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Summary

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学位題名論文

Application of Alkali-Activated Materials to Solidification of the Wastes Generated from On-Site and Off-Site of Fukushima Dai-Ichi Nuclear Power Station
（福島第一原子力発電所のオンサイトとオフサイトで発生している廃棄物固化へのアルカリ刺激材の応用）

The catastrophic incident at the Fukushima Daiichi Nuclear Power Station (FDNPS) on 11 March 2011, precipitated by an earthquake and subsequent tsunami, led to severe nuclear reactor meltdowns, resulting in the release of significant quantities of radioactive substances. The primary radionuclides released were cesium-134 (Cs-134) and cesium-137 (Cs-137). In the wake of this disaster, decommissioning activities at the site have concentrated on the safe removal and management of various radionuclides. This includes Cs-137, which is characterised by its high radioactivity, as well as iodine-129 (I-129) and selenium-79 (Se-79), both noted for their extended half-lives.

In Chapter 1, during the initial stages of water treatment at the FDNPS, the Simplified Active Water Retrieve and Recovery System (SARRY) implemented a system that incorporated engineered zeolite specifically for the extraction of Cs. However, this approach exhibited limited effectiveness and resulted in the generation of secondary waste. To address these limitations, the system was subsequently enhanced with the Advanced Liquid Processing System (ALPS), which improved the treatment capabilities for contaminated water. This upgrade enabled the removal of a wider range of radionuclides, with the notable exception of tritium. The process also led to the

production of slurries containing adsorbed I and Se. The spent adsorbents derived from these treatment processes are currently stored in high-integrity containers (HIC).

In areas beyond the FDNPS site (off-site), the incident led to extensive soil contamination, particularly with Cs-134 and Cs-137, predominantly adhering to the upper layers of the soil. In response, the Japanese government initiated a comprehensive soil remediation effort within a designated evacuation zone. This initiative focused on differentiating more heavily contaminated soil from less contaminated soil, with a long-term plan to permanently dispose of the highly contaminated soil outside the Fukushima Prefecture by 2045.

A significant challenge in this scenario is the effective management of low- and intermediate- level radioactive wastes, such as Cs-137, Se-79, and I-129. Conventional disposal methods, including burial in pits or trenches sites, are under investigation for their efficacy. However, the search for efficient encapsulation materials for the long-term immobilisation of these radionuclides is ongoing, as cement-based materials, typically employed for such purposes, exhibit limitations, particularly in the immobilisation of specific radionuclides.

Consequently, this study aims to explore the potential of alkali-activated materials (AAM) as a viable alternative for the encapsulation of radioactive waste. The research objectives include the assessment of capability of AAM in immobilising hazardous radionuclides, the identification of additive materials to enhance anion immobilisation, the development of effective solidification methods for offsite waste, and the proposition of suitable disposal strategies for the long-term secure storage of these wastes. This study is pivotal in bridging the gaps in existing waste management practices, particularly in the context of major nuclear disaster sites such as FDNPS.

Chapter 2 introduces Alkali-Activated Materials (AAMs), including geopolymers, tracing their history from ancient Roman times to modern developments. It highlights the evolution from early 'pozzolanic' concrete to the sophisticated materials known today, emphasizing significant contributions by scientists like Hans Kühl, Emil Langin, Glukhovsky, and Joseph Davidovits. The chapter distinguishes between geopolymers and AAMs, noting their different structural properties and formation processes.

It delves into the specifics of AAMs, focusing on binders with low calcium content, known for rapid curing and strong bonds with silicate-based aggregates. These materials are praised for their environmental sustainability and versatility in various applications, ranging from construction to hazardous waste treatment. Further, the chapter explores the mechanism and properties of AAMs, differentiating them from zeolites due to their amorphous alumina-silica structures. It covers the polymerisation models by Glukhovsky, P. Duxson, and J. Deventer, detailing the stages from dissolution to crystallisation. The importance of the dissolution process and the role of hydroxide ions in forming aluminosilicate solutions are emphasized.

The molecular architecture of AAMs is examined, discussing the principles of electrovalency and the formation of stable octet configurations through electron transfer. The chapter describes the formation of anionic stability through electron acceptance from metallic ions and oxygen-sharing interactions, leading to the formation of a disordered, zeolite-like framework. Additionally, it notes the challenges in forming Al-O-Al bonds, the importance of alkali-cations in balancing the negative charges, and the final crystallisation phase of AAMs, leading to a structure with short-range order.

The chapter concludes by focusing on potassium-based alkali-activated materials (K-AAMs). It explains the genesis of K-AAM involving metakaolin and potassium water glass, detailing the dissolution and polycondensation processes. The unique properties of K-AAMs, such as superior flowability and stability in waste encapsulation applications, are highlighted, emphasising their adaptability and long-term structural integrity.

Chapter 3 delves into the mechanisms underlying the retention of Cs, particularly Cs-137, in chabazite-type zeolite incorporated into metakaolin-based AAM. The investigation assesses the efficacy of synthetic chabazite, a zeolite mineral, in the immobilisation of Cs-137. Conventional immobilisation methods, such as vitrification and cement-based materials, have been found to be either costly or less effective, particularly in the context of Cs immobilisation. AAMs, particularly those with low calcium content, have emerged as a viable alternative, owing to their zeolite-like characteristic and their ability to form a continuous, cross-linked network of aluminate and silicate tetrahedra.

The study demonstrates that K-AAM outperforms sodium-based AAM (Na-AAM) and Ordinary Portland Cement (OPC) in immobilising Cs, as evidenced by the reduced leaching rates of Cs in K-AAM. This superior performance is attributed to the presence of chabazite within the AAM matrix. The study identifies distinct mechanisms of Cs retention at different stages of leaching. Initially, Cs is released from K-AAM but subsequently exhibits relative stability, indicating its potential for effective long-term immobilisation.

Elemental distribution analysis indicates that Cs is retained within the chabazite and AAM matrix both before and after the leaching process, although some Cs is released during the AAM fabrication. Additionally, the study notes the migration of potassium into chabazite, suggesting ion exchange processes at play. Advanced analytical techniques, including Field Emission-Electron Probe Micro Analyser (FE-EPMA), Transmission Electron Microscopy (TEM), and Raman spectroscopy, reveal that the introduction of a K-alkali activator leads to the formation of pollucite, a more stable phase for Cs retention. This finding is corroborated by observed structural changes in chabazite and the formation of new phases at ambient temperatures, a process previously believed to require high temperatures for pollucite formation.

Chapter 4 of the study delves into the application of Cs-contaminated soil from the Fukushima Daiichi Nuclear Power Station incident as a natural pozzolan in the formulation of AAM. This initiative was necessitated by the substantial radionuclide contamination, predominantly of Cs-137, which called for extensive soil remediation. The research aimed to devise an efficient strategy for the immobilisation of Cs in contaminated soil, focusing on reducing waste volume and streamlining the production process.

The experimental phase involved mixing both raw and finely ground soils with a potassium-based alkali-activator. It was observed that while mixtures with raw soils remained in a liquid state, those with finely ground soils exhibited potential for forming stable structures. The study highlighted that the amorphisation of soil contributed to the enhanced solubility of aluminium, a key factor in the generation of AAMs. Mixtures incorporating finely ground soils proved more effective in achieving structural stability, particularly at lower soil-to-water ratios.

The research identified an optimal AAM formulation comprising 60% soil and 40% alkali-activator, with a water content of 28.2%. This composition not only achieved high compressive strength but also significantly reduced the final waste volume compared to traditional Portland cement mixtures. X-ray diffraction (XRD) analysis indicated that the process of grinding the soil into finer particles increased its amorphous nature, thereby facilitating the formation of AAM. Cs leaching tests revealed that the selected AAM formulation effectively immobilised Cs, with only a minimal percentage leached after 90 days. Analyses conducted using FE-EPMA and TEM-EDS demonstrated the efficacy of the AAM structure in retaining Cs, particularly within the weathered biotite interlayers.

Chapter 5 of the study explores the interaction of 2-line ferrihydrite from iron slurry waste with K-AAM. This chapter aims to understand whether Fe^{3+} from the iron slurry dissolves and interacts with K-AAM during the manufacturing process, a critical factor in determining the stability and efficacy of K-AAM for radioactive waste encapsulation.

The study employs various analytical techniques, including XRD, FE-EPMA, and TEM, to investigate the encapsulation of 2-line ferrihydrite in K-AAM. The XRD analysis shows that the original phase of the iron slurry remains largely unchanged in the K-AAM matrix, even after 90 days of leaching. This suggests that Fe^{3+} does not significantly dissolve or incorporate into the K-AAM matrix during the fabrication process.

FE-EPMA analysis provides insight into the elemental composition of K-AAM-Fe samples. At 0 and 90 days of leaching, it is observed that silicon (Si) and aluminium (Al) penetrate the surface of 2-line ferrihydrite, while K predominantly resides on its surface. Importantly, there is minimal to no accumulation of Fe within the K-AAM matrix, indicating that Fe^{3+} from the 2-line ferrihydrite remains largely undissolved.

TEM analysis further elucidates the potential incorporation of Fe^{3+}. It reveals no Fe^{3+} incorporation in the K-AAM area, and the selected area electron diffraction (SAED) pattern shows an amorphous phase typical of AAM. At the interface between K-AAM and 2-line ferrihydrite, and in the iron slurry area, the SAED ring patterns show increased Fe concentration, suggesting a low solubility of 2-line ferrihydrite, particularly at elevated pH levels.

The study concludes that 2-line ferrihydrite exhibits low solubility in the K-AAM environment during the fabrication process, mainly because potassium binds to its surface. This binding, along with the presence of Si and Al, plays a crucial role in inhibiting the dissolution of 2-line ferrihydrite. The study demonstrates the structural integrity of K-AAM, which remains preserved even after 90 days of leaching, suggesting that 2-line ferrihydrite remains largely intact without significant dissolution or Fe^{3+} incorporation into the K-AAM.

Chapter 6 of the study investigates the immobilisation of I-129, a radionuclide characterised by its volatility and extended half-life, within AAM. The high volatility and prolonged half-life of I-129 render it a significant environmental hazard, and its complex chemical nature and mobility present challenges in its effective immobilisation. This study focused on the immobilisation of I^- rather than IO_3^- because the former is more common in environmental contexts.

The initial findings of the study revealed rapid leaching of I^- from K-AAM in the absence of additives, indicating a lack of effective immobilisation. To address this, the research incorporated various additives into the K-AAM matrix, including layered double hydroxides (LDH), magnesium oxide (MgO), and silver nitrate ($AgNO_3$), to enhance the retention of I-129.

The incorporation of LDH into K-AAM demonstrated limited success in immobilising I^-, with complete leaching observed within a day. This phenomenon was attributed to the transient adsorption of I^- onto the interlayers of LDH, which was subsequently displaced by other anions. TEM analysis affirmed the structural stability of LDH within the K-AAM matrix but also indicated weak adsorption of I^-.

The addition of MgO to K-AAM was similarly less effective in immobilising I-129, with a leaching rate of 94% within 7 hours. Initially, MgO led to the formation of brucite, which gradually dissolved, and the Mg/Al ratio proved unfavourable for the formation of hydrotalcite, an anion-immobilising structure. Conversely, $AgNO_3$ emerged as the most effective additive in immobilising I^- within the K-AAM matrix. The study observed a significant reduction in I^- leaching, particularly when the Ag/I molar ratio was optimally adjusted. Notably, in the K-AAM-2Ag50 sample, where the Ag/I molar ratio was 2:1 with an I^- concentration of 50 ppm, I-129 leaching was reduced to zero. This outcome was linked to the formation of stable silver iodide (AgI) within the matrix, as evidenced by XRD and FE-EPMA analyses.

Chapter 7 of the study delves into the intricate mechanisms behind the retention of selenite (SeO_3^{2-}) in metakaolin-based AAM, with a particular emphasis on comparing the immobilisation capabilities of K-AAM and Na-AAM. This investigation is driven by the urgent need for effective long-term strategies to immobilise anionic radionuclides like Se-79, which present significant challenges due to their high concentrations and prolonged half-lives, especially in the context of the Fukushima Daiichi Nuclear Power Station disaster.

The study uncovers that the K-AAM matrix exhibits a notably superior ability to immobilise SeO_3^{2-} compared to Na-AAM. While Na-AAM demonstrated complete Se leaching within 19 days, K-AAM showed only a 12.50% Se leaching rate after 90 days, stabilising after 19 days. This finding highlights the enhanced efficacy of K-AAM in retaining SeO_3^{2-}.

In terms of elemental leaching and distribution, the study observed distinct differences in the leaching of Si, Al, and alkali cations (Na or K) between control samples and those containing SeO_3^{2-}. In Na-AAM, the presence of SeO_3^{2-} seemed to encourage the formation of phases requiring higher concentrations of Si and Al. However, in K-AAM, the leaching rates of Si and Al remained consistent, suggesting that Si might not play a significant role in SeO_3^{2-} retention within the matrix.

FE-EPMA analysis indicated an even distribution of SeO_3^{2-} in K-AAM, in stark contrast to its complete leaching in Na-AAM after 90 days.

XRD analysis revealed that both K-AAM and Na-AAM predominantly maintained an amorphous phase, with no secondary phase formations observed in K-AAM, irrespective of SeO_3^{2-} addition. This implies that the incorporation of SeO_3^{2-} does not significantly alter the amorphous structure of K-AAM. TEM analysis showed that K-AAM retained its amorphous structure even after 90 days of leaching, with SeO_3^{2-} integrated into its structure. In contrast, Na-AAM evolved into a more defined zeolitic form after 90 days, devoid of any SeO_3^{2-} traces, indicating the release of $SeO_3^{2-}$from Na-AAM.

Raman spectroscopy findings suggested that the introduction of SeO_3^{2-} into K-AAM led to alterations in the ring and chain structures, indicating interactions between SeO_3^{2-} and Al, thereby modifying the matrix structure. The ^{27}Al- and ^{29}Si-MAS-NMR analyses corroborated the tetrahedral positioning of Al in the presence of SeO_3^{2-} and demonstrated an increased coordination of Al with Si in K-AAM. This points to a distinct binding mechanism of SeO_3^{2-} within the K-AAM matrix.

Chapter 8 of the study undertakes a critical evaluation of the safety and efficacy of various underground disposal methods for managing radioactive waste from the Fukushima Daiichi Nuclear Power Station (FDNPS). Utilizing the advanced capabilities of GoldSim software, the research simulates the migration of radionuclides through different disposal strategies, including trench, pit, and subsurface disposal. The primary objective is to ensure that radiation exposure remains within the stringent safety threshold of 10 μSv/y.

The study presents significant findings regarding the disposal of Cs-137, particularly when embedded in K-AAM. It identifies pit disposal as a more suitable method than trench disposal for Cs-137 in chabazite embedded in K-AAM. This conclusion is drawn from the observation that the highest exposure in trench disposal was approximately 1 mSv/y, primarily affecting livestock grazing on the soil. In stark contrast, pit disposal demonstrated a significantly lower exposure level of around 0.001 μSv/y, underscoring its effectiveness for long-term underground disposal of Cs.

Additionally, the study assesses the release of Cs-137 from contaminated soil in Fukushima when embedded into K-AAM. The findings indicate that trench disposal is adequate for managing this type of waste, with no pathways exceeding the established safety limits. The highest exposure level recorded was a mere 1.7×10^{-3} mSv/y through the intake of crops grown in the contaminated soil. This suggests that trench disposal is a sufficient and cost-effective method for handling Cs-contaminated soil from Fukushima, negating the need for the more expensive pit disposal methods.

Furthermore, the research explores the disposal of I-129 and Se-79 when embedded in iron slurry within K-AAM. The study reveals that both trench and pit disposal methods are viable options for these waste forms. The highest level of radioactive exposure was observed in residents consuming crops grown in contaminated areas, with selenium showing a slightly higher exposure level of approximately 1×10^{-2} μSv/y, compared to iodine's exposure level of around 1×10^{-3} μSv/y. This finding confirms the feasibility of using either disposal method for these types of radioactive waste.

In summary, the comprehensive study conducted on the management of radioactive waste from FDNPS presents several key findings across various chapters. The research demonstrates the effectiveness of K-AAMs in trapping Cs in spent chabazite and soil. The charge-balancing cation K^+ aids in forming stable ceramic phases, such as pollucite, which efficiently retain Cs^+. K-AAMs also excel in binding with fine Cs-contaminated soil particles, creating a compact honeycomb-like structure that encapsulates Cs ions securely.

The study highlights K-AAMs' ability to immobilise long-lived radionuclides like I^- and SeO_3^{2-} in iron slurry waste. The addition of $AgNO_3$ significantly improves the immobilisation of I^-, outperforming other additives. K-AAMs' amorphous structure promotes strong interactions with elements like aluminium, enhancing the immobilisation of SeO_3^{2-}.

For waste disposal, K-AAMs meet safety standards for handling Cs in chabazite and soil, recommending pit and trench disposal methods, respectively. They also effectively encapsulate I- and SeO_3^{2-} in iron slurry, suggesting their viability for long-term containment. K-AAMs' adaptability in cation exchange and bond formation with various radionuclides is noted, especially in creating stable containment phases and accommodating coordination numbers of 4 to 12.

The study concludes that K-AAMs offer an ecologically responsible option for sustainable radioactive waste management. They reduce waste volume and adapt to various disposal methods, highlighting their suitability for long-term waste management strategies. The findings endorse the integration of K-AAMs into FDNPS's waste management strategy, emphasizing their superiority in managing diverse types of waste.

Future research is suggested to focus on optimising the fabrication process for large-scale encapsulation and broadening the scope of immobilisation studies to include additional oxyanions and other spent wastes from FDNPS. This includes refining the initial mixing approach, exploring the immobilisation of other radionuclides, and examining alternative methods for elements resistant to immobilisation within the K-AAM matrix. The expanded scope of this research aims to enhance our understanding of these materials' interactions with the K-AAM matrix and assess broader waste encapsulation applications. This will contribute significantly to developing safer and more efficient strategies for radioactive waste management.