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Geochemical Behavior of Heavy Metal Elements in Tailings Ponds and Solidification/Stabilization Remediation

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ABSTRACT
Tailings dams are indispensable infrastructure for mining operations, storing processed tailings and waste residues while enabling wastewater recycling. As high-potential artificial hazards, their safe and stable operation is critical, necessitating strict regulatory oversight categorized into hazardous, high-risk, impaired, and standard dam classifications. Achieving efficient tailings management while balancing safety and environmental risks poses challenges, particularly regarding secondary pollution from heavy metal elements. This paper, therefore, explores the geochemical behavior characteristics of heavy metals within tailings dam systems and key solidification/stabilization remediation technologies, aiming to support optimized environmental risk management and enhanced closed-loop treatment efficiency for tailings dams.

KEYWORDS
Tailings dam; Heavy metal elements; Chemical behavior

1 Introduction

A tailings dam is a specialized industrial storage facility constructed by mining operations to intercept valley heads or enclose land areas. It is designed to store solid waste (tailings) generated during mineral processing and to reuse clarified wastewater. The primary structure comprises a tailings storage system, a flood control and drainage system, and a water recycling treatment system. Its spatial layout varies, including terrain-utilizing types (valley-type) and regionally segmented types (flat-land type). Mandatory regulations now govern the compliant operation of tailings dams in China. Under the Mining Safety Law of the People's Republic of China, the Measures for the Prevention and Control of Environmental Pollution from Tailings, and the Technical Guidelines for Environmental Risk Assessment of Tailings Dams, new projects are prohibited near residential areas or water sources. Simultaneous closure and rehabilitation systems are mandatory, with operational focus on preventing dam failure and environmental pollution risks. Against this backdrop, the focus of environmental conflicts surrounding tailings dams is gradually shifting from risk mitigation to ecological value restoration. Identifying the behavior mechanisms of heavy metals in tailings and controlling their mobility represents key technical challenges in reshaping governance approaches. This article will explore the behavior patterns of heavy metals in tailings and investigate solidification/stabilization remediation strategies.

2 Geochemical behavior of heavy metal elements in tailings ponds

2.1 Distribution characteristics of heavy metal elements

The combined effects of ore characteristics, discharge methods, and natural conditions primarily influence the spatial distribution of heavy metals in tailings ponds. Horizontally, heavy metal concentrations decrease from the central discharge area toward the periphery. High-concentration contaminated clumps typically accumulate near discharge pipes, as initially settled coarse mineral particles carry primary metal enrichment. In intermediate zones, hydraulic sorting effects become evident, with fine-grained sediments adsorbing highly mobile elements like lead and cadmium during deposition. In the still water areas at the tail end of the dam, colloidal metals may form secondary enrichment points through flocculation and sedimentation with organic matter [1]. Vertical distribution is governed by environmental gradient depth. The oxidation layer (0 – 50 cm) undergoes acid production due to sulfide mineral oxidation upon air exposure, causing leaching of soluble components like zinc and copper downward. The transition zone (50 – 150 cm) develops iron-manganese oxide films and experiences pH recovery in seepage water, forming a retention barrier for heavy metals—lead and chromium commonly exhibit relative enrichment within this depth range. The deep reduction zone (150 cm) operates under anoxic conditions where sulfate-reducing bacteria promote metal sulfide precipitation, significantly immobilizing elements like arsenic and mercury.

2.2 Migration patterns of heavy metals

Heavy metal migration within the tailings body fundamentally involves interfacial transport across solid-liquid-gas-

biological multiphase media. Liquid-phase migration relies on pore water flow. Dissolved metals like zinc and manganese migrate directionally within the reservoir along hydraulic gradients. After penetrating the tailings layer, they enter the surrounding groundwater systems. The solubility of heavy metals controls their effective release, while soil/tailings permeability coefficients determine flow rates. Reservoir bottom geology (e.g., clay layer thickness) directly influences retention capacity. Gas-phase migration primarily occurs through wind erosion, where dry, exposed tailings dust (particle size <75 microns) carries bound elements like nickel and copper into the atmosphere. Under monsoon influence, these suspended particles can impact farmland environments kilometers away, typically manifesting as increased heavy metal concentration gradients in downwind soils. Furthermore, biogenic migration cannot be overlooked. Pioneer plant roots in reservoir areas absorb cadmium and arsenic, transferring these elements to aboveground parts. Through decomposition of plant litter or animal consumption, they re-enter environmental cycles. The bioaccumulation effect in aquatic organisms further amplifies heavy metal transfer along food chains, forming ecological risk chains that extend beyond reservoir boundaries. All these migration pathways interact synergistically, resulting in complex network-like diffusion patterns of heavy metal pollution impacts [2].

2.3 Analysis of influencing factors

The regulatory framework governing heavy metal environmental behavior encompasses two major categories: natural constraints and human interventions. Geochemistry represents the fundamental constraint: pH fluctuations in reservoir areas directly alter the hydrolytic equilibrium of heavy metals. Under acidic conditions (pH < 5), the destruction of aluminosilicate lattices releases structural metals, while alkaline environments (pH > 8) promote hydroxide precipitation but may cause arsenic dissolution. Oxidation-reduction potential (Eh) regulates the activity of multivalent elements. At low Eh, hexavalent chromium reduces to trivalent chromium and precipitates; at high Eh, trivalent antimony oxidizes to highly mobile pentavalent forms. Mineral composition also profoundly influences regulation: iron-manganese oxides sequester lead and zinc through specific adsorption, while carbonate dissolution releases competitive calcium ions that weaken clay's cadmium retention capacity [3]. Human interference disrupts natural equilibrium. Engineering defects, such as compromised impermeable liners, create direct shortcut pathways that bypass geological barriers. Reservoir water level fluctuations induce alternating wet and dry conditions, accelerating sulfide mineral oxidation and acid release. Extreme rainfall erodes tailings pile slopes, causing rapid vertical migration of heavy metal-laden clumps.

3 Principles of solidification/stabilization remediation technology

3.1 Fundamental principles of solidification/stabilization remediation

Solidification/stabilization technology reconfigures pollutants' form and spatial distribution through material interactions with tailings, primarily involving physical encapsulation and chemical sealing. Physical encapsulation utilizes binders such as cement or lime to form dense network structures that envelop tailings particles and seal pore spaces, isolating heavy metals beyond the reach of biological contact. This process requires binders with appropriate hydration rates and ultimate strength to ensure the stability of the solidified matrix. Chemical sequestration relies on directed reactions between active components and heavy metal ions to alter their solubility and mobility. For instance, phosphate-based materials convert lead into thermodynamically stable chlorite lead, reducing bioavailability; organic clays adsorb aqueous cadmium ions through ion exchange and surface complexation, trapping them in a deeply retained state. These two actions are inherently synergistic: the structural integrity of the solidified mass ensures the continuity of the chemical sealing environment, while the chemical fixation effect reduces the potential for pollutant release due to physical structural failure [4].

3.2 Mechanism of solidification process

The solidification mechanism initiates with the multiphase dissolution and reorganization of the binder. Taking cement-based solidification as an example, when cement is added to the tailings slurry, a chain reaction occurs. The hydration of tricalcium silicate releases calcium hydroxide, rapidly raising the liquid-phase pH above 12. This forces metal ions such as zinc and copper to convert into hydroxide precipitates. Subsequently, calcium silicate hydrate (CSH) gel synergizes with calcium aluminate hydrate (CAH) crystals to grow within tailings particle voids, progressively cementing loose tailings sand into a solidified matrix. This formation is governed by three critical parameters: water-cement ratio affects gel porosity, with excessively low ratios causing localized encapsulation failure; curing temperature determines crystal growth rate, with low temperatures significantly delaying strength development cycles; The particle size distribution of tailings affects interfacial bonding efficiency; excessive acceptable powder content adsorbs excess moisture, weakening ultimate strength. However, sulfide oxidation risks require preemptive intervention. High-sulfur

tailings still generate expansive calcium aluminate in alkaline solidification environments, destroying the structure. Therefore, oxidation inhibitors must be added, or iron-based consolidation systems should replace cement-based solutions.

3.3 Principles and mechanisms of stabilization

Stabilization deeply locks pollutant activity through point-to-point chemical reactions between materials and heavy metals. According to solubility product (Ksp) rules, anion donor materials drive chemical reactions. For instance, S^{2-} generated by sodium sulfide reacts with zinc ions to form zinc sulfide, sharply reducing solubility migration to parts per million levels. Phosphate ions released from apatite selectively form fluorapatite under controlled calcium ion activity, achieving over 98% lead ion fixation. Such reactions are susceptible to competitive effects from high ionic strength solutions, with high chloride environments diminishing fixation efficiency. Porous materials rely on chemical adsorption and inner-sphere coordination to restrict metal activity. Defective sites and oxygen-containing functional groups (hydroxyl/carboxyl) on iron-based biochar surfaces facilitate the formation of bidentate binuclear complexes with arsenic. Interlayer anions in layered double hydroxides (LDHs) undergo ion exchange with chromate ions, enabling "memory effect"-like electron capture. This mechanism is governed by interfacial reaction kinetics equilibrium. Environmental pH changes from the optimal range (typically 6–8) trigger desorption chain reactions [5].

4 Current application status of solidification/stabilization remediation technology

4.1 Scope of application for solidification/stabilization technology

Solidification/stabilization technology is primarily applicable for in-situ and ex-situ risk management of heavy metal pollutants. In mine tailings pond remediation, in-situ solidification applied to surface wind-erosion zones forms a hard crust covering that prevents dust and heavy metals from dispersing with the wind. For closed tailings piles, ex-situ solidification is commonly used for pollution containment before pond expansion or land reuse, involving excavation and transferring contaminated materials to designated areas for batch processing. In emergency pollution incidents, such as heavy metal-containing liquid waste leaking into soil, injection-based solidification rapidly injects slurry to form underground barriers. However, the technology has apparent limitations: conventional solidification struggles to block biotransformation pathways when pollutants exist in organic forms like methylmercury. Additionally, solidified bodies exhibit significantly reduced freeze-thaw cycle resistance when treating high soluble salt concentrations of tailings. Current core applications remain concentrated on surface and shallow-layer remediation of sites contaminated with inorganic heavy metals like lead, zinc, copper, and arsenic. For contaminated areas exceeding five meters in depth, material mixing homogeneity issues necessitate the integration of complementary technologies.

4.2 Application effects of common solidifiers

Using cement-based materials, leveraging their high hydration strength and low cost, is the primary solution for immobilizing medium-to-low concentration mixed heavy metals. The resulting calcium silicate hydrate gel encapsulates various metal hydroxide precipitates, with solidified bodies in arid climates maintaining compressive strength for over a decade. However, when treating acidic sulfide tailings, ordinary cement is susceptible to sulfate erosion and expansion cracking. In such cases, cement with high slag content or alkali-activated cementitious materials should be used instead. Lime solidifiers significantly raise substrate pH, making them suitable for rapidly treating copper-nickel contaminated soils. However, pure lime solidification often leads to "efflorescence," causing surface powdering, so it is commonly blended with fly ash to enhance structural stability. Polymer-based solidifiers, such as epoxy resin materials, demonstrate superior performance in complex site conditions. Their hydrophobic properties block water-salt migration, and when applied to cadmium-contaminated farmland topsoil remediation, they reduce plant uptake.

4.3 Application of stabilization technologies

Stabilizers precisely control the activity of specific heavy metals through chemical transformation. Phosphate materials are the preferred choice for lead removal; injecting phosphate rock suspensions converts lead into hydroxyapatite structures, achieving nearly 100-fold reductions in leaching toxicity when treating lead-contaminated battery waste piles. Iron-based materials—such as red mud modifiers—dominate by forming iron arsenate precipitates for arsenic-contaminated sites, demonstrating superior fixation efficacy in acidic red soil regions compared to lime solidification. Sodium sulfide exhibits high efficiency in immobilizing arsenic and mercury pollutants, though sulfide oxidation may generate secondary acids; thus, slow-release sulfur formulations or oxygen-isolating composite layers are now

predominantly used. Composite systems combining zero-valent iron and iron salts for chromium remediation achieve dual locking by reducing hexavalent chromium and precipitating trivalent chromium. Current trends favor multi-stage sequential approaches: first neutralizing acidic tailings with calcium carbonate, then adding potassium dihydrogen phosphate to precipitate heavy metals, and finally applying slag-based solidification layers to enhance overall stability.

5 Conclusion

This paper discusses the geochemical behavior of heavy metal elements in tailings ponds, which essentially involves migration-driven release and transformation of speciation under environmental conditions. Solidification/stabilization remediation effectively intervenes in natural release patterns by blocking migration pathways through physical compaction barriers while suppressing heavy metal activity via chemical conversion reactions. Future practice should deepen in three areas: prioritizing the development of acid-resistant cementitious systems to overcome stability constraints in high-sulfur tailings environments; synergistically designing composite stabilizers with both precipitation capacity and adsorption capacity to meet complex demands of multi-metal coexisting contaminated matrices; and establishing controllable deep remediation process standards to address homogenization challenges in slurry injection. Through a tiered environmental risk control pathway, this approach shifts remediation technology from short-term indicator management toward long-term ecological safety maintenance, ultimately achieving synergistic development of tailings pond pollution control and land regeneration objectives.

About the Author

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