

# Chloride Profile Development in Cement Paste under Immersion and Wet–Dry Cycling Determined by Neutron Activation Analysis

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## 1. Introduction

Chloride ingress is one of the primary deterioration mechanisms affecting the durability of reinforced concrete structures exposed to marine and de-icing environments. The transport of chloride ions into cementitious materials is strongly influenced by exposure conditions, particularly continuous immersion and cyclic wet–dry regimes, which govern moisture distribution and ion mobility within the pore network. While numerous studies have evaluated chloride penetration using conventional titration or potentiometric methods, high-precision depth-resolved quantification remains challenging. Neutron Activation Analysis (NAA) offers a reliable and sensitive approach for determining total chloride content without chemical extraction, enabling accurate characterization of chloride concentration profiles. This study investigates the development of chloride profiles in cement paste subjected to immersion and wet–dry cycling, with emphasis on differences in transport behavior under distinct exposure regimes.

## 2. Methods and Results

### 2.1 Chloride exposure protocols

Cement paste specimens were prepared with ordinary Portland cement and a fixed water-to-binder ratio, followed by sealed curing to minimize moisture loss prior to exposure. After curing, specimens were subjected to two chloride exposure regimes using the same NaCl solution: (i) continuous immersion and (ii) cyclic wetting–drying consisting of alternating wetting in solution and drying under controlled laboratory conditions. At selected exposure times, specimens were retrieved, rinsed to remove residual surface salt, and conditioned prior to characterization.

### 2.2 Experimental methods

Depth-resolved chloride profiles were obtained by sequentially removing material from the exposed surface and collecting powdered samples at defined depth intervals. Total chloride contents were quantified

by NAA, enabling direct determination of chloride without acid extraction and minimizing potential analytical bias associated with dissolution efficiency. The NAA-derived chloride concentration data were used to construct chloride concentration–depth profiles for each exposure condition and exposure time. Apparent diffusion parameters were determined by fitting the experimental profiles to the analytical solution of Fick’s second law for a semi-infinite medium, with the surface chloride concentration and apparent diffusion coefficient treated as fitting parameters.

To relate transport behavior to microstructural and phase changes, X-ray diffraction (XRD) was conducted on powdered samples taken from near-surface and inner regions. Phase assemblages were examined with a focus on chloride-related products and changes in hydration phases that may affect chloride binding capacity and pore structure. Complementary microstructural observations were performed using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). Polished cross-sections were prepared to evaluate morphology and spatial distribution of chloride-bearing regions across the penetration depth. Elemental maps and spot analyses (notably Cl, Al, Ca, and Si) were used to identify chloride enrichment zones and to support interpretation of chloride binding/association with aluminate-bearing hydrates.

### 2.3 Results

The results showed distinct chloride profile development between exposure conditions, evidenced by clear differences in concentration gradients, near-surface enrichment, and microstructural/phase signatures. Under continuous immersion, chloride profiles exhibited a smooth and monotonic decrease with depth, indicating progressive inward transport under persistently saturated conditions. The concentration gradient near the exposed surface was comparatively moderate and the profile shape remained stable, suggesting that chloride uptake was governed primarily by sustained ionic transport through a

continuously connected pore solution without significant drying-induced redistribution.

In contrast, wet-dry cycling produced markedly stronger near-surface chloride accumulation and a more pronounced extension of chloride presence into the interior. The elevated chloride content in the outermost region is consistent with cyclic moisture fluctuations: during wetting, chloride-bearing solution is absorbed into near-surface pores, while subsequent drying promotes evaporation-driven concentration increases and salt accumulation close to the exposed boundary. Repetition of these cycles can intensify the chloride build-up at shallow depths and facilitate intermittent advancement of chloride fronts, resulting in deeper measurable chloride occurrence compared with continuous immersion at similar exposure durations. Importantly, the wet-dry profiles were characterized not only by higher surface-adjacent concentrations but also by steeper gradients and broader penetration zones, implying that exposure-driven moisture gradients significantly modulate the spatial distribution of chlorides.

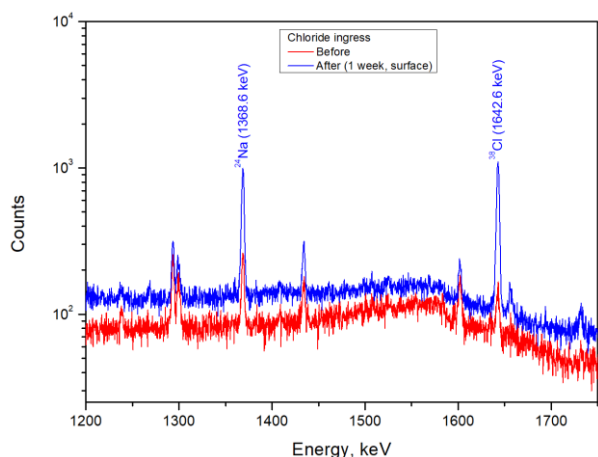


Fig. 1. NAA gamma-ray spectra of cement paste before (red) and after 1 week of chloride ingress (blue). The enhanced <sup>38</sup>Cl (1642.6 keV) peak confirms chloride ingress.

Complementary phase and microstructural analyses supported these interpretations. XRD measurements on powders collected from the near-surface region indicated exposure-dependent differences in phase assemblage, including signals attributable to Friedel's salt and changes in aluminates-bearing hydrates that are relevant to chloride association. SEM-EDS observations of polished cross-sections further revealed that chloride was not uniformly distributed; instead, localized enrichment zones were detected near the exposed surface and along microstructural features. Elemental mapping and point analyses (Cl, Ca and Al) suggested that a portion of the detected chloride was associated with specific hydrate regions rather than being solely present as freely distributed pore-solution salt. This combined evidence indicates that the observed chloride

profiles reflect the interplay of physical transport processes controlled by moisture state and chemical association with hydration products, both of which are strongly influenced by the exposure regime.

Overall, continuous immersion resulted in comparatively smooth, diffusion-like profile development under stable saturation, whereas wet-dry cycling promoted surface enrichment and extended chloride occurrence through repeated wetting-induced intake and drying-induced concentration effects. The integrated NAA quantification with XRD and SEM-EDS therefore demonstrates that realistic cyclic exposure conditions can substantially alter both the magnitude and spatial characteristics of chloride ingress in cement paste.

### 3. Conclusions

This study demonstrates that chloride profile development in cement paste is strongly dependent on exposure regime. Continuous immersion produces diffusion-controlled transport behavior, whereas wet-dry cycling promotes surface enrichment and accelerated penetration due to moisture fluctuations. Neutron Activation Analysis proved to be an effective and precise technique for depth-resolved chloride quantification, enabling robust evaluation of transport characteristics. The findings highlight the importance of considering realistic exposure conditions when assessing chloride ingress and durability performance of cementitious materials.

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