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Interfacial Control of B_4C-Filled Boron Geopolymers for Enhanced Neutron Shielding

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Abstract

Metakaolin-based geopolymers incorporating boron carbide (B_4C) as a neutron-absorbing filler show promise for radioactive waste remediation. However, B_4C's weakly polar, negatively charged surface causes poor interfacial bonding, leading to reduced mechanical and chemical stability. In this study, cetyltrimethylammonium bromide (CTAB) was introduced to modify the B_4C surface, reversing its charge and improving dispersion. Although CTAB slightly hindered metakaolin dissolution, it preferentially interacted with B_4C, mitigating negative effects on geopolymerisation. CTAB also promoted gel formation in the interfacial transition zone, forming a dense, stable microstructure. The synergistic effect of B_4C and CTAB enhanced interfacial bonding, mechanical strength, and neutron shielding performance, offering a viable pathway to develop multifunctional geopolymer composites for nuclear applications.

Keywords: Alkali-activated metakaolin-based geopolymer; Boron carbide; CTAB; Interface transition zone (ITZ); Neutron shielding

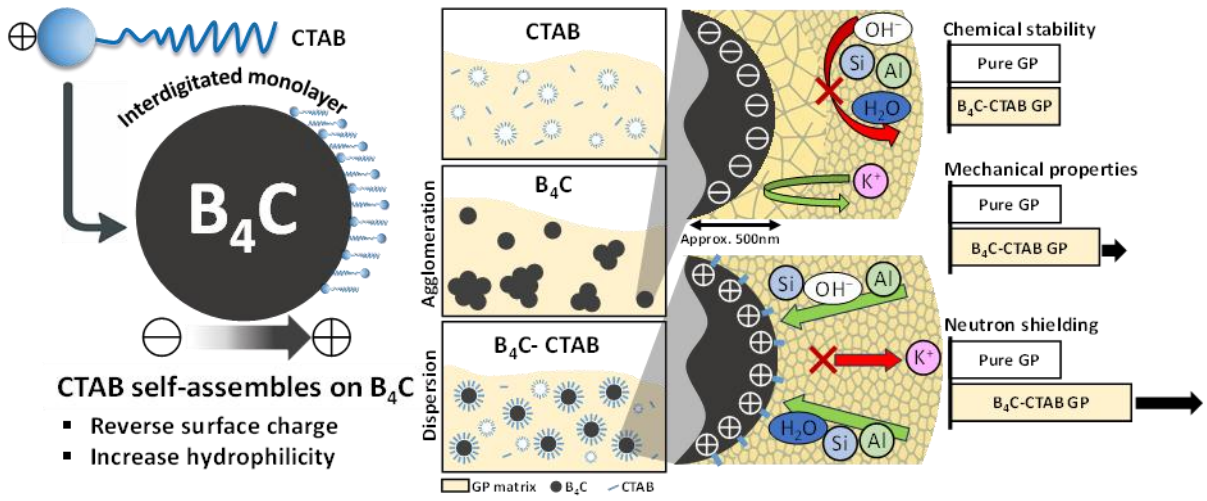

Figure 1: Schematic representation of CTAB-induced surface modification of B_4C, promoting uniform dispersion in the geopolymer matrix and facilitating the formation of dense interfacial transition zones.

1 Introduction and methodology

The Fukushima Daiichi Nuclear Power Plant (1F) accident in 2011 resulted in the generation of complex radioactive waste streams, including molten core–concrete interaction (MCCI) debris, activated structural materials, and radionuclide-contaminated water and solids [1]. Among the various radiation types emitted, neutron radiation poses unique and significant challenges. Neutrons are electrically neutral and highly penetrating, making them difficult to shield. Additionally, neutron interactions with matter can induce secondary activation, complicating long-term storage and increasing biological hazards such as internal irradiation and DNA damage [2].

To address these challenges, alkali-activated geopolymers have emerged as promising encapsulation matrices due to their high chemical durability, mechanical strength, and ability to immobilise cationic radionuclides (e.g., Cs^{+}, Sr^{2+}, Co^{2+}) [3]. However, geopolymers lack inherent neutron attenuation capacity. Therefore, incorporating neutron-absorbing materials such as boron carbide (B_4C) offers a viable strategy to improve shielding performance. B_4C contains a high fraction of ^{10}B, which has a strong neutron capture cross-section (~3837 barns) [4].

Previous studies have explored the addition of boric acid (H_3BO_3) into geopolymers, enabling partial incorporation of BO_4 units into the matrix, though concerns remained regarding long-term stability and permeability. B_4C, by contrast, is chemically inert and has been investigated as a filler in cementitious materials. However, due to its hydrophobicity, negative surface charge, and poor wettability, B_4C tends to agglomerate and segregate during mixing and curing, resulting in weak interfacial bonding and poor mechanical performance.

To overcome these interfacial challenges, this study introduces cetyltrimethylammonium bromide (CTAB), a cationic surfactant, to modify the B_4C surface. CTAB has shown effectiveness in modifying particle surface charge and improving dispersion in cementitious systems [5]. Its quaternary ammonium head group reverses the negative charge on B_4C, enabling electrostatic attraction with aluminosilicate species in the matrix and promoting the formation of a denser interfacial transition zone (ITZ).

In this study, metakaolin-based geopolymer pastes were prepared with varying B_4C contents (1–10 wt.%) and CTAB levels (index 3–30). Zeta potential and solubility tests were conducted to evaluate particle interaction and MK dissolution. Slump flow and chemical deformation tests were used to assess rheological properties and early-stage reaction kinetics. Hardened samples were characterised via compressive strength testing, solid-state MAS NMR (^{29}Si, ^{27}Al, ^{11}B), XRD, FE-EPMA, and TEM/STEM. Elemental leaching was examined under simulated near-field conditions, and neutron shielding was quantified using cold neutron transmission imaging at AISTANS.

This integrated approach clarifies how CTAB-mediated interfacial engineering improves B_4C dispersion, strengthens the matrix–filler interface, and enables the design of multifunctional geopolymers with improved neutron attenuation, durability, and mechanical performance.

2 Conclusion

(1) CTAB-assisted interfacial control and charge reversal

Zeta potential measurements confirmed that B_4C and MK particles both carried negative surface charges in alkaline media. Upon the addition of CTAB, the surface charge of B_4C reversed from negative to positive, promoting better dispersion and facilitating electrostatic interactions with negatively charged silicate and aluminate species. CTAB formed an interdigitated monolayer on the B_4C surface, improving wettability and stabilising particle distribution in the matrix. Molecular simulation of CTAB demonstrated its positive electrostatic potential at the quaternary ammonium site, supporting its strong surface activity.

(2) Influence on geopolymerisation and fresh paste behaviour

Dissolution tests showed that CTAB slightly inhibited the dissolution of MK, especially in the absence of B_4C. This inhibition was mitigated in

B_4C-containing systems due to the preferential adsorption of CTAB onto B_4C particles. Flowability tests revealed that B_4C enhanced initial paste fluidity, while CTAB further delayed setting and reduced flowability loss. Chemical deformation analysis showed volumetric expansion during early curing, which was suppressed by CTAB due to micelle-induced porosity acting as strain buffers.

(3) Mechanical and microstructural performance

Despite increased porosity, CTAB significantly improved compressive strength in B_4C-filled systems by enhancing filler dispersion and strengthening the ITZ. XRD patterns confirmed the preservation of B_4C crystallinity and the development of typical amorphous geopolymer structures. MAS NMR revealed that CTAB slightly suppressed MK depolymerisation but improved network formation at the B_4C interface. ^{29}Si and ^{27}Al spectra showed a higher proportion of oligomeric species and lower Al_6 content in CTAB-free samples, while CTAB-containing systems exhibited increased crosslinking.

Microscopic analyses demonstrated a dramatic transformation of the ITZ upon CTAB addition. Without CTAB, a weak, porous shell formed around B_4C due to repulsive interactions with OH^- and silicate species. With CTAB, a dense, K^+-deficient, but electrostatically stabilised gel structure was formed around the filler, ensuring mechanical integration and stress transfer. TEM/STEM mapping confirmed the elemental accumulation (Si, Al, K) and improved interface continuity.

(4) Environmental stability and neutron shielding performance

Leaching tests revealed that elemental release of Si and Al remained low in all systems but decreased further with CTAB. B leaching was mainly dependent on the exposed surface area of B_4C, which was minimised in dense matrices. CTAB promoted matrix densification and suppressed the mobility of unreacted monomeric species, contributing to higher chemical stability.

Neutron transmission imaging showed that B_4C incorporation significantly enhanced shielding performance, with $\geqslant$80% attenuation observed in 10 mm thick samples. CTAB-containing samples exhibited more compact grayscale profiles, indicating denser internal structure and improved neutron absorption.

3 Significance

This study provides a comprehensive understanding of how surfactant-assisted interface engineering can overcome key limitations in neutron-shielding geopolymer design. The synergistic interaction between CTAB and B_4C not only improves filler dispersion and mechanical strength but also enhances chemical stability and neutron attenuation capacity. These findings offer a viable pathway toward the development of multifunctional, radiation-resistant geopolymers for the safe solidification and long-term disposal of radioactive wastes.

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