Leaching Behavior of Heavy Metals from Cement Pastes Containing Solid Wastes

YUAN Xiaolu

Key Laboratory of Geological Hazards on Three Gorges Reservoir Area (China Three Gorges University), Ministry of Education, Yichang 443002, China

Email: 544529920@qq.com

Abstract. The leaching behavior of heavy metals from the cement pastes containing solid wastes including fly ash (FA), or municipal solid waste incineration fly ash (MSWI), was investigated by means of the tank test. Effects of two kinds of curing conditions (standard curing and natural curing) and carbonation on the leaching characteristics of heavy metals were studied. The environmental assessment relating to the leaching of heavy metals was also discussed. Results indicate that the leached heavy metals are mostly produced at early age of 28d, and subsequently decrease sharply to be undetected. Specimens subjected to the standard curing exhibit the lower \( \Sigma_{64d} \) leaching concentrations of heavy metals than those exposed to the natural curing. Specimens under carbonation show the highest \( \Sigma_{64d} \) leaching concentrations of heavy metals, compared with those at the standard curing and the natural curing. The long-term exposure of cement concrete containing MSWI and FA to the water environment may lead to the Cr pollution and the Cd pollution, respectively.

1. Introduction

With the rapid development of global economy, large quantities of solid waste materials have been generated. Owing to economic, technical, and environmental considerations, the use of various solid wastes has become very common in modern concrete construction. Most of these solid wastes contain various hazardous heavy metals, which can be solidified into the cement concrete. The solidification process is mainly attributed to the C-S-H phase, which can sorb large amounts of heavy metals, and prevent them from migration due to the low permeability of C-S-H. Owing to the high alkalinity of cement matrix, heavy metals also form the low soluble products to reduce the leaching. In addition to sorption and precipitation, heavy metals may enter the lattice of the hydrates, being firmly bound within the cement matrix \[1\].

In spite of the immobilization of heavy metals within the cement concrete, some studies show the risk of heavy metals leaching from the cement products containing solid wastes, especially when exposed to the flowing water or various severe environments \[2\]. Hardened cement paste is seriously attacked by these severe conditions, which induce the decrease in the alkalinity of cement matrix and the degradation of cement hydrates such as C-S-H, leading to the desorption of heavy metals from the cement matrix \[3\].

Curing conditions and carbonation are known as the important factors to affect the formation of cement hydrates, as well as the composition and alkalinity of cement matrix \[4\]. Therefore, this paper investigates the leaching behavior of heavy metals from the cement pastes containing two kinds of solid wastes (FA and MSWI). The effects of two types of curing conditions (standard curing and natural curing) and carbonation on the leaching characteristics are also studied. Finally, the quantities
of heavy metals leached during the course of the tank test are compared with the parametric values of GB 3838-02 to assess the leaching toxicity.

2. Experimental

2.1. Raw materials

42.5 moderate heat Portland cement (MHPC), Class I fly ash (FA) and municipal solid waste incineration fly ash (MSWI) were used in this study. Chemical compositions of these raw materials are given in Table 1. The total contents of heavy metals in these materials are shown in Table 2.

| Sample  | CaO  | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | R₂O | Loss |
|---------|------|------|-------|-------|-----|-----|-----|------|
| MHPC    | 62.1 | 21.7 | 4.1   | 5.0   | 4.8 | 0.8 | 0.4 | 0.2  |
| FA      | 3.24 | 58.95| 21.59 | 9.60  | 1.24| 0.14| 0.76| 0.92 |
| MSWI    | 20.37| 41.65| 7.46  | 13.2  | 14.3| 0.30| —   | —    |

| Sample | Cr  | Pb  | Cd  | Zn  | Cu  |
|--------|-----|-----|-----|-----|-----|
| MHPC   | 111.3| 662.5| 9.232| 838.5| 60.90|
| FA     | 45.22| 210.0| 32.54| 185.2| 96.62|
| MSWI   | 433.5| 323.1| 8.559| 1870 | 434.7|

2.2. Specimens preparation

Mix proportions used in making cement pastes are listed in Tables 3. Cement paste specimens (20×20×20 mm) were made and cured until 28d in accordance with the standard curing method (20 ± 3 °C, RH > 95%) and the outdoor natural curing method, respectively. Then half of the specimens subjected to the standard curing were moved into the carbonation chamber (20 ± 5 °C, RH = 70 ± 5%, CO₂ = 20 ± 3%) for 14d.

2.3. Experimental methods

The total contents of heavy metals in cement pastes were conducted in accordance with the acid digestion. The specimens were crushed and ground until more than 95% of the particles passing a 125μm sieve. 0.50g of ashed sample was weighed and put into a 10mL polytetrafluoroethylene beaker. 20mL of aqua regia and 20mL of HF were added and the slurry was heated until it nearly dried out. The beaker was washed with deionized water and dried out again by heating. After cooling, 1mL of nitric acid and 20mL deionized water were added to the beaker and heated at 90 ℃~100 ℃ until the sample dissolved completely. After cooling, the digestate was diluted to 100 ml with deionized water. Atomic absorption spectrophotometer was used to measure the contents of Cr, Pb, Cd, Zn and Cu.

| Set | w/b | MHPC | FA | MSWI |
|-----|-----|------|----|------|
| A   | 0.3 | 50%  | 50%| 0    |
| B   | 0.3 | 50%  | 0  | 50%  |

The successive leaching concentrations of heavy metals from cement pastes within 64d were conducted referring to the tank test defined by NEN 7375. The cement samples were immersed in the acetic acid solution (pH 7 and liquid/solid ratio =3) and kept in static conditions at a temperature of 20±2°C. At the end of each normalized immersion step (3, 7, 14, 21and 28 days), the eluate was separated, filtered, acidified, and stored for analysis and also replaced with fresh acetic acid solution. The final sample was taken after an immersion period of 64 days. The leachates corresponding to each immersion step were analyzed by inductively coupled plasma (ICP) to quantify the heavy metals.
3. Results and discussion

3.1. Total contents of heavy metals in cement pastes

The total content of the heavy metal is an essential parameter for the leaching characterization of cement concrete. The total contents of heavy metals in cement pastes are given in Table 4. The curing conditions and carbonation do not significantly modify the total heavy metal contents of specimens, which indicates that no evident heavy metals is leached during the curing and carbonation process. The composition of the cement paste is the main factor to affect the total contents of heavy metals within cement pastes. Owing to the highest amounts of Pb and Zn in cement, all the specimens exhibit the highest amounts of them. A specimens show higher amounts of Cd than B specimens, which is due to the higher numbers of Cd in FA than in MSWI. B specimens have higher contents of Cr, Pb, Zn and Cu than A specimens, which is also because MSWI possesses the higher contents of these heavy metals than FA.

Table 4  Total contents of heavy metals in cement pastes mg/kg

| Elements | A                                      | B                                      |
|----------|----------------------------------------|----------------------------------------|
|          | Standard Natural Carbonation            | Standard Natural Carbonation            |
| Cr       | 80.05 78.97 79.83                      | 262.1 261.9 262.1                      |
| Pb       | 393.9 385.8 395.6                      | 489.5 492.9 494.3                      |
| Cd       | 18.08 17.73 18.04                      | 7.287 8.181 7.286                      |
| Zn       | 514.7 511.7 514.5                      | 1309 1310 1306                         |
| Cu       | 74.28 74.24 74.68                      | 248.6 248.1 247.7                     |

Table 5  Leaching concentrations of Cr and its leached fraction for ∑64d

| Items | Conditions | 3d  | 7d  | 14d  | 21d  | 28d  | 64d  | ∑64d | GB3838 (≤, mg/L) |
|-------|------------|-----|-----|------|------|------|------|------|-----------------|
| A     | Standard   | 0.0185 | 0.0083 | 0.0015 | 0.0007 | ED   | ED   | 0.029 | 0.1              |
|       | Natural    | 0.0185 | 0.0135 | 0.0080 | 0.0005 | ED   | ED   | 0.040 |                 |
|       | carbonation| 0.0250 | 0.0130 | 0.0060 | 0.0010 | ED   | ED   | 0.045 |                 |
| B     | Standard   | 0.0755 | 0.0435 | 0.0115 | 0.0010 | ED   | 0.0010 | 0.132 |                 |
|       | Natural    | 0.0740 | 0.0455 | 0.0125 | 0.0050 | ED   | ED   | 0.137 |                 |
|       | carbonation| 0.0820 | 0.0665 | 0.0285 | 0.0085 | 0.0005 | 0.0025 | 0.188 |                 |

Table 6  Leaching concentrations of Pb and its leached fraction for ∑64d

| Items | Conditions | 3d  | 7d  | 14d  | 21d  | 28d  | 64d  | ∑64d | GB3838 (≤, mg/L) |
|-------|------------|-----|-----|------|------|------|------|------|-----------------|
| A     | Standard   | 0.0305 | 0.0110 | 0.0035 | 0.0005 | ED   | ED   | 0.045 | 0.1              |
|       | Natural    | 0.0320 | 0.0180 | 0.0105 | ED   | ED   | 0.0040 | 0.064 |                 |
|       | carbonation| 0.0370 | 0.0195 | 0.0080 | ED   | ED   | 0.0010 | 0.065 |                 |
| B     | Standard   | 0.0265 | 0.0122 | 0.0015 | 0.0008 | ED   | ED   | 0.041 |                 |
|       | Natural    | 0.0310 | 0.0174 | 0.0035 | 0.0006 | ED   | ED   | 0.052 |                 |
|       | carbonation| 0.0395 | 0.0165 | 0.0090 | ED   | ED   | 0.0005 | 0.065 |                 |
3.2. Successive leaching concentrations of heavy metals during the tank test

To investigate the leaching behavior of heavy metals from cement pastes, variation of heavy metals leached during the tank test over 64d was measured. The leaching concentrations for all the heavy metals fall sharply with increased length of immersion, regardless of the compositions of cement specimens, the curing conditions and carbonation (seen in Tables 5-9). In most cases, the leaching of heavy metals becomes undetected after 28d immersion. This behavior indicates that most of leached heavy metals are produced at early age, which is possibly because that the heavy metals are solidified within the cement matrix and the cement hydrates dissolve and diffuse into the solution during immersion. However, owing to the good density of cement pastes, the penetration of the solution into the cement paste becomes more slow and difficult with time. Once the balance of diffusion and dissolving is obtained, the leaching of heavy metals becomes insignificant.

| Items | Conditions | 3d  | 7d  | 14d | 21d | 28d | 64d | ∑64d |
|-------|------------|-----|-----|-----|-----|-----|-----|------|
| A     | Standard   | 0.0105 | 0.0051 | 0.0018 | 0.0006 | ED   | ED   | 0.0180 |
| A     | Natural    | 0.0120 | 0.0040 | 0.0015 | 0.0005 | ED   | ED   | 0.0190 |
|       | carbonation| 0.0165 | 0.0042 | 0.0020 | 0.0008 | ED   | ED   | 0.0235 |
| B     | Standard   | 0.0014 | 0.0006 | ED   | ED   | 0.0005 | ED   | 0.0025 |
| B     | Natural    | 0.0049 | 0.0010 | ED   | 0.0006 | ED   | ED   | 0.0065 |
|       | carbonation| 0.0055 | 0.0017 | 0.0008 | ED   | ED   | ED   | 0.0080 |

Table 8 Leaching concentrations of Zn and its leached fraction for ∑64d

| Items | Conditions | 3d  | 7d  | 14d | 21d | 28d | 64d | ∑64d |
|-------|------------|-----|-----|-----|-----|-----|-----|------|
| A     | Standard   | 0.2950 | 0.1170 | 0.0485 | 0.0120 | 0.0035 | 0.0105 | 0.486 |
| A     | Natural    | 0.3205 | 0.1445 | 0.0375 | 0.0115 | 0.0005 | 0.0080 | 0.522 |
|       | carbonation| 0.3455 | 0.1285 | 0.0495 | 0.0105 | 0.0020 | 0.0120 | 0.548 |
| B     | Standard   | 0.6865 | 0.3595 | 0.1005 | 0.0495 | 0.0110 | 0.0265 | 1.233 |
| B     | Natural    | 0.7170 | 0.3590 | 0.1225 | 0.0630 | 0.0245 | 0.0355 | 1.321 |
|       | carbonation| 0.7935 | 0.4790 | 0.1860 | 0.0630 | 0.0275 | 0.0415 | 1.590 |

3.3. ∑64d Leaching concentrations versus the parametric values (GB 3838-02)

Not all of the heavy metals in concrete are dissolved, even under the extremely severe environmental exposure. Thus, the soluble amounts of heavy metals are more suitable to evaluate the environmental safety of materials. In this paper, ∑64d Leaching concentrations of heavy metals are used to represent the soluble amounts of heavy metals in cement pastes, and compared with the parametric values of GB 3838-02 (Assessment standard for surface water environmental quality- Grade V surface water) to assess the risk of contamination due to the leaching of heavy metals from cement pastes.

| Items | Conditions | 3d  | 7d  | 14d | 21d | 28d | 64d | ∑64d |
|-------|------------|-----|-----|-----|-----|-----|-----|------|
| A     | Standard   | 0.0190 | 0.0060 | 0.0010 | 0.0005 | ED   | ED   | 0.026 |
|       | GB383       | 8   | ≤   |     |     |     |     | 1.0  |
Comparison of the leaching concentrations of heavy metals for $\Sigma 64d$ against the parametric values of GB 3838-02 is shown in Tables 5-9. It can be seen that most of the specimens exhibit lower values than those of GB 3838-02. However, the $\Sigma 64d$ leaching concentrations of Cr for B specimens and Cd for A specimens are higher than the parametric values. Since Grade V surface water is heavily polluted, it is supposed that the concrete incorporating solid wastes may cause relatively low risk of contamination by heavy metals; while the long-term exposure of cement concrete containing MSWI and FA to the water environment may lead to the Cr pollution and the Cd pollution, respectively.

4. Summary
This paper investigates the leaching behavior of heavy metals from cement pastes containing solid wastes. The leached heavy metals are mostly produced at early age of 28d, and subsequently decrease sharply to be undetected. Curing conditions and carbonation have large influence on the leaching of heavy metals from cement pastes. Specimens subjected to the standard curing exhibit the lower $\Sigma 64d$ leaching concentrations and leached fractions of heavy metals than those exposed to the natural curing. Specimens under carbonation show the highest $\Sigma 64d$ leaching concentrations and leached fractions of heavy metals, compared with those at the standard curing and the natural curing.

$\Sigma 64d$ Leaching concentrations of heavy metals are compared with the parametric values of GB 3838-02 to assess the risk of contamination due to the leaching of heavy metals. It is supposed that the long-term exposure of cement concrete containing MSWI and FA to the water environment may lead to the Cr pollution and the Cd pollution, respectively.

Acknowledgement
The authors acknowledge support from China Hubei Province Education Department Natural Science Research Item (SN: D20141204).

References
[1] Q.Y. Chen, M. Tyrer, C.D. Hills, et al. Immobilisation of heavy metal in cement-based solidification/stabilisation: A review [J]. Waste Management, 2009, 29(1): 390-403.
[2] Anne-Marie Marion, Michel De Lanèève, Alain De Grauw. Study of the leaching behaviour of paving concretes: quantification of heavy metal content in leachates issued from tank test using demineralized water [J]. Cement and Concrete Research, 2005, 35: 951-957.
[3] ZHOU Shihua, WANG Yingchun, SU Jie, et al. Review on leaching methods of heavy metal ions in concrete [J]. Concrete, 2009, (7): 8-10.
[4] Evi Aprianti, Payam Shafigh, Rodiah Zawawi, et al. Introducing an effective curing method for mortar containing high volume cementitious materials [J]. Construction and Building Materials, 2016, 107: 365-377.