Phase Evolution, Iron Speciation, and Elemental Profiles of Cements: An Integrated XRD–NAA–Mössbauer study

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1. Introduction

Cement is one of the most essential construction materials in modern society, produced in enormous quantities worldwide. Its performance and durability are strongly influenced by the mineralogical phase composition, the oxidation states of iron, and the distribution of trace elements. These characteristics not only govern structural strength but also play a crucial role in long-term degradation behavior and environmental sustainability.

To achieve a comprehensive understanding of these features, advanced analytical techniques are indispensable. X-ray diffraction (XRD) provides valuable insights into the quantitative determination and phase evolution of clinker and hydration products. Mössbauer spectroscopy is particularly effective in elucidating the oxidation state and coordination environment of iron-bearing phases such as brownmillerite. Neutron activation analysis (NAA), on the other hand, enables precise quantification of both major and trace elements, thus supporting assessments of environmental safety and quality control. Portland cement hydration governs the evolution of phase assemblages and microstructural properties that critically affect the long-term durability of concrete. Despite its importance, limited systematic data are available for the mineralogical and compositional characteristics of commercial cement in Korea.

In this study, representative types of cement were selected and investigated using an integrated approach combining XRD, Mössbauer spectroscopy, and NAA. The results are expected to reveal complementary structural, electronic, and compositional information, offering a holistic understanding of cement chemistry. Ultimately, the findings will provide scientific evidence that can contribute to durability assessment, low-carbon material design, and the development of environmentally friendly cement.

2. Methods and Results

In this study, Korean ordinary Portland cements (OPC) were selected and characterized in an unhydrated state using XRD and NAA. Hydration was subsequently carried out for 1, 3, 7, and 30 days under controlled curing conditions. At each curing age, hydration was stopped by solvent exchange, and the samples were subjected to quantitative phase analysis by XRD. To complement these results and provide insights into the iron-bearing phases, Mössbauer spectroscopy was performed.

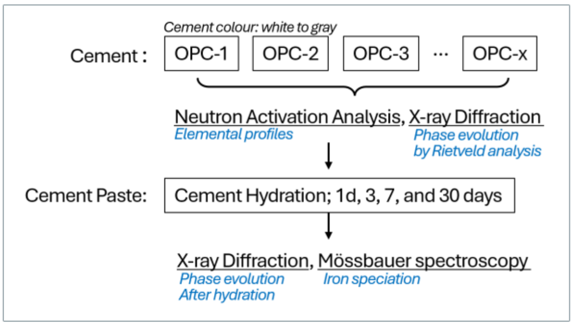

Fig.1. Simplified diagram of the experimental procedure.

NAA results revealed distinct differences in iron content between white and grey Portland cements. Grey cement consistently exhibited higher Fe concentrations, attributable to the presence of C_4AF and Fe_2O_3 phases, which during clinkering generate brown-to-black iron oxides responsible for the grey–greenish coloration of the powder. In contrast, the Fe_2O_3 content in white cement was significantly lower, consistent with the deliberate use of Fe-poor limestone and clay as raw materials. As a result, the mineralogical assemblage of white cement is dominated by Ca-rich crystalline phases such as CaO, alite (C_3S), and belite (C_2S), imparting the white appearance.

XRD analysis of the unhydrated samples confirmed this compositional distinction: alite, belite, and aluminate were the main phases in white OPC, whereas grey OPC additionally contained ferrite (C_4AF) peaks. Upon hydration, clinker peaks decreased progressively with curing time, accompanied by the development of new hydration products. In the early stage (1–3 days), ettringite and portlandite were clearly detected, while prolonged hydration (7–30 days) led to a marked increase in portlandite intensity and a gradual consumption of belite, consistent with ongoing silicate hydration.

Complementary Mössbauer spectroscopy provided further insights into Fe-bearing phases. The spectra confirmed the presence of Fe in ferrite in grey cement, in contrast to the negligible Fe signals observed for white cement. These results collectively demonstrate that the compositional differences in Fe content not only govern cement color but also influence the mineralogical evolution during hydration, highlighting the critical role of Fe-bearing phases in OPC characterization.

3. Conclusions

This study presents a novel case of integrated analysis of cement phase composition, iron oxidation states, and elemental distribution. By employing three complementary techniques—XRD, Mössbauer spectroscopy, and NAA—the research demonstrates their synergistic relationship and extends the depth of materials science interpretation in cement chemistry. From an industrial perspective, the findings provide a foundation for establishing durability and chemical resistance evaluation criteria according to the microstructural and chemical characteristics of different types of cement. Furthermore, the quantitative verification of alternative raw materials offers practical evidence for performance optimization. From an environmental perspective, the precise analysis of trace elements ensures the safe utilization of recycled materials and contributes to the development of low-carbon cements and service life prediction. Overall, this research elucidates the structural and chemical features of cement in a multidimensional manner, thereby opening new avenues for the design and quality control of sustainable and durable cementitious materials.

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