Concrete Engineering   **콘크리트공학**

Thermodynamic Modeling of Long-Term Phase Development of Slag Cement in Seawater

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해수에 노출된 슬래그 시멘트의 장기 상변이 열역학 모델링

ABSTRACT

Known to improve resistance to chloride ingress, blast furnace slag is a widely used supplementary cementitious material. However, a detailed characterization of cements blended with slag exposed to seawater remains unavailable. This study employs thermodynamic modeling as a toolkit for assessing the long-term phase evolution of slag cement in seawater. The modeling result shows that slag incorporation leads to the formation of phases that are less prone to structural alteration in seawater. Formation of more ettringite is expected to induce expansion in both plain and blended cements, while brucite is unstable in the blended systems. Despite this, the porosity is expected to increase in the blended cements, and aluminate hydrates with a higher chloride binding capacity are more abundant in the blended cements. The results suggest that the use of slag in concrete improves the durability performance of concrete in marine environments.

Key words : Portland cement, Blast furnace slag, Seawater, Thermodynamic modeling

초 록

고로슬래그는 콘크리트의 염소이온침투 저항성능 개선 목적으로 가장 널리 활용되는 혼화재이나, 해수에 노출된 고로슬래그 혼입 콘크리트의 장기거동 및 상변이에 대한 보고는 부족한 실정이다. 본 연구에서는 열역학 모델링을 통해 해수에 노출된 슬래그 시멘트의 장기 상변이를 모사하였다. 모델링 결과 슬래그 혼입은 해수에 노출되었을 때 상변이가 쉽게 일어나지 않는 안정적인 상을 생성시킬 것으로 예측되었다. 해수에 노출되었을 때 ettringite 생성으로 인해 포틀랜드 시멘트 및 슬래그 시멘트에서 모두 팽창이 일어날 것으로 예측되었으나, 슬래그 시멘트에서는 brucite가 덜 생기는 것을 확인하였다. 공극률은 슬래그 혼입 시멘트의 경우 더 높았으나, 염소 흡착능이 높은 알루미네이트 수화물이 슬래그 시멘트에서 더 활발히 생성되는 것을 확인하였다. 따라서 슬래그 혼입을 통해 해양 환경에서 사용되는 콘크리트의 내구성능을 크게 증진시킬 수 있는 것으로 나타났다.

검색어 : 포틀랜드 시멘트, 고로슬래그, 해수, 열역학 모델링

1. Introduction

Seawater contains various ions that may interact with cement hydrates. In addition to chloride which induces corrosion of steel rebars embedded in concrete, seawater also contains carbonates and sulfates that lead to precipitation of salts and induce volumetric changes

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(De Weerdt et al., 2019). It is mandatory that marine concrete has high chloride binding capacity and high resistance against chloride ingress, as well as good resistance against structural changes that can be induced by ions contained in seawater.

It is a common practice that concrete blended with supplementary cementitious materials such as blast furnace slag, fly ash and silica fume is used instead of plain concrete with Portland cement as a sole binder (Otieno et al., 2014). It has been shown that blended concrete exhibits better performance in terms of resistance to chloride penetration (Song and Saraswathy, 2006), time-to-corrosion initiation (Mangat et al., 1994) and corrosion rate (Otieno et al., 2010; Scott and Alexander, 2007), when compared to plain concrete in both cracked and uncracked conditions (Aldea et al., 1999; Boulfiza et al., 2003). The improved chloride resistance of concrete blended with slag is attributed to the densification of microstructure (Yeau and Kim, 2005), while phase development of slag cement in seawater has not been investigated in detail.

This study therefore explores the long-term evolution of hydration products that forms in slag-blended concrete in seawater by employing thermodynamic calculations, thereby predicting stable hydration assemblages that are difficult to be obtained in laboratory timescale. This technique has been previously employed to simulate the hydration phase assemblages of various cementitious binders and to assess their likely durability performance (Park et al., 2019; Park, 2020; Park et al., 2020a; Park et al., 2020b; Yoon et al., 2020). The results of this study may have important implications for designing concrete with enhanced performance in marine environments.

2. Methods

The modeled Portland cement containing 63.6 % C_3S, 8.9 % C_2S, 6.5 % C_3A, 14.2 % C_4AF, 0.4 % periclase, 4.0 % anhydrite and 2.3 % arcanite (by mass) was adapted from a previous study (Snellings et al., 2014). The modeled blast furnace slag was also adapted from (Snellings et al., 2014), which contains 36.6 % SiO_2, 12.2 % Al_2O_3, 0.85 % FeO, 41.6 % CaO, 7.2 MgO, 0.6 % SO_3, 0.2 % Na_2O, 0.3 % K_2O and 0.4 % TiO_2 (by mass) based on the oxide composition obtained by X-ray fluorescence.

The hydration phase assemblages of plain Portland cement, and that blended with 30, 50 and 70 mass- % slag at a water-to-binder ratio of 0.4 were predicted by thermodynamic calculations.

The reaction degrees of Portland cement clinkers (C_3S, C_2S, C_3A and C_4AF) were simulated using the hydration model proposed by Parrot's hydration model (Parrot, 1984). The reaction degrees of slag at varying dosages were obtained from previous studies (Durdziński et al., 2017a; Durdziński et al., 2017b; Escalante et al., 2001), and were linearly extrapolated to the slag-to-binder compositions of 30 and 70 mass- %. In short, the reaction degrees of slag in the system with 30 and 70 % slag were 39 % and 31 %, respectively.

The thermodynamic calculations were conducted using the Gibbs free energy minimization software GEM-Selektor v.3.5. (Kulik et al., 2013; Wagner et al., 2012). CEMDATA18 (Lothenbach et al., 2019) which is a database containing thermodynamic properties of solids, solid-solutions and aqueous phases encountered in hydration of cements was also employed. The activity coefficients for aqueous species that may be present during the hydration were calculated using the Trusdell-Jones extension to the Debey Hückel equation (Helgeson et al., 1981), which is given as follows:

$$\log_{10}\gamma_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1+\dot{a}B_\gamma \sqrt{I}}+b_\gamma I+\log_{10}\frac{X_{jw}}{X_w} \qquad (1)$$

where γ_i: activity coefficient; z_i: charge; A_γ: temperature-dependent coefficient; B_γ: pressure-dependent coefficient; I: effective molal ionic strength; X_{jw}: molar quantity of water; X_w: total molar amount of the aqueous phase; $\dot{a}$: common ion size parameter; and b_γ: short-range interaction parameter. The common ion size parameter and the short-range interaction parameter were set to 3.72 Å and 0.064 kg/mol respectively, to simulate NaCl-dominated background electrolyte.

The thermodynamic modeling procedure was as follows: first, the thermodynamic database to be used in the calculation was imported (CEMDATA18, in this case), then the aqueous electrolyte model was selected. Here, Trusdell-Jones extension to the Debey Hückel equation was chosen, since it is known to give reasonably accurate values for ionic strength relevant to cement hydration. After defining elements which are present in the calculation, their bulk elemental composition was defined according to the reaction degrees reported in previous studies. Specifically, the portion of binder(s) which have not reacted is ignored in the calculation, thus assuming that the local equilibrium has been reached at the point of analysis. To simulate

the effect of seawater, the hydrated systems consisting of plain Portland cement, 30 % slag, 50 % slag or 70 % slag were titrated with seawater by following the procedure described in (Shi et al., 2017), which showed that chloride profiling experimental results and the thermodynamic calculations were in reasonable agreement. The chemical composition of the seawater used in the calculations was adopted from (Millero et al., 2008).

3. Results

The thermodynamic calculations have been conducted in this study to predict the phases that are stable upon exposure to seawater beyond the experimental timescale. The thermodynamic modeling predicts that C-S-H (CaO-$_x$SiO$_2$-$_y$H$_2$O), portlandite (Ca(OH)$_2$), Fe-hydrogarnet and ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$26·H$_2$O) are stable phases of the plain cement before exposure to seawater (Fig. 1). Replacing Portland cement with and increasing the

dosage of slag are expected to reduce the volume of overall solid phases, specifically, decreasing the volume of C-S-H portlandite, ettringite and Fe-hydrogarnet, while leading to formation of monosulfate and hydrotalcite. The simulation result suggests that portlandite is not fully consumed even when the slag replacement ratio is as high as 70 %, since a large volume of slag remains anhydrous.

Exposure of both plain and blended cements to seawater is calculated to destabilize monosulfate to Kuzel's salt which is gradually destabilized to Friedels' salt, while hydrotalcite that increasingly forms at higher slag contents remains mostly unaffected. Hydrotalcite is formed as a transient phase to which Friedel's salt is destabilized in the plain cement, unlike the blended cements in which the volume of hydrotalcite slightly changes upon destabilization of Friedel's salt and formation of brucite. Both plain and blended cements are predicted to undergo a volumetric change due to ettringite and brucite, which are most
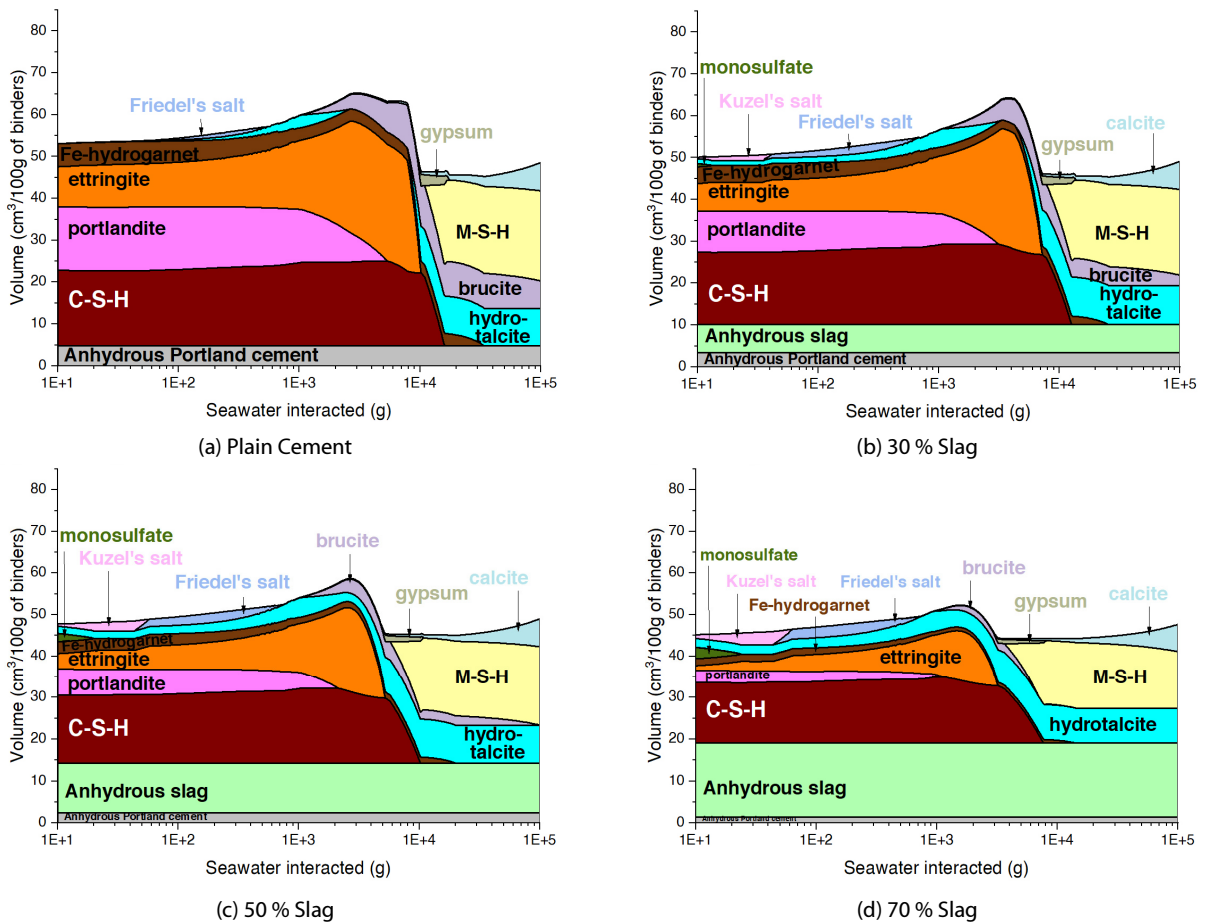

Fig. 1. Predicted Phase Assemblages of (a) Plain Cement and Blended Cements Containing (b) 30 %, (c) 50 %, and (d) 70 % Slag in Seawater
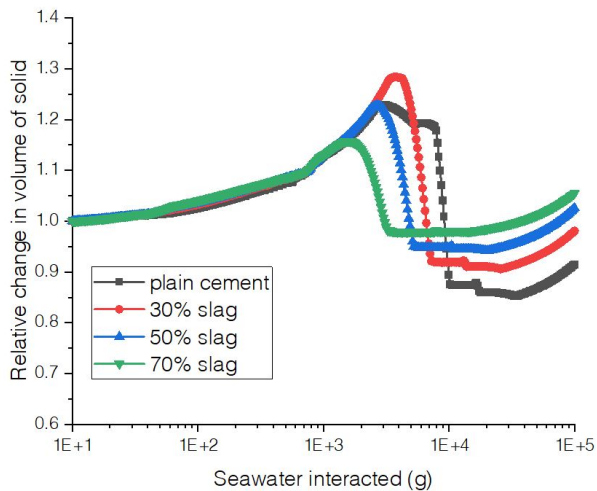
Fig. 2. Simulated Volume Change in Plain and Blended Cements in Seawater

Table 1. Simulated Porosity, pH, and Ca/Si of C-S-H in Plain and Blended Cements in Seawater

	Plain cement	30 % slag	50 % slag	70 % slag
Porosity	0.21	0.31	0.35	0.39
pH	13.98	13.75	13.31	13.35
Ca/Si of C-S-H	1.35	1.34	1.34	1.34

abundantly formed in the plain cement, while the volume change relative to the initial hydration phase assemblage is noticeably less in the blended cements, except for that containing 30 % slag (Fig. 2).

All the phases that are predicted stable before exposure to seawater are destabilized except for hydrotalcite in the cements blended with 50 % and 70 % slag, while M-S-H and calcite are predicted stable after extended time of exposure. In addition, gypsum can be formed as a transient phase upon destabilization of ettringite, and brucite is predicted unstable in the 50 % and 70 % slag-blended cements.

The modeling results suggest that the enhanced chloride resistance of slag-blended cements can be attributed to the higher amount of aluminate hydrates with a high chloride binding capacity, namely hydrotalcite and monosulfate. It is interesting to note that the simulated porosity results in Table 1 do not support for densification of microstructure when a certain amount of slag is blended with Portland cement, and that the amount of C-S-H tends to decrease with an increasing dosage of slag. Additionally, it is found from the thermodynamic modeling results in Table 1 that slag incorporation in Portland cement (up to 70 %) is unlikely to lead to substantial changes in the chemistry of C-S-H.

The modeled phase assemblage is expected to take very long time to take place and certainly exceed the laboratory timescale, thus it is difficult to observe the modeled evolution in the literature.

4. Conclusion

The evolution of phases in slag-blended cements when exposed to seawater is simulated by thermodynamic modeling in this study. The predicted hydration phase assemblages of blended cements suggest that hydrotalcite and monosulfate are stable phases in cements blended with <50 % slag, in addition to C-S-H, portlandite and ettringite which are also observed in the plain cement. Formation of hydrotalcite in blended cements destabilizes brucite, which otherwise abundantly forms and significantly induces mineralogical changes. Thus, it can be concluded that slag incorporation in cement not only leads to enhancing the chloride binding capacity, but also reduces susceptibility to mineralogical alteration in marine environments.

Acknowledgement

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