

柠檬酸钠对碱激发粉煤灰滤液中钢筋的阻锈机制

周霄骋, 李 曼, 施锦杰

(东南大学材料科学与工程学院, 江苏省土木工程材料重点实验室, 南京 211189)

摘 要: 碱激发粉煤灰是一种兼具低碳与环保优势的建筑材料, 具备应用于海洋等氯盐侵蚀环境的潜力。作为一种典型的羧酸盐阻锈剂, 柠檬酸钠可进一步保障碱激发粉煤灰中钢筋的耐蚀性。然而, 柠檬酸钠对碱激发粉煤灰体系中钢筋的阻锈机制尚未明确。基于此, 本研究通过电化学测试、钝化膜表征技术和腐蚀形貌及产物分析方法研究了氯盐侵蚀作用下柠檬酸钠对碱激发粉煤灰滤液中钢筋腐蚀行为的影响, 并揭示了其阻锈机制。结果表明: 虽然柠檬酸钠会一定程度上影响碱激发粉煤灰体系中钢筋钝化膜的稳定性, 但其不仅能与氯离子产生竞争吸附效应, 还能在钢筋表面形成吸附膜, 从而有效提高钢筋的耐氯盐侵蚀能力。

关键词: 碱激发粉煤灰; 钢筋; 柠檬酸钠; 钝化膜; 阻锈机制

中图分类号: TU503 文献标志码: A 文章编号: 0454-5648(2024)02-0603-11

网络出版时间: 2023-12-05



碱激发胶凝材料是利用具有(潜在)火山灰活性的硅铝质材料与碱性激发剂反应而生成的一种胶凝材料^[1]。常用的硅铝质材料主要有粉煤灰、高炉矿渣、偏高岭土等工业副产品^[2]。碱激发胶凝材料的制备无需高温煅烧, 碱激发剂激发代替硅酸盐水泥(OPC)水化可减少 80%以上的二氧化碳排放量, 因此采用碱激发胶凝材料具有可持续发展潜力^[3-4]。

近年来, 在中国“双碳目标”背景下, 碱激发胶凝材料体系中钢筋的钝化及腐蚀行为研究得到了更多的关注^[5-6]。由于碱激发胶凝材料的反应产物、孔结构和孔溶液组成与普通硅酸盐水泥存在显著差异, 其反应过程主要包括粉煤灰等原材料被碱性激发剂破坏, 高度无序、交联的铝硅酸盐等凝胶结构的形成^[7]。研究表明, 碱激发粉煤灰(AAFA)砂浆中钢筋钝化膜的稳定性主要取决于激发剂中碱的种类和浓度^[8]。与 OPC 相比, 碱激发环境的高碱性、反应形成的类沸石吸附层使得钢筋具备更优异的耐氯盐腐蚀性能^[9-10]。但需要注意的是, 对于耐蚀性较低的普通低碳钢筋而言, 高浓度氯盐或氯盐长期侵蚀作用下 AAFA 体系不能完全抑制钢筋锈蚀^[11]。

已有研究表明, 阻锈剂对 AAFA 砂浆中钢筋腐

蚀的抑制效率较高^[12], 因此使用阻锈剂可以作为保障碱激发体系中钢筋耐蚀性的方法之一, 具备潜在的应用价值。在种类繁多的绿色有机阻锈剂中, 羧酸盐类阻锈剂可以有效提高碱性溶液中钢筋的耐蚀性^[13-15]。研究表明, 在较高氯盐浓度下, 羧酸盐类阻锈剂作用下钢筋的点蚀电位(E_{pit})明显高于胺盐和氨基酸盐, 羧酸盐能有效提高钢筋的耐氯盐点蚀能力^[16]。此外, 加入适量羧酸盐类阻锈剂(柠檬酸钠)可提高混凝土的初始黏度和抗分散性, 从而改善其混凝土孔结构, 提高抗压强度及耐久性^[17-18], 但其在碱激发胶凝材料体系中的适应性及阻锈机制尚未明确^[19]。

基于此, 本研究通过在含柠檬酸钠的碱激发粉煤灰滤液中直接加入氯盐和预先钝化钢筋后再加入氯盐的方式, 分析柠檬酸钠对未钝化钢筋/预钝化钢筋腐蚀行为的影响, 并提出柠檬酸钠对碱激发粉煤灰滤液中钢筋耐蚀性提升的作用机制。

1 实验

1.1 材料

钢筋为直径 16 mm 的 HRB400E 热轧螺纹钢,

收稿日期: 2023-06-27。 修订日期: 2023-07-23。

基金项目: 国家重点研发计划(2021YFB3802000; 2021YFB3802005)。

第一作者: 周霄骋(1991—), 女, 博士研究生。

通信作者: 施锦杰(1983—), 男, 博士, 副教授。

Received date: 2023-06-27. Revised date: 2023-07-23.

First author: ZHOU Xiaocheng (1991—), female, Doctoral candidate.

E-mail: zhxc512@126.com

Correspondent author: SHI Jinjie (1983—), male, Ph.D., Associate Professor.

E-mail: jinjie@seu.edu.cn

其化学成分(质量分数)为 C 0.24%, Si 0.33%, Mn 1.26%, P 0.032%, S 0.035%, 其余为 Fe。所用粉煤灰为低钙粉煤灰, 其主要化学组分(质量分数)为 SiO₂ 51.07%, Al₂O₃ 36.24%, CaO 1.25%, Fe₂O₃ 2.88%, K₂O 1.43%, MgO 0.74%, SO₃ 0.39%, Na₂O 0.44%。

碱激发粉煤灰滤液的制备在(25±2) °C 进行: 首先将粉煤灰与碱激发剂(80 g/L NaOH 溶液)以质量比 1:1 混合; 然后在封闭容器中搅拌 24 h; 最后采用快速定性滤纸过滤密封保存备用。其中, 含柠檬酸钠(Cit)的 AAFA 滤液通过向 AAFA 滤液中添加 100 mmol/L 柠檬酸钠得到。采用电感耦合等离子体发射光谱仪(ICP-OES)测定 AAFA 滤液的化学组成, 结果如表 1 所示。

表 1 AAFA 滤液的化学组成

Table 1 Chemical composition of alkali-activated fly ash (AAFA) solution

Solution		Na	Mg	Ca	K	Si	S	Al
AAFA		>291.7	0.3	16.9	289.7	90.2	232.0	0.8

w is mass fraction.

1.2 电化学测试

电化学测试在 DH7000 电化学工作站(东华分析, 江苏东华分析仪器有限公司)完成, 采用经典的三电极测试体系。工作电极为 HRB400E 钢筋电极: 将直径为 16 mm 的钢筋切成 10 mm 厚的电极, 通过 180[#]、400[#]、800[#]、1 200[#]和 2 000[#]的碳化硅砂纸逐级打磨后, 用粒径 2.5 μm 的金刚石抛光剂进行抛光, 最后用去离子水和乙醇清洗、干燥。参比电极为饱和甘汞电极(SCE), 辅助电极为铂电极。电化学阻抗(EIS)谱测试在开路电位下进行, 交流扰动电压幅值为 10 mV, 测量频率范围为 100 kHz~10 mHz。动电位循环极化(CPP)的扫描速率为 1 mV/s, 由腐蚀电位以下 0.1 V 扫描至电流密度为 1 mA/cm²时再回扫至腐蚀电位(E_{corr})。CPP 测试中自阴极扫描至阳极过程中腐蚀电流密度(i_{corr})最小时的电位即为腐蚀电位; 钢筋在钝化区间维持的恒定电流密度即为钝化电流密度(i_{pass}); 当阳极极化达到某一电位值时, 钢筋钝化膜破坏出现电流密度迅速增大时的电位即为点蚀电位(E_{pit})。

1.3 钝化膜表征

原子力显微镜(AFM)技术的扫描尺寸为 10 μm×10 μm, 扫描频率为 1 Hz。X 射线光电子能谱(XPS)测试的激发源为 Al K_α 射线($h\nu=1\ 486.6\ \text{eV}$), 束斑 400 μm, 以 C 1s 结合能(284.80 eV)为能量标准进行荷电校正。

1.4 腐蚀形貌及产物分析

钢筋腐蚀形貌及产物表征采用 QUANTA250 扫描电子显微镜(SEM)和能谱仪(EDS)联用进行分析。

2 结果与讨论

2.1 柠檬酸钠对未钝化钢筋氯盐腐蚀行为的影响

图 1 为未经预钝化的钢筋直接在含 3 mol/L 氯盐的 AAFA 滤液中的 EIS 谱。随着腐蚀时间自 1 d 延长至 7 d, 空白组钢筋(Blank)的容抗弧半径变小, 相应的钢筋阻抗模值 $|Z|$ 也有所降低, 表明氯盐直接侵蚀作用下钢筋的耐蚀性明显降低(见图 1a~图 1b)。虽然 AAFA 滤液的 pH 值较高(pH 值>13), 有利于钢筋保持钝化状态并具备较高的耐蚀性; 但较高浓度氯盐仍会破坏相对致密的钝化膜, 从而逐渐降低钢筋的耐蚀性^[10]。

值得注意的是, 柠檬酸钠作用的钢筋(Cit)容抗弧半径和钢筋阻抗模值 $|Z|$ 在 7 d 内不降反升(见图 1c~图 1d)。对比图 1a 和图 1c, 侵蚀 7 d 后, 柠檬酸盐作用的钢筋容抗弧半径大约是空白组的 3 倍, 表明高浓度氯盐环境下柠檬酸盐能明显提高钢筋的耐蚀性, 可能的原因在于柠檬酸根离子会和氯离子在钢筋表面产生竞争吸附作用^[20]。

采用双时间常数等效电路对 EIS 数据进行定量分析(见图 2a)^[21], 其中: R_s 是溶液电阻; R_f 代表钢筋电极表面钝化膜电阻; R_{ct} 是电荷转移电阻。常相位角元件 CPE_f 代表电极表面的钝化膜电容, CPE_{dl} 表征电极表面/溶液界面双电层电容。

CPE 的阻抗可由 CPE 参数 Q 和 n 定义, 如式(1)所示^[22]:

$$Z_{\text{CPE}} = (j\omega)^{-n} / Q \quad (1)$$

式中: Q 是 CPE 的导纳($\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^n$); j 为虚数单位($j^2=-1$); ω 是角频率; n 是 CPE 的指数。当 n 趋近 1 时, CPE 代表纯电容; 当 n 趋近 0 时, CPE 代表理想电阻。拟合结果如表 2 所示。由表 2 可知, 随着腐蚀时间的延长, 空白组钢筋的 R_{ct} 值显著下降, 柠檬酸钠作用的钢筋 R_{ct} 值不降反升, 且远高于空白组钢筋, 表明柠檬酸钠可有效作用于电极/溶液界面双电层, 提升钢筋的耐蚀性。

2.2 柠檬酸钠对钢筋钝化及耐氯盐腐蚀的影响

图 3 为钢筋在不含氯盐的 AAFA 滤液中预先钝化的 EIS 结果。随着钝化时间的延长, 空白组钢筋(P-Blank)的容抗弧半径不断变大, 与之对应的阻抗模量值增大且相位角增大, 表明钝化膜不断形成(见图 3a~图 3b)。但在整个钝化期内, 柠檬酸盐作用的

钢筋(P-Cit)容抗弧半径都明显小于空白组钢筋(见图 3c~图 3d), 表明柠檬酸盐不利于 AAFA 滤液中钢

筋钝化膜的形成, 且这种负面作用随着钝化时间的延长更为显著。

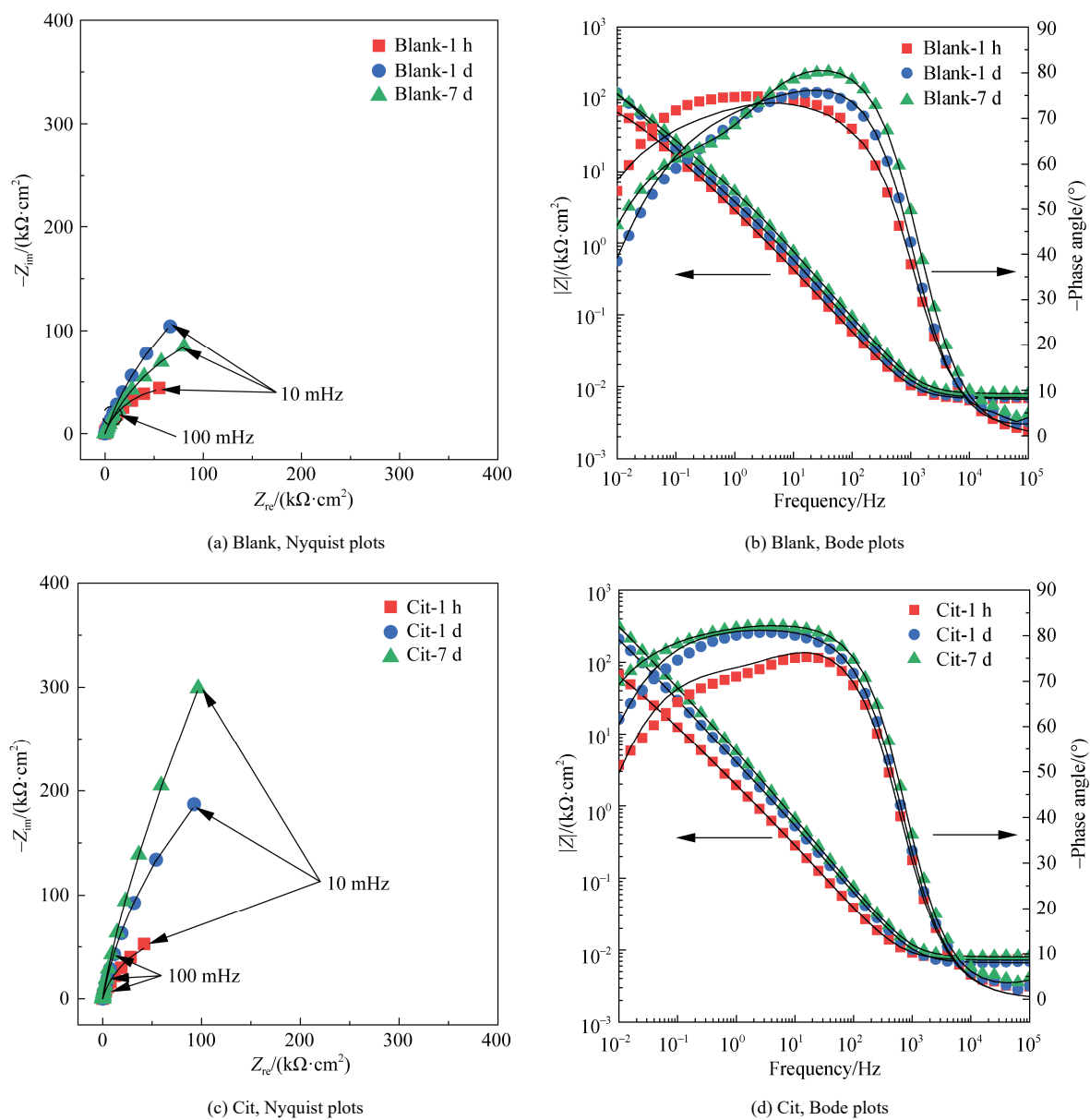


图 1 未钝化钢筋在含氯盐 AAFA 滤液中的 EIS 谱

Fig. 1 EIS (electrochemical impedance spectroscopy) spectra of bare steel in AAFA solution containing chlorides

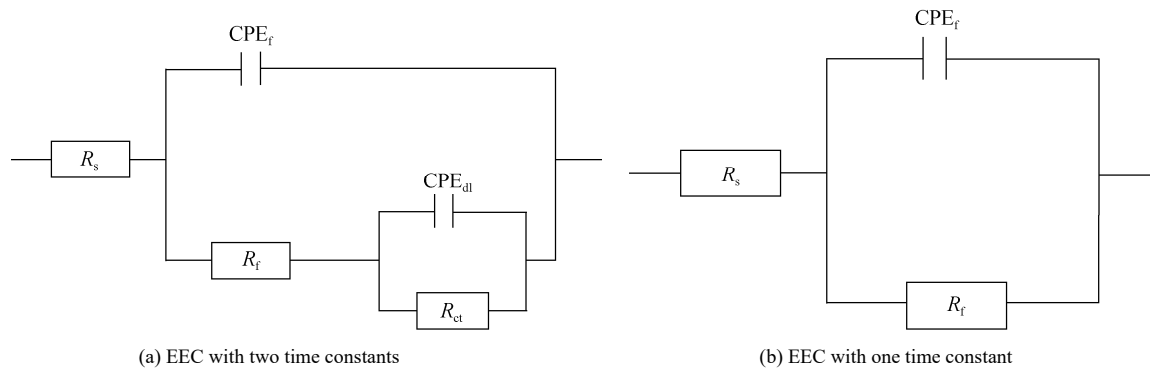


图 2 用于拟合钢筋 EIS 数据的等效电路

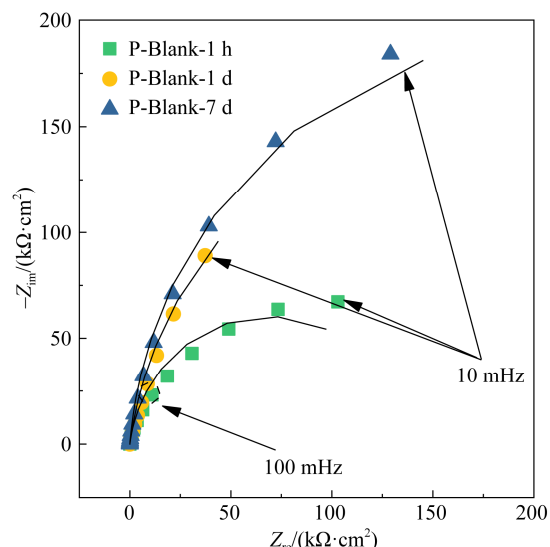
Fig. 2 Equivalent electrical circuits used for fitting EIS data of steel

表 2 含氯盐的 AAFA 滤液中未钝化钢筋的 EIS 拟合结果

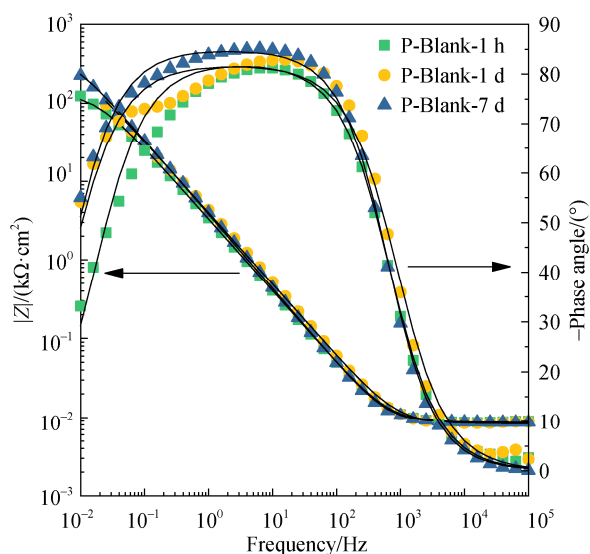
Table 2 Fitted EIS results of bare steel in AAFA solution containing chlorides

Specimen	Time/d	$R_s/(\Omega \cdot \text{cm}^2)$	$R_f/(\text{k}\Omega \cdot \text{cm}^2)$	CPE_f		$R_{ct}/(\text{k}\Omega \cdot \text{cm}^2)$	CPE_{dl}	
				$Q_f/(10^{-5} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n)$	n_f		$Q_{dl}/(10^{-5} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n)$	n_{dl}
Blank	1	6.9	5.9	3.8	0.9	289	3.3	0.7
Blank	7	7.9	8.4	2.7	0.9	164	4.8	0.6
Cit	1	6.4	0.4	3.4	0.8	1 004	1.6	1.0
Cit	7	8.0	2.5	2.8	1.0	1 953	7.9	0.7

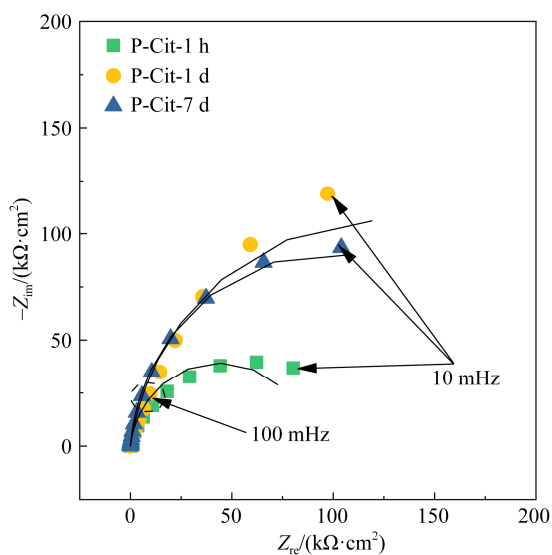
CPE_f is passive film capacitance on electrode surface. CPE_{dl} is double layer capacitance at electrode surface/solution interface. R_s is solution resistance. R_f is surface passivation film resistance of steel electrode. R_{ct} is charge-transfer resistance. Q is admittance of CPE. n is index of CPE.



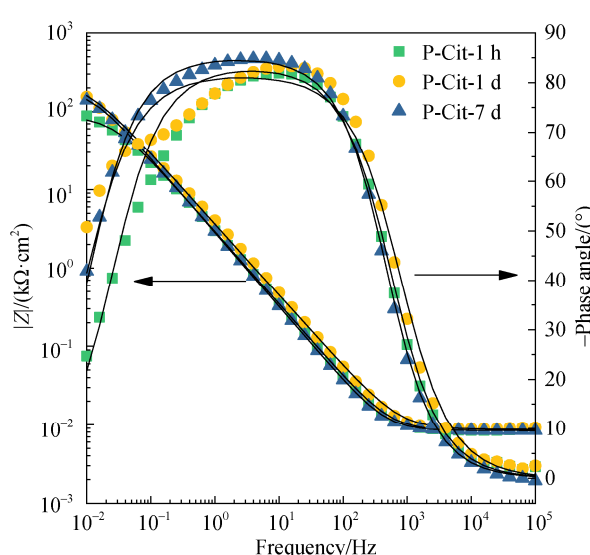
(a) P-Blank, Nyquist plots



(b) P-Blank, Bode plots



(c) P-Cit, Nyquist plots



(d) P-Cit, Bode plots

图 3 钢筋在 AAFA 滤液中钝化阶段的 EIS 谱

Fig. 3 EIS spectra of steel for passivation in AAFA solution

经 7 d 预钝化, 向 AAFA 滤液中加入 3 mol/L NaCl 以模拟氯盐的侵蚀作用, 相应的 EIS 结果如图 4 所示。由图 4a~图 4b 可见, 随侵蚀时间延长, 空白组钢筋的容抗弧半径整体变小, 表明钢筋受到氯盐侵

蚀作用, 耐蚀性下降。然而, 与钝化阶段柠檬酸盐对钢筋钝化膜的破坏作用不同(见图 3), 柠檬酸钠作用下钢筋的容抗弧半径随侵蚀时间的延长而增大, 表明柠檬酸钠提升了钢筋的耐氯盐侵蚀能力(见图 4c~

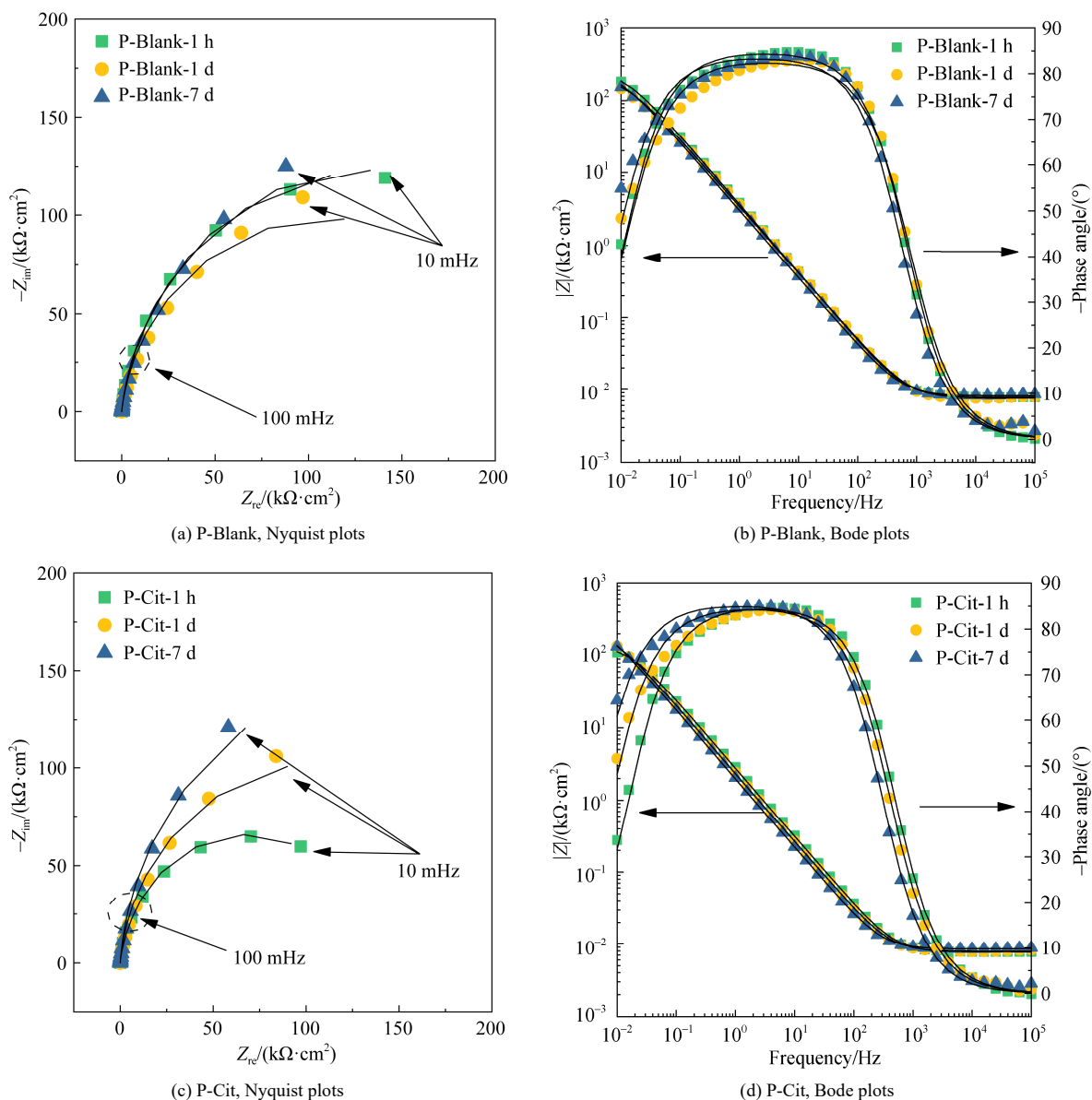


图 4 含氯盐 AAFA 滤液中预钝化钢筋的 EIS 谱

Fig. 4 EIS spectra of pre-passivated steel in AAFA solution containing chlorides

图 4d)。因而, 在氯盐存在时, 柠檬酸钠对预钝化钢筋的作用效果与未钝化钢筋的情况一致, 表明其降低了氯盐对钢筋的侵蚀作用。

采用单时间常数等效电路(见图 2b)对预钝化钢筋在含氯盐的 AAFA 滤液中不同腐蚀阶段的 EIS 数据进行拟合^[23], 拟合结果如表 3 所示。由表 3 可知, 空白组钢筋的 R_f 值在 7 d 内有所下降; 而柠檬酸钠作用的钢筋在腐蚀期间 R_f 值不断升高。

图 5 为钢筋在含氯盐 AAFA 滤液中的 SEM/EDS 结果。由图 5a 可见, 空白组预钝化钢筋的表面出现明显的腐蚀坑和疏松的腐蚀产物。柠檬酸钠作用的预钝化钢筋表面仅出现轻微点蚀(见图 5b), 且无明显腐蚀产物, 验证了柠檬酸钠对钢筋的耐蚀性具

表 3 含氯盐的 AAFA 滤液中预钝化钢筋的 EIS 拟合结果
Table 3 Fitted EIS results of pre-passivated steel in AAFA solution containing chlorides

Specimen	Time	$R_s/(\Omega \cdot \text{cm}^2)$	$R_f/(\text{k}\Omega \cdot \text{cm}^2)$	CPE_f	
				$Q_f/(10^{-5} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n)$	n_f
P-Blank	1 h	7.8	261.7	4.8	0.94
	1 d	7.5	222.1	5.3	0.92
	7 d	6.6	190.4	4.7	0.95
P-Cit	1 h	7.7	141.3	6.3	0.95
	1 d	7.9	225.2	7.5	0.94
	7 d	8.1	303.5	8.3	0.92

有提升作用。此外, 由图 5b 可见, 柠檬酸钠作用的钢筋表面还出现少量沉淀物, 这可能与柠檬酸根离子和钙离子的反应有关。

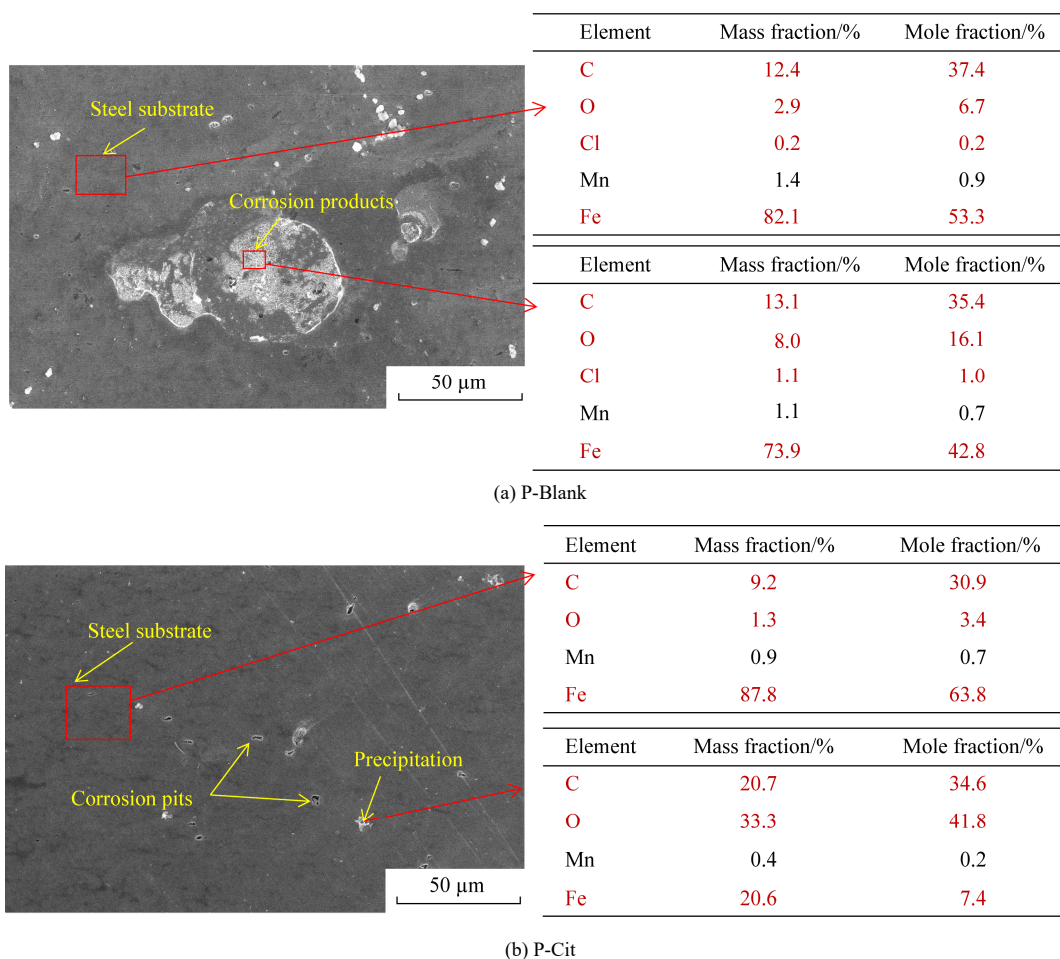


图5 含氯盐 AAFA 滤液中钝化钢筋的 SEM/EDS 结果

Fig. 5 SEM/EDS results of pre-passivated steel in AAFA solution containing chlorides

2.3 柠檬酸钠对钢筋耐点蚀行为的影响

通过 CPP 测试表征钢筋的腐蚀电位(E_{corr})、点蚀电位(E_{pit})和钝化电流密度(i_{pass}), 以分析阻锈剂对钢筋氯盐点蚀敏感性的影响, 未钝化钢筋及预钝

化钢筋的氯盐点蚀行为分别如图 6 和图 7 所示。由图 6a 可见, 腐蚀 1 h 后, 空白组及柠檬酸钠组未钝化钢筋均出现正滞回环, 且 2 组钢筋的 E_{pit} 值基本相同, 表明氯盐作用初期钢筋均出现氯盐点蚀现象,

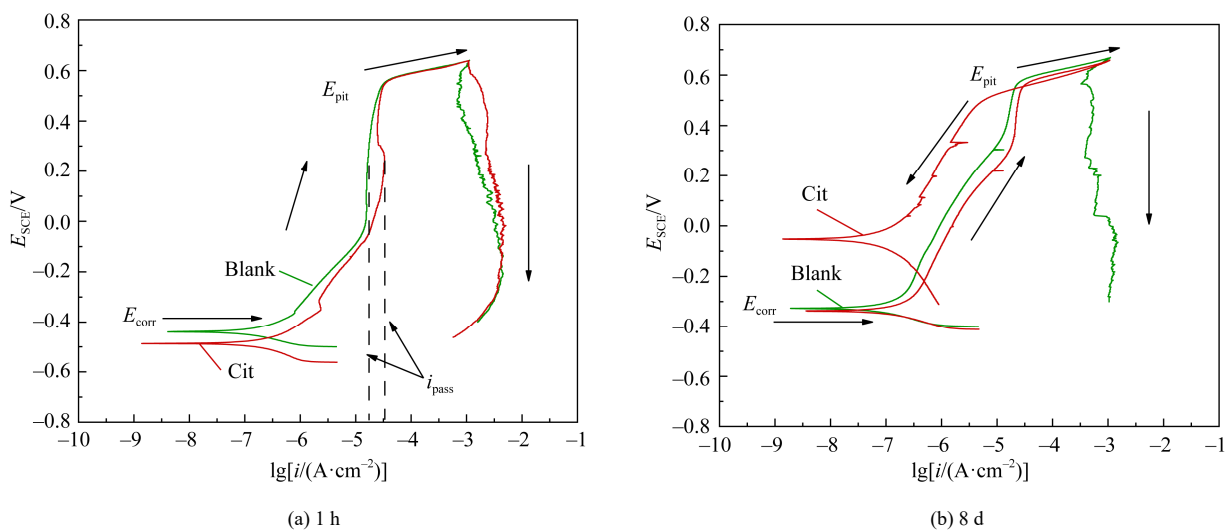


图6 含氯盐 AAFA 滤液中未钝化钢筋的 CPP 图

Fig. 6 CPP (cyclic potentiodynamic polarization) curves of bare steel in AAFA solution containing chlorides

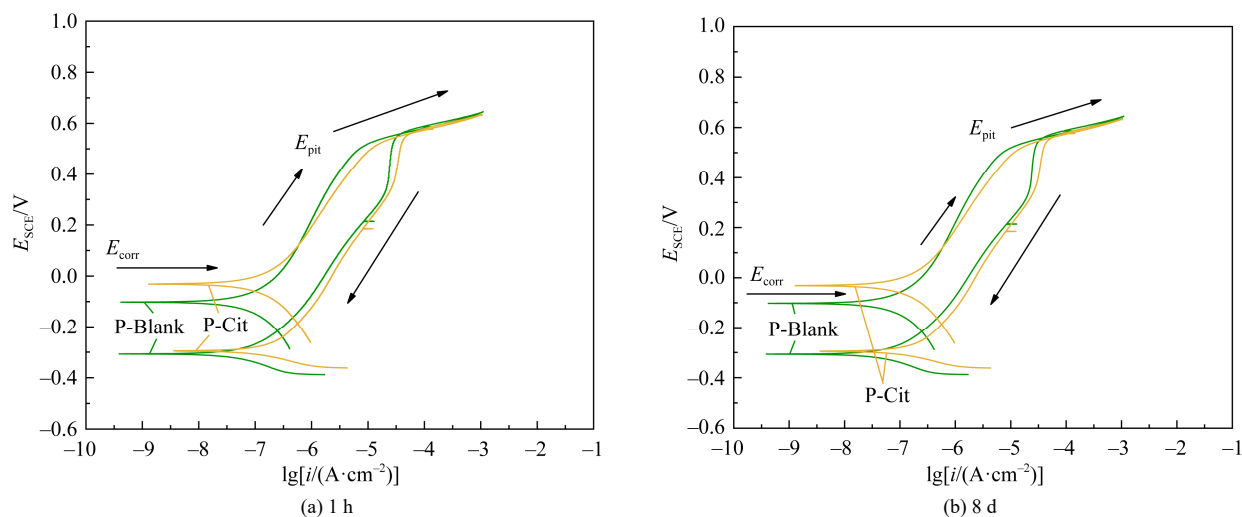


图 7 含氯盐 AAFA 滤液中钝化钢筋的 CPP 图

Fig. 7 CPP curves of pre-passivated steel in AAFA solution with chlorides

氯盐对钢筋钝化膜具有明显破坏作用^[24]。值得注意的是, 氯盐腐蚀初期(1 h), 柠檬酸钠作用的钢筋 i_{pass} 值较空白组稍高, 表明柠檬酸钠对钢筋钝化膜的形成具有一定的溶解作用。由图 6b 可见, 腐蚀 8 d 后, 空白组钢筋仍呈现正滞回环, 且钝化区间不明显, 而柠檬酸钠作用的钢筋表现出负滞回环, 表明柠檬酸盐显著提升了钢筋的耐氯盐点蚀能力^[22]。

图 7 为钝化钢筋暴露在含氯盐 AAFA 滤液中的 CPP 测试结果。由图 7 可见, 在含氯盐的 AAFA 滤液中浸泡 1 h 与 8 d 后, 钝化钢筋都出现负滞回环, 均未发生明显点蚀, 表明钢筋在 AAFA 滤液中钝化后, 耐氯盐点蚀能力得到明显提升。此时, 柠檬酸钠抑制氯盐点蚀的能力无法得到直观体现。

3 阻锈机制分析

根据前期的试验结果, 无论钢筋预先钝化与否, 柠檬酸钠均可提升钢筋的耐氯盐腐蚀性能, 因此对预钝化钢筋钝化膜进一步分析, 以明确柠檬酸钠对钢筋耐蚀性提升的作用机制。图 8 为钢筋在 AAFA 滤液中钝化后的 AFM 形貌, 并分析了钝化钢筋的表面粗糙度(表 4)。

综合图 8a 和表 4 可知, 空白组钢筋表面存在较大颗粒, 表现为均方根粗糙度 R_q 值和平均粗糙度 R_a 值均较高, 这可能与钢筋表面形成的非均匀钝化膜有关^[25]。由于柠檬酸钠的吸附效应, 钢筋表面存在大量细小颗粒, 表面粗糙度较小, 更为均匀(见图 8b 和表 4)。

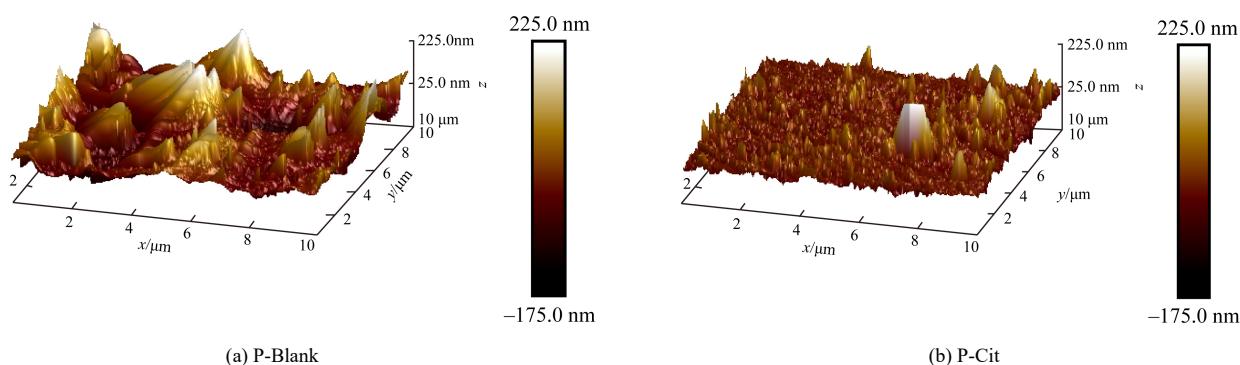


图 8 钢筋在 AAFA 滤液中钝化后的 AFM 形貌

Fig. 8 AFM images of steel after 7 d of passivation in AAFA solution

表 4 钝化钢筋的表面粗糙度

Table 4 Surface roughness of passivated steel

Specimen	R_q/nm	R_a/nm
P-Blank	51.3	38.2
P-Cit	21.1	14.0

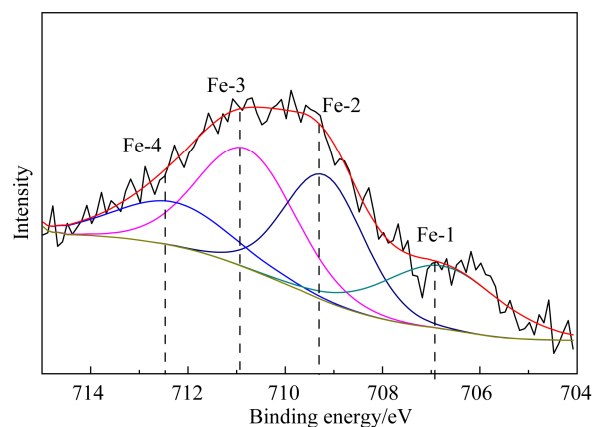
R_q is root mean square roughness. R_a is average roughness.

通过 XPS 可进一步表征钢筋钝化膜的化学组成。图 9 为钢筋钝化膜中特征元素的高分辨率 XPS 谱。其中, $\text{Fe } 2p_{3/2}$ 谱包括 4 个峰: 706.4 (Fe 基体)、709.2 (Fe^{2+} 氧化物)、710.8 eV (Fe^{3+} 氧化物)和 712.8 eV (FeOOH); $\text{O } 1s$ 谱包括 3 个峰: 530.0、531.2 eV 和

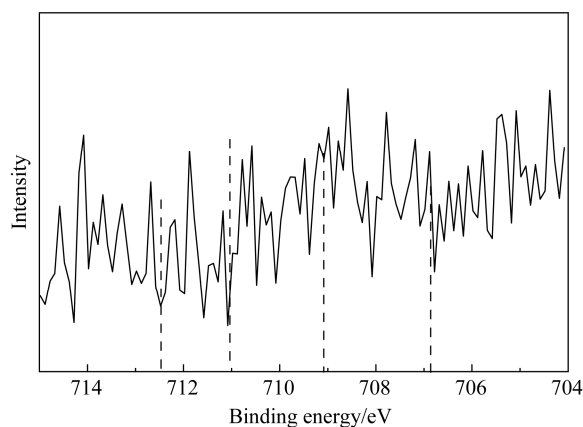
532.8 eV, 分别与 O^{2-} 、 OH^- 和 H_2O 对应相关; C 1s 谱包括 3 个峰: 284.7、286.1 eV 和 288.1 eV, 分别与 C—C/C—H、C—O 和 C=O 对应^[26–27]。

由图 9 可见, 柠檬酸钠显著改变了钢筋表面钝化膜的组成。一方面, 与空白样不同(见图 9a), 在含柠檬酸钠的 AAFA 滤液中浸泡后, Fe 2p_{3/2} 谱的表达被抑制, 这可能与钢筋表面形成的较厚吸附膜有关(见图 9b)^[28]; 另一方面, 经过计算, 柠檬酸钠作

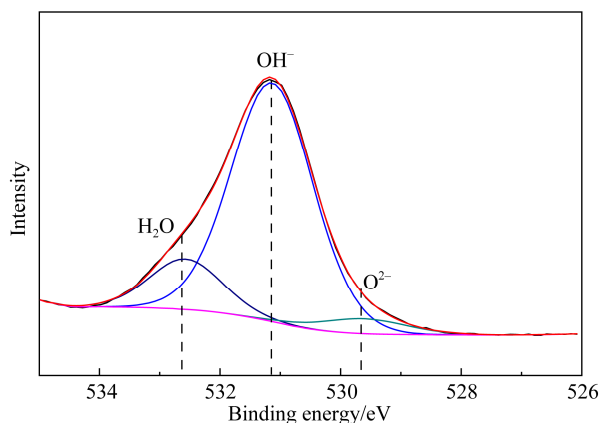
用的钢筋表面 $\text{O}^{2-}/\text{OH}^-$ 值略有下降趋势, 表明钢筋钝化膜中保护性 2 价金属氧化物含量降低, 不利于钢筋自身钝化(见图 9c~图 9d)^[22]。但是, 相比与空白试样(见图 9c), 含柠檬酸钠的钢筋钝化膜中的结合水含量显著下降(见图 9d), 证实其保护性有所提升。在钝化过程中, 由于钢筋表面一部分铁离子未参与钝化膜的形成或钝化膜中的部分铁离子处于非稳定状态, 这部分铁离子与柠檬酸根离子在钢筋表



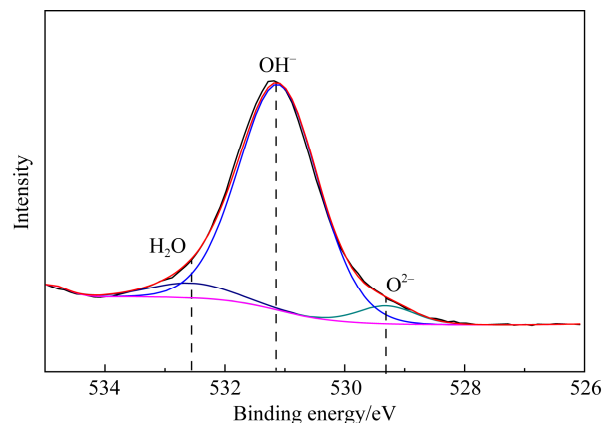
(a) P-Blank, Fe 2p_{3/2}



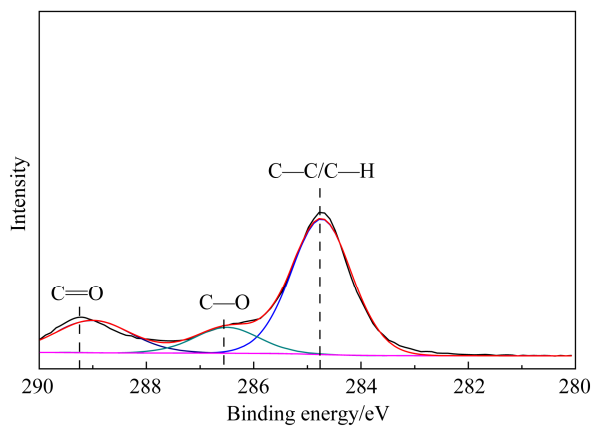
(b) P-Cit, Fe 2p_{3/2}



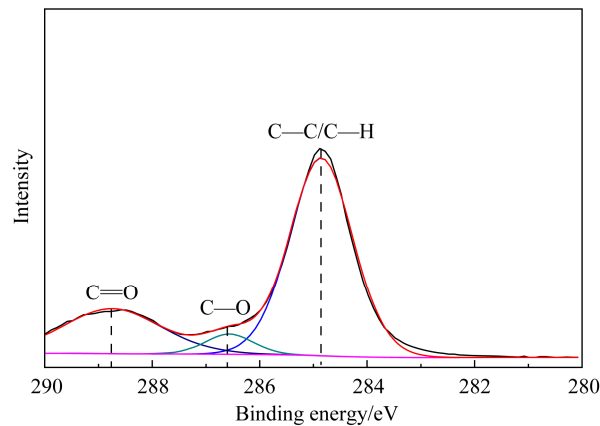
(c) P-Blank, O 1s



(d) P-Cit, O 1s



(e) P-Blank, C 1s



(f) P-Cit, C 1s

图 9 钝化钢筋的高分辨 XPS 谱

Fig. 9 High-resolution XPS spectra of passivated steel

面生成可溶性络合物, 抑制了钝化膜的形成或溶解了部分钝化膜, 因此一定程度上削弱了钢筋钝化膜自身的保护性, 这与前期钢筋钝化阶段的电化学结果一致。此外, 由图 9e~图 9f 可见, 加入柠檬酸钠后, 羧基中主要的 C=O 峰和 C—C/C—H 峰的强度明显增强, 这一结果证实了柠檬酸钠在钢筋表面的吸附与沉淀作用。

当钢筋受到氯盐侵蚀作用时, 柠檬酸根离子在钢筋表面的吸附膜可以阻止部分氯离子到达钢筋表面; 其次, 带负电的羧酸基团在与氯离子的竞争中占优势, 有效抑制氯离子的去极化作用, 进一步阻止氯离子侵入, 最终提高了钢筋的耐蚀性。

4 结论

1) 柠檬酸钠适用于碱激发粉煤灰体系中钢筋耐蚀性的提升。无论钢筋是否发生预钝化, 柠檬酸钠均可显著提升钢筋的耐氯盐侵蚀能力, 一方面是柠檬酸根离子会与氯离子竞争吸附, 降低了氯离子对钢筋的侵蚀风险; 另一方面柠檬酸根离子与钢筋表面的铁离子(Fe^{2+} 与 Fe^{3+})生成吸附膜, 形成了有效的物理屏障。

2) 柠檬酸钠的吸附作用一定程度抑制钢筋自身钝化膜的形成, 影响钝化膜的稳定性。其原因是柠檬酸根与钢筋钝化膜形成可溶性络合物, 溶解部分已形成的钝化膜, 因此削弱了钢筋钝化膜的保护性。

参考文献:

- [1] 聂松, 周健, 徐名凤, 等. 低碳胶凝材料的研究进展[J]. 材料导报, 2024, 38(2): 1–19.
NIE Song, ZHOU Jian, XU Mingfeng, et al. Mater Rep, 2024, 38(2): 1–19.
- [2] SHI C J, QU B, PROVVIS J L. Recent progress in low-carbon binders[J]. Cem Concr Res, 2019, 122: 227–250.
- [3] 阎培渝. 碱激发胶凝材料发展瓶颈在哪里[J]. 硅酸盐学报, 2022, 50(8): 2067–2069.
YAN Peiyu. J Chin Ceram Soc, 2022, 50(8): 2067–2069.
- [4] ZHONG H, ZHANG M Z. Engineered geopolymers composites: A state-of-the-art review[J]. Cem Concr Compos, 2023, 135: 104850.
- [5] TAHRI W, HU X, SHI C J, et al. Review on corrosion of steel reinforcement in alkali-activated concretes in chloride-containing environments[J]. Constr Build Mater, 2021, 293: 123484.
- [6] RUNCI A, PROVVIS J L, SERDAR M. Revealing corrosion parameters of steel in alkali-activated materials[J]. Corros Sci, 2023, 210: 110849.
- [7] FERNÁNDEZ-JIMÉNEZ A, PALOMO A, CRIADO M. Microstructure development of alkali-activated fly ash cement: A descriptive model[J]. Cem Concr Res, 2005, 35(6): 1204–1209.
- [8] BASTIDAS D M, FERNÁNDEZ-JIMÉNEZ A, PALOMO A, et al. A study on the passive state stability of steel embedded in activated fly ash mortars[J]. Corros Sci, 2008, 50(4): 1058–1065.
- [9] TITTARELLI F, MOBILI A, GIOSUÈ C, et al. Corrosion behaviour of bare and galvanized steel in geopolymers and Ordinary Portland Cement based mortars with the same strength class exposed to chlorides[J]. Corros Sci, 2018, 134: 64–77.
- [10] ZHANG Z M, CHEN R, HU J, et al. Corrosion behavior of the reinforcement in chloride-contaminated alkali-activated fly ash pore solution[J]. Compos B Eng, 2021, 224: 109215.
- [11] MONTICELLI C, NATALI M E, BALBO A, et al. Corrosion behavior of steel in alkali-activated fly ash mortars in the light of their microstructural, mechanical and chemical characterization[J]. Cem Concr Res, 2016, 80: 60–68.
- [12] CRIADO M, MONTICELLI C, FAJARDO S, et al. Organic corrosion inhibitor mixtures for reinforcing steel embedded in carbonated alkali-activated fly ash mortar[J]. Constr Build Mater, 2012, 35: 30–37.
- [13] ORMELLESE M, BOLZONI F, LAZZARI L, et al. Organic substances as inhibitors for chloride-induced corrosion in reinforced concrete[J]. Mater Corros, 2011, 62(2): 170–177.
- [14] JOHARI M, ALLAHKARAM S R, TEYMOURI F, et al. The effect of carboxylate compounds on controlling nitrite's environmental side effects for carbon steel corrosion protection in the simulated concrete pore solution[J]. Constr Build Mater, 2021, 308: 125037.
- [15] DIAMANTI M V, PÉREZ ROSALES E A, RAFFAINI G, et al. Molecular modelling and electrochemical evaluation of organic inhibitors in concrete[J]. Corros Sci, 2015, 100: 231–241.
- [16] ORMELLESE M, LAZZARI L, GOIDANICH S, et al. A study of organic substances as inhibitors for chloride-induced corrosion in concrete[J]. Corros Sci, 2009, 51(12): 2959–2968.
- [17] LIU Y, HUANG L, LI M Y, et al. The effects of sodium citrate on compressive strength and paste microstructure of self-compacting concrete[J]. Constr Build Mater, 2020, 260: 120467.
- [18] MA C, FAN L L, SHI J Y, et al. Direct electric curing in high early-strength sodium citrate-doped Portland cement systems for sustainable energy saving applications[J]. Appl Energy, 2023, 347: 121381.
- [19] MONTICELLI C, NATALI M E, BALBO A, et al. A study on the corrosion of reinforcing bars in alkali-activated fly ash mortars under wet and dry exposures to chloride solutions[J]. Cem Concr Res, 2016, 87: 53–63.
- [20] TEYMOURI F, ALLAHKARAM S R, SHEKARCHI M, et al. A comprehensive study on the inhibition behaviour of four carboxylate-based corrosion inhibitors focusing on efficiency drop after the optimum concentration for carbon steel in the simulated concrete pore solution[J]. Constr Build Mater, 2021, 296: 123702.
- [21] 马麒, 蔡景顺, 穆松, 等. 混凝土模拟孔隙液中吡啶衍生物对钢筋的阻锈性能与机制[J]. 硅酸盐学报, 2021, 49(5): 939–947.
MA Qi, CAI Jingshun, MU Song, et al. J Chin Ceram Soc, 2021, 49(5): 939–947.
- [22] ZHOU X C, YAO N, SHI J J. Unraveling electrochemical performance of a 10CrMo steel in alkaline concrete pore solutions with red mud and ground granulated blast-furnace slag[J]. Corros Sci, 2022, 207: 110568.
- [23] CUI L, HANG M Y, HUANG H H, et al. Experimental study on multi-component corrosion inhibitor for steel bar in chloride environment[J]. Constr Build Mater, 2021, 313: 125533.

- [24] XIAO Y, TANG J L, WANG Y Y, et al. Corrosion behavior of 2205 duplex stainless steel in NaCl solutions containing sulfide ions[J]. *Corros Sci*, 2022, 200: 110240.
- [25] CHEN R, HU J, MA Y W, et al. Characterization of the passive film formed on the reinforcement surface in alkali activated fly ash: Surface analysis and electrochemical evaluation[J]. *Corros Sci*, 2020, 165: 108393.
- [26] CHAN-ROSADO G, PECH-CANUL M A. Influence of native oxide film age on the passivation of carbon steel in neutral aqueous solutions with a dicarboxylic acid[J]. *Corros Sci*, 2019, 153: 19–31.
- [27] JIANG S B, JIANG L H, WANG Z Y, et al. Deoxyribonucleic acid as an inhibitor for chloride-induced corrosion of reinforcing steel in simulated concrete pore solutions[J]. *Constr Build Mater*, 2017, 150: 238–247.
- [28] ZHOU X C, LI M, GUAN X D, et al. Insights into the enhanced corrosion resistance of carbon steel in a novel low-carbon concrete with red mud and phytic acid[J]. *Corros Sci*, 2023, 211: 110903.

Inhibition Mechanism of Sodium Citrate on Reinforcing Steel in Extracted Alkali-Activated Fly Ash Solution

ZHOU Xiaocheng, LI Man, SHI Jinjie

(School of Materials Science and Engineering, Jiangsu Key Laboratory of Construction Materials, Southeast University, Nanjing 211189, China)

Extended Abstract

Introduction Alkali-activated fly ash (AAFA) can reduce the carbon emissions from the production of ordinary Portland cement (OPC) by >80%. The utilization of AAFA and the research on the electrochemical behavior of steel in AAFA have thus attracted much attention. Compared with OPC, a higher resistance to chloride-induced corrosion can be achieved in AAFA due to its high alkalinity and zeolite-like adsorption layer. However, the corrosion of steel in AAFA cannot be completely inhibited in harsh environments contaminated with chlorides.

Carboxylate groups-based corrosion inhibitors (such as sodium citrate) improve the pore structure and compressive strength of concrete, and have a high inhibition efficiency for steel. Especially at a high chloride concentration, the pitting potential (E_{pit}) of steel treated with carboxylate groups-based corrosion inhibitors is greater than that treated with amine salt and amino acid. Therefore, sodium citrate can be considered as a promising organic corrosion inhibitor to enhance the corrosion resistance of steel in AAFA. However, the inhibition mechanism of sodium citrate for steel in AAFA is still unclear. In this paper, the effect of sodium citrate on the corrosion behavior of reinforcing steel in extracted AAFA solution under chloride attack was investigated by electrochemical measurements and surface characterization techniques, and the inhibition mechanism of sodium citrate was revealed.

Methods In this study, the preparation of AAFA solution was carried out at room temperature ($(25 \pm 2)^\circ\text{C}$). Firstly, a low calcium fly ash was mixed with an alkali-activated solution (80 g/L NaOH solution) at a mass ratio of 1:1, then the mixture was stirred in a closed vessel for 24 h, and finally it was filtered to remove the residues. The concentration of sodium citrate added into the AAFA solution was 100 mmol/L.

Conventional ribbed carbon steel (HRB400E) with a diameter of 16 mm was used. The electrochemical measurements, namely electrochemical impedance spectroscopy (EIS) and the cyclic potentiodynamic polarization (CPP), were performed in a classic three-electrode electrochemical system, *i.e.*, the working electrode (HRB400E steel), the reference electrode (saturated calomel electrode, SCE) and the counter electrode (platinum electrode). The surface morphology and chemical composition of steel passive films were characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. After chloride attack, the corrosion morphology and corrosion products of steel were analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) in a model FEI Quanta 3D FEG environmental scanning electron microscope.

Results and discussion In the absence of protective passive film, the capacitive loop of the non-passivated steel (the Blank specimen) decreases in AAFA solution containing chlorides, thereby gradually reducing the corrosion resistance of steel. However, the capacitive loop and impedance modulus ($|Z|$) of steel treated with citrate (the Cit specimen) increase. Citrate can effectively improve the corrosion resistance of the non-passivated steel in AAFA solution containing chlorides.

Moreover, the EIS results of pre-passivated steel in chlorides-free AAFA solution show that the capacitive loop of steel treated with citrate (the P-Cit specimen) is somehow smaller than that of the blank group (the P-Blank specimen), indicating that citrate is unfavorable to the formation of steel passive films in AAFA solution. However, in the presence of chlorides, an enhanced corrosion resistance can be obtained for the P-Cit specimen, which is the same as that of the non-passivated steel.

According to the results of AFM and XPS measurements, citrate can modify the surface morphology and chemical composition of steel passive film in AAFA solution. There are a large number of fine particles on the steel surface in AAFA solution, and the

surface roughness of steel is less and more uniform due to the adsorption effect of citrate, compared with that without citrate. For steel with citrate, the intensities of C—C/C—H and C=O peaks increase and the oxidation of Fe may be suppressed to a great extent. Furthermore, O^{2-}/OH^{-} ratio of steel passive film treated with citrate slightly decreases, and the corresponding content of bound water in steel passive film decreases.

Clearly, citrate ions can combine with iron ions to form an adsorption film on the steel surface, therefore suppressing the formation of passive film to some extent. However, when steel is attacked by chlorides, the adsorption film of citrate can prevent chloride ions from reaching steel surface. In addition, the negatively charged carboxylic acid group is also dominant in the competition with chloride ions, effectively inhibiting the depolarization of chloride ions, and finally improving the corrosion resistance of steel in AAFA solution.

Conclusions Although sodium citrate had a negative effect on the formation of a stable steel passive film, it was suitable for improving the corrosion resistance of steel in AAFA solution. Citrate ions could be adsorbed on the steel surface to form an adsorption film, thereby acting an effective physical barrier. Also, citrate ions played a dominant role in the competitive adsorption with chloride ions on the steel surface. The corrosion resistance of steel in AAFA solution contaminated with chlorides was improved by the addition of sodium citrate.

Keywords alkali-activated fly ash; reinforcing steel; sodium citrate; passive film; inhibition mechanism