論 文 の 要 旨

題 目　IMPACT OF VARIOUS CHLORIDE SOLUTIONS ON THE LEACHING CAPACITY AND ADSORPTION/DESORPTION CHARACTERISTICS OF HEAVY METALS IN CEMENT-BASED MATERIALS
(各種塩化物溶液がセメント系材料中の重金属の溶出能力および吸脱着特性に与える影響)

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In light of growing environmental concerns, the construction industry, particularly in concrete production, has significantly contributed to global carbon dioxide emissions and resource depletion. Promoting sustainable development within the construction sector is crucial for mitigating its environmental footprint. In response, many cities are now using urban waste, industrial by-products, and construction and demolition waste (CDW) as alternative materials for concrete. For instance, granulated blast furnace slag, municipal solid waste incineration bottom ash, and fly ash are widely used as supplementary cementitious materials (SCMs). However, these additives often lead to substantial leaching of heavy metals. There is growing concern about the potential leaching of heavy metals from concrete structural components. Heavy metals typically leach through direct leaching from the surface phases and/or diffusion to the concrete surface through pore solutions, seeping into the water in contact with the concrete surface. Many past studies have shown that the leaching of heavy metals from cementitious materials depends on environmental conditions. Given that previous studies have not fully clarified how chlorides affect the fixation and leaching of heavy metals in cement hydrates, analyzing the behavior of heavy metals in concrete under different chloride environmental conditions is vital for ensuring the safety of this issue.

Limited prior research has addressed the leaching of heavy metals from concrete in chloride environments, particularly regarding how chloride influences the immobilization and leaching of heavy metals from cement hydrates. Although the effect of contact solutions has been discussed, the systematic compilation of data on the leaching of heavy metals from hardened cements with immobilized heavy metals is lacking. When the contact solution is a chloride, previous studies focused on sodium chloride. Consequently, the comprehensive understanding of the effects of various chlorides is still limited. The aim of this study was to comprehensively assess the long-term leaching of copper (Cu), zinc (Zn), and lead (Pb) from mortars exposed to sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride ($MgCl_2$), and calcium chloride ($CaCl_2$), as well as to investigate the adsorption behavior of Pb on cement hydrate and calcium silicate hydrate (CSH) under these conditions. Additionally, the study aims to explore how variations in pH, influenced by different nitric acid additions or liquid-solid ratios, impact Pb's adsorption characteristics in these chloride environments.

To achieve the aforementioned objectives, the structure of this thesis is arranged as follows:

Chapter 1 introduces the background, objectives, and methodology of this study.

Chapter 2 presents a literature review on the content of heavy metals in cement and SCMs. This chapter explores the mechanisms of heavy metal fixation and examines the impact of environmental factors, such as pH and chlorides, on heavy metal leaching. Additionally, it discusses various leaching tests used for assessing the safety of heavy metals in cement-based materials.

Chapter 3 provides a description of the experimental program, including detailing the experiments conducted to study the leaching and adsorption behavior of heavy metals in cement-based materials under various chloride environments. The experiments start by preparing sand mortar specimens using Ordinary Portland Cement (OPC) that conforms to Japanese Industrial Standards, combined with quartz sand and deionized water. The focus is on three heavy metals: Cu, Zn, and Pb, chosen due to their prevalence in supplementary cementitious materials (SCMs) and recycled aggregates. These metals are introduced into the cement mixtures in nitrate form, at a 1% ratio by mass relative to the cement, to ensure uniform distribution within the cement matrix. The specimens are prepared with two different water-to-cement ratios (0.40 and 0.55) and are subjected to a tank leaching test. This test involves placing the cured mortar specimens in polyethylene tanks filled with different chloride solutions (10 mass% concentration of NaCl, KCl, $MgCl_2$, $CaCl_2$) and deionized water, simulating various environmental conditions. The leaching behavior of heavy metals from these specimens is monitored over time, with periodic renewal of the leaching solutions and measurement of their pH values. The concentration of the leached heavy metals is quantitatively analyzed using flame atomic absorption spectrophotometry.

Additionally, the porosity of the mortar specimens is assessed both before and after their exposure to the chloride solutions using mercury intrusion porosimetry. This analysis helps understand the effect of environmental exposure on the pore structure of cement-based materials.

Furthermore, the study extends to the X-ray diffraction (XRD) analysis of the mortar samples, aiming to identify any changes in the crystalline phases of the specimens before and after immersion in the tank leaching tests. This analysis provides insights into the structural alterations within the mortar specimens and the state of the heavy metals post-exposure. To identify the reasons for the differences in the varying effects of different chlorides on Pb leaching, the study examined the penetration of chloride ions from KCl and $CaCl_2$ solutions into the mortar, as well as the distribution of Pb and Ca in the specimens post-exposure, using electron probe microanalysis (EPMA).

The chapter also delves into the adsorption characteristics of Pb, on cement paste and CSH. This analysis is achieved through adsorption tests using various chloride solutions and a nitric acid solution for pH adjustment. The study examines the impact of pH on lead adsorption by altering the liquid-to-solid ratio and using nitric acid. These tests aim to understand the interaction between lead and the cementitious materials under different environmental conditions. The synthesized CSH samples are then analyzed using XRD and energy dispersive X-ray spectroscopy (EDX) to investigate the adsorption properties and determine the Ca/Si ratios after exposure to different solutions.

Chapter 4 delves into the impact of chloride-based salts on the leaching and immobilization of heavy metals like Cu, Zn, and Pb in cement hydrates. The chapter meticulously examines how different chloride solutions affect the leaching behavior of these metals over a prolonged duration of 625 days. Observations indicated that leaching was highest in the presence of $CaCl_2$, significantly exceeding the leaching levels observed with other chloride solutions such as NaCl, KCl, and $MgCl_2$, as well as in deionized water. This finding underscores the unique role of $CaCl_2$ in enhancing heavy metal leaching from cement-based materials.

The chapter also explores how these chloride solutions influence the internal crystalline structure of the cement hydrates. Through XRD analysis, it was found that exposure to $MgCl_2$ led to the transformation of portlandite into brucite, resulting in a reduction in pH and consequently in the leachate quantities of Cu, Zn, and Pb. This transformation was not observed with other chloride solutions. Additionally, EPMA results revealed that in the case of KCl solutions, the weaker binding capacity of chloride ions compared to $CaCl_2$

may explain the lower leaching of Pb. These findings underscore the significant and varied influences of different chloride solutions on the long-term leaching behavior of heavy metals from cement-based materials.

Chapter 5 centers on the influence of various chloride solutions on the adsorption and desorption properties of Pb in hardened cement and CSH. Key findings reveal that the adsorption behavior of Pb is significantly impacted by the type of chloride solution used. Among the tested solutions, $MgCl_2$ showed the highest Pb adsorption, while $CaCl_2$ resulted in the lowest. This indicates that different chloride solutions can alter the adsorption capacity of cement hydrates for heavy metals.

The study further highlights the effect of pH on Pb adsorption, noting an increase in adsorption as the pH shifts from alkaline towards neutral. This trend, however, is not evident in the presence of chlorides, suggesting other influencing factors beyond pH. Furthermore, XRD analysis did not definitively identify Pb compounds in any samples, indicating the complexity of these interactions.

In the case of CSH, the adsorption characteristics differed based on the Ca/Si ratio and the chloride solution used. The study confirms that lower Pb adsorption on CSH correlates with higher leachate quantities in chloride solutions. It was also found that $CaCl_2$ plays a role in retaining calcium in CSH, which in turn affects Pb adsorption.

Chapter 6 describes the conclusions of this study and makes recommendations for future work.