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Thermodynamic Modeling of Chemical Acidification of Cementitious Paste

by Feyza Nur Sahan, W. Jason Weiss, and O. Burkan Isgor

The role of limestone (LS) powder replacement and changes in calcium-silicate-hydrate (C-S-H) due to pozzolanic reactions on the acid resistance of cementitious pastes are studied using thermodynamic modeling. Simulations are performed under equilibrium conditions, while hydration products are exposed to increasing levels of sulfuric acid. LS replacement does not show sacrificial characteristics against sulfuric acid attack, and LS acidification starts only after full consumption of portlandite and most C-S-H. Increased LS replacement causes the dilution of the formed portlandite and C-S-H volumes, which results in their full consumption at lower acid concentrations than mixtures without LS replacement. Pozzolanic reactions of supplementary cementitious materials (SCMs) result in C-S-H phases with lower Ca/Si than their ordinary portland cement (OPC) counterparts, increasing acid resistance. However, highly reactive and/or high-volume SCM replacements might further decrease the available portlandite, reducing the buffer acid resistance capacity. This issue is particularly critical for portland-limestone cement (PLC)-based systems.

Keywords: acid attack; calcium-silicate-hydrate (C-S-H); limestone (LS); portland-limestone cement (PLC); supplementary cementitious materials (SCMs); thermodynamic modeling.

INTRODUCTION

Acid resistance of concrete is critical for wastewater transmission and treatment facilities. The construction industry has been moving toward using ASTM C595 Type IL cement (that is, portland-limestone cement [PLC]) across the United States, and there is a significant drive to reduce the clinker content of concrete using supplementary cementitious materials (SCMs) to reduce the carbon footprint of concrete.[1,2] However, it is not clear how clinker reduction will affect acid resistance. Few studies have examined the impact of replacing clinker with limestone (LS) on the acid resistance of cement paste,[3-11] and the literature shows contradictory findings. Senhadji et al.[4] examined the acid resistance of mortars by replacing 5, 10, and 15% by mass of the clinker with LS and showed a lower mass loss for mortars with a higher LS replacement level. The improvement in acid resistance with LS replacement was attributed to reduced permeability and porosity; consumption of calcium carbonate ($CaCO_3$) as a sacrificial material; reduced calcium hydroxide (portlandite, $Ca(OH)_2$, or CH) content, which is considered to be more susceptible to acidification; and the possible role of LS as a filler material that can affect the transport properties of the system.[5,6] Furthermore, the mixtures with LS aggregates showed a greater resistance to sulfuric acid; Chang et al.[5] attributed this to the LS aggregates acting as a sacrificial material to neutralize the acid and decrease the acid degradation of the paste. Supporting this hypothesis, Fernandes et al.[7] showed through a microscopic study the formation of gypsum crystals along the interface of the LS aggregate and paste, indicating that acid attacks both the cement paste (likely the portlandite-rich region of the paste) and LS aggregate. In addition, finer LS fillers showed greater resistance to sulfuric acid attack, presumably due to the increased surface area of the LS, which resulted in a more rapid neutralization of the acid.[8]

Siad et al.[9] reported contradictory results while studying acid resistance of self-consolidating concrete with mixtures containing LS, natural pozzolan, and fly ash. They reported that the mixtures containing LS filler had the greatest mass loss and significant visual deterioration after 12 weeks of immersion, which the authors correlated to higher neutralization capacity of LS and increased kinetics of the reaction with sulfuric acid due to fineness of LS in the study. House[10] reported that while the use of LS coarse aggregate increased concrete resistance to sulfuric acid attack, replacing a portion of cement with finely ground LS did not have positive effects on concrete resistance to sulfuric acid. The lower acid consumption with ground LS replacement was interpreted as lower neutralization capacity of LS than the cementitious material, even though the mass loss was less with LS replacement. Liu and Wang[11] suggested that when cement is replaced with LS filler, the sulfuric acid is more readily available to react with portlandite, reducing acid resistance. These contradictory results indicate a need for a systematic investigation of the role of LS in the acid resistance of cementitious pastes.

Furthermore, studies examined the influence of pozzolanic reactions on sulfuric acid resistance.[12-15] Pozzolanic reactions consume portlandite. Further, the calcium-silicate-hydrate (C-S-H) produced by pozzolanic reactions of SCMs has a lower calcium-silicate ratio (Ca/Si) than C-S-H produced by ordinary portland cement (OPC) hydration. The properties of C-S-H with different Ca/Si were investigated by several researchers.[16-19] Kunther et al.[18] reported that the compressive strengths improved with decreasing Ca/Si when four different Ca/Si (0.83, 1.0, 1.25, and 1.50) were tested. Another study examining the micro/nanostructure of C-S-H[16] reported that with the increase in Ca/Si (0.83, 1.0,

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Table 1—Oxide composition of OPC, LS, and SF

	Eq. Na_2O^*, %	MgO, %	SO_3, %	CaO, %	SiO_2, %	Fe_2O_3, %	Al_2O_3, %	LOI	SG	DOR[*†]
OPC	0.57	3.80	2.80	62.00	19.90	3.20	4.60	0.96	3.15	—
LS	0.11	0.47	0.05	55.62	1.83	0.05	0.09	41.68	2.70	—
SF	0.48	0.26	0.15	0.70	95.88	0.12	0.69	4.30	2.20	76%
GS	—	—	—	—	>99.00	—	—	—	2.65	0%

[*] Eq. $Na_2O = Na_2O + 0.658\ K_2O$.

[†] Maximum degree of reactivity as per pozzolanic reactivity test.[28]

Note: LOI is loss on ignition; SG is specific gravity.

and 1.50), there was a decrease in the degree of polymerization, resulting in more discrete silica chains. Alizadeh et al.[19] suggested that adsorbed and interlayer water contribute significantly to the dynamic mechanical properties of C-S-H. Wanna et al.[14] examined the effect of low- and high-CaO fly ash on the sulfuric acid resistance and found that the addition of fly ash improved the acid resistance of cement pastes by promoting pozzolanic reactions that consume portlandite and produce C-S-H, which is more resistant to acid attack, in addition to the role of the reaction products in refining pore size and pore connectivity. Low-CaO fly ash was more effective in improving the sulfuric acid resistance of cement pastes than the high-CaO fly ash. Bassuoni and Nehdi[15] investigated the acid resistance of self-consolidating concrete mixtures to sulfuric acid attack. The testing was conducted in two 6-week-long phases: Phase I, with the initial pH (0.9) of the solution controlled at a maximum threshold value of 2.5; and Phase II, with the refreshment of the solution with pH (0.9) controlled at a maximum threshold value of 1.0. They reported that the decalcification of C-S-H became the governing factor for mass loss in Phase II. The authors reported that the decalcification of C-S-H with a high Ca/Si resulted in a surface that is susceptible to direct acid attack. Conversely, the decomposition of C-S-H with a lower Ca/Si generated a protective zone, effectively restricting acid diffusion into the cementitious matrix. This protective mechanism consequently diminished mass loss in specimens derived from blended-binder mixtures. These limited studies indicate a need to study the role of pozzolanic reactions, C-S-H type, and Ca/Si on the acid resistance of cementitious pastes.

The main objective of this study is to systematically investigate the role of LS replacement and Ca/Si of the C-S-H (that is, different types of C-S-H) on the acid resistance of cementitious pastes using thermodynamic modeling. This study aims to simulate chemical acidification of paste samples with varying LS, ground silica (GS), and silica fume (SF) contents using thermodynamic calculations where the concentration of sulfuric acid is gradually increased. It should be noted that unreacted clinker phases were excluded by considering 100% degree of hydration (DOH) for the systems, which simply reduces the extent of unreacted cement (which is highly acid-resistant). The water-cementitious materials ratio (*w/cm*) was considered higher than in realistic conditions to enable the availability of pore solution and surrounding solution for the reactions. This assumption allowed the authors to study the role of LS replacement and Ca/Si of the C-S-H at the thermodynamic level, without the complication of unhydrated cement phases or ionic transport.

RESEARCH SIGNIFICANCE

The acid resistance of concrete is important for septic tanks, sewer pipes and risers, and water treatment facilities. Experimental tests can be time-consuming, and it is often difficult to isolate the influence of specific changes in a mixture. This study uses computational models to assess the resistance of the unreacted and reacted phases to acid exposure. The results provide a clear indication of the phases that are most susceptible to damage and the reaction products that form for a given level of acid reaction. This approach can enable the design of binder systems that are more resistant to acid attack.

THERMODYNAMIC MODELING

In this study, thermodynamic simulations were performed using the open-source GEMS3K code[20,21] combined with the default PSI/Nagra Chemical Thermodynamic Database and the Cemdata v18.1 thermodynamic database.[22] GEMS3K uses Gibbs free energy minimization to predict the output phase assemblage of a cementitious system in equilibrium. Following the well-established practice,[22,23] the CSHQ model was used to model OPC and OPC + pozzolanic SCM systems. The CSHQ model can predict the changes in four different C-S-H types: jennite D (JenD) with a Ca/Si of 2.25, jennite H (JenH) with a Ca/Si of 1.33, tobermorite D (TobD) with a Ca/Si of 1.25, and tobermorite H (TobH) with a Ca/Si of 0.67. Based on empirical evidence from the literature, the formation of carbonate-ettringite,[24,25] hydrotalcite,[26] hydrogarnet,[26] and thaumasite[27] was blocked in the GEMS-CEMDATA framework because these phases are not observed to form in substantial quantities in cementitious systems at 25°C—the temperature at which the simulations were conducted.

Thermodynamic calculations were performed for systems at 100% DOH for cement and complete pozzolanic reaction for the reactive phases of the SCM, which was chosen as SF in this study. Table 1 provides the chemical composition of the materials used in the simulations (that is, OPC, LS, SF, and GS) and the degree of reactivity (DOR* as per the pozzolanic reactivity test[28]) of SF, which represents the portion of the SCM that is pozzolanically reactive. Note that OPC does not contain any LS, so the effect of LS replacement can be compared to a control case with no LS. All LS is assumed to be available for reaction. In all simulated mixtures, the *w/cm* was 0.70 to ensure the high DOR of the simulated cementitious systems and for sufficient pore solution for acidification.

The first set of thermodynamic simulations investigated the effect of LS replacement. Four mixtures were studied with 0, 5, 10, 15, and 25% (mass) LS replacement, labeled as OPC, 5LS, 10LS, 15LS, and 25LS, respectively. To investigate the dilution effect of LS replacement on the hydration products, the 5, 10, 15, and 25% (mass) nonreactive GS replacements were considered and labeled as 5GS, 10GS, 15GS, and 25GS, respectively. Finally, the effect of C-S-H type (and Ca/Si) was studied by incorporating 15% (mass) SF—this mixture was labeled 15SF. The authors acknowledge that this level of SF replacement is higher than the standard industry designs, which are typically 5 and 9%, but the goal of this simulation was to provide comparative pozzolanic reaction data with the same dilution level to 15% LS replacement. Chemical acidification in the simulations was achieved by incrementally adding H_2SO_4 to the hydrated cementitious systems at 100% DOH. The changes of the hydrated solid-phase volumes, the Ca/Si of C-S-H, and the pH of the system at equilibrium were recorded with H_2SO_4 addition for each simulation. Unhydrated phases were excluded in the sulfuric acid attack simulations to develop a clear understanding of the acid resistance of the hydrated phases.

RESULTS AND DISCUSSION

Effect of LS

Figures 1 and 2 show the results of the thermodynamic calculations in the form of volumetric distribution of phases with increasing sulfuric acid addition for OPC and OPC + LS systems, respectively. It should be noted that this modeling was conducted for 100% DOH. The cementitious system hydration phase volume was 100%; the additional phase volume represents the unreacted volume of H_2SO_4. Realistically, there would be unreacted cementitious phases in the system, which might also react with sulfuric acid.

As shown in Fig. 1, for the 100% OPC mixture, monosulfate depleted first with sulfuric acid addition, producing ettringite, which remained in the system until all portlandite and most C-S-H were consumed. During this time, the pH dropped below 10.7. The degradation of ettringite occurred below 10.7, as reported by Gabrisová et al.,[29] who studied ettringite stability in aqueous solutions. As also expected from the literature,[30-32] portlandite was shown to be highly susceptible to sulfuric acid attack even at low acid concentrations. For the 100% OPC system, C-S-H consumption began with H_2SO_4 addition after monosulfate and portlandite were consumed completely. The reaction of C-S-H phases started with high Ca/Si C-S-H (JenD then JenH), followed by low Ca/Si C-S-H (TobD then TobH), decreasing the overall Ca/Si of C-S-H in the system with increasing acidification. Ettringite, portlandite, and C-S-H converted to gypsum with increasing acidification. When the last form of C-S-H with the lowest Ca/Si (that is, TobH with a Ca/Si of 0.67) was consumed by the acid, quartz was formed with the released Si in the system. It is noted that the pH of the system had no obvious change during the portlandite consumption due to the neutralization of the sulfuric acid. The pH started to decrease at a slow rate, from ~13 to ~10, after portlandite depletion while C-S-H was being consumed. When there was no hydration product left to neutralize the sulfuric acid in the system, a rapid decrease in the pH was observed.

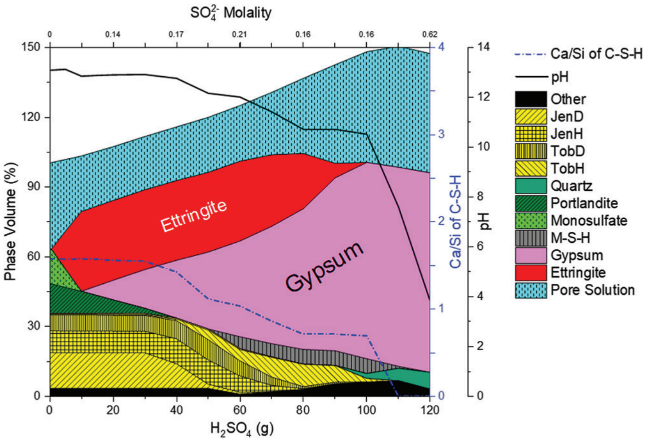
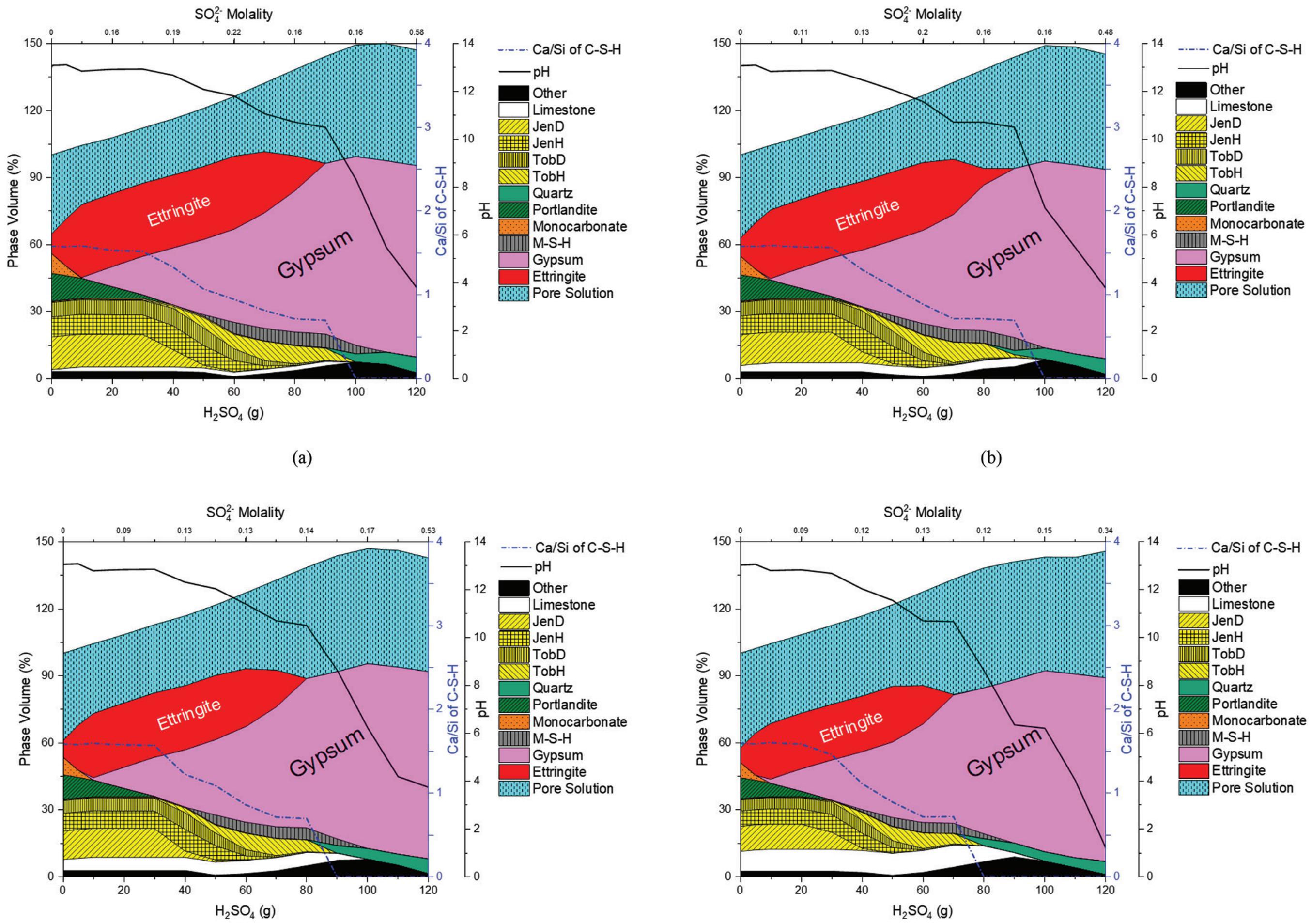


Fig. 1—Phase assemblage of OPC system reacting with H_2SO_4. (Phase volume beyond 100% reflects volume change due to addition of H_2SO_4. Chemical shrinkage is not shown in plot for clarity, but this accounts for why phase volume starts at less than 100%.)

Figure 2 shows that LS replacement causes lower volumes of hydrated phase (for example, portlandite, C-S-H, and so on) formation before acidification, due primarily to dilution. Unlike the OPC mixture, OPC + LS mixtures contained monocarbonate phases instead of monosulfate phases. These monocarbonate phases were the first to acidify to produce ettringite, which remained in the system until all portlandite and most C-S-H were consumed. Other than this difference, 100% OPC and OPC + LS systems showed similar trends under chemical acidification with sulfuric acid. However, a negative effect of increased LS replacement is the dilution of the formed portlandite and C-S-H volumes, which results in their full consumption at lower H_2SO_4 concentrations, as shown in Fig. 2(a) to (d), with progressive increase of LS from 5 to 25%. For example, the mixture with OPC + 15% LS replacement (representing PLC) showed complete portlandite and C-S-H depletion at 25% and 45% lower sulfuric acid concentrations than the 100% OPC mixture, respectively. Note that the OPC used in this study did not contain any LS, and commercial OPC would typically contain up to 5% LS. When this comparison is done with respect to the OPC + 5% LS mixture (Fig. 2(a)), which represents typical commercial OPC, the mixture with OPC + 15% LS replacement (Fig. 2(c)), representing PLC, showed complete portlandite and C-S-H depletion at 20% and 25% lower sulfuric acid concentrations, respectively. Figure 2 also shows that LS (at any replacement level) does not show sacrificial characteristics against sulfuric acid addition. In fact, LS acidification does not start until all portlandite and most C-S-H phases (JenD, JenH, and TobD) are consumed. This observation is supported by an earlier experimental work by Sahan et al.[33] on the acidification of mixed pure phases, which showed when LS was still present after portlandite depletion while other phases were being consumed.

The pH of the pore solution influences the formation of other hydration products in the presence of magnesium oxide



(a)

(b)

(c)

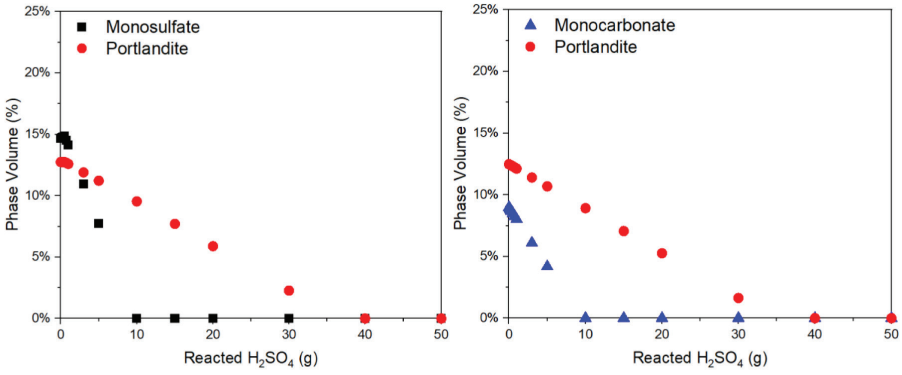
(d)

Fig. 2—Phase assemblage of OPC + LS systems reacting with H_2SO_4: (a) 5LS; (b) 10LS; (c) 15LS; and (d) 25LS. (Phase volume beyond 100% reflects volume change due to addition of H_2SO_4. Chemical shrinkage is not shown in plot for clarity, but this accounts for why phase volume starts at less than 100%.)

(MgO). It is reported in the literature that if the pH exceeds 10.5, brucite will be the primary reaction product.[34] When the pH decreases below 10.5, the progressive formation of magnesium-silicate-hydrate (M-S-H) gel occurs.[34] The formation of M-S-H gels in thermodynamic simulations was attributed to decomposition of brucite at lower pH and an available Si source due to decomposition of C-S-H. With the decomposition of M-S-H, the excess Si source forms quartz.

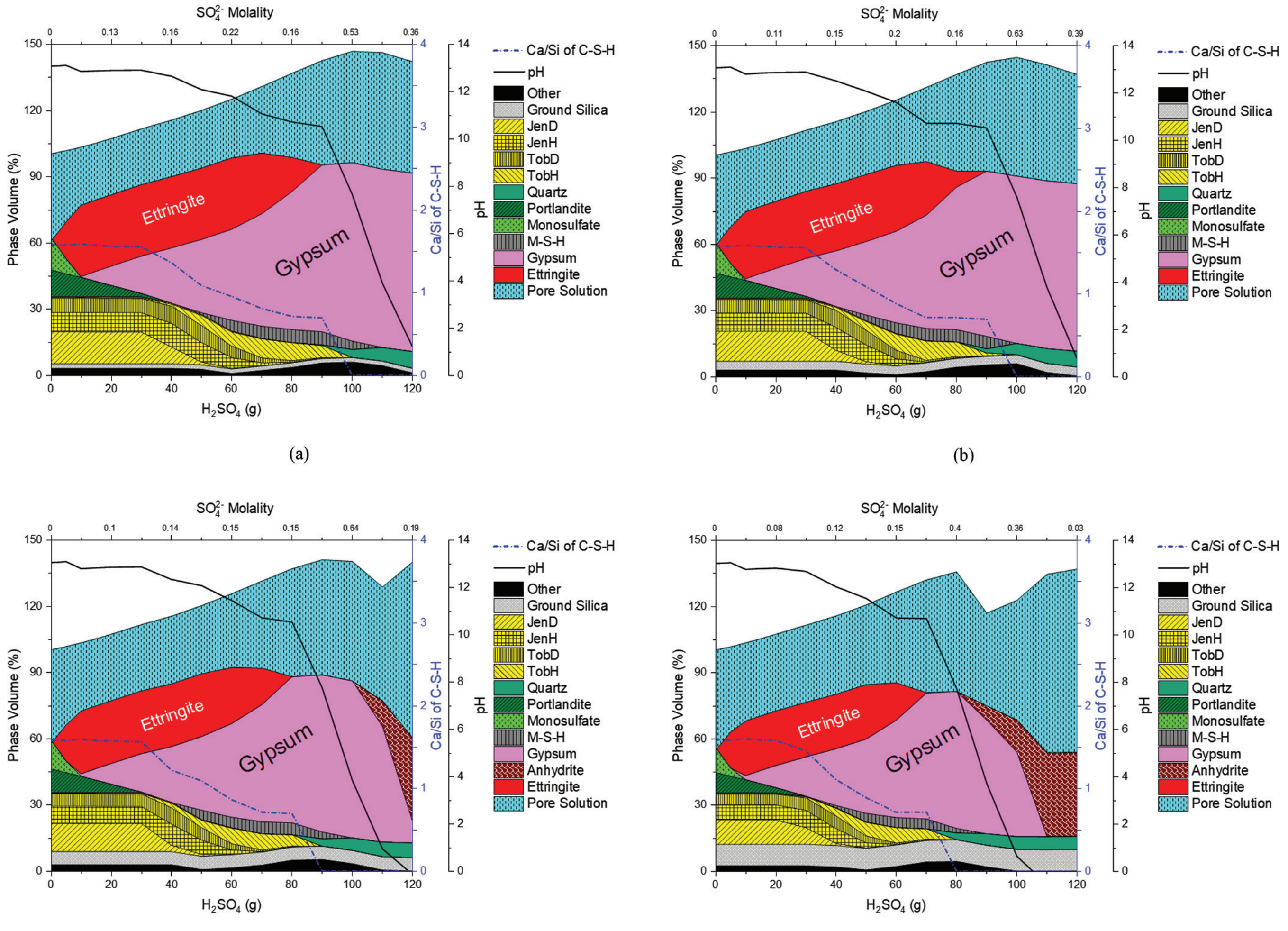
The changes in portlandite, monosulfate, and monocarbonate phases are clearly shown in Fig. 3 for the OPC and 25LS systems. Although portlandite is traditionally considered to be the most susceptible hydration product to acid attack, the consumption rate of monosulfate and monocarbonate phases is more likely to be higher with the initial sulfuric acid exposure. As the amount of reacted sulfuric acid increases, the phase volume percentage of monosulfate and monocarbonate decreases steadily. The portlandite decreases as the amount of reacted sulfuric acid increases, but at a less rapid rate than monosulfate for both cases.

The observations in Fig. 2 reflect the influence of LS replacement on the acid resistance of OPC pastes; however, they contain both the chemical effects and the effects due to the dilution of the OPC with the LS replacement. To isolate the dilution effect, additional simulations were performed with nonreactive GS replacement at corresponding LS mass replacement levels—that is, 5, 10, 15, and 25%. Figures 4(a), (b), (c), and (d) represent the changes in phase volume (%) as a function of H_2SO_4 addition for 5GS, 10GS, 15GS, and 25GS, respectively. As expected, the reduced hydration phases due to reduced cement hydration with unreactive GS replacement caused these phases to be consumed more readily than the OPC mixture, as shown in Fig. 4. As shown in Fig. 4, with the increase of GS from 5 to 25%, the required H_2SO_4 addition for the depletion of C-S-H decreased from approximately 100 to 80 grams of H_2SO_4. While LS reacted with the H_2SO_4 after C-S-H depletion for the OPC + LS mixtures, unreactive GS did not react in the acidic environment. The further increase in H_2SO_4 caused the conversion of gypsum ($CaSO_4 \cdot 2H_2O$) to anhydrite ($CaSO_4$) and a further decrease in pH. These results confirm earlier simulations on the effect of LS that until the complete consumption of portlandite and C-S-H, LS acts as an inert filler under chemical acidification, similar to inert GS. However, after the consumption of all portlandite and C-S-H, LS provides additional acid resistance and delays the sharp pH decrease to levels below 2.



(a) (b)

Fig. 3—Comparison of reaction with sulfuric acid for: (a) monosulfate versus portlandite for OPC system; and (b) monocarbonate versus portlandite for OPC + 25LS system.



(a) (b) (c) (d)

Fig. 4—Phase assemblage of OPC + GS systems reacting with H_2SO_4: (a) 5GS; (b) 10GS; (c) 15GS; and (d) 25GS. (Phase volume beyond 100% reflects volume change due to addition of H_2SO_4. Chemical shrinkage is not shown in plot for clarity, but this accounts for why phase volume starts at less than 100%.)

Effect of C-S-H type

Figure 5 shows the results of the thermodynamic calculations in the form of volumetric distribution of phases with increasing sulfuric acid addition for the OPC + SF system. All simulations (OPC in Fig. 1, OPC + LS in Fig. 2, and OPC + GS in Fig. 4) show that portlandite is highly susceptible to acid attack, as also reported in the literature,[30-32] and decalcification of C-S-H does not occur until the portlandite in the system is mostly consumed.

Figure 5 shows that the pozzolanic reactions consumed all the portlandite in the system. When portlandite is not present in the 15SF system, the initial acid attack promotes the consumption of monosulfate and C-S-H phases. It is shown that the decalcification of C-S-H with acid attack begins with high Ca/Si C-S-H type. The JenD type (high Ca/Si) was followed successively by the lower Ca/Si types, and eventually all converted to the TobH type (the lowest Ca/Si type) with increasing acid volume. Finally, the TobH reacted with sulfuric acid and formed gypsum and quartz by following Eq. (1)

$$CaO_x(SiO_2)_y \cdot H_2O_z + {}_xH_2SO_4 \leftrightarrow {}_xC\overline{S}H2 + {}_ySiO_2 + (z-x)H_2O \quad (1)$$

The main phases identified in conventional cement paste, following sulfuric acid attack, are gypsum and amorphous silica gels, rather than ettringite.[35]

It is established in the literature that C-S-H generally remains stable at high pH until the pH is reduced to a value of 8.8.[36,37] In the absence of portlandite, the decalcification process of C-S-H starts as soon as acid is introduced and continues until only amorphous silica gel remains. Although the present work only focuses on the chemical aspect of acidification, previous work by Bassuoni and Nehdi[15] and Gu et al.[35] proposed that during sulfuric acid exposure, the decalcification of C-S-H results in the formation of a protective layer composed of silica and aluminosilicate gels. This layer effectively protects the undegraded cement paste from further degradation.

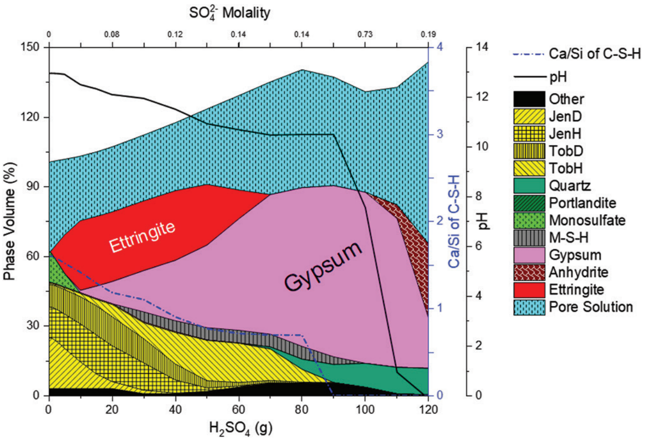
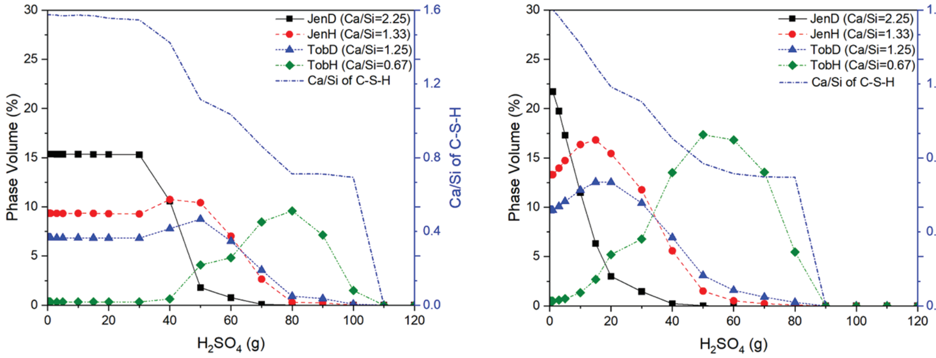


Fig. 5—Phase assemblage of OPC + SF system reacting with H_2SO_4. (Phase volume beyond 100% reflects volume change due to addition of H_2SO_4. Chemical shrinkage is not shown in plot for clarity, but this accounts for why phase volume starts at less than 100%.)

Figures 6(a) and (b) demonstrate the phase volume conversions of different C-S-H types with varying H_2SO_4 amount for the OPC and 15SF mixture, respectively. Figure 6(a) shows a delayed consumption of C-S-H due to consumption of other phases for the OPC system, while the consumption of C-S-H and the decrease in Ca/Si began immediately with H_2SO_4 addition. The comparison of OPC and 15SF systems in Fig. 6 shows an increase in the phase volume of C-S-H due to pozzolanic reaction, which resulted in greater acid consumption by C-S-H in the 15SF system compared to OPC. The degradation of C-S-H began initially with the JenD type, which has a high Ca/Si and deteriorates compared to other types, which were deteriorating and forming from the decalcified material. The temporary increase observed in JenH and TobD types suggests a gradual conversion of C-S-H. TobH is the final product consumed during the acid attack. This study used a CSHQ model incorporating four types of C-S-H with varying Ca/Si, noting the possibility of observing C-S-H structures with different average Ca/Si compositions during the attack.

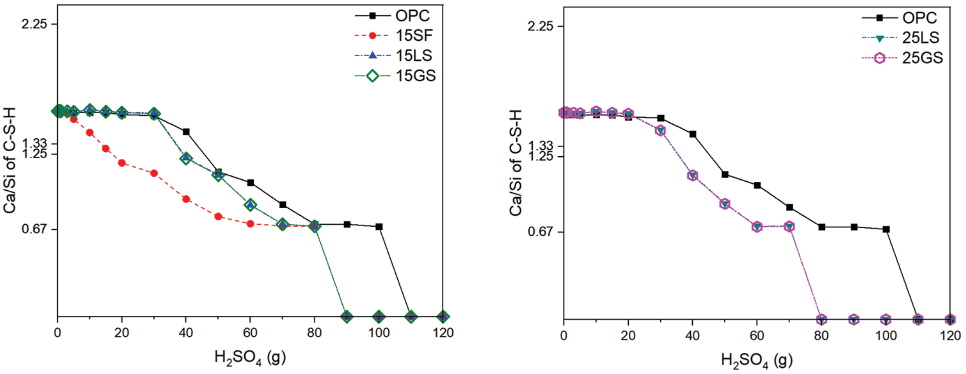
Figure 7 compares the Ca/Si of the C-S-H in the system for the different mixtures. Figure 7(a) compares OPC with 15% replacement systems, while Fig. 7(b) compares OPC with 25% replacement systems. As can be seen in Fig. 7(a), the decomposition of C-S-H was delayed for the OPC mixture due to the availability of other hydration products, such as portlandite and monosulfate. The LS and GS mixtures followed a nearly identical trend based on the replacement percentages; the higher replacement percentage enabled the decomposition of C-S-H at lower $H_2SO_4(g)$ addition due to dilution of other reaction products. While other hydration products were not available for reaction with sulfuric acid, the decomposition of C-S-H was promoted at lower concentration with the sulfuric acid addition for the 15SF mixture. As can be seen in Fig. 7(a) and (b), the Ca/Si of C-S-H for 25LS and 25GS showed a decrease in Ca/Si at lower H_2SO_4 addition compared to 15LS and 15GS. Besides, the C-S-H was depleted at lower H_2SO_4 addition for 25% replacement systems due to the reduced amount of C-S-H. Although C-S-H was being consumed at a higher rate for 15SF, the higher amount of C-S-H due to pozzolanic reaction led to later depletion compared to 25LS and 25GS mixtures. This provides insight into how the presence of different substitute



(a)

(b)

Fig. 6—Phase volume alteration of C-S-H types with exposure to H_2SO_4 for: (a) OPC system; and (b) 15SF system.



(a) (b)

Fig. 7—Comparison of average Ca/Si of C-S-H for: (a) OPC and 15% replacement systems exposed to H_2SO_4; and (b) OPC and 25% replacement systems exposed to H_2SO_4.

materials and proportions influences C-S-H's stability and decomposition in the presence of sulfuric acid. The Ca/Si appears to play an important role in the reaction with sulfuric acid.[38] The incorporation of SCMs decreases portlandite in the system with pozzolanic reaction and promotes the formation of C-S-H; however, this also promotes the formation of C-S-H with a lower Ca/Si, which appears more stable when exposed to acid.

Thermodynamic simulations presented in this paper focus on the chemical equilibrium of the phases under increased levels of acidification and do not consider the impact of transport properties. This is one area where the pozzolanic reactions may have additional benefits that are not captured here. Furthermore, the change in pore structure due to acidification reactions plays a significant role in transport properties, which affects the degradation rate.

CONCLUSIONS

This study systematically investigated the influence of limestone (LS) as a replacement of cement in terms of the acid resistance of cementitious pastes. In addition, silica fume (SF) was used to assess the influence of the calcium-silicate ratio (Ca/Si) of the calcium-silicate-hydrate (C-S-H) (that is, different types of C-S-H) on acid resistance. The primary conclusions are based on 100% degree of hydration (DOH) and include:

- LS replacement as a filler material did not show sacrificial characteristics to sulfuric acid attack, contrary to many discussions in the literature. In fact, LS acidification did not start until all portlandite and most C-S-H phases (JenD, JenH, and TobD) were consumed.
- Increased LS replacement caused the dilution of portlandite and C-S-H volumes, which resulted in their complete consumption at lower H_2SO_4 concentrations than mixtures without LS replacement. For example, the mixture with 15% LS replacement (representing a portland-limestone cement [PLC] mixture) showed complete portlandite and C-S-H depletion at 20% and 25% lower sulfuric acid concentrations than corresponding ordinary portland cement (OPC) mixtures, respectively.
- Although portlandite is traditionally considered to be the most susceptible hydration product to acid attack, the consumption rates of monosulfate and monocarbonate phases were higher with sulfuric acid exposure.
- The acidification of C-S-H phases started with high Ca/Si C-S-H (JenD then JenH), followed by low Ca/Si C-S-H (TobD then TobH), decreasing the overall Ca/Si of C-S-H in the system with increasing acidification.
- Pozzolanic reactions resulted in C-S-H phases with lower Ca/Si than the OPC-only counterparts, increasing acid resistance. The level of pozzolanic reaction depends on the reactivity of the pozzolan and the volume of the pozzolan used. However, if pozzolanic reactions consume all portlandite in the mixtures, the buffer acid resistance capacity of the mixtures might decrease. This issue is particularly critical for PLC systems, for which additional LS further dilutes the available portlandite (by approximately 13% for 15% LS mass replacement) and C-S-H in the mixture before acidification.
- Further experimental and/or modeling research is needed to explore the role of changes in transport properties of the hardened systems due to pozzolanic reactions and chemical acidification, particularly for typical degrees of hydration and pozzolanic reactions of PLC-based systems.

AUTHOR BIOS

ACI member **Feyza Nur Sahan** *is a PhD Student at Oregon State University, Corvallis, OR. She received her BS from Özyeğin University, Istanbul, Turkey, and her MS from Oregon State University. Her research interests include microbially induced corrosion of concrete, acid attack, and service life modeling.*

W. Jason Weiss, *FACI, is the Miles Lowell and Margaret Watt Edwards Distinguished Chair in Engineering in the School of Civil and Construction Engineering at Oregon State University. He is the former Editor-in-Chief of the* ACI Materials Journal *and is a member of the ACI Technical Activities Committee.*

O. Burkan Isgor, *FACI, is the Eric H.I. and Janice Hoffman Professor in Civil and Construction Engineering at Oregon State University. He is past Chair and a current member of ACI Committee 222, Corrosion of Metals in Concrete, and a member of ACI Committees 236, Material Science of Concrete, and 365, Service Life Prediction. His research interests include corrosion of steel in concrete, service life modeling of concrete, and thermodynamic modeling of cementitious systems.*

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