

极端低温环境下混凝土力学性能及其演变机制研究进展

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摘 要: 极端温度环境对混凝土服役性能与结构安全具有负面影响, 其劣化过程涉及诸多复杂物理化学作用。本文概述了混凝土在超低温环境下的宏观力学性能及微结构特征演变, 阐释了超低温作用下混凝土的性能增强机制, 归纳了低温冻融循环后混凝土性能劣化机制, 探讨了目前极端低温环境下混凝土研究存在的关键问题, 并对未来相关研究进行了展望。

关键词: 极端低温环境; 混凝土; 力学性能; 微结构特征; 劣化机制

中图分类号: TU528 文献标志码: A 文章编号: 0454-5648(2024)05-1698-12

网络出版时间: 2024-02-22



极端条件下材料的物理与化学研究是 21 世纪材料学探索的前沿领域之一, 常不为人所熟知, 但具有极大的探索空间。作为最为常见的极端条件之一, 极端低温环境不仅会对混凝土的力学性能产生较大影响, 严重时还会对混凝土结构的正常服役安全构成极大威胁。目前, 混凝土材料因其优异的力学性能、耐久性能、可建造性能与安全性能, 已被广泛应用于严寒环境条件下的工程中, 如中国哈大高速铁路、青藏铁路以及南北极工程建设等。同时, 由于混凝土材料也具备优异的耐超低温服役性能, 近年来也在极端温度环境下的特殊结构工程中备受关注, 诸如深冷冷藏仓库(-80℃)、液化天然气储罐(-161.5℃)、液化氢气储罐(-253℃)及液化氦气储罐(-268.9℃)等^[1-2]。由此可见, 超低温会对混凝土材料与结构产生极大负面作用, 探明极端低温环境下的混凝土性能演变及其劣化机制对揭示材料本质具有重要意义。

混凝土作为现代结构工程中最为重要的建设材料, 已被广泛用于各种环境中的工程应用。然而在极端低温环境中由于其服役条件与常温时相差甚大, 会致使混凝土性能出现一定程度的劣化。此时,

研发出一种能耐极端温变作用的混凝土材料对解决极端环境下工程耐久性问题具有重要意义^[3]。目前, 关于超低温环境下的普通混凝土研究相对较多且完善, 故近年来一些研究人员已着手研究超低温下钢筋混凝土、超高性能混凝土(UHPC)及地聚物混凝土等, 同时通过优化原材料组分以期进一步提高混凝土的耐极端温变性能^[4-6]。超低温环境下, 钢筋混凝土的性能劣化主要源于钢筋与混凝土间粘结作用失效及基体脆性增加, 而通过提高箍筋比或采用预应力钢筋可提高钢筋混凝土的延展性和延迟开裂作用^[7-9]。采用钢纤维增强 UHPC 可极大提高混凝土在超低温下的力学性能, PVA 纤维和 PP 纤维的增强效果则较差^[2]。当然, UHPC 填充高强度钢管也不失为一种改善混凝土耐超低温作用的方法^[10]。此外, 地聚物混凝土也被证实具有相对优异的耐超低温冻融作用^[6]。

值得注意的是, 混凝土材料具有极强的可塑性, 通过不断对其进行原材料优选、配合比优化、结构设计及性能调控等, 可开发出满足不同应用场景需求且适用性能突出的新型建筑材料, 特别是面向极端低温环境下的混凝土工程^[11-12]。因此, 为解决普

收稿日期: 2023-08-30。 修订日期: 2023-11-07。

基金项目: 国家自然科学基金资助项目(U22B2076, 51878480, 52078369, 52108241); 2021 年产业技术基础公共服务平台(2021-H029-1-1); 上海市优秀学术带头人计划资助(22XD1403300); 中央高校基本科研业务费专项资金资助。

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Received date: 2023-08-30. Revised date: 2023-11-07.

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通混凝土在极端温度环境下的应用受限难题, 本文系统综述了极端低温环境下的混凝土力学性能及劣化机制, 以期开发出可满足极端低温服役需求的混凝土材料提供重要思路, 同时也对我国未来前沿性战略研究与探索方向提供一定的参考。

1 超低温环境下混凝土力学性能

1.1 抗压强度

超低温下, 混凝土的抗压强度呈现出异于常温时的规律, 主要与混凝土强度等级、温度及含水量有关^[13-14]。随着温度降低, 混凝土中的孔隙水逐渐冻结会导致对外部荷载的抵抗力显著增加, 最终抗压强度随之提高^[15-16]。混凝土含水率或强度等级的增加, 均会提高超低温下混凝土的抗压强度^[17]。而关于超低温下混凝土的极限抗压强度值, 目前尚未得出明确统一^[18]。有人认为混凝土抗压强度在 -125°C 附近会出现极大值, 此后将随温度的降低而降低^[13]。另一部分人则认为混凝土的强度在到达一定低温后将不再增加, 在 $0\sim-120^{\circ}\text{C}$ 范围内, 混凝土的强度主要取决于温度和含水量, 当温度低于 120°C 时, 强度则仅与初始含水率有关, 而与温度无关^[19-20]。图 1 为超低温下混凝土抗压强度的增长规律^[17-18]。

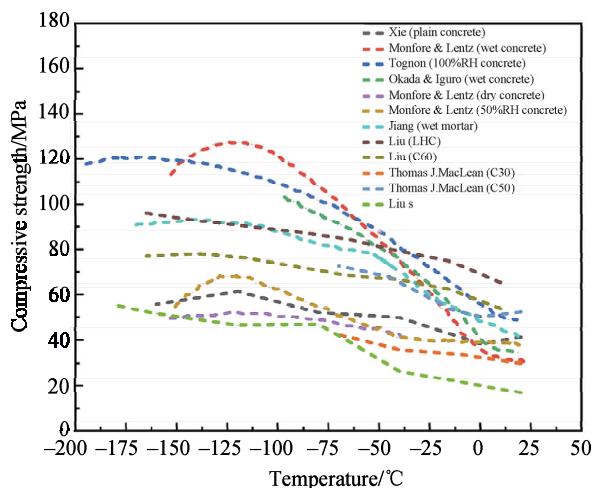


图 1 超低温下混凝土抗压强度演变规律^[17-18]

Fig. 1 Evolution law of compressive strength of concrete at cryogenic temperature^[17-18]

1.2 抗拉强度

与抗压强度类似, 超低温下混凝土的抗拉强度随温度的降低及含水率的升高而逐渐增加(见图 2)^[21-22]。饱水混凝土抗拉强度增长明显, 干燥混凝土的抗拉强度增长则较小。相较于普通骨料混凝土,

轻骨料混凝土抗拉强度受温度的影响相对较小^[22-23], 钢纤维的掺入同样能显著改善 UHPC 在超低温下的拉伸性能^[24]。现有研究认为, 混凝土的抗拉强度会在一定温度下达到最大值, 但不同研究中的极限抗拉强度对应的温度则不尽相同, 其主要原因可能是由于混凝土配合比、养护时间、试件的含水量和孔隙率等不同所致^[20, 25]。此外, 混凝土内孔溶液会随温度的降低而逐渐冻结, 并在基体内部形成由冰组成的网状结构。然而, 由于混凝土孔隙结构的不同, 其在降温过程中的结冰时间也各异, 加之不同混凝土内部冰网结构也有区别, 同样是引起混凝土抗拉强度不同的原因^[26]。

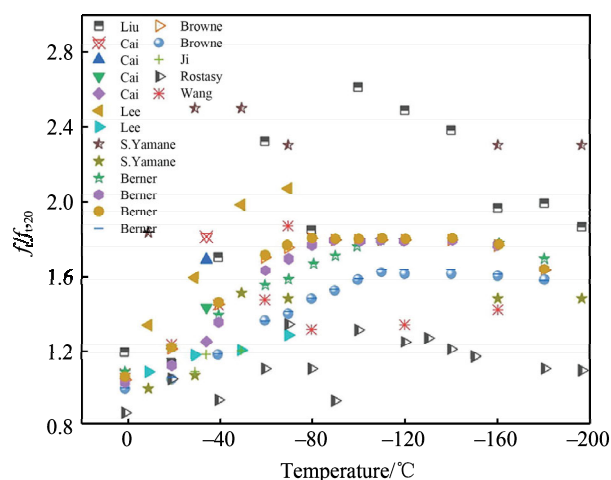


图 2 混凝土在超低温下与室温下的抗拉强度之比^[21-22]

Fig. 2 Tensile strength ratio of concrete at cryogenic temperature to ambient temperature^[21-22]

1.3 抗弯强度

抗弯强度, 亦称抗折强度, 目前在超低温环境下的相关研究相对较少。相较于抗压强度, 抗弯强度对混凝土中孔隙分布和孔结构演变更加敏感, 其在超低温下更易受含水率的影响^[27-28]。一些学者认为混凝土的抗弯强度会随混凝土含水率的增加和温度的降低而逐渐增加。也有学者认为混凝土抗弯强度会在 -60°C 时达到峰值, 之后不再随温度的降低而增加^[25]。超低温环境下, UHPC 相较于普通混凝土具有更好的抗弯性能、抗温变性能以及抑制微裂缝扩展能力^[29]。钢纤维增强 UHPC 比 PP 纤维和 PVA 纤维具有更明显的抗超低温性能, 其在超低温下的抗弯强度将大幅增加, 且混凝土的脆性也随之增大^[12, 30]。

1.4 粘结强度

对于不同类型混凝土而言, 混凝土的粘结性能主要包括钢筋与混凝土间的粘结强度以及钢纤

维与混凝土间的粘结强度。超低温环境下, 随着温度的降低, 钢筋的屈服强度逐渐增加而韧性随之降低^[31], 其劣化模式从延性破坏变为脆性破坏^[32], 钢筋混凝土的粘结强度则随温度的降低而呈线性增加的趋势^[33]。同时, 含水率、约束条件、混凝土抗压强度与保护层厚度也与钢筋混凝土的粘结性能具有正相关关系^[34–37]。然而对 UHPC 而言, 其粘结强度主要来源于纤维与 UHPC 基体间的界面性能。超低温下, UHPC 的粘结强度大幅提高, 但基体界面和拔出纤维的表面损伤程度也会明显加重^[38]。

1.5 弹性模量

与抗折强度类似, 混凝土在超低温下的弹性模量也存在争议。大多数研究者认为^[39–40], 混凝土在超低温下的弹性模量随温度的降低而增加, 且无极值。少数研究者则持相反观点, 他们认为在超低温下混凝土弹性模量的增加与含水量、降温速率及骨料含量密切相关^[41]。含水量越高, 弹性模量的增长速率越快, 同时弹性模量的增长率明显低于抗压强度的增长率。饱水混凝土在 -30 、 -70 、 -160 °C 的弹性模量增量分别达到 30%、50% 和 70%。绝干混凝土明显不同于饱水混凝土, 当温度低于 -30 °C 时, 绝干混凝土的弹性模量便保持稳定^[22]。在 -190 °C 时, 饱水混凝土和绝干混凝土的弹性模量分别是常温下的 1.75 倍和 1.65 倍^[42]。对于普通混凝土, 谢剑等^[43]提出了超低温环境下混凝土弹性模量的预测模型。Kang 等^[44]研究了寒冷地区 UHPC 的静态力学性能, 发现 UHPC 的弹性模量随温度的降低而明显增加。同时, 冻结水填充 UHPC 的凝胶孔和毛细孔, 强化了水泥基体-骨料界面过渡区。

2 超低温冻融循环后混凝土微结构特征演变

2.1 孔隙水相变

超低温环境下, 混凝土孔隙水存在过冷水现象, 即水在低于 0 °C 时仍未冻结成冰^[45]。过冷水的热力学性质较为独特, 具有很强的温度依赖性。当温度低至 -46 °C 时, 过冷水的性质将发生突变, 这一临界温度便是冰均匀成核的温度^[46]。通常而言, 混凝土内毛细孔与凝胶孔中的孔隙水在 20 °C 至 -80 °C 会相继发生相变和迁移, 纳米孔中孔隙水则会在 -80 °C 至 -170 °C 发生冰型转化^[1, 47]。实际上, 孔隙

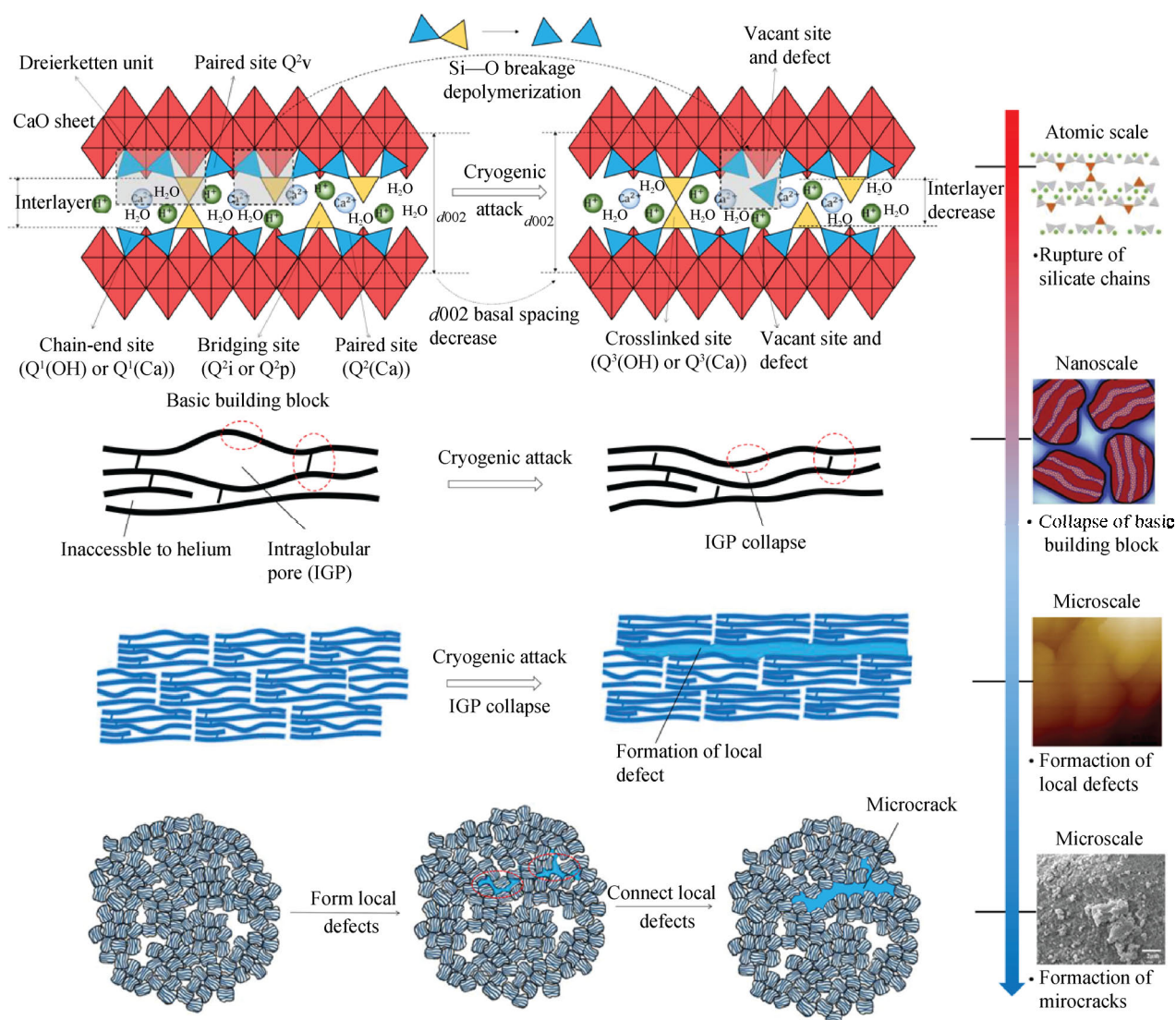
水的相变温度取决于孔径尺寸^[48–50], 孔径越小则相变温度越低。在温度降至 -20 °C 时, 混凝土内部大量凝胶孔中的孔隙水逐渐结冰并产生较大的体积膨胀, 对孔结构造成严重的破坏。同时, 相同孔径内孔隙水的结冰温度低于冰结晶的融化温度, 这使得在冻融循环过程中孔隙水和冰结晶的相变进程并不完全重合^[51]。在超低温冻融循环过程中, 混凝土存在内部孔隙水的迁移和外界水分交换。内部孔隙水迁移可由渗透压理论^[52]和微冰晶理论^[53–54]解释, 外界水分交换则是由于内部水迁移使得细小孔隙(20 nm 以下)处于失水状态, 在低温泵吸的作用下对外吸水, 最终使得混凝土在超低温冻融循环过程中含水率持续升高^[52, 54]。

2.2 界面过渡区

超低温也会对混凝土的界面过渡区造成破坏, 使其产生大量微裂缝, 并由此导致混凝土的宏观劣化现象^[55]。混凝土在冻融破坏过程中的界面过渡区破坏主要原因在于, 混凝土内部毛细水发生膨胀导致界面过渡区发生开裂并出现微裂缝^[56]。同时, 骨料和硬化水泥浆体之间的热膨胀系数差亦会使得两者热变形不协同, 从而在界面过渡区产生应力集中并诱发微裂缝^[57]。此外, 混凝土界面过渡区的破坏还与骨料特性和状态有关, 若骨料结构疏松且具有较高吸水率, 当骨料接近饱水状态时, 部分孔隙水会随温度的降低而迁移或扩散, 并在骨料与基体间的界面处产生静水压, 最终加剧界面过渡区微结构的破坏^[55, 58]。

2.3 C-S-H 凝胶

C-S-H 凝胶作为水泥混凝土的主要胶结组分, 其在超低温下的性能与微纳结构变化同样会诱发混凝土宏观性能劣化(见图 3)^[59]。超低温后, C-S-H 凝胶的平均杨氏模量将降低, 而低 Ca/Si 比体系的 C-S-H 纳米结构通常较高 Ca/Si 比体系具有更高的稳定性^[60–61]。原因在于: C-S-H 的硅氧链主层结构在超低温作用下会发生解聚断裂或层间离子键合重组, 并在纳米结构层次上形成新的缺陷部位。这些缺陷又将导致 C-S-H 基本胶粒单元的层间孔发生坍塌收缩, 并进一步使该缺陷逐渐扩展贯通而形成微裂缝。为此, Zhu 等^[62–63]提出了可改善 C-S-H 凝胶超低温稳定性的方法, 一是可采用低掺量的铝原子来提高 C-A-S-H 纳米结构及纳米力学性质的超低温稳定性, 二是采用有机无机自组装策略来制备出一种有序排列的 C-S-H 超结构材料。

图 3 超低温下 C-S-H 自上而下的多尺度劣化路径^[63]Fig. 3 Multi-scale degradation path of C-S-H from top to bottom at cryogenic temperature^[63]

3 超低温作用下混凝土性能增强机制

超低温下混凝土强度大幅提高,其主要原因在于基体内部的 C-S-H 凝胶强度增加^[64]和孔隙水相变^[1, 47, 55]。C-S-H 凝胶作为混凝土的主要产物相,其层间区域为结构薄弱面,其破坏原因在于层间分解导致的裂缝扩展和最终失效。Zhu 等^[64]首次发现超低温下 C-S-H 的抗拉强度、杨氏模量、断裂能、断裂过程区长度均遵从温度-应变速率耦合的 Zhurkov 标度律。随着温度的降低, C-S-H 的抗拉强度、杨氏模量与断裂能呈线性增加趋势,而其断裂过程区长度则呈现相反规律。Ca/Si 比越低, C-S-H 的破坏强度越高。C-S-H 的化学组成对其抗拉强度的影响主要通过影响其内部电荷分布密度和原子分布状态实现。C-S-H 达到拉破坏跃迁态的活化能随

温度的降低而增大,从而在较低温度下产生较高的破坏应力。Ca/Si 比为 1.7 和 1.1 时, C-S-H 破坏的最大活化能减小量分别为 0.413 eV 和 0.428 eV。

超低温下,水将冻结成冰。在-63 ℃时,冰的应力为 70 MPa,其破坏会由延性破坏转变为脆性破坏^[65]。同时,随着温度的降低,孔隙水结冰对混凝土强度的影响包括^[47]: 1) 冰晶填充与粘结效应:在 0 至-80 ℃内,混凝土宏观孔、微孔及凝胶孔内水分逐渐被冻结成冰并填充内部孔隙,同时冰与基体粘结强度的提高也会极大强化微结构的密实程度。2) 冰晶强度提升效应:孔隙冰的抗压强度在 0 至-120 ℃内随温度降低而增加,在-120 ℃至-170 ℃之间则逐渐趋于稳定。3) 冰晶预应力效应:主要存在于-20 ℃至-120 ℃之间,此时混凝土内部大部分孔隙水在-20 ℃时已结冰。随着温度的降低,冰晶

产生的预应力作用会进一步促进基体强度的增长。

4) 冰的晶型转变: 当温度为 $-120\text{ }^{\circ}\text{C}$ 时, 冰的晶型由六方晶系转变为斜方晶系, 其体积减小 20%并导致材料密实性降低, 强度不再增长, 甚至出现下降。

4 低温冻融循环后混凝土性能劣化机制

4.1 静水压理论

当混凝土处于低温环境时, 其热传递通常从混凝土表面向内传递并在试件内部形成温差。该温差会使试件表层水分被冻结并阻隔水分向外扩散。此时, 混凝土外侧的孔隙水将会结冰并发生体积膨胀, 同时将未冻结水通过毛细孔道挤向饱和度较小的内部。随着温度的降低, 孔隙冰的体积逐渐增加, 并不断挤压孔隙中未结冰水。因此, 当混凝土内部的未结冰水难以在孔隙中自由迁移时, 其会在基体毛细孔中形成一定的压力并随温度降低而随之增加, 并在混凝土内的毛细孔壁产生拉应力。若该拉应力继

续增长并超过结构拉伸承载极值后, 则会诱使毛细孔发生开裂, 最终导致试件结构发生宏观劣化^[66]。

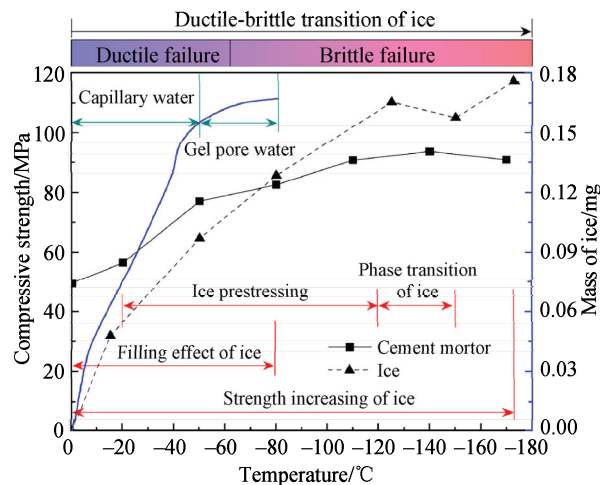


图 4 超低温下混凝土强度增强机制^[1, 47]

Fig. 4 Enhancement mechanism of concrete strength at cryogenic temperature^[1, 47]

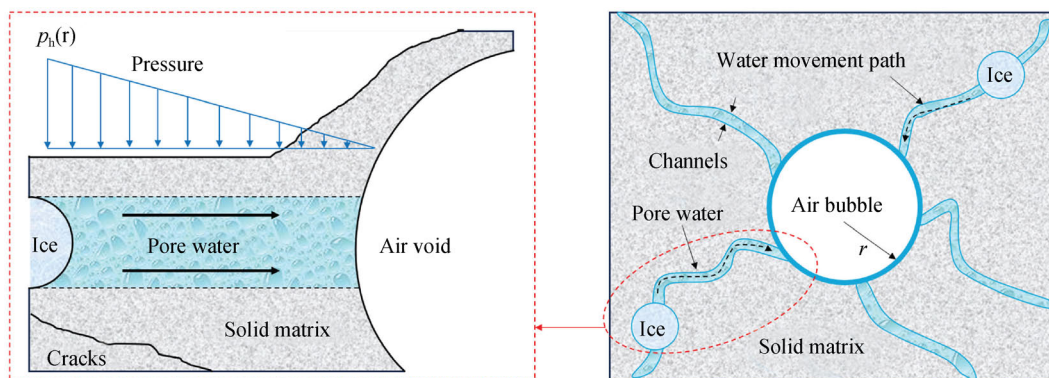


图 5 静水压理论图^[1]

Fig. 5 Hydrostatic theory diagram^[1]

4.2 渗透压理论

在低温环境下, 混凝土大孔与毛细孔内的部分溶液会随温度的降低而快速被冷却并形成冰晶。此时, 由于孔结构中部分溶液的冻结作用会造成剩余溶液的浓度增加, 并会使混凝土内毛细孔和凝胶孔中的溶液产生一定的浓度差。该浓度差不仅会使过冷水从凝胶孔向毛细孔迁移或扩散, 还会在混凝土孔隙内产生较大的渗透压, 最终对硬化水泥浆体中的孔结构造成极大损伤^[52]。

4.3 结晶压理论

如图 6 所示, 该理论假设混凝土内部孔隙为理想圆柱形, 当孔隙内的水分在低温下被冻结成冰时, 由于冰水半球形界面与圆柱形孔界面存在曲率差异而导致孔隙周围出现一定的压力差。因此, 为了平衡混凝土基体与孔隙之间的压力差, 此时试件内孔

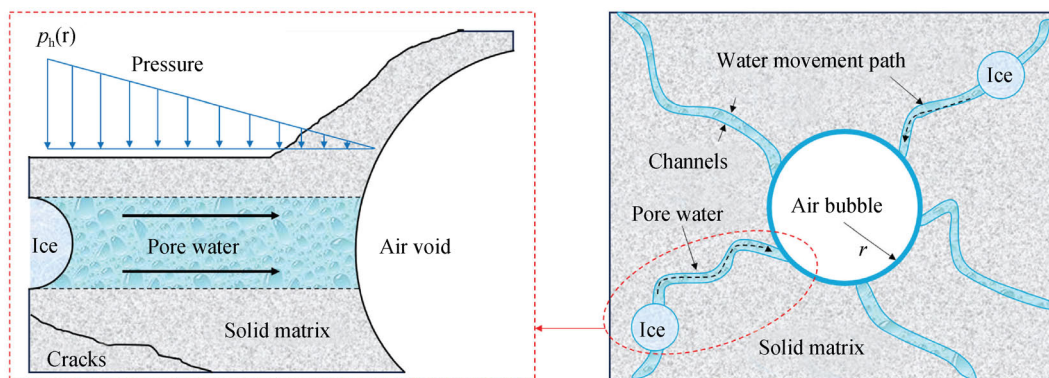
隙壁将会对冰晶结构施以额外的结晶压作用。然而, 当结晶压不足且难以平衡来自冰晶结构四周的压力时, 此时会使得处于高压区的冰晶结构逐渐融化并向低压区运动。如果该结晶压过高且远大于多孔材料的强度极限值时, 则会导致结构发生劣化^[67]。

4.4 微冰晶理论

图 7 为微冰晶理论示意图。该理论认为混凝土内部并非完全饱水, 内部孔结构中通常同时存在液态水、冰以及水蒸汽的三相物态, 通过三者之间的平衡关系可解析得到混凝土内孔隙水在低温下的迁移或扩散规律。在低温下, 混凝土内的孔隙水将冻结成冰并产生一定的低温泵吸现象, 由此使孔隙水形成过饱和状态。该理论旨在探讨低温冻融循环作用下孔隙中微冰晶结构的水热传输机制。当温度降低时, 混凝土内部孔隙水会在热力学作用下产生相

较冰更高的化学势能, 故而使得临近孔隙水与凝胶水呈现出更易向结冰点迁移的行为。当温度升高时, 混凝土基体内大毛细孔中的冰逐渐融化成水并向小毛细孔和凝胶孔内迁移或扩散, 该行为可源于孔隙

水的蒸发与凝聚现象以及冰晶融化过程。在此过程中, 当混凝土表面有水时, 外部水会向材料内部迁移或扩散并使得孔隙水饱和度逐渐增加, 且该增加趋势随冻融循环次数的增多而愈加明显^[53-54]。



(a) Schematic diagram of the forces acting on cylindrical pores due to ice formation

(b) Schematic diagram of pore freezing^[1, 67]

Note: r_p is the radius of cylindrical ice crystals, δ_w is the thickness of the unfrozen water layer between crystal and pore wall, P_A is the additional crystallization pressure from pore wall, and P_L is the liquid pressure.

图 6 结晶压理论图

Fig. 6 Crystallization pressure theory diagram

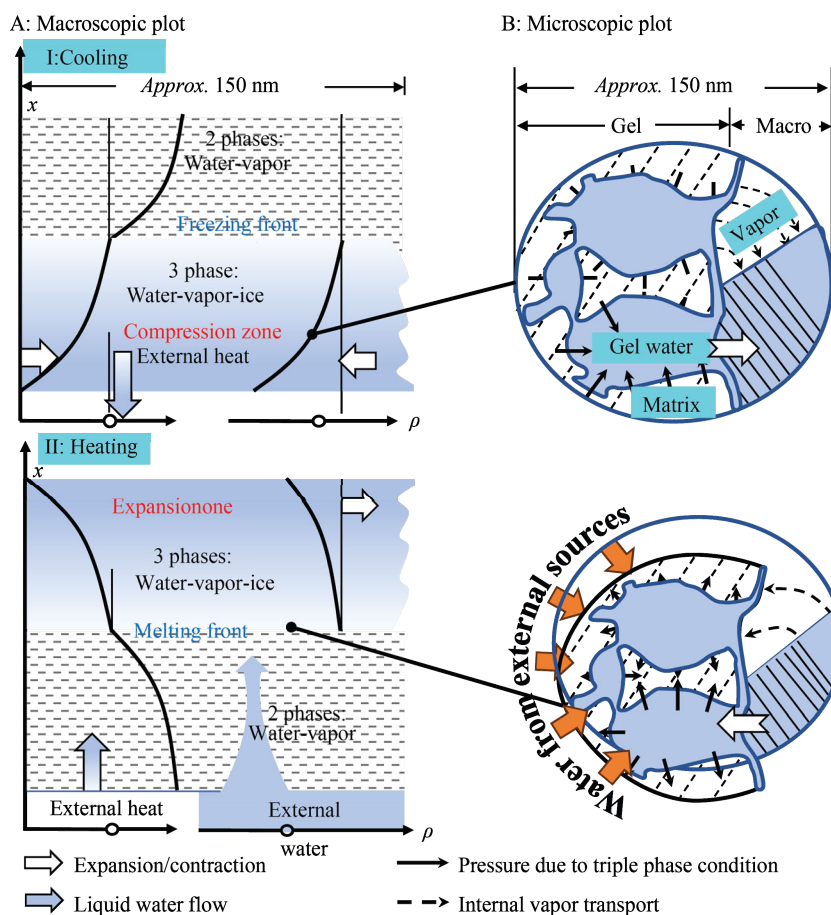


图 7 微冰晶理论示意图^[1]

Fig. 7 Schematic diagram of micro ice crystal theory^[1]

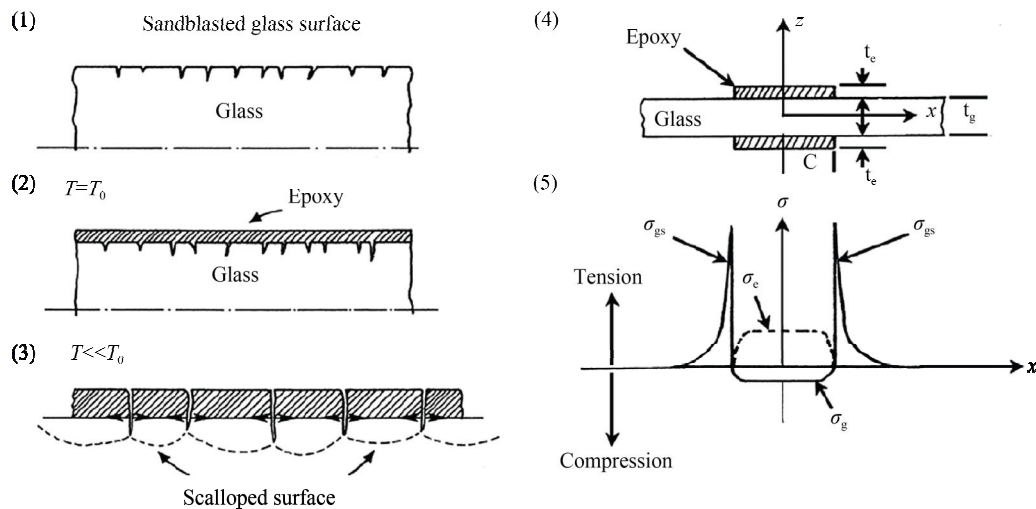
4.5 粘结剥落理论

为阐释混凝土材料在低温环境下的表面剥蚀

劣化现象与机理, 一些研究人员提出了粘结剥落理论^[67-68]。如图 8 所示, 该理论认为混凝土试件

表层的盐溶液在低温环境下将会结冰并产生热膨胀变形, 而其变形产生的热膨胀系数($-10\text{ }^{\circ}\text{C}$ 时为 $50\times 10^{-6}\text{ K}^{-1}$)通常远大于混凝土材料的热膨胀系数($-10\text{ }^{\circ}\text{C}$ 时为 $10\times 10^{-6}\text{ K}^{-1}$)。此时, 混凝土表面

结冰将产生一定的应力作用, 从而使得混凝土表面发生剥落破坏。在 $-20\text{ }^{\circ}\text{C}$ 时, 混凝土表面结冰可产生 2.6 MPa 的应力, 并使混凝土材料出现剥落劣化^[69]。



Note: (1) Rough glass surface; (2) Epoxy/glass composite at initial temperature T_0 ; (3) Interface of composite, illustrating the islands of epoxy and the thin scallops of glass removed when $T \ll T_0$; (4 and 5) Schematic representation of an epoxy/glass/epoxy sandwich seal and the stress that arises in the composite. where: σ_g is the surface stress of glass under epoxy resin, σ_e is the surface stress of epoxy resin, σ_{gs} is the glue spall stress around the boundary of the epoxy.

图8 粘结剥落理论示意图^[1]

Fig. 8 Schematic diagram of adhesive peeling theory^[1]

4.6 孔隙介质力学理论

多孔材料在自然界中无处不在, 研究人员基于多孔材料的特点提出了孔隙介质力学理论, 并在岩土工程、生物工程及材料工程中的到极大推广应用。该理论将多孔材料的宏观应力分解为热应力、孔隙介质内部应力及基体材料应力^[70–71], 而混凝土作为一种最常见的多孔材料, 低温下其内部孔隙水相变将使孔隙压大幅增加, 并导致基体发生变形。然而, 由于混凝土表面冻结以及表面能的组合作用, 冻结混凝土孔隙水饱和度极大程度依赖当前温度。因此, 当混凝土孔隙中同时存在液态水和冰晶时, 混凝土的力学性能则可通过饱和和孔隙弹性延伸至非饱和条件的方法获得。

$$\sigma = K\varepsilon - bP - 3K\alpha_s\Delta T \quad (1)$$

其中: σ 为材料宏观应力; b 为 Biot 系数; P 为有效孔隙压力; K 为固体材料体积模量; α_s 为固体的线性热膨胀系数; ΔT 为温度变化。

Couss 等^[72]基于上式推导出孔隙压力公式(式 1.2)与多孔材料宏观应变公式(式 1.3)。

$$P_L - P_{\text{atm}} \approx \left(\frac{V_C - V_L}{V_C} \right) \frac{\varnothing_C}{\varnothing_C / K_C + (1 - \varnothing_C) / K_L} \quad (2)$$

P_{atm} 为大气压; V_C 、 V_L 为冰、水的摩尔体积;

K_C 、 K_L 为冰、水的体积模量; $\varnothing_C$ 为冰的含量。

$$\varepsilon_x \approx \left(\frac{1}{3K_p} - \frac{1}{3K_s} \right) [\varnothing_C p_A + (1 - \varnothing_C) p_L] + \alpha \Delta T \quad (3)$$

其中: K_p 和 K_s 分别为基体和固相的体积模量; α 为热膨胀系数; p_A 为冰晶对孔隙壁的压力。

根据以上公式可见, 孔隙介质力学理论可准确地计算多孔材料的孔隙压及预测其宏观变形。

4.7 经典冻融破坏理论比较

不同学者根据混凝土内部不同孔隙的水结冰膨胀以及该过程中的热力学过程提出了以上几种低温环境下混凝土冻融破坏机理, 然而不同冻融破坏理论均有其适用范围与计算条件, 在使用时还需充分结合自身材料特性进行考虑。在微观层面, 静水压理论、渗透压理论及结晶压理论阐释了多孔材料冻融过程中水分迁移及局部受力状态, 对多孔材料的冻融破坏过程与机制作出解释。在宏观层面, 微冰晶理论则基于热力学平衡条件, 对冻融作用下混凝土内部孔隙水的迁移行为及其传输特性作出很好的阐释。粘结剥落理论则主要关注混凝土表面的盐冻破坏。孔隙介质理论基于多孔材料微观变形和宏观应变间联系构建了低温变形与力学性能计算模型, 明确了多孔材料在低温环境下的内外受力状态。然

而混凝土内部组成极为复杂且均质程度较低, 上述理论虽在一定程度上为我们探明混凝土低温破坏机理提供了参考, 却难以完全揭示超低温环境下的混凝土冻融破坏现象。目前, 尽管已有不少学者在超低温领域开展了相关研究, 但主要集中于宏观性能方面, 而在微观性能与理论机制方面涉及尚少且未形成系统结论, 仍难以清晰阐释超低温环境下的混凝土破坏机理, 故后续研究还需深入探讨。

5 总结与展望

5.1 总结

极端低温环境作为生活中较为罕见的自然现象之一, 会使材料显露出极其复杂且难以预知的潜在本征属性, 常常超越人类已知科学理论的理解范畴。开展相关研究, 不仅是为揭秘材料在极端环境下的未知属像, 更是为探索其在未来极端环境下应用的潜在可能性, 已成为近年来材料学研究的前沿性课题与科学壁垒突破点。本文主要结论如下:

1) 在极端低温环境下, 普通混凝土的力学性能会显著劣化。为此, 通过提高箍筋比、采用预应力钢筋、掺入纤维、使用 UHPC 填充高强度钢管可极大提高混凝土结构的耐超低温性能。

2) 超低温环境下, 混凝土的强度主要与其强度等级、温度、含水量及孔隙率有关。随着温度的降低, 混凝土的抗压强度、抗弯强度与抗拉强度先增加后降低, 粘结强度则呈线性增加趋势。混凝土在力学破坏极限时对应的临界温度值不同, 目前尚未完全取得统一。

3) 超低温冻融循环后, 混凝土内孔隙水的结冰、冻融和迁移均会破坏孔结构, 热变形不协同以及骨料结构疏松和吸水率较高会诱使混凝土界面过渡区开裂, C-S-H 凝胶将发生解聚断裂或层间离子键合重组并导致层间孔坍塌与收缩开裂。

4) 超低温作用下, C-S-H 凝胶的强度增加与孔隙水相变是导致混凝土性能增强的内因。低温冻融循环过程中, 基于孔隙水结冰产生的体积膨胀及其热力学过程, 学者们提出了静水压理论、渗透压理论、结晶压理论、微冰晶理论、粘结剥落理论及孔隙介质力学理论。相关理论虽可解释低温环境下的冻融破坏, 但并不能完全适用于超低温环境下的混凝土破坏机制。

5.2 展望

纵观现有研究, 尽管一些学者在相关领域开展了大量研究, 对混凝土的宏观性能、微观结构及破

坏机理已有初步结论。然而, 极端温度环境下的混凝土材料研究与应用涉及多层级的物理化学变化, 再加之多重外界因素的叠加效应, 使其性能演化呈现出复杂多变的现象, 对人类利用客观规律去适应或改造自然产生了一定的技术限制。该领域仍存在诸多亟待研究和解决的关键问题:

1) 对于普通混凝土而言, 其耐极端温变性能因受限于材料本身属性而表现较差, 而相应优化技术提升效果也并不明显。因此, 急需研发出耐极端低温性能优异且兼具长久服役性能的新型混凝土材料(如 UHPC 或地聚物混凝土等), 并深入解析其在极端温度环境下的性能演化与耐低温增效机理。

2) 现有极端低温环境下的混凝土研究主要集中于宏观力学性能与热工性能方面, 而关于混凝土在超低温下的微结构特征原位演化研究尚少。同时, 相关低温冻融破坏理论仅针对温度范围较小的普通冻融循环破坏而提出, 并不适用于复杂且极端低温环境下的混凝土性能劣化机制。

3) 从技术手段角度来看, 超低温环境下的温变作用会对混凝土的力学性能测试及如何协调其热力耦合效应带来极大挑战, 同时在极端低温环境下如何实现混凝土在荷载作用下的性能原位监测也尤为重要。在该环境下, 诸多针对混凝土宏观或微观性能的常规测试设备、技术与方法将不再适用。

4) 在超低温环境下, 混凝土的宏观性能与微结构均会同时出现增强效应和劣化效应, 且该效应在不同温度区间内呈现出不同的主导趋势。因此, 后续研究还需进一步探讨并明确超低温混凝土的增强或劣化行为在不同温度区间的主导效应及其温度-性能转变内因。

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Review on Mechanical Properties and Evolution Mechanism of Concretes under Extreme Cryogenic Environmen

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Extended Abstract

As one of the frontier domains of modern materials research, extreme cryogenic environments often expose materials with intrinsic properties that are completely different from those at ambient temperature. The existing concrete engineering in extreme cryogenic environments is ubiquitous, such as railway in northern or plateau cold regions of China ($-40\text{ }^{\circ}\text{C}$), cryogenic refrigeration warehouses ($-80\text{ }^{\circ}\text{C}$), the construction of the North and South Poles ($-94.5\text{ }^{\circ}\text{C}$), liquefied natural gas storage tanks ($-161.5\text{ }^{\circ}\text{C}$), liquid nitrogen storage tank ($-196\text{ }^{\circ}\text{C}$), liquefied hydrogen storage tank ($-253\text{ }^{\circ}\text{C}$), liquid helium storage tank ($-268.9\text{ }^{\circ}\text{C}$), etc.. In addition, the construction of future lunar bases has attracted recent attention and been put on the agenda by major aerospace countries, and the lunar concrete used for its construction will be subjected to long-term cryogenic temperatures as low as $-183\text{ }^{\circ}\text{C}$. Concrete is widely applied in structural engineering at ambient temperature due to its superior performance. Therefore, conducting a research on the synergistic mechanism between the macroscopic mechanical behavior and microstructure evolution of concrete under extreme temperature environments has a practical engineering application value for developing new concrete materials that can meet the requirements of extreme temperature service.

Extreme cryogenic environments have a negative impact on the service performance and structural safety of concrete, and their deterioration process involves many complex physical and chemical reactions. In this review, the cryogenic concrete application and various methods to improve their cryogenic temperature resistance were systematically introduced. The macroscopic mechanical properties of concrete in cryogenic environments, such as compressive strength, tensile strength, flexural strength, bonding strength, and elastic modulus evolution, were elaborated in detail. The evolution of microstructure characteristics of concrete under cryogenic freeze-thaw cycles was summarized, *i.e.*, pore water phase transition, interface transition zone destruction, and C-S-H gel degradation. From the point of view of the strength increase of C-S-H gel at cryogenic temperature and the enhancement of pore water icing, the enhancing mechanism of concrete performance at cryogenic temperature was summarized. Based on the hydrostatic pressure theory, osmotic pressure theory, crystallization pressure theory, micro-ice lens theory, glue spall theory, and unsaturated poroelasticity theory, the mechanism of concrete performance degradation after cryogenic freeze-thaw cycles was discussed. Finally, some key issues on concrete performance in extreme cryogenic environments were analyzed, and the research prospects in the future were proposed.

Summary and prospects As one of the most extreme environments, the cryogenic temperature can make materials expose extremely complex and unpredictable potential intrinsic properties. Conducting the relevant research is to reveal the unknown attributes of materials in extreme environments, and to explore their potential applications in the future. This becomes a frontier topic and breakthrough point of scientific barriers in materials science research. The main conclusions are as follows: 1) In cryogenic environments, the mechanical properties of ordinary concrete can deteriorate. Therefore, the cryogenic temperature resistance of concrete structures can be greatly improved *via* increasing the ratio of stirrups, using prestressed steel bars, adding fibers, and filling high-strength steel pipes with UHPC. 2) The concrete strength is mainly related to its strength grade, temperature, water content, and porosity. As the temperature decreases, the compressive strength, flexural strength, and tensile strength of concrete firstly increase and then decrease, while the bonding strength shows a linear increasing trend. The critical temperature corresponding to the mechanical failure limit of concrete is different. 3) After cryogenic freeze-thaw cycles, the freezing, freeze-thaw and migration of pore water in concrete can destroy the pore structure. The uncoordinated thermal deformation, loose aggregate structure and high water absorption induce cracking in concrete interface transition zone. The C-S-H gel can undergo depolymerization fracture or interlayer ion bonding recombination, leading to interlayer pore collapse and shrinkage cracking. 4) At cryogenic temperature, the strength increase of C-S-H gel and the phase transition of pore water are the internal factors that enhance the concrete performance. During the cold freeze-thaw cycle, based on the volume expansion caused by pore water freezing and its thermodynamic process, the theories of hydrostatic pressure, osmotic pressure, crystallization pressure, micro-ice lens, glue spall and unsaturated poroelasticity are proposed. Although the relevant theories can explain a freeze-thaw failure at low temperatures, they are not fully applicable to explain the failure mechanism of concrete in cryogenic environments.

The existing research are conducted in the related fields, but the preliminary conclusions are only drawn on the macroscopic properties, microstructure, and failure mechanism of concrete. However, the research and application of concrete materials in extreme environments involve multiple levels of physical and chemical reactions, coupled with a superposition effect of multiple external factors, which presents complex and variable characteristics. This has certain technical limitations for human-being to utilize the existing cognition to adapt or modify nature. There are still some key issues that need to be solved in this field, *i.e.*, 1) For ordinary concrete, its extreme temperature-variation resistance is inferior due to the limitation of material properties, and the optimization

technology and improvement effect are not effective. Therefore, there is an urgent need to develop new concrete materials with an excellent resistance to cryogenic temperatures and long-term service, and deeply analyze their performance evolution and enhancement mechanism in extreme environments. 2) The existing research on cryogenic concrete mainly focuses on macroscopic mechanical and thermal properties, while there is little research on the in-situ evolution of concrete microstructure characteristics at cryogenic temperatures. Meanwhile, the relevant failure theory is only proposed for ordinary freeze-thaw cycles in a small temperature range, and is not applicable to the deterioration mechanism of concrete in complex and extreme cryogenic environments. 3) From the perspective of technical methods, the temperature-variation effect in cryogenic environments has great challenges to the performance testing of concrete and how to coordinate its thermal coupling effect. Simultaneously, it is particularly momentous to achieve *in-situ* monitoring of concrete performance in extreme environments. That is because many conventional testing equipment, techniques, and methods for macroscopic or microscopic properties of concrete will no longer be applicable. 4) In cryogenic environments, the macroscopic properties and microstructure of concrete exhibit enhancement and degradation effects, and these effects show different dominant trends in different temperature ranges. It is thus necessary for further research to make clear the dominant effects of the reinforcement or deterioration behavior of cryogenic concrete in different temperature ranges and the internal causes of temperature-performance transition.

Keywords extreme cryogenic environment; concrete; mechanical properties; microstructural characteristics; deterioration mechanism