Estimation of Cement Composition using Thermodynamic Model in Subsurface Environment

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1. Introduction

Cementitous materials have been used for the conditioning of nuclear and non-nuclear hazardous waste materials and for the construction of an engineered barrier in deep geological repositories for radioactive waste. Some disposal facilities for low- and intermediate-level waste (LILW) have been constructed in water-saturated environments. The concrete structure of the disposal facilities is degraded due to reactions with groundwater or sodium salts. Therefore, it is very important to understand or estimate the physic-chemical change of the concrete structure to guarantee the long-term safety of the disposal facilities.

2. Approach

Thermodynamic modeling was conducted to estimate the leaching properties of concrete structure and consequential composition change of the concrete structure in groundwater saturated environments. Batch experiments were also carried out to verify the simulation results and understand the dissolution of the concrete structure in equilibrium environments.

2.1 Thermodynamic modeling

A thermodynamic model was applied to estimate the hydration reaction of cement clinker and the subsequent reaction of the cement paste with groundwater using PHREEQC-2 (Parkhurst and Apello, 1999). The initial mineralogical composition of the cement clinker is listed in Table I.

2.2 Experimental method

A cement paste in cylinder type was prepared using Type-I ordinary Portland cement (OPC). Groundwater was sampled at the depth of 130 m below sea level at the Wolsong LILW Disposal Center, and it was used in the leaching solution. The chemical composition of the groundwater is shown in Table II. It is clearly shown that the groundwater was in the reduced condition. A leaching experiment was carried out as shown in Fig. 1. A cement paste was prepared in 10 cm in diameter and 15cm in length. The groundwater and the cement paste

were added in the reactor. Then, the reactor was sealed, and argon gas was injected to the reactor to maintain the reduced condition. The experiment was carried out for 6 months. During the experiment, ORP, temperature, the concentration of dissolved oxygen, and pH were continuously monitored. After the experiment, the mineralogical composition and porosity of the cement paste were analyzed. The chemical composition of the groundwater was also analyzed.
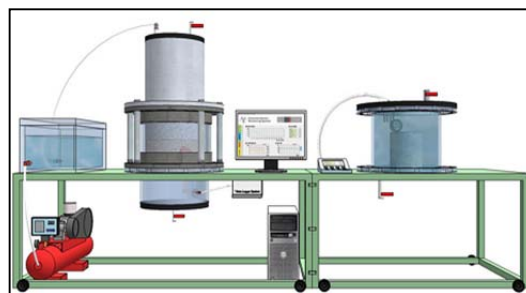

Fig. 1. Experimental set-up for the leaching experiment.

Table Ⅰ: Mineralogical composition of OPC

Mineral	Weight percent (%)
C3S	51.86
C2S	22.29
C3A	9.49
C4AF	8.51
Gypsum	2.03

3. Results and Discussion

Fig. 1 shows the chemical composition of the solution before and after the experiment. The simulation result is also compared in Fig. 2.

After 6 months of the reaction, the pH of groundwater increased from 8.0 to 12.5. This seemed to be caused by the dissolution of $Ca(OH)_2$ from the cement paste. The modeling work also estimated the same pH level. The Ca^{2+} concentration in the simulation was approximately 15 times higher than those in the solution of the dissolution experiment. However, K^+ concentration of the dissolution experiment was 10 times higher than those of the simulation. This result implies that the simulation relatively well estimated the

pH change in the dissolution of cement paste in the reduced condition which is expected in geological disposal. However, the dissolution of minor phases, such as K^+ was not exactly simulated in this study. This seems to be highly influenced by the chemical composition of the groundwater.

Fig. 2. Chemical composition of leaching solution.

4. Conclusions

A thermodynamic model was applied to estimate the dissolution of the cement paste and subsequent composition change. The simulation relatively well estimated the pH change in the dissolution of the cement paste in the reduced condition which is expected in geological disposal. However, the dissolution of minor phases, such as K^+ was not exactly simulated in this study.

5. Acknowledgments

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[8] Barbara Lothenbach, Frank Winnefeld, Corinne Alder, Erich and Peter Lunk, Effect of temperature on the pore solution, microstructure and hydration products of Portland cement paste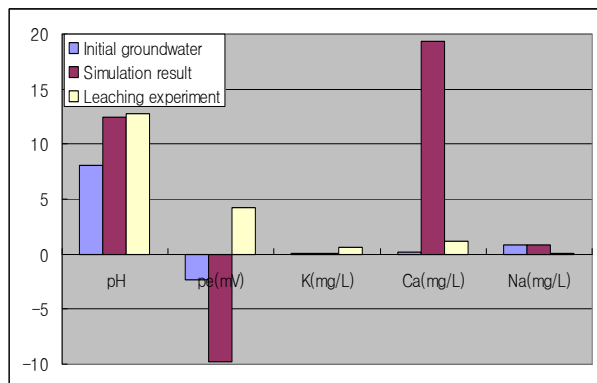s, Cement and Concrete Research 37, pp.483-491.