

溶蚀作用下中热硅酸盐水泥净浆劣化机理

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摘 要: 溶蚀是大坝混凝土不可忽略的耐久性问题。本工作对中热硅酸盐水泥(MHC)净浆、中热硅酸盐水泥-粉煤灰净浆和普通硅酸盐水泥(OPC)净浆进行加速溶蚀试验, 通过强度测试、溶蚀深度、孔结构、X 射线衍射、热重分析和硅谱固体核磁研究了溶蚀劣化机理。结果表明: 与 OPC 净浆相比, MHC 净浆水化产物中 $\text{Ca}(\text{OH})_2$ 含量更少, 在溶蚀过程中具有更好的力学性能和更慢的溶蚀深度发展, 因此抗溶蚀性更好。30%粉煤灰掺入降低 MHC 水化产物中 $\text{Ca}(\text{OH})_2$ 含量, 并增加其孔隙率, 但是降低了抗压强度下降率和孔隙增长率。溶蚀前后 MHC 净浆中 C-(A)-S-H 凝胶硅链长度大于 OPC 净浆, 但其溶蚀后硅链增长率却较低。溶蚀后 30%粉煤灰掺量的 MHC 净浆中 C-(A)-S-H 凝胶劣化程度最高, 出现了层间交联并部分转变为硅胶。

关键词: 中热硅酸盐水泥; 粉煤灰; 溶蚀; 结构和组成; 水化硅(铝)酸钙凝胶

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中热硅酸盐水泥在保证混凝土早期强度的同时, 还能有效降低水化热, 提高混凝土抗开裂能力, 是建造大坝最重要的基础材料。三峡大坝共浇筑了 1 600 万 m^3 的中热硅酸盐水泥-粉煤灰混凝土^[1]。这种胶凝材料也成功运用在丹江口大坝、溪洛渡水电站大坝和锦屏水电站大坝。混凝土具有高耐久性是大坝长期安全稳定运行的关键, 然而其大部分区域长期位于水中, 溶蚀是不可忽略的耐久性问题。现有文献^[2-4]报道了瑞典某大坝、美国胡佛大坝和中国丰满大坝均发生过不同程度的溶蚀危害。

混凝土与水接触时, 氢氧化钙会率先溶解降低混凝土内部碱度, 随后钙矾石、C-(A)-S-H 凝胶等水化产物和未水化熟料发生分解^[5]。在这一过程中, 水化产物、未水化水泥颗粒等的溶出与分解会显著增加混凝土孔隙率, 造成混凝土力学性能和抗渗性能的下降。此外, C-(A)-S-H 凝胶作为水泥基材料的强度基因, 其在溶蚀过程中的脱钙会进一步加大水泥基材料力学性能的劣化程度^[6]。目前关于混凝土溶蚀劣化的研究多集中在混凝土材料性能演变, 例如溶蚀深度发展、力学性能下降、微结构劣化、

物相组成变化等^[7-10]。也有一些文献研究了矿物掺合料对水泥基材料抗溶蚀性能的影响: 刘仍光等^[11]研究表明, 矿渣掺量不超过 70%时可以提升水泥基材料抗溶蚀性能; 文献[12-14]研究表明, 较低掺量粉煤灰有助于提升水泥基材料抗溶蚀性能, 大掺量粉煤灰则显著降低抗溶蚀性能。现有研究多集中在普通硅酸盐水泥-矿物掺合料胶凝材料, 鲜有关于大坝建造常用的中热硅酸盐水泥-粉煤灰胶凝材料的溶蚀研究。

混凝土在自然界中遭受淡水溶蚀是一个缓慢的过程, 因此研究人员多采用室内加速溶蚀试验的方法进行混凝土溶蚀试验。研究表明^[15]使用化学试剂加速混凝土溶蚀与淡水溶蚀具有相似性, 其中最常用的加速溶蚀试剂为 NH_4NO_3 溶液。考虑到 NH_4NO_3 具有易爆性, 近些年来众多溶蚀试验采用 NH_4Cl 溶液替代 NH_4NO_3 溶液作为加速溶蚀试剂。左晓宝等^[16]、蒋林华等^[17]的研究结果证明了 NH_4Cl 溶液进行混凝土溶蚀与淡水溶蚀具有良好的相似性。因此, 本工作选用 5 mol/L NH_4Cl 溶液对中热硅酸盐水泥净浆和中热硅酸盐水泥-粉煤灰净浆进

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行了加速溶蚀试验,并与普硅水泥净浆溶蚀进行了对比。研究了净浆试块溶蚀过程中溶蚀深度和抗压强度随时间发展规律。并采用排水称重法、X 射线衍射(XRD)、热重分析(TGA)和硅谱固体核磁(^{29}Si NMR)分析了溶蚀对净浆试块孔隙率、物相组成以及 C-(A)-S-H 化学结构的影响,探究溶蚀劣化机理。

1 实验

1.1 原材料及配合比

采用中国建材总院生产的 P·I-42.5 基准水泥

(OPC),四川嘉华水泥股份有限公司生产的中热硅酸盐水泥(MHC),以及云南宣威电厂生产的 I 级粉煤灰(FA)。原材料的组成和性质如表 1 所示。由表 1 可知,OPC 与 MHC 之间在氧化物组成及基本物理性质上并无显著区别,最主要的差异在于 MHC 具有更高的 C_2S 含量以及更低的 C_3S 含量。

净浆配合比如表 2 所示,选用了大坝混凝土常用的水胶比(0.5)和粉煤灰掺量(30%)。试块尺寸为 40 mm×40 mm×40 mm,成型后表面覆盖塑料保鲜膜,在室温带模养护 24 h 后脱模,放置在混凝土标准养护室内养护 2 年后进行溶蚀试验。

表 1 原材料的组成和性质
Table 1 Composition and properties of raw materials

Composition and property		OPC	MHC	FA
Mass fraction of chemical compositions/%	CaO	66.43	64.30	5.75
	SiO_2	18.96	20.69	47.37
	Al_2O_3	4.10	2.77	21.85
	Fe_2O_3	4.08	5.71	15.79
	SO_3	2.34	3.08	2.08
	MgO	2.07	2.04	0.68
	R_2O	0.39	0.27	0.72
	LOI	1.69	1.13	4.13
Mass fraction of mineral composition/%	C_3S	63.7	50.5	
	C_2S	11.4	25.4	
	C_3A	4.7	1.5	
	C_4AF	13.4	15.0	
	Gypsum	1.3	2.0	
Physical properties	Specific gravity/($\text{g}\cdot\text{cm}^{-3}$)	3.10	3.20	2.35
	Specific surface area /($\text{m}^2\cdot\text{kg}^{-1}$)	357	338	348
	Initial setting time/min	216	225	
	Final setting time/min	302	327	
	Fineness (45 μm)/%			6.8
	Water demand ratio/%			94

Alkali content(R_2O)= $\text{Na}_2\text{O}+0.658\text{K}_2\text{O}$. OPC is Ordinary Portland cement. MHC is Moderate heat Portland cement. FA is fly ash. LOI is loss on ignition. C_3S is tricalcium silicate. C_2S is dicalcium silicate. C_3A is tricalcium aluminate. C_4AF is tetra calcium aluminoferrite.

表 2 净浆试块配合比
Table 2 Mix proportions of pastes

Sample	OPC	MHC	FA	Water
P0	100	0	0	50
M0	0	100	0	50
M30	0	70	30	50

w is mass fraction.

1.2 溶蚀制度及样品制备

待试块养护 2 年后,用毛巾擦干表面残余水分,在试块的 5 个面涂上环氧树脂,仅保留 1 个非浇筑面作为暴露面。将试块浸泡在 5 mol/L NH_4Cl 溶液

中进行加速溶蚀试验,溶液与试块的体积比为 10:1。待试块浸泡至 7、14、28 d 和 56 d,从溶液中取出试件用于溶蚀深度和抗压强度测试。测完溶蚀深度后,对浸泡至不同时期的试块溶蚀区与未溶蚀区分别取样,切成厚度为 5 mm 的水泥片,用于孔隙率测试。此外,对浸泡时长 56 d 的试块距离暴露面 0~3、3~6 mm 和试块中心未溶蚀区域分别进行取样并破碎,在异丙醇溶液中浸泡 7 d(期间更换 3 次异丙醇溶液),随后在 40 $^{\circ}\text{C}$ 的真空干燥箱中干燥 7 d。使用玛瑙研钵对干燥样品进行磨粉并过 200 目筛网,制样后进行真空密封保存并进行编号。净浆试

块取样示意图如图 1 所示: 将距离溶蚀面 0~3 mm 的区域记为溶蚀外层, P0、M0 和 M30 的溶蚀外层分别编号为 P0-Ext.、M0-Ext. 和 M30-Ext.; 将距离溶蚀面 3~6 mm 的区域记为溶蚀内层, P0、M0 和 M30 溶蚀内层分别编号为 P0-Int.、M0-Int. 和 M30-Int.; 试块中心未溶蚀区记为 P0-Un.、M0-Un. 和 M30-Un.。将制备好的粉末样品分别进行 XRD、TGA 和 ^{29}Si NMR 测试。

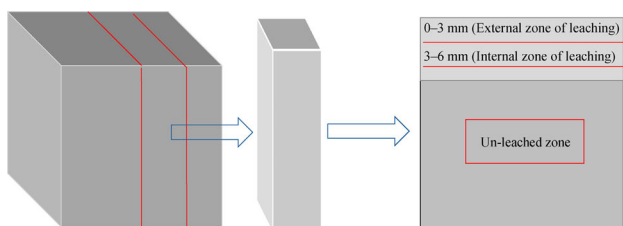


图 1 溶蚀净浆试块制样示意图

Fig. 1 Schematic diagram of the paste sample preparation process

1.3 测试

抗压强度测试加载方向垂直于溶蚀面, 加载速率为 2.4 kN/s。每组测试 6 个试块取平均值, 并控制误差范围为 15% 以内。

采用酚酞法进行溶蚀深度测定, 用切割机将溶蚀至不同龄期的试块沿溶蚀面径向切开, 均匀喷散质量分数 1% 的酒精酚酞溶液。未溶蚀的区域显现红色, 溶蚀区域不变色。用游标卡尺测量溶蚀区域的深度, 每个试块记录 5 个溶蚀深度数据, 计算平均值。

孔隙率测试按照文献[18]所述的排水称重法。先将待测试块用排水法测得体积 V , 随后将其放入 105 °C 干燥箱中干燥 24 h, 冷却至室温后称重 m_1 , 再将试块放入水中 24 h 进行保水, 测其饱和面干质量 m_0 。则试块的孔隙率 P 可由公式(1)确定。

$$P = (m_0 - m_1) / V \quad (1)$$

使用 D-MAX 1200 X 射线粉末衍射仪(日本理学公司)进行 XRD 测试。工作电压为 40 kV, 工作电流为 40 mA, 辐射源为 Cu K_α , 扫描范围为 5°~70°, 扫描速率为 2 (°)/min。

使用 SDT Q600 热分析仪(美国 TA 公司)进行 TGA 测试。将 10~15 mg 净浆粉末在氮气氛围中加热至 1000 °C, 升温速率为 10 °C/min。为避免初始样品中自由水的影响, 待测样品先在热分析仪中加热至 50 °C 并保持 10 min。

使用 Burkert AvanceIII 400M 核磁共振波谱仪进

行硅谱固体核磁测试。将待测净浆粉末装满于 7 mm 转子, 在 10 kHz 的工作频率下采集核磁共振信号, 以四甲基硅烷作为化学位移分析外标物, 扫描次数为 1 024 次, 弛豫延迟为 10 s。使用 Gauss-Lorentz 函数对硅谱固体核磁结果进行解卷积处理, 解卷积过程中保持配位硅氧四面体与桥接硅氧四面体的面积比例为 2:1, 具体处理方法见文献[19]。

2 结果与讨论

2.1 溶蚀深度

净浆试块溶蚀深度发展如图 2 所示。净浆试块的溶蚀深度与溶蚀天数的平方根成线性正比, 符合 Fick 定律, 公式(2)可用来拟合溶蚀深度与溶蚀时间的关系。从图 1 中的拟合结果可得知, 相较于 P0, M0 的 K 值减小了 10.3%, M30 的 K 值增加了 12.1%, 表明 MHC 净浆的溶蚀深度发展慢于 OPC 净浆, 而 30% 的粉煤灰掺量显著加快了 MHC 净浆的溶蚀深度发展。

$$y = k\sqrt{t} \quad (2)$$

式中: y 为溶蚀深度(mm); t 为溶蚀天数(d); k 为与溶蚀速率相关的系数。

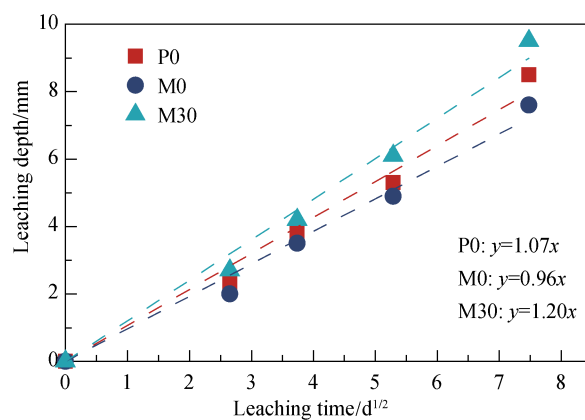


图 2 净浆试块溶蚀深度发展

Fig. 2 Evolution of leaching depth of pastes specimens

2.2 抗压强度

净浆试块溶蚀抗压强度发展如图 3 所示。图中的柱状图为净浆试块的抗压强度值, 折线图为归一化抗压强度。溶蚀前, M0 的抗压强度高于 P0, 这是由于其长期水化过后具有更密实的孔隙结构, 且会生成更多的 C-(A)-S-H 凝胶^[20-21]。掺入粉煤灰的水泥基材料的抗压强度发展主要取决于粉煤灰活性、反应时间以及掺量等因素^[22-23]。图 3 表明 M30 在水化 2 年之后的抗压强度仍低于 M0, 这可能归因于粉煤灰掺量过高且 MHC 净浆水化产物碱含量

较低,不利于粉煤灰发挥火山灰活性。溶蚀试验过程中,不同净浆试块抗压强度均随溶蚀时间增长而下降,其中 M0 抗压强度始终最高, M30 始终最低。根据强度归一化结果可知,与 P0 相比, M0 不仅具有较高初始抗压强度,而且抗压强度下降率也较低,这将有利于其长期的抗溶蚀性能。尽管 M30 初始抗压强度最低,但抗压强度下降较慢,对于长期溶蚀作用下的力学性能发展有利。

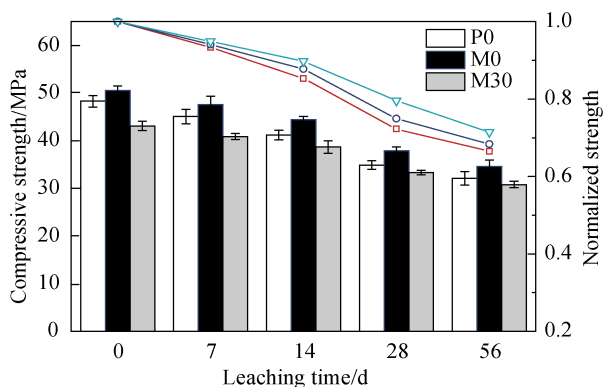


图3 净浆试块溶蚀抗压强度发展

Fig. 3 Evolution of compressive strength of the pastes specimens during leaching

2.3 孔隙率

净浆试块溶蚀过程中孔隙率演变如图4所示。孔隙增长率变化如图5所示。溶蚀前, M30 的孔隙率最大, M0 最小, 溶蚀使样品孔隙率增大, 但是仍保持这一大小次序。孔隙率越大, 水分越容易传输, 溶蚀深度发展也就越快, 这与 2.1 中溶蚀深度发展的规律相一致。尽管 M30 的孔隙率最大, 但是其在溶蚀过程中的孔隙增长率却最小, P0 的孔隙增长率最大。氢氧化钙是溶蚀过程中最容易溶出的物质, 是造成孔隙率增长的最主要因素^[24-25]。通过热重-热重微分曲线(TG-DTG)(图6)数据可知,

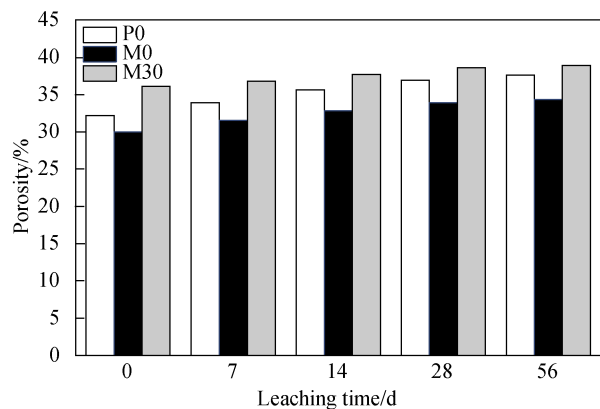


图4 净浆试块溶蚀过程中孔隙率演变

Fig. 4 Evolution of porosity of the pastes specimens during leaching

在未溶蚀区域中, P0 的氢氧化钙的含量高于 M0, 而 M30 的氢氧化钙含量远低于 P0 和 M0, 与孔隙增长率大小次序一致。同理, 这也可以用于解释 M30 具有最低的初始抗压强度, 但其抗压强度下降率却远低于 M0 和 P0。

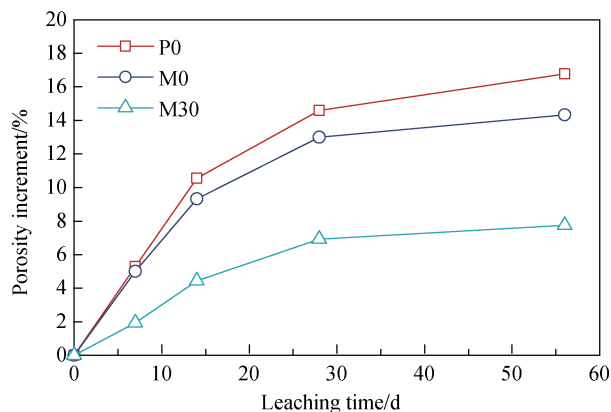


图5 净浆试块溶蚀过程中孔隙增长率发展

Fig. 5 Evolution of porosity increment of the pastes specimens during leaching

2.4 溶蚀前后净浆水化产物组成分析

2.4.1 XRD 溶蚀后净浆不同区域的 XRD 谱如图7所示。从整体上看, 3种净浆未溶蚀区域水化产物的种类并无明显的差异, 主要物相包括氢氧化钙、钙矾石、水镁铁石和碳酸钙, 以及未水化的硅酸三钙、硅酸二钙和铁铝酸四钙, M30-Un.则另含石英峰(来自粉煤灰)。对于 P0 和 M0 的溶蚀外层, 主要物相包括碳酸钙、钙矾石和水镁铁石, 以及硅酸三钙、硅酸二钙和铁铝酸四钙; 氢氧化钙的峰全部消失, 钙矾石的峰显著下降, 可能有2部分原因: 一是因为较长养护龄期中试块外层发生碳化使得钙矾石分解; 二是因为溶蚀导致钙矾石分解。此外, 可能由于养护或溶蚀过程中的碳化^[11], 溶蚀外层样品的碳酸钙峰较未溶蚀区域显著增加。溶蚀后内层的氢氧化钙峰全部消失, 且钙矾石的峰也发生了显著的降低, 这主要是由于溶蚀所造成的。对于 M30, 溶蚀外层区域可见碳酸钙(包括方解石和球霏石)、单碳酸盐, 铁铝酸四钙、C-(A)-S-H 凝胶和石英峰, 且硅酸三钙和硅酸二钙峰变得极为微弱; 此外, M30 外层样品与其他溶蚀样品的外层相比, 钙矾石的峰消失。以上现象表明, M30 外层样品发生了更严重的劣化, 这可能是由于 M30 的孔隙率更大, 更易于水、气介质传输。M30 溶蚀内层的物相中没有氢氧化钙和碳酸钙, 但仍有部分钙矾石, 其受溶蚀程度与外层相比较轻。

得 Q^1 比例降低, Q^2 比例增加, 增加了 $\bar{l}$ 长度。C-(A)-S-H 凝胶的结构类似于带有缺陷的托贝莫来石, 硅链结构中存在着大量空位点, 这些空位点需要阳离子来平衡末端硅氧四面体 Q^1 所带的负电荷, 例如钙离子、钾离子、钠离子和氢离子, 其中最主要的是钙离子^[37]。溶蚀使得大量钙离子脱去, 硅链为了保持电荷平衡进而发生缩聚, 共用更多硅氧四面体, 因此 $\bar{l}$ 增长。硅链缩聚过程会同时使得末端硅氧四面体 Q^1 比例降低, 中间硅氧四面体 Q^2 比例增加。对于溶蚀外层区域而言, P0、M0 和 M30 的 $\bar{l}$ 相对于未溶蚀区域分别增加 102.7%, 57.4% 和 133.1%。对于溶蚀内层, P0、M0 和 M30 的 $\bar{l}$ 相对于未溶蚀区域分别增加 54.2%、37.7% 和 102.7%。无论是在内层还是外层, M30 的 $\bar{l}$ 增长比例最大, M0 的 $\bar{l}$ 增长比例最小。这是由于, 对于未溶蚀区域, M30 中的氢氧化钙含量远低于 P0 和 M0, 溶蚀

受到的缓冲作用与 P0 和 M0 相比极弱, C-(A)-S-H 凝胶会更早的发生脱钙, 造成其结构转变。而 M0 中的氢氧化钙含量低于 P0, 其溶蚀缓冲作用与 P0 相比较弱, 但其硅链的变化程度却仍然小于 P0。通过表 3 的 $\bar{l}$ 数据可得知, 尽管溶蚀过后 M0 的内层与外层 $\bar{l}$ 均高于 P0, 但是其硅链增长幅度却小于 P0。所有样品外层浸泡在同样的溶蚀溶液中, 所接触的外界 pH 值接近, 相对于 M0, 由于 P0 生成 C-(A)-S-H 凝胶时 pH 值更高, 因此溶蚀后 C-(A)-S-H 凝胶面临的 pH 环境变化也更大, 造成其硅链结构发生的转变也更为剧烈。此外, 未水化 MHC 净浆中 C_2S 含量较高, C_2S 含量高的水泥水化过程中会生成更多高密度 C-(A)-S-H 凝胶^[40], 这可能对其抗溶蚀性能也有所提升。以上结果表明, C-(A)-S-H 凝胶在溶蚀过程中的结构转变不仅受氢氧化钙缓冲作用影响也受硅链的初始状态影响。

表 3 ^{29}Si NMR 解卷积结果及硅链结构计算Table 3 Deconvolution results of ^{29}Si NMR spectra and the calculation of silicate chain structure

^{29}Si Site	Intensity/%								
	P0-Un.	M0-Un.	M30-Un.	P0-Int.	M0-Int.	M30-Int.	P0-Ext.	M0-Ext.	M30-Ext.
C_2S	2.8	4.5	5.0	2.5	4.4		2.9	2.4	
C_3S	4.4	3.9	5.5	7.7	6.9		8.1	5.3	
$Q^2(1Al_6)$	8.1	9.0	8.0	4.9	5.9	1.9	4.3	4.7	1.6
Q^1	32.0	24.6	14.3	19.8	17.0	5.8	14.6	15.2	4.5
$Q^2(1Al_4)$	9.0	12.6	13.3	8.7	10.3	2.5	4.8	8.8	2.3
Q_6^2	14.5	15.5	18.0	18.8	18.5	16.0	21.7	21.2	13.5
Q_6^2	29.0	31.0	36.0	37.6	37.0	32.0	43.4	42.4	27.0
$Q^3(0Al)$						11.6			15.5
$Q^3(1Al)$						10.6			7.7
$Q^3(\text{Si-Al gel})$						5.3			13.3
$Q^4(\text{Si-Al gel})$						11.5			14.6
Calculation $\bar{l}$	6.32	8.26	14.0	9.75	11.37	31.22	12.82	13.00	32.64
of silicate chain	$n(Al_{4+6})/n(\text{Si})$	0.10	0.10	0.12	0.08	0.09	0.04	0.05	0.04
	$n(Al_4)/n(\text{Si})$	0.05	0.06	0.07	0.05	0.06	0.02	0.03	0.02
	$n(Al_6)/n(\text{Si})$	0.05	0.04	0.05	0.03	0.03	0.02	0.02	0.02

M30 不仅内外层的硅链转变程度均最大, 还产生了层间交联的硅氧四面体 Q^3 , 并伴随大量硅铝胶生成。然而, M30 具有最低的抗压强度下降率。普遍认为, 溶蚀中造成的水泥基材料力学性能下降主要有 2 方面因素, 一是水化产物的溶出造成微结构发生破坏进行影响强度, 另外是 C-(A)-S-H 凝胶脱钙转变为低弹性模量的硅铝胶对力学性能产生负面影响^[6]。结合孔隙率下降率的规律, 这一结果表明, 可溶性物质溶出引发的孔结构变化对力学性能下降

的影响可能大于 C-(A)-S-H 凝胶脱钙产生硅胶的影响。溶蚀过后, 所有样品的内外层 $n(Al_{4+6})/n(\text{Si})$ 均发生了降低, 说明溶蚀过程中不仅发生了脱钙, 也发生了脱铝。然而, P0 与 M0 的内层溶蚀较轻, $n(Al_4)/n(\text{Si})$ 几乎不变, 而 $n(Al_6)/n(\text{Si})$ 出现了降低。说明在脱钙过程中四面体配位的铝 IV 的稳定性大于八面体配位的铝 VI。而低钙硅比的 C-(A)-S-H 凝胶中铝 IV 含量较高, 这对于其溶蚀过程中 C-(A)-S-H 凝胶的结构稳定性起到提升作用。

$$\bar{l} = \frac{2}{\left[\frac{l(Q^1)}{l(Q^1) + l(Q_b^2) + l(Q_p^2) + \frac{3}{2}(l(Q^2(1Al_6)) + l(Q^2(1Al_4)) + l(Q^3(0Al)) + l(Q^3(1Al)))} \right]} \quad (4)$$

$$\frac{n(Al_{4+6})}{n(Si)} = \frac{n(Q^2(1Al_4)) + n(Q^2(1Al_6))}{n(Q^1) + n(Q_b^2) + n(Q_p^2) + \frac{3}{2}(n(Q^2(1Al_6)) + n(Q^2(1Al_4)))} \quad (5)$$

$$\frac{n(Al_4)}{n(Si)} = \frac{n(Q^2(1Al_4))}{n(Q^1) + n(Q_b^2) + n(Q_p^2) + \frac{3}{2}(n(Q^2(1Al_6)) + n(Q^2(1Al_4)))} \quad (6)$$

$$\frac{n(Al_6)}{n(Si)} = \frac{n(Q^2(1Al_6))}{n(Q^1) + n(Q_b^2) + n(Q_p^2) + \frac{3}{2}(n(Q^2(1Al_6)) + n(Q^2(1Al_4)))} \quad (7)$$

3 结论

1) 中热硅酸盐水泥净浆水化产物中氢氧化钙含量与初始孔隙率均低于普硅水泥, 30%粉煤灰的掺入显著降低了中热水泥中氢氧化钙含量并增大了其孔隙率。氢氧化钙在溶蚀过程中既是缓冲物质也是易溶解物质, 其含量的降低虽然减弱了溶蚀的缓冲作用, 但也降低了孔隙增长率以及强度下降率。因此, 溶蚀过程中, 中热水泥净浆与普硅水泥净浆相比具有更慢的溶蚀深度发展、更小的孔隙增长率、更高的初始抗压强度以及更低的抗压强度下降率, 体现了更优的抗溶蚀性能。尽管掺入 30%粉煤灰加速了中热水泥净浆溶蚀深度的发展并降低其抗压强度, 但同时也减缓了强度下降率与孔隙增长率, 整体上效果偏负面。

2) 溶蚀显著增加净浆试件中 C-(A)-S-H 凝胶的硅链长度。溶蚀后中热水泥净浆试件内外层 C-(A)-S-H 凝胶硅链长度均大于普硅水泥净浆, 但其硅链长度增长率低于普硅水泥净浆。不论在试件的内层还是外层区域, 中热硅酸盐水泥-粉煤灰净浆中 C-(A)-S-H 凝胶硅链长度最大且增长幅度最快, 产生了层间交联并伴随硅胶的生成。溶蚀过程中硅链中四面体配位的铝 IV 的稳定性强于八面体配位的铝 VI。溶蚀过程中可溶性物质溶出导致的孔结构变化对试件力学性能的影响可能大于 C-(A)-S-H 凝胶脱钙转变为硅胶的影响。

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Deterioration Mechanism of Moderate Heat Portland Cement Pastes Under Leaching

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Extended Abstract

Introduction Moderate heat Portland cement (MHC) enhances early concrete strength, reduces hydration heat, and increases crack resistance, making it widely used for dam construction. Most dams located underwater therefore having to face to leaching issues.

Prolonged concrete exposure to water leads to the dissolution of $\text{Ca}(\text{OH})_2$ from hydration products, thus decreasing internal alkalinity so as to cause the breakdown of ettringite, C-(A)-S-H, and clinker. The phenomena result in deterioration of mechanical properties and impermeability. Current research on the leaching of cementitious material mainly focuses on ordinary Portland cement (OPC) and its blends with mineral admixtures, while little attention is paid to MHC and moderate heat Portland cement-fly ash (MHC-FA) systems. The latter two MHCs are commonly employed in dam construction. In this work, leaching tests were conducted on MHC pastes and MHC-FA pastes. Comparison with OPC pastes system was further carried out, focusing on the evolution of leaching depth, deterioration of compressive strength, and the impact on phase composition and C-(A)-S-H structure.

Methods Specimens with a water-to-cement ratio of 0.5 were prepared from MHC pastes (M0), MHC with 30% FA pastes (M30), and OPC pastes (P0). The size of the formed specimens was 40 mm×40 mm×40 mm. After curing in a standard concrete curing room for two years, five surfaces of the specimens were sealed with epoxy resin, leaving one surface exposed for accelerated leaching in a 5 mol/L NH_4Cl solution. The specimens were taken out from the solution after 7, 14, 28 d, and 56 d, following a test on compressive strength and leaching depth. The leaching depth is determined by spraying a 1% phenolphthalein solution in alcohol on the cut-open specimens. Samples were taken from areas 0–3 mm and 3–6 mm from the leaching exposure surface and pristine surface at 56 d. The thickness of 0–3 mm is labeled as the external layer of the leaching zone, and the thickness of 3–6 mm is labeled as the internal layer of the leaching zone. Characterization techniques included X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), and Solid-State ^{29}Si Nuclear Magnetic Resonance (^{29}Si NMR) spectroscopy. In addition, the porosity of samples was evaluated using the hydrostatic weighing method.

Results and discussion The Leaching depth of M0 develops slower than OPC, while the M30 is the fastest. Initially, the compressive strength of M0 is higher than P0, but adding 30% fly ash to M0 lowers its compressive strength. Before leaching, the compressive strength of M0 is higher than that of P0, and the M30 has the lowest compressive strength. The compressive strength of the specimens decreases as the leaching time increases. Among them, the compressive strength of M0 is always the highest, and M30 is always the lowest. Compared with OPC, MHC has higher initial compressive strength and a lower strength decline rate, benefiting its long-term corrosion resistance. Although M30 has the lowest initial intensity, its intensity decreases more slowly. Additionally, before leaching, M30 has the highest porosity, P0 is in the middle, and M0 the lowest. Leaching increases the porosity of all samples evenly. Despite M30 has the highest initial porosity, the increasing rate of porosity is the lowest. Similar phenomena are observed for M0 and P0, while P0 shows the highest increasing rate of porosity. There is no significant difference in hydration products among the P0, M0 and M30 in the unleaching regions. The prominent XRD diffraction peaks of the sample before dissolution include $\text{Ca}(\text{OH})_2$, sjogrenite, ettringite, CaCO_3 and gypsum, and C_3S , C_2S and C_4AF . M30 also contains quartz peaks. The long-time curing leads to carbonation in the external layers. Thus, after leaching, a significant CaCO_3 peak appears. For the leached external layers of P0 and M0, the main phases include CaCO_3 , sjogrenite, ettringite and gypsum, as well as C_3S , C_2S and C_4AF . All ettringite dissolves in the leached external layers of M30, showing weakened peaks of C_3S and C_2S , yet ettringite remains in the internal layer. TGA reveals the $\text{Ca}(\text{OH})_2$ contents of 26.0% for P0, 22.1% for M0, and 5.3% for M30, showing that P0 has the strongest leaching buffering effect. Based on the former result that M0 has the best leaching resistance, the experiments reveals no guaranteed relationship between strong buffering and optimal leaching resistance. This can be understood as that $\text{Ca}(\text{OH})_2$ is the most soluble, and is therefore easier to create more pathways for leaching, leading to significant microstructural damage. The ^{29}Si NMR results reveal that a significant increase in MCL is observed in all the samples due to the decalcification of C-(A)-S-H. Both the internal and external layers of M30 exhibit the highest growth proportions, accompanied by the formation of Si-Al gel. Although the MCL of M0 exceeds that of P0 in both the internal and external layers after leaching, the growth of silicate chain is still lower than that of P0. However, M30 experiences the lowest compressive strength reduction rate, suggesting that microstructural changes from soluble substance leaching may show greater impact on declining mechanical properties than silica gel formation due to C-(A)-S-H decalcification. During the leaching, the stability of AIVI is greater than AIIV.

Conclusions The main conclusions are summarized as follows: Compared to OPC pastes, MHC pastes experience a slower leaching depth development, leading to enhanced residual compressive strength, decreased pore degradation, mitigated declines in compressive strength and changes in C-(A)-S-H gel structure. Before leaching, OPC pastes has the highest $\text{Ca}(\text{OH})_2$ content, MHC pastes the middle and MHC-FA pastes the lowest. Leaching leads to a significant increase in the MCL of C-(A)-S-H in the paste. After leaching, both the internal and external layers MHC-FA pastes exhibit the largest increase in MCL, accompanied by the production of silica-alumina gel. The average increase of silicate chain length is observed greater in C-(A)-S-H of OPC pastes than that of MHC pastes. During leaching, the stability of AIVI exceeds that of AIIV.

Keywords moderate heat Portland cement; fly ash; leaching; structure and composition; calcium silicate aluminate hydrate gel