

掺膨胀剂水泥净浆膨胀变形的低场磁共振原状解析

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摘 要:应用膨胀剂补偿水泥基材料干燥收缩时,其补偿效果的发挥与化学结合水和物理吸附水的演化密切相关,多数细微观测测试分析手段都要求对试件进行干燥预处理,难以辅助分析补偿收缩的时间发展历程。利用原位无损的低场磁共振弛豫技术,结合宏观质量和长度测试,对持续水养和高湿度空养的掺膨胀剂净浆进行长期监测,从水分状态和含量角度,定量分析化学结合水与物理吸附水的演化规律,进而解析净浆的补偿收缩变形。结果表明:在持续水养过程中,从水养第 3 d 起算,净浆质量、膨胀变形、可蒸发水含量均持续增大,但增加速率逐渐降低。掺硫铝酸钙类或氧化镁类膨胀剂可明显增大净浆化学结合水增量及其单位增量导致的膨胀变形,但几乎不影响物理吸附水的演变规律及其单位增量导致的膨胀变形。在高湿度(98%相对湿度)空养过程中,从空养第 0 d(水养第 56 d)起算,净浆质量先降低、后升高;净浆先收缩、后膨胀;可蒸发水含量在前 28 d 内迅速降低,后保持稳定。掺硫铝酸钙类或氧化镁类膨胀剂会增大净浆前期可蒸发水含量降幅,也会增大后期膨胀变形以补偿收缩。掺膨胀剂水泥基材料的膨胀过程极其复杂,利用低场磁共振技术并结合其它测试方法实现膨胀变形的精确解析,有助于完善膨胀机理,并协助选用膨胀剂。

关键词:膨胀剂;化学结合水;物理吸附水;低场磁共振技术

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水泥基材料的体积稳定性等诸多性质与水分紧密关联^[1-2]。合理选择高效的测试技术,对孔隙水特征进行测试分析,是开展水泥基材料理论与试验研究的重要基础^[3]。低场磁共振技术利用水中氢核为探针,可原状、无损、快速、准确地表征试件内部孔隙水含量及其分布^[4],有助于精确解析孔隙水微量变化与宏观物理力学性能之间的联系,在水泥基材料科学研究领域具有独特技术优势^[5-6]。

在凝结、硬化和服役过程中,受水泥水化与温湿度变化影响,水泥基材料会发生体积变形^[7-8]。在限制条件下,过量体积收缩可能导致水泥基材料开裂,严重威胁结构的长期性能与耐久性能^[9]。作为补偿收缩、控制开裂的重要外加剂,膨胀剂在工程建设中广泛应用^[10-11],主要有硫铝酸钙类(CSA)、氧化镁类(MEA)以及氧化钙类(CEA)。CSA 的膨胀产物主要为钙矾石,其水化速率适宜、早期膨胀效能较高,但需水量较大^[12]; MEA 的膨胀

产物为氢氧化镁,其具有早期放热量小、膨胀期长、膨胀量稳定等特点^[13-14]; CEA 的膨胀产物为氢氧化钙,其早期放热量大、膨胀极快^[15-16]。膨胀剂的作用机理主要包括结晶膨胀与吸水肿胀,其过程与效能均与水分含量、分布、状态、运移密切相关^[17-18]。

掺膨胀剂后,水泥基材料体积变形的过程与规律更为复杂。水泥熟料和膨胀剂组分的综合水化反应会导致其体积发生变化^[19-20];水化硅酸钙(C-S-H)凝胶等物质还存在干缩湿胀行为^[21-22]。原状测试与精确分析材料内部水分,对解析水泥基材料的体积变形具有重要价值。为深度剖析掺膨胀剂水泥基材料膨胀变形与水分演化的关联,在持续水养与高湿度空养过程中,对掺与不掺膨胀剂的净浆试件进行质量、长度与低场磁共振监测,从水分含量及其状态角度,定量解析化学结合水与物理吸附水演化对净浆膨胀变形的影响。

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1 实验

1.1 材料与试件

为避免铁磁性物质对低场磁共振横向弛豫测试及结果解析的干扰^[23], 选用 Fe_2O_3 含量极低的白色硅酸盐水泥作为胶凝材料; 从水化速率和后期膨胀量角度考虑, 选用 SY-G 高性能膨胀抗裂剂(CSA)与 MAC 镁质高性能混凝土抗裂剂(MEA) 2 类膨胀剂, 化学组成见表 1, 二者均由武汉三源特种建材有限责任公司生产。

表 1 白水泥与膨胀剂的化学组成

Type	CaO	MgO	SiO ₂	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	R ₂ O	Reactivity value/s
Cement	63.00	2.00	21.60	2.35	2.80	0.20	0.50	
CSA	50.60	2.08	1.50	15.61	27.50	1.37	1.19	
MEA	2.15	94.31	2.10	0.24	0.29	0.00	0.82	270

w is mass fraction. CSA and MEA are expansive agents.

制作足够数量的不掺膨胀剂(WP-BLK)、掺 CSA(WP-CSA)、掺 MEA(WP-MEA)共 3 类白水泥净浆试件, 膨胀剂内掺 5%, 水胶比恒为 0.4, 具体配合比见表 2。

表 2 水泥净浆配合比

Sample No.	Water	Cement	CSA	MEA
WP-BLK	400	1 000	0	0
WP-CSA	400	950	50	0
WP-MEA	400	950	0	50

将原材料按照表 2 称重并倒入搅拌机内充分搅拌, 将其浇筑在 20 mm×20 mm×280 mm (尺寸 A) 与 20 mm×20 mm×50 mm (尺寸 B) 的模具中。在尺寸 A 试件两端, 各嵌入 1 个伸出长度为 10 mm 的铜钉, 以便开展长度测试。尺寸 B 试件则主要用于低场磁共振测试。所有试件经振捣、覆膜养护 24 h 后脱模, 用环氧树脂密封其端面, 待凝固后再放入(20±2)℃的饱和石灰水中养护, 直至开展后续试验。

从水养 3 d 龄期开始, 每类材料、每种尺寸各取 3 个试件, 定期进行质量、长度和低场磁共振测试。此外, 在水养 56 d 龄期时, 每类材料、每种尺寸另取 3 个试件, 放入高湿度条件下(20℃、98%相对湿度(RH))进行空养, 定期进行质量、长度和低场磁共振测试。

1.2 测试方案

1.2.1 长度测试 试件长度通过精度为 1 μm 的比

长仪测得, 进而由式(1)计算试件应变 ε 。

$$\varepsilon = \frac{l_t - l_0}{l} \quad (1)$$

式中: l (mm) 为试件有效长度, 取 280 mm; l_0 (mm) 为 0 时刻的试件长度; l_t (mm) 为 t 时刻的试件长度。持续水养试件的 0 时刻取作第 3 d 龄期, 高湿度空养试件的 0 时刻取作第 56 d 龄期(即空养第 0 d)。

1.2.2 质量测试 试件质量通过精度为 0.001 g 的电子天平测得, 进而由式(2)计算试件的相对质量变化量 α_m (mg/cm³)。

$$\alpha_m = \frac{m_t - m_0}{V_0} \times 10^3 \quad (2)$$

式中: m_t (g) 为 t 时刻的试件质量; m_0 (g) 为 0 时刻的试件质量; V_0 (cm³) 为 0 时刻的试件体积。持续水养与高湿度空养试件的 0 时刻取值与长度测试一致。

1.2.3 低场磁共振测试 试件可蒸发水含量采用低场磁共振弛豫技术进行测试。为避免试件与环境发生水分交换, 测试前需用保鲜膜严密包裹试件。对持续水养试件, 从水中取出后立即用干布擦去表面多余水分, 以保持饱和面干状态。

为进一步抑制铁磁性物质的影响, 选用磁场强度 0.047 T、主频为 2 MHz 的低场磁共振仪器, 并利用 CPMG 脉冲序列, 采集试件孔隙水的横向弛豫信号。回波间隔 τ_e (s) 设置为仪器允许的最小值 60 μs, 回波个数 N 取 10 000~40 000, 扫描次数取 256~512, 相邻 2 次扫描间隔 5~15 s。除回波间隔外, 其余参数根据试件含水状态灵活调整, 保证弛豫数据的信噪比高于 240。按以上参数设置进行 CPMG 测试, 即可得到脉冲回波序列 $M(\tau)$ ($\tau = n\tau_e$, $n=1, 2, 3, \dots, N$)。利用多指数反演算法对 $M(\tau)$ 进行拟合, 即可计算出 $\tau=0$ 时的总信号量 M_0 (V)^[23]。此外, 按相同的 CPMG 测试方法, 对含水量为 m_{wb} (g) 的硫酸铜溶液进行测试, 拟合可得其总信号量 M_{wb} (V)。由于横向弛豫总信号量与水分质量严格成正比^[24], 根据式(3)可计算试件孔隙水含量 m_w (g)。按照上述 CPMG 测试和分析方法, 所得孔隙水含量 m_w 恰为可蒸发水含量^[4]。

$$m_w = m_{wb} \frac{M_0}{M_{wb}} \quad (3)$$

试件在 t 时刻的可蒸发水含量变化 α_w (mg/cm³) 可由式(4)计算。

$$\alpha_w = \frac{m_{wt} - m_{w0}}{V_0} \times 10^3 \quad (4)$$

式中: m_{wt} (g) 为 t 时刻的试件可蒸发水含量; m_{w0} (g)

为 0 时刻的试件可蒸发水含量; $V_0(\text{cm}^3)$ 为 0 时刻的试件体积。持续水养与高湿度空养试件的 0 时刻取值与长度测试一致。

2 持续水养过程分析

2.1 相对质量变化

在持续水养过程中, 随养护时间延长, 试件相对质量不断增大, 增加速率逐渐降低, WP-CSA 和 WP-MEA 的相对质量增量逐渐高于 WP-BLK, 如图 1 所示。由于试件端部封闭, 且仅通过侧面与水接触, 两种尺寸试件的相对质量变化基本不受其长度影响。对尺寸 A 试件, 截止第 196 d 龄期, WP-BLK、WP-CSA 和 WP-MEA3 类试件的相对质量增幅分别为 16.99、21.21 mg/cm^3 和 22.88 mg/cm^3 , 后两者分别比 WP-BLK 高出 24.8% 和 34.7%。对尺寸 B 试件, WP-BLK、WP-CSA 和 WP-MEA 3 类试件的相对质量增幅分别为 17.10、21.96、23.23 mg/cm^3 。由此可见, 在持续水养过程中, 从第 3 d 起算, 掺 CSA 或 MEA 的净浆试件会结合或吸收更多水分, 导致其相对质量增量更大。

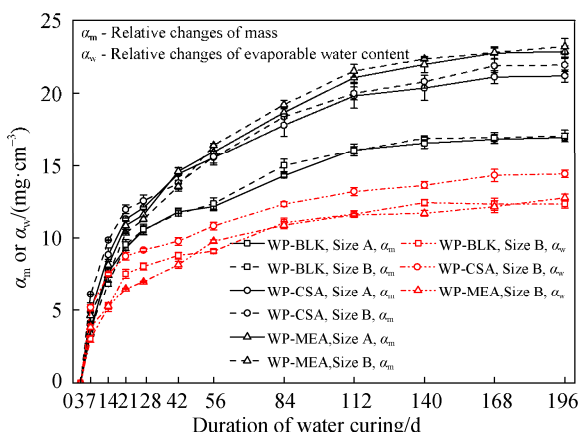


图 1 持续水养过程中试件的相对质量与可蒸发水含量变化
Fig. 1 Relative changes of mass and evaporable water content of specimens during water-curing process

2.2 膨胀变形

在持续水养过程中, 随着水泥与膨胀剂水化反应的进行, 净浆试件同时发生膨胀变形。与相对质量变化规律类似, WP-CSA 与 WP-MEA 的膨胀变形也逐渐高于 WP-BLK, 且差异显著, 见图 2。以第 3 d 的试件长度为基准, 截止第 196 d, WP-BLK、WP-CSA 和 WP-MEA3 类试件的膨胀变形分别为 417×10^{-6} 、 718×10^{-6} 、 1405×10^{-6} , 后两者比 WP-BLK 分别高出 72.2%、236.9%。如上所述, 掺 CSA 或 MEA 后, 试件的膨胀应变也显著增大。

从图 2 还可见, WP-BLK、WP-CSA 和 WP-MEA 3 类试件在前 28 d 的膨胀变形分别为 241×10^{-6} 、 445×10^{-6} 、 573×10^{-6} , 各占 196 d 总膨胀变形的 57.7%、62.0% 与 40.8%, 28 d 后的膨胀变形占比仍较高。为进一步分析膨胀变形随养护时间的发展规律, 将 3 类试件的平均膨胀速率 $\beta_{n+1}(10^{-6}/\text{d})$ 定义为:

$$\beta_{n+1} = \frac{\varepsilon_{n+1} - \varepsilon_n}{t_{n+1} - t_n} \quad (5)$$

式中: $\varepsilon_n (\times 10^{-6})$ 为第 n 次长度测试时的试件膨胀变形; $t_n (\text{d})$ 为第 n 次长度测试时刻, n 取最小值 1 时, t_n 为第 3 d。WP-BLK、WP-CSA 和 WP-MEA 3 类试件在第 3~7 d 内的平均膨胀速率分别为 33×10^{-6} 、 49×10^{-6} 、 $51 \times 10^{-6}/\text{d}$, 前两者在 28 d 后迅速降低至 $5 \times 10^{-6}/\text{d}$ 以下, 后期膨胀速率与变形均较小; 而 WP-MEA 在第 21~28 d 的平均膨胀速率为 $10 \times 10^{-6}/\text{d}$, 此后缓慢下降, 直至第 112 d, 其平均膨胀速率仍超过 $5 \times 10^{-6}/\text{d}$ 。由此可见, 在水养后期, 未水化水泥颗粒与 CSA 的膨胀效能已消耗殆尽, 但低活性的 MEA 仍具有较大膨胀能, 使得试件持续膨胀。

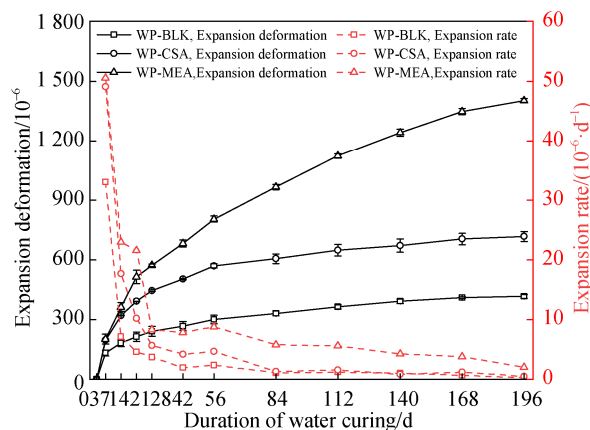


图 2 持续水养过程中试件的膨胀变形与膨胀速率
Fig. 2 Expansion deformation and expansion rate of specimens during water-curing process

2.3 可蒸发水含量变化

随养护时间延长, 持续水养试件内部的可蒸发水含量不断增大, 其增加速率也逐渐降低, 3 类试件可蒸发水含量增幅的差距较小, 见图 1。从第 3 d 起算, 第 196 d 时 WP-BLK、WP-CSA 和 WP-MEA3 类试件的可蒸发水含量增加 12.33、14.44、12.79 mg/cm^3 。与相对质量增幅相比, 3 类试件的可蒸发水含量增幅明显较小。这意味着, 未水化颗粒(水泥熟料与膨胀剂组分)会结合较多水分, 水化产物的生成导致试件产生明显膨胀变形。

3 高湿度空养过程分析

3.1 相对质量变化

在高湿度(98% RH)空养过程中, 随养护时间延长, 3 类试件的相对质量变化均呈先降低、后升高的趋势, 且分别在空养第 42 d、第 42 d 与第 28 d 时达到最低, 见图 3。与持续水养试件类似, 试件长度对空养试件的相对质量变化几乎无影响。对尺寸 A 试件, 从空养第 0 d 起算, WP-BLK、WP-CSA 和 WP-MEA 3 类试件的相对质量最大降幅分别为 9.49、11.72 mg/cm^3 和 10.49 mg/cm^3 , 后两者比 WP-BLK 分别高出 23.5%和 11.0%。截至第 196 d, WP-BLK、WP-CSA 和 WP-MEA 的相对质量增幅分别是其相对质量最大降幅的 17.5%、15.4%和 18.7%。如上所述, 在高湿度空养前期, 掺 CSA 或 MEA 的净浆试件相对质量降幅更大; 而在高湿度空养后期, 3 类试件的相对质量增幅差距较小。

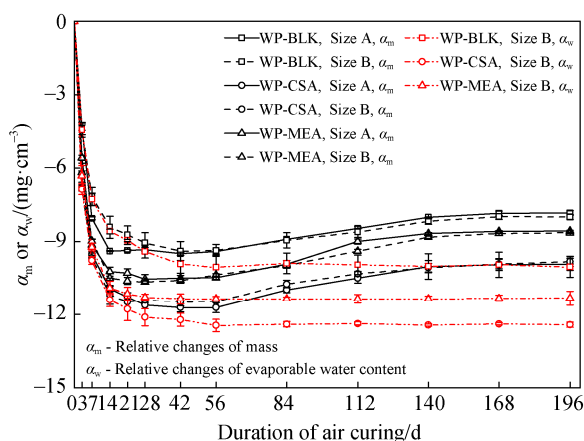


图 3 高湿度空养过程中试件相对质量与可蒸发水含量变化
Fig. 3 Changes of relative mass and evaporable water content of specimens during air-curing process at high humidity

3.2 收缩变形

在高湿度空养过程中, 试件先收缩后膨胀, 且分别在空养第 56 d、第 56 d 和第 28 d 时, WP-BLK、WP-CSA 和 WP-MEA 的收缩变形达最大值(绝对值), 如图 4 所示。若以空养第 0 d 时的长度为基准, 在 98%较高相对湿度下, 3 类试件仍发生一定收缩, 其最大收缩变形分别为 282×10^{-6} 、 316×10^{-6} 、 291×10^{-6} , 但相差不超过 12%。由于空养后期膨胀效应重新占据主导作用, 在空养第 196 d 时, 3 类试件已分别恢复 37×10^{-6} 、 87×10^{-6} 、 204×10^{-6} 的膨胀变形, 占其收缩变形最大值的 11.7%、27.5%、70.1%。由此可见, 在高湿度空养前期, CSA 和 MEA 对净

浆收缩变形影响较小, 但在高湿度空养后期, 掺膨胀剂尤其是 MEA 的净浆试件仍会发生明显膨胀。

结合试件相对质量变化分析可知, 在高湿度空养前期, 试件内部孔隙持续失水, 试件质量不断降低, 收缩变形也逐渐增大; 但在空养后期, 未水化颗粒继续水化, 试件质量因吸湿而逐渐增加, 水化产物的持续生成将补偿部分收缩。

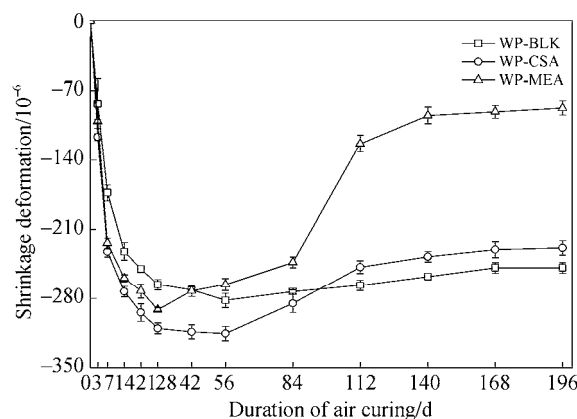


图 4 高湿度空养过程中试件的收缩变形
Fig. 4 Shrinkage deformation of specimens during air-curing process at high humidity

3.3 可蒸发水含量变化

在高湿度空养的前 28 d, 3 类试件的可蒸发水含量均快速降低, 此后 WP-CSA 和 WP-MEA 的可蒸发水含量降幅明显大于 WP-BLK, 见图 3。高湿度条件下, 试件可蒸发水含量降低主要源于部分粗孔失水, 且 WP-CSA 和 WP-MEA 的粗孔比 WP-BLK 多。在空养第 28 d 至第 196 d 期间, 3 类试件可蒸发水含量保持稳定, 且其降幅均大于相对质量降幅。此时, 试件的质量增加与膨胀变形由继续水化控制。

4 膨胀变形解析

4.1 高湿度空养过程

净浆试件的质量和体积变化取决于水化进程及试件与外部环境的水分交换, 前者可从化学结合水角度进行定量分析, 后者则为物理吸附水, 在数值上与低场磁共振测试所得可蒸发水含量一致。

在高湿度空养过程中, 试件化学结合水逐渐增加, 物理吸附水逐渐损失直至稳定, 化学结合水增量等于相对质量与可蒸发水含量变化的差值。由图 3 可见, 若从收缩变形最大时(i 时刻)起算, 在高湿度空养后期, 试件可蒸发水含量基本不变, 试件相对质量增量 $\Delta\alpha_{m, \text{air}}$ (mg/cm^3) 仅由化学结合水增量 $\alpha_{c, \text{air}}$ (mg/cm^3) 决定, 二者应相等, 见式(6), 对应地, 试件的膨胀变形恢复也仅由水化产物生成、补偿收

缩导致, 其膨胀变形 $\Delta\epsilon$ 可由式(7)计算。

$$\alpha_{c,air} = \Delta\alpha_{m,air} = \alpha_{m,j} - \alpha_{m,i} \quad (6)$$

$$\Delta\epsilon = \epsilon_j - \epsilon_i \quad (7)$$

式中: $\alpha_{m,i}$ (mg/cm^3)与 $\alpha_{m,j}$ (mg/cm^3)分别为 i 时刻与此后 j 时刻试件的相对质量降幅; ϵ_i 与 ϵ_j 分别为 i 时刻与 j 时刻试件的收缩变形。WP-BLK 与 WP-CSA 的 i 时刻取空养第 56 d; WP-MEA 的 i 时刻取空养第 28 d, 此时 3 类试件的收缩变形达最大。

由式(6)与式(7), 可计算尺寸 A 试件在高湿度空养后期的化学结合水增量 $\alpha_{c,air}$ (mg/cm^3)与膨胀变形 $\Delta\epsilon$, 如图 5 所示。WP-BLK、WP-CSA 和 WP-MEA3 类试件的化学结合水增量与其膨胀变形近似线性相关, 拟合直线的斜率分别为 19.62×10^{-6} 、 42.54×10^{-6} 、 104.57×10^{-6} , 此即化学结合水单位增量导致的膨胀变形 λ_c ($10^{-6} \text{ cm}^3/\text{mg}$)。掺 CSA 或 MEA 后, 化学结合水单位增量导致的膨胀变形明显增大, 且 WP-MEA 远大于其它 2 类试件, 凸显 MEA 膨胀期长、后期膨胀量大的特点。

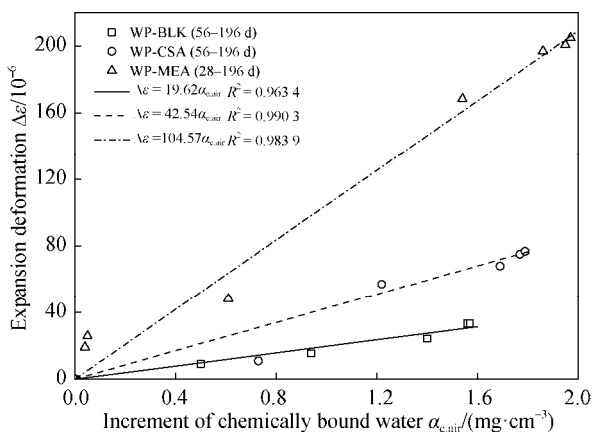


图 5 在高湿度空养后期试件的化学结合水增量与膨胀变形
Fig. 5 Increment of chemically bound water and expansion deformation of specimens in the later stage of air curing at high humidity

在高湿度空养前 28 d 内, 物理吸附水损失导致试件收缩变形, 化学结合水增加又补偿其收缩。利用试件相对质量与可蒸发水含量变化, 同样可计算出空养前期的化学结合水增量, 再结合 λ_c 可算出化学结合水增量对应的膨胀变形, 进而得到物理吸附水损失对应的收缩变形, 结合物理吸附水损失量(即可蒸发水含量降幅), 分析二者关系, 见图 6。WP-BLK、WP-CSA 和 WP-MEA 3 类试件物理吸附水损失与其收缩变形同样近似线性相关, 其拟合直线斜率均在 $25 \times 10^{-6} \text{ cm}^3/\text{mg}$ 左右, 此为试件损失单位质量物理吸附水导致的收缩变形。

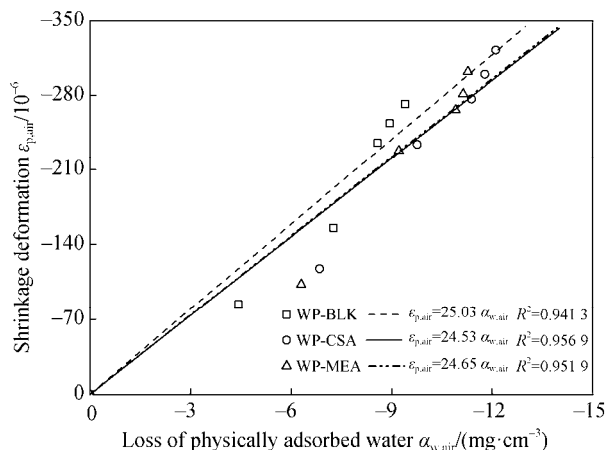


图 6 在高湿度空养前期试件的物理吸附水损失与其导致的收缩变形

Fig. 6 Loss of physically adsorbed water and its resulting shrinkage deformation of specimens in the early stage of air curing at high humidity

4.2 持续水养过程

在持续水养过程中, 试件相对质量变化同样取决于化学结合水与物理吸附水含量的综合变化。在利用低场磁共振技术无损测得试件可蒸发水含量并计算得到其变化量 $\alpha_{w,water}$ (mg/cm^3)后, 其化学结合水增量 $\alpha_{c,water}$ (mg/cm^3)可由式(8)计算。

$$\alpha_{c,water} = \alpha_{m,water} - \alpha_{w,water} \quad (8)$$

根据图 1 数据并结合式(8), 计算所得持续水养过程中的化学结合水增量见图 7。

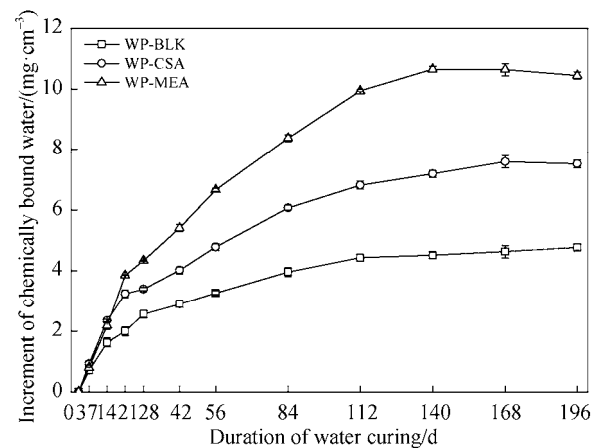


图 7 持续水养过程中试件的化学结合水增量
Fig. 7 Increment of chemically bound water of specimens during water-curing process

随水养时间延长, 3 类试件内部化学结合水量逐渐增加, 且差异显著。从水养第 3 d 起算, 截止第 196 d, WP-BLK、WP-CSA 和 WP-MEA 3 类试件的化学结合水增量分别为 4.77、7.52 mg/cm^3 和 10.44 mg/cm^3 , 后两者比 WP-BLK 高 57.7%与

118.8%。由此可见, 掺 CSA 或 MEA 后, 试件的化学结合水增量显著增大, 且 WP-MEA 的化学结合水增量最大, 同样凸显出 MEA 活性低、膨胀期长的特点。

对高湿度空养与持续水养试件, 假设二者化学结合水单位增量导致的膨胀变形一致, 且试件物理吸

附水增量与其对应膨胀变形同样线性相关, 则持续水养试件物理吸附水单位增量对应的膨胀变形 λ_p ($10^{-6} \text{ cm}^3/\text{mg}$) 为:

$$\lambda_p = \frac{\varepsilon - \lambda_c \alpha_{c, \text{water}}}{\alpha_{w, \text{water}}} \quad (9)$$

计算结果见表 3。

表 3 持续水养试件膨胀变形的解析结果

Table 3 Analytical results of expansion deformation of specimens during water-curing process

Sample No.	WP-BLK	WP-CSA	WP-MEA
Expansion deformation caused by unit increment of chemically bound water $\lambda_c/(10^{-6} \text{ cm}^3 \cdot \text{mg}^{-1})$	19.62	42.54	104.57
Increase of chemically bound water of specimens during water-curing process $\alpha_{c, \text{water}}/(\text{mg} \cdot \text{cm}^{-3})$	4.77	7.52	10.44
Expansion deformation caused by increase in chemically bound water of specimens during water-curing process/ 10^{-6}	94.00	320.00	1 092.00
Total expansion deformation of specimens during water-curing process $\varepsilon/10^{-6}$	417.00	718.00	1 405.00
Expansion deformation caused by increase in physically adsorbed water of specimens during water-curing process/ 10^{-6}	323.00	398.00	313.00
Increase of physically adsorbed water of specimens during water-curing process $\alpha_{w, \text{water}}/(\text{mg} \cdot \text{cm}^{-3})$	12.33	14.44	12.79
Expansion deformation caused by unit increment of physically adsorbed water $\lambda_p/(10^{-6} \text{ cm}^3 \cdot \text{mg}^{-1})$	26.23	27.27	24.49

由表 3 可知, 在持续水养过程中, WP-BLK、WP-CSA、WP-MEA 3 类试件物理吸附水增加所导致的膨胀变形分别占试件总膨胀变形的 77.5%、55.7%、22.3%。不掺膨胀剂时, 净浆试件水养 3 d 后的膨胀变形仅 417×10^{-6} , 且主要源于物理吸附水增加。掺 CSA 或 MEA 后, 试件膨胀变形分别显著增大至 718×10^{-6} 、 $1 405 \times 10^{-6}$, 且膨胀剂水化导致的化学结合水增加对膨胀变形起控制作用。同时, 3 类试件的物理吸附水单位增量与总增量对应的膨胀变形几乎一致, 前者在 $25 \times 10^{-6} \text{ cm}^3/\text{mg}$ 左右, 该值与是否掺膨胀剂无关。

膨胀剂的作用机理主要包括结晶膨胀与吸水膨胀。前者可从化学结合水角度表征, 后者则可从物理吸附水角度分析。对掺膨胀剂水泥净浆来说, 化学结合水含量取决于水泥与膨胀剂的水化动力学过程, 其单位增量导致的膨胀变形与膨胀产物的种类密切相关。掺 CSA 与 MEA 可明显提高净浆化学结合水增量及其单位增量所导致的膨胀变形, 后者是不同膨胀剂膨胀效能存在差异的关键。物理吸附水增量与净浆内部非饱和孔隙的含量与养护条件密切相关, 仅就持续水养过程来说, CSA 与 MEA 的掺入, 几乎不影响净浆物理吸附水的演变规律及其单位增量导致的膨胀变形。

如上所述, 水泥基材料膨胀变形与其化学结合水、物理吸附水密切相关。将低场磁共振技术与质量、长度测试结合, 可无损监测并定量分析水化过程中化学结合水与物理吸附水的演化规律, 进而深

入解析水泥基材料的收缩与膨胀过程。

5 结论

利用低场磁共振技术, 原位监测持续水养与高湿度空养净浆的可蒸发水含量, 结合质量与长度测试结果, 从水分状态与含量角度, 深入解析膨胀剂补偿收缩的动力学过程, 主要结论有:

1) 在持续水养长达 6 个月的时间范围内, 净浆质量、膨胀变形和可蒸发水含量均持续增大, 但增加速率逐渐降低。硫铝酸钙类或氧化镁类膨胀剂持续水化并增大净浆化学结合水含量, 同时提高化学结合水单位增量导致的膨胀变形, 这显著影响其补偿收缩效果, 但物理吸附水的演变规律及其对体积变形的影响与是否掺膨胀剂无关。

2) 在高湿度(98%)空养过程中, 掺硫铝酸钙类或氧化镁类膨胀剂后, 净浆前期可蒸发水含量降幅显著增大, 但其收缩变形差异较小, 后期膨胀剂的补偿收缩效能仍旧能够有效发挥。

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Low-Field Nuclear Magnetic Resonance Characterization of Deformation Behaviour of Cement Pastes with Shrinkage-Compensating Agents

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Extended Abstract

Introduction The volumetric deformation of cement-based materials continues over setting, hardening and service periods, as a result of both cement hydration and changes in temperature and humidity. Under restricted conditions, excessive volume shrinkage may lead to cracking in cement-based materials, seriously threatening the long-term performance and durability of structure. As an important admixture to compensate for shrinkage and to control cracking, expansive agents are widely used in engineering construction. The influence of expansive agents on the compensatory effect for drying shrinkage of cement-based materials is closely linked to the evolution of chemically bound water and physically adsorbed water. Since most mesoscopic and microcosmic testing techniques require drying preparations for specimens, it is challenging to analyze the development process of shrinkage-compensating. Low-field nuclear magnetic resonance (LF-NMR) technique has a unique technological advantage for investigating cement-based materials. Taking hydrogen nuclei in water as a probe, LF-NMR technique can non-destructively, rapidly and accurately characterize the pore water content and water distribution in specimens in situ, which promotes to accurately analyze the connection between

micro change of pore water and macro volumetric deformation. Therefore the cement paste samples mixed with expansive agents are monitored by non-destructive LF-NMR technique in this work, the weight and length are also measured. From the perspective of water content and its state, the quantitative analysis on evolution of chemically bound water and physically adsorbed water is conducted. Furthermore, the shrinkage-compensating deformation of cement paste is thoroughly analyzed.

Methods White cement, calcium sulfoaluminate and MgO expansive agents (CSA and MEA) are used to prepare cement paste specimens. Water to cement ratio (W/C) is 0.40, and the weight ratio of expansive agent to cement is 5%. The expansion agents are produced by Wuhan Sanyuan Special Building Materials Co. The sizes of cement paste specimens are 20 mm×20 mm×280 mm (size A) and 20 mm×20 mm×50 mm (size B).

Starting from the 3rd day of water-curing, the weight and length of 3 specimens of each sample are measured at regular time intervals, as well as the low-field magnetic resonance tests. In addition, at 56th day of water-curing, another 3 specimens of each mixture proportion and each size are transferred into a high humidity environment (20°C, 98% relative humidity (RH)) for air-curing, and measurements of weight and length, and low-field magnetic resonance tests are conducted periodically. The length test is carried out using a length gauge with an accuracy of 0.001 mm. An electronic balance with an accuracy of 0.001 g is used in the weight test. The low-field magnetic resonance test is performed by a low-field magnetic resonance instrument with a magnetic field strength of 0.047 T and a main frequency of 2 MHz. And the transverse relaxation signal of pore water in specimen is characterized with a CPMG pulse sequence.

Results and discussion After curing in water for 3 d, the weight, expansion deformation and evaporable water content of paste continuously increased during curing process, while the rate of increase gradually decreased. CSA and MEA can significantly increase the increment of chemically bound water and the expansion deformation caused by each unit increment. However, their influences on the evolution of physically adsorbed water and the expansion deformation are both insignificant. During the process of air curing in high humidity (98% RH), starting from the day 0 of air curing (*i.e.*, water curing 56 d), the weight of paste decreases initially and then increases. Similarly, the paste initially shrinks and then expands. Additionally, the evaporable water content decreases rapidly in the first 28 days and then stabilizes. Both CSA and MEA can increase the loss of evaporable water content of paste in the early stage and also enhance the expansion deformation in the later stage to compensate for shrinkage. Considering the complicated expansive process of cement-based materials mixed with expansive agents, the utilization of low-field nuclear magnetic resonance relaxation technique and other testing methods can accurately analyze the expansion deformation, which can improve the expansion mechanism and assist the selection of expansive agents.

Conclusions The main conclusions of this paper are summarized as following. During the period of 6-month water-curing, all the tested indicators, including weight, expansion deformation, and evaporable water content of paste, continuously increase, while the increasing rate keeps declining. Both CSA and MEA continue to hydrate, resulting in the larger content of chemically bound water. In the meanwhile, they increase the expansion deformation caused by unit increment of chemically bound water. The evolution of chemically bound water significantly influences the effect of expansive agents on compensating for shrinkage. Nevertheless, the evolution of physically adsorbed water and its effect on volumetric deformation is independent of the addition of any expansive agent.

After air-curing at a high humidity (98% RH), the reduction rate of evaporable water content of cement paste with CSA and MEA increases significantly in the early stage, but the difference in its shrinkage deformation is relatively small. And the compensatory effect of expansive agents on shrinkage is still effective in the later stage.

Keywords expansive agent; chemically bound water; physically adsorbed water; low-field nuclear magnetic resonance technique