

## Article

# Influence of Pore Solution Chemistry on the Evolution of Steel Passive Films in Ferrite–Aluminate Cement and Fly Ash-Blended Systems

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## Abstract

Based on comparative experiments conducted on conventional Portland cement (OPC) systems, ferraluminate cement (FAC) systems, and FAC–fly ash (FA) composite systems, this study systematically investigates the ion evolution in pore solutions and the transformation of hydration products, as well as the compositional and microstructural evolution of the passive film formed on steel reinforcement surfaces under simulated pore solution conditions and natural passivation conditions. The results show that: ① FAC and FA-mixed systems produce different product types from OPC in the early stage (mainly AFt/AFm, C–(A)–S–H), thereby altering the pH and the evolution of the main ion concentration in the pore solution. ② An appropriate amount of FA (10%) refines the pore structure through pozzolanic reaction, enhances low-frequency electrochemical impedance, and facilitates the evolution of the steel passive film toward a more favorable composition; however, excessive incorporation (20%) induces a “dilution effect” and reduces the early-age densification rate, which is ultimately detrimental to long-term corrosion resistance. ③ The passive film exhibits a characteristic chemical gradient evolution, comprising an outer  $\text{Fe}^{3+}$ -enriched phase and an inner  $\text{Fe}^{2+}$ -enriched phase. Its thickness and the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio are significantly influenced by the chemical environment of the pore solution (pH,  $\text{SO}_4^{2-}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , etc.), which plays a decisive role in the protective efficiency of the steel reinforcement. These findings establish the intrinsic relationship between pore solution chemistry, hydration product evolution, and passive film development, providing new mechanistic insight into the passivation behavior of reinforcing steel in FAC–FA systems. Based on these findings, key guidelines for the proportioning and microstructural–electrochemical design of ferroaluminate cement are proposed, providing scientific support for the durability-oriented application of FAC-based materials in aggressive environments. It should be noted that the beneficial effect of incorporating 10 wt.% FA is limited to the optimization of FAC-based systems and should not be interpreted as indicating superior overall corrosion resistance compared with OPC.



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**Keywords:** ferroaluminate cement; pore solution ion evolution; electrochemistry; passivation

## 1. Introduction

With the continuous advancement of national marine strategies, large-scale marine infrastructure projects such as subsea tunnels and cross-sea bridges have been increasingly implemented. Consequently, the scientific exploitation and rational utilization of marine resources, together with in-depth investigations into marine environments and ecosystems,

have become critical pathways for expanding national development space and ensuring long-term sustainable growth. Meanwhile, in 2022, global carbon dioxide emissions from fossil fuel combustion and cement production reached  $36.1 \pm 0.3$  Gt, representing an increase of approximately 1.5% compared with 2021 [1]. Therefore, the development of marine engineering infrastructure and offshore resource utilization carries significant economic and environmental implications. China is currently at a critical stage of marine engineering construction, in which subsea tunnels, as key strategic projects, have received strong national attention and substantial financial investment [2]. However, relevant statistics indicate that both domestically and internationally, submarine tunnels that have been completed and put into operation have encountered varying degrees of diseases or defects during service. Additionally, maintenance costs are substantial. Globally, corrosion causes losses amounting to 2.2 trillion US dollars annually, exceeding 3% of the global GDP [3,4]. Strengthening research on quality control techniques for concrete in submarine tunnels contributes to ensuring the long-term safety and reliability of the projects.

Marine engineering structures, particularly subsea tunnels, impose more stringent durability requirements on concrete and embedded steel reinforcement. In marine environments containing seawater and sea sand, high concentrations of chloride ions, sulfate species, and complex ionic combinations can disrupt the chemical equilibrium of the pore solution, thereby triggering the breakdown of steel passivation and promoting localized corrosion. As a result, concrete structures produced with ordinary Portland cement (OPC) may suffer from pronounced durability challenges when exposed to aggressive marine conditions [5–8]. In recent years, cement/composite cementitious systems based on FAC (ferroaluminate cement), known for their low-carbon and corrosion-resistant properties, have attracted increasing attention in the field of marine structures [9–11]. On the one hand, such binders contribute to reductions in carbon emissions; on the other hand, their distinct mineral compositions result in markedly different hydration products (e.g., AFt, AFm, and C-(A)-S-H) and pore solution chemistries, which in turn influence the composition, phase assemblage, and electrochemical behavior of the passive film on reinforcing steel. Although some studies have addressed the corrosion resistance of sulfoaluminate cement (SAC), ferrite-rich aluminate cement (FAC) exhibits performance characteristics that differ from those of conventional systems due to its higher iron-phase content [12]. During the sintering process, part of the alumina is substituted by ferric oxide, endowing FAC with a higher iron phase content compared to SAC [13–15]. Recent studies have demonstrated that FAC exhibits excellent mechanical strength and volumetric stability. Its superior performance has been further confirmed through laboratory seawater immersion tests and coastal tidal-zone exposure experiments [16]. These findings indicate that FAC holds strong potential for application in marine environments. Therefore, a systematic understanding of the interactions among ion evolution in the pore solution, hydration product development, and the microstructural and chemical characteristics of the steel passivation film is of critical importance for achieving long-term durability design of concrete used in subsea tunnel engineering [17–19]. Although previous studies have extensively investigated hydration characteristics and chloride resistance of FAC-based materials, the intrinsic coupling relationship among pore solution chemistry, hydration evolution and passive film formation on reinforcing steel remains insufficiently understood. Existing studies generally focus on either hydration products or electrochemical performance, whereas the physicochemical linkage between these processes has rarely been systematically established. Therefore, the novelty of this study lies in integrating pore solution chemistry, hydration product evolution and passive film characterization into a unified framework. By combining pore solution extraction, electrochemical measurements, XRD, XPS and AFM analyses, this work systematically reveals the coupled evolution mechanism governing steel passivation in

FAC–FA systems, thereby providing new theoretical support for the durability-oriented design of low-carbon ferroaluminate cement.

## 2. Materials and Methods

### 2.1. Materials

In this study, two commercially available cements were used: P·I 52.5 ordinary Portland cement (OPC) and ferrite–aluminate cement (FAC). According to the preliminary test results, at a water-to-binder ratio of 0.4, the initial setting times of OPC and FAC were 115 min and 11 min, respectively, indicating a pronounced difference in their setting characteristics. The main chemical compositions of the two cements and the incorporated fly ash (FA) are listed in Tables 1 and 2. As shown in the tables, FAC contains significantly higher proportions of  $\text{Al}_2\text{O}_3$ ,  $\text{SO}_3$ , and  $\text{Fe}_2\text{O}_3$  compared with OPC.

**Table 1.** Main Chemical Constituents of Cement (%).

| Materials | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ | $\text{TiO}_2$ | $\text{Fe}_2\text{O}_3$ | CaO   | MgO  | $\text{SO}_3$ |
|-----------|----------------|-------------------------|----------------|-------------------------|-------|------|---------------|
| OPC       | 22.01          | 5.31                    | 0.19           | 2.82                    | 58.04 | 5.93 | 4.11          |
| FAC       | 7.23           | 18.60                   | 0.87           | 4.30                    | 45.30 | 1.35 | 12.5          |

**Table 2.** Main Chemical Constituents of FA (%).

| Materials | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ | CaO  | $\text{Fe}_2\text{O}_3$ | gO   | $\text{P}_2\text{O}_5$ | $\text{K}_2\text{O}$ | $\text{Cl}^-$ |
|-----------|----------------|-------------------------|------|-------------------------|------|------------------------|----------------------|---------------|
| FA        | 45.13          | 35.74                   | 7.98 | 6.43                    | 1.27 | 0.68                   | 0.45                 | 0.19          |

The fine aggregate used in the experiments was standard sand supplied by Xiamen ISO Standard Sand Co., Ltd., with a particle size range of 0.08–2 mm. To improve the workability of the mortar, a polycarboxylate-based high-performance water-reducing admixture was added during mixing, and tap water was used as the mixing water. The steel bars used in this study were HRB400, with the following chemical composition: C = 0.22%, Si = 0.65%, Mn = 1.54%, S = 0.045%, and P = 0.045%.

### 2.2. Experimental Programme

#### 2.2.1. Mixing Proportions

Based on the mix design specifications for subsea tunnel engineering (with reference to TB10005-2010), the mortar mixtures were designed using the equal-mass replacement method [20]. A mass replacement ratio of 10% was adopted as the incremental control variable, while the water-to-binder ratio was fixed at 0.4. Accordingly, four comparative systems were established: (1) PC group: 100% OPC; (2) FAC group: 100% FAC; (3) F10 group: 10% of FAC replaced by FA on an equal-mass basis; and (4) F20 group: 20% of FAC replaced by FA on an equal-mass basis. The total binder content was strictly kept constant for all mixtures, and the detailed mix proportions are presented in Table 3.

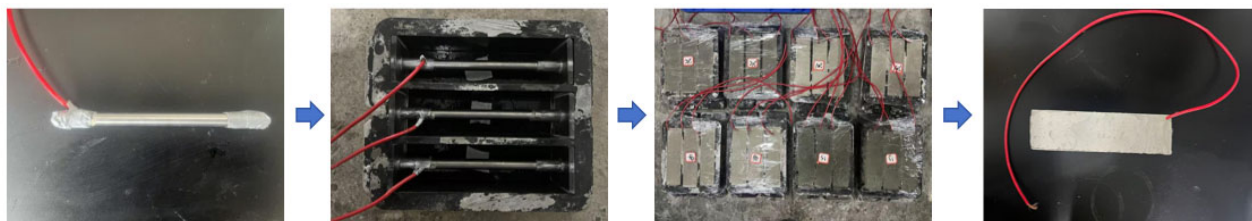
**Table 3.** Mortar mixing proportions ( $\text{kg}/\text{m}^3$ ).

| Group | OPC | FAC | FA | Aggregate | Water | Superplasticizer |
|-------|-----|-----|----|-----------|-------|------------------|
| PC    | 450 | 0   | 0  | 1350      | 180   | 0.3              |
| FAC   | 0   | 450 | 0  | 1350      | 180   | 1                |
| F10   | 0   | 405 | 45 | 1350      | 180   | 1                |
| F20   | 0   | 360 | 90 | 1350      | 180   | 1                |

### 2.2.2. Mortar Preparation

#### Specimen Preparation

Prismatic specimens with dimensions of  $40 \times 40 \times 160 \text{ mm}^3$  were prepared, in which an HRB400 steel bar with a diameter of 10 mm and a length of 158 mm was embedded, with a concrete cover thickness of 15 mm. Prior to specimen preparation, the steel bars were acid-cleaned to remove surface rust and ensure a smooth surface. Copper wires were connected to both ends of the steel bar using a soldering technique to meet the conductivity requirements for electrochemical testing, and the welded regions were sealed with a high-temperature-resistant epoxy resin. The specific procedure was as follows: epoxy resin was uniformly applied to both ends of the specimen, leaving only the central 100 mm section exposed as the working surface for electrochemical testing. After curing at room temperature for 24 h, the coated regions were further reinforced with electrical insulating tape. The prepared electrode specimens were then sealed and stored in a vacuum desiccator for subsequent use. The preparation process of the mortar specimens is illustrated in Figure 1. The specimens used for ion transport tests were cylindrical, with a diameter of 50 mm and a height of 50 mm. All specimens were demolded after 24 h and then cured in a standard curing room at a temperature of  $20 \pm 3^\circ\text{C}$  and a relative humidity of 95% for 28 days [21].

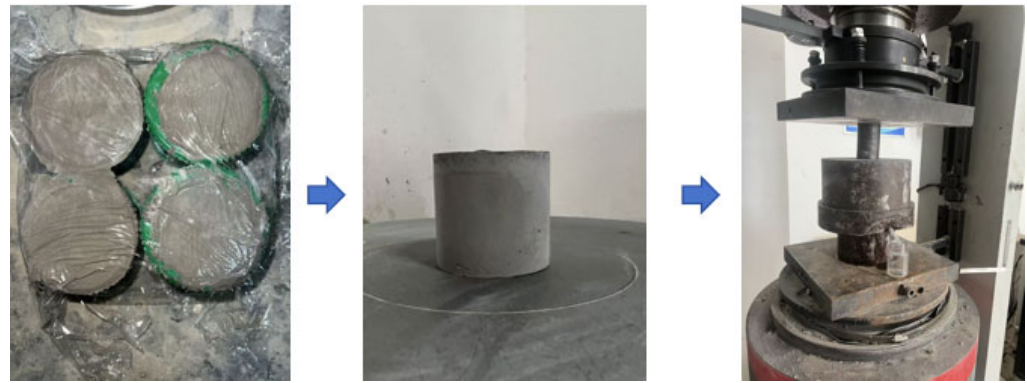


**Figure 1.** Flow chart of specimen preparation.

### 2.2.3. Experimental Methods

#### Squeezing Pore Solution of Mortar

In this study, the pore solution of the mortar was extracted using a high-pressure squeezing device, following the method proposed by Martin Cyr and co-workers [22]. A schematic illustration of the extraction process is shown in Figure 2. The specific procedure was as follows: pressure was applied using a hydraulic testing machine at a loading rate of 12.8 MPa/s until a maximum pressure of 600 MPa was reached and maintained for 10 s to ensure sufficient extrusion of the pore solution. The collected solution was immediately filtered through qualitative filter paper with a pore size of  $0.45 \mu\text{m}$ , and then sealed and stored in centrifuge tubes for subsequent analysis. Although the applied extraction pressure was relatively high (600 MPa), the pressure holding time was limited to only 10 s to minimize secondary dissolution of hydration products. This extraction protocol follows the procedure proposed by Martin Cyr et al. [22] and has been widely used for cementitious materials. Because all mixtures were subjected to identical extraction conditions, the measured ion concentrations are considered suitable for comparative analysis of pore solution chemistry, although slight deviations from true in-situ pore solution for trace species cannot be completely excluded.



**Figure 2.** Pore solution of mortar squeezing.

#### Ions of Pore Solution Analysis

Inductively coupled plasma-optical emission spectrometry (ICP-OES) was employed to determine the concentrations of K, Ca, Na, Al, and Si in the pore solution, while ion chromatography (IC) was used for the analysis of sulfur-containing anions.

#### Electrochemical Measurements

Electrochemical measurements were conducted at an ambient temperature of  $23 \pm 2$  °C using a Princeton Versa STAT 3 potentiostat/galvanostat (Princeton Applied Research, Oak Ridge, TN, USA). A conventional three-electrode system was employed, in which the embedded steel bar served as the working electrode, a saturated Hg/HgO electrode was used as the reference electrode, and a platinum electrode functioned as the counter electrode. During the measurements, the open-circuit potential (OCP) was first monitored and recorded to analyze the evolution of the potential with time, thereby evaluating the corrosion state of the reinforcing steel [23]. After the OCP stabilized, a sinusoidal perturbation signal with an amplitude of  $\pm 10$  mV relative to the OCP was applied, and electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of  $10^{-2}$  to  $10^5$  Hz [24]. The obtained impedance data were subsequently analyzed using ZsimpWin 3.6 software. An equivalent circuit model was employed for impedance fitting, and the fitting quality was evaluated using the chi-square ( $\chi^2$ ) values generated by the software. The validity of the selected equivalent circuit was confirmed by the satisfactory agreement between the experimental and fitted impedance spectra.

#### Characterization of Surficial Morphology

The paste specimens prepared according to the above mix proportions were demolded after 24 h and then cured for 28 days under conditions of  $20 \pm 2$  °C and a relative humidity of  $\geq 95\%$ . After curing, specimens with dimensions of  $10 \times 10 \times 10$  mm were cut from the central region of the hardened paste. The samples were dried in a vacuum oven for 24 h, embedded in epoxy resin, and successively ground using 400#, 800#, 1200#, and 2500# silicon carbide papers. Finally, the specimens were polished with a  $0.25 \mu\text{m}$  polishing suspension for 10 min. Prior to observation, the sample surfaces were cleaned with absolute ethanol.

To promote the formation of a stable passive film on the steel surface, the steel bars were first subjected to a 28-day passivation treatment by embedding them in mortar specimens. After removal, the samples were cleaned with absolute ethanol, dried, and stored under vacuum prior to testing. To further obtain information on surface roughness and nanoscale morphology, atomic force microscopy (AFM) was employed for characterization. AFM tests were conducted in tapping mode with a commercial silicon probe (nanometer-scale tip radius as specified by the manufacturer), over a scanning area of

5.0  $\mu\text{m} \times 5.0 \mu\text{m}$ . The chemical composition of the passive film was analyzed by X-ray photoelectron spectroscopy (XPS), and depth profiling was carried out using a 2 keV argon ion beam for stepwise sputtering (with a sputtering rate calibrated against  $\text{Ta}_2\text{O}_5$ , approximately 0.29 nm/s) to obtain compositional information at different depths. All XPS data were fitted and analyzed using Avantage software 6.6.0.

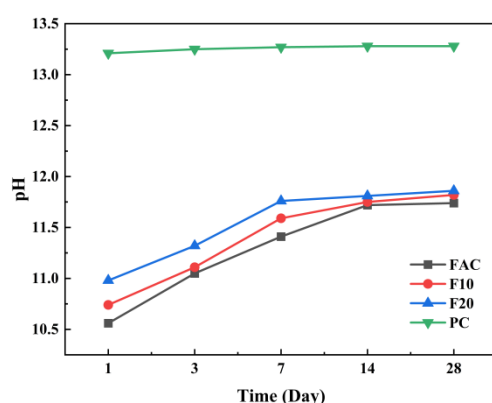
The surface morphology was characterized using a high-resolution field-emission scanning electron microscope (HR-FESEM, ZEISS Sigma 300 (Carl Zeiss AG, Oberkochen, Germany)). Secondary electron (SE) imaging mode was employed with an accelerating voltage of 5 kV and a beam current of 10  $\mu\text{A}$ . For elemental analysis, energy-dispersive X-ray spectroscopy (EDS) was performed at an accelerating voltage of 15 kV with a probe current of 1.2 nA. To improve the accuracy and reproducibility of the measurements, each selected area was analyzed with a dwell time of 60 s and scanned three times.

### 3. Results and Discussion

#### 3.1. Ion Evolution in Pore Solution

##### 3.1.1. pH in Real Pore Solution

Figure 3 illustrates the variation in pore solution pH with curing time. As shown, a clear correlation exists between the pore solution pH of the FAC system and curing duration. During curing, the pH of the FAC system gradually increases to values above 11.2, indicating that cement hydration becomes progressively more complete with time. The incorporation of FA further elevates the system pH, which can be attributed to enhanced ion release and modifications in the type of hydration products formed. In the PC system, the presence of highly reactive silicate minerals leads to rapid early-stage hydration, accompanied by calcium ion release and the formation of alkaline hydration products such as calcium hydroxide (CH), resulting in the highest pore solution pH. In contrast, in FAC systems containing FA, the physical dilution effect of FA increases the effective water-to-binder ratio, thereby reducing the ionic concentration in the liquid phase. Moreover, owing to its lower intrinsic cementitious activity compared with cement, FA participates in pozzolanic reactions with CH generated during FAC hydration, forming C-S-H gel and consequently influencing the hydration process. This observation is consistent with the findings reported by Guo [25].



**Figure 3.** Evolution of pore solution pH during curing.

During the early hydration stage (0–30 min), rapid dissolution of  $\text{C}_4\text{AF}$  releases  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  ions, leading to a rapid increase in pore solution alkalinity. Simultaneously, FAC rapidly forms Aft, while FA mainly acts as a physical filler because its pozzolanic activity remains limited under the relatively moderate alkalinity of the

system [26]. Consequently, the pore solution pH is maintained at approximately 11.0–11.5 during this stage.

During the setting and hardening stage, the pozzolanic reaction of FA consumes dissolved  $\text{Ca}^{2+}$  and  $\text{OH}^-$  while generating additional C-(A)-S-H gel. Together with the continued precipitation of FAC hydration products, these reactions establish a dynamic equilibrium that stabilizes the pore solution pH within 11.2–11.6.

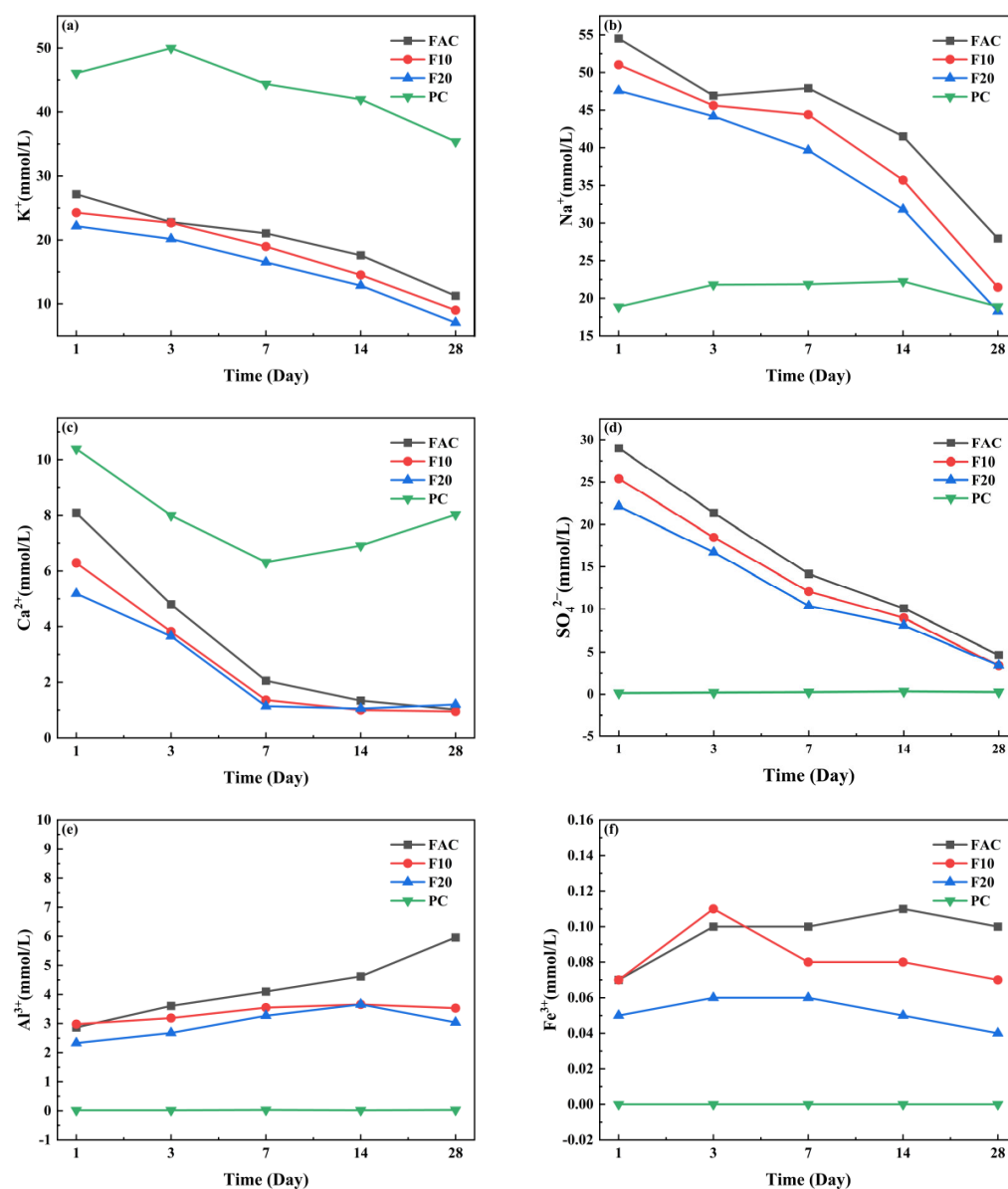
After 14 d, hydration gradually approaches equilibrium. The continued formation of hydration products and the pozzolanic reaction of FA further refine the pore structure, while the dissolution and precipitation of solid phases reach a dynamic balance. Consequently, the pore solution pH stabilizes within the range of 11.3–11.8 [27].

From a thermodynamic perspective, the pore solution pH is governed by the dynamic equilibrium between the dissolution of cement clinker phases and the precipitation of hydration products, rather than solely by the generation of  $\text{OH}^-$  ions. In the FAC system, the rapid precipitation of AFt and AFm continuously consumes  $\text{Ca}^{2+}$  and Al-bearing species while maintaining a moderately alkaline environment. After FA incorporation, the pozzolanic reaction further modifies the dissolution–precipitation equilibrium by consuming dissolved calcium species and producing additional C-(A)-S-H gel. Consequently, the measured pH represents the equilibrium state established by coupled hydration reactions and phase transformations instead of a simple accumulation of hydroxyl ions.

### 3.1.2. Ion Evolution in Real Pore Solution

Figure 4 illustrates the evolution of ion concentrations in the pore solution as a function of curing time. The concentration profiles of  $\text{K}^+$  and  $\text{Na}^+$  in the pore solution of cement-based materials are jointly governed by the type and structure of hydration products and their interactions with ions, and essentially reflect a dynamic equilibrium involving mineral dissolution, product formation, and ion adsorption/binding. For the PC group, the typical hydration products C-S-H gel and  $\text{Ca}(\text{OH})_2$  play a dominant role in regulating ionic behavior. The  $\text{K}^+$  concentration increases at the early stage due to its release during the hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ , and then gradually decreases at later ages as the binding capacity of C-S-H is enhanced and the encapsulation effect of  $\text{Ca}(\text{OH})_2$  becomes more pronounced. In contrast,  $\text{Na}^+$  is released at early ages and subsequently remains relatively stable as an adsorption equilibrium with C-S-H is established, followed by a slight decrease at later stages with progressive densification of the system. In the FAC system, calcium ferroaluminate hydrates constitute the main hydration products, and no  $\text{Ca}(\text{OH})_2$  is formed, resulting in a relatively lower alkalinity of the pore solution. Consequently, the  $\text{K}^+$  concentration exhibits a continuous decreasing trend. In contrast,  $\text{Na}^+$  displays a more complex evolution, characterized by an initial decrease followed by an increase and then a subsequent decrease, due to its substantial early release, enhanced adsorption at intermediate stages, and the dominance of binding effects at later ages. In the FA-incorporated FAC system, both the physical dilution effect and the pozzolanic reaction of FA further modify ionic behavior. At early ages, the dilution effect reduces the initial concentrations of  $\text{K}^+$  and  $\text{Na}^+$ . At later ages, the C-(A)-S-H gels generated by the pozzolanic reaction markedly enhance the ion adsorption capacity, leading to an accelerated decrease in  $\text{K}^+$  and  $\text{Na}^+$  concentrations with increasing FA content. Ultimately, the concentrations of both ions are significantly lower than those of the FA-free reference system. Overall, the evolution of ion concentrations reflects fundamental differences among cementitious systems in terms of hydration product assemblage, pore solution alkalinity, and microstructural development. In addition, the concentration evolution of alkali ions is governed not only by their release and adsorption but also by changes in ionic activity during hydration. As hydration products progressively reduce the effective pore solution volume and refine the pore network, the activity

coefficients of dissolved ions decrease, contributing to the reduction in measurable ion concentrations, particularly for  $K^+$ , which mainly remains in the liquid phase rather than participating directly in hydration products.



**Figure 4.** Evolution of ions concentration in the pore solution of mortar: (a)  $K^+$ ; (b)  $Na^+$ ; (c)  $Ca^{2+}$ ; (d)  $SO_4^{2-}$ ; (e)  $Al^{3+}$ ; (f)  $Fe^{3+}$ .

The evolution of  $Ca^{2+}$  and  $SO_4^{2-}$  concentrations in the pore solution of cement-based materials shows distinct trends among different systems. In the PC group, the  $Ca^{2+}$  concentration exhibits a typical decrease–increase pattern. At early ages, rapid hydration of  $C_3S$  and  $C_2S$  leads to a peak  $Ca^{2+}$  level due to intensive ion release; this is followed by a sharp decline caused by the precipitation of  $Ca(OH)_2$  and its incorporation into C–S–H gel. At later stages, as hydration approaches completion,  $Ca^{2+}$  is slowly released again, resulting in a gradual increase. In contrast, the  $SO_4^{2-}$  concentration in the PC system remains negligible throughout curing, reflecting its inert behavior under non-aggressive conditions. In the FAC system, owing to the hydration characteristics of the dominant  $C_4AF$  phase and the absence of  $Ca(OH)_2$  formation among the hydration products, the  $Ca^{2+}$  concentration continuously decreases. Although the initial  $SO_4^{2-}$  level

is relatively high due to its incorporation during mixing, it progressively declines as the matrix becomes denser. For FAC systems incorporating FA, a combined effect of “physical dilution–chemical consumption” and “structural modification–enhanced adsorption” is observed. At early ages, the dilution effect of FA lowers the initial concentrations of both  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . At later stages, pozzolanic reactions of FA are activated under moderately alkaline conditions, and the newly formed C–(A)–S–H gel further consumes  $\text{Ca}^{2+}$  while enhancing the adsorption of  $\text{SO}_4^{2-}$ . Meanwhile, significant pore refinement accelerates the reduction in both ion concentrations with increasing FA content, ultimately resulting in levels markedly lower than those of the FA-free reference system. These findings are in good agreement with the conclusions reported by Criado [28].

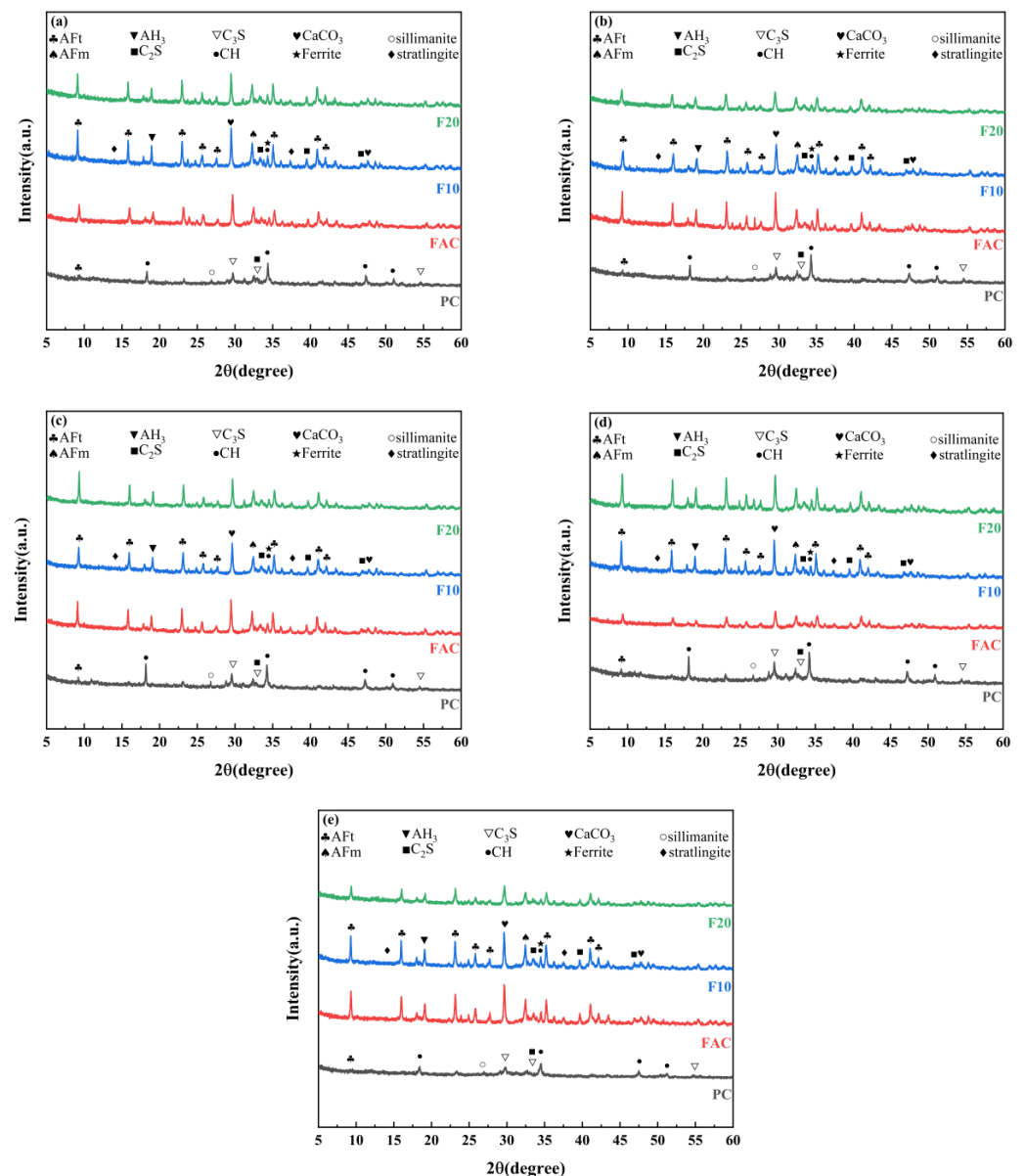
The concentration behavior of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in the pore solution, serving as important indicators of cement hydration chemistry and microstructural evolution, exhibits pronounced differences among different systems. These differences fundamentally depend on the compositional design and reaction pathways of the cementitious materials. In the PC system, owing to the very low contents of iron and aluminum in the clinker mineral phases and their preferential incorporation into stable crystal lattices or hydration products (such as C–S–H gel and ettringite), free  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are essentially undetectable in the pore solution. In sharp contrast, the FAC system is dominated by the iron-rich mineral phase  $\text{C}_4\text{AF}$  [26,29]. In this system, the dissolution of  $\text{Fe}^{3+}$  is governed by the competition between hydration kinetics and product binding. At early ages, the rapid dissolution of  $\text{C}_4\text{AF}$  leads to a sharp increase in  $\text{Fe}^{3+}$  concentration. With the formation of calcium ferroaluminate hydrates and related products,  $\text{Fe}^{3+}$  is immobilized through chemical bonding, and its concentration subsequently decreases. At later ages, system densification restricts ionic transport, maintaining the  $\text{Fe}^{3+}$  concentration at a relatively low level. The evolution of  $\text{Al}^{3+}$  follows a different trajectory. Under the continuous hydration of  $\text{C}_4\text{AF}$ ,  $\text{Al}^{3+}$  is persistently released, while the C–A–H and related gels formed in the system exhibit a relatively limited capacity for its adsorption and immobilization. Consequently, the  $\text{Al}^{3+}$  concentration shows a gradual accumulation and increase with time. When FA is incorporated into the FAC system, the ionic environment is subject to the combined effects of physical dilution and chemical activation. The addition of FA directly reduces the relative content of the reactive mineral  $\text{C}_4\text{AF}$ , thereby decreasing the initial dissolution of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . More importantly, FA undergoes a pozzolanic reaction under the moderately alkaline environment provided by FAC, generating large amounts of gels such as C–(A)–S–H, which is consistent with previous studies [26,30]. These gels exhibit a strong adsorption affinity for  $\text{Al}^{3+}$ , causing its concentration to decrease rather than increase at higher FA dosages (e.g., 20%). In contrast, the adsorption capacity of the newly formed gels for  $\text{Fe}^{3+}$  is relatively weak, and the evolution of its concentration is mainly constrained by the reduced early-stage release and the densification of the pore structure at later ages. Consequently, the final concentrations of both  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  decrease markedly with increasing FA content.

### 3.2. Hydrated Product

The composition and evolution of hydration products in cement-based materials are the core determinants of their macroscopic properties (such as strength and durability). Based on XRD patterns obtained at five curing ages (1 d, 3 d, 7 d, 14 d, and 28 d), this study systematically analyzes the characteristics, temporal evolution, and underlying mechanisms of hydration products in PC, FAC, and FA-incorporated FAC systems (F10 and F20).

Figure 5 presents a comparative XRD analysis of hydration products for different cement systems at curing ages of 1 d, 3 d, 7 d, 14 d, and 28 d. As can be seen, at 1 d the hydration products of PC are dominated by CH and calcium silicates (C3S and C2S). This is

because the rapid hydration of C3S and C2S leads to a pronounced increase in the diffraction intensity of CH, while the characteristic peaks of C3S and C2S are markedly weakened due to mineral consumption [31]. For the FAC group, distinct AFt hydration products are observed, which can be attributed to the rapid hydration of C4AF and the formation of AFt under sulfate-rich conditions. In addition to AFt peaks, characteristic peaks of stratlingite are detected in the F10 and F20 groups. This is likely because FA contains reactive siliceous and aluminous components that participate in early-age hydration reactions, leading to the formation of this phase. Closer examination reveals a broadened “hump” in the XRD patterns between  $25^\circ$  and  $35^\circ$ . Since C–S–H gel is essentially amorphous and poorly crystalline, it does not exhibit sharp diffraction peaks. This observation is consistent with previous findings that large amounts of C–S–H gel are formed during the early stages of cement hydration [32].



**Figure 5.** XRD patterns of concrete with FAC different age: (a) 1 d; (b) 3 d; (c) 7 d; (d) 14 d; (e) 28 d.

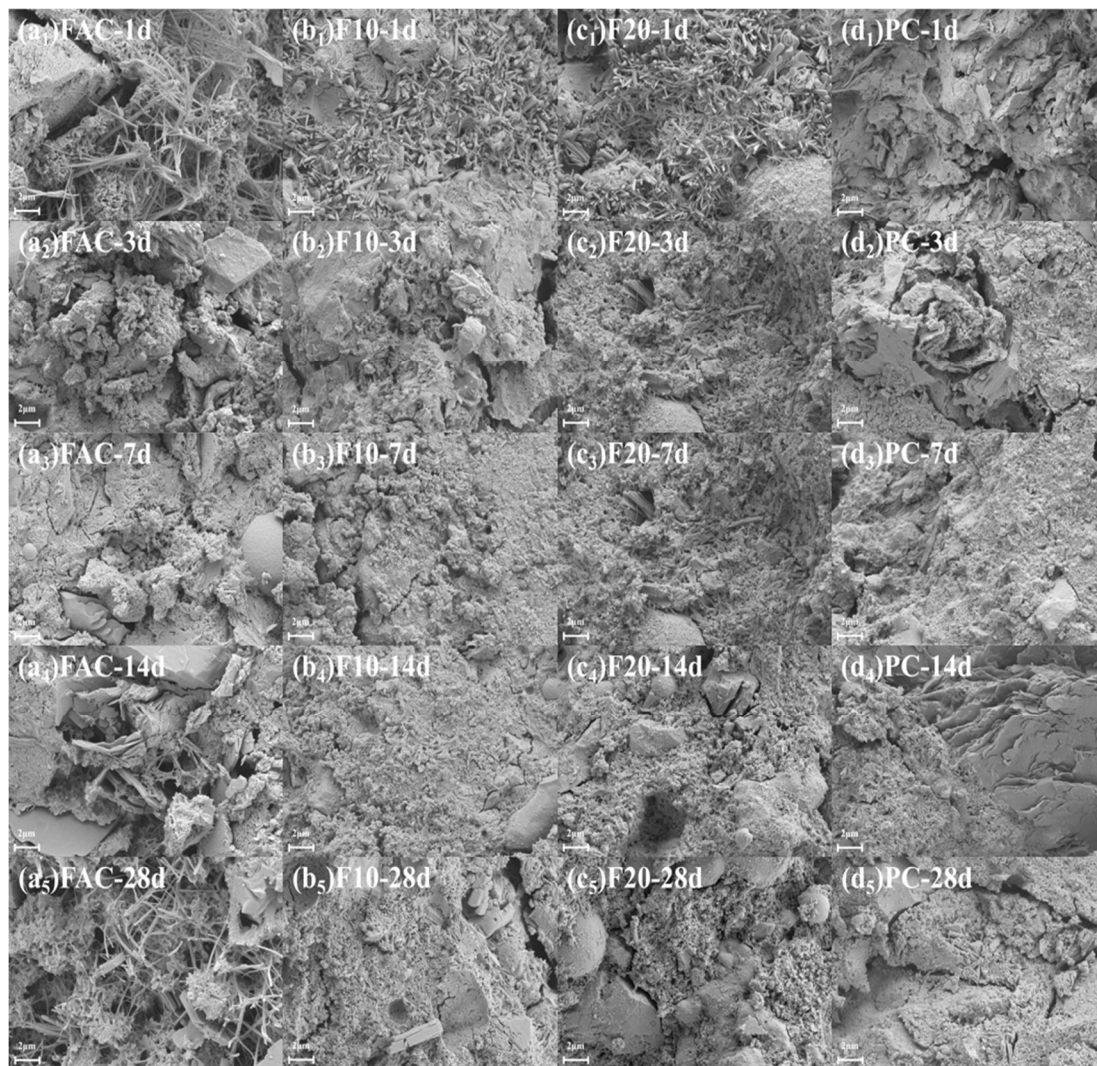
From the XRD patterns at 3 d, 7 d, 14 d, and 28 d, it can be observed that with increasing curing age, the intensities of the characteristic peaks corresponding to C3S and C2S in PC are lower than those at 1 d, whereas the diffraction peaks associated with CH

are markedly higher than those of the 1 d specimen. This phenomenon can be reasonably explained as follows: during hydration, C3S and C2S are progressively transformed into other products, such as C–S–H gel. As the hydration of C3S and C2S continues, the amount of CH increases, leading to enhanced CH diffraction peaks in the XRD patterns. This evolution reflects the dynamic nature of the cement hydration process. Moreover, the CH crystals formed at early ages are relatively small and finely dispersed; with increasing age, these crystals gradually coarsen, resulting in a pronounced increase in diffraction peak intensity. In the FAC system, the diffraction peaks of AFt gradually weaken, while those of AFm continuously intensify. This behavior arises because, as hydration proceeds, sulfates in the liquid phase are progressively consumed, leading to a decrease in the stability of AFt and its gradual transformation into the more stable AFm phase. A comparison of XRD patterns at different curing ages further reveals that, in FA-incorporated cementitious systems, the diffraction intensities corresponding to ferroaluminate minerals are markedly reduced. This phenomenon indicates that FA promotes the hydration of ferroaluminate phases. The silicon- and aluminum-rich components in FA form Si and Al rich layers during hydration, which can effectively adsorb and immobilize ions in the pore solution, thereby accelerating the hydration process. This observation is consistent with the findings reported by Sanjuán, M.Á [33].

At 28 d, the CaCO<sub>3</sub> diffraction peaks in the PC group become discernible and increase in intensity, indicating that carbonation resulting from the interaction between the specimens and atmospheric CO<sub>2</sub> intensifies with curing age. In the FAC system, the AFm peak intensity continues to increase, reflecting its intrinsic hydration mechanism dominated by sulfoaluminate–ferrite reactions with no formation of Ca(OH)<sub>2</sub>. In FA-incorporated FAC systems, the intensity of stratlingite peaks increases with curing age, and the peaks in the F20 group are stronger than those in the F10 group, demonstrating the promoting effect of FA dosage on the pozzolanic reaction. These observations are consistent with the findings reported by Jing [34].

Figure 6 presents SEM observations of specimens at different curing ages, revealing pronounced microstructural differences among the four binder systems. The PC system exhibits a typical interwoven morphology composed of plate-like Ca(OH)<sub>2</sub> crystals and amorphous C–S–H gel, with noticeable defects distributed in the interfacial regions. In contrast, the FAC system shows a distinct “framework–filling” microstructure. At early ages, needle-shaped ettringite crystals form a three-dimensional skeletal network, while at later stages, the generated C–(A)–S–H gel effectively fills the pore space. This divergence in microstructural features originates from fundamental differences in hydration products. Hydration of PC is dominated by C–S–H gel and Ca(OH)<sub>2</sub>, whereas FAC forms a composite system consisting of ettringite and C–(A)–S–H gel. The latter provides improved microstructural continuity and compactness.

In the FAC system, the FA dosage exerts a significant influence on microstructural development. The incorporation of an appropriate amount of FA optimizes the pore structure through the pozzolanic effect; in specimens with a 10% FA replacement, secondary hydration products can be observed effectively filling capillary pores, resulting in pore refinement. However, when the FA content is increased to 20%, SEM images reveal a pronounced dilution effect, manifested by an increased presence of unreacted FA particles and a reduction in the continuity of the hydration product network. This deterioration in microstructure primarily arises from excessive FA, which leads to insufficient formation of early-age hydration products and incomplete pozzolanic reactions at later stages, thereby creating structurally weak regions.



**Figure 6.** SEM micrographs.

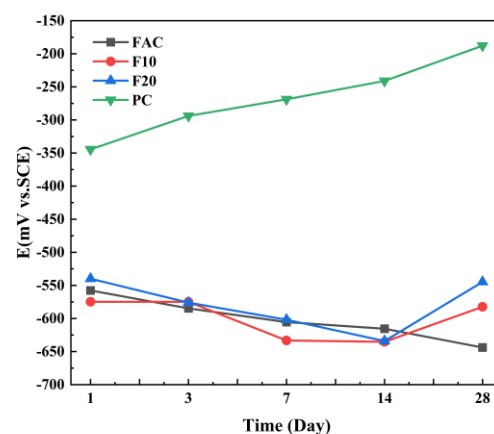
In summary, the XRD patterns and SEM micrographs at five different curing ages clearly illustrate the evolution of hydration products in PC, FAC, and FAC blended with FA. Hydration in PC is driven by silicate minerals, leading to the formation of CH and C–S–H. In contrast, FAC hydration relies on ferroaluminate minerals, producing AFt and AFm phases without CH. FA participates through pozzolanic reactions, generating products such as Stratlingite, which contributes to the optimization of the product assemblage and enhancement of material performance. These observations are consistent with the previously discussed trends in ionic concentration evolution and align well with findings reported in the literature [35,36].

### 3.3. Study on Passivation Behavior of Steel Bars in Real Mortar Environment

#### 3.3.1. Open Circuit Potential Method

Previous studies have demonstrated that this corrosion potential can effectively reflect the corrosion tendency of steel reinforcement in concrete environments, while also characterizing the growth and evolution of surface film layers on the steel [37]. The time-dependent evolution of the open-circuit potential of the steel electrode at different passivation stages is shown in Figure 7. It can be seen that the incorporation of mineral admixtures does not significantly alter the overall time-dependent trend of the steel open-circuit potential. The addition of FA shifts the open-circuit potential in the positive direction, indicating a

tendency to promote steel passivation. This behavior arises because the passivation process of steel is primarily governed by the properties of the pore solution. Previous studies have shown that an increase in solution pH can markedly improve the quality of the passive film formed on steel [38]. In contrast, the OCP of the FAC system is relatively low, which is attributed to the dense pore structure of the FAC matrix. This limits oxygen availability at the steel surface and constrains the cathodic reaction, resulting in a lower potential. This observation is consistent with the conclusion that the pore structure becomes increasingly dense as hydration progresses. Moreover, as shown by the previous pore solution measurements, during the early stages of hydration, FA physically dilutes the cement, reducing the formation of alkaline species such as  $\text{Ca}(\text{OH})_2$  and thereby suppressing the pH of the system. In the later stages of hydration, the effective activation of the pozzolanic reaction relies on the alkaline environment ( $\text{pH} \geq 11.5$ ) provided during the dissolution of FAC. The newly formed hydration products not only regulate alkalinity but also optimize the pore structure, enhancing the long-term stability of the pH. The complex composition of FA alters the concentrations of key ions in the pore solution, making its characteristics more intricate and resulting in differences in steel passivation behavior across different systems.



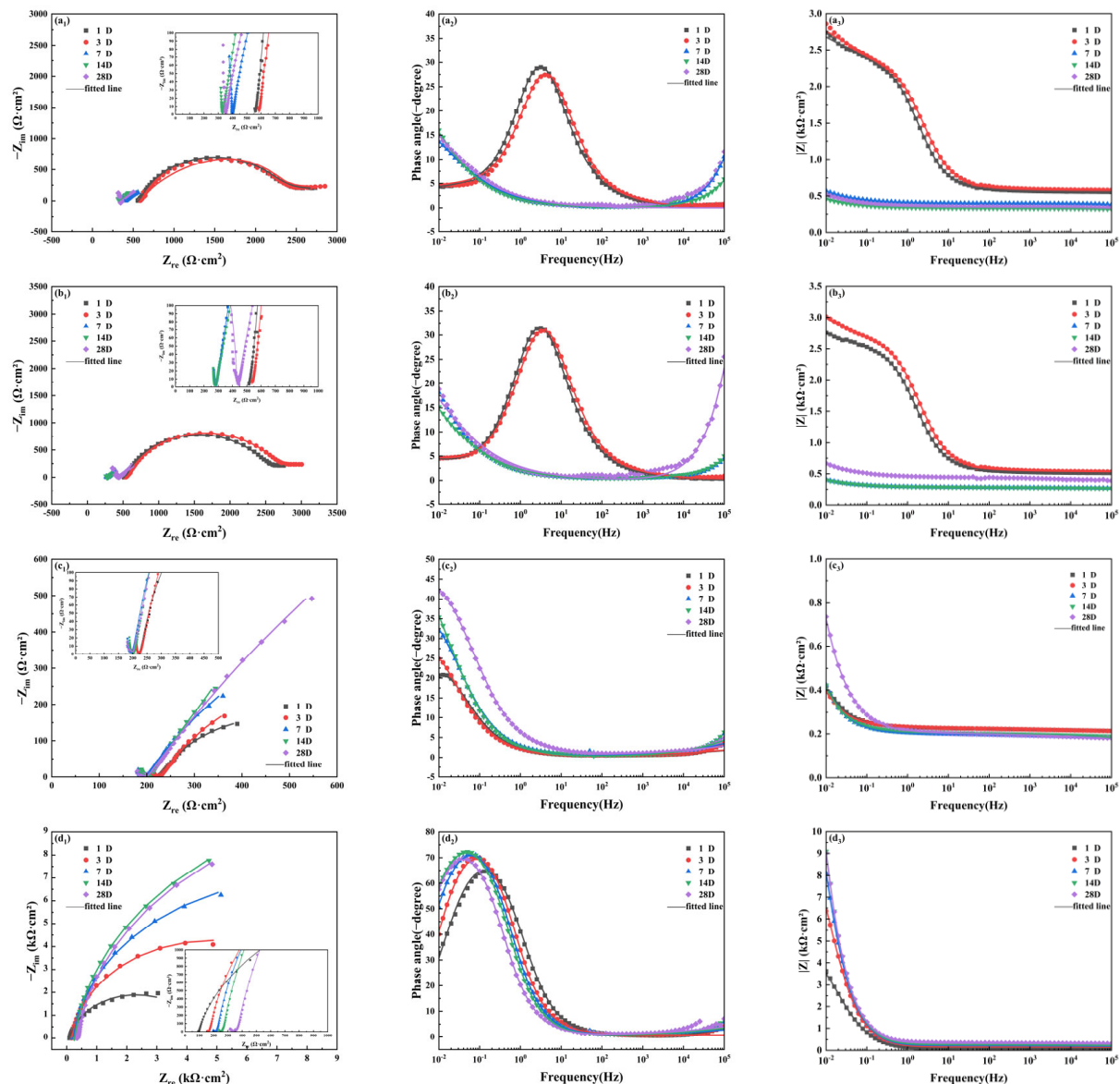
**Figure 7.** OPC of steel reinforcement at different curing ages.

### 3.3.2. EIS

To further analyze the electrochemical behavior at the steel-mortar interface and to elucidate the formation process and quality differences in the passive film on steel within the mortar system, electrochemical impedance spectroscopy (EIS) was immediately performed on the steel electrodes following the completion of the open-circuit potential tests.

Figure 8(a1–d3) present the Nyquist plots of different reinforced mortar systems under standard curing conditions. From the Nyquist plots, it can be observed that the capacitive arcs all exhibit a typical semicircular feature. Previous studies have indicated that the radius of the capacitive arc can reflect the degree of steel passivation [39]. As shown in the figure, within the first three days of passivation, the low-frequency capacitive arcs of the steel in all four cement-based systems gradually increase over time, indicating a rise in charge transfer resistance and the initiation of passive film growth. This is attributed to the hydration reactions of the cementitious materials, which release a large amount of  $\text{OH}^-$  and, in the FAC-based system, produce  $\text{Fe}(\text{OH})_2$  that is further oxidized to stable iron oxides, resulting in increased impedance at the steel surface. This trend is consistent with the previously discussed evolution of pore solution pH. From the perspective of electrochemical kinetics, the increase in impedance indicates that the charge-transfer process at the steel/passive film interface becomes progressively inhibited during passivation. The continuous formation of compact iron oxides increases the energy barrier for anodic iron dissolution while simultaneously restricting ionic migration through the passive film. Consequently, both

electron-transfer kinetics and ionic transport are suppressed, leading to an increase in charge-transfer resistance and improved passivation behavior.



**Figure 8.** EIS diagrams of steel in different mortars during the curing time: (a<sub>1</sub>–a<sub>3</sub>) FAC mortar; (b<sub>1</sub>–b<sub>3</sub>) F10 mortar; (c<sub>1</sub>–c<sub>3</sub>) F20 mortar; and (d<sub>1</sub>–d<sub>3</sub>) PC mortar.

This study, through a comparative analysis of Nyquist plots for FAC and its composite systems incorporating 10% and 20% FA at different hydration ages, reveals the significant influence of FA content on the electrochemical behavior and hydration process of the systems. For the pure FAC system, the diameter of the Nyquist semicircle increases markedly during the early hydration period, indicating a continuous rise in charge transfer resistance ( $R_{ct}$ ). This behavior is attributed to the synergistic pore-structure optimization by typical FAC hydration products, including the rapidly formed Aft at early ages and the continuously generated C-(A)-S-H gel at later stages. The needle-like Aft crystals, together with the amorphous C-(A)-S-H gel, effectively fill capillary pores, enhancing the matrix density and impeding ionic transport [40].

When 10% FA is incorporated, the system exhibits higher impedance values (Figure 8), The fitted charge transfer resistance ( $R_{ct}$ ) remained on the order of  $10^4$ – $10^5 \Omega \cdot \text{cm}^2$  throughout the passivation process, indicating the development of a stable passive film. This

improvement arises from the pozzolanic effect of FA. The reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in FA react with  $\text{Ca}(\text{OH})_2$  produced during hydration to form additional C–S–H gel and AFm/AFt phases, a process referred to as the “pore refinement effect.” This not only increases the total amount of gel phases but, more importantly, transforms larger capillary pores into finer gel pores, significantly reducing pore connectivity and greatly enhancing the matrix’s resistance to ionic transport [35].

However, when the FA content is increased to 20%, both the diameter of the Nyquist semicircle and the impedance values decrease noticeably, indicating insufficient densification of the system. This is mainly attributed to two factors: first, the “dilution effect” reduces the relative content of cement clinker, weakening the ability of early-age hydration products (such as AFt) to form a structural framework, resulting in higher initial porosity; second, the excess FA does not fully participate in the pozzolanic reaction within 28 days, and its reactive components are not sufficiently activated to effectively fill the large number of pores generated by the dilution effect. Consequently, the microstructure exhibits more defects during the observation period, and ion transport pathways remain relatively unobstructed [41]. This observation is consistent with the previously discussed conclusion that the pore structure becomes increasingly dense during hydration.

With increasing hydration time, the Nyquist plots of the FAC-incorporated systems exhibit shortened capacitive arcs, indicating a decrease in the polarization resistance at the steel–mortar interface. This electrochemical response suggests that the passive film formed in the FAC-based systems becomes less protective during prolonged hydration. Considering the evolution of pore solution chemistry presented in Section 3.1, the deterioration of the electrochemical response is more reasonably attributed to the combined effects of changes in pore solution alkalinity, ionic composition, and passive film stability. Although variations in sulfate concentration were observed in the pore solution, the XPS survey spectra did not reveal detectable sulfur enrichment on the steel surface, and no direct evidence of sulfur incorporation into the passive film or sulfur-containing corrosion products was obtained in this study. Therefore, the specific role of sulfur species in passive film degradation cannot be confirmed based on the present results and requires further investigation.

In summary, an appropriate amount of FA (e.g., 10%) can serve as an effective functional admixture for FAC, optimizing long-term microstructure and durability through active pozzolanic reactions. In contrast, excessive incorporation (e.g., 20%) may negatively affect the formation of the system’s structure due to early-stage dilution and insufficient later-stage reactions. This observation is consistent with the previously discussed conclusion that the pore structure becomes increasingly dense during hydration.

For comparison, the PC system exhibits extremely rapid impedance growth kinetics during early hydration, with  $R_{ct}$  exceeding several  $\text{k}\Omega\cdot\text{cm}^2$  within 24 h. This behavior is primarily attributed to the rapid hydration of the dominant  $\text{C}_3\text{S}$  mineral in OPC, which leads to the rapid nucleation, growth, and interweaving of a large amount of nanoscale C–S–H gel, forming a dense microstructure with very low pore connectivity even at early ages [42,43]. In the early-age Nyquist plot, a very small capacitive arc near the origin is observed. This stage corresponds to the initial dissolution and induction period of cement particles. The pore solution is saturated with high concentrations of ions such as  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , resulting in extremely high electrolyte conductivity and, consequently, very low overall system impedance [44]. At this stage, a continuous network of hydration products has not yet formed, and the paste structure remains loose. Unlike the FAC system, where early-age performance relies on the structural framework provided by ettringite crystallization, the early-age enhancement in the PC system is primarily attributed to the efficient and continuous filling of pore space by C–S–H gel.

During the early hydration stage, the phase-angle curves in the Bode plots of the FAC system gradually develop characteristic peaks in the mid-frequency range (approximately 10–100 Hz) and exhibit slight broadening. This phenomenon indicates the emergence of a significant distribution of time constants within the system. Correspondingly, the impedance modulus plots, particularly at low frequencies ( $<0.1$  Hz), show a steady increase. This electrochemical behavior is primarily attributed to the rapid formation of a large amount of AFt at early ages. The needle-like or rod-like AFt crystals interlock to form the initial physical framework of the cement matrix, effectively subdividing large capillary pores and thereby enhancing the system's resistance. However, at this stage, the amount of C-(A)-S-H gel is relatively limited, and its pore-filling effect at the nanoscale has not yet fully manifested. Consequently, the increase in impedance is moderate, in sharp contrast to the rapid early-age impedance growth observed in the PC system.

The evolution trend of the Bode plots for the F10 group is similar to that of the FAC group, but at 28 d it exhibits higher low-frequency impedance modulus and broader, higher phase-angle peaks. This confirms that a 10% FA addition induces a positive pozzolanic effect. The reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in FA react with  $\text{Ca}(\text{OH})_2$  released during cement hydration to generate additional gel phases, achieving more efficient pore filling and resulting in a denser and more protective microstructure compared with pure FAC.

In the F20 group, both the absolute value ( $<1.0 \text{ k}\Omega\cdot\text{cm}^2$ ) and the increase in low-frequency impedance modulus are much lower than those of the previous two groups. This electrochemical behavior indicates that an excessive FA content (20%) induces a pronounced “dilution effect,” delaying early-age hydration. Additionally, a large portion of FA does not fully react within the observation period, resulting in a less dense microstructure and higher porosity at later ages, thereby limiting impedance development.

For the PC system, a high and broad phase-angle peak is already observed at 1 d, and it continues to extend toward higher frequencies as hydration progresses, indicating that a very dense microstructure forms at an early age and is further optimized over time. Its most notable feature is the extremely high low-frequency impedance modulus (exceeding  $100 \text{ k}\Omega\cdot\text{cm}^2$  at 28 d), with most of the increase occurring during early hydration. This behavior is closely related to the rapid hydration of the dominant  $\text{C}_3\text{S}$  mineral in OPC, which produces a large amount of C-S-H gel that quickly fills the pores. Compared with the FAC system, OPC achieves high early-age resistance primarily through the physical pore-filling effect of C-S-H gel, whereas the impedance development in the FAC system relies more on the synergistic and progressive growth of multiple hydration products, including AFt and C-(A)-S-H.

To further obtain electrochemical parameters associated with steel passivation, the EIS spectra were fitted using ZsimpWin software based on the equivalent circuit shown in Figure 9, and the corresponding fitting parameters are summarized in Tables 4–7. The selected equivalent circuit has been widely adopted for describing the electrochemical response of passive steel in cementitious materials because it appropriately represents the contributions of the mortar matrix resistance, passive film characteristics, and charge-transfer process at the steel/mortar interface. The fitting quality was evaluated using the chi-square ( $\chi^2$ ) values generated by ZsimpWin. As shown in Tables 4–7, the relatively low  $\chi^2$  values indicate satisfactory agreement between the experimental impedance spectra and the fitted results, confirming that the selected equivalent circuit provides a reliable description of the electrochemical behavior of the steel/passive film system. In the circuit,  $R_s$  represents the resistance of the cement-based material,  $Q_f$  denotes the capacitance of the passive film,  $R_f$  is the passive film resistance,  $R_{ct}$  corresponds to the charge-transfer resistance, and  $Q_{dl}$  represents the double-layer capacitance at the steel/mortar interface.

The satisfactory fitting quality demonstrated by the  $\chi^2$  values indicates that the fitted electrochemical parameters ( $R_s$ ,  $R_f$  and  $R_{ct}$ ) can be reliably used to analyze the evolution of steel passivation during hydration. As shown in Tables 4–7, the  $R_s$  values of all samples gradually increase with passivation time. This is because, in the mortar environment, as cement hydration accelerates, the resulting hydration products progressively form and fill the original pores, reducing the porosity of the cement matrix. Consequently, the migration paths of ions in the pore solution become narrower, leading to a continuous increase in resistance.

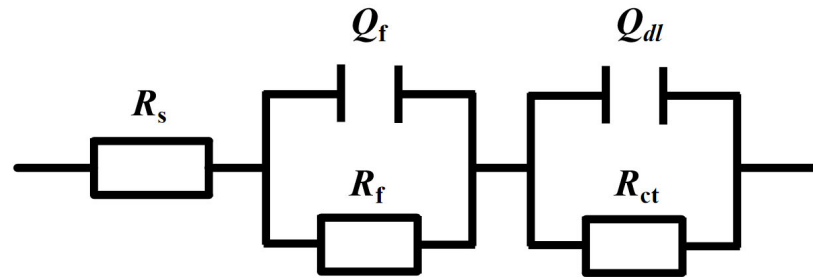


Figure 9. EIS fitted equivalent circuit diagram.

Table 4. EIS Data Fitting Results for the Full Passivation Process of Steel in the FAC Group.

| Time<br>(D) | $R_s$<br>( $k\Omega \cdot cm^2$ ) | $R_f$<br>( $k\Omega \cdot cm^2$ ) | $Q_f$                                              |      | $R_{ct}$<br>( $\Omega \cdot cm^2$ ) | $Q_{dl}$                                           |      | Chi-Square<br>Value ( $\chi^2$ ) |
|-------------|-----------------------------------|-----------------------------------|----------------------------------------------------|------|-------------------------------------|----------------------------------------------------|------|----------------------------------|
|             |                                   |                                   | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                                     | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                                  |
| 1           | 0.54                              | 1.26                              | $2.89 \times 10^{-5}$                              | 0.76 | $1.02 \times 10^5$                  | $9.68 \times 10^{-5}$                              | 0.59 | $1.58 \times 10^{-4}$            |
| 3           | 4.58                              | 1.52                              | $2.41 \times 10^{-5}$                              | 0.85 | $1.14 \times 10^5$                  | $7.22 \times 10^{-5}$                              | 0.63 | $2.24 \times 10^{-4}$            |
| 7           | 6.51                              | 0.41                              | $5.46 \times 10^{-5}$                              | 0.56 | $0.24 \times 10^5$                  | $7.83 \times 10^{-5}$                              | 0.55 | $3.36 \times 10^{-4}$            |
| 14          | 8.45                              | 0.33                              | $8.76 \times 10^{-5}$                              | 0.49 | $0.25 \times 10^5$                  | $8.56 \times 10^{-5}$                              | 0.53 | $3.37 \times 10^{-4}$            |
| 28          | 10.35                             | 0.32                              | $1.22 \times 10^{-4}$                              | 0.36 | $0.26 \times 10^5$                  | $9.13 \times 10^{-5}$                              | 0.57 | $2.63 \times 10^{-4}$            |

Table 5. EIS Data Fitting Results for the Full Passivation Process of Steel in the F10 Group.

| Time<br>(D) | $R_s$<br>( $k\Omega \cdot cm^2$ ) | $R_f$<br>( $k\Omega \cdot cm^2$ ) | $Q_f$                                              |      | $R_{ct}$<br>( $\Omega \cdot cm^2$ ) | $Q_{dl}$                                           |      | Chi-Square<br>Value ( $\chi^2$ ) |
|-------------|-----------------------------------|-----------------------------------|----------------------------------------------------|------|-------------------------------------|----------------------------------------------------|------|----------------------------------|
|             |                                   |                                   | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                                     | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                                  |
| 1           | 0.56                              | 1.39                              | $2.65 \times 10^{-5}$                              | 0.72 | $0.98 \times 10^5$                  | $6.68 \times 10^{-5}$                              | 0.57 | $1.22 \times 10^{-4}$            |
| 3           | 3.68                              | 1.98                              | $1.97 \times 10^{-5}$                              | 0.91 | $1.03 \times 10^5$                  | $4.22 \times 10^{-5}$                              | 0.66 | $3.28 \times 10^{-4}$            |
| 7           | 5.61                              | 0.64                              | $4.47 \times 10^{-5}$                              | 0.84 | $0.25 \times 10^5$                  | $5.83 \times 10^{-5}$                              | 0.57 | $2.87 \times 10^{-4}$            |
| 14          | 7.54                              | 0.47                              | $6.22 \times 10^{-5}$                              | 0.56 | $0.21 \times 10^5$                  | $5.56 \times 10^{-5}$                              | 0.54 | $3.11 \times 10^{-4}$            |
| 28          | 9.46                              | 0.43                              | $8.04 \times 10^{-5}$                              | 0.53 | $0.26 \times 10^5$                  | $7.13 \times 10^{-5}$                              | 0.58 | $2.78 \times 10^{-4}$            |

Table 6. EIS Data Fitting Results for the Full Passivation Process of Steel in the F20 Group.

| Time<br>(D) | $R_s$<br>( $k\Omega \cdot cm^2$ ) | $R_f$<br>( $k\Omega \cdot cm^2$ ) | $Q_f$                                              |      | $R_{ct}$<br>( $\Omega \cdot cm^2$ ) | $Q_{dl}$                                           |      | Chi-Square<br>Value ( $\chi^2$ ) |
|-------------|-----------------------------------|-----------------------------------|----------------------------------------------------|------|-------------------------------------|----------------------------------------------------|------|----------------------------------|
|             |                                   |                                   | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                                     | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                                  |
| 1           | 0.54                              | 1.32                              | $2.74 \times 10^{-5}$                              | 0.74 | $0.18 \times 10^5$                  | $6.28 \times 10^{-5}$                              | 0.47 | $1.89 \times 10^{-4}$            |
| 3           | 3.70                              | 2.08                              | $1.79 \times 10^{-5}$                              | 0.95 | $0.19 \times 10^5$                  | $6.52 \times 10^{-5}$                              | 0.62 | $3.55 \times 10^{-4}$            |
| 7           | 4.62                              | 1.01                              | $5.01 \times 10^{-5}$                              | 0.86 | $0.24 \times 10^5$                  | $5.83 \times 10^{-5}$                              | 0.63 | $2.69 \times 10^{-4}$            |
| 14          | 6.58                              | 0.68                              | $9.22 \times 10^{-5}$                              | 0.61 | $0.36 \times 10^5$                  | $4.56 \times 10^{-5}$                              | 0.60 | $4.58 \times 10^{-4}$            |
| 28          | 8.44                              | 0.45                              | $1.78 \times 10^{-4}$                              | 0.54 | $0.53 \times 10^5$                  | $5.13 \times 10^{-4}$                              | 0.59 | $3.22 \times 10^{-4}$            |

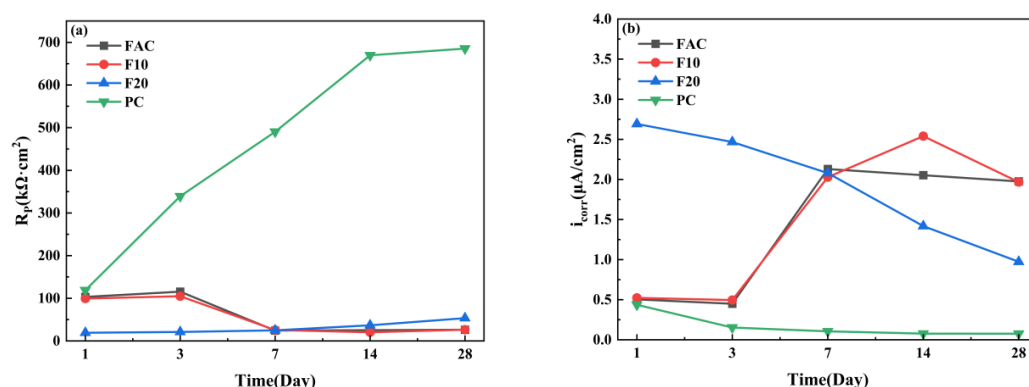
**Table 7.** EIS Data Fitting Results for the Full Passivation Process of Steel in the PC Group.

| Time | $R_s$                    | $R_f$                    | $Q_f$                                              | $R_{ct}$ | $Q_{dl}$                | Chi-Square Value ( $\chi^2$ )                      |      |                       |
|------|--------------------------|--------------------------|----------------------------------------------------|----------|-------------------------|----------------------------------------------------|------|-----------------------|
| (D)  | ( $k\Omega \cdot cm^2$ ) | ( $k\Omega \cdot cm^2$ ) | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n        | ( $\Omega \cdot cm^2$ ) | $Y_0$<br>( $\Omega^{-1} \cdot cm^{-2} \cdot s^n$ ) | n    |                       |
| 1    | 0.38                     | 0.94                     | $2.26 \times 10^{-5}$                              | 0.94     | $1.18 \times 10^5$      | $1.87 \times 10^{-5}$                              | 0.89 | $1.33 \times 10^{-4}$ |
| 3    | 1.70                     | 2.18                     | $1.79 \times 10^{-5}$                              | 0.93     | $3.37 \times 10^5$      | $1.43 \times 10^{-5}$                              | 0.94 | $2.53 \times 10^{-4}$ |
| 7    | 2.62                     | 2.34                     | $1.01 \times 10^{-5}$                              | 0.91     | $4.88 \times 10^5$      | $1.33 \times 10^{-5}$                              | 0.93 | $4.89 \times 10^{-4}$ |
| 14   | 4.58                     | 2.63                     | $6.42 \times 10^{-6}$                              | 0.92     | $6.67 \times 10^5$      | $1.46 \times 10^{-5}$                              | 0.92 | $3.49 \times 10^{-4}$ |
| 28   | 8.47                     | 2.45                     | $1.78 \times 10^{-6}$                              | 0.91     | $6.83 \times 10^5$      | $1.34 \times 10^{-5}$                              | 0.93 | $4.28 \times 10^{-4}$ |

Based on the fitted data in the above tables and using Equation (1), the polarization resistance ( $R_p$ ) of the steel can be calculated. To further analyze the evolution of  $R_p$  with passivation time under curing conditions in the FAC and PC systems, the relationship between  $R_p$  and passivation time is presented in Figure 10.

$$R_p = R_f + R_{ct} \quad (1)$$

The results indicate that the  $R_p$  of steel serves as a key parameter for characterizing its passivation state and protective performance in the FAC system. As shown in Figure 10a, during the early hydration stage,  $R_p$  values for all four groups increase, indicating rapid formation of the passive film. However, with prolonged hydration, the  $R_p$  values of the FAC and F10 groups decrease, demonstrating that extended hydration adversely affects the steel passive film in these systems. Notably, during standard curing, the  $R_p$  values of steel in the PC and F20 groups continue to increase, indicating ongoing passivation under standard conditions. In contrast, the  $R_p$  values of steel in FAC-containing systems remain at a relatively low level and tend to stabilize, suggesting that passive film growth is hindered under these conditions and an effective protective layer is not formed. This differential behavior highlights the influence of FA on steel passivation in FAC systems.



**Figure 10.** Time-Dependent Plot of Polarization Resistance ( $R_p$ ) and Corrosion Current Density ( $i_{corr}$ ): (a)  $R_p$ ; (b)  $i_{corr}$ .

Based on the  $R_p$  data obtained from the above equivalent circuit fitting, the corrosion current density ( $i_{corr}$ ) of steel can be calculated using the Stern–Geary equation (Equation 2), which is one of the key parameters for assessing steel corrosion behavior. During the initial stage of steel passivation, active electrochemical reactions continuously occur at the electrode interface, resulting in relatively high current densities. As the passive film gradually forms and approaches completeness, this high-resistance layer effectively inhibits charge transfer, hindering anodic oxidation reactions and consequently causing a significant reduction in corrosion current density. Therefore, measuring  $i_{corr}$  provides an effective

means to determine whether steel has reached a stable passive state. In general, the lower the  $i_{\text{corr}}$  value, the higher the degree of passivation on the steel surface and the denser and more intact the resulting passive film.

$$i_{\text{corr}} = \frac{B}{R_p} \quad (2)$$

Here,  $i_{\text{corr}}$  is the corrosion current density in  $\mu\text{A}/\text{cm}^2$ ;  $R_p$  is the polarization resistance of steel in  $\text{k}\Omega\cdot\text{cm}^2$ ; and  $B$  is the Stern–Geary constant in mV. Since the electrochemical measurements were performed during the passivation stage under standard curing conditions, a Stern–Geary constant of 52 mV, commonly adopted for passive steel in alkaline cementitious environments, was used to calculate the apparent corrosion current density. The calculated  $i_{\text{corr}}$  values are mainly intended for comparative evaluation among different cement systems rather than as absolute corrosion rates.

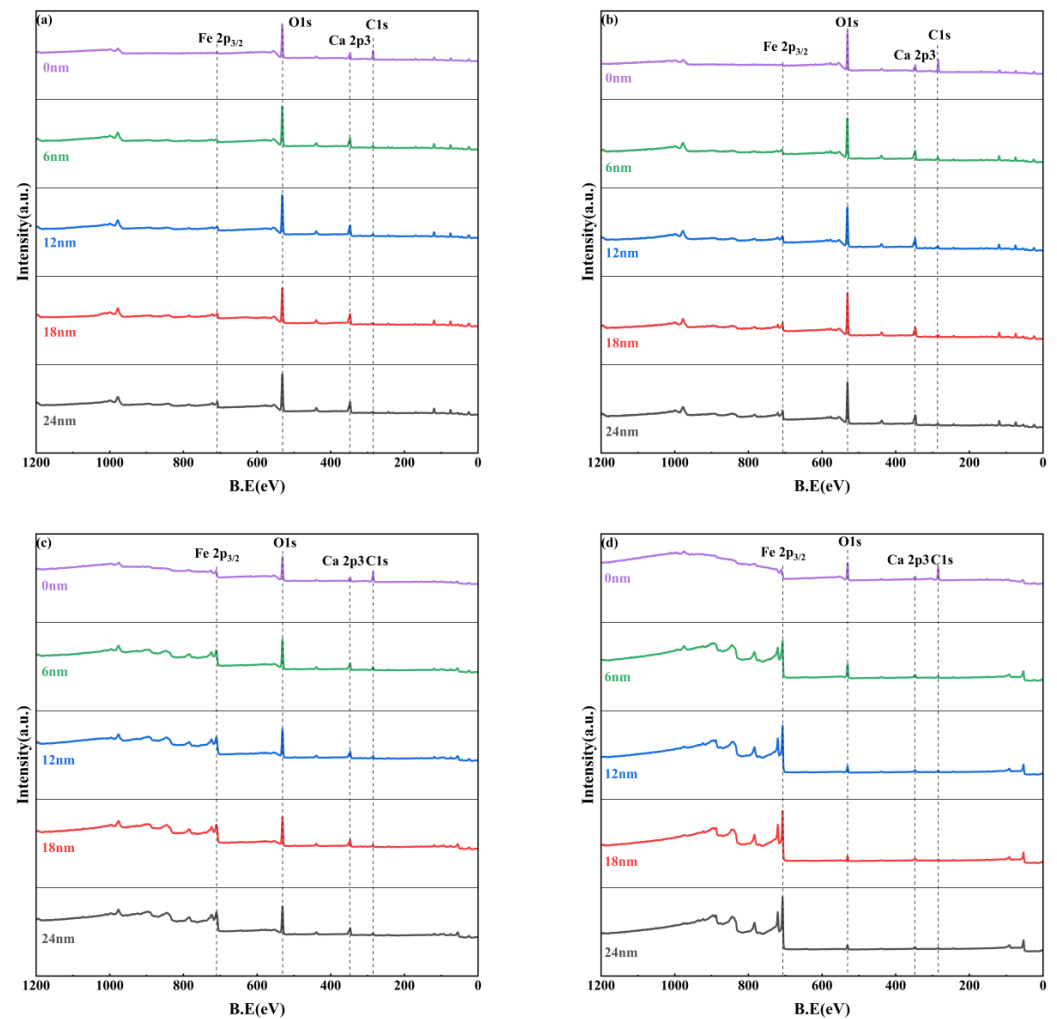
Based on the characteristics of the curves, the PC group exhibited the most pronounced passivation behavior. Its corrosion current density  $i_{\text{corr}}$  rapidly decreased from an initial value of approximately  $0.5 \mu\text{A}/\text{cm}^2$  and stabilized at an extremely low level below  $0.1 \mu\text{A}/\text{cm}^2$  after 7 days, indicating the formation of a continuous and dense passive film on the steel surface. In contrast, the FAC and F10 groups displayed markedly different behavior:  $i_{\text{corr}}$  remained relatively high throughout the observation period and showed a clear trend of initial decrease followed by continuous increase. This suggests that the passive film remained incomplete or locally unstable under the present curing conditions, resulting in relatively high apparent corrosion current densities. Since no direct morphological evidence of pitting was obtained, localized pitting cannot be conclusively confirmed. This indicates that the passivation tendency was comparable to that of the PC group. However, the sustained high corrosion current suggests that, despite slightly higher pH values compared to the FAC and F10 groups, the overall low-pH environment likely hindered the formation of a stable passive film, leaving the steel in a long-term activated corrosion state.

### 3.4. Composition of the Steel Passive Film

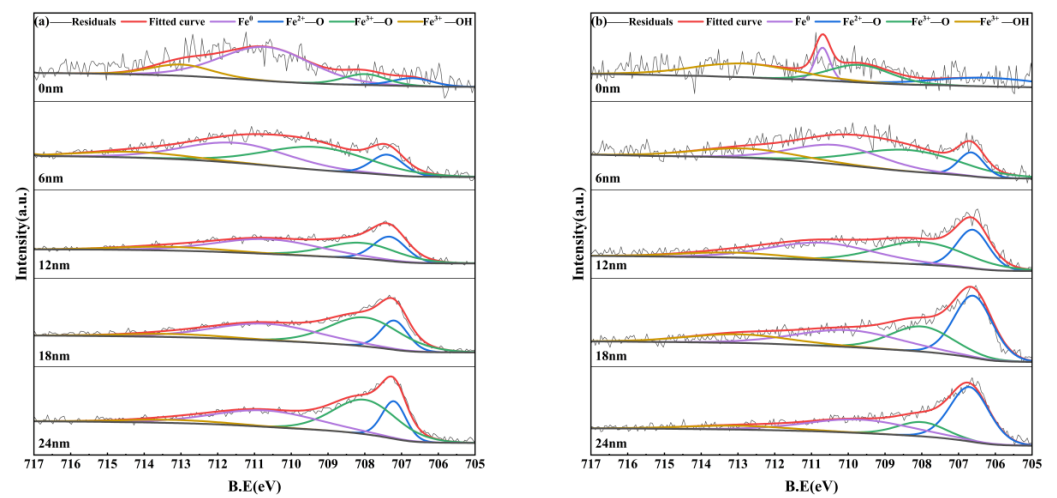
XPS analysis provides key information for revealing the chemical composition of the passive film formed on steel in simulated pore solutions. As shown in the spectra (Figure 11), characteristic signals of Fe, O, Ca, and C are clearly identified, while trace elements dissolved in the solution, such as Na, K, and S, are not prominently detected. This result indicates that sulfur-containing species were not significantly incorporated into the passive film under the present experimental conditions, and therefore no direct evidence of sulfur-induced passive film degradation was obtained. The combined signals of Fe and O indicate that the surface passive layer is primarily composed of iron oxides and hydroxides. The detected Ca originates from calcium-containing compounds deposited from the solution [44], whereas the C peak generally arises from atmospheric hydrocarbon contaminants adsorbed on the sample during preparation or testing.

Further peak deconvolution of the Fe2p high-resolution spectra (Figure 12) indicates that the iron on the steel surface coexists in both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  chemical states, confirming that the passive film is a mixture of various iron oxides and hydroxides [45]. Based on the deconvolution of the O1s spectra (Figure 13), specific phases within the passive film can be assigned. The O1s spectra can be resolved into three sub-peaks: the lowest binding energy peak (O-1) corresponds to lattice oxygen ( $\text{O}^{2-}$ ), primarily originating from  $\text{Fe}_3\text{O}_4$ , FeO, and  $\text{Fe}_2\text{O}_3$ ; the O-2 peak represents hydroxyl oxygen ( $\text{OH}^-$ ), mainly derived from  $\text{FeOOH}$  and  $\text{Fe}(\text{OH})_3$ ; and the highest binding energy peak (O-3) corresponds to chemisorbed or physisorbed water molecules ( $\text{H}_2\text{O}$ ). Together, these results reveal that the passive film is a

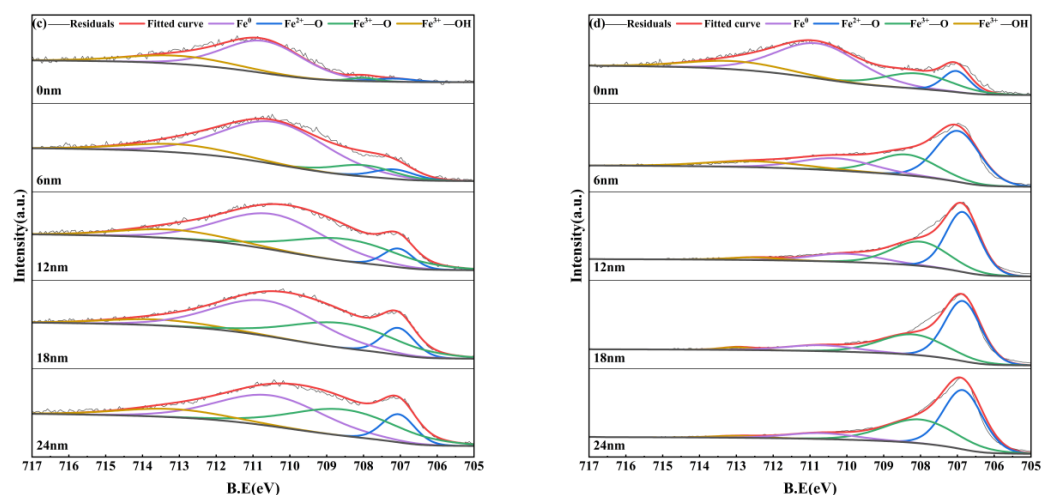
complex, heterogeneous system composed of crystalline oxides, amorphous hydroxides, and adsorbed water.



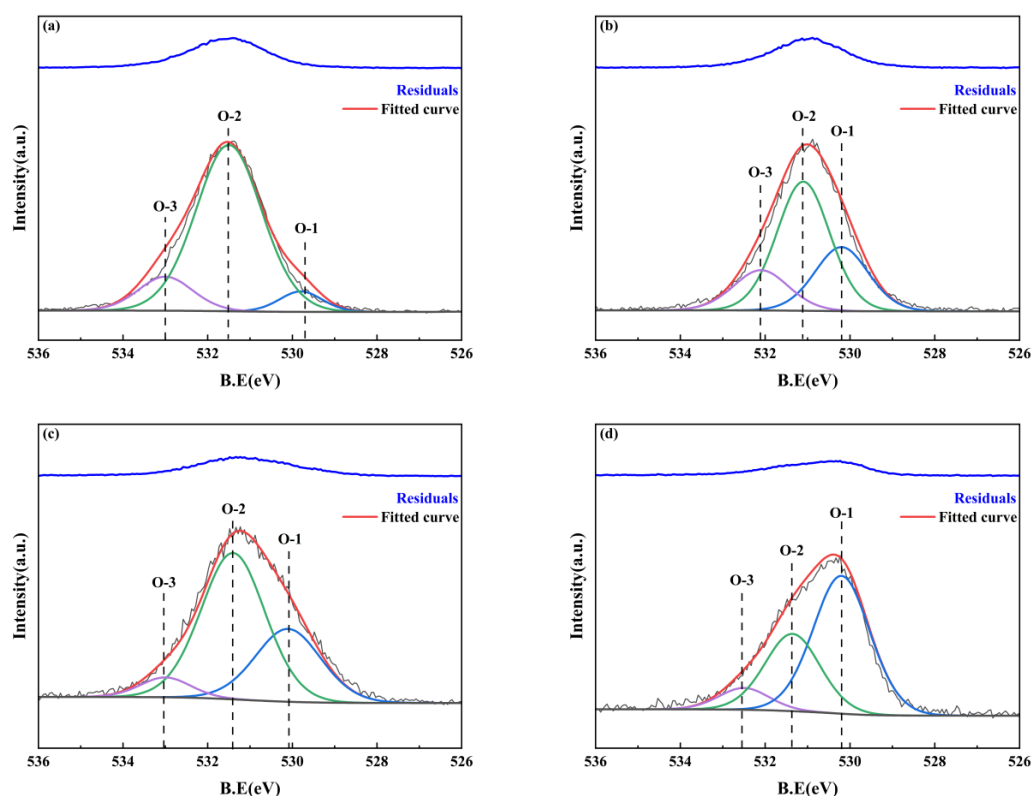
**Figure 11.** XPS Full Survey Spectra of Steel in Mortar: (a) FAC, (b) F10, (c) F20, (d) PC.



**Figure 12.** Cont.

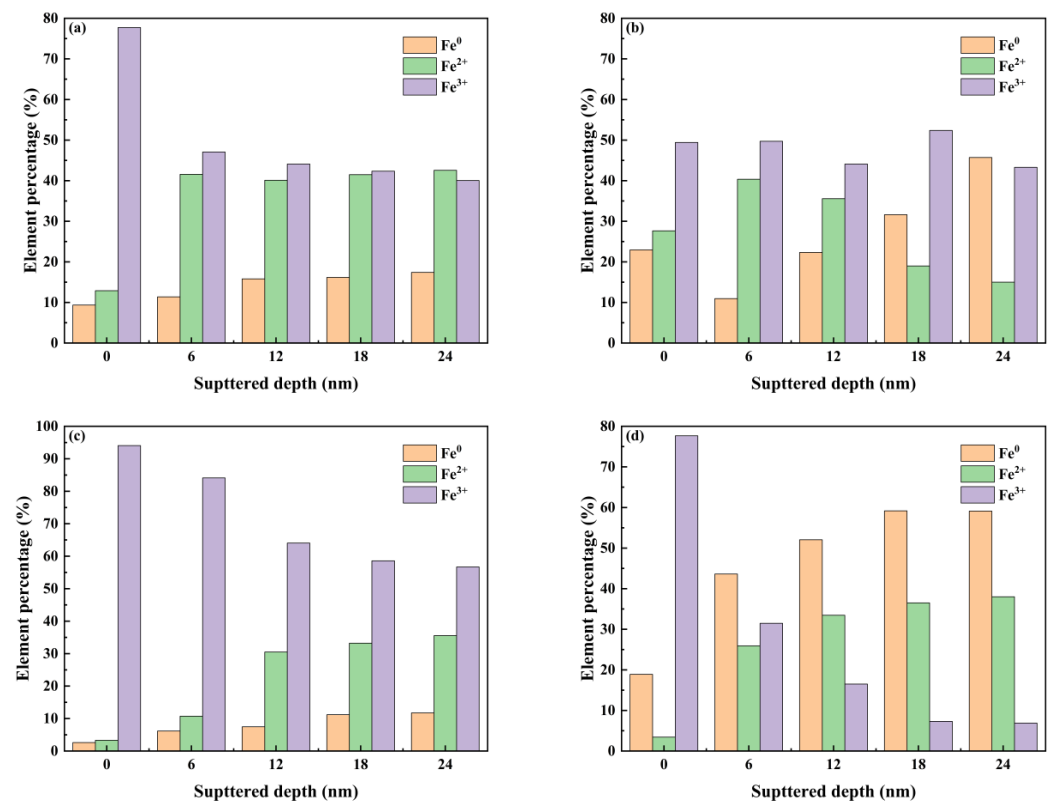


**Figure 12.** XPS Fe2p Spectra of Steel at Different Sputtering Depths in Mortar: (a) FAC, (b) F10, (c) F20, (d) PC.



**Figure 13.** High-Resolution O 1s Spectra of Steel in Mortar after 28 Days of Natural Passivation: (a) FAC, (b) F10, (c) F20, (d) PC.

Based on the above information, the composition, structure, and protective performance of the passive film can be correlated. According to the classical double-layer model of passive films, the inner layer is primarily composed of more protective  $\text{Fe}^{2+}$  oxides (such as  $\text{Fe}_3\text{O}_4$ ), while the outer layer mainly consists of relatively less protective  $\text{Fe}^{3+}$  oxides and hydroxides (such as  $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$ ) [41]. The quantitative analysis in Figure 14. indicates that the passive film formed on the steel surface is predominantly composed of  $\text{Fe}^{3+}$  phases ( $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$ ), while the more protective  $\text{Fe}^{2+}$  phases are present at relatively lower levels. This compositional feature is closely related to the chemical composition of the steel substrate and suggests that the protective effectiveness of such passive films may be partially influenced by their specific phase distribution.

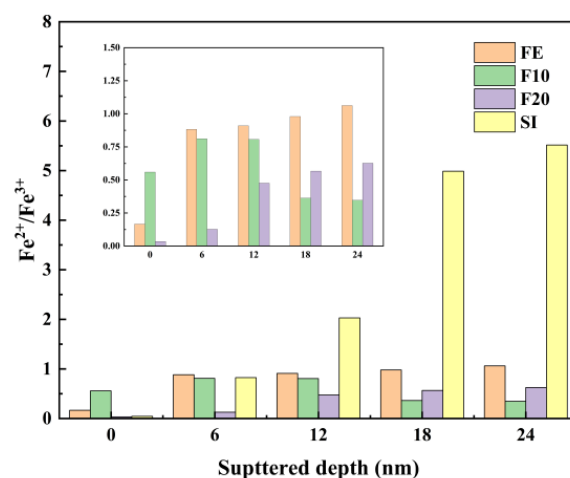


**Figure 14.** Effect of Sputtering Depth in Pore Solution on the Content of Iron and Iron Ions on the Steel Surface: (a) FAC, (b) F10, (c) F20, (d) PC.

Figure 15 shows the evolution of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio with sputtering depth within the passive films formed in the four simulated pore solutions. Overall, the ratio increases with depth, with a particularly pronounced rise in the near-surface region from 0 to 6 nm, followed by a more gradual change. This trend indicates that from the film surface toward the film/substrate interface, the relative content of divalent iron oxides (such as FeO) gradually increases, while trivalent iron compounds (such as  $\text{Fe}_2\text{O}_3$ ) correspondingly decrease, revealing a distinct chemical gradient. The formation of this gradient is likely related to the continuous phase transformation during passive film growth: the surface-rich hematite ( $\text{Fe}_2\text{O}_3$ ) gradually transitions inward to magnetite ( $\text{Fe}_3\text{O}_4$ ), a transformation that simultaneously affects both the film thickness and its chemical composition. This observation is consistent with the findings of MESQUITA [46].

Fitting analysis of the high-resolution XPS spectra (O1s and Fe2p) indicates that the naturally formed passive film is a complex, heterogeneous system rather than a single compound. Oxygen exists in three chemical states: lattice oxygen ( $\text{O}^{2-}$ ), primarily originating from oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ; hydroxyl oxygen ( $\text{OH}^-$ ), mainly corresponding to hydroxides such as  $\text{FeOOH}$ ; and adsorbed water ( $\text{H}_2\text{O}$ ). Correspondingly, iron is present in three valence states:  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ , with their proportions varying continuously with depth, forming a characteristic chemical gradient. Specifically, in the outermost layer (0–6 nm),  $\text{Fe}^{3+}$  dominates, corresponding to an enrichment of the less protective phases  $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$ . Moving inward (approximately 6–18 nm), the  $\text{Fe}^{2+}$  content rapidly increases and becomes predominant, marking the beginning of the “inner layer” dominated by the more protective  $\text{Fe}_3\text{O}_4$  and FeO. Near the metal substrate (>18 nm), the  $\text{Fe}^0$  signal strengthens, indicating the transition to the steel bulk. This structural model—“ $\text{Fe}^{3+}$ -enriched outer layer  $\rightarrow$   $\text{Fe}^{2+}$ -enriched inner layer  $\rightarrow$  metal substrate”—reflects the spatial manifestation of the dynamic balance between  $\text{Fe}^{2+}$  oxida-

tion and  $\text{Fe}^{3+}$  transformation/precipitation during passivation, and forms the structural basis for the protective function of the passive film.



**Figure 15.** Variation in the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  Ratio with Sputtering Depth in Different Pore Solutions.

In the highly alkaline PC pore solution ( $\text{pH} > 13.5$ ), the strong oxidative environment promotes the formation of a thick and dense  $\text{Fe}^{3+}$  oxide layer on the surface, while the  $\text{Fe}^{2+}$ -enriched inner layer remains relatively thin. In FA-blended systems, the pozzolanic reaction consumes  $\text{Ca}(\text{OH})_2$ , moderately lowering the pore solution pH; as a result, the surface  $\text{Fe}^{3+}$  layer becomes thinner, whereas the  $\text{Fe}^{2+}$ -enriched inner layer forms earlier and develops more thickly. This indicates that a relatively mild alkaline environment is more favorable for the growth of stable and protective  $\text{Fe}^{2+}$  oxides, such as  $\text{Fe}_3\text{O}_4$ . The FAC system exhibits a different scenario: its unique combination of early high aluminum, high sulfate, and moderately high pH environment may influence the crystallization of oxide phases through ion adsorption or co-precipitation mechanisms, forming a gradient structure with specific thickness and composition that differs from that of silicate cement systems. These contrasts clearly demonstrate that the passive film is not static; its final structure is a direct product of the interfacial reactions between the metal and the specific ionic environment.

According to the double-layer model, the overall protective effectiveness of the passive film relies primarily on the integrity of the  $\text{Fe}^{2+}$ -rich inner layer (such as  $\text{Fe}_3\text{O}_4$ ), which is dense, closely adherent to the metal substrate, and exhibits low conductivity. The  $\text{Fe}^{3+}$ -rich outer layer (such as  $\text{Fe}_2\text{O}_3$ ) mainly serves as a physical barrier and provides relatively weaker protection. Studies indicate that passive films formed in the highly alkaline environment of OPC, although possessing a thick  $\text{Fe}^{3+}$  outer layer, have a relatively thin  $\text{Fe}^{2+}$  inner layer, which may compromise long-term stability when exposed to localized pH decreases or aggressive ion penetration [47,48]. In contrast, passive films formed in FA-blended systems, while having a thinner  $\text{Fe}^{3+}$  surface layer, feature a thicker and better-developed  $\text{Fe}^{2+}$ -enriched inner layer. This structural characteristic suggests that, in corrosive environments, such films can offer more durable and stable electrochemical protection, as the inner layer is less susceptible to complete reduction or damage. The unique film structure formed in FAC systems may also provide corrosion resistance mechanisms distinct from those in conventional silicate cement systems.

### 3.5. Microstructure of the Passive Film

Figure 16 shows the AFM morphology of steel surfaces after passivation in pore solutions of different mix proportions. The images reveal that the steel surface is covered by an oxide film, on which nanoscale near-spherical particles are distributed. This method

allows for a more comprehensive characterization of the surface topography, and the random distribution of the particles helps to eliminate interference from surface flatness variations caused by polishing, thereby providing a more objective representation of the actual surface condition. The observed heterogeneity in particle size and distribution corroborates the multiphase chemical composition of the passive film revealed by XPS analysis.

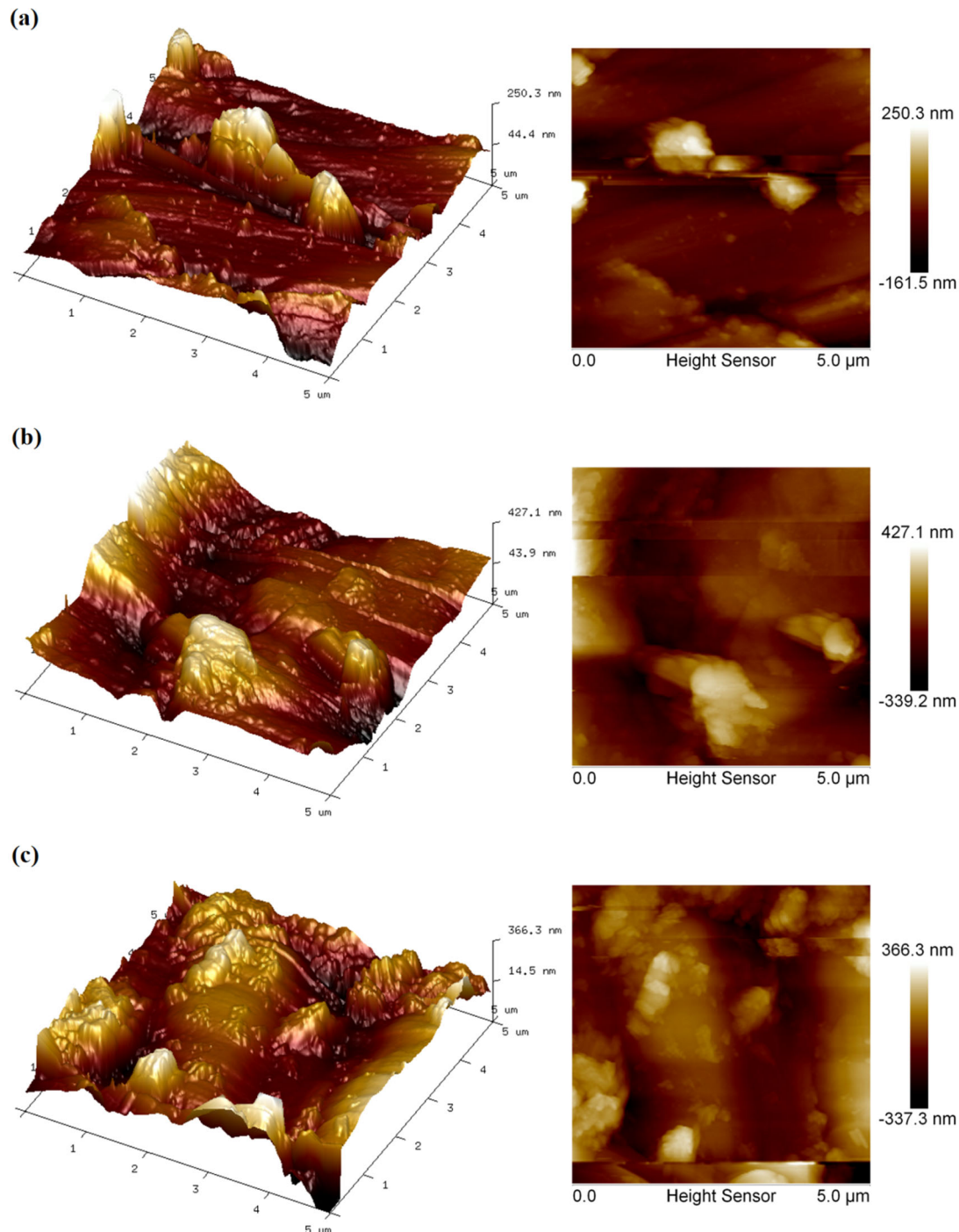
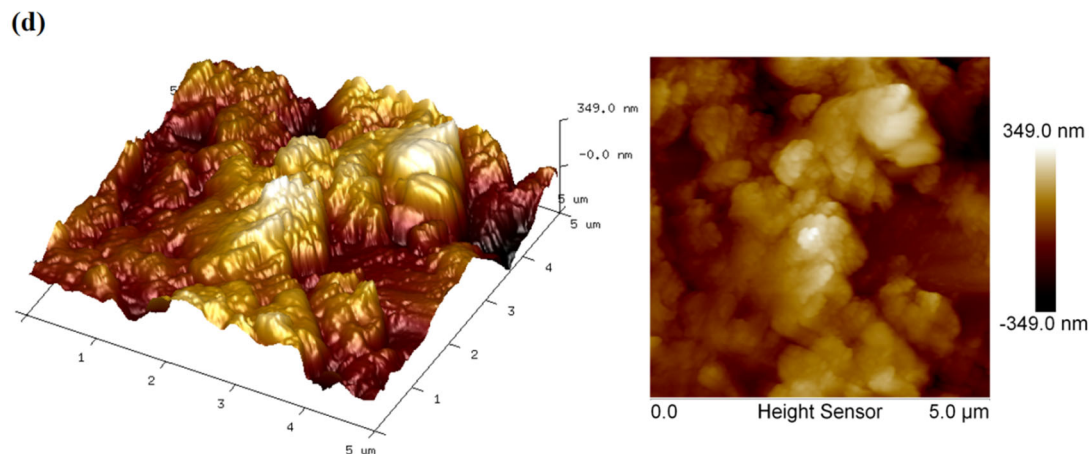


Figure 16. Cont.

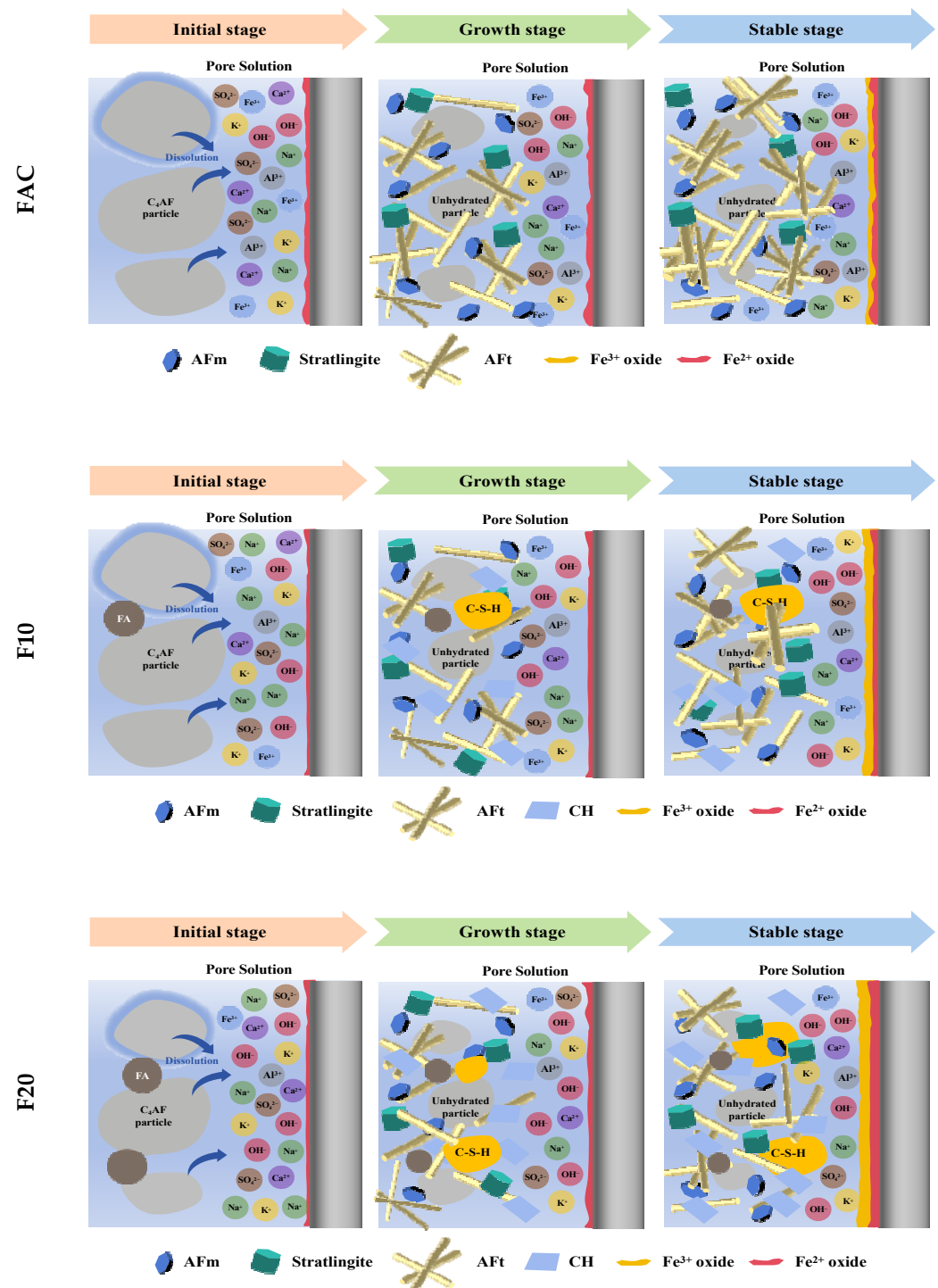


**Figure 16.** AFM Images of Steel Passivated in Mortar: (a) FAC, (b) F10, (c) F20, (d) PC.

### 3.6. Pore Solution Evolution and Reinforcement Passivation Mechanism in Ferroaluminate Systems

Figure 17 schematic illustration of the formation mechanisms of passive films on steel surfaces subjected to passivation in pore solutions with different mix proportions. Based on the combined analysis of hydration product evolution, pore solution chemistry, electrochemical response, and surface characterization, the formation and development of steel passive films in the four cementitious systems exhibit distinct mechanisms. In the PC system, the rapid hydration of  $C_3S$  and  $C_2S$  generates abundant  $Ca(OH)_2$  and C–S–H gel, establishing an extremely high-alkaline environment ( $pH > 13.5$ ) and a dense early-age microstructure. This condition promotes fast steel passivation characterized by a thick  $Fe^{3+}$ -rich outer layer ( $Fe_2O_3/FeOOH$ ) and a relatively thin  $Fe^{2+}$ -rich inner layer ( $Fe_3O_4$ ), resulting in low corrosion current densities but potentially limited long-term stability under pH reduction or aggressive ion ingress. In contrast, the FAC system, dominated by the hydration of ferroaluminate phases, forms AFt-, AFm-, and C–(A)–S–H-based matrices without  $Ca(OH)_2$  generation. Although the pore structure becomes dense, the moderate alkalinity and restricted oxygen availability constrain the growth of a well-developed  $Fe^{2+}$  inner layer, leading to incomplete passivation and persistently high electrochemical activity. When 10% FA is incorporated, the pozzolanic reaction effectively refines the pore structure and stabilizes the pore solution alkalinity, creating a favorable environment for the sustained development of a compact  $Fe^{2+}$ -enriched inner layer. The resulting passive film exhibits a pronounced chemical gradient with a thinner  $Fe^{3+}$  outer layer and a thicker, more continuous  $Fe^{2+}$  inner layer, providing enhanced and more durable electrochemical protection. However, excessive FA addition (20%) induces a dominant dilution effect, weakening early hydration and limiting later pozzolanic activation, which leads to insufficient densification of both the cement matrix and the passive film. Consequently, the  $Fe^{2+}$  inner layer remains underdeveloped, and long-term passivation stability is compromised. Overall, the results demonstrate that the protective performance of steel passive films is governed not solely by alkalinity but by the synergistic regulation of hydration products, pore structure, and pore solution chemistry, with the integrity of the  $Fe^{2+}$ -rich inner layer being the critical determinant of long-term corrosion resistance. Among the FAC-based systems investigated, the incorporation of 10 wt.% fly ash provides the most favorable balance between passive film stability, pore structure refinement, and resistance to chloride ingress. Although the OPC system exhibited superior early-age passivation owing to its higher pore solution alkalinity, the FAC–F10 system demonstrates a more balanced combination of chloride resistance, passive film stability, and

sustainability, indicating its potential as a low-carbon cementitious material for reinforced concrete exposed to chloride environments.



**Figure 17.** Pore Solution Evolution and Reinforcement Passivation Mechanism in Ferroaluminate Systems Illustration.

#### 4. Conclusions

This study employed high-pressure extraction to investigate the ion evolution in the true pore solution of ferroaluminate (FAC) cementitious mortars blended with fly ash, and examined the passivation behavior of steel in the pore solution. Triplicate parallel samples were tested for each group; however, standard deviation values are not provided herein, as

the complete raw experimental data could not be fully preserved. The main conclusions are as follows:

- (1) In the actual pore solution of FAC–fly ash mortars, the concentrations of  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ , and  $SO_4^{2-}$  decrease over time, while Al content continuously increases, and Fe exhibits a trend of initial increase followed by a decrease.
- (2) Among the FAC-based systems investigated, the incorporation of 10 wt.% fly ash provided the optimum overall performance. Compared with plain FAC, the electrochemical impedance  $R_{ct}$  remained at approximately  $0.26 \times 10^5 \Omega \cdot cm^2$ , while F10 improved pore refinement, passive film stability, and chloride resistance. Considering its low-carbon characteristics and balanced durability performance in chloride environments, the FAC–F10 system shows considerable potential for reinforced concrete exposed to chloride environments.
- (3) The passive film exhibits a chemical gradient structure of “ $Fe^{3+}$ -enriched outer layer/ $Fe^{2+}$ -enriched inner layer,” with its composition and thickness influenced by the pore solution pH and the concentrations of S, Al, and Fe. The development of the  $Fe^{2+}$ -rich inner layer is particularly critical for long-term protective performance. More importantly, this study establishes, for the first time, the coupling relationship between pore solution chemistry, hydration evolution and passive film development in FAC–FA systems.

## 5. Future Perspectives

Although this study systematically investigated the evolution of pore solution chemistry, passive film characteristics, and electrochemical behavior in FAC–FA systems, moisture transport properties were not directly evaluated. Future work will therefore include water sorptivity testing to quantitatively characterize capillary water absorption and pore connectivity. Previous studies have demonstrated that water sorptivity is an effective indicator of capillary transport characteristics, pore connectivity, and durability performance of cementitious materials [49,50]. By integrating sorptivity measurements with pore solution chemistry, electrochemical characterization, and microstructural analyses, the relationships among moisture transport, passive film evolution, and long-term corrosion resistance of FAC–fly ash systems can be more comprehensively understood.

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