

杂质离子对水化硅(铝)酸钙微纳结构的影响

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摘 要: 作为硅酸盐水泥最主要的水化产物, 水化硅(铝)酸钙[C-(A-)S-H]及其在杂质离子作用下的微纳结构演变决定了水泥基材料的各项性能。近年来, 在大量先进表征技术、计算机模拟以及机器学习技术加成下, C-(A-)S-H 微纳结构模型发展迅速。随着对 C-(A-)S-H 微纳结构认识的不断深入, 杂质离子作用下 C-(A-)S-H 微纳结构演变规律逐渐清晰。本文总结了 C-(A-)S-H 的微纳结构表征、微纳结构模型发展、杂质离子作用对其微纳结构的影响机制和面向海洋服役环境的硅酸盐水泥基材料延寿策略, 分析了当前研究进展及未来发展方向, 旨在为硅酸盐水泥基材料的性能精准调控提供理论借鉴。

关键词: 水化硅(铝)酸钙; 杂质离子; 微纳结构; 耐久性

中图分类号: TU528 文献标志码: A 文章编号: 0454-5648(2025)01-0212-13

网络出版时间: 2024-11-06



作为硅酸盐水泥最主要的水化产物, 水化硅酸钙 $[(\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z]$, 简记 C-S-H 的微纳结构直接决定了硅酸盐水泥基材料的力学性能和耐久性^[1-3]。随着矿渣等高铝辅助性胶凝材料的广泛应用, 部分 C-S-H 被水化硅铝酸钙[C-(A-)S-H]替代^[4], 大量研究逐步聚焦于 C-(A-)S-H^[5-9]。研究表明, 源于 C-(A-)S-H 结构的不稳定性, 硅酸盐水泥基材料服役时易受温度、湿度、压力、pH 值和杂质离子等^[10-13]因素干扰。其中, 杂质离子的影响最为复杂, 或吸附在层间, 或在 C-(A-)S-H 中发生原子置换并参与结构重构, 或诱导 C-(A-)S-H 脱钙^[14-19]。典型的, 海工混凝土易受 Mg^{2+} 、 Na^+ 、 Cl^- 、 SO_4^{2-} 等离子侵蚀, 从而出现性能劣化, 其主要原因在于 Mg^{2+} 、 Na^+ 、 Cl^- 、 SO_4^{2-} 等杂质离子诱导 C-(A-)S-H 等水化产物的微纳结构演变^[15-17, 19]。通常 Mg^{2+} 取代 C-S-H 中的 Ca^{2+} , 则形成 $(\text{MgO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z$ ^[17-18, 20], 简记 M-S-H。此外, 杂质离子还会改变水泥孔溶液的 pH 值, 进而影响 C-S-H 稳定性^[21], 最终导致水泥基材料强度和体积稳定性等性能劣化^[17, 22-23]。因此, 揭示杂质离子对 C-(A-)S-H 微纳结构的影响利于针对

性提出防护措施, 从而提高混凝土服役寿命。

水泥基材料中的 C-(A-)S-H 组成多样且多为非晶, 表征难度大, 相关微纳结构模型发展缓慢。近年来, 随着分析手段的飞速发展, 尤其是核磁共振(NMR)、小角散射(SAS)、液细胞透射电子显微镜(LCTEM)等技术的发展, 大量的 C-(A-)S-H 本征结构信息得以获取^[24-28]。此外, 随着计算机技术的发展, 以热力学模拟和基于第一性原理的分子动力学模拟为代表的计算机模拟为揭示 C-(A-)S-H 的原子尺度信息提供了极大助力^[29-30], 机器学习与分子动力学模拟的联合使用大幅提升了模拟效率^[31]。

本文在 C-(A-)S-H 的经典结构模型及近年来在杂质离子作用下 C-(A-)S-H 微纳结构解析方面的研究的基础上, 系统综述了基于先进表征及模拟技术的 C-(A-)S-H 微纳结构解析、微纳结构模型发展、和杂质离子作用下微纳结构的演变规律, 展望了其微纳结构模型的优化和海工服役环境中 C-(A-)S-H 结构演变方面的研究前景, 旨在为水泥基材料延寿技术提供基础理论指导。

收稿日期: 2024-08-06。 修订日期: 2024-09-06。

基金项目: 国家重点研发计划专项(2022YFC3803404); 国家自然科学基金基金(52378255, 52278270, 52302030)。

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Received date: 2024-08-06. Revised date: 2024-09-06.

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1 微纳结构

1.1 C-S-H 微纳结构模型

尽管 C-S-H 结构呈现出长程无序性,但在 3~5 nm 的结构单元内则具有原子有序性^[32-34]。这意味着可通过以托贝莫来石(Tobermorite)和尖乃特石(Jennite)为代表的天然矿物入手研究 C-S-H 微纳结构^[35]。C-S-H 的结构特征与其化学计量比密切相关,尤其是钙硅比(Ca/Si 比),由硅酸三钙和硅酸二钙水化所得 C-S-H 的 Ca/Si 比通常在 1.5~2.0 之间^[36]。Richardson^[37]整理了常见水化硅酸钙晶体的结构信息,揭示了不同种类水化硅酸钙晶体的化学式、Ca/Si 比和晶体结构信息。C-S-H 的 Ca/Si 比差异往往对应于水化硅酸钙类型的差异,且水化硅酸钙中硅氧四面体链的聚合度会随着 Ca/Si 比的增加而降低^[38]。此外,温度和压力也会显著影响 C-S-H 的微纳结构,高温有利于高 Ca/Si 的 C-S-H 生成,而高压则会诱导 C-S-H 层间脱水、结晶度提高^[10]。选区电子衍射为 C-S-H 结晶度精细化表征提供了技术支撑,Zheng 等^[11]联用原位透射电子显微镜和选区电子衍射观察到了 20~800 °C 升温过程中一部分 C-S-H 转为晶态。

由于 C-S-H 具有类托贝莫来石结构,故常用托贝莫来石模型^[39-41]描述其微纳结构。托贝莫来石模型认为硅氧四面体按照 Dreierketten 规则排列,与层状排列的钙氧层相互插层。按照结构单元的间距,托贝莫来石可分为 9、11 Å 和 14 Å 托贝莫来石^[37]。水化产物 C-S-H 与 14 Å 托贝莫来石的结构最为相似^[35]。其为层状结构,主层可细分为 Dreierketten 链和钙氧层,前者通过共价作用连接在钙氧层两侧。进一步的,Dreierketten 链中的硅氧四面体可分为配对硅氧四面体(P)和桥接硅氧四面体(B),前者与钙氧层连接,后者则与 2 个配对硅氧四面体相连^[42]。层间被电解质溶液所填充,以维持整体电中性^[29]。图 1^[37]展示了 14 Å 托贝莫来石结构,其中四面体为硅氧四面体(中心原子为硅原子,氧原子分布于四面体顶点),菱形单元组成了钙氧层(中心原子为钙原子,氧原子分布于菱形单元顶点)。根据 C-S-H 中的 Dreierketten 链之间是否存在交联,可划分为交联和非交联 C-S-H 结构,11 Å 托贝莫来石的(非)交联结构如图 2^[43]所示。C-S-H 中的聚合单元可通过固体核磁共振(NMR)技术量化,常用 Q^n ($n=0, 1, 2, 3, 4$)代表聚合态,即与该聚合单元共价键合的硅(铝)氧四面体数^[44]。基于不同聚合单元的数量可算得 C-S-H

的平均链长(MCL),非交联 C-S-H 的 MCL 如式(1)所示^[45]。

$$\text{MCL} = 2(Q^1 + Q_p^2 + Q_b^2) / Q^1 \quad (1)$$

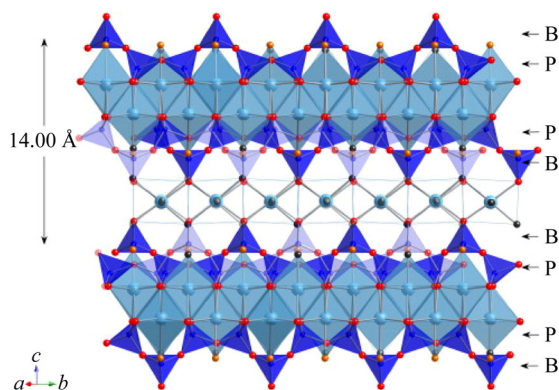


图 1 14 Å 托贝莫来石结构示意图^[37]

Fig. 1 14 Å tobermorite structure schematic diagram^[37]

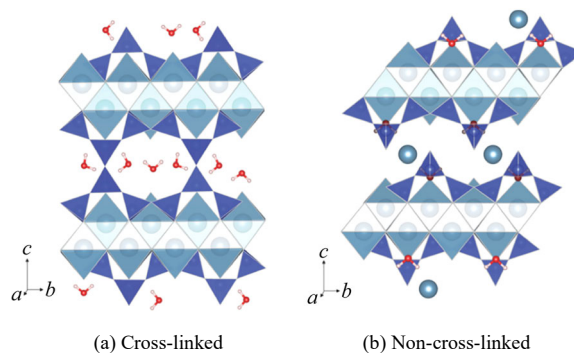


图 2 11 Å 托贝莫来石的交联和非交联结构示意图^[43]

Fig. 2 11 Å tobermorite cross-linked and non-cross-linked structure schematic diagrams^[43]

为实现 C-S-H 微纳结构的精细化表征,并推动 C-S-H 微纳结构模型的发展,需量化 C-S-H 的微纳结构信息。飞行时间二次离子质谱仪(TOF-SIMS)技术赋能 C-S-H 微结构精细化表征在水泥基材料中具有较大应用潜力,TOF-SIMS 技术通过高能离子束加速聚焦后轰击样品可将其表面溅射成大小不均的二次离子碎片,由于荷质比差异导致各碎片飞行时间不同,可通过各碎片的飞行时间获得其质量信息^[46-47]。利用该技术可获取 C-S-H 的化学计量信息,对 C-S-H 微纳结构的精细化研究和定量表征具有重要意义。周珩^[48]使用了 TOF-SIMS 技术构建了 C-S-H 碎片中阴阳离子基团峰强与硅氧四面体聚合度的量化关系,量化分析了微米尺度区域 C-S-H 的局部组成。结果表明,水合程度较高的 C-S-H 多为硅酸盐长链结构,且 C_3S 紧密堆积的空间会促进 C-S-H 聚合度提高。

在建立起 C-S-H 的微纳结构模型后,还需结合

C-S-H 的生成过程探索其微纳结构演变规律。为更好地阐明 C-S-H 生成过程中的微纳结构演变, Zhu 等^[49]使用了小分子封端技术捕捉到了正硅酸乙酯 (TEOS) 和氯化钙溶液-凝胶反应过程中 C-S-H 的中间体, 并解析了其微纳结构, 图 3 为小分子封端技术和 C-S-H 中间体的原子结构模型。所用小分子封端技术巧妙利用了三乙醇胺 (TEA) 和乙醇 (EtOH) 挥发时诱导 C-S-H 缩聚, 进而阻碍 Si—O—Si 键生成。该方法可以原位捕获 C-S-H 生成过程中的中间体, 而 C-S-H 中间体的结构解析则为 C-S-H 微纳结构模型发展及 C-S-H 成核与生长方式的研究提供了重要参考。

当前, 计算机科学的蓬勃发展为水泥基材料研究带来了极大便利, 尤其在机器学习等技术的加成下, C-S-H 的结构模型有望迎来突破性发展。例如, 利用第一性原理、从头算算法 (*ab initio*) 和分子动力学模拟获取 C-S-H 内部原子排列信息、键角和键长信息和荷载作用下 C-S-H 的应力-应变关系等^[31, 50–55]。

在深度学习算法加成下, 模拟效率提高的同时稳定性也得到了保障^[31]。此外, 分子动力学还为研究 C-S-H 表面的相互作用提供了便利, 尤其是为水和电解质离子在 C-S-H 表面的动力学、能量学研究提供了全新视角^[56]。在分子动力学模拟过程中, 为使系统达到平衡过程, 通常需要松弛过程, 松弛过程的高昂成本在极大程度上制约了分子动力学模拟在 C-S-H 模拟中的应用^[31]。Wang 等^[57]基于无松弛过程的分子动力学低保真结果和有松弛过程的高保真结果, 借助高保真物理信息神经网络解析了 NaCl 溶液对 C-S-H 微纳结构参数的影响, 获得了预测误差低于 3% 的高精度结果。基于上述研究结果不难发现, 机器学习技术赋能 C-S-H 微纳结构解析可以极大程度降低分子动力学模拟过程的计算成本。随着机器学习技术在水泥基材料领域的成熟应用, 或可用于指导 C-S-H 的结构改性与定向调控。

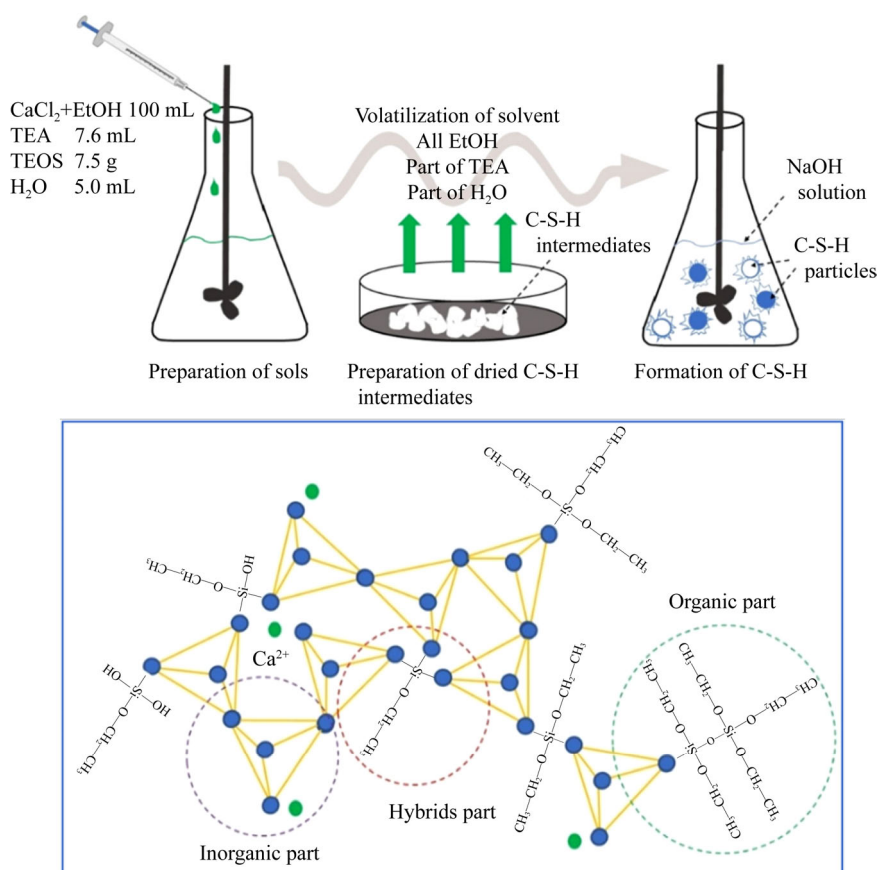


图 3 小分子封端技术及 C-S-H 中间体原子结构模型^[49]

Fig. 3 Small molecule capping techniques and atomic structure models of C-S-H intermediates^[49]

1.2 C-A-S-H 微纳结构模型

Al 可以自发进入 C-S-H 中的 Dreierketten 链, 取代硅氧四面体中的硅, 形成铝氧四面体, 结构自

由能降低^[58]。与 C-S-H 相同, C-A-S-H 也可用 $Q^n(m\text{Al})$ 表示聚合单元及其聚合态, 其中 m 表示该聚合单元连接的铝酸盐结构数量, 一般为 0 或 1^[59]。关于

C-A-S-H 的原子结构, 目前存在 2 点不明确的地方: 1) Al 在 Dreierketten 链中的取代位点; 2) Al 的配位数^[8]。多数学者认为铝的取代主要以四面体配位的

形式[Al(IV)]发生在桥位点(Q_b^2)^[4, 60-62], 或发生在 Q^3 位点[连接 2 个 Dreierketten 链的硅(铝)氧四面体], 如图 4^[63]所示。

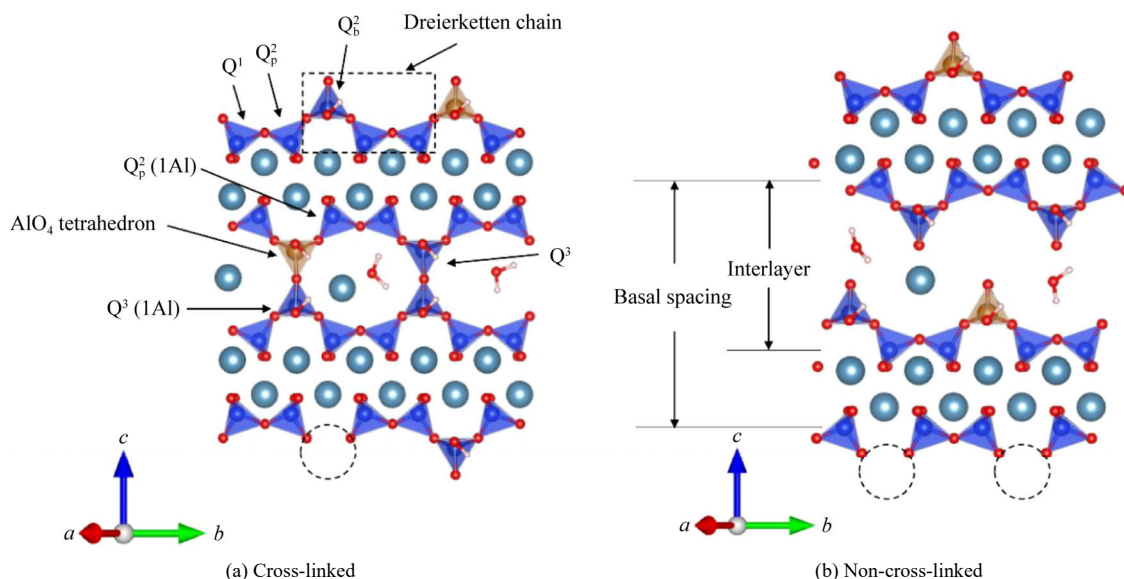


图 4 交联型和非交联型 C-A-S-H 结构示意图^[63]

Fig. 4 Cross-linked and non-cross-linked C-A-S-H structure schematic diagrams^[63]

Al 掺杂会促进 Dreierketten 链交织、提高 $Q^2(1Al)$ 与 $Q^3(1Al)$ 聚合态的相对含量, 并会降低 Q^1 的相对含量, 使得 C-S-H 整体聚合度增长。此外, 根据式(2)和式(3)^[63], Al 掺杂还会导致 C-S-H 平均链长增加^[64-65]。在高 Ca/Si 比下, C-S-H 中更多六配位铝[Al(VI)]出现^[61-62, 66-67], 它们或吸附在 C-S-H 表面的无定形氢氧化铝或第三水化铝(TAH), 抑或在 C-S-H 内部层间^[67], 但也有研究认为水化产物中不存在 TAH^[28]。此外, Al 参与 C-(A)-S-H 形成的过程中, 会造成缺陷、电荷失衡及层间距扩大^[62]。为保持电荷平衡, 一些电荷较少且半径较大的碱金属阳离子(例如 Na^+ 和 K^+)会进入层间^[62, 68]。因此, Al 掺杂会导致 C-(A)-S-H 吸附碱金属离子, 为杂质离子侵入提供条件; 相应的, 层间距的扩大也使 C-A-S-H 与服役环境的物质交换更通畅。

$$MCL (Cross-linked) = 4[Q^1 + Q^2 + Q^2(Al) + Q^3 + 2Q^3(Al)]/Q^1 \quad (2)$$

$$MCL (Non-cross-linked) = 2[Q^1 + Q^2 + 1.5Q^2(1Al)]/Q^1 \quad (3)$$

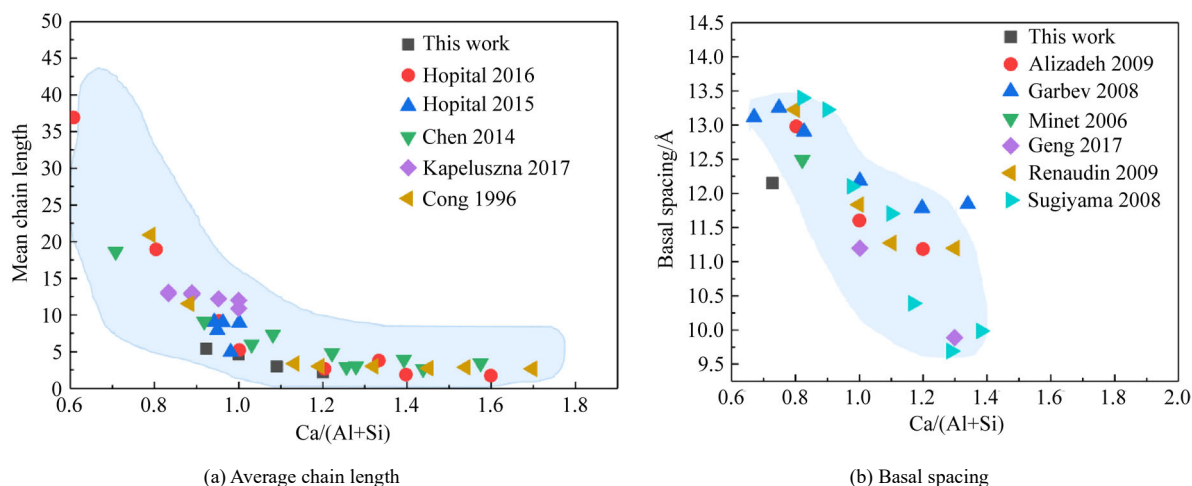
Li 等^[69]进一步提出了面向环境温度的 C-(A)-S-H 结构模型。他们指出, 7~50 °C 时, C-(A)-S-H 保持“类托贝莫来石”结构, 其 Dreierketten 链呈高度扭曲的状态, 交联位点的 Si 易被 Al 取代^[29], 造成 C-(A)-S-H 微结构重构, 交联位点减少。当温度升至 80 °C, C-S-H 交联位点数量增加, 即可供 Al 取代的位

点增多, 大量 Al 取代会导致 C-S-H 微结构显著畸变^[70]。

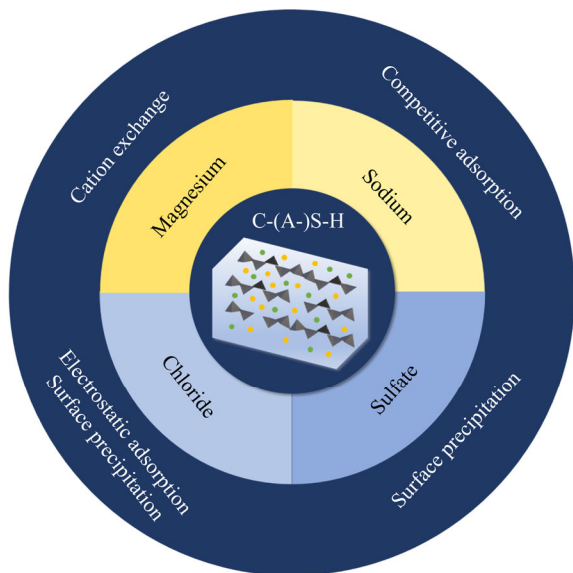
随着对 C-(A)-S-H 认知的日渐深入, 诸多学者尝试阐述 C-(A)-S-H 微纳结构(如 Ca/Si 比和 Al/Si 比)与其微观力学性能之间的联系。研究发现, 高 Ca/Si 比利于氢氧化钙的沉淀, 使得 C-(A)-S-H 的弹性模量和蠕变模量增大^[70-71], 纳米压痕和定量能量色散光谱的结果也证实了这一点^[70, 72-75]。但也有研究表明, Ca/Si 比的提高不利于 C-(A)-S-H 微观力学性能发展^[1, 38, 70]。例如, Ca/Si 比为 1.2 的 C-(A)-S-H 的弹性模量低于 Ca/Si 比为 0.8 的 C-(A)-S-H^[70], 这或可归因于高 Ca/Si 的 C-(A)-S-H 中 Dreierketten 链缺陷浓度^[1]和聚合度^[38]更高。随着 Ca/(Al+Si)比升高, 平均链长和片层间距减小, 如图 5 所示^[70, 76-83]。

2 杂质离子作用下 C-(A)-S-H 的微纳结构演变

为提高硅酸盐水泥基材料在盐蚀环境中耐久性, 延长其服役寿命, 水化产物 C-(A)-S-H 微纳结构演变的研究尤为关键。总体来说, 杂质离子与 C-(A)-S-H 的相互作用多可归纳为以下 4 类^[84-96]: 1) 直接诱导结构重组, 杂质离子取代 C-S-H 中的部分钙或硅, 通过改变 Ca/Si 或 Al/Si 实现 C-(A)-S-H 微纳结构重构, 例如 Mg^{2+} 对 C-S-H 中 Ca^{2+} 的取代。

图5 不同 Ca/(Al+Si)比下 C-(A-)S-H 的微结构特征^[4, 70, 76–83]Fig. 5 Microstructure characteristics of C-(A-)S-H at different Ca/(Al+Si) ratios^[4, 70, 76–83]

2) 在静电引力的作用下吸附在 C-S-H 表面。3) 与硅氧四面体或 Ca^{2+} 发生沉淀反应, 消耗了大量的硅(铝)酸盐和 Ca^{2+} , 从而改变 C-S-H 的 Ca/Si 比。4) 间接诱导结构重组, 通过破坏 C-(A-)S-H 结构, 使其发生解体形成大量硅(铝)酸盐、钙离子, 再通过硅(铝)酸盐、钙离子及杂质离子间的反应实现 C-(A-)S-H 的重构。本文关注 Cl^- 、 SO_4^{2-} 、 Na^+ 和 Mg^{2+} 与 C-(A-)S-H 的作用机制, 图 6 给出了概述^[68, 92, 96]。

图6 Cl^- 、 SO_4^{2-} 、 Na^+ 和 Mg^{2+} 与 C-S-H 的作用机制^[68, 92, 96]Fig. 6 Interaction mechanisms of Cl^- , SO_4^{2-} , Na^+ and Mg^{2+} on C-S-H^[68, 92, 96]

2.1 Cl^- 对 C-(A-)S-H 微纳结构的影响

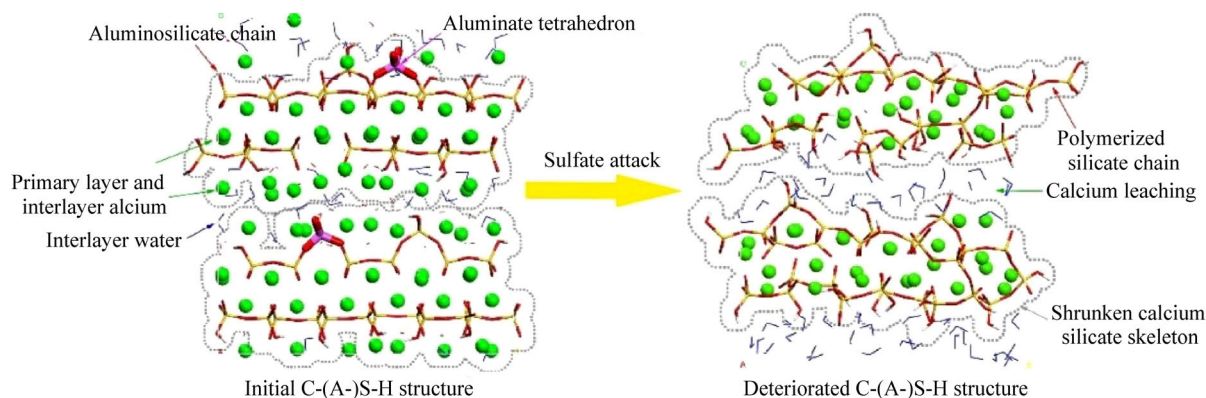
作为最常见的杂质离子, Cl^- 大量存在于海洋、盐碱地等多种服役环境中。尽管 Cl^- 难以侵入稳态水化产物, 也难以影响 C-S-H 中硅氧四面体的聚合

态^[88], 但可在水化初期促进低密度 C-S-H 的生成^[89], 或在静电作用下吸附在稳态 C-S-H 表面, 并与 Ca^{2+} 、 OH^- 反应形成稳定且难溶水合物^[35, 88]。分子建模技术直观地展示了 C-S-H 表面吸附的 Cl^- 与 Ca^{2+} 的稳态及非稳态结合; 稳态结合时 Cl^- 与表层 Ca^{2+} 、表层 Ca^{2+} 与氧原子间的间距均较小, 分别为 2.175 Å 和 2.342 Å, 这赋予了 Cl^- 与 C-S-H 间更强的静电结合力, 如图 7 所示^[3]。 Cl^- 会与 C-A-S-H 中解离的铝酸盐离子反应生成 Frediel's 盐, 使得 Al/Si 比降低, 导致原子结构重排、结构稳定性劣化^[90]。

Cl^- 对 C-(A-)S-H 微纳结构的影响程度与其本征特征(Ca/Si 比和 Al/Si 比等)和环境因素均有关。研究表明, 在 NaCl 溶液环境中, C-S-H 早期结晶度降低, 且低 Ca/Si 比的 C-S-H 含量增加; 而低 Ca/Si 比的 C-S-H 由于表面吸附位点较少使得其 Cl^- 吸附能力较弱^[91]。另有研究表明, C-S-H 的压痕模量和压痕硬度均随 NaCl 溶液浓度增大而增大, 尤其是当 NaCl 浓度提升到 0.05 mol/L 时, HD C-S-H 的压痕模量和压痕硬度提升较为显著; 同时, LD C-S-H 压痕模量提升较快^[92]。此外, 阳离子种类往往影响着氯盐环境中 C-(A-)S-H 的结构演变机制, Jin 等^[93] 将 C-(A-)S-H 在 NH_4Cl 溶液中的解体分为轻度脱钙和重度脱钙 2 大阶段, 结构演变大致如图 8 所示。该研究揭示了 Ca/(Si+Al) 对其主链长度、凝胶孔尺寸的影响规律, 为 NH_4Cl 环境中 C-(A-)S-H 的微纳结构演变研究提供了重要参考。

2.2 SO_4^{2-} 对 C-(A-)S-H 微纳结构的影响

不同于 Cl^- , SO_4^{2-} 会直接参与 C-S-H 结构重组, 诱导其微纳结构畸变。 SO_4^{2-} 会诱导 C-S-H 脱去 Ca^{2+} 形成硫酸钙晶体, C-S-H 的聚合度随之提高。相比

图9 硫酸盐诱导 C-(A-)S-H 结构解体^[94]Fig. 9 Sulphate-induced decomposition of C-(A-)S-H structure^[94]

SO_4^{2-} 对 C-(A-)S-H 微纳结构的影响程度同样取决于 C-(A-)S-H 的本征特征和环境因素。高 Ca/Si 比的 C-(A-)S-H 中 Q^1 聚合态含量较高,更易被 SO_4^{2-} 脱钙;而低 Ca/Si 比的 C-A-S-H,由于其中铝氧四面体大多分布于交联位点,增加了硅链聚合度,阻碍了 SO_4^{2-} 渗透,从而降低了对 SO_4^{2-} 的敏感程度^[94]。Elkhadiri 等^[95]发现,高温会促进 C-S-H 中 S/Ca 比的提高并抑制钙矾石的生成,即高温会促进 SO_4^{2-} 渗透进入 C-S-H 结构。

2.3 Na^+ 对 C-(A-)S-H 微纳结构的影响

Na^+ 是硅酸盐水泥中常见的碱金属离子之一,主要来自水泥熟料中的 NaO 及外界服役环境。当熟料中 Na_2O 完全溶解后,孔溶液中 Na^+ 的浓度约在 0.1~1.0 mol/L 间^[96]。辅助性胶凝材料、外加剂的使用、海洋和盐碱服役环境还会引入额外的 Na^+ 。 Na^+ 会在静电引力牵引下吸附在 C-S-H 颗粒表面或通过扩散作用进入其层间空间,以维持电荷平衡^[87]。C-S-H 对 Na^+ 的吸附作用会随其 Ca/Si 比的升高而减弱,这可能是因为增多的 Ca^{2+} 与 Na^+ 竞争吸附带负电硅链上的有限吸附位点(例如因去质子化作用而残留的表面硅烷醇位点)^[14, 59]。此外, Na^+ 断键作用还会降低早期 C-S-H 聚合度,且对高 Ca/Si 比的 C-S-H 影响较大。水化后期, Na^+ 还可抑制 $\text{Ca}(\text{OH})_2$ 的溶解,降低孔溶液中 Ca^{2+} 浓度,从而降低后期生成 C-S-H 的 Ca/Si 比^[91]。 Na^+ 对 C-S-H 微纳结构的影响程度呈现出随 Na^+ 浓度的增加而增加的趋势^[6, 59, 87, 97]。Liu 等^[87]归纳了不同 Na^+ 浓度下, C-S-H 中 Na/Si 比与 Ca/Si 比之间存在近似线性关系,即 C-S-H 的 Na/Si 比提高会伴随其 Ca/Si 比的降低。这进一步揭示了 Na^+ 与 C-S-H 结构中 Ca^{2+} 的位点竞争关系。

铝掺杂可以通过促进 C-A-S-H 中硅氧四面体链

的聚合程度进而提高 C-(A-)S-H 的 Ca/Si 比, Ca/Si 比的提高则会降低 C-(A-)S-H 对以 Na^+ 为代表的碱金属离子吸附,这同样被归因于 Na^+ 和 Ca^{2+} 之间的竞争吸附^[59, 98]。此外,基于密度泛函的计算结果显示,当孔溶液中碱金属离子浓度较高时,水泥基材料中 AFm 相易分解为 $\text{Al}(\text{OH})_4^-$ 和 OH^- ,为使 C-(A-)S-H 能适应 OH^- 浓度的增加,优先发生铝的桥位点掺杂^[98–99]。

2.4 Mg^{2+} 对 C-(A-)S-H 微纳结构的影响

与 Ca^{2+} 的化学性质的相似性使得 Mg^{2+} 也可与硅氧四面体结合,形成水化硅酸镁(M-S-H)^[17, 100–105]。当 C-S-H 的 Ca/Si 比较低时, M-S-H 才易生成,且其生长则较为缓慢^[17, 91, 103]。常见的 M-S-H 的 Mg/Si 比约为 0.8~1.3,且 pH 值在 8.0~10.4 间才稳定存在^[17, 91, 104, 106]。此外, Mg^{2+} 还可进入 C-S-H 层间。尤其是在高 Ca/Si 比的 C-S-H 中,由于 M-S-H 的生长受抑制,致使更多的 Mg^{2+} 进入层间^[91]。

Mg^{2+} 在高 Ca/Si 比(1.8)的 C-(A-)S-H 凝胶中以四配位的形式掺入, Mg^{2+} 或以镁氧四面体的形式掺入 Dreierketten 链之间的八配位位点或 Q_6^2 硅氧四面体的间距^[107]。因此,在 C-(A-)S-H 中 Mg^{2+} 的反应位点在很大程度上取决于其 Ca/Si 比^[108]。此外,相比于 C-(A-)S-H 中的其他结构位点, Q^1 位点更易成为 Mg^{2+} 反应位点,这归因于其结构不稳定性^[109]。 Mg^{2+} 可以直接和 C-S-H 结构中的 Ca^{2+} 发生置换,形成 $\text{MgO-CaO-SiO}_2\text{-H}_2\text{O}$ (M-C-S-H),但该相难以捕捉,极可能是亚稳态^[110–111]。 Mg^{2+} 不仅会置换 C-A-S-H 的 Ca^{2+} ,还提高了 C-A-S-H 对 SO_4^{2-} 的敏感程度^[90]。高 Ca/Si 比的 C-S-H 在富 Mg^{2+} 环境中常伴随 $\text{Mg}(\text{OH})_2$ 的沉淀,导致溶液 pH 值降低,致使 C-S-H 和 M-S-H 的结构失稳, Mg^{2+} 与 C-S-H 反应加剧,形成正反馈效应^[91]。

尽管上述 4 种离子与 C-(A-)S-H 反应机制不尽

相同, 但均会通过沉淀或离子竞争等作用实现对 C-S-H 的脱钙。其中, Cl^- 会与 C-(A-)S-H 发生表面吸附并与 Ca^{2+} 和 OH^- 结合形成水合物沉淀^[35, 88]; SO_4^{2-} 通过与 Ca^{2+} 结合形成硫酸钙水合物^[87]; 孔溶液和 C-S-H 层间的 Na^+ 和 Mg^{2+} 则会通过离子竞争作用和阳离子置换作用实现对 C-S-H 的脱钙^[59, 110–111]。C-(A-)S-H 的脱钙一般先发生于层间, 层间脱钙会导致 C-S-H 层间距及其分子体积缩小; 当 Ca/Si 比降低至 0.67 以下时, 脱钙主要发生于钙氧层, 而钙氧层内脱钙则会诱导 C-(A-)S-H 解体及硅酸盐溶出^[19, 112]。

2.5 多离子耦合作用对 C-(A-)S-H 微纳结构影响

实际工程中, 硅酸盐水泥基材料中的 C-(A-)S-H 往往面临多离子耦合环境, 相比于单一盐溶液环境, C-(A-)S-H 在多离子耦合作用下的微纳结构演变更加复杂。这种复杂性主要体现在 2 个方面, 其一是当 C-(A-)S-H 与某一种或多种杂质离子作用后其微纳结构会出现一定程度的畸变, 这种畸变可能会改变 C-(A-)S-H 与其他杂质离子的反应机制。例如: 当 C-(A-)S-H 受到 SO_4^{2-} 脱钙后其 Ca/Si 比会降低且聚合度和平均链长增加^[23, 91, 94], 根据 2.1、2.3 节和 2.4 节所述, 此时 Cl^- 吸附减弱^[91], Na^+ 吸附增强^[14, 59, 98], M-S-H 则更易生成^[17, 91, 103]。其二是杂质离子会改变 C-(A-)S-H 周围孔溶液的 pH 值, 从而影响 C-(A-)S-H 和 M-S-H 等物相结构稳定性。例如: M-S-H 稳定存在的 pH 值范围是 8.0~10.4^[104, 106]。

基于 Na^+ , Mg^{2+} , Cl^- 和 SO_4^{2-} 与 C-(A-)S-H 的反应机制, 可以针对性提出海洋服役环境中硅酸盐水泥基材料的延寿方案。首先 Ca/Si 比是影响 C-(A-)S-H 耐久性的主要内因, 在满足其他服役性能要求的前提下, 基于不同杂质离子种类及其浓度定向调控水化产物中 C-(A-)S-H 的 Ca/Si 比可有效实现硅酸盐水泥基材料延寿。其次, 在水泥基材料制备过程中添加 pH 缓冲组分以调控孔溶液 pH 值, 进而抑制杂质离子与 C-(A-)S-H 间的反应。

3 结论与展望

介绍了 C-(A-)S-H 结构模型, 并总结了 C-(A-)S-H 在 Cl^- 、 SO_4^{2-} 、 Na^+ 和 Mg^{2+} 作用下微纳结构演变的研究进展, 并阐述了 C-(A-)S-H 形成机制。表征手段的进步及分子模拟和机器学习等技术的引入推动了 C-(A-)S-H 微纳结构模型的发展, 目前正在逐步建立 C-(A-)S-H 的原子比与其形貌特征和服役性能间的映射关系; 此外, 还推动了 Dreierketten 链中硅/铝氧四面体序列研究。进一步的, 海洋及盐

碱服役环境下 C-(A-)S-H 微纳结构的演变规律也得到进一步揭示。但是, 还存在以下方面有待进一步研究:

1) C-(A-)S-H 微纳结构模型的优化。基于第一性原理计算、分子动力学模拟和机器学习技术建立 C-(A-)S-H 微纳结构模型, 实现基于 C-S-H 微纳观结构的硅酸盐水泥基材料力学性能和耐久性预测;

2) C-(A-)S-H 原子排列解析。受益于核磁共振(NMR)技术的发展, 当前已经可以获取 C-(A-)S-H 中硅(铝)氧四面体的相对含量, 以 X 射线光电子能谱为代表的化学环境分析技术也可以实现 C-(A-)S-H 中元素价态分析, 需在此基础上进一步实现 C-(A-)S-H 原子排列解析, 为实现 C-(A-)S-H 性能的定向调控奠定基础;

3) C-(A-)S-H 在海洋环境中的微纳结构演变机制研究。通过建立不同温度和压力环境中单一盐溶液作用下 C-(A-)S-H 微纳结构数据库, 借助热力学模拟等手段进一步模拟海洋服役环境中 C-(A-)S-H 的微纳结构演变机制, 并进一步与真实海洋服役环境中获取的 C-(A-)S-H 微纳结构对比验证, 为调控 C-(A-)S-H 的微纳结构、开发设计出高耐久性的水泥基材料奠定基础。

4) 低碳绿色建筑材料的发展。基于优化后的 C-(A-)S-H 微纳结构模型, 通过定向调节 C-(A-)S-H 的 Ca/Si 比, 在保证满足工程需求的前提下优化水泥原材料配比, 降低水泥生产过程中的碳排放, 助力低碳绿色建材开发。

参考文献:

- [1] ABDOLHOSSEINI QOMI M J, KRAKOWIAK K J, BAUCHY M, et al. Combinatorial molecular optimization of cement hydrates[J]. Nat Commun, 2014, 5: 4960.
- [2] HU Z L, HILAIRE A, STON J, et al. Intrinsic viscoelasticity of C-S-H assessed from basic creep of cement pastes[J]. Cem Concr Res, 2019, 121: 11–20.
- [3] 刘新, 冯攀, 沈叙言, 等. 水泥水化产物——水化硅酸钙(C-S-H)的研究进展[J]. 材料导报, 2021, 35(9): 9157–9167.
LIU Xin, FENG Pan, SHEN Xuyan, et al. Mater Rep, 2021, 35(9): 9157–9167.
- [4] L'HÔPITAL E, LOTHEBACH B, LE SAOUT G, et al. Incorporation of aluminium in calcium-silicate-hydrates[J]. Cem Concr Res, 2015, 75: 91–103.
- [5] IRBE L, BEDDOE R E, HEINZ D. The role of aluminium in C-A-S-H during sulfate attack on concrete[J]. Cem Concr Res, 2019, 116: 71–80.
- [6] YAN Y, MA B, MIRON G D, et al. Al uptake in calcium silicate hydrate and the effect of alkali hydroxide[J]. Cem Concr Res, 2022, 162: 106957.

- [7] BALDERMANN A, PREISSEGGGER V, DIETZEL M. Solubility of C-A-S-H phases with high degree of heavy metal ion substitution[J]. *Constr Build Mater*, 2022, 327: 126926.
- [8] ZHU X P, VANDAMME M, BROCHARD L, et al. Nature of aluminates in C-A-S-H: A cryogenic stability insight, an extension of DNA-code rule, and a general structural-chemical formula[J]. *Cem Concr Res*, 2023, 167: 107131.
- [9] LI D B, QI Q D, LIU Q L, et al. Uniaxial tensile study of calcium aluminosilicate hydrate (C-A-S-H): Structure, dynamics and mechanical properties[J]. *Mater Today Commun*, 2024, 38: 107854.
- [10] WANG Z P, CHEN Y T, XU L L, et al. Insight into the local C-S-H structure and its evolution mechanism controlled by curing regime and Ca/Si ratio[J]. *Constr Build Mater*, 2022, 333: 127388.
- [11] ZHENG Q, JIANG J Y, LI X L, et al. *In situ* TEM observation of calcium silicate hydrate nanostructure at high temperatures[J]. *Cem Concr Res*, 2021, 149: 106579.
- [12] GAJEWICZ-JAROMIN A M, MCDONALD P J, MULLER A C A, et al. Influence of curing temperature on cement paste microstructure measured by ¹H NMR relaxometry[J]. *Cem Concr Res*, 2019, 122: 147–156.
- [13] LI J Q, ZHANG W X. Preferred orientation of calcium silicate hydrate and its implication to concrete creep[J]. *Compos Part B Eng*, 2022, 247: 110297.
- [14] SHI Z G, LOTHENBACH B. The combined effect of potassium, sodium and calcium on the formation of alkali-silica reaction products[J]. *Cem Concr Res*, 2020, 127: 105914.
- [15] CHEN W, BROUWERS H J H. Alkali binding in hydrated Portland cement paste[J]. *Cem Concr Res*, 2010, 40(5): 716–722.
- [16] BACH T T H, CHABAS E, POCHARD I, et al. Retention of alkali ions by hydrated low-pH cements: Mechanism and Na⁺/K⁺ selectivity[J]. *Cem Concr Res*, 2013, 51: 14–21.
- [17] KIM G, IM S, JEE H, et al. Effect of magnesium silicate hydrate (M-S-H) formation on the local atomic arrangements and mechanical properties of calcium silicate hydrate (C-S-H): *In situ* X-ray scattering study[J]. *Cem Concr Res*, 2022, 159: 106869.
- [18] LOTHENBACH B, NIED D, L'HÔPITAL E, et al. Magnesium and calcium silicate hydrates[J]. *Cem Concr Res*, 2015, 77: 60–68.
- [19] 张紫薇, 刘振陶, 李国新. 钙硅比对水化硅酸钙脱钙过程的影响及机理[J]. *硅酸盐学报*, 2023, 51(11): 2924–2930.
- ZHANG Ziwei, LIU Zhentao, LI Guoxin. J Chin Ceram Soc, 2023, 51(11): 2924–2930.
- [20] LIU X, FENG P, YU X H, et al. The physiochemical alterations of calcium silicate hydrate (C-S-H) under magnesium attack[J]. *Cem Concr Res*, 2022, 160: 106901.
- [21] SHEN X Y, FENG P, ZHANG Q, et al. Toward the formation mechanism of synthetic calcium silicate hydrate (C-S-H)-pH and kinetic considerations[J]. *Cem Concr Res*, 2023, 172: 107248.
- [22] VIALIS H, FAUCON P, PETIT J C, et al. Interaction between salts (NaCl, CsCl) and calcium silicate hydrates (C-S-H)[J]. *J Phys Chem B*, 1999, 103(25): 5212–5219.
- [23] LIU X, FENG P, LI W, et al. Effects of pH on the nano/micro structure of calcium silicate hydrate (C-S-H) under sulfate attack[J]. *Cem Concr Res*, 2021, 140: 106306.
- [24] KURUMISAWA K, NAWA T, OWADA H, et al. Deteriorated hardened cement paste structure analyzed by XPS and ²⁹Si NMR techniques[J]. *Cem Concr Res*, 2013, 52: 190–195.
- [25] MARUYAMA I, IGARASHI G, MATSUI K, et al. Hinderance of C-S-H sheet piling during first drying using a shrinkage reducing agent: A SAXS study[J]. *Cem Concr Res*, 2021, 144: 106429.
- [26] ALLEN A J, THOMAS J J. Analysis of C-S-H gel and cement paste by small-angle neutron scattering[J]. *Cem Concr Res*, 2007, 37(3): 319–324.
- [27] DONG P, ALLAHVERDI A, ANDREI C M, et al. Liquid cell transmission electron microscopy reveals C-S-H growth mechanism during Portland cement hydration[J]. *Materialia*, 2022, 22: 101387.
- [28] SHIRANI S, CUESTA A, MORALES-CANTERO A, et al. 4D nanoimaging of early age cement hydration[J]. *Nat Commun*, 2023, 14(1): 2652.
- [29] HAAS J, NONAT A. From C-S-H to C-A-S-H: Experimental study and thermodynamic modelling[J]. *Cem Concr Res*, 2015, 68: 124–138.
- [30] MORALES-MELGARES A, CASAR Z, MOUTZOURI P, et al. Atomic-level structure of zinc-modified cementitious calcium silicate hydrate[J]. *J Am Chem Soc*, 2022, 144(50): 22915–22924.
- [31] ZHOU Y, ZHENG H J, LI W H, et al. A deep learning potential applied in tobermorite phases and extended to calcium silicate hydrates[J]. *Cem Concr Res*, 2022, 152: 106685.
- [32] TAYLOR H F W. Nanostructure of C-S-H: Current status[J]. *Adv Cem Based Mater*, 1993, 1(1): 38–46.
- [33] XU Z, VIEHLAND D. Observation of a mesostructure in calcium silicate hydrate gels of Portland cement[J]. *Phys Rev Lett*, 1996, 77(5): 952–955.
- [34] XU Z K, VIEHLAND D. Reply to “comment on ‘mesostructure of calcium silicate hydrate (C-S-H) gels in Portland cement paste: Short-range ordering, nanocrystallinity, and local compositional order’”[J]. *J Am Ceram Soc*, 1997, 80(11): 2961–2962.
- [35] TAYLOR H F W. *Cement chemistry*[M]. 2nd ed. London: Thomas Telford, 1997.
- [36] 赵不琪, 孙乾, 杨新月, 等. 水化硅酸钙凝胶的研究进展[J]. *硅酸盐学报*, 2024, 52(5): 1710–1721.
- ZHAO Piqi, SUN Qian, YANG Xinyue, et al. J Chin Ceram Soc, 2024, 52(5): 1710–1721.
- [37] RICHARDSON I G. The calcium silicate hydrates[J]. *Cem Concr Res*, 2008, 38(2): 137–158.
- [38] KIM J J, FOLEY E M, REDA TAHA M M. Nano-mechanical characterization of synthetic calcium-silicate-hydrate (C-S-H) with varying CaO/SiO₂ mixture ratios[J]. *Cem Concr Compos*, 2013, 36: 65–70.
- [39] MERLINO S, BONACCORSI E, ARMBRUSTER T. The real structures of clinotobermorite and tobermorite 9 Å: OD character, polytypes, and structural relationships[J]. *Ejm*, 2000, 12(2): 411–429.
- [40] MERLINO S, BONACCORSI E, ARMBRUSTER T. The real structure of tobermorite 11A: Normal and anomalous forms, OD character and polytypic modifications[J]. *Ejm*, 2001, 13(3): 577–590.
- [41] BONACCORSI E, MERLINO S, KAMPF A R. The crystal structure of tobermorite 14 Å (plombierite), a C-S-H phase[J]. *J Am Ceram Soc*, 2005, 88(3): 505–512.
- [42] LOTHENBACH B, NONAT A. Calcium silicate hydrates: Solid and liquid phase composition[J]. *Cem Concr Res*, 2015, 78: 57–70.
- [43] LI J Q, ZHANG W X, GARBEV K, et al. Influences of cross-linking and Al incorporation on the intrinsic mechanical properties of

- tobermorite[J]. *Cem Concr Res*, 2020, 136: 106170.
- [44] SCHNEIDER J, CINCOTTO M A, PANEPUCCHI H. ^{29}Si and ^{27}Al high-resolution NMR characterization of calcium silicate hydrate phases in activated blast-furnace slag pastes[J]. *Cem Concr Res*, 2001, 31(7): 993–1001.
- [45] YAN Y R, YANG S Y, MIRON G D, et al. Effect of alkali hydroxide on calcium silicate hydrate (C-S-H)[J]. *Cem Concr Res*, 2022, 151: 106636.
- [46] 包泽民. TOF-SIMS 二次离子检测技术研究[D]. 长春: 吉林大学, 2016.
BAO Zemin. Study on TOF-SIMS secondary ion detection technology[D]. Changchun: Jilin University, 2016.
- [47] 包泽民, 刘光达, 龙涛, 等. 铜合金表面元素的飞行时间二次离子质谱微区原位分析[J]. *质谱学报*, 2016, 37(3): 229–235.
BAO Zemin, LIU Guangda, LONG Tao, et al. *J Chin Mass Spectrom Soc*, 2016, 37(3): 229–235.
- [48] 周玥. 水化硅酸钙微纳结构及其组成的量化研究[D]. 上海: 同济大学, 2023.
ZHOU Yue. The quantitative study on the micro-nano structure and composition of calcium silicate[D]. Shanghai: Tongji University, 2023.
- [49] ZHU Z Y, WANG Z P, XU L L, et al. Synthesis and characterization of an intermediate for C-S-H structure tailoring[J]. *Cem Concr Res*, 2022, 160: 106923.
- [50] DHARMAWARDHANA C C, MISRA A, CHING W Y. Quantum mechanical metric for internal cohesion in cement crystals[J]. *Sci Rep*, 2014, 4: 7332.
- [51] SHAHSAVARI R, BUEHLER M J, PELLENQ R J M, et al. First-principles study of elastic constants and interlayer interactions of complex hydrated oxides: Case study of tobermorite and jennite[J]. *J Am Ceram Soc*, 2009, 92(10): 2323–2330.
- [52] YOUSSEF M, PELLENQ R J M, YILDIZ B. Glassy nature of water in an ultraconfining disordered material: The case of calcium-silicate-hydrate[J]. *J Am Chem Soc*, 2011, 133(8): 2499–2510.
- [53] ZHANG N, SHAHSAVARI R. Balancing strength and toughness of calcium-silicate-hydrate via random nanovoids and particle inclusions: Atomistic modeling and statistical analysis[J]. *J Mech Phys Solids*, 2016, 96: 204–222.
- [54] CHURAKOV S V, LABBEZ C, PEGADO L, et al. Intrinsic acidity of surface sites in calcium silicate hydrates and its implication to their electrokinetic properties[J]. *J Phys Chem C*, 2014, 118(22): 11752–11762.
- [55] NGUYEN M T, WANG Z M, ROD K A, et al. Atomic origins of the self-healing function in cement-polymer composites[J]. *ACS Appl Mater Interfaces*, 2018, 10(3): 3011–3019.
- [56] KALINICHEV A G, WANG J W, KIRKPATRICK R J. Molecular dynamics modeling of the structure, dynamics and energetics of mineral-water interfaces: Application to cement materials[J]. *Cem Concr Res*, 2007, 37(3): 337–347.
- [57] WANG T F, CAO J, GUO T, et al. The role of deep learning in reducing computational cost when simulating chloride ion attack on hydrated calcium silicate with molecular dynamics[J]. *Constr Build Mater*, 2024, 417: 135257.
- [58] KALOUSEK G L. Crystal chemistry of hydrous calcium silicates: I, substitution of aluminum in lattice of tobermorite[J]. *J Am Ceram Soc*, 1957, 40(3): 74–80.
- [59] L'HÔPITAL E, LOTHENBACH B, SCRIVENER K, et al. Alkali uptake in calcium alumina silicate hydrate (C-A-S-H)[J]. *Cem Concr Res*, 2016, 85: 122–136.
- [60] KOMARNENI S, ROY R, ROY D M, et al. ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy of Al-substituted tobermorites[J]. *J Mater Sci*, 1985, 20(11): 4209–4214.
- [61] PARDAL X, BRUNET F, CHARPENTIER T, et al. ^{27}Al and ^{29}Si solid-state NMR characterization of calcium-aluminosilicate-hydrate[J]. *Inorg Chem*, 2012, 51(3): 1827–1836.
- [62] SUN G K, YOUNG J F, KIRKPATRICK R J. The role of Al in C-S-H: NMR, XRD, and compositional results for precipitated samples[J]. *Cem Concr Res*, 2006, 36(1): 18–29.
- [63] LOTHENBACH B, JANSEN D, YAN Y, et al. Solubility and characterization of synthesized 11 Å Al-tobermorite[J]. *Cem Concr Res*, 2022, 159: 106871.
- [64] MAEDA H, ABE K, ISHIDA E H. Hydrothermal synthesis of aluminum substituted tobermorite by using various crystal phases of alumina[J]. *J Ceram Soc Japan*, 2011, 119(1389): 375–377.
- [65] GARCÍA LODEIRO I, FERNÁNDEZ-JIMENEZ A, PALOMO A, et al. Effect on fresh C-S-H gels of the simultaneous addition of alkali and aluminium[J]. *Cem Concr Res*, 2010, 40(1): 27–32.
- [66] FAUCON P, DELAGRAVE A, RICHET C, et al. Aluminum incorporation in calcium silicate hydrates (C-S-H) depending on their Ca/Si ratio[J]. *J Phys Chem B*, 1999, 103(37): 7796–7802.
- [67] RENAUDIN G, RUSSIAS J, LEROUX F, et al. Structural characterization of C-S-H and C-A-S-H samples—Part II: Local environment investigated by spectroscopic analyses[J]. *J Solid State Chem*, 2009, 182(12): 3320–3329.
- [68] MUDRAKOVSKII I L, MASTIKHIN V M, SHMACHKOVA V P, et al. High-resolution solid-state ^{29}Si and ^{31}P NMR of silicon-phosphorous compounds containing six-coordinated silicon[J]. *Chem Phys Lett*, 1985, 120(4–5): 424–426.
- [69] LI J Q, GENG G Q, MYERS R, et al. The chemistry and structure of calcium (alumino) silicate hydrate: A study by XANES, ptychographic imaging, and wide- and small-angle scattering[J]. *Cem Concr Res*, 2019, 115: 367–378.
- [70] WANG J W, HU Z L, CHEN Y, et al. Effect of Ca/Si and Al/Si on micromechanical properties of C(-A)-S-H[J]. *Cem Concr Res*, 2022, 157: 106811.
- [71] HU Z L, WYRZYKOWSKI M, GRIFFA M, et al. Young's modulus and creep of calcium-silicate-hydrate compacts measured by microindentation[J]. *Cem Concr Res*, 2020, 134: 106104.
- [72] MEJDI M, WILSON W, SAILLIO M, et al. Quantifying glass powder reaction in blended-cement pastes with the Rietveld-PONKCS method[J]. *Cem Concr Res*, 2020, 130: 105999.
- [73] WILSON W, RIVERA-TORRES J M, SORELLI L, et al. The micromechanical signature of high-volume natural pozzolan concrete by combined statistical nanoindentation and SEM-EDS analyses[J]. *Cem Concr Res*, 2017, 91: 1–12.
- [74] KRAKOWIAK K J, WILSON W, JAMES S, et al. Inference of the phase-to-mechanical property link via coupled X-ray spectrometry and indentation analysis: Application to cement-based materials[J]. *Cem Concr Res*, 2015, 67: 271–285.
- [75] WILSON W, SORELLI L, TAGNIT-HAMOU A. Unveiling

- micro-chemo-mechanical properties of C–(A)–S–H and other phases in blended-cement pastes[J]. *Cem Concr Res*, 2018, 107: 317–336.
- [76] GENG G Q, MYERS R J, QOMI M J A, et al. Densification of the interlayer spacing governs the nanomechanical properties of calcium-silicate-hydrate[J]. *Sci Rep*, 2017, 7(1): 10986.
- [77] RENAUDIN G, RUSSIAS J, LEROUX F, et al. Structural characterization of C–S–H and C–A–S–H samples—Part I: Long-range order investigated by Rietveld analyses[J]. *J Solid State Chem*, 2009, 182(12): 3312–3319.
- [78] L'HÔPITAL E, LOTHENBACH B, KULIK D A, et al. Influence of calcium to silica ratio on aluminium uptake in calcium silicate hydrate[J]. *Cem Concr Res*, 2016, 85: 111–121.
- [79] CHEN J J, THOMAS J J, TAYLOR H F W, et al. Solubility and structure of calcium silicate hydrate[J]. *Cem Concr Res*, 2004, 34(9): 1499–1519.
- [80] CONG X D, KIRKPATRICK R J. Effects of the temperature and relative humidity on the structure of C–S–H gel[J]. *Cem Concr Res*, 1995, 25(6): 1237–1245.
- [81] ALIZADEH A. Nanostructure and engineering properties of basic and modified calcium-silicate-hydrate systems[D]. Ottawa: University of Ottawa, 2009.
- [82] MINET J, ABRAMSON S, BRESSON B, et al. Organic calcium silicate hydrate hybrids: A new approach to cement based nanocomposites[J]. *J Mater Chem*, 2006, 16(14): 1379–1383.
- [83] SUGIYAMA T, RITTHICHAUY W, TSUJI Y. Experimental investigation and numerical modeling of chloride penetration and calcium dissolution in saturated concrete[J]. *Cem Concr Res*, 2008, 38(1): 49–67.
- [84] BERNARD E, DAUZÈRES A, LOTHENBACH B. Magnesium and calcium silicate hydrates, Part II: Mg-exchange at the interface “low-pH” cement and magnesium environment studied in a C-S-H and M-S-H model system[J]. *Appl Geochem*, 2018, 89: 210–218.
- [85] KRATTIGER N, LOTHENBACH B, CHURAKOV S V. Sorption and electrokinetic properties of ASR product and C-S-H: A comparative modelling study[J]. *Cem Concr Res*, 2021, 146: 106491.
- [86] JALLAD K N, SANTHANAM M, COHEN M D. Stability and reactivity of thaumasite at different pH levels[J]. *Cem Concr Res*, 2003, 33(3): 433–437.
- [87] LIU X, FENG P, CHEN J, et al. A critical review on the interaction between calcium silicate hydrate (C-S-H) and different ions[J]. *Constr Build Mater*, 2024, 413: 134931.
- [88] HIRAO H, YAMADA K, TAKAHASHI H, et al. Chloride binding of cement estimated by binding isotherms of hydrates[J]. *J Adv Concr Technol*, 2005, 3(1): 77–84.
- [89] JUENGER M C G, MONTEIRO P J M, GARTNER E M, et al. A soft X-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydration[J]. *Cem Concr Res*, 2005, 35(1): 19–25.
- [90] JIN S C, LIU K, ZHANG G Z, et al. Effect of corrosive ions (Cl^- , SO_4^{2-} , and Mg^{2+}) on the nanostructure and chloride binding property of C-A-S-H gel[J]. *J Wuhan Univ Technol Mater Sci Ed*, 2020, 35(6): 1061–1072.
- [91] 陈钰婷. 不同结构水化硅酸钙在离子侵蚀下的演化机理[D]. 上海: 同济大学, 2022.
- CHEN Yuting. Study on the mechanism of calcium silicate hydrates with different structure under corrosive ions attack[D]. Shanghai: Tongji University, 2022.
- [92] SUN Y J, YAPHARY Y L, POON C S. Experimental and mesoscale simulation studies of micro-mechanical properties of alite mixed with NaCl solutions[J]. *Cem Concr Res*, 2022, 159: 106890.
- [93] JIN M, MA Y F, LI W W, et al. Multi-scale investigation on composition-structure of C-(A)-S-H with different Al/Si ratios under attack of decalcification action[J]. *Cem Concr Res*, 2023, 172: 107251.
- [94] YANG J, DING Q J, ZHANG G Z, et al. Effect of sulfate attack on the composition and micro-mechanical properties of C-A-S-H gel in cement-slag paste: A combined study of nanoindentation and SEM-EDS[J]. *Constr Build Mater*, 2022, 345: 128275.
- [95] ELKHADIRI I, PUERTAS F. The effect of curing temperature on sulphate-resistant cement hydration and strength[J]. *Constr Build Mater*, 2008, 22(7): 1331–1341.
- [96] VOLLPRACHT A, LOTHENBACH B, SNELLINGS R, et al. The pore solution of blended cements: A review[J]. *Mater Struct*, 2016, 49(8): 3341–3367.
- [97] HONG S Y, GLASSER F P. Alkali binding in cement pastes[J]. *Cem Concr Res*, 1999, 29(12): 1893–1903.
- [98] WEI S H, ZHENG K R, CHEN W, et al. The correlation between Al incorporation and alkali fixation by calcium aluminosilicate hydrate: Observations from hydrated C_3S blended with and without metakaolin[J]. *Cem Concr Res*, 2023, 172: 107249.
- [99] MOHAMED A K, MOUTZOURI P, BERRUYER P, et al. The atomic-level structure of cementitious calcium aluminate silicate hydrate[J]. *J Am Chem Soc*, 2020, 142(25): 11060–11071.
- [100] LI Z H, ZHANG T S, HU J, et al. Characterization of reaction products and reaction process of $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system at room temperature[J]. *Constr Build Mater*, 2014, 61: 252–259.
- [101] SZCZERBA J, PROROK R, ŚNIEŻEK E, et al. Influence of time and temperature on ageing and phases synthesis in the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system[J]. *Thermochim Acta*, 2013, 567: 57–64.
- [102] LIMEIRA J, ETXEBERRIA M, AGULLÓ L, et al. Mechanical and durability properties of concrete made with dredged marine sand[J]. *Constr Build Mater*, 2011, 25(11): 4165–4174.
- [103] ZHANG Y, LI Y W, DAI Y J, et al. Hydration evolution of MgO-SiO_2 slurries in the presence of sodium metasilicate[J]. *Ceram Int*, 2018, 44(6): 6626–6633.
- [104] NIED D, ENEMARK-RASMUSSEN K, L'HOPITAL E, et al. Properties of magnesium silicate hydrates (M-S-H)[J]. *Cem Concr Res*, 2016, 79: 323–332.
- [105] TANG Y J, SCHOLLBACH K, BROUWERS H J H, et al. Effects of soluble magnesium on the structure of calcium silicate hydrate[J]. *Constr Build Mater*, 2021, 302: 124402.
- [106] ROOSZ C, GRANGEON S, BLANC P, et al. Crystal structure of magnesium silicate hydrates (M-S-H): The relation with 2:1 Mg-Si phyllosilicates[J]. *Cem Concr Res*, 2015, 73: 228–237.
- [107] FERNANDEZ L, ALONSO C, HIDALGO A, et al. The role of magnesium during the hydration of C_3S and C-S-H formation. Scanning electron microscopy and mid-infrared studies[J]. *Adv Cem Res*, 2005, 17(1): 9–21.
- [108] FERNANDEZ L, ALONSO C, ANDRADE C, et al. The interaction of magnesium in hydration of C_3S and CSH formation using ^{29}Si MAS-NMR[J]. *J Mater Sci*, 2008, 43(17): 5772–5783.
- [109] 朱效宏, 李青, 陈平, 等. 硫酸盐侵蚀条件下 C–(A)–S–H 组成-结构

- 演化的量化分析[J]. 硅酸盐学报, 2021, 49(5): 901–909.
- ZHU Xiaohong, LI Qing, CHEN Ping, et al. J Chin Ceram Soc, 2021, 49(5): 901–909.
- [110] KOMARNENI S, BREVAL E, ROY D M, et al. Reactions of some calcium silicates with metal cations[J]. Cem Concr Res, 1988, 18(2): 204–220.
- [111] SHRIVASTAVA O P, KOMARNENI S, BREVAL E. Mg^{2+} uptake by synthetic tobermorite and xonotlite[J]. Cem Concr Res, 1991, 21(1): 83–90.
- [112] ZHANG Y, GUO L, SHI J Y, et al. Full process of calcium silicate hydrate decalcification: Molecular structure, dynamics, and mechanical properties[J]. Cem Concr Res, 2022, 161: 106964.

Effect of Impurity Ions on Micro-/Nano-Structure of Calcium Silicate (Aluminate) Hydrate

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Extended Abstract

Calcium silicate (aluminate) hydrate (C-(A-)S-H) as a predominant hydration product formed in Portland cementitious materials plays a pivotal role in determining the mechanical strength, durability, and creep resistance of Portland cementitious materials. The complex and intricate micro-/nano-structures of C-(A-)S-H become a challenge in deciphering its characteristics of micro-/nano-structures. Furthermore, the sensitivity of C-(A-)S-H to service environments exacerbates the complexity of micro-/nano-structures analysis. Throughout the operational lifespan of Portland cementitious materials, fluctuations in temperature, mechanical stresses, water flow dynamics, and attack of ions (*i.e.*, Na^+ , Mg^{2+} , Cl^- and SO_4^{2-}) lead to continuous and dynamic changes in the micro-/nano-structures of C-(A-)S-H. Recent work on the methods for characterizing C-(A-)S-H micro-/nano-structures, computational simulations of C-(A-)S-H, and the integration of machine learning techniques are carried out to clarify the micro-/nano-structures of C-(A-)S-H. These advancements facilitate iterative improvements in micro-/nano-structure models, enabling more precise predictions and control of macroscopic properties in micro-/nano-scale in Portland cementitious materials, accurately forecasting the evolution of C-(A-)S-H micro-/nano-structures under ions attack conditions, having a significant promise for further refining micro-/nano-structure models. Such advancements can provide theoretical insights and offer practical avenues and strategies for optimizing the performance and durability of Portland cementitious materials through informed materials design and engineering strategies.

It is necessary to explore the advanced characterization of C-(A-)S-H micro-/nano-structures and clarify the intricate development of models depicting micro-/nano-structures of C-(A-)S-H, micro-/nano-structures evolution under ions attack environments and the specific mechanisms by ions (*i.e.*, Na^+ , Mg^{2+} , Cl^- and SO_4^{2-}) interact. A C-(A-)S-H micro-/nano-structure model is developed *via* utilizing the advanced techniques such as small molecule capping, time-of-flight secondary ion mass spectrometry (TOF-SIMS), molecular simulations and machine learning. The overarching goal remains to provide theoretical foundations for optimizing C-(A-)S-H micro-/nano-structure model.

In addition, predicting the evolution of C-(A-)S-H micro-/nano-structures under ions attack conditions accurately is a multifaceted endeavor with a potential to advance theoretical understanding and provide practical solutions. The significance of this undertaking is that it paves a way for Portland cementitious materials optimization through intelligent design, thereby creating cementitious materials that are more durable, efficient, and environmentally sustainable to meet the demands of modern construction and other related fields.

Summary and Prospects This review represents the micro-/nano-structure models of C-(A-)S-H and discusses recent advancements in understanding its evolution under common marine ions attack (*i.e.*, Na^+ , Mg^{2+} , Cl^- and SO_4^{2-}). This review elucidates the mechanisms by which aluminum-rich supplementary cementitious materials promote the formation of C-A-S-H, highlighting advancements in characterization techniques and the integration of molecular simulation and machine learning. These innovations significantly advance the development of models describing the micro-/nano-structures of C-(A-)S-H.

Advancements in characterization techniques supported by cutting-edge technologies such as molecular dynamics simulations and machine learning deepen our understanding of atomic ratios within C-(A-)S-H in relation to its degree of polymerization, average chain length, micro-mechanical properties, and durability. These developments facilitate the establishment of mappings between the micro-/nano-structures of C-(A-)S-H and its properties. Furthermore, this can contribute to advancing sequential studies of silicate (aluminate) tetrahedra on the Dreierketten chains.

At present, some aspects merit a further investigation and have a potential to emerge as future research focal points as follows: 1) the micro-/nano-structure model of C-(A-)S-H can be optimized and a framework utilizing first-principles calculations, molecular dynamics simulations, and machine learning techniques needs to be proposed. These aim to predict the mechanical properties and durability of Portland cementitious materials based on the micro-/nano-structure of C-(A-)S-H. It is thus feasible to enhance

understanding and predictive capabilities concerning the performance and longevity of Portland cementitious materials at the microstructural level *via* integrating these advanced computational methodologies. 2) Atomic arrangement analysis of C-(A-)S-H is needed. It is thus feasible to determine the relative abundance of structural units within C-(A-)S-H by nuclear magnetic resonance (NMR). Chemical environment analysis techniques, such as X-ray photoelectron spectroscopy (XPS), enable elemental valence state analysis in C-(A-)S-H. The detailed atomic arrangement analysis of C-(A-)S-H can be obtained, which is crucial for directing the targeted production of Portland cementitious materials. 3) The micro-/nano-structures evolution mechanisms of C-(A-)S-H in marine environments need to be investigated. The micro-/nano-structures evolution mechanisms of C-(A-)S-H under complex ions attack conditions are investigated. The degradation mechanisms of C-(A-)S-H in simulated marine environment need to be further simulated *via* establishing a database of products under single-factor attack environments and employing thermodynamic simulation techniques, and the simulation results with the micro-/nano-structures of C-(A-)S-H in real marine service environments need to be compared. 4) Low-carbon green building materials are developed. The Ca/Si ratio in C-(A-)S-H can be adjusted based on the optimized models of micro-/nano-structures of C-(A-)S-H, meeting engineering requirements, while optimizing the raw material composition of cement. This approach can reduce CO₂ emissions during cement production, thereby promoting the development of low-carbon green building materials.

Keywords calcium silicate (aluminate) hydrate; impurity ions; micro-nanostructures; durability