extraction results and the actual leaching on site. Therefore, the development of a leaching procedure that can well simulate actual leaching is needed. When the priority of environment safety is to be taken into the first consideration, in our opinions, a laboratory leaching condition severer than actual leaching one is also adoptable.

The leachability of heavy metals in wastes is greatly influenced by the geochemistry of waste, morphology of metals and leachant pH, particularly, at an elevated pH some metals will have much reduced leachability due to the decrease in solubility and/or the formation of insoluble phases. Therefore, the same metal but existing in different wastes or stabilized by different methods will exhibit varying leachability. For making a comprehensive comparison of the leachability of heavy metals in various wastes, it is of most important to conduct leaching/extraction test under a constant pH condition. The TCLP was developed to evaluate the leaching behaviors of cement-stabilized wastes, using acetic acid to buffer the alkaline of leachant. But the fact is that the content of alkalis released from cement hydrates is high enough to quickly consume the acetic acid, resulting in a final pH around 12. In Japan, a shaking extraction method is usually applied, in which leachant pH is also free of control. A lowered leaching of some metals in cement-stabilized waste may be possibly estimated by it. Hence, an improvement upon it is also needed.

3. Raw Materials and Experiments

Fly ash A and fly ash E, ordinary Portland cement (OPC), B type slag cement (SC), blast-furnace slag powder (SP) with Blaine surface of 4040 cm^2/g and pure water (>18.0 MΩ・cm) were used in the following ways: (1) 40×40×160 mm cement mortar specimens, called A00, A25 and A40, were made with OPC at W/B=0.60, S/B=2.00 and with 0%, 25% and 40% fly ash A replacement of OPC. After cured at R.H. >90% for 28 days they were crushed to 1-5 mm particles and, dried at 60±2℃ for 24 hr and then in vacuum for 2 hr; (2) Mixtures of: (a) 100% fly ash E; (b) 94%E+6%SC; (c) 88%E+6%SC+6%SP and (d) 82%E+6% SC+12%SP were compacted into cylinders of φ100×127 mm at the optimum moisture content (OMC for short, 24 -25%) accord-

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ing to JIS A 1210. In addition, they were made to slurries with flow of about 240 mm at water to solid ratios between 42% and 45%. After cured at 100% R.H. for 28 days all the specimens were crushed (<2 mm in size) and dried at the same conditions as above.

Two shaking extraction procedures were commenced in this experiment. One is the traditional procedure, using pure water that has been previously modified to pH 6.2 with HCL solution as leachant (W_L/W_S =10.0) and shaking sample bottles for 6 hr in a frequency of 250 rpm and amplitude of 50 mm. In another one, CO_2 was continuously introduced to the bottles at a rate of about 0.6L/min so as to buffer the increase of leachant pH. **Fig. 1** shows the effect of the induced CO_2 on the leachant pH of OPC mortar.

The obtained leachates were filtered to remove particulates and larger colloids and, after measurement of pH, acidified with HNO_3 solution to pH 0.9-1.1. Cr, Mn, Cu, Zn, Cd and Pb in the leachates were analyzed by an ICP equipped with an ultrasonic nebulizer, using Yttium as internal standard material. The results are respectively shown in **Tables 1 and 2**.

4. Results and Conclusions

CO_2 induced at the above rate had a very good pH buffering effect and made all the leachants be close to neutral. At the same time, the leaching of some heavy metals both in the mortars and solidified fly ashes, such as Mn, Zn, Cr and Pb, was greatly increased. Arguments against the intrusion of CO_2 may yield because (1) cement hydrates may have been decomposed by the induced CO_2; and (2) the leaching environment differs from the actual one, which is of absence of CO_2 or only under low P_{CO2}. But based on the fact that the heavy metals in the consolidated fly ashes without cement addition, also exhibited higher leachability in the presence of CO_2, it can be said that the change of leachant from alkaline to neutral, not the possible damaging effect of CO_2 on cement hydrates, is the main reason for the more leaching of heavy metals. From **Table 1** it can be also found that the leaching of Cr from cement mortar is increased when cement mortar has been carbonated. Considering the fact that neutral or slightly acidic/alkaline condition is of the most occurrence in the nature and the internal environment of cement-stabilized wastes will gradually change to neutral as degradation of cement hydrates occurs, it is appropriate to conduct a leaching test in which leachant remains neutral in the estimation of the environmental impact of heavy metals in them.

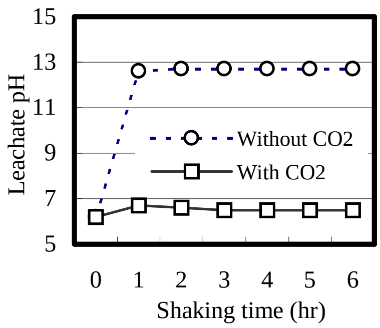

Fig. 1 pH of the leachate of cement mortar

Table 1 Concentrations of metals in the leachates of mortars (ppb)

No	CO_2	pH	Zn	Cr	Cu	Mn	Cd	Pb
A00	No	12.7	8	59	4	N	4	38
A25	No	12.8	6	86	10	N	3	36
A40	No	12.6	7	99	14	N	3	33
A00	Yes	6.3	124	150	35	101	5	70
A25	Yes	6.4	121	140	47	94	3	66
A40	Yes	6.5	142	171	38	205	3	55
A25-1	No	11.3	2	369	18	N	3	27
A25-1	Yes	6.2	148	305	25	282	3	52

* 1: neutralized mortar; N: below analytical detection

Table 2 Concentrations of metals in the leachates ofsolidified fly ash E (ppb)

Item	OMC (a)		Slurry (a)		OMC (b)		Slurry (b)		OMC (c)		Slurry (c)		OMC (d)		Slurry (d)	
	○	●	○	●	○	●	○	●	○	●	○	●	○	●	○	●
pH	11.6	7.0	11.5	6.8	11.7	7.3	11.6	7.0	11.7	7.2	11.7	7.1	11.4	7.2	11.5	6.9
Zn	7	90	24	33	N	39	22	63	N	46	22	63	N	33	31	39
Cr	112	558	133	596	144	418	90	189	78	175	51	135	49	138	27	140
Cu	2	13	N	13	3	30	2	25	2	29	N	28	2	24	2	15
Mn	N	471	N	457	N	1467	N	1876	N	1616	N	1900	N	1594	N	934
Cd	N	8	N	12	N	6	N	6	N	5	N	6	N	4	N	4
Pb	25	81	24	83	23	109	19	87	26	91	21	74	25	82	18	55

* ●: with induced CO_2; ○: without CO_2; a, b, c and d in () represent different mixtures

Generally speaking, leached heavy metals from fly ash slurries are more than those from the fly ashes solidified at OMC. But there are exceptions, e.g., less Cr was observed in the leachates of slurries with cement addition. Consolidating fly ash at OMC can make specimen's structure compact, it is helpful to prevent leaching. In another aspect, more cement hydrates, being capable to fix some heavy metals, can be formed in slurry due to the high water content, which can also lead to decreased leaching. The less leaching of Cr from slurry observed in this study may be a typical example of this effect. The main conclusions of this study are:

(1) Heavy metals do leach out from cement mortars and solidified fly ashes and, their leachability bears largely on leachant pH. At lower pH, more leaching occurs. Only conducting a leaching/extraction test under an uncontrolled leachant pH condition cannot wholly and reliably estimate the leachability of heavy metals in fly ashes, especially for the fly ashes solidified by cement. The method of bubbling CO_2 to leachant can overcome the shortage of present leaching procedures and is recommended by the authors.

(2) With cement addition, especially the addition of both cement and slag, the leaching of heavy metals in fly ash is decreased.