

提升结构混凝土耐久性的外加剂研究进展

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摘 要: 结构混凝土耐久性是公认的世界性难题, 随着全球气候变暖, 服役环境恶劣, 混凝土耐久性能过早失效的问题日益突出。化学外加剂作为混凝土的关键组分, 在改善混凝土微结构、提升耐久性方面表现出显著的技术优势。本文从混凝土裂缝控制、孔结构调控与钢筋阻锈性能提升 3 个影响耐久性的关键因素出发, 综述了耐久性提升外加剂的发展现状与最新研究动态, 并对耐久性提升外加剂的未来发展进行展望, 助力混凝土耐久性提升技术的创新与低碳、可持续社会的发展。

关键词: 混凝土耐久性; 外加剂; 混凝土开裂; 冻融; 疏水改性; 纳米密实; 钢筋锈蚀

中图分类号: TU528 文献标志码: A 文章编号: 0454-5648(2025)03-0553-21

网络出版时间: 2025-02-08



钢筋混凝土是当今世界用量最大的建筑材料, 也是重大工程建设的基础材料。钢筋混凝土兼具钢与混凝土的优点 坚固又耐用, 但是人们却低估了环境因素对它的影响, 为此也付出了巨大的代价。中国工程院重大咨询项目“我国腐蚀状况及控制战略研究”调查结果显示^[1], “中国 2014 年腐蚀成本为 21 278.2 亿, 占当年国内生产总值的 3.34%”, 其中钢筋混凝土相关的腐蚀约占交通、能源等基础设施腐蚀的 40%。随着国家建设规模的不断扩大, 未来钢筋混凝土面临的耐久性失效以及由此引发的安全问题将日益凸显。

混凝土耐久性失效是指混凝土结构在环境或荷载作用下导致性能下降, 无法有效抵抗物理、化学或其他侵蚀作用^[2]。由于混凝土中骨料大多是天然材料, 自身耐久性良好, 耐久性失效主要与水化产物水化硅酸钙(C-S-H)凝胶组成以及 C-S-H 凝胶与骨料形成的界面过渡区微结构相关。因此, 调控胶凝材料组成与结构, 改善界面过渡区性能, 减少水分、离子以及气体等侵蚀性介质在混凝土中的传输, 是提升混凝土耐久性的根本。

化学外加剂作为混凝土的第 5 组分, 在调控水

化产物微结构、浆体/骨料界面, 改善混凝土流变、力学及耐久性等方面显示出越来越重要的作用^[3], 特别是在控制混凝土裂缝发生与发展、抑制介质传输、抗硫酸盐腐蚀、抗冻融破坏、提升钢筋阻锈等性能方面优势显著。为了深入了解化学外加剂在结构混凝土耐久性提升方面的作用, 本文从混凝土裂缝控制、孔结构调控和钢筋阻锈性能提升 3 个关键影响因素出发, 归纳总结了相关耐久性提升类外加剂的研究进展与最新动态(图 1), 并对相关耐久性提升外加剂的未来发展进行了展望。随着现代工程建设需求的复杂多样化, 采用各类外加组分提升水泥基材料性能的方法越来越多, 本文基于此将化学外加剂的概念和范围拓展, 将混凝土拌制前或拌制中加入用以改善硬化后混凝土结构耐久性能的外加材料(非胶材、骨料和水), 均统称为“耐久性提升外加剂”。

1 混凝土裂缝控制

裂缝是加剧混凝土耐久性能劣化的重要因素, 采用有效措施降低裂缝及其影响是提高混凝土耐久性的前提。混凝土结构物 80% 以上的裂缝是由收缩

收稿日期: 2024-07-31。 修订日期: 2024-09-13。

基金项目: 国家重点研发计划(2023YFB11400); 江苏省自然科学基金(BK20221550)资助。

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Received date: 2024-07-31. Revised date: 2024-09-13.

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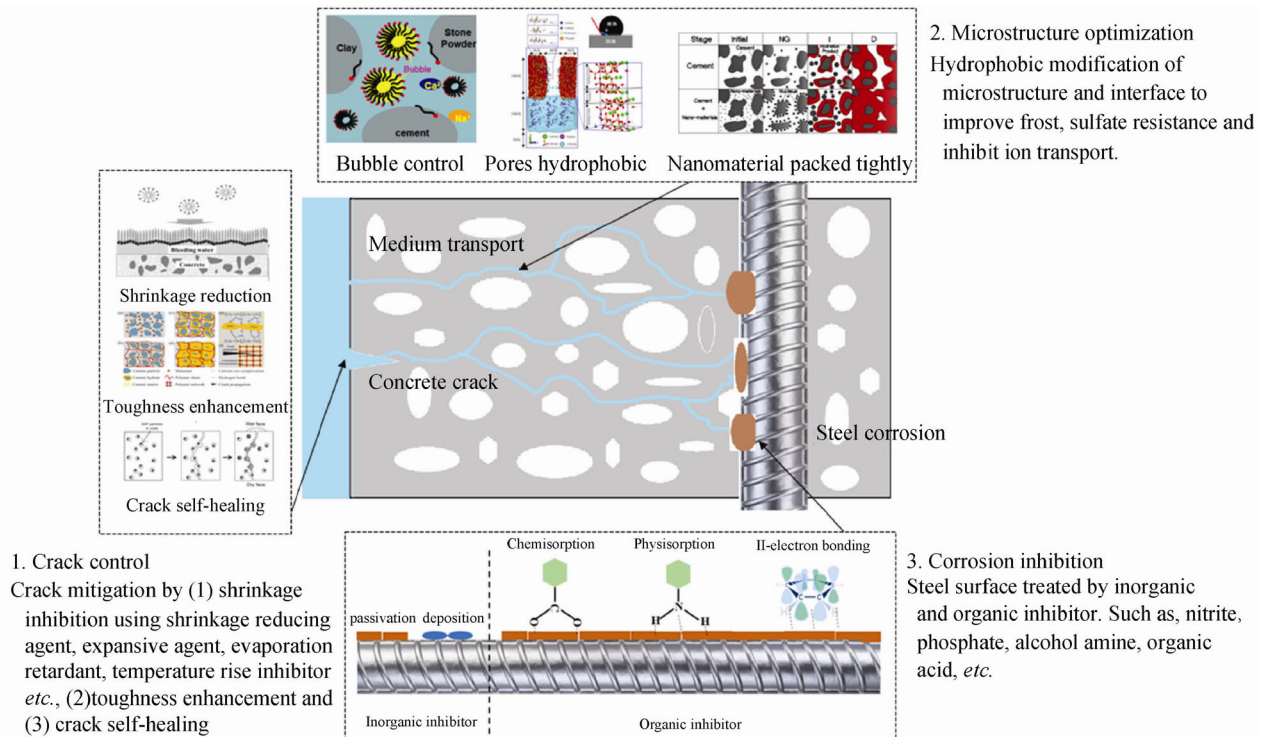


图 1 结构混凝土耐久性提升关键技术：裂缝控制、孔结构优化与钢筋阻锈^[9, 51, 85, 102]

Fig. 1 Schematic diagram of key technologies for improving durability of structural concrete: Crack control, pore structure optimization and corrosion inhibition of reinforcement^[9, 51, 85, 102]

变形引起，现有研究从不同的诱因出发，发展出一系列通过抑制收缩来预防开裂的外加剂，但其在复杂工况以及极端干燥、温度疲劳等严苛环境下，仍难以满足混凝土抗裂性需求。近年来，混凝土韧性提升与裂缝自修复等技术也不断发展，为裂缝控制提供了新的技术途径。本节分别从收缩抑制、韧性提升及裂缝自修复这 3 个角度介绍外加剂的研究进展，并将相应的外加剂统称为收缩抑制类、韧性提升类和裂缝自修复类外加剂，代表性文献汇总于表 1。

1.1 收缩抑制类外加剂

混凝土的收缩变形，除塑性阶段的沉降收缩变形外，均可以归结为混凝土湿度降低(塑性收缩、自收缩、干燥收缩)或温度降低(温度收缩，也叫温降收缩)所造成的收缩。基于不同收缩诱因，发展了诸如减缩剂、膨胀剂、内养护剂、水分蒸发抑制剂及水化温升抑制剂等抑制混凝土宏观收缩变形、提高体积稳定性的外加剂。

减缩剂是通过直接降低毛细收缩应力来减少收缩的外加剂。减缩剂按组成大致可分为醇类、聚醚类和大分子聚合物类。尽管其减缩机理目前仍存在一定争议，但主要可以归结为 3 个方面：1) 降低孔溶液表面张力从而减小毛细管收缩应力^[4]；2) 改变孔溶液离子浓度进而提高氢氧化钙和钙矾石的结晶

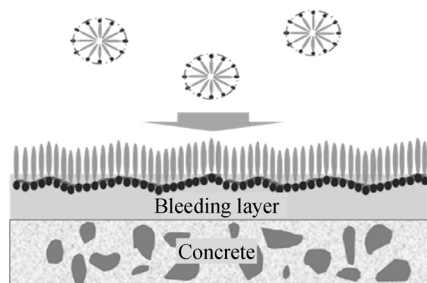
压力(产生膨胀效应)^[5]；3) 延缓水泥水化并改变孔隙结构进而缓解内部相对湿度下降^[5]。对于不同种类减缩剂，上述影响往往同时存在，但程度不一。鉴于醇类、聚醚类减缩剂因掺量高、影响混凝土强度导致无法大规模推广应用的问题，多功能(如同时具有减水和减缩功能)的聚合物类减缩剂^[4, 6]的研究是近年来的热点之一，但如何实现减缩功能与其他功能的平衡，是减缩剂多功能化发展亟待解决的一大难题。

膨胀剂是通过在混凝土中产生膨胀来补偿收缩的一类外加剂，其机理、性能和应用技术的研究较为广泛。根据其膨胀组分的不同，可分为硫铝酸钙类膨胀剂、氧化钙类膨胀剂、氧化镁膨胀剂以及同时具有两种或多种膨胀组分的复合类膨胀剂。鉴于不同膨胀组分水化膨胀特性的差异，其对混凝土的补偿收缩效能也有较大差别。根据工程混凝土收缩历程，精准设计并调控膨胀材料的膨胀历程^[7-8]是近年来的一大研究方向。

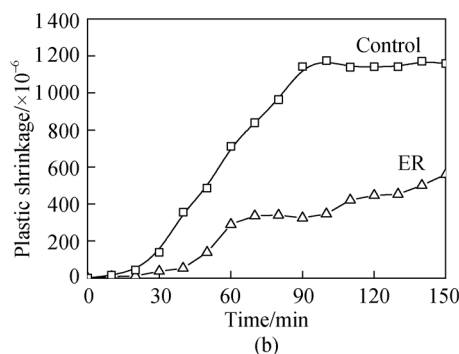
混凝土水分蒸发抑制剂和水化温升抑制剂是近年来新发展起来的外加剂。水分蒸发抑制剂通过在尚处于塑性阶段的混凝土表面形成单分子膜以抑制表面水分蒸发，进而降低塑性收缩，其原理如图 2 所示。该材料的作用效果取决于单分子膜的稳定性

和致密性^[9]。而其能否在混凝土表面稳定、致密成膜主要受所用两亲性化合物的结构(疏水性、亲水性和链长等)、起稳定作用的乳液分子及浓度、混凝土泌水层的离子浓度、环境温湿度和风速等因素的影响。Liu 等^[10]研究发现,在温度 35℃、湿度 30%、风速 5 m/s 的条件下,水分蒸发抑制剂可以降低混

凝土的水分蒸发 60%, 进而显著抑制塑性开裂。近年来的应用研究发现,由于高风速下(10 m/s 及以上)可能难以形成稳定、致密单分子膜,其作用效果显著减弱^[11]。因此,如何提升单分子膜在高风速下混凝土表面的成膜稳定型,是水分蒸发抑制剂亟待攻克的技术难题。



(a)



(b)

ER is abbreviation of evaporation retardant.

图 2 水分蒸发抑制剂的作用原理及效果: (a) 水分蒸发抑制机理; (b) 塑性收缩影响^[9]

Fig. 2 Principle and effect of evaporation retardants: (a) mechanism of water evaporation inhibition; (b) effect on plastic shrinkage^[9]

水化温升抑制剂是一种可以有效降低水泥水化加速期放热速率且基本不影响水化总放热量的外加剂^[12]。该类外加剂目前主要是淀粉类衍生物^[13],可以缓解水泥早期集中水化放热,从而能够降低混凝土中心温升值 5℃ 以上,已在隧道、桥梁等大体积混凝土结构中得到应用。有限的机理研究结果显示,水化温升抑制剂的作用效果和其溶解吸附特性相关,其溶解后吸附在水泥颗粒表面,降低了 C-S-H 的成核密度,进而降低加速期水化放热速率^[14];随着水化的进行,残余的水化温升抑制剂伴随着钙矾石的生成被逐渐耗尽,体系水化恢复正常^[15]。近期研究还表明,水化温升抑制剂的溶解吸附特性和作用效能对胶凝体系组成、pH 值、温度等因素较为敏感^[16],相关溶解吸附特性的调控机制与构效关系亟需深入研究。

1.2 韧性提升类外加剂

混凝土的脆性来自其结构中的众多“缺陷”,宏观尺度表现为大量空隙结构的存在、局部水胶比增加导致大尺寸水化产物(钙矾石、氢氧化钙等)在骨料-基体界面过渡区疏松堆积;在纳微米层次,微观断裂韧性受水化产物、未水化水泥颗粒等之间氢键、范德华力等相互作用影响,而 C-S-H 凝胶内 Ca—O 离子键、H₂O 氢键和 Si—O—Si 共价键等也至关重要^[17]。添加纳米二氧化硅^[18]、纳米碳材料^[19]、纳米纤维^[20]、矿物掺合料等可以从多尺度减少缺陷、优化水化产物尺寸、诱导水化产物有序生长,抑制微

裂纹发展,但未能从纳微米相互作用的层次解决根本问题。

有机聚合物拉伸性能显著优于混凝土,若与水泥基材料发生较强的相互作用,则可以从根本上提高混凝土断裂韧性。然而,有机聚合物抗压强度和模量显著低于混凝土,当添加量过大时,聚合物在水泥基材料中容易形成分离的相结构,成为水泥基材料的“缺陷”^[21],易发生界面滑移或破坏,从而导致界面粘结力下降,降低抗压强度。例如,聚合物乳液颗粒(丁苯乳液、聚醋酸乙烯乳液等)通过干燥形成聚合物膜可以普遍提高水泥基材料抗折和抗拉强度(20%~60%)^[22],但抗压强度普遍降低(10%~50%)^[23]。当强极性聚合物以更小的尺寸附着于水泥、水化产物颗粒表面,水泥基材料的韧性可以得到极大增强。Pan 等^[24]通过聚合物[掺量各 1%~4%(质量分数)的聚丙烯酰胺和聚乙烯醇]、水泥混合研磨、热压成型,成功制备了具有“砖-泥”结构的高韧性水泥基材料,弯曲韧性增加 27 倍,抗折强度提高 71%。

若聚合物能以分子单体的形式进入 C-S-H 硅氧四面体链间、C-S-H 晶粒之间、水化产物颗粒间等关键位置,则可针对性增强键合强度,优化“弱点”^[25],同时降低聚合物用量,避免相分离。最近的研究发现,向水泥基材料中添加小分子单体和引发剂,通过原位聚合可以实现净浆/砂浆的抗折强度、断裂韧性的显著提高^[26]。单体和引发剂往往以溶液

形式均匀的分布于浆体中(图 3a), 且单体含有可产生氢键、配位键或静电相互作用的极性官能团[如丙烯酰胺^[27]、丙烯酸(盐)^[28]、2-丙烯酰胺基-2-甲基丙磺酸^[29]等], 也有研究人员引入交联剂如 N,N'-亚甲基二丙烯酰胺^[30]以及可水解产生羧基的单体(如甲基丙烯酸 2-羟基乙酯^[31])等, 在引发剂作用下聚合在几个小时内完成(图 3b), 最终形成聚合物网络。

单体及生成聚合物量是影响水泥基材料韧性的的重要因素。单体用量不超过 5%(质量分数)可以使抗折强度提高 50%~200%^[26], 不同文献报道水泥基材料断裂能、韧性指数、峰值荷载、初裂挠度等有大幅提升(弯曲和拉伸试验), 主要结果见表 1。原位聚合对 20~100 MPa 的水泥基材料(净浆或砂浆)都表现出良好的增韧效果^[26], 当聚合物含量 $\leq 1\%$ (质量分数)时, 水泥基材料抗压强度与对照组相当。添加 3%~6%(质量分数)单体可以轻微的提高抗压强度^[32], 但大部分情况下原位聚合导致抗压强度轻微下降, 且随着单体用量的增加, 强度进一步降低^[27], 这是因为过量的聚合物倾向于形成单独的聚合物相。

在水化初期, 聚合物网络的形成显著缩短了初凝时间^[33], 但延长了终凝时间^[34]。聚合物吸附水泥颗粒上或通过配位方式与 Ca(II)发生强烈的相互作用^[27], 形成的薄薄的膜层, 抑制水泥颗粒表面与溶

液相的物质交换(溶解、扩散等), 使水化变慢(图 3c)。随着水化反应进行, 水化产物不断填充聚合物骨架之间的空隙^[35], 形成聚合物-水化产物复合结构。Ca²⁺与聚合物中的羧基络合作用连接了 C-S-H 纳米颗粒^[27], 并增强了聚合物网络的稳定性(图 3e)^[36], 富集的 Ca—Si 进一步促进了 C-S-H 在聚合物网络上的成核生长^[33]。在水化反应后期, 聚合物膜的内养护效应, 促进了水化过程, 不断生长的水化产物穿透聚合物膜相互连接(图 3d), 聚合物层的抑制作用逐渐减弱, 空间成为水化的主要控制因素^[26], 最终形成了一个兼具强韧性的聚合物-水泥/水化产物网络结构。聚合物具有体积膨胀和抗剪切应变能力^[37], 在裂纹尖端产生压应力, 阻碍裂纹扩展(图 3f), 从而提高了水泥基体的变形能力。

目前, 原位聚合生成的聚合物无法准确表征其分子量、结构、位置和形态, 对原位聚合的调控尚处于调整聚合单体、条件、更换胶凝材料体系或与其他掺合料(纤维^[38]、晶须^[30])复合使用等方面, 对其作用机制尚未完全明晰, 且未能实现对聚合-水化历程进行设计, 例如, 调控聚合启动、持续的时间及其位置等。此外, 该方法在混凝土中的增韧特性以及更长期龄的各种效应(强度、耐久性)等也有待系统性研究。

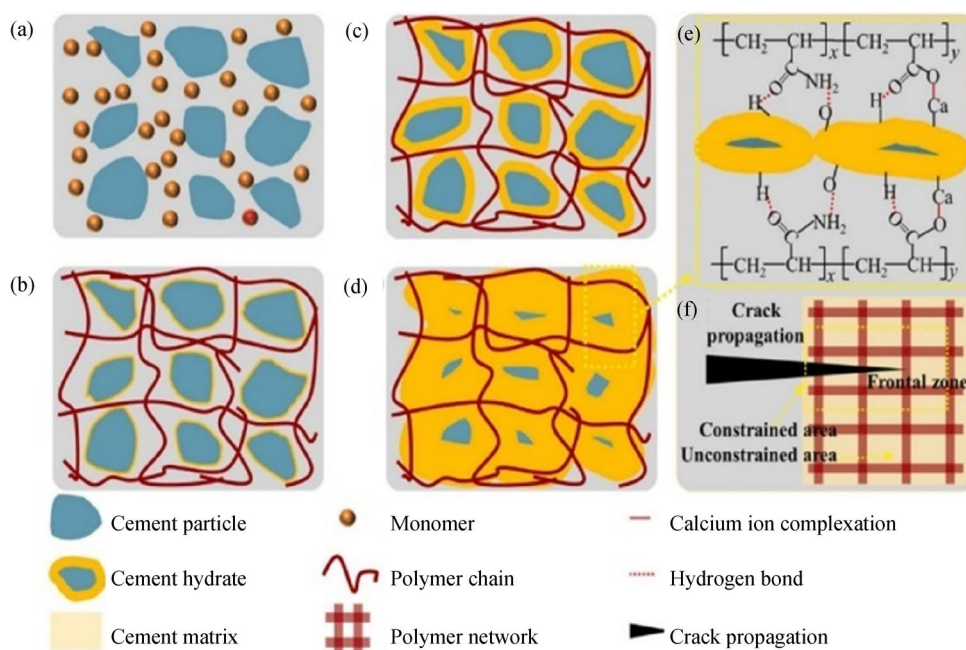


图 3 基体中聚合物-水泥/水化产物网络示意图^[26]。(a) 初始状态(聚合、水化发生前); (b) 聚合物骨架的形成; (c) 水泥持续水化与聚合物膜; (d) 硬化后聚合物-水泥/水化产物网络; (e) 聚合物与水化产物相互作用; (f) 裂纹扩展示意图

Fig. 3 Schematic diagram of polymer-cement/hydrates in matrix^[26]. (a) Initial state before polymerization and hydration; (b) Formation of polymer skeleton; (c) Continuous hydration and formation of polymer film; (d) Structure of hardened state; (e) Interaction between polymer and hydration products (coordination); (f) Schematic diagram of propagation of microcracks

表 1 混凝土裂缝控制类外加剂对水泥基材料性能的影响及其机理

Table 1 Influence of concrete crack prevention and healing admixtures on properties of cement-based materials and its mechanism

Categories	Types	Composition	System	Parameters	Effect and mechanism	Reference	Time
Admixtures for shrinkage reducing inhibition	Shrinkage reducing admixtures (SRA)	Polyether	Cement paste	Water cement ratio (w/c)=0.3, SRA dosage: 2% (mass fraction) of cement	Autogenous shrinkage at 7 d reduced by 55% with expansion occurring from 6 h to 28 h due to synergistic effects of reduced surface tension	[5]	2017
		Shrinkage reducing polycarboxylate superplasticizer(SR-PCA)	Cement paste	w/c=0.29, SR-PCA dosage:0.4% (mass fraction) of cement	Drying shrinkage reduced by 23% and 17.72% at 28 d and 90 d due to reduced surface tension attributed by unabsorbed SR-PCA and unreacted esterification macromonomers	[4]	2022
	Expansive agent (EA)	CaO-based EA modified by polylactic acid encapsulation	Cement paste	w/c=0.35, EA dosage: 6% (mass fraction) of cement	Restrained and unrestrained expansion increased by 25% and 35% at early age	[52]	2016
		CaO-C4A3S type EA modified by carbonation	Mortar	w/c=0.4, EA dosage: 6% (mass fraction) of cement	Low carbonation degree of 1.55% and 3.63% increased the restrained expansion before 5 d, high carbonate degree of 13.24% reduced restrained expansion before 3 d, while increased expansion rate from 3 d to 7 d, with the 28 d restrained expansion increased by 1.6 times	[7]	2020
	Evaporation retardants (ER)	Octadecanol (OA) emulsion	Concrete	w/c=0.5	Water evaporation reduced by 41%	[9]	2010
		Poly (lauryl methacrylate) emulsion	Concrete	w/c=0.5	Water evaporation reduced by 60%.	[10]	2011
	Temperature rise inhibitor (TRI)	Modified starch	Concrete	water-binder ratio (w/b)=0.4, TRI dosage: 0.3% (mass fraction) of binders	Temperature peak reduced by 10.4 °C	[13]	2016
Admixtures for Polymer toughness enhancement	Polymer	Polyacrylic acid (PAA), polyvinyl alcohol (PVA), polyethylene glycol(PEG)	C-S-H	Simulation	Young's modulus and tensile strength increased by 22.27% and 19.2%, fracture strain increased 66.7%; PAA>PVA>PEG	[25]	2019
		Acrylamide (AM)	Cement paste	w/c=0.4; 0-5%; 80~100 MPa	Bending strength 8.7 MPa to 25.7 MPa; PAM-Ca ²⁺ formation of a chemical bond, polymer-cement dual network	[27]	2022
	Acrylate (AANA)	Acrylamide (AM), cross-linking agent	Cement paste	w/c=0.4; 4%, 8%	Bending and compress strength increased 109% and 11%; Bending and compression deformation increased by 458.8% and 161.0%; polymer phase accumulation occurred in 8% AM then influence the hydration	[28]	2022
			Concrete	w/c=0.47; 3%~5%, wollastonite whisker,	The peak bending stress and fracture energy are increased by 31.5% and 91.4% respectively, and the compressive strength is -5.4%; the porosity is reduced, the interfacial transition zone is optimized	[30]	2024
	AM		Cement paste	4%, 1.75% (volume fraction) PVA fiber, w/c=0.4	The flexural strength increased by 151.7%, the peak load increased by 174%, and the bending toughness index was 4-5 to form a uniform polymer-fiber organic network structure.	[38]	2024

(to be continued)

(continued to above table)

Categories	Types	Composition	System	Parameters	Effect and mechanism	Reference	Time
Admixtures for crack self-healing	Crystalline admixture (CA)	Portland cement, very fine treated silica and other active chemicals	FRSHCC	w/c=0.25, 1.5% (mass fraction) CA	CA slightly improved the deflection recovery capacity. Mechanical properties recovery capacity: wet/dry cycles>tap water immersion> indoor air exposure	[42]	2013
		Portland, cement, brucite, gypsum, calcite, and quartz	Cement paste	w/b=0.3, 1.5% (mass fraction) CA	Self-healing capability: cracks induced at 7 d>cracks induced at 28 d	[43]	2018
		Mg-based CA	High performance fiber reinforced concrete (HPFRC)	w/b=0.43, CA dosage: 2% (mass fraction) of cement	Mg-based CA has favored aragonite formation in cracks of HPFRC, slowed down the self-healing process, but provided a greater mechanical recovery under tension	[44]	2018
	EA	MgO with reactivity value of 70s or 130s	Concrete	w/c=0.45	Cracks with width < 0.40mm were better healed. Self-healing capacity: MgO 70 s > MgO 130 s	[53]	2018
		CaO + calcium sulphoaluminate (CSA)	Concrete	Dosage of EA: 35 kg/m ³	Cracks formed in the early stages of actual engineering concrete healed after three months or six months	[47]	2018
		CSA	Concrete	w/c=0.4, dosage of EA: 0–12%	Cracks induced at 3d with width ≤0.15 mm were completely healed with more than 8% EA. Self-healing capacity: cracks induced at 3 d>cracks induced at 7 d.	[46]	2022
	Super absorbent polymer (SAP)	Acrylate/acrylamide copolymers	Cement paste	w/c=0.3, 0.5, SAP dosage: <1% (volume fraction)	Flowrate through a 0.34 mm wide model crack can be reduced	[51]	2010
		Polyacrylate or polyacrylate-co-acrylamide	Paste, mortar, concrete	w/c=0.3, 0.4, 0.5, 5% (volume fraction) SAP	Peak flow rate and total flow of 0.3 mm cracks can be reduced by 85% and 98%	[54]	2016
		Cross-linked potassium salt polyacrylate	Mortar	w/c=0.3, 0.35, SAP dosage: 0.5%	Crack healing capacity: wet/dry cycles>RH higher than 90% > 60% RH	[49]	2018
	Combination of CA, EA, and SAP	CA+CSA	Mortar	w/c=0.25	Surface crack with width ≤0.4 mm was completely closed by adding 10% (mass fraction) CSA and 1.5% (mass fraction) CA.	[42, 55]	2012 2013
		CA+SAP, CA+CSA	Concrete	w/b=0.43, 3.33% CSA, 2% CA, 0.5% SAP	Average strength regains capacity: long-term outdoor > wet/dry cycles> water immersion	[56]	2022

1.3 裂缝自修复类外加剂

采用各种自修复方法愈合或闭合裂缝，以提高混凝土抗渗和耐久性能，是近年来混凝土裂缝控制技术的一大重要研究方向。根据技术途径不同，自修复方法主要分为自主修复和自生修复 2 大类^[39]。自主修复是指借助外来结构或组分，作为或诱导修复材料对基体裂缝进行愈合的一类技术，但由于成本等限制，其目前主要还停留在研究阶段。而自生修复则是指仅采用水泥基材料固有组分或常用外加剂组分，依靠自身水化或活性反应等达到愈合裂缝的一类技术，包括利用未水化水泥、使用矿物掺合

料、采用纤维增强混凝土以及采用渗透结晶材料等具有自愈功能的外加剂。相较于自主修复技术，自生修复技术具有经济性和使用便捷性的优势，当下具有较大的应用价值。

渗透结晶材料是目前研究和应用最多的混凝土裂缝自修复材料之一。结晶材料中含有的活性化学物质通过渗透、扩散和迁移等作用，与混凝土内部游离的 Ca²⁺、SiO₃²⁻、AlO₃³⁻发生络合及结晶沉淀反应^[40–41]，进而起到填充愈合裂缝的作用。因此活性化学物质的成分、含量、渗透/扩散速度、反应速度显著影响结晶材料的裂缝愈合效果。结晶材料中活性化学

物质化学成分主要包括 CaO 、 SiO_2 , 此外还含有不同比例的 Al_2O_3 、 MgO 、 SO_3 、 Na_2O 、 K_2O 等^[42-44], 矿物成分包括铝酸钙、石膏、碳酸钠、硅酸钠、铝酸钠、离子螯合剂等^[43]。除了结晶材料的成分和用量外, 养护条件、开裂时间、裂缝宽度等因素也会影响结晶材料对结构性能的改善和裂缝的修复效果^[42, 45]。由于渗透结晶材料的作用发挥需要有水的参与, 养护环境中含水量会显著影响其效果。不同养护环境下的对比研究结果显示, 渗透结晶材料对裂缝的愈合效果在浸水环境或适宜的干湿循环下最好, 在标准养护环境下次之, 而在空气暴露环境下极其有限^[40-41]。

除了渗透结晶材料外, 近年来也有大量文献^[46-54]报导了膨胀剂、高吸水性树脂(SAP)等的单独掺入或与渗透结晶材料的复合使用对裂缝的自愈合作用, 虽然膨胀剂、高吸水性树脂在传统概念上并不归类于裂缝自修复外加剂的范畴。对不同类型膨胀剂的研究结果表明, 其提升混凝土裂缝自愈合的能力一方面来源于潮湿条件下未水化膨胀颗粒继续水化产生的膨胀^[46-47], 另一方面来源于膨胀水化产物如氢氧化钙、氢氧化镁及其碳化后转变为方解石、镁碳酸氢盐而起到的沉淀修复作用^[46-48]。因此不同膨胀

剂水化膨胀行为的差异势必影响其裂缝愈合作用。 CaO 类膨胀剂水化速率较快, 可能仅对早期几天之内产生的裂缝能起到愈合作用; 而 MgO 膨胀剂的自愈合效应与其活性密切相关, 常温条件下, MgO 膨胀剂活性越高, 其膨胀作用越快, 自愈合作用越好。对 SAP 的研究结果表明, 裂缝处前期释水后的 SAP 在遇水情况下重新吸水膨胀, 其体积可以增加到自身重量的数百倍从而堵塞裂缝^[49](图 4), 而 SAP 重新吸收的水分在后期自愈合过程中可以进一步释放到胶凝基体, 促进未水化水泥和矿物掺合料的水化以及碳酸钙结晶^[50]。鉴于 SAP 的吸液性能受其自身结构和溶液特性的影响, 其在不同结构或溶液环境下对裂缝的愈合作用也会有较大差异。

总结已有研究结果(表 1), 渗透结晶材料、膨胀剂和 SAP 主要对宽度小于 0.5 mm 的裂缝有较好的愈合作用, 对毫米级以上宽度裂缝的作用极其有限。同时, 这几种材料的组合使用相较于单一使用效果更好。但需要注意的是, 在混凝土成型时即掺入到混凝土拌合物中的膨胀剂、SAP 首先是作为一种减缩防裂外加剂, 而后再起到裂缝自愈合作用, 如何使其 2 种作用能够根据不同的需要受控激活是极具挑战的一个问题。

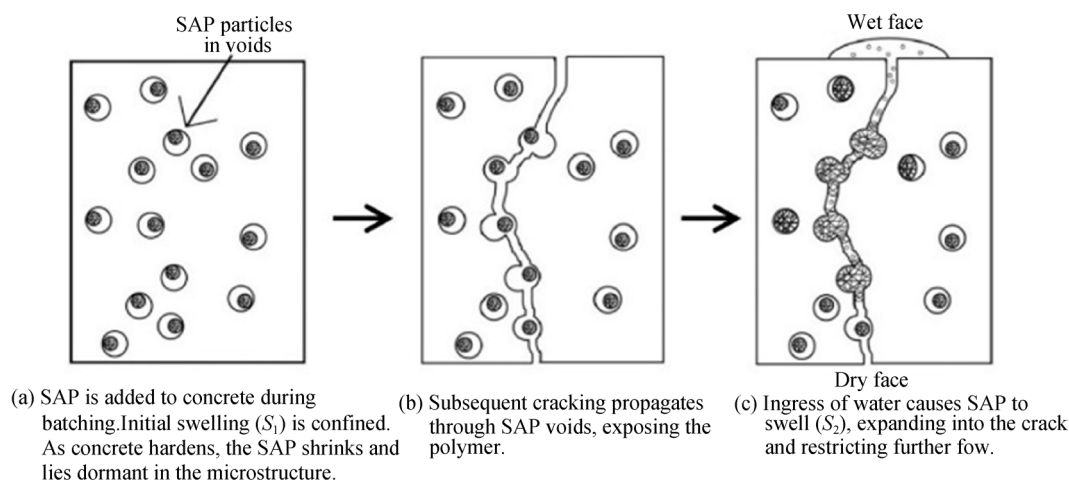


图 4 基于 SAP 的裂纹自愈合机理示意图^[51]

Fig. 4 Schematic of the crack self-sealing mechanism using SAP^[51]

2 混凝土孔结构调控

混凝土的孔结构是影响耐久性的关键。通常, 混凝土的孔包括无害孔(<20 nm)、少害孔(20~100 nm)、有害孔(100~200 nm)和多害孔(>200 nm), 减少 100 nm 以上的有害孔、增加 50 nm 以下的少害或无害孔, 才能改善水泥混凝土材料的宏观性能和耐久性能^[57]。此外, 混凝土孔结构形状、联通性、孔径分布、孔

隙率、孔隙界面的亲疏水性以及对离子的吸附特性等也是影响耐久性的重要方面。本节将从混凝土气孔、孔隙界面疏水性和孔隙致密性调控 3 个方面介绍相关外加剂的研究进展。

2.1 引气剂

在新拌混凝土中引入适量细小、均一、稳定的气泡, 有利于提高新拌混凝土的和易性以及硬化后混凝土的抗冻融耐久性^[58], 这些气泡的引入需要借

助混凝土引气剂的使用。从化学结构来看, 引气剂是一种两亲性的表面活性剂, 由疏水部分和亲水部分构成。早期的引气剂多为改性天然分子, 如松香、皂苷等; 现阶段使用的引气剂则多为人工合成的分子, 如十二烷基硫酸钠(K12)、脂肪醇聚醚硫酸钠(AES)、 α -烯基磺酸钠(AOS)等^[59]。

传统的引气剂由于分子间存在同种离子基团的静电排斥力, 使得它们在气泡表面只能呈现松散无序地排列, 从而导致生成的气泡稳定性较差。因此, 让引气剂分子在气泡表面更加紧密有序地排列, 是提高混凝土气泡稳定性的有效办法, 目前报道的稳泡方法主要如表 2 所示。单广程等^[60]发现将非离子表面活性剂的椰油二乙醇酰胺(CDEA)引入阴离子引气剂 AES 中, CDEA 与 AES 通过它们疏水部分的疏水缔合作用, 能够共同排列在气泡表面。CDEA 的存在有效地削弱了 AES 中硫酸根的静电排斥作用(图 5), 使得表面活性剂分子能够更加紧密有序地在气泡表面排列, 从而有效提高气泡的稳定性。Chen 等^[61]和 Qiao 等^[62]首次报道了将双子型表面活性剂用作混凝土引气剂(图 6), 这类分子在化学结构上相当于 2 个传统的单链引气剂, 在靠近离子基团的位置用桥接单元共价连接起来。相比于传统的单

链引气剂(K12、AES、AOS 等), 双子型引气剂能在气泡表面更加紧密有序地排列, 具有更高的表面活性, 生成的气泡也更加细密、稳定, 硬化后的混凝土气孔数量也更多, 尺寸更加细小、均匀, 气孔结构也更加合理。在双子引气剂的基础上, 又衍生出了三聚、四聚等低聚型引气剂^[63], 研究发现引气剂的聚合度越高, 其稳泡性能越强, 对应的混凝土硬化后的抗冻融耐久性越好。She 等^[64]报道了表面带负电荷的硅纳米粒子和两性离子引气剂(甜菜碱)发生静电吸附作用, 硅纳米粒子能吸附在气泡表面并使引气剂分子更加紧密有序的排列, 另外可以减少气泡间因物理碰撞而导致的气泡的破裂合并, 从而使气泡变得更加稳定^[65]。Shen 等^[66]讨论了硅纳米粒子的粒径、亲疏水性、表面电荷对稳泡效果的影响, 发现亲疏水性适中(接触角在 60° ~ 110° 之间), 尺寸较小(粒径 50 nm 左右), 带有和引气剂相反电荷的硅纳米粒子, 具有更好的稳泡效果。

气泡在混凝土的多尺度体系中极不稳定, 本质上趋向聚并、上浮和溢出, 导致气泡尺寸分布极不规律, 尺度从几微米级到几毫米级, 同时气液界面难测试、气泡行为难观察, 给混凝土中的气泡调控带来了极大难度。借助分子动力学模拟、数值模拟

表 2 几种常见的混凝土稳泡方法对比

Table 2 Comparison of common concrete foam stabilization methods

Foam stabilization methods	Optimum structure	Air-void parameters	Reference
Synergistic effects of nonionic surfactants for stabilizing air bubbles	Coconut diethanol amide	$D=68.5\text{--}103.2\text{ }\mu\text{m}$, $L=153.6\text{--}215.5\text{ }\mu\text{m}$	[61]
Novel gemini/oligomeric surfactants	Anionic groups (sulfate groups) hydrophobic groups(C12), linker group (C2)	$D=109.9\text{--}219.2\text{ }\mu\text{m}$, $L=97.8\text{--}190.6\text{ }\mu\text{m}$	[64]
Synergistic effects of nano particles for stabilizing air bubbles	Water contact angles (60° ~ 110°), particle size (50 nm), opposite charge to air entraining agents	$D=95\text{--}150\text{ }\mu\text{m}$, $L=110\text{--}170\text{ }\mu\text{m}$	[66]

Note: D is mean air-void diameters; L is air-void spacing factors

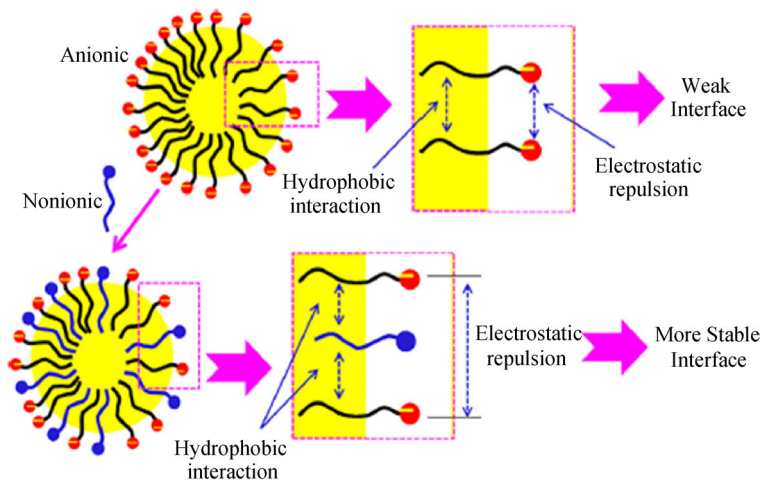
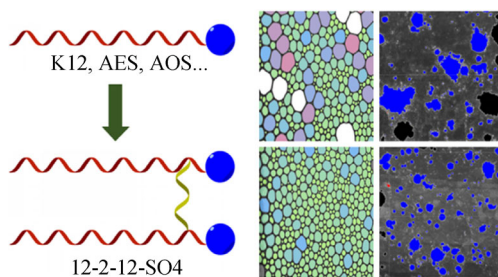


图 5 非离子表面活性剂与离子引气剂的协同作用

Fig. 5 Synergistic effects of nonionic and anionic surfactants

图 6 双子型引气剂与单链引气剂的性能对比^[61]Fig. 6 Properties of gemini and single air entraining agent^[61]

等计算机辅助方法研究气液界面和气泡行为, 弥补现有测试表征方法的不足, 是引气剂分子结构设计优化的重要手段。行业内的引气剂一般泊来于日化领域, 在高盐碱、高细粉颗粒的悬浮态体系中的作用效果严重受限, 从分子结构设计出发, 制备耐盐、抗吸附的专用引气剂, 是实现混凝土气孔结构高效调控的重要发展方向。

2.2 疏水改性剂

侵蚀性介质渗透进入混凝土内部是引起结构混凝土加速劣化的主要原因, 而水分是侵蚀性介质渗透的载体。因此, 抑制水分在混凝土中传输是改善混凝土结构耐久性的关键。

混凝土拌合过程中加入硅烷、金属皂类、石蜡和聚合物乳液等疏水材料^[67]是实现混凝土孔隙疏水的有效途径。这些材料均具有低的表面活性, 能够增强混凝土孔隙疏水性, 但也容易吸附在水泥颗粒表面, 降低水化产物与骨料界面粘结性能, 从而造成混凝土力学性能和压力作用下的抗水渗透性能下降^[29, 68]。Feng 等^[68]发现 1.0%(质量分数)掺量的硬脂酸乳液可以显著增强水泥基材料整体疏水性, 无论是表面和内部, 接触角均大于 130°, 吸水率降低 86.06%, 但过高掺量的硬脂酸乳液会带来力学性能的损失约 10%~20%。通过纳米颗粒表面疏水化是改善疏水材料对混凝土力学性能影响的有效措施。Mora 等^[69]通过正十二烷基硅氧烷改性纳米硅表面,

在 1.5%(质量分数)掺量下能够使得混凝土表面接触角达到 122°, 吸水率降低 45%, 且对混凝土抗压强度基本没有影响。而利用缓释技术控制疏水组分释放速率也是减少直接掺入疏水材料对水泥水化和力学性能影响的有效措施。Meng 等^[70]设计制备了纳米二氧化硅胶囊包覆辛酸的新型缓释疏水材料, 证实了疏水性化合物缓慢释放有助于提升水化程度、细化孔隙结构, 从而减少疏水材料对混凝土力学性能的影响。

由于混凝土耐久性影响因素较多, 常规的孔隙疏水在抑制离子渗透、抗硫酸盐腐蚀、抗风化等方面表现突出^[71], 但在改善混凝土压力渗透、冻融破坏、钢筋锈蚀等方面仍有争议^[72-74]。脂肪酸盐、硅烷等疏水材料会增大水泥基材料总孔隙率和凝胶孔隙率^[72], 加速 O₂ 传输, 影响钢筋耐锈蚀性能^[74]。而将疏水组分与纳米二氧化硅组合制备成乳液^[75-76]则可以改善疏水材料的分散性, 增强水泥基材料在干湿交替环境下的抗氯离子渗透性能, 从而提升水泥基材料的耐腐蚀和钢筋耐锈蚀性能。然而, 乳液型疏水材料也会影响混凝土含气量, 对混凝土抗冻性改善甚微, 粉体颗粒表面疏水化是解决这一问题的有效途径。Yang 等^[77]和 Pang 等^[78]通过硬脂酸改性云母粉实现混凝土抗冻性能提升, 该类材料产生疏水性同时可以细化混凝土孔隙结构, 减少了有害孔, 从而抑制了冻融过程中微裂缝发展。此外, 混凝土孔隙疏水还可以抑制混凝土的碱骨料反应^[79], 增强特种混凝土的耐久性^[80]。

在混凝土孔隙疏水化作用机制方面, 界面润湿模型是较为广泛应用的理论模型。孔隙疏水化会改变材料表面润湿性, 而表面润湿性主要取决于材料表面结构与组成(表面自由能、粗糙度), 一般通过接触角, 滑动角和表面自由能来计算, 常用计算模型包括 Young's、Wenzel、Cassie-Baxter 和 Partial wetting 等(表 3)。

表 3 材料表面润湿模型
Table 3 Wetting model of material surface

Model	Equation	Reference
Young's	$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$	[81]
Wenzel	$\cos\theta^* = r \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} = r \cos\theta_c$	[82]
Cassie-Baxter	$\cos\theta = f_{sl}(\cos\theta_0 + 1) - 1$	[83]
Partial wetting	$\cos\theta = [f_{sl} + r - f_{sl}f]\cos\theta_0 + (1 - f_{sl})(1 - f)\cos 180^\circ$	[84]

Note: θ is contact angle; γ_{sg} , γ_{sl} , γ_{lg} are solid-gas, solid-liquid, liquid-gas interfacial surface tension; r is roughness; θ^* is apparent contact angle of rough surface; θ_c is intrinsic contact angle of smooth surface; f_{sl} , f_{lg} are solid-liquid, liquid-gas contact area fraction, $f_{sl} + f_{lg} = 1$; f is effective wetting rate.

上述模型能够较好的解释不同结构固体表面, 固体-液体-气体三相平衡时固/液界面接触角的差异。对于混凝土而言, 疏水材料能够改变内部孔隙结构和孔隙界面自由能, 增大孔隙界面的接触角, 从而增大了水等液体介质在混凝土孔隙中的传输阻力。即使混凝土内部存在毛细孔负压, 介质仍旧难以渗透进入孔隙内部, 这也是孔隙疏水抑制混凝土中水分和离子在干湿交替环境下快速传输与富集

主要机制(图 7a)。

除了影响混凝土毛细孔外, 最新的理论计算也发现, 疏水材料还会在孔径更细的纳米级凝胶孔中产生作用^[85–86](图 7b), 如脂肪酸类疏水物质会与凝胶孔表面的钙离子等络合吸附凝胶孔表面, 当没有水分时, 疏水物质以平铺形式附着凝胶孔壁内, 当水分渗透至凝胶孔时, 疏水物质会站立起来形成栓塞效应, 抑制水分及离子的渗透。

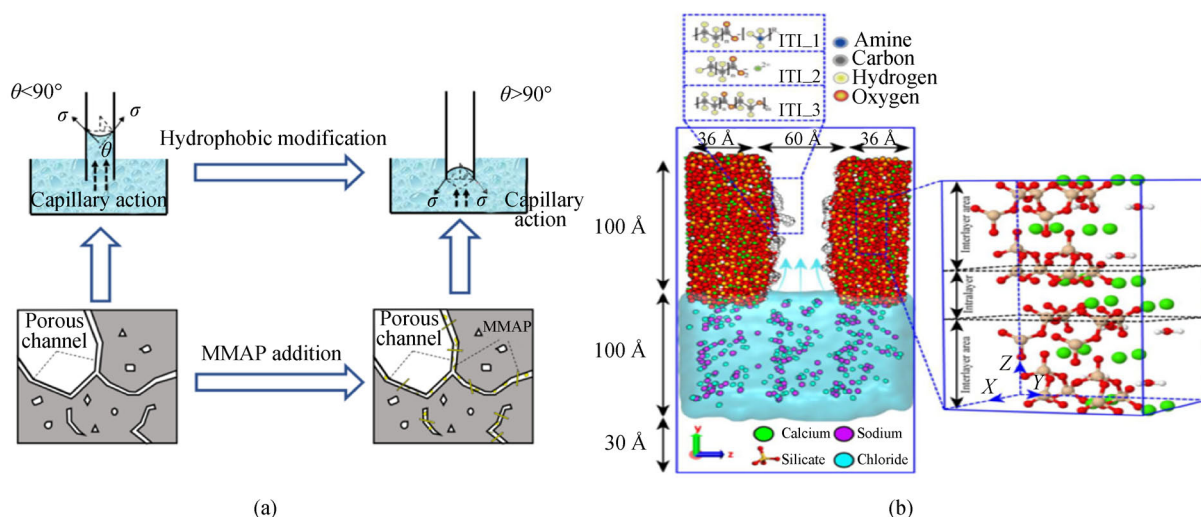


图 7 疏水材料混凝土中作用机制: (a) 毛细孔渗透抑制^[78], (b) 凝胶孔渗透抑制^[85]

Fig. 7 Mechanism of hydrophobic material in concrete: (a) transportation inhibition of water in capillary pore, (b) transportation inhibition of water in gel pore

疏水改性显著提升混凝土耐久性已逐渐形成共识, 但在气体渗透、微生物腐蚀抑制等方面仍不明确。此外, 内掺疏水改性剂难免会影响水泥水化及微结构形成, 如何在水泥水化完成后形成高效孔隙疏水效应, 减少疏水改性剂对水泥水化的影响, 是未来需要长期攻克的技术难题。

2.3 纳米密实剂

近几十年来, 纳米技术得到飞速发展, 随着人们对纳米材料应用于水泥基材料的深入认知, 使用纳米材料改善混凝土性能的研究迅速兴起, 混凝土中加入纳米材料可以有效改善混凝土的微观结构、力学性能和抗渗等耐久性, 延长混凝土的服役年限^[87]。

Liu 等^[88]研究了不同水灰比下纳米二氧化硅掺量对碳纤维增强混凝土性能的影响, 发现纳米二氧化硅可以有效降低水灰比为 0.3 的混凝土孔隙率。同时, 当水灰比从 0.3 增加到 0.4 时, 纳米二氧化硅的掺入对试件抗渗性的提升更为明显。Hosan 等^[89]研究了掺入纳米碳酸钙和纳米二氧化硅对界

面过渡区(ITZ)微观结构的影响, 结果表明: 与对照样品相比, 纳米添加剂的微观结构明显致密, 孔隙率更低, ITZ 区域周围的裂纹较少。Zhang 等^[90]对掺入纳米二氧化硅和纳米氧化锌的混凝土进行了 Cl⁻侵蚀和碳化的联合效应实验, 微观测试表明纳米颗粒可以优化混凝土孔隙结构, 生成 C-S-H 凝胶, 使混凝土内部结构致密; 在混凝土中掺入纳米二氧化硅和纳米氧化锌, 可以显著提高混凝土抗 Cl⁻渗透和碳化共同作用的能力, 有效提高混凝土的耐久性。

总体来说, 纳米材料对混凝土耐久性能的影响主要是由于降低了水泥基材料的总孔隙率, 综述了目前广泛应用到混凝土材料中的纳米材料, 如纳米二氧化硅(SiO₂)、二氧化钛(TiO₂)、三氧化二铝(Al₂O₃)、氧化石墨烯(GO)、碳纳米管(CNT)、碳酸钙(CaCO₃)、纳米粘土(Nanoclay)等对混凝土总孔隙率的影响, 如表 4 所示, 纳米材料降低了混凝土的总孔隙率, 但孔隙细化程度取决于纳米材料的类型、用量。

表 4 纳米材料对混凝土总孔隙率的影响
Table 4 Effect of nano-materials on total porosities of concrete

Nano material type	Mineral admixture	Nano material properties				Mass fraction of nano material /%	Variation of porosity/%	Reference
		Solid structure	Size/nm	Specific surface area/(m ² ·g ⁻¹)	Form			
SiO ₂	RCCP/GBFS	Amorphous	10		Powder	1.2	-8.9	[91]
	RCCP/GBFS	Amorphous	10		Powder	3.0	-1.0	
Al ₂ O ₃	RCCP/GBFS	Crystal	10		Powder	1.6	-16.27	
	RCCP/GBFS	Crystal	10		Powder	2.4	-16.76	
SiO ₂	None		15	100	Powder	0.5	-19.4	[92]
	None		15	100	Powder	1.0	-28.3	
	None		15	100	Powder	3.0	-31.1	
TiO ₂	None	Anatase	10	210	Powder	0.5	-20.5	
	None	Anatase	10	210	Powder	1.0	-24.4	
	None	Anatase	10	210	Powder	3.0	-27.6	
Graphene oxide (GO)	None	Crystal	10-50	100-300	Flaky	0.08	-51.2	[93]
	None		15±5	163±20	Powder	0.5	-4.0	[94]
Al ₂ O ₃	None		15±5	163±20	Powder	1.0	-9.0	
	None		15±5	163±20	Powder	1.5	-7.0	
	None		15±5	163±20	Powder	2.0	-2.0	
Carbon nano tube (CNT)	FA		10		Powder	0.08	-2.5	[95]
GO	FA		100 000		Flaky	0.08	-27.5	[96]
CNT@GO	FA				Powder	0.16	-37.0	
GO	FA/SF		200-10 000		Flaky	0.02	-3.5	
	FA/SF		200-10 000		Flaky	0.04	-9.8	
	FA/SF		200-10 000		Flaky	0.06	-13	
	FA/SF		200-10 000		Flaky	0.08	-11.8	
TiO ₂	None	Anatase	15	240±50	Powder	1	-16.9	[97]
SiO ₂	None		10±5	640±50	Powder	1	-6.22	[98]
CaCO ₃	FA		40-50		Powder	1	-46	
Nanoclay	None				Powder	4	-43	[99]

Note: RCCP is recycled concrete fine powder; GBFS is granulated blast furnace slag; FA is fly ash; SF is silica fume.

纳米材料在细化混凝土孔隙结构，改善混凝土耐久性能方面的机理主要有填充效应、火山灰效应和成核效应^[100]。首先，纳米材料利用其自身的超细颗粒优势，有效填充了混凝土内部的微孔隙和微裂纹，减少了混凝土中的有害孔数量，细化了混凝土的微观结构，降低了水泥基材料的孔隙率，进而可以在 ITZ 区域减少传输通道，从而使渗透率和吸水率大幅度降低^[101]，抵抗了各种硫酸盐、氯化物、二氧化碳和水等侵蚀介质对混凝土结构的破坏。

另一方面，纳米材料还具有较高的火山灰反应活性、较大的比表面积，可以和水水泥水化产生的 Ca(OH)₂ 反应生成强度较高的 C-S-H 凝胶，同时纳米材料发挥晶核效应，为 C-S-H 凝胶提供较多的成核位点，使 C-S-H 凝胶由松散、簇状结构转变为致密的网状结构，可以有效促进水泥的水化反应速率

和水化效果，生成更多的 C-S-H 凝胶，提高孔隙网络的互联性，有效填充水泥基材料基体和 ITZ 区域的微孔隙和微裂纹，降低混凝土基体中的孔隙率，改善混凝土微观结构，进而提高混凝土的早期力学性能、相对动弹性模量及抗渗等耐久性能^[102]，如图 8 所示。

值得注意的是，在低水胶比条件下，纳米密实剂改善混凝土密实性的作用受到限制。另外，纳米密实剂比表面积高，强碱高盐环境下易发生团聚，对水泥基材料流动性和强度发展不利，其耐久性提升效应也受到影响。尽管有研究采用不同的分散剂改善团聚问题，但尚不能完全解决。因此，对纳米密实剂的研究，需要综合考量其对水泥基材料施工、力学和耐久性的影响，实现水泥基材料宏观性能的协同提升。

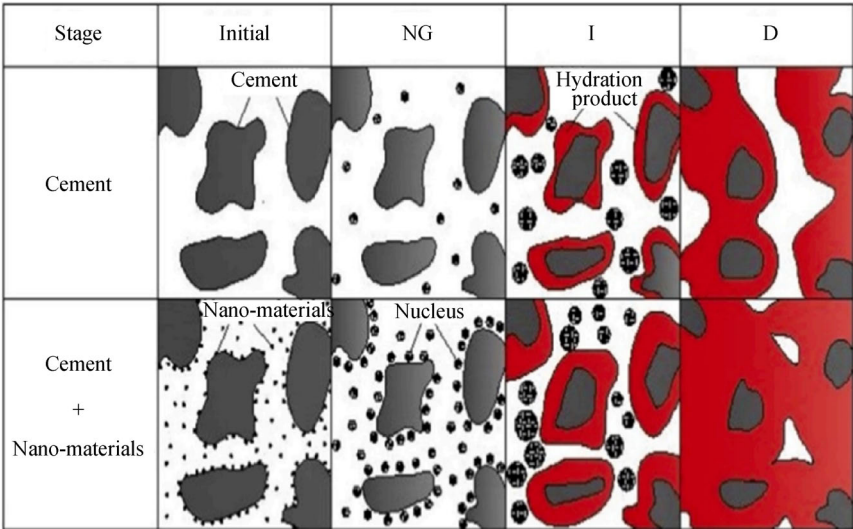


图 8 纳米颗粒对混凝土微观结构和水泥水化的影响(NG:晶体生长阶段, I:边界反应, D:扩散反应)^[102]

Fig. 8 Effects of NPs on the microstructures and cement hydration of the concretes (NG: stage of crystal growth, I: boundary reaction, and D: diffusion reaction)^[102]

3 钢筋阻锈性能提升

钢筋锈蚀是影响结构混凝土耐久性的最重要因素之一。阻锈剂由于使用方便、应用成本低，在改善和提升混凝土结构耐久性方面优势突出，被认为是有效的钢筋阻锈技术。由于筋阻锈剂种类多样、作用机制不同、应用形式及作用效果差异巨大，为此对近年来相关研究进行了归纳分类，详见表 5。

总结发现，研究较多的无机阻锈组分包括亚硝酸盐、磷酸盐、硼酸盐、钼酸盐和钨酸盐等。然而，无机组分大多具有毒性、对环境有害，实际应用受到限制。新型有机阻锈剂，绿色阻锈剂和智能型阻锈剂具有环境友好、应用方便和智能高效等特点，正成为研究的热点，近年来受到广泛关注。本节将以这 3 类阻锈剂为主，对新型钢筋阻锈剂的研究动态进行简要阐述。

表 5 钢筋阻锈剂代表性文献汇总

Table 5 Summary of representative literature on corrosion inhibitors for reinforced concrete									
Classes	Composition	System	Parameters	Environment	Inhibitor concentration	Test method	Effect	Reference	Time
Nitrite	LiNO ₂	Concrete	w/c=0.55, 0.6, and 0.65		0.2 mol	Pressure:1MPa, 1.5MPa Time: 24, 48, 96 h	$n(\text{NO}_2^-)/n(\text{Cl}^-)=0.6$, Diffusion efficiency: 0.427	[126]	2021
	NaNO ₂ , Ca(NO ₂) ₂ , NaNO ₃ , Ca(NO ₃) ₂	SCPs	pH=12.6; 25, 35, 45, 55℃	0.6 mol Cl ⁻	$n(\text{NO}_2^-)/n(\text{Cl}^-)=1:1$	PDP	IE: NO ₂ ⁻ >NO ₃ ⁻ , Na ⁺ >Ca ²⁺ , max 85%	[127]	2022
Phosphate	TSP, DHP, MFP	Paste/ Mortar	w/c =0.35 w/s/c=0.5/3/1	3% NaCl vs. cement	0.2 mol, immersion 60 d	LPR	IE: MFP>DHP >TSP	[128]	2013
Borate	Na ₂ B ₄ O ₇	SCPs	pH	0.6 mol Cl ⁻	0.02–0.08 mol	EIS	IE 86%	[129]	2023
amine	DMEA	Mortar	w/c=0.6	1–5% NaCl	2% of cement	LPR, CV, WL	ML: 43%	[130]	2013
	HPP	SCPs	pH=12.45	0.1 mol Cl ⁻	0.0076–0.076 mol	EIS	IE: 99.7%	[105]	2014
	TETA	Concrete	BIEM:1–5 A/m ² , 7–30 d	1–5% NaCl		EIS		[106]	2016
	PA	Concrete	w/c=0.35		0.5%~3% of cement	PDP, EIS	IE 94.5%	[131]	2024
	APTS	SCPs	pH=12.45	3.5% (mass fraction) NaCl	1–30 mmol	LPR, EIS	IE 97.4%	[104]	2018

(to be continued)

(continued to above table)

Classes	Composition	System	Parameters	Environment	Inhibitor concentration	Test method	Effect	Reference	Time
Organic acid	TA, GA, BA etl.	SCPs	pH=13	0.1, 0.3 mol or 1 mol Cl ⁻	0.0001–0.3 mol	PDP	IE: GA > TA > TETA > BA > DMEA	[109]	2015
	BA/DMEA	SCPs	pH=12.45	0.05–0.6 mol Cl ⁻	1.2%(mass fraction) of SCPs	LPR, EIS	CTL: 0.2 mol·L ⁻¹ Cl ⁻	[108]	2017
	Polycarboxylic	SCPs	pH	0.3, 0.6 mol Cl ⁻	0.07–7%	Tafel, EIS	IE: 63% IE: 92.35%	[114]	2018
	Polyacrylamide	SCPs	pH=12.45	Passivation 7 d, 0.03–0.15% 0.01 mol/L Cl ⁻ accumulated	0.01 mol IP6	LPR, PDP	CTL:0.1 mol/L IE: 99%	[115]	2020
	Phytic acid (IP6)	SCPs	pH=13.3, bare/pre-paasivation	0.01, 0.3mol/L Cl ⁻	0.01 mol IP6	EIS	IP6 prove dissolution	[111]	2022
	EDTA-Na EDTA-Ca	SCPs	pH=13	0.2 mol/L Cl ⁻	0.01–0.1 mol	EIS, PDP	IE: 95.2%	[113]	2023
Hetrocycles	Serine, cysteine	SCPs	pH=9	Carbonation	0.05 mol and 0.1 mol	PDP, EIS	IE: >90%	[132]	2023
	Imidazole liquid	SCPs	pH=12.5	0.3 mol	0.5–10 mmol	PDP	IE: 88.9%	[118]	2020
	BTA/DSP	SCPs	pH=9.97	Carbonation	DSP:BTA=1:0–1mmol: 10 mmol	LPR, PDP	IE: 94.7%	[117]	2020
	2-aminopyridine	Concrete	BIEM: 0.5–1A/m ²	1%, 3% NaCl	0.3 mol and 0.15 mol		IE: 99.99%	[133]	2024
Green corrosion inhibitor	Carbohydrate derivatives	SCPs	pH=12.5	3.5% NaCl	0.5–10 mmol	PDP, EIS	IE: 94.8%	[125]	2016
	Rose leaf extract	SCPs			12 % (volume fraction)		IE: 82%	[121]	2019
	Coconut powder extract	SCPs		0.3, 0.5, 0.76 mol/L Cl ⁻	0.1–0.5 g/L		IE: 99.8%	[122]	2024
Smart corrosion inhibitor	MBD@hydroxyapatite	SCPs		0.5% H ₂ SO ₄	0.01–5 mmol	PDP	IE: 88.5%	[134]	2017
	/pH response	SCPs	pH=7, 9, 11, 13		0.5 g/L	Ultraviolet spectrum	EC: 2.1 mg/mg RA: 9% IE: 93%	[135]	2017
	Paraffin@MFP/ Microwave	SCPs	Saturated Ca(OH) ₂	3.5% NaCl			IE: 85.99%	[136]	2022
	LDHs@NO ₂ 、BTA、EDTA /Cl ⁻ exchange	SCPs Mortar	pH=9.5–12.5 w/c=0.36	0.01–0.3 mol (SCP) 3.5% NaCl (Mortar)	1–25 g/L	EIS PDP	IE: 79.7%–98.6%	[137] [138] [139]	2017 — 2024
								[123]	

Note: IE is inhibition efficiency; WL is weight loss; CTL is chloride threshold level; BIEM is biodirection eletrochemical migration; n is in mole: w/s/c is water/sand/cement.

3.1 有机阻锈剂

常见有机阻锈剂包括有机胺、氨基醇、氨基硅氧烷、有机羧酸、杂环化合物等。胺类化合物由于具有孤对电子,能够在钢筋表面吸附形成膜层,保护钢筋免于锈蚀,但胺类阻锈剂多为小分子化合物,长期应用会有渗漏和耗散风险,致使其作用效果存在争议。Bolzoni 等^[103]证实二甲基乙醇胺(DMEA)能够提高钢筋的临界氯离子浓度,相对于水泥用量最高达到 1.2%~1.3%(质量分数)。然而,在较高氯

离子浓度侵蚀下,DMEA 的阻锈效率较低且不及其他类型的有机阻锈剂^[104]。为了提升醇胺类阻锈剂的性能,Cai 等^[105]通过增加吸附中心数量以及通过调控烷基链长及结构,制备了一系列多吸附中心氨基醇,通过吸附能力及阻挡层结构致密性调控,实现氨基醇阻锈效果增强,阻锈效率最高达 99%。除了氨基醇外,氨基硅氧烷也是新型有机阻锈剂^[106]。Liu 等^[104]发现氨丙基三乙氧基硅烷(APTS)具有非常显著的钢筋锈蚀抑制效果,与常规 DMEA 相比,在

高浓度的氯离子侵蚀环境下, 阻锈效率由 78% 左右提升至 97.4%。此外, APTS 还可以通过电迁移渗入混凝土内部, 在结构锈蚀修复过程中表现更好的效果^[107]。

芳香酸、氨基酸、多羟基羧酸、植酸等有机羧酸类化合物, 因其结构中含有羧酸根, 吸附与络合能力强, 能够在钢筋表面形成吸附膜抑制钢筋锈蚀, 是有机阻锈剂的重要组成部分之一^[108–111]。Liu 等^[108]发现苯甲酸盐能够在钢筋表面形成吸附与沉积复合膜, 可将钢筋腐蚀的临界氯离子浓度由 0.06 mol/L 提升至 0.2 mol/L 以上。Diamanti 等^[109]和 Zhou 等^[112]通过分子模拟, 揭示了羧酸基团更容易与钢筋表面钝化膜发生相互作用(图 9), 相比于 DMEA 或 TETA 等有机胺, 酒石酸(双羟基羧酸结构)吸附能力更强,

谷氨酸次之。Teymouri 等^[110]也发现多羧酸结构化合物具有较强的吸附与络合能力, 能够增强钢筋的阻锈性能; 同等掺量下, 柠檬酸钠(3 个羧酸基团)具有最好的腐蚀抑制效果, 而乙二胺四乙酸钠(EDTA-4Na) (4 个羧酸基团)会引起钝化膜溶解, 导致阻锈效率降低。然而将 EDTA-4Na 中 Na^+ 换成 Ca^{2+} 后, EDTA 的阻锈效果得到改善^[113], 主要是由于 Ca^{2+} 会影响 EDTA 分子构象, 从而改善吸附膜的致密性和稳定性。除小分子有机羧酸外, 最近的研究发现, 聚羧酸、聚丙烯酰胺等聚合物也具有良好的阻锈效果。如聚羧酸在 1.8% (质量分数) NaCl 模拟孔隙液中, 能够提升钢筋阻锈效率高达 92.35%^[114]; 而掺量仅有 0.15% (质量分数) 的聚丙烯酰胺能够提升钢筋的阻锈效率达 99%^[115], 表现出非常优异的阻锈效果。

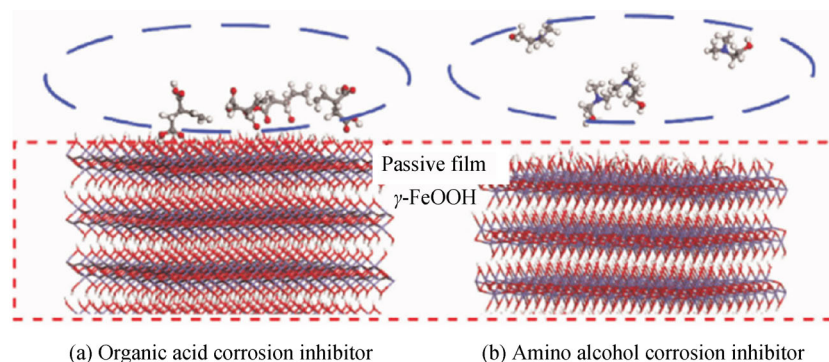


图 9 有机羧酸与醇胺在钢筋界面的吸附过程分子动力学模拟^[112]

Fig. 9 Molecular dynamics simulation of adsorption process between organic carboxylic acid and alkanol amine at the interface of reinforced steel

此外, 咪唑、苯并三氮唑(BTA)等杂原子环状化合物由于具有 p- π 共轭成键特性, 能够增强有机化合物在钢筋表面的吸附成膜效应, 也可以改善钢筋阻锈性能^[116]。如 BTA 能与钢筋表面铁原子形成 BTA-Fe 螯合物, 抑制 Cl^- 对钝化膜的溶解, 当它与阳极型阻锈剂或沉淀膜型钢筋阻锈剂复合时会产生协同增强效应; 但 BTA 由于存在强的吸附络合特征, 也会抑制钝化膜的形成, 导致钝化膜厚度小于单一氧化性阻锈剂^[117]。除 BTA 外, 新型咪唑、吡啶^[118–119]等化合物也是广泛研究的杂环类阻锈剂, 该类阻锈剂能够通过季铵化形成阳离子结构, 还可以作为电迁移阻锈剂应用于结构混凝土锈蚀修复中。

3.2 绿色阻锈剂

尽管有机阻锈剂相比无机阻锈剂表现出更好的环境友好性, 在应用端减少了阻锈剂对人体和环境的污染, 但有机阻锈剂多是化石原料提炼加工而成, 实际生产中不可避免产生环境污染和能源消耗。为

了更好的减少阻锈剂在全链条生产及应用过程中对环境和人体的危害, 也有大量学者开展了生物基绿色阻锈剂的研究^[120–121]。Anitha 等^[121]对 Rose 叶提取物的钢筋锈蚀抑制性能进行评估, 发现随着提取物浓度的增加, 钢筋表面电化学腐蚀反应得到显著抑制, 最高锈蚀抑制效率达到 82%。Liu 等^[122]分析了椰子粉提取物作为绿色阻锈剂应用混凝土中钢筋锈蚀抑制的潜力, 发现该类生物提取物展现出非常优异的阻锈性能, 0.1 g/L 的乙醇提取物可以显著延缓点蚀的产生, 较高浓度的氯化物侵蚀环境下浸泡 6 个月, 钢筋的阻锈效率仍保持 90% 以上, 最高阻锈效率达到 99.8%。目前, 绿色阻锈剂主要集中在植物或其他生物提取, 利用提取物中有机化合物增强钢筋阻锈性能。通常所述的植物提取物或生物制剂多为小分子有机化合物, 如灌木等经济植物的茎、叶提取物^[123]、木质素^[124]、糖类衍生物^[125]等, 其提取物结构中含有苯环、羟基以及羧酸等结构, 能够通过化学、物理或静电吸附等方式在钢筋表面形成

吸附膜, 从而保护钢筋免于腐蚀。

3.3 智能阻锈剂

在钢筋混凝土结构体系中, 阻锈剂除了直接作用于钢筋表面产生锈蚀抑制效果外, 阻锈剂与水泥的适应性, 对混凝土微结构与钢筋/混凝土界面的影响, 以及在混凝土中自身渗漏或失效的风险等也是需要重点考虑的问题。通过微/纳胶囊、层状氢氧化物(LDHs)以及多孔材料的负载或封装, 有望解决上述问题。此外, 利用封装材料的环境响应释放特性, 还可以实现阻锈剂的智能释放, 从而为结构混凝土长效阻锈提供了可能, 因此也成为当前研究的新热

点^[123, 134–135, 137–138, 140]。智能阻锈剂主要包括阻锈芯材和壳层材料。亚硝酸盐、磷酸盐或 BTA 是常用的阻锈芯材, 由于体系相容性以及包覆效果差异, 氨基醇或有机羧酸作为芯材包覆的研究还较少。壳层材料的组成与结构对阻锈芯材的包覆效率以及智能释放行为起直接影响, 现有研究中壳层材料的响应释放机制包括 Cl^- 浓度诱导微胶囊破裂, LDHs 中负载组分与环境中的 Cl^- 交换, 微波响应刺激, 多孔材料或微胶囊材料在 pH 值变化时响应释放以及时间依赖自然释放等, 不同体系的智能阻锈材料作用机制如图 10 所示。

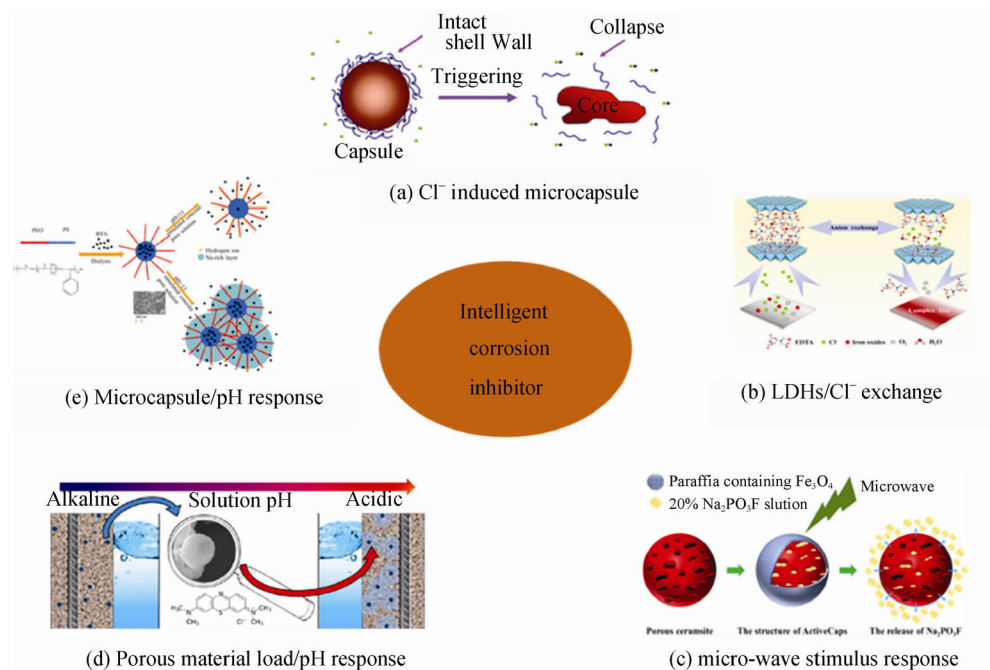


图 10 智能型阻锈剂作用机制 (a) Cl^- 诱导, (b) 离子交换, (c) 微波刺激, (d) 多孔材料/pH 响应和 (e) 微胶囊/pH 响应^[134–137]
Fig. 10 The mechanism of intelligent corrosion inhibitors (a) Cl^- induction, (b) ion exchange, (c) microwave stimulation, (d) porous material /pH response and (e) microcapsule /pH response^[134–137]

有机阻锈剂作为新的发展方向, 近 30 年来取得了长足的进步, 但现有的研究仍多聚焦于模拟液中钢筋阻锈性能的改善及作用机制的探究, 对混凝土体系的适应性以及在混凝土中的长期阻锈性能研究仍有不足。

需要指出的是绿色与智能代表了阻锈剂未来发展方向, 特别是智能阻锈剂可以解决钢筋阻锈剂长效性不足的难题, 但现有的研究大多处于理论探索阶段。智能阻锈剂包覆材料的制备技术研究还不够深入, 智能阻锈剂的响应灵敏度、材料自身的耐久性以及添加智能阻锈剂对混凝土的影响等还不明确, 仍需开展深入研究。

此外, 借助于人工智能技术的发展, 在阻锈剂分子设计方面也不断有新的进展, 如通过量子化学、

分子动力学模拟、人工智能机器学习可以极大的减少试验试错量, 大大缩短新型阻锈剂的开发周期, 且能较为准确的分析不同结构的阻锈剂分子与钢筋表面钝化膜的相互作用, 为阻锈剂作用机制研究与性能提升提供支撑。

4 总结与展望

本文综述了混凝土裂缝控制、孔结构调控及钢筋阻锈性能提升等方面耐久性提升外加剂的研究进展, 并对各类外加剂存在的问题进行评述, 基于此对耐久性提升类外加剂研究进展进行总结与展望:

1) 混凝土裂缝控制是结构混凝土耐久性提升的前提。控制混凝土裂缝可以从减缩抗裂、韧性提升以及裂缝自修复等方面着手, 然而如何针对混凝

土材料体系特征的变化以及环境需求, 进一步提升外加剂的作用效能及适应性, 是其发展的重要方向。此外, 韧性提升以及自修复外加剂仍处于探索研究阶段, 仍需进一步明晰材料结构与性能的关系, 拓展不同混凝土体系的应用效果。

2) 混凝土孔结构调控是提升混凝土耐久性的关键。引气剂、疏水改性剂、纳米密实剂是改善混凝土孔结构的有效手段, 可以解决冻融、硫酸盐腐蚀、氯离子侵蚀等环境下混凝土耐久性失效难题, 但对于耦合腐蚀环境, 多种外加剂共同应用仍存在相互适应性不足。此外, 孔结构调控类外加剂与水泥水化的交互作用过程, 孔结构的稳定调控与优化以及由此产生的耐久性影响机制仍不够清晰, 有待深入研究。

3) 钢筋阻锈性能提升是结构混凝土耐久性提升的根本。无机和有机阻锈剂是阻锈剂的重要组分, 合理发挥不同种类阻锈剂的作用效果是实现复杂体系下钢筋阻锈性能提升的关键。阻锈剂通过内掺、外涂、电迁移、压力渗透等不同应用方式, 可以实现结构混凝土钢筋锈蚀防护与修复。绿色和智能化是阻锈剂未来的发展方向, 但在精确智能控制以及高效绿色化利用方面仍有不足, 需要结合应用实际开展深入研究。

尽管混凝土耐久性问题极其复杂, 但外加剂在改善混凝土耐久性方面已表现出显著的技术优势。未来需要进一步加大外加剂的微观作用机制及构效关系研究, 借助于分子动力学模拟、人工智能等理论分析, 提出新型外加剂结构设计与制备方法, 突破现有外加剂的性能局限。同时结合水泥水化的特点, 利用微胶囊包覆、层状及多孔材料负载等缓控释技术, 增强耐久性提升外加剂与混凝土的适应性, 实现混凝土体系中外加剂定时、定点高效利用, 避免外加剂对水泥水化、微结构形成以及长期性能的影响, 实现全生命周期结构混凝土耐久性精准调控。

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Research Progress on Chemical Admixtures for Improving Durability of Structural Concrete

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Extended Abstract

Concrete durability is recognized as a worldwide problem. With global warming and harsh service environment, the problem of premature failure of structural concrete durability becomes more prominent. Chemical admixtures as the key components of concrete show significant technical advantages in improving the microstructure and durability of structural concrete. This review represents research progress on the durability enhancement admixtures for the innovation of concrete durability enhancement technology and the development of low-carbon and sustainable society.

Some admixtures used for concrete crack control (i.e., expanding agent, water evaporation inhibitor, heat of hydration inhibitor) are described. The addition of nanomaterials and polymers as well as the use of monomer *in-situ* polymerization are summarized. In addition, SAP, osmotic crystallization and expansion agents for realizing the self-healing of cracks are also discussed.

Air entraining agent, pore hydrophobic agent and nano-pore compacting agent are summarized to enhance concrete microstructure, thus solving the durability failure problem of concrete under freeze-thaw, sulfate attack and chloride ion attack.

Corrosion inhibitor is induced. Recent research progress on organic rust inhibitors, green rust inhibitors and intelligent rust inhibitors is reviewed, and the existing problems of current rust inhibitors are summarized, and the development direction of future rust inhibitors is prospected.

Summary and Prospects Durability failure is a challenge facing the sustainable development of society. How to improve the durability of structural concrete with low cost and high efficiency is a key problem to be solved. This review represents the research progress on durability enhancing admixtures in concrete crack control, microstructure regulation and reinforcement rust resistance improvement, and points out the existing problems of various admixtures.

1) Concrete crack control is a premise of structural concrete durability improvement. However, how to further improve the effectiveness and adaptability of admixtures according to the changes of concrete material system characteristics and environmental requirements is a major development direction. In addition, toughness enhancement and self-healing admixtures are still in the research stage, and the key properties are still unclear. How to realize the application needs, further reveal the structure-activity

relationship of key materials and achieve the improvement of toughness and self-healing properties is a problem worthy of in-depth study.

2) The control of concrete microstructure is a key to improving the durability of concrete. Air entraining agent, pore hydrophobic agent and nano-pore compacting agent are effective technical means to enhance concrete microstructure, which can solve the durability failure problem of concrete under freeze-thaw, sulfate attack and chloride ion attack. However, for coupled corrosion environment, there are still insufficient mutual adaptability of various admixtures applied together, and a further research is needed. In addition, the relations among air entrainment agent, pore hydrophobic agent, nano densifier, cement hydration, stable regulation/optimization of pore structure, and the resulting durability impact mechanism are still unclear, which need to be further investigated.

3) The improvement of rust resistance of steel bars is a fundamental to the improvement of structural concrete durability. Inorganic and organic rust inhibitors are important components of rust inhibitors, and the reasonable use of different kinds of rust inhibitors is a key to achieve the improvement of rust resistance performance of steel bars in complex systems. The corrosion protection and repair of structural concrete can be improved *via* different application methods such as internal mixing, external coating, electromigration and pressure penetration. The future development direction of rust inhibitors can be green and intelligent, but it still needs to be further studied in combination with practical applications.

Although the durability of concrete is extremely complex, admixtures have some technical advantages in improving the durability of concrete. In the future, it is necessary to further analyze the micro-action mechanism and structure-activity relationship of admixtures, and propose an effective method of structural design and preparation of admixtures by theoretical calculation (i.e., molecular simulation, artificial intelligence and other theoretical analysis). Also, slow and controlled release technologies such as microcapsule coating, layered and porous material loading are used with the characteristics of cement hydration to enhance the durability and improve the adaptability of admixtures to cement concrete, thus realizing the efficient use of admixtures in concrete systems at regular and fixed points, avoiding the influence of admixtures on cement hydration, microstructure formation and long-term performance, and achieving an accurate control of structural concrete durability throughout the life cycle.

Keywords durability of concrete; admixture; concrete cracking; freeze-thaw; hydrophobic modification; concrete compacted by nanomaterial; corrosion of reinforcement