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研究課題名(和文) Predicting long-term durability performance of cement systems from the nanostructure and properties of calcium aluminosilicate hydrate (C-A-S-H) gels

研究課題名(英文) Predicting long-term durability performance of cement systems from the nanostructure and properties of calcium aluminosilicate hydrate (C-A-S-H) gels

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研究成果の概要(和文)：本研究では、Ca/(Si+Al)比の異なるC-(A)-S-Hを合成し、SiOH基及びAlOH基には反応性の異なる2つのサイトが存在すると仮定した。これらのサイトにおける表面錯体反応の平衡定数を算出し、吸着量予測を行うことで、合成系におけるモデルの構築を行った。C-S-HおよびC-A-S-Hへのカルシウムおよび塩化物の吸着の実験データを予測することによってモデルの検証を行った。

研究成果の学術的意義や社会的意義

This research links C-S-H and C-A-S-H properties to durability of cementitious materials. Therefore, this research provides an excellent embodiment of the concept of material design for required properties and long-term durability in various environments.

研究成果の概要(英文)：The density of the surface groups was determined by analysing the structure of C-S-H and C-A-S-H through ^{27}Al and ^{29}Si MAS NMR. The surface sites of SiOH and AlOH are available in C-A-S-H whereas C-S-H has SiOH groups. The incorporation of aluminium decreases the number of total adsorption sites in C-A-S-H. Furthermore, the site density increased with Ca/(Si+Al). To understand the C-A-S-H/solution interface, a triple-layer surface complexation model was developed and the associated equilibrium constants for deprotonation, calcium, and chloride adsorption were determined by fitting the experimental data of potentiometric titration and zeta potential measurement results. The estimated surface complexation modelling parameters were verified by predicting the experimental data of calcium and chloride adsorption on C-S-H and C-A-S-H.

研究分野：工学

キーワード：Cement chemistry C-A-S-H Modelling

様式 C-19、F-19-1、Z-19 (共通)

1. 研究開始当初の背景

Alumina-rich supplementary cementitious materials (SCMs) increase the incorporation of aluminium in calcium silicate hydrate (C-S-H) and forms calcium aluminosilicate hydrate (C-A-S-H) gel, which is the main hydration products of SCMs containing materials consist of more than 70 % in weight [1,2]. The nanostructure and physical, chemical, surface electrical and mechanical properties of C-A-S-H gel are significantly different from the conventional C-S-H that affects the performance (durability and strength) of concrete. The durability of concrete highly depends on the phase assemblage, characteristics of the hydration products, and microstructure in the hydrated cement system. The interaction between ionic species and hydration products is important in the durability because each aggressive specie behave differently (adsorption, absorption, and exchange) towards hydration product. Since the C-A-S-H gel the primary products of hydrated cement systems, durability of the cement systems is controlled by the structure and the properties of the C-A-S-H gel. Despite being studied, the structure, solubility, physicochemical and electrostatic properties of the gel have not yet well understood. This information is essential in understanding the chemistry of cement system to describe the ionic transport, solubility, and sorption processes for long-term durability performance.

2. 研究の目的

The aim of this research project is to develop a quantitative link between nanostructure, and physicochemical and surface electrical properties of C-A-S-H gel and durability performance of cement system.

3. 研究の方法

(1) Synthesis of C-S-H and C-A-S-H

Both C-S-H and C-A-S-H were synthesised at 50 °C. The $\text{Ca}(\text{OH})_2$ (special grade reagent manufactured by Kanto Chemical Co.) and SiO_2 (AEROSIL200 with purity of 99.9% or higher by Nippon Aerosil Co., Ltd.) in different proportions were mixed with pure water with a water to powder ratio of 20 mL/g, and the mixture was cured for 10 days. The targets of the Ca/Si ratios were 0.8, 1.0, and 1.5. In the preparation of C-A-S-H, $\text{Ca}(\text{OH})_2$, SiO_2 , and CaAl_2O_4 were mixed for the target of Ca/(Si+Al) of 0.8, 1.0, and 1.5, and Al/Si of 0.19. The mixing water to powder ratio was 45 mL/g, and the mixture was sealed after N_2 purging and cured for 5 weeks at 50 °C. After the curing time, the solid and liquid phases were separated by suction filtration, and the solid phase was washed with deionised water three times and then dried for 2 days by freeze-drying before use.

(2) Experimental procedure

C-S-H and C-A-S-H were characterised by a Rigaku X-ray generator with CuK α radiation. A fluorescent X-ray analyser element monitor EA1200VX manufactured by Hitachi High-Tech Science was used to determine the solid composition of C-S-H and C-A-S-H. Thermogravimetry/Differential Thermal Analysis (TG/DTA) was performed in nitrogen using a HITACHI TG/DTA 7220 analyser at a heating rate of 293 K/min up to 980 °C. The specific surface areas of C-S-H and C-A-S-H were measured using the Brunauer–Emmett–Teller (BET) water adsorption method. Titration experiments for C-S-H and C-A-S-H suspensions were conducted using an automated titration system. A 0.01 mol/L NaNO_3 solution (50 mL) was prepared, and the pH of the solution with 5g/L of C-S-H/C-A-S-H and without C-S-H/C-A-S-H was measured by titrating the solution with 0.25 mol/L NaOH. The ^{29}Si MAS NMR experiment was conducted on MSL 400 9.4 T BRUKER at 79.48 MHz. The Q_8M_8 ($\text{Si}(\text{CH}_3)_8\text{Si}_8\text{O}_2$) manufactured by Wako Pure Chemical Industries was used as a reference material for the measurement. A JEOL ECA-700 was used to obtain ^{27}Al spectra, where $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was used as a reference material. A C-S-H/C-A-S-H suspension with a solid to liquid ratio of 0.1 g/L was prepared for zeta potential measurement using a Zetasizer Nano series. A batch experiment was performed with $\text{Ca}(\text{OH})_2$ solution to determine calcium adsorption on C-S-H/C-A-S-H. The sample was immersed in different concentrations of 10 mL $\text{Ca}(\text{OH})_2$ solution for one day, where 5 g/L of solid to liquid ratio was adopted. After equilibrium, the solid and liquid phases were separated by handshaking, and then the liquid phase was filtered with a 0.45 μm syringe filter. The concentration of calcium in the filtered solution was measured by ICP-OES. The calcium concentration difference between the blank and C-S-H/C-A-S-H suspensions was the adsorbed calcium. The same experimental procedure was adopted for chloride adsorption. C-S-H/C-A-S-H was equilibrated with different concentrations of 5 mL CaCl_2 for 5 days, and the solid to liquid ratio for the chloride adsorption was 100 g/L. After equilibrium, the solid and liquid phases were separated and the chloride concentration

in the liquid phase was measured using ion chromatography to determine its adsorption.

(3) Modelling approach

The geochemical code PHREEQC was used for the speciation, thermodynamic equilibrium, and surface complexation modelling calculations [3]. The charge-distribution-multi site complexation model (CD-MUSIC) available in PHREEQC was adopted for the surface complexation reaction between C-S-H/C-A-S-H and ionic species [4]. The model can be implemented in PHREEQC using the keyword data block of SURFACE and SURFACE_SPECIES with the charge distribution and the capacitance of the inner and outer Stern layers.

4. 研究成果

(1) Characterisation and determination of surface site density of C-S-H and C-A-S-H

To calculate the ionic adsorption using a surface complexation model, the types of surface functional groups and their densities must be evaluated. The synthesised C-S-H/C-A-S-H samples were characterised, and this information was used to evaluate the surface site densities. The XRD patterns of the synthesised samples are aligned with the results reported by Myer et al. [5], which was again confirmed by the TG/DTA. In addition, XRF measurements were conducted on the synthesised samples to examine if the actual Ca/(Si+Al) ratio reaches the target value.

In this study, it was assumed that the synthesised C-S-H corresponded to β -C-S-H, and the layers were calculated from the results of the specific surface area. It increases with an increase in Ca/(Si+Al). Information about the number of layers was used to estimate the surface site density of C-S-H and C-A-S-H. It was assumed that the structure of C-S-H and C-A-S-H is close to tobermorite-type crystal structure, and the C-S-H has surface functional group of $\equiv\text{SiOH}$, whereas C-A-S-H possesses both $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ groups. The basic unit is a tetrahedron of the two silicates that make up the dimer, and the surface reactive groups are present in the bridges and end chains of silica and aluminium. The estimated total surface site densities of C-S-H and C-A-S-H as a function of the Ca/(Si+Al) ratio is shown in **Fig. 1**. The site density increased with increasing Ca/(Si+Al) ratio due to the increase in the number of stacking layers. The quantified total surface site densities of C-S-H and C-A-S-H were 4.3–6.3 and 3.5–5.2 sites/nm², respectively. These values are not significantly different from those reported in the literature [6-8]; a value of 4.8 sites/nm² has been reported for C-S-H in many studies [6,7].

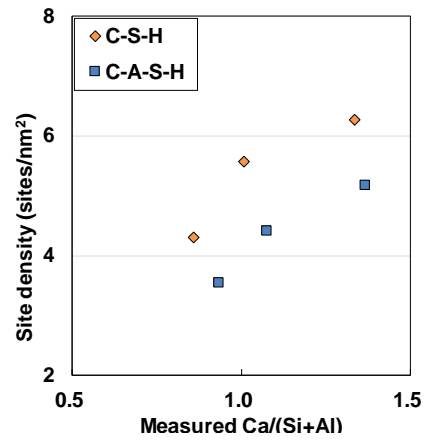
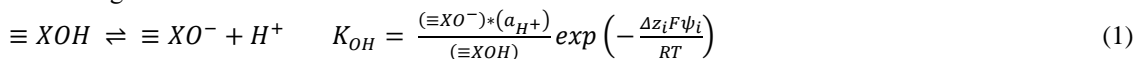


Fig. 1. Estimated total surface site density of C-S-H and C-A-S-H

(2) Electrostatic interaction between C-A-S-H and hydroxyl, calcium, and chloride ions

The total sites determined in section (1) were divided further into strong and weak sites, where the weak sites were easy to dissociate, while the strong sites were difficult to dissociate. Charukov et al. performed a simulation based on the different degrees of dissociation in Q¹ and Q^{2b}, each of which exists at a ratio of 1:1 [6]. A similar approach was adopted in this study to estimate the density of weak and strong sites. In the silicate chain, Q^{2b} exists only on the flat surface and is distributed to sites with different dissociation ratios of 1:1. However, Q¹ exists on both flat surface and edge, and the surface area ratio between the end surface and the layer surface can be calculated based on the layered structure proposed by Haas et al. [7]. The Q¹ sites on the flat surface can form a hydrogen bond and are considered to be strong sites, whereas the sites at the edge surface are less affected by hydrogen bonds and considered as weak sites. The strong and weak surface site densities of C-S-H and C-A-S-H are presented in **Table 1**.

The strong and weak of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface sites are dissociated in the alkaline solution as follows:

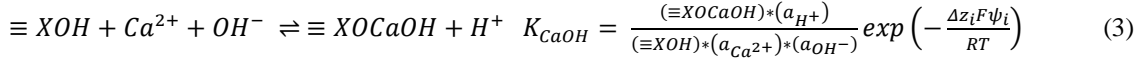
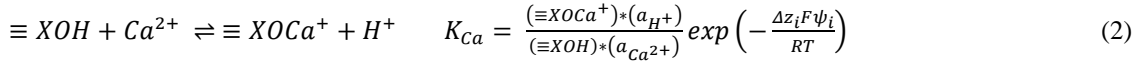


X: Si or Al

where K_{OH} is the intrinsic equilibrium constant for dissociation, $(\equiv\text{XOH})$, $(\equiv\text{XO}^-)$ are concentrations of the surface species of surface sites (mol/m²), a_{H^+} is the activity of H^+ (mol/L), ψ_i is the potential at the 0-, 1-, or 2-plane (V), Δz_i is the charge distribution, R is the universal gas constant equal to 8.31451 J/(mol·K), and T is the absolute temperature (K).

The titration experimental results were fitted to the surface complexation modelling results to estimate the K_{OH} of both strong and weak sites. The estimated equilibrium constant for the dissociation of surface sites is presented in **Table 1**.

The adsorption of Ca^{2+} and $CaOH^+$ on strong and weak $\equiv SiOH$ and $\equiv AlOH$ surface sites was considered as the following inner-sphere surface complexation reaction:

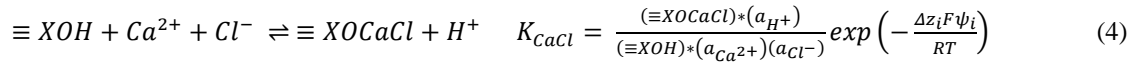


X: Si or Al

where K_{Ca} and K_{CaOH} are the intrinsic equilibrium constants for calcium adsorption, $(\equiv XOCa^+)$ and $(\equiv XCaOH)$ are the concentrations of the surface species of surface sites (mol/m²), and $a_{Ca^{2+}}$ is the activity of Ca^{2+} (mol/L).

The experimental data for the C-S-H/C-A-S-H in $Ca(OH)_2$ solution were fitted to the modelling results to estimate K_{Ca} and K_{CaOH} . The results are given in **Table 1**.

The positive surface of C-S-H/C-A-S-H strong and weak sites in the presence of calcium can adsorb chloride ions via the following surface complexation reaction:



X: Si or Al

where K_{CaCl} is the intrinsic equilibrium constant for chloride adsorption, $(\equiv XOCaCl)$ is the concentration of the surface species of surface sites (mol/m²), and a_{Cl^-} is the activity of Cl^- (mol/L). The estimated equilibrium constants for both C-S-H and C-A-S-H are presented in **Table 1**.

Table 1: Estimated surface complexation modelling parameters for C-S-H/C-A-S-H

			Site density (sites/nm ²)	pK _{OH}	pK _{Ca}	pK _{CaOH}	pK _{CaCl}
CSH-0.8	SiOH	weak site	1.54	6.6	5.8	3.7	5.7
		strong site	2.76	13.0	6.6	6.6	7.0
CSH-1.0	SiOH	weak site	1.44	6.6	5.8	3.8	5.7
		strong site	4.12	13.0	7.1	6.8	7.3
CSH-1.5	SiOH	weak site	1.13	6.6	5.8	3.7	5.7
		strong site	5.14	13.0	7.9	6.9	8.0
CASH-0.8	SiOH	weak site	1.22	6.6	5.8	3.5	5.7
		strong site	2.02	13.0	6.8	6.8	6.5
	AlOH	weak site	0.15	6.6	5.8	3.5	4.5
		strong site	0.15	13.0	6.8	6.8	6.0
CASH-1.0	SiOH	weak site	1.07	6.6	5.8	3.5	5.7
		strong site	2.89	13.0	7.3	6.9	7.5
	AlOH	weak site	0.22	6.6	5.8	3.5	5.5
		strong site	0.22	13.0	7.3	6.9	7.5
CASH-1.5	SiOH	weak site	1.06	6.6	5.8	3.5	5.7
		strong site	3.73	13.0	7.6	7.0	7.8
	AlOH	weak site	0.16	6.6	5.8	3.5	4.8
		strong site	0.22	13.0	7.6	7.0	7.0

(3) Prediction of calcium and chloride adsorption on C-A-S-H

The estimated surface complexation modelling parameters (**Table 1**) were used to predict the adsorption of calcium and chloride. The predicted calcium adsorption on CSH:1.0 and CASH:1.0 was compared with experimental data in **Fig. 2**. A similar comparison was performed for other C-S-H and C-A-S-H. The model successfully predicted calcium adsorption as a function of calcium concentration. As can be seen from the model prediction, both Ca^{2+} and $CaOH^+$ adsorb on the surface sites, but the adsorption of $CaOH^+$ contributes at a high concentration of calcium. Therefore, both surface complexation reactions (Eqs. (2) and (3)) are

necessary to understand calcium adsorption on C-S-H and C-A-S-H. Both experimental and modelling results indicate that aluminium incorporation in C-A-S-H does not influence the total calcium adsorption. The substitution of silica by aluminium decreases the total surface sites in C-A-S-H, but a fraction of available silica sites changes to $\equiv\text{AlOH}$ sites. Therefore, both $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ sites contribute to calcium adsorption in C-A-S-H and show an equal amount of adsorption as in C-S-H. The surface complexation reactions given in Eqs. (1) - (4) were used to predict chloride adsorption on C-S-H and C-A-S-H in CaCl_2 solution. A high concentration of CaCl_2 solution was selected to enhance chloride adsorption on C-S-H and C-A-S-H, as reported in

ref. [9] where 20–70% of chloride adsorption was observed when cement paste was exposed to CaCl_2 solutions. Both the strong and weak of the $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ sites compete for chloride adsorption via the surface complexation reaction given in Eq. (4). However, the surface site density and equilibrium constants presented in **Table 1** control the amount of adsorption. A comparison between the predicted and measured chloride adsorption on CSH:1.0 and CASH:1.0 is shown in **Fig. 3**. A similar comparison was performed for other C-S-H and C-A-S-H. A very good agreement between the predicted results and experimental data indicates the validity of the model and estimated parameters. Both experimental data and modelling results show that aluminium incorporation in C-S-H reduces chloride adsorption. More details results are presented in ref. [10].

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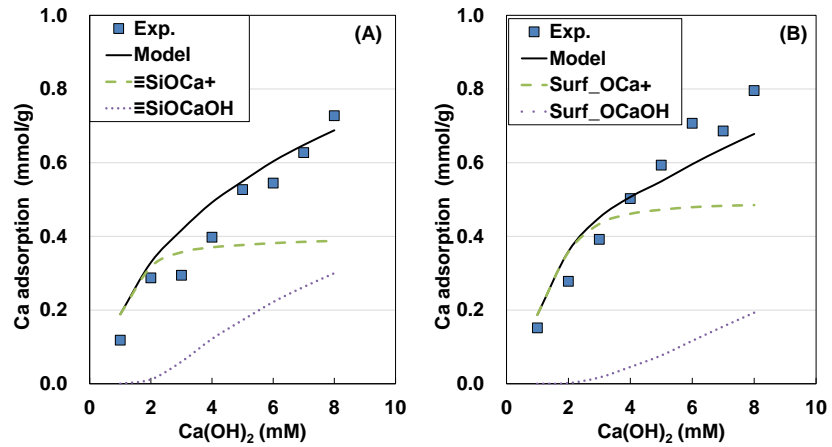


Fig. 2. Comparison of the predicted and measured calcium adsorption on (A) CSH:1.0; (B) CASH:1.0

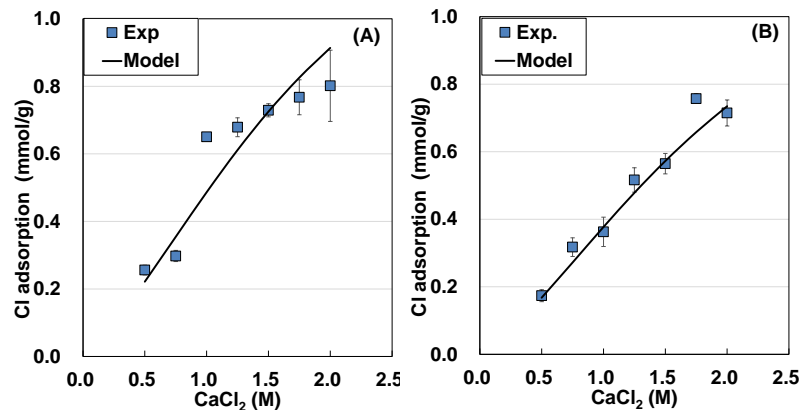


Fig. 3. Comparison of the predicted and measured chloride adsorption on (A) CSH:1.0; (B) CASH:1.0

5. 主な発表論文等

〔雑誌論文〕 計2件（うち査読付論文 2件/うち国際共著 0件/うちオープンアクセス 1件）

1. 著者名 Elakneswaran Yogarajah, Owaki Eiji, Nawa Toyoharu	4. 巻 8
2. 論文標題 Modelling Long-Term Durability Performance of Cementitious Materials under Sodium Sulphate Interaction	5. 発行年 2018年
3. 雑誌名 Applied Sciences	6. 最初と最後の頁 2597 ~ 2597
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/app8122597	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 -

1. 著者名 Satoshi Yoshida, Yogarajah Elakneswaran, Toyoharu Nawa	4. 巻 122
2. 論文標題 Electrostatic properties of C-S-H and C-A-S-H for predicting calcium and chloride adsorption	5. 発行年 2021年
3. 雑誌名 Cement and Concrete Composites	6. 最初と最後の頁 Accept
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 -

〔学会発表〕 計3件（うち招待講演 0件/うち国際学会 3件）

1. 発表者名 Yogarajah Elakneswaran, Satoshi Yoshida, Toyoharu Nawa
2. 発表標題 Relationship between electrokinetic properties of C-A-S-H and ionic adsorption
3. 学会等名 International conference on innovative materials for sustainable civil engineering（国際学会）
4. 発表年 2019年

1. 発表者名 Yogarajah Elakneswaran, Satoshi Yoshida, Toyoharu Nawa
2. 発表標題 Influence of electrokinetic properties of C-A-S-H and chloride binding in slag-blended cementitious materials
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3. 学会等名 RILEM SPRING CONVENTION and SUSTAINABLE MATERIALS, SYSTEMS AND STRUCTURES CONFERENCE (国際学会)
4. 発表年 2019年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関