

Modeling of Coupled Mass Transport and Chemical Equilibrium in Cement-Solidified Soil Contaminated with Heavy Metal Ion

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ABSTRACT

The purpose of this research is to simulate and predict the stabilization and leaching process of hexavalent chromium from cement-solidified soil. An existing analytical system named DuCOM, which principally deals with cementitious materials, is expanded to apply to soil materials in this study. Firstly, mass conservation equation of chromium is formulated and added to the existing system. In order to obtain the solid-liquid equilibrium, chromium binding capacity of cement hydrates is experimentally identified with different ratios of chromium concentration and cement hydrates amounts. After that, tank leaching tests in the previous research are simulated with the proposed analytical model for verification. Leached amounts of chromium from cement-solidified soil are calculated and the results show that the system can simulate the tank leaching test under various conditions reasonably. Furthermore, by coupling the system with geochemical calculations, the effects of different redox conditions of soils are studied and discussed.

Keywords. Hexavalent Chromium, Leaching, Cement-Soil Composites, Thermodynamic model, Redox condition

INTRODUCTION

Cement products are now made from not only raw materials such as lime stone and clay, but also by-products and waste materials. It is known that all the ingredients often contain tiny amounts of hazardous components, among which chromium compounds are usually regarded as with the highest environmental risk. In the process of burning cement clinkers, trivalent chromium contained in clinkers turns into hexavalent chromium, which is a strong oxidizer. The existence of a tiny amount of hexavalent chromium in cement matrix is not so critical because the chromium is fixed chemically and physically by the hydrates. However, the cement-solidified soil is more porous and permeable, so some amounts of hexavalent chromium can leach from the mass and contaminate the surrounding water.

To assess the environmental risks regarding chromium in cemented soils, standard shaking tests with 2 mm size crushed specimens or tank leaching tests with small mass specimens are

often used (Takahashi *et al.* 2007). However, those tests can evaluate only leaching properties of small specimens, whereas in real sites other critical factors exist, such as disturbance or buffering effect with soils. In order to evaluate the leaching process appropriately, it is necessary to consider chemo-physical reactions such as hydration and chromium stabilization, as well as mass transport and equilibrium simultaneously.

To access this issue, in this study, a new model for chromium leaching is proposed. Based on the existing analytical system for cement-soil composite materials, the transport and equilibrium model of chromium is added and the applicability is verified with systematic experimental data. Studies about the influence of other co-existing ions and redox condition by geochemical models are also reported.

MODELING OF CHROMIUM LEACHING

Thermodynamic analytical system. As previously indicated, chromium leaching from cemented soil is strongly related with the processes of cement hydration, micro-pore structure formation and moisture distribution. To simulate the life-span properties of cementitious and soil materials, a multi-scale computational system called DuCOM has been developed (Maekawa *et al.* 2008) (Figure 1). This system consists of a series of thermo-chemo-physical models dealing with cement hydration, pore structure formation, moisture transport, and transport and equilibrium of various ions in pore solution. In the pore structure model, a multi-distribution formula is used to describe the nano/micrometre-scale pores in cement as well as millimetre scale pores in soil, thus the system is applicable to cement-soil composite materials. In this study, chromium transport and equilibrium model is established and integrated into this analytical scheme.

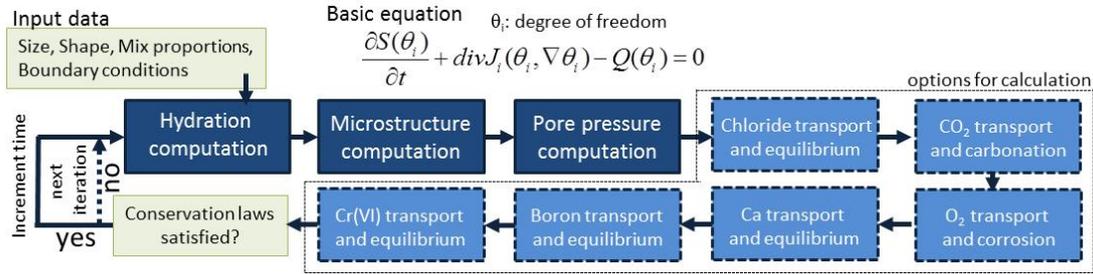


Figure 1. Overall scheme of DuCOM chemo-physical coupled system

Mass Conservation Law for Chromium. The transport and equilibrium of chromium must obey the conservation law. Accordingly, a mass conservation equation is established as below, referring to the calcium model formulated by Nakarai *et al.* (2005)

$$\frac{\partial}{\partial t}(\phi \cdot S \cdot C_{ion}) + \frac{\partial C_{bound}}{\partial t} - divJ_{ion} = 0 \quad (1)$$

where ϕ is the porosity [m^3/m^3], S is the degree of saturation in pore spaces, C_{ion} is the molar concentration of chromate ions in the liquid phase [$mmol/m^3$], C_{bound} is the amount of bound chromium per unit volume [$mmol/m^3$], and J_{ion} is the flux of chromate ions [$mmol/m^2/s$]. The first and second terms in Eq. 1 represent the increments in the amount of chromium in the liquid and solid phases per unit time and volume respectively. Here, valence of chromium ion is regarded unchanged, because pH and redox potential are generally high enough to

keep the hexavalent shape (Takahashi, 2008). Effects of pH and redox conditions are discussed and described later.

The flux of chromate ions in a porous media is written as

$$J_{ion} = -\left(\frac{\phi \cdot S}{\Omega} \cdot \delta \cdot D_{ion}\right) \cdot \nabla C_{ion} + \phi \cdot S \cdot \mathbf{u} \cdot C_{ion} \quad (2)$$

where Ω is tortuosity, δ is constrictivity, D_{ion} is the diffusion coefficient [m^2/s], \mathbf{u} is the velocity vector of a solution flow in pores [m/s]. The first term in Eq. 2 represents the flux of chromate ion due to diffusion by concentration gradient and the second term represents the advection constituent part in chromate ion flux.

Solid-liquid equilibrium for chromium. To formulate the liquid-solid equilibrium about chromium, binding test with cement paste was conducted. Using ordinary Portland cement and 19.2 mmol/l K_2CrO_4 solution, cement paste specimens were made with $\phi 50 \times 100$ mm cylinder molds. W/C ratios are 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0. To reduce the segregation, 0.5-2.0 % [of water weight] amount of viscosity improvers were added to the specimens.

After 7-day sealed curing, specimens were crushed into 1-2 mm size and then shaken for 2 hours in the water with specific specimen-to-water ratios shown as Table 1. During the shaking, chromium in specimen was leached into the water and thought to reach the equilibrated state. After that, the water was filtrated and chromium amounts in the filtrated water were measured with inductively-coupled plasma atomic emission spectroscopy (ICP). The measured results are shown in Figure 2. Higher W/C and lower specimen-to-water ratio show the high chromium concentrations. It reveals the fact that the equilibrium point depends on hydrates volume and water volume, which vary according to W/C or specimen-to-water ratios.

Table 1. Shaking Condition

Specimen-to-water ratio	Specimen weight [g]	Water weight [g]
5	5.0	25
10	5.0	50
20	5.0	100
40	2.5	100
100	1.0	100
400	0.25	100

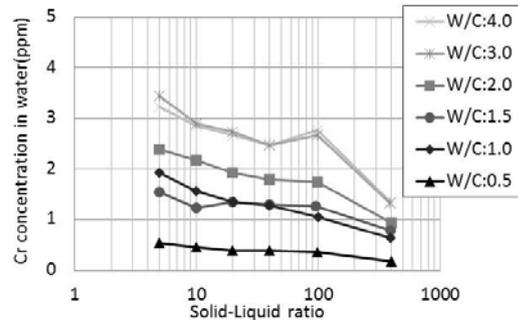


Figure 2. ICP measurement results

Crushed specimens were also used to measure the cement hydrate volumes. Specimens were soaked into acetone to prevent the hydration, dried for 24hours in 40°C- RH60% condition, and crushed into powder with 10 μm size by agate mortars. Then, powdered specimens were analysed with thermogravimetical analyser (TGA) and X-ray diffractometer (XRD). In the TGA measurement, temperature rise rate was 20°C/min. Weight decrements from 40 °C to 600 °C were measured. The influence of decarboxylation of $CaCO_3$ is assumed negligible in the temperature range, so this temperature is considered suitable to measure the total water amount in the cement hydrates. In the XRD analyses, 10% of sample powder was replaced by $\alpha-Al_2O_3$ as standard substance, and Rietveld

analyses were conducted with C_3S , C_2S , C_3A , C_4AF , $Ca(OH)_2$, $CaCO_3$, ettringite, monosulfate, and Al_2O_3 as object substances. Results of TGA measurements are shown in Table 2. Weight decrement during 40-600°C increases slightly as W/C increases, which is thought to be caused by the porosity increase in high W/C cement hydrates. With these TGA measurement results and the hydration degree of each clinker obtained by Rietveld analyses, degrees of hydration are calculated as Table 2.

Table 2. The results of TGA and XRD analyses

Water to cement ratio	0.5	1.0	1.5	2.0	3.0	4.0
(40-600°C weight decrement) / (600°C weight) [%]	18.6	19.7	20.4	20.7	21.3	20.9
Calculated degree of hydration [%]	81.0	77.2	67.7	76.2	80.1	76.7

Calculated degrees of hydration have variations in spite of the same material ages. One possible reason is the object substances of the Riedveld analyses. In this study, object substances which do not contain chromium were used in the analyses, since databases of substances containing chromium is unavailable. In future, it is needed to collect the XRD data of chromium-contained hydrates, and the accuracy of the analyses will be further improved.

Using ICP measurement results and calculated degree of hydration above, solid-liquid relations about chromium in cement matrix are plotted as Figure 3. C_{ion} is the molar concentration of chromate ions in the liquid phase [mmol/m³], C_{bound} is the amount of bound chromium per unit volume [mmol/m³]. It can be found that higher concentration of chromate ions makes bound chromium amount higher.

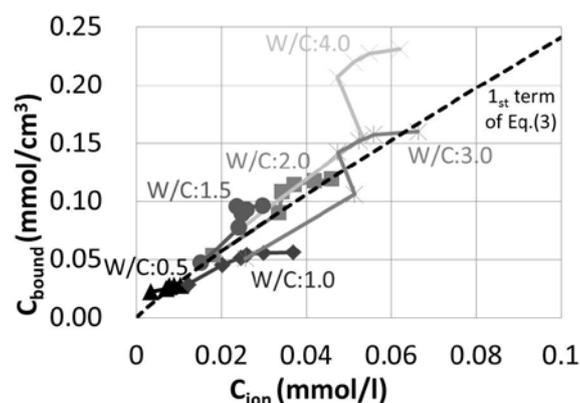


Figure 3. Solid-liquid relationship about chromium in cement paste matrix

Table 3. The results of beaker leaching test with sand(PWRI, 2000)

Cr concentration in liquid phase [mg/l]	0.026	0.19	0.5	6.5	87
Bound Cr amount [mg/kg]	0.71	3.4	6.1	34	131

For sandy soil, beaker leaching tests were conducted by PWRI (2001) and the results shown in Table 3 were reported. From these relationships in Figure 3 and Table 3, solid-liquid equilibrium of chromium in cement-soil composite materials is formulated as Eq. 3.

$$C_{bound} = 1.8 \times 10^6 \cdot C_{ion}^{0.90} \cdot V_h + 2.0 \times 10^3 \cdot C_{ion} \cdot V_s \quad (3)$$

where V_h is the volume of cement hydrates [m^3/m^3], V_s is volume of sand [m^3/m^3]. The first term in Eq. 3 corresponds to the bound chromium amount to cement hydrates. It is the summation of adsorbed chromium on the hydrates surface and bound chromium as a solid solution phase in the hydrates. The second term corresponds to the adsorbed chromium amount to sandy soil and is formulated by the linear isotherm. It should be noted that the formula is only applicable to sandy soil, while for other soil types the formula should be reconstructed based on their intrinsic adsorption properties. In the analyses, volume of cement hydrates, V_h , is calculated by the hydration and micro-pore structure models in DuCOM, so the time-dependent chromium binding capacity in cement hydrates can be simulated quantitatively.

VERIFICATION

Test methods and analytical conditions. The proposed model is verified by tank leaching test conducted by PWRI (2000). In the experiment, specific amounts of potassium bichromates were added to the sandy soil and after one day, the contaminated sands were solidified with ordinary Portland cement in the $\phi 50 \times 100$ mm cylinder molds or 400mm*400mm*400mm cubic molds. Tamping procedure is based on JGS0811 Standard and after specific sealed curing, the specimens were soaked into water with 1:10 of specimen-water weight ratio. Then, time-dependent changes of chromium concentration in water were measured with diphenylcarbazide method. Experimental parameters are shown in Table 4. Chrome amount [mg/l] represents shaking test results of each contaminated soil before solidification with cement.

Table 4. Experimental parameters

Test series	Chrome amount [mg/l]	Cement Amount [kg/m^3]	Curing time [day]	Specimen Size [mm]
1d-100	2.91	100	1	$\phi 50 \times 100$
1d-100-m	7.59	100	1	$\phi 50 \times 100$
1d-100-h	12.56	100	1	$\phi 50 \times 100$
0d-0	2.91	0	0	$\phi 50 \times 100$
1d-50	2.91	50	1	$\phi 50 \times 100$
0d-100	2.91	100	0	$\phi 50 \times 100$
7d-100	2.91	100	7	$\phi 50 \times 100$
1d-100-h-L	11.61	100	1	400*400*400

Table 5. Mix proportions in analyses

Cement amount [kg/m^3]	Unit weight [kg/m^3]			Void [%]
	Water	Cement	Sand	
0	0	0	2140	21
50	188	50	2090	2
100	182	100	2030	3

Based on the proposed model, analyses are conducted with fully saturated condition in one dimension. The meshes for calculations consist of cemented-soil part and water part and the volume ratio of the two parts is the same as experimental situation. Mix proportions in analyses are shown in Table 5. Each weight is determined by supposing that the specimens have been tamped with the optimal moisture content. Void means the rate of large pores existing between sand particles.

Test results. Figure 4 shows the results of tank leaching tests with different conditions, i.e. (i) different chrome amounts, (ii) different cement amounts, (iii) different curing times, and (iv) different specimen sizes. Vertical axis is the measured chromium concentration [mg/l] in water surrounding the specimen, and horizontal axis is the time [day] from start of leaching. Dots represent the experimental results (PWRI, 2000) and lines are the analytical results with proposed model.

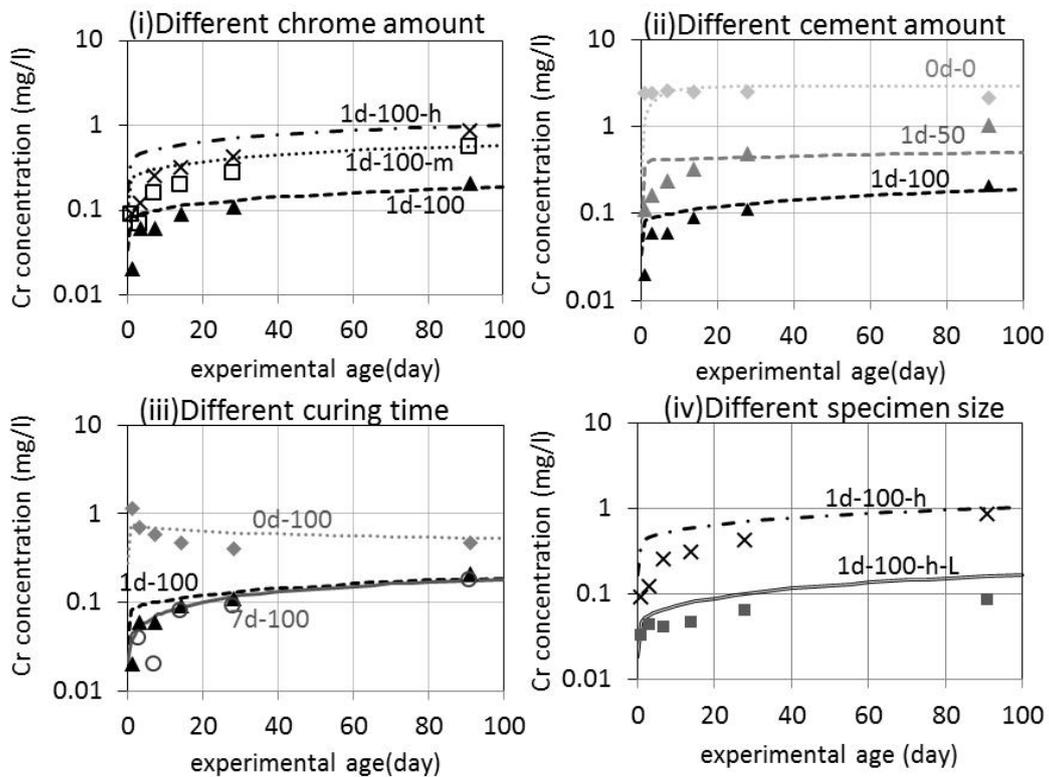


Figure 4. Results of tank leaching test

For all those conditions, it can be found that the analytical results well trace the trends of experiment. Larger chrome amount case (i) and lighter cement amount case (ii) show faster leaching from cemented soil specimens. In the curing time case (iii), both experiments and analyses show little difference between 1 day and 7 days. Furthermore, it is noticeable and significant that the unique trend of the 0d-100 case in the experiment can be well simulated. In this case, chromium concentration rises instantaneously at very early age and then decreases gradually as the cement hydration proceeds. Only with the coupled hydration and leaching process this phenomenon can be simulated, which is the highlight and advantage of the proposed model. Moreover, size effect can be reflected (iv) with the proposed model as well. Overall, the applicability of the proposed model to chromium leaching phenomena from cement-solidified soil is confirmed according to the above verifications.

EFFECTS OF REDOX CONDITIONS

Coupling analysis with the geochemical model. In the previous section, the applicability of thermodynamic system DuCOM to chromium leaching process from cemented soil is confirmed. As introduced, the premise is that the valence of leached chromium is assumed unchanged. However, in actual situations, phase or valence of leached chromium may change according to the surrounding pH and redox conditions. In this section, to discuss these influences, the DuCOM-PhreeqC coupling system (Elakneswaran, 2012) (Figure 5) are used. PhreeqC is a geochemical program designed to perform geochemical calculations including equilibrium between minerals and solution, ion exchanges, surface complexes, solid solution and gases (Parkhurst and Appelo, 1999). As the results of equilibrium calculations, pH value and the parameter regarding redox condition, pe, can be obtained in PhreeqC. Accordingly, those values are used in the equilibrated phase of each ion. Herein, the chromium leaching model in the previous section is integrated into this coupling system as shown in Figure 5. Decrement of chromate ions due to phase change is added to C_{bound} to maintain the mass conservation law.

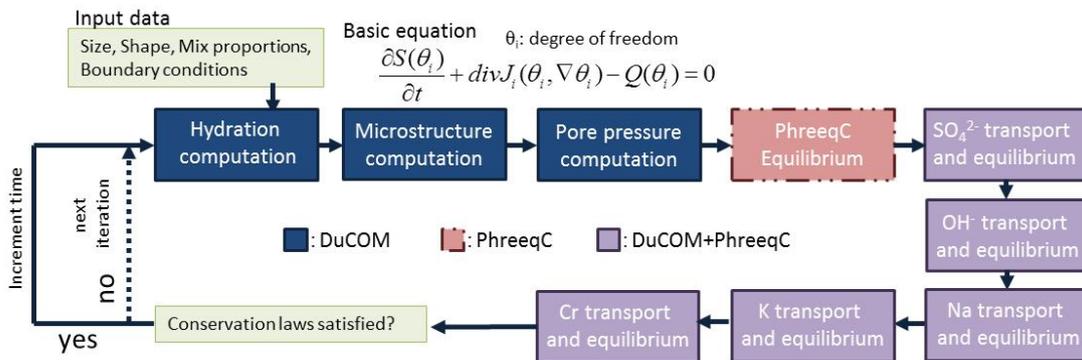


Figure 5. Overall scheme of DuCOM-PhreeqC coupling system

Analyses of tank leaching. With the coupling system, tank leaching test by PWRI (2000) is simulated again. Figure 6 shows the comparison of analytical results about 1d-100 case without and with PhreeqC coupled. No obvious difference can be seen between the two analyses. In DuCOM-PhreeqC coupling system, calculated pH and pe values at the beginning of leaching are 12.9 and 8.33. From the pH-pe diagrams of chromium (Takahashi

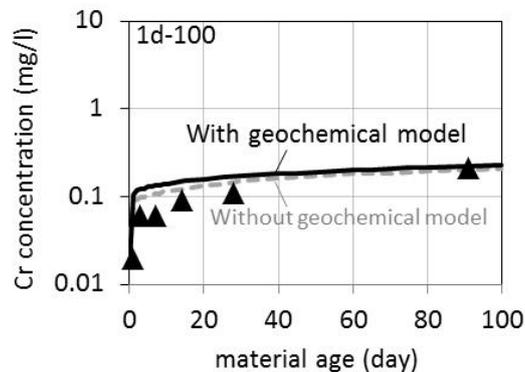


Figure 6. Effect of considering the geochemical model

2008), the dominant phase of chromium seems to be chromate ion under those pH and pe values. That is the reason why the both analytical results do not have the significant differences. This means that the proposed model can evaluate the chromium leaching behaviour properly in tank leaching conditions, even without geochemical calculations.

Effect of different redox conditions. Finally, leaching behaviors under different redox conditions are simulated with DuCOM-PhreeqC coupling system. Analytical conditions are almost same as previous analysis in Figure 6 but different pe values (10, 5, 0, -3 and -5) are configured in the water part as input parameters, so the phase of each ion can change due to the input pe values with geochemical calculation. The analytical results are shown in Figure 7.

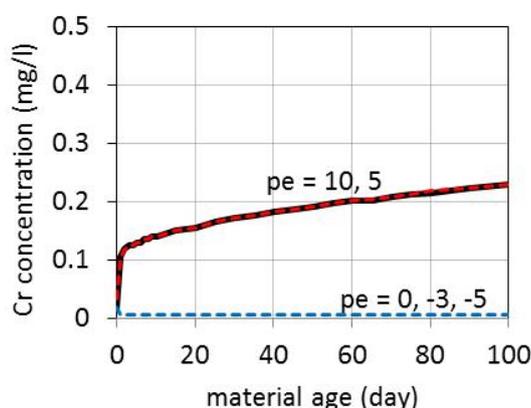


Figure 7. Effect of different redox condition in water

As Figure 7 shows, at high pe cases (10 and 5), the analytical results are totally same as those with equilibrated pe values in Figure 6. In those cases, the dominant phase of chromium seems to be stay in chromate ion shape. In contrast, at low pe cases (0, -3, -5), both leaching speed and leached chromium amount are significantly lower than the high cases, while the speeds among those low pe cases do not change any longer. This means the main phase of chromium might change from chromate ion to others, for example, chromium oxide. It is analytically shown that the reducing condition in redox atmosphere can decrease the speed and amount of chromium leaching. In this way, influence of different redox condition can be considered in the coupling analytical system.

CONCLUSION

A model for chromium transport and equilibrium is installed to the existing analytical system DuCOM so as to assess the chromium leaching from the cement-solidified soils, which is strongly related to the process of cement hydration and micro-pore formation. Solid-liquid equilibrium considering the chromium binding to the cement matrix is formulated based on the experiment results of cement paste specimens containing chromate ion. Then, the proposed model is verified by tank leaching experiments. As a result, for different chromium amount, cement amount, curing time, and specimen size, the proposed model can reflect the trends observed in the experiments successfully. Hence, it can be concluded that the proposed model shows high applicability to the chromium leaching phenomena from cemented soils.

Furthermore, the proposed model is installed to the DuCOM- PhreeqC coupling system, in order to investigate the effects of redox conditions and other co-existing ions and minerals on leaching. It is shown that, with the coupling analytical system, the main phase of chromium does not change from chromate ion shape in cement paste matrix, whereas leaching speed and amount of chromium can be reduced at the reducing condition in redox atmosphere.

REFERENCES

- Elakneswaran, Y., Ishida, T. (2012). "Coupled Physical and Geochemical Model for External Sulfate Attack in Concrete", *Proceedings of JCI*, 34(1), 754-759
- Maekawa, K., Ishida, T., Kishi, T. (2008). *MULTI-SCALE MODELLING OF STRUCTURAL CONCRETE*, Taylor and Francis
- Nakarai, K., Ishida, T., Maekawa, K. (2006). "Modeling of Calcium Leaching from cement Hydrates Coupled with Micro-pore Formation", *Journal of Advanced Concrete Technology*, Vol.4, No.3, 395-407
- Notification No.46 of Environmental agency of Japan (1991). "Environmental quality standards for soil pollution" (in Japanese)
- Parkhurst, D. L., Appelo, C. A. J. (1999). "A Computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations". *USGS report*
- Public Works Research Institute (PWRI) in Ministry of Land, Infrastructure and Transport (2001). *Report of joint research study about development of construction technology in the scope of conserving geo-environments*, 73-91 (in Japanese)
- Takahashi, S., Sakai, E., Sugiyama, T. (2007). "Study on Leaching of Hexavalent Chromium form Hardened Concretes Using Tank Leaching Test", *Journal of Advanced Concrete technology*, Vol.5, No.2, 201-207
- Takahashi, S. (2008). "Leaching behaviors of hexavalent chromium from cement hydrates and method of its analysis and evaluation", *Ph.D. thesis*, Tokyo institute of technology