

Fabrication and Performance Study of Nano-Aluminum-Based Modified Positively Charged Purification Materials for Nuclear Power Plant Coolants

Authors: Tao Liu

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Abstract

In nuclear power plant operation, coolant impurity filtration constitutes a critical component for ensuring safe and efficient system operation and extending equipment lifespan. However, existing filtration materials exhibit prominent issues including high import dependence (resulting in elevated procurement costs and prolonged after-sales cycles), high leaching rates of soluble silicon and sulfate ions from conventional glass fiber filter media (reaching 21 ppm and 141 ppm respectively), and insufficient filtration efficiency (0.45 μ m particle retention rate of merely 86.83%). This study proposes a domestic solution based on nano-aluminum powder modified glass fiber: through a one-step hydrothermal method, an AlOOH nanolayer was in-situ grafted onto the glass fiber surface, successfully fabricating a novel composite filter material featuring stable positive Zeta potential (+11 mV). Experimental results demonstrate that this material enhances the retention efficiency for 0.45 μ m latex spheres to 99.95%, reduces the leaching rates of soluble silicon and sulfate ions by 87.64% and 84.43% respectively compared to imported products, while maintaining a dirt holding capacity comparable to imported filter media (60.57 g/cm³). This achievement breaks through the “bottleneck” technical constraints of nuclear-grade filter materials, providing crucial technical support for improving primary loop coolant purification efficiency and reducing radiation exposure risks for operation and maintenance personnel.

Full Text

Construction and Properties of Positively Charged Purification Material for Nuclear Power Plant Coolant Based on Nano-Aluminum Modification

Tao Liu, Yongguo Li*, Haixia Kong, Jia Wang, Mang Wang, Xin Chen, Xu Shi, Shuwei Liang, Zhixin Liu, Yingzhong Shuang

1. Institute of Environmental Engineering Technology, China Institute for Radiation Protection, Taiyuan, Shanxi 030006, China
2. CNNC Key Laboratory of Radioactive Gas Purification Technology, China Institute for Radiation Protection, Taiyuan, Shanxi 030006, China
3. Shanxi Provincial Engineering Center for Radioactive Gas Purification, Taiyuan, Shanxi 030006, China

Abstract

In nuclear power plant operations, the filtration of coolant impurities is a critical link for ensuring safe and efficient system operation and extending equipment lifespan. However, existing filter materials suffer from several prominent issues: high import dependence (resulting in high procurement costs and long after-sales cycles), high leaching rates of soluble silicon and sulfate ions from traditional glass fiber filter materials (reaching 21 ppm and 141 ppm, respectively), and insufficient filtration efficiency (0.45 μ m particle retention rate is only 86.83%). This study proposes a domestic solution based on nano-aluminum powder modified glass fiber: a novel composite filter material with stable positive Zeta potential (+11 mV) was successfully prepared by in-situ grafting of AlOOH nanolayers onto glass fiber surfaces via a one-step hydrothermal method. Experimental results demonstrate that the material's retention efficiency for 0.45 μ m latex spheres increased to 99.95%, while the leaching rates of soluble silicon and sulfate ions decreased by 87.64% and 84.43%, respectively, compared with imported products, all while maintaining equivalent dirt-holding capacity (60.57 g/cm³). This achievement breaks through the technical bottleneck of "chokepoint" issues in nuclear-grade filter materials and provides important technical support for improving primary coolant purification efficiency and reducing radiation exposure risks for operation and maintenance personnel.

Keywords: Nuclear power plant; Glass fiber; Positive Zeta potential; Soluble silicon; Sulfate

Introduction

As of April 2024, China has become the world's largest nuclear power capacity nation [1]. According to the latest data, China's nuclear power capacity exceeds 50 units with total installed capacity surpassing 50 GW, accounting for over 40% of global nuclear power capacity. These nuclear plants typically employ pressurized water reactor (PWR) technology, which represents the most common and mature nuclear power technology currently available [2]. The primary coolant circuit conditions constitute a crucial aspect of nuclear power plant operation. Primary coolant serves as the medium that removes heat generated in the nuclear reactor. In PWRs, purified water is typically used as the coolant, which flows through fuel assemblies in the reactor core to absorb heat before transferring it to the steam generator [3]. The stability of primary coolant conditions directly affects nuclear power plant operational safety and efficiency. Plants require regular chemical analysis and treatment of coolant to prevent corrosion, deposition, and other adverse phenomena [4].

AlOOH has been widely used as a modification material due to its excellent electrostatic adsorption properties and large specific surface area. Lu Mingxia et al. prepared fibrous AlOOH using aluminum powder as the aluminum source and verified its adsorption effectiveness for Cd^{2+} metal ions in water, demonstrating that AlOOH possesses good electrostatic adsorption properties [5]. Regarding fiber modification, Miao et al. [6] grafted specifically morphological AlOOH onto electrospun glass fibers via hydrothermal reaction, achieving favorable adsorption effects for Congo red dye. Guo Xiaorui et al. [7] prepared hierarchical AlOOH structures using hydrothermal methods and ultimately verified their electrostatic adsorption performance. Hsing-Wang Li et al. [8] developed a novel alumina nanofiber filter demonstrating good potential for removing and retaining viral aerosols.

In recent years, fiber modification research has become a hot topic in materials science, as it not only maintains the inherent characteristics of fibers but also imparts superior properties tailored to practical application requirements. This study employs glass fiber as the substrate material and nano-scale aluminum powder as the raw material to generate AlOOH via a one-step hydrothermal method for surface modification. This approach endows the material with positive Zeta potential on its surface [9] while improving filtration efficiency and reducing leaching of soluble silicon and sulfate, which holds significant importance for the safe operation of PWR primary circuits and improving nuclear power generation efficiency.

Experimental Methods

2.1 Materials and Reagents

Nano-scale aluminum powder (50 nm, Shanghai Maoguo Nano Technology), glass fiber (diameter approximately 1 μm), Congo red dye (Shanghai Aladdin Biochemical Technology Co., Ltd.), deionized water, latex sphere suspension

(Thermo Fisher Scientific).

2.2 Preparation of Modified Glass Fiber Filter Material

Nano-scale aluminum powder (0.5 g) was ultrasonically dispersed in 300 ml deionized water, followed by addition of 1.0 g glass fiber and thorough mixing. The prepared mixture was heated to boiling before terminating the reaction, then naturally cooled to room temperature. Finally, the reaction product was formed into sheets using a sheet-making machine.

2.3 Filtration Efficiency and Dirt-Holding Capacity Tests

Filter material efficiency experiments monitor the filtration performance for particles of specific sizes. During testing, the experimental fluid consisted of deionized water containing latex sphere particles at a concentration of approximately 10^5 particles/ml (0.2 μ m latex spheres). The experimental flow rate was 75 L/h, with continuous injection of contaminants into the test chamber. A differential pressure gauge monitored the pressure drop across the filter. The experiment concluded after 1 hour. During the test, downstream samples were collected every 5 minutes and upstream samples every 10 minutes. A liquid particle counter was used for particle counting and statistics to calculate filter efficiency. Filtration efficiency represents a critical performance metric for filter materials. Upstream and downstream samples were collected at identical time intervals and counted using an SLS-1200 particle counter (EMIN GROUP), with filtration efficiency calculated using Equation (4.1).

Dirt-holding capacity testing employed experimental dust from PTI Company (USA) at an injection concentration of 10 ppm and flow rate of 75 L/h. The test was terminated when the pressure differential across the filter reached 0.25 MPa, at which point the experimental time was recorded and dirt-holding capacity was calculated according to Equation (4.1).

Equation (4.1)

Where: N is the dirt-holding capacity (g/m^2); t is the dirt-holding time; Q is the experimental flow rate (L/h); c is the test solution concentration (g/L); S is the filter area (m^2).

2.4 Dye Static Adsorption Test

To verify the electrostatic adsorption capacity of modified glass fiber for negatively charged colloids in coolant, an anionic dye (Congo red) was selected to demonstrate this capability. The adsorption effect was characterized using C/C_0 , where concentrations after adsorption at identical time intervals were determined via calibration curves.

Glass fiber filter materials of identical area were cut, surface-cleaned, and placed into three identical polytetrafluoroethylene bottles. Simulated coolant water (boric acid: 2500 ppm, lithium hydroxide: 3.4 ppm) was added to each bottle.

Samples were taken on days 1, 3, 5, 7, and 14 post-immersion. Soluble silicon leaching was measured using the silicon molybdenum blue method, while SO_4^{2-} concentration was determined via liquid chromatography.

The grafted ALOOH can serve as a positively charged adsorbent [10] for removing negatively charged impurities from water. Congo red, a common azo dye in the textile industry, was selected as a typical water pollutant and anionic dye for adsorption measurements. Adsorption tests were conducted using fixed fiber weight and fixed Congo red solution volume (50 mg/L). At selected time intervals, Congo red solution concentration was measured at 500 nm using a QQJFS-01 UV-Vis spectrophotometer. A calibration curve was prepared by measuring absorbance of samples at predetermined concentrations. Relative adsorption capacity was characterized by C/C_0 (where C_0 and C represent initial and post-adsorption Congo red concentrations, respectively). Simultaneously, saturation adsorption of Congo red dye by different grafted fibers was determined at identical mass.

2.5 Filter Element Leaching Experiment

A 100 cm² filter material was cut into four equal portions, rinsed and wetted with deionized water, then placed in a sample bottle containing 250 ml leaching solution (water quality: B-2500 ppm, Li-3.4 ppm), ensuring complete immersion. Labeled sample bottles were placed in a 60°C water bath for periodic sampling and analysis at 1, 3, 5, 7, and 14 days.

Soluble silicon detection employed the silicon molybdenum blue method. This method's principle involves reaction of ammonium molybdate with silicon dioxide in the leachate under acidic conditions to form a yellow soluble silicomolybdic acid complex, which is then reduced by 1,2,4-aminonaphtholsulfonic acid to silicon molybdenum blue. The blue color intensity is directly proportional to silica concentration within a certain range—deeper blue indicates higher silica content. Leachate silica concentration was determined by measuring absorbance against a silica standard curve. Sulfate ion concentration was measured using liquid ion chromatography.

2.6 Filtration Process Simulation

Ansys Workbench software was utilized to simulate pressure and velocity variations during filtration, comparing the effects of unmodified versus modified filter materials on pressure drop and flow rate [11]. The simulation workflow is shown in [Figure 1: see original paper].

Figure 1. Simulation flowchart

Results and Discussion

3.1 Morphology and Crystal Characterization

[Figure 2: see original paper] shows SEM images of glass fibers before and after grafting: (a) pure glass fiber; (b) post-grafting glass fiber. Pure glass fibers exhibit smooth surfaces with diameters of approximately 1 μm . In contrast, post-grafting glass fiber surfaces are coated with a dense, flaky structured material approximately 50 nm thick, with a grafting thickness of about 1 μm .

[Figure 3: see original paper] presents FTIR spectra of grafted glass fibers. Literature [10] indicates that the peak near 3450 cm^{-1} arises from hydroxyl vibration in water. Additionally, the peak near 2090 cm^{-1} can be attributed to superposition of -OH group vibrations on the AlOOH surface [12]. The characteristic peak near 1635 cm^{-1} is associated with stretching vibrations of -OH groups in hydroxide structures and physically adsorbed water [13], while the peak near 1070 cm^{-1} originates from Al-O-H vibrations in AlOOH. To ensure experimental accuracy, different amounts of glass fiber were used for grafting, with consistent results obtained.

Figure 3. FTIR spectra of glass fibers before and after modification

3.2 Dye Static Adsorption Results

[Figure 4: see original paper] illustrates static dye adsorption: (a) linear fitting equation; (b) static adsorption curve. The calibration curve shows an R^2 value exceeding 99.9%, indicating excellent model fit. Using this calibration curve to obtain concentrations at different adsorption times and plotting C/C_0 curves reveals that modified glass fiber exhibits superior Congo red dye adsorption compared to pure glass fiber, achieving complete adsorption of certain dye concentrations after 90 minutes. As shown in [Figure 5: see original paper], this is primarily attributed to the positive charge of AlOOH attached to the glass fiber surface, enabling effective adsorption of anionic Congo red dye.

Figure 5. Zeta potential values of glass fiber filter media before and after modification

3.3 Filtration Efficiency and Dirt-Holding Capacity Results

[Figure 6: see original paper] presents filtration efficiency and dirt-holding capacity comparisons: (a) 0.2-2 μm latex sphere filtration efficiency; (b) 0.45 μm latex sphere filtration efficiency and dirt-holding capacity comparison. For 0.2-2 μm latex spheres, modified glass fiber filter material demonstrates overall superior performance compared to Canadian NTI series products and pure glass fiber filter material. For 0.45 μm latex spheres, modified glass fiber filter material achieves 99.84% filtration efficiency, significantly higher than NTI company products and pure glass fiber filter material. In terms of dirt-holding capacity, both Canadian NTI company products and modified glass fiber filter material

outperform pure glass fiber filter material, with modified glass fiber filter material maintaining high filtration efficiency while achieving dirt-holding capacity essentially equivalent to NTI company products. This is attributed to the increased diameter and thickness of modified glass fiber filter material compared to the original.

3.4 Filter Element Leaching Results

[Figure 7: see original paper] compares soluble silicon and sulfate leaching concentrations for our experimental samples against unmodified filter material and NTI company products. Our experimental sample shows significantly lower 14-day soluble silicon leaching compared to both pure glass fiber filter material and NTI company products. This is likely because the grafted AIOOH effectively encapsulates the glass fiber surface, preventing direct contact between the leaching solution and glass fiber, thereby substantially reducing soluble silicon leaching. For sulfate leaching, our experimental sample shows levels essentially equivalent to pure glass fiber filter material but far lower than NTI company products, primarily because our experimental design optimized the process to avoid sulfate introduction from the source, thus reducing sulfate leaching.

Figure 7. Comparison chart of soluble silicon and sulfate leaching concentrations: (a) soluble silicon leaching amount (b) sulfate leaching amount

3.5 Filtration Process Simulation Results

[Figure 8: see original paper] demonstrates that at the filter material location, fluid velocity decreases due to the blocking effect. However, the velocity change trends differ between pre- and post-modification materials. Pre-modification filter material causes greater velocity changes before and after passing through the filter, while post-modification filter material shows relatively smaller velocity variations, indicating better permeability of the modified filter material.

Figure 8. Velocity simulation effect cloud map: (1) Simulation of filter material before modification (2) Simulation of filter material after modification

[Figure 9: see original paper] shows that at the filter material location, fluid pressure decreases due to the blocking effect, with different pressure trends for pre- and post-modification materials. Pre-modification filter material exhibits larger pressure differentials, suggesting greater thickness or poorer water permeability. Post-modification filter material shows smaller pressure drop effects, with less pressure reduction compared to pre-modification material, demonstrating that modified filter material can reduce thickness while maintaining equivalent filtration efficiency and improving filtrate permeability.

Figure 9. Cloud diagram of pressure drop simulation effect: (1) Simulation of filter material before modification (2) Simulation of filter

material after modification

Conclusion

To address issues of high soluble silicon and sulfate leaching in currently used glass fiber filter materials in power plants, this study employed nano-aluminum powder as raw material to load AlOOH onto glass fiber surfaces via a one-step hydrothermal method, preparing positively charged Zeta potential glass fiber filter material. The electrostatic adsorption, filtration efficiency, soluble silicon leaching, sulfate leaching, and dirt-holding capacity of the modified glass fiber filter material were evaluated.

1. FT-IR spectra reveal distinct AlOOH characteristic peaks in modified glass fiber. SEM images show a dense flaky substance grafted onto the glass fiber surface. Combined FT-IR and SEM results confirm successful grafting of flaky AlOOH crystals onto glass fiber surfaces.
2. Modified filter material electrical properties changed from original -40 mV to approximately +11 mV positive potential, demonstrating that grafted AlOOH altered fiber charge characteristics. The material exhibits good electrostatic adsorption capacity for anionic dyes, with 0.45 μm latex sphere filtration efficiency improved to 99.95%.
3. Due to effective encapsulation of glass fiber surfaces by grafted AlOOH crystals, direct contact between filter material and test solution was reduced, resulting in 87.64% reduction in soluble silicon leaching compared with pre-modification. Additionally, eliminating sulfuric acid from the experimental protocol reduced sulfate leaching by 84.43% compared with foreign filter materials.
4. While improving the aforementioned filter performance characteristics, the modified material maintained dirt-holding capacity essentially equivalent to foreign products. Simulation results demonstrate that compared with pre-modification, filter material pressure drop and permeability were effectively improved.

These experimental results establish a foundation for domestic filter material development and hold significant importance for maintaining primary coolant water quality stability, reducing nuclear power plant operational safety risks, and decreasing occupational personnel radiation exposure.

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