Differences in the desorption properties of heavy metals from cement hydrates in various chloride solutions

Akihiko Hayashi[1], Hiromitsu Kikuchi[2], Shinya Yokoyama[3] and Kenji Kawai[4]

[1]*Hiroshima University, Japan*
[2]*IHI Corporation, Japan*
[3]*Kobe University, Japan*
[4]*Hiroshima University, Japan*
[*1]*1-3-2 Kagamiyama Higashi-Hiroshima, Hiroshima 739-8511 Japan ,*
nicolasdeka@gmail.com
[*2]*TOYOSU IHI BUILDING., 1-1, Toyosu 3-chome, Koto-ku, Tokyo 135-8710, Japan,*
hiromitsu_kikuchi@iis.ihi.co.jp
[*3]*1-1 Rokkodai-cho, Nada-ku, Kobe-shi, Hyogo 657-8501, Japan,*
shinyayokoyoko@gmail.com
[*4]*1-3-2 Kagamiyama Higashi-Hiroshima, Hiroshima 739-8511 Japan ,*
kkawai@hiroshima-u.ac.jp

ABSTRACT

Recently, it has been expected that municipal wastes and industrial by-products can be used as concrete materials, but there is a possibility that municipal wastes and industrial by-products may contain heavy metals. Accordingly, heavy metals in concrete may be leached into the environment. It is important that the heavy metals leaching mechanisms are understood to evaluate and to prevent heavy metals leaching. In this study, the adsorption and desorption properties of cement pastes in various chloride solutions were investigated. Lead was used as the heavy metal. As a result, after lead ions have been adsorbed on the cement hydrate, a large number of lead ions desorbed from the cement hydrate in a calcium chloride solution, while very few lead ions desorbed in deionized water and in lithium, sodium, and potassium chloride solutions. Especially about 70 % of lead ions desorbed when 35 % and 40 % of calcium chloride solutions were used.

Keywords. Heavy metal, adsorption, desorption, lead, chloride

INTRODUCTION

Recently, it has been expected that municipal wastes and industrial by-products can be used as concrete materials to reduce the environmental impact, and in the future it is estimated that more and more various municipal wastes and industrial by-products will be used for concrete materials. However, there is a possibility that municipal wastes and industrial by-products may contain hazardous substances such as heavy metals which affect both humans and the environment. Accordingly, heavy metals in concrete may be leached into the environment. (JSCE, 2003) In addition, concrete changes from original state because

concrete products are reused as recycled aggregates as well as roadbed materials, and would be exposed to various environments. Therefore, heavy metal leaching evaluation must include service, reuse, and final disposal, and it is necessary to understand the heavy metals leaching mechanisms with regards to usage, deteriorations as well as exposed environment of concrete.

It is known that heavy metal ions are easily fixed in cement hydrates. (Takahashi, 1973) On the other hand, it is supposed that they contact with chlorides such as de-icing salt when reused as roadbed materials as well as seawater when used as coastal structures, but in such situations, the behavior of adsorbed heavy metals is not clear. Therefore, in this study, the desorption behavior of heavy metals adsorbed on cement hydrates attacked by chlorides were investigated, and based on these knowledge, this study aims at understanding the leaching mechanisms of heavy metal.

EXPERIMENTS

Materials. As fundamental research in this study, cement pastes were used. Cement pastes with a water-cement ratio of 0.40 pulverized to less than 40 μm was prepared. Ordinary Portland cement and deionized water were used as cement and mixing water, respectively. Lead ions were dealt with as a heavy metal, and lead(II) nitrate solution was used as the heavy metal solution.

Adsorption Test. One gram of cement paste powder was added in 20 mL of deionized water, and was stirred for 10 hours. After that, 1mL of solution containing a certain concentration of lead ions was added, and then stirred for 6 more hours. In this test, 0.5, 1, 2, 4, 8, 10, 12, 16, 20, and 25 g/L of lead ions were used as heavy metal solutions. After stirring, the solution was filtrated with a membrane-filter and the concentration of heavy metal ions in the solution was determined with an atomic adsorption spectrophotometer. **Figure 1** illustrates the experimental methodology of the adsorption test.

Desorption Tests. Tests (a), (b), (c), and **(d)** were carried out to understand the desorption characteristics of heavy metals adsorbed on cement pastes.

(a) Time Dependent Test for Desorption Amount. The residue after filtration in the adsorption test and deionized water were used in this test. In this test, the residue used was obtained from filtration of solution containing 1mL of 5 g/L of lead ions that was stirred for 6 hours in the adsorption test. In this test, One gram of the sample was added in 20 mL of deionized water, and was stirred for fixed periods of times (1, 3, 5, 10, 20, 30, 60, 120, 240, 360, 540, 720, and 1440 minutes). After stirring, the solution was filtrated with a membrane-filter and the concentration of heavy metal ions in the solution was determined with an atomic adsorption spectrophotometer.

(b) Desorption Test with Deionized Water. The residue after filtration in the adsorption test and deionized water were used in this test. In addition, the residue used was obtained from filtration of solution containing every concentration of lead ions in the adsorption test. One gram of the sample was added in 20 mL of deionized water, and was stirred for 10 hours. After stirring, the solution was filtrated with a membrane-filter and the concentration of heavy metal ions in the solution was determined with an atomic adsorption spectrophotometer.

(c) Desorption Test with Chloride Solutions. The residue after filtration in the adsorption test and chloride solutions were used in this test. In addition, the residue used was obtained from filtration of solution containing 1mL of 10, 12, 16, 20, and 25 g/L of lead ions that was stirred for 6 hours in the adsorption test. NaCl, KCl, LiCl, and $CaCl_2.2H_2O$ solutions were dealt with chloride solutions, and concentrations of each chloride solution were 1, 3, and 10 mass%. Only when the solution was $CaCl_2.2H_2O$ solution, 20, 25, 30, 35, 40, and 45 mass% of $CaCl_2.2H_2O$ solutions were used. One gram of the sample was added in 20 mL of chloride solutions, and was stirred for 10 hours. After stirring, the solution was filtrated with a membrane-filter and the concentration of heavy metal ions in the solution was determined with an atomic adsorption spectrophotometer.

(d) Repeated Desorption Test. The residue after filtration in the adsorption test and $CaCl_2.2H_2O$ solution (20 %) were used in this test. In addition, the residue used was obtained from filtration of solution containing 1mL of 12, 16, 20, and 25 g/L of lead ions that was stirred for 6 hours in the adsorption test. One gram of the sample was added in 20 mL of $CaCl_2.2H_2O$ solution (20 %), and was stirred for 2 hours. After stirring, the solution was filtrated with a membrane-filter and the concentration of heavy metal ions in the solution was determined with an atomic adsorption spectrophotometer. (process 1) The residue after filtration in process 1 was added into 20 mL of $CaCl_2.2H_2O$ solution (20 %) again, and was stirred for 2 hours. After stirring, the solution was filtrated with a membrane-filter and the concentration of heavy metal ions in the solution was determined with an atomic adsorption spectrophotometer. (process 2) The same operation as process 2 was carried out. (process 3)

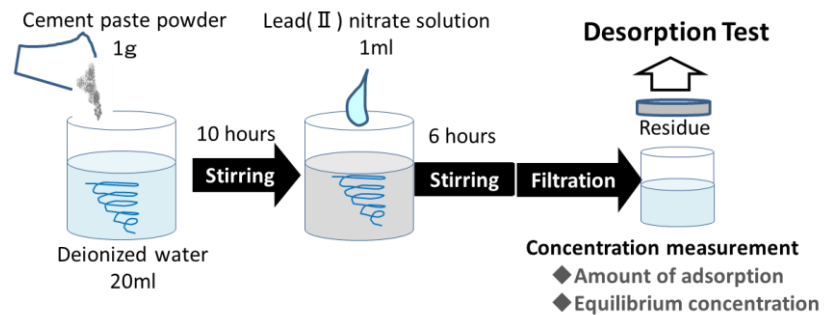**Figure 2** illustrates the experimental methodology of **Tests (a), (b), (c),** and **(d).**

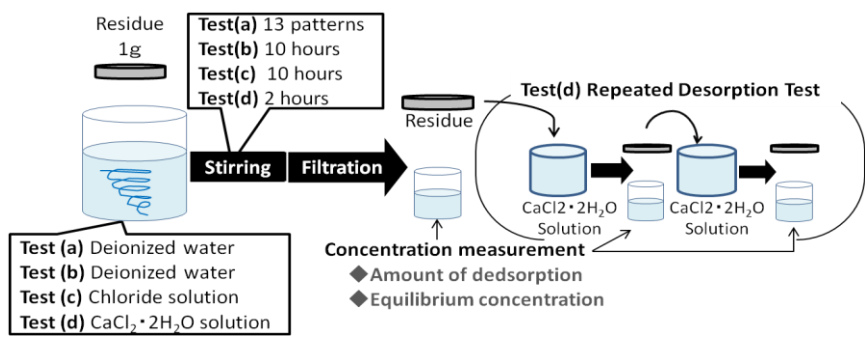
Figure 1. Adsorption test

Figure 2. Desorption test

RESULTS AND DISCUSSIONS

Adsorption Test. The adsorption isothermal curve of lead ions for cement pastes is shown in **Figure 3**. It is known that the adsorption isothermal curve for lead ions and cement hydrates can be approximated by the Freundlich isotherm equation represented as **Eq. (1)**. For the specimens in this test, the isothermal curve can also be classified into the Freuindlich equation represented in **Eq. (2)**

$$V = aC^{\frac{1}{n}} \tag{1}$$

$$V = 2.0C^{\frac{1}{1.41}} \tag{2}$$

where V is the amount of adsorption, C is the equilibrium concentration, and a and n are constants given for adsorbate and adsorbent at a particular temperature.

Desorption Test.

(a) Time Dependent Test for Desorption Amount. Time-dependent change in the depsoption amount of lead ions is shown in **Figure. 4**. In this figure, it is found that the desorption amount was 0.06 mg/cement-g at 1minutes, thereafter, the values were steady within the range from 0.08 to 0.09 mg/cement-g. The initial adsorption amount in this test was about 5 mg/L. Therefore, the desorption amount corresponds to 2 % of the adsorption amount, and is very small.
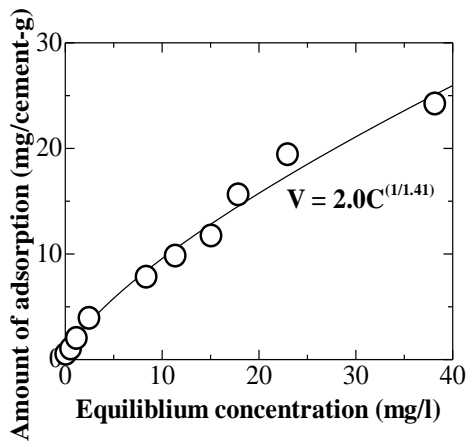

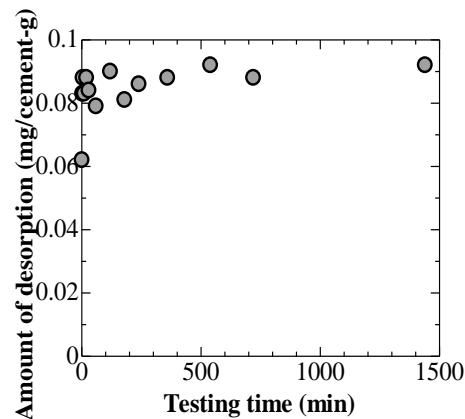**Figure 3. Adsorption test; the adsorption isothermal curve**

Figure 4. Test (a); the time dependent change for the amount of desorption

(b) Desorption Test with Deionized Water. Figure 5 shows the relationship between the adsorption amount and the desorption amount. In addition, **Figure 6** shows the relationship between each equilibrium concentration of lead ions and the amount of adsorption after the adsorption test and the desorption test.
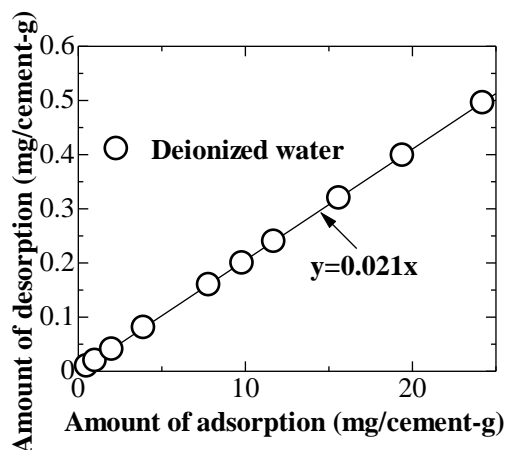

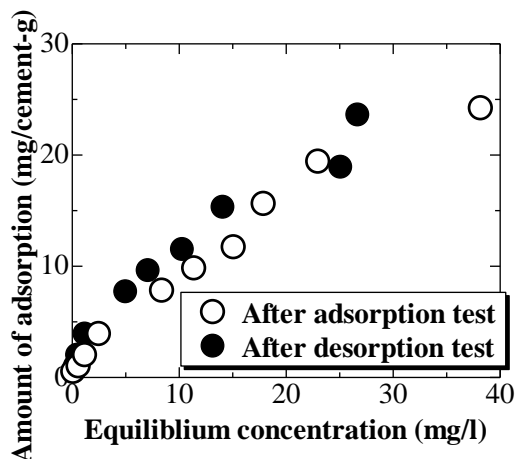**Figure 5. Test (b); the relationship between the amount of desorption and the amount of adsorption.**

Figure 6. The adsorption isothermal curves after the adsorption test and the desorption test.

Figure 5 shows a linear relationship between the initial adsorption amount and the desorption amount. The slope of the approximate line was 0.021; which implies that, almost 2 % of adsorbed lead ions were desorbed from cement hydrates in proportion to the adsorption amount. On the other hand, in the previous study, adsorption of lead ions by cement hydrates depended on C-S-H, and decomposition of C-S-H such as carbonation and diffusion resulted in the change of adsorption amount of lead ions. (Sato, 2008) However, **Figure 6** shows the isothermal curves after the adsorption test and the desorption test, and there is little or no difference between both curves. This result indicates that decomposition of cement hydrates resulting in effecting adsorption and desorption properties did not occur at least during 10 hours desorption process in this test. From the above, it is thought that lead ions adsorbed on fine cement hydrates barely desorbed into deionized water.

(c) Desorption Test with Chloride Solutions. Figures 7, 8, 9, and **10** show the relationship between the adsorption amount and the desorption amount of each concentration of NaCl, KCl, LiCl, and $CaCl_2.2H_2O$ solutions. **Figure 11** shows the comparison of desorption amount between four chloride solutions and their concentrations for the sample whose initial adsorption amount is about 24 mg/cement-g.
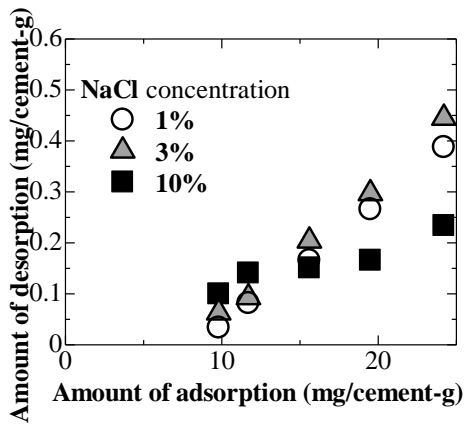
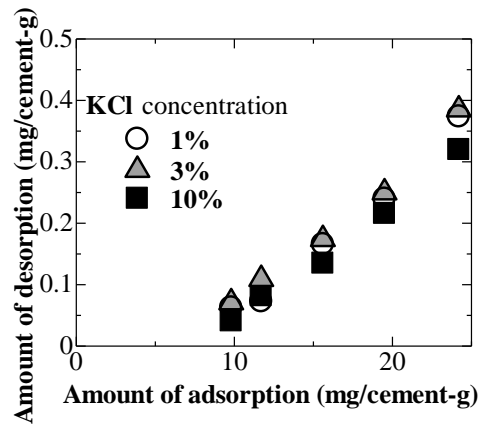**Figure 7. Test (c); the amount of desorption in NaCl solution.**

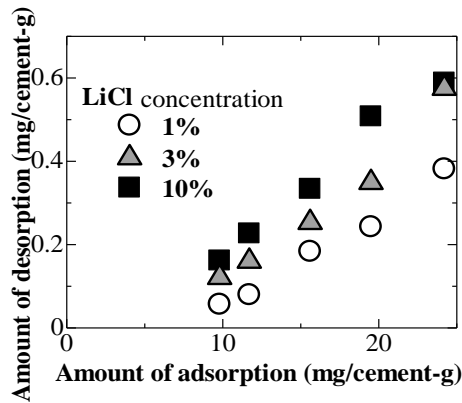**Figure 8. Test (c); the amount of desorption in KCl solution**

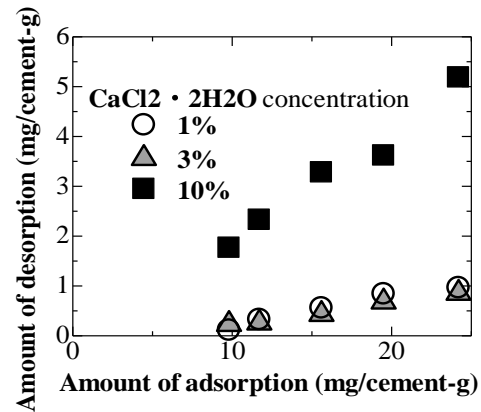**Figure 9. Test (c); the amount of desorption in LiCl solution**

Figure 10. Test (c); the amount of desorption in CaCl$_2$.2H$_2$O solution
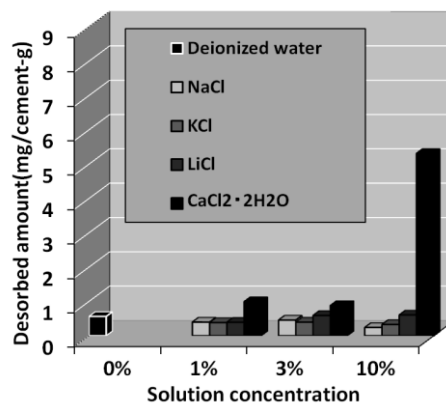

Figure 11. The amount of desorption in each solution
(The initial amount of adsorption is about 24 g/cement-g)

From **Figure 7**, a linear relationship can be seen between the initial adsorption amount and the desorption amount for NaCl solution, such as in the case of deionized water. In addition, the desorption amount was about 1-2 % of the initial adsorbed amount for each concentration, although the desorption amount differed slightly between the concentrations of the solution. The results for KCl and LiCl solutions shown in **Figure 8** and **Figure 9** are also similar to the result for NaCl solution, and it is found that the desorption amount of lead ions for these solutions is not significantly large.

On the other hand, **Figure 10** and **Figure 11** show that the desorption amount of lead ions is about 4 % of the initial adsorption amount for 1 and 3 % of $CaCl_2.2H_2O$ solution, and a little larger than for the other solutions. Furthermore, the desorption amount increased to 20% of the initial adsorption amount for 10 % of $CaCl_2.2H_2O$ solution, and the different tendency with the other chloride solutions was observed.

The desorption test was carried out to understand the maximum desorption ratio (the ratio of the desorption amount to the initial adsorption amount) of lead ions with 20, 25, 30, 35, 40, and 45 % of $CaCl_2.2H_2O$ solutions. **Figure 12** shows the relationship between the desorption amount and the initial adsorption amount for each concentration of the solutions, as well as **Figure 13** shows concentration of lead ions in each concentration of the solution and the adsorbed amount after the desorption test.
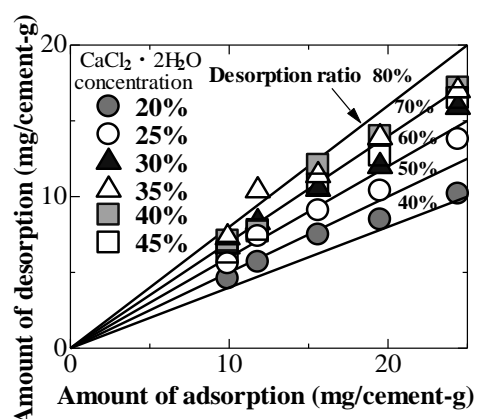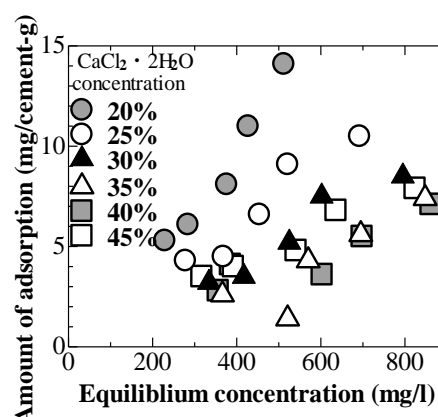

Figure 12. Test (c); the amount of desorption in $CaCl_2.2H_2O$ solution

Figure 13. The isothermal curves after the desorption test in $CaCl_2.2H_2O$ solution

The five lines in **Figure 12** represent the percentage of the desorption amount in relation to the adsorption amount, and the percentage was defined as the desorption ratio. The desorption ratio for each line is 80 %, 70 %, 60 %, 50 %, and 40 %. The desorption ratio of lead ions increased with the increase in the concentration of the solution within the range of the concentration from 20 % to 40 %, be maximum for 40 % of $CaCl_2.2H_2O$ solution, and the value of the desorption ratio was over 70 %. In addition, the desorption ratio for 45 % $CaCl_2.2H_2O$ solution was about the same as for 40 % of $CaCl_2.2H_2O$ solution. On the other hand, in **Figure 13**, focusing on the desorption amount for 20 % of $CaCl_2.2H_2O$ solution, the desorption amount of lead ions increased drastically at the lead ions concentration of about 400 mg/L, and the drastic increase in the desorption amount was also noticed for the other concentrations of $CaCl_2.2H_2O$ solution, though the concentration of lead ions at the increase point differed with the concentration of $CaCl_2.2H_2O$ solution. It is thought that some lead ions could be precipitated, and this causes the apparent increase in the adsorption amount.

(d) Repeated Desorption Test. Figure 14 shows the relationship between cumulative desorption amount after this test and the initial adsorption amount of lead ions. **Figure 15** shows the relationship between the adsorption amount of lead ions at the start of each process in this test and the desorption amount of lead ions at the end of each process.
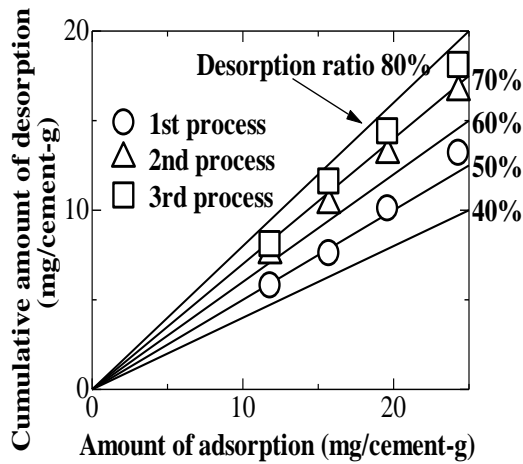

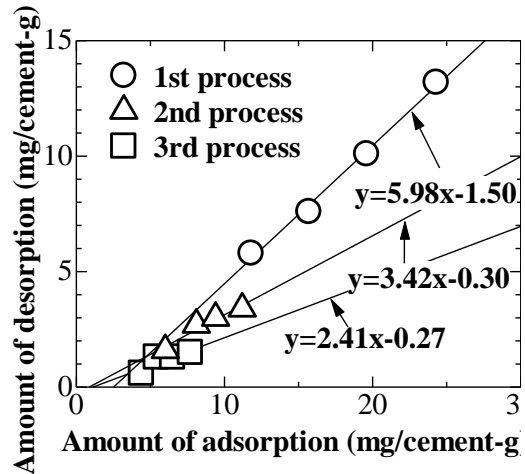**Figure 14. Test (d); the cumulative amount of desorption of lead ions**

Figure 15. Test (d); the amount of desorption at each process

Figure 14 shows that desorption of lead ions proceeds by repeating the desorption process for $CaCl_2.2H_2O$ solution. Furthermore, **Figure 15** shows the ratio of the desorption amount to the adsorption amount at the start of each process decreased in every process. If cement hydrates as solid phase and $CaCl_2.2H_2O$ solution as liquid phase had not been changed, the ratio of the desorption amount to the adsorption amount at the start of each process could be constant in every process, but in this test, the ratios were different in every process. A previous study reports that $Ca(OH)_2$ reacts with $CaCl_2$ such as **Eq. (3)**, (Kuga, 2011), and in this test, it is suggested that the cement hydrates altered by the same reaction as **Eq. (3)**.

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3CaO \cdot CaCl_2 \cdot 15H_2O \tag{3}$$

CONCLUSIONS

(1) Lead ions adsorbed on cement hydrates begin to be desorbed quickly in deionized water, and the desorption of lead ions is in equilibrium on three minutes.

(2) A linear relationship is obtained between the initial adsorption amount and the desorption amount for every chloride solution of NaCl, KCl, LiCl, and $CaCl_2.2H_2O$ solution, and deionized water.

(3) The desorption amount is about 1-2 % of the initial adsorbed amount for each concentration of NaCl, KCl, and LiCl solution, and deionized water. The desorption amount of lead ions is about 4 % of the initial adsorption amount for 1 and 3 % of $CaCl_2.2H_2O$ solution, and the desorption amount increased to 20 % of the initial adsorption amount for 10 % of $CaCl_2.2H_2O$ solution.

(4) The desorption ratio of lead ions increases with the increase in the concentration of the solution within the range of the concentration from 20 % to 40 %. When 40 % of $CaCl_2.2H_2O$ solution was used, the desorption ratio was maximum, and was about 70 %.

(5) Desorption of lead ions proceeded by repeating the desorption process for $CaCl_2.2H_2O$ solution. On the other hand, the ratio of the desorption amount relative to the initial adsorption amount in each process decreased by repeating the desorption process.

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