Transactions of the Korean Nuclear Society Autumn Meeting
Changwon, Korea, October 30-31, 2025

Solubility of C-S-H Phase in the Presence of Polycarboxylate Superplasticizer

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Keywords : Concrete barrier, C-S-H solubility, polycarboxylate superplasticizer

1. Introduction

When calculating the chemical durability of concrete barriers in radioactive waste repositories, the solubility of the C-S-H phase is of critical importance [1]. Polycarboxylate ether (PCE)-based superplasticizers are widely used in modern concrete structures, including low- and intermediate-level radioactive waste repositories. PCE improves workability, allowing a reduction in the water content of the mix and thereby enhancing early mechanical strength [2]. However, since PCE binds with calcium, it can increase the solubility of the C-S-H phase [3]. An increase in C-S-H solubility can weaken the long-term durability of concrete and lead to an increase in porosity. This study explores the effect of PCE on the solubility of C-S-H (C/S~1) phase through the formation of Ca-PCE complexes. Furthermore, this results offer homologous insight into complexation between radioactive Sr and PCE, which has not yet been reported.

2. Methods

2.1 Synthesis of C-S-H

C-S-H was prepared via the double precipitation method. $CaCl_2$ ($CaCl_2\cdot 2H_2O$, ACS reagent, ≥99%, Sigma-Aldrich) and Na_2SiO_3 ($Na_2SiO_3\cdot 9H_2O$, BioReagent, ≥98%, Sigma-Aldrich) solutions were prepared using deionized water (18.2 MΩ·cm, Milli-Q Direct 8, Millipore) in an Ar glovebox (96% Ar, 4% H_2, O_2 < 10 ppm). PCE (Hunan Zhongyan Building Materials Technology) was added, and the two solutions were slowly mixed to achieve a Ca/Si ratio of 1. The pH of the synthesized solution was 12.5 and the total ionic strength was approximately 0.08 M. Fig. 1 and Fig. 2 show the thermodynamic calculations under conditions without PCE. The calculations were performed using PHREEQC Ver. 3 with the CEMDATA18 database [4]. At pH 12.5, the most stable solid phase is CSH_2 ($CaO\cdot SiO_2\cdot 2H_2O$).

2.2 Solubility measurement

After synthesizing C-S-H, the suspension was allowed to settle for 1 day, and the supernatant was collected. Centrifugation (10,000×*g*) was performed to determine the total dissolved Ca concentration after removing solids. Additionally, ultrafiltration (10 kDa) was conducted to quantify the non-chelated Ca concentration, effectively excluding Ca-PCE complexes, as commercial PCEs are massive polymers with a molecular weight (M_w) of approximately 40 kDa [5]. Ca concentrations were analyzed using ICP-OES (Optima 8300, Perkin Elmer).

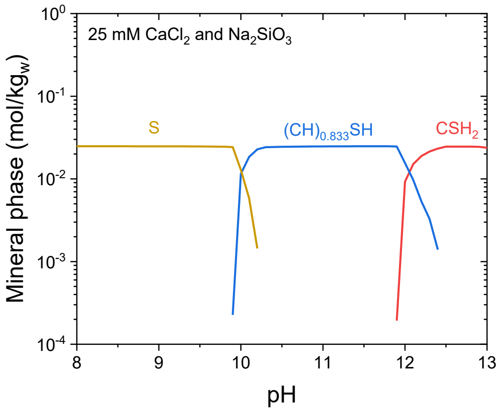

Fig. 1. Mineral phases speciation calculation using CEMDATA18 database ([Ca] = [Si] = 25 mM). S: SiO_2, $(CH)_{0.833}SH$: $(CaOH)_{0.833}\cdot SiO_2\cdot H_2O$, CSH_2: $CaO\cdot SiO_2\cdot 2H_2O$.

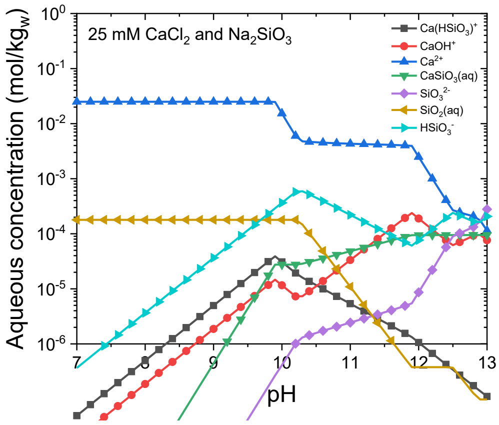

Fig. 2. Aqueous phases speciation calculation using CEMDATA18 database ([Ca] = [Si] = 25 mM).

3. Results and discussion

3.1 Solubility of C-S-H

Fig. 2 shows that the solubility of C-S-H decreases as pH increases. At PCE concentrations below 0.001%, ultrafiltration does not remove Ca. However, since PCE itself is removed by ultrafiltration, any Ca chelated with PCE is also eliminated. Typically, higher pH and Ca concentrations favor the presence of C-S-H with a higher CaO/SiO_2 (C/S) ratio. However, because the overall Ca:Si molar ratio in this system is fixed, only C-S-H with a C/S ratio of 1 can exist even at pH 13. At low PCE concentrations, the solubility of C-S-H is comparable to the values predicted by the database as shown in Fig. 3. However, the solubility increases with higher PCE concentrations due to the formation of Ca-PCE complexes, which promote the continuous release of Ca^{2+} ion from C-S-H structure.

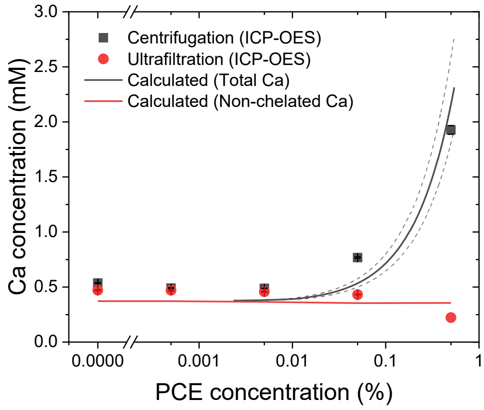

Fig. 3. Measured Ca concentration of C-S-H suspension as a function of PCE concentration. Calculated lines were calculated using CEMDATA18 database [4] with Ca-PCE complexation reaction (log $\beta = 2.9 \pm 0.1$).

3.2 Ca-PCE complexation

The interaction between Ca and PCE involves a complexation reaction with the carboxylate (L^-) groups of PCE. A previous study has shown that under low PCE concentrations, Ca predominantly forms 1:1 complex with carboxylate groups and reported a formation constant of log $\beta = 0.48$ for Ca-PCE complex (chemical equation (1)) [3]. The ligand concentration of the PCE used in this study was determined to be 5.55 mmol/g through pH titration. The formation constant derived from the observed increase in solubility was log $\beta = 2.9 \pm 0.1$. Activity coefficients were corrected using the Davies equation. Although this value deviates markedly from the previously reported one, it appears more reasonable when compared with the formation constants of other Ca-carboxylate complexes listed in Table I [6,7].

$$L^- + Ca^{2+} \leftrightarrow LCa^+ \quad \log \beta_{(1,1)} \qquad (1)$$

Table I: Complexation constants (log $\beta_{(1,1)}$) of Ca-carboxylate complexes

Ligand	log $\beta_{(1,1)}$	I (M)	Reference
Oxalate	2.46	0.1 (37°C)	[7]
Polyacrylate	3.25	0.1	[6]
Humate	3.4	0.1	[6]
PCE	0.48	0.3	[3]
PCE	2.9±0.1	0.08	This study

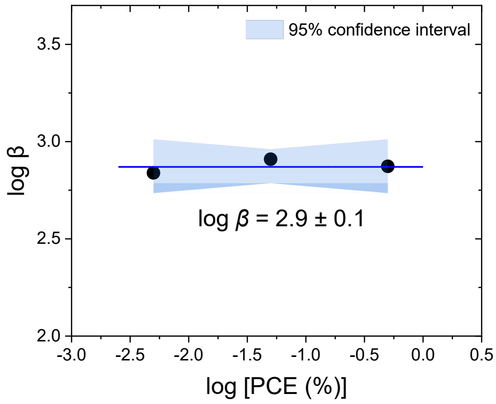

Fig. 4. Ca-PCE complexation constants calculated from the solubility enhancement. The shaded area represents the 95% confidence interval of the constant.

4. Conclusions

The increase in the solubility of the C-S-H phase was observed in the presence of PCE, from which the Ca-PCE complexation constant was derived. The obtained constant, log $\beta = 2.9 \pm 0.1$, is significantly higher than previously reported values but is comparable to those of other Ca-carboxylate complexes. While high PCE concentrations enhance workability and improve early strength, they may also accelerate the dissolution of the C-S-H phase, thereby compromising the long-term durability of concrete. The complexation constant of Ca-PCE determined in this study allows for a more accurate estimation of the solubility of the C-S-H phase, which is expected to enhance the reliability of chemical thermodynamic calculations for concrete barriers. This also indicates the possibility of complex formation between radioactive Sr, a chemical analog of Ca, and PCE.

Acknowledgment

This work was supported by Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by Korea government Ministry of Trade, Industry and Energy (MOTIE) (RS-2023-00236697).

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