Current Pollution Reports (2018) 4:35–48
https://doi.org/10.1007/s40726-018-0078-8

Subsurface Submergence of Mine Waste Materials as a Remediation Strategy to Reduce Metal Mobility: an Overview

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Abstract

The most common lead (Pb) and zinc (Zn) ore minerals are galena (PbS) and sphalerite (ZnS). Milling and mining operations of these ores produce huge amounts of waste known as chat and tailings. Chat is composed of gravel, sand, and silt-sized rock materials, whereas tailings are often fine-grained and silt-sized particles with higher toxic element concentrations. Upon oxidation, tailings with high pyritic materials release Pb, Zn, Cadmium (Cd), and other elements associated with ores affecting plant productivity, the ecosystem, and human health. This article is an overview on utilizing the subsurface submergence technique for mitigating environmental impacts from abandoned mine waste materials. In the past, researchers have studied the influence of submergence on these elements; however, an emphasis on gathering a detailed understanding of such redox-based remediation processes is not that common. We reviewed literature that evaluated water chemistry, solid phases, and association of trace elements, and addressed utilization of surface amendments of mine tailings for predicting their interactions within sediments and overlying waters. Case studies specifically focused on mining of Pb and Zn, including a recent study conducted in the Tri-State mining district (Kansas, Missouri, and Oklahoma), are presented to add a more comprehensive understanding of biogeochemical transformations of trace elements present in mine waste materials under a long-term submergence. The purpose of this article is to present evidence on the viability of subsurface disposal of mine waste materials, in order to design effective remediation and mitigation strategies to protect human and environmental health in the global dimension.

Keywords Lead · Zinc · Mine waste material · Subsurface submergence · Sulfides · Colloids

Background

Mine Waste and Its Mineralogy

Mining operations impact the local and regional environment, leaving a legacy of mining that may persist for many years after the site is abandoned. During mining operations, less than 1% of processed material is recovered as useful metal [54], and the rest is discarded as chat and tailings [90]. Chat is composed of gravel, sand, and silt-sized rock materials. In contrast, tailings are often more fine-grained and silt-sized particles with higher metal concentrations [77, 119]. Further, tailings contain negligible amount of organic matter or macronutrients, and exhibit mostly acidic pH, although some tailings may be alkaline, depending on the parent material and carbonate concentration [77, 116]. Mine tailings usually contain sulfide-rich materials acting as persistent toxic metal sources [55, 101].

A complete understanding of the mineralogical composition of mine waste materials and their interaction with water is highly important when predicting their environmental impact, and developing satisfactory and cost-effective control and remediation measures [53, 105]. Galena (PbS) is often deposited as a lead (Pb) mineral with variable amounts of accessory silicate and carbonate gangue minerals. Under oxidized conditions, PbS results in the formation of various secondary minerals including cerussite ($PbCO_3$), anglesite ($PbSO_4$),

Data Extraction Data were extracted from peer-reviewed articles and books identified on Google Scholar, Web of Science, and publications available through the US EPA.

This article is part of the Topical Collection on *Land Pollution*

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and plumbojarosite ($PbFe_6(SO_4)_4(OH)_{12}$). Sorbed species of Pb are often associated with jarosite ($KFe_3(SO_4)_2(OH)_6$), and Fe (oxyhydr) oxides [88, 98]. Each of these minerals has specific solubility and bioavailability [49, 67]. About 65% in vitro and 56% in vivo bioavailability for $PbCO_3$ has been reported from swine feeding studies (stomach phase) conducted by the US EPA Region 8 and the University of Missouri ($r^2 = 0.85$, $n = 15$) in the Jasper County mining region [45]. In general, relative bioavailability (relative to lead acetate from several in vivo and in vitro studies) varies from high for cerussite $PbCO_3$ and Pb sorbed to manganese (Mn) oxide (> 75%); to medium for Pb phosphate (pyromorphite) and PbO (25 to 75%); to low for anglesite, galena, Fe-Pb species, and remaining Pb-based oxides (< 25%) [120, 121]. Common zinc (Zn) compounds found in mine waste materials include $ZnCl_2$, ZnO, $ZnSO_4$, and ZnS [73]. Other Zn minerals identified in mine waste materials include willemite (Zn_2SiO_4), hopeite ($Zn_3(PO_4)_2.4H_2O$), scholzite ($Zn_2Ca(PO_4)_2.2H_2O$), smithsonite ($ZnCO_3$), hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$), and Zn-phosphates ($Zn_3(PO_4)_2$) [7, 8, 58, 74, 79]. Zinc is originally presented as ZnS in mine waste materials; however, it is oxidized when exposed to the surface. Upon oxidation, ZnS is redistributed into Zn hydroxide and/or ZnFe hydroxide phases in contaminated ground water and sediments [44, 85, 127]. Cadmium (Cd) minerals are found in combination with other elements such as CdO, $CdCl_2$, $CdSO_4$, and CdS. Under sulfide-rich environments, CdS has been found as the dominant Cd mineral, or Cd sorbs to FeS and pyrite (FeS_2) due to their high reactivity [9, 15].

Issues with Abandoned Mine Waste

Several issues associated with abandoned mine waste materials that impact water quality as well as the surrounding environment are listed as (a) acid mine drainage (AMD) (formation and movement of highly acidic water rich in heavy metals), (b) alkaline mine drainage (occurs when parent material at the mining site is high in calcite and dolomite, and (c) metal mine drainage (occurs when high levels of lead or other metals drain from metalliferous mine waste materials) (US EPA [118]). Overall, oxidation of FeS_2 and/or pyrrhotite (Fe_7S_8) causes formation of AMD with the subsequent release of sulfate, iron (Fe), and elements such as Al, Mn, Zn, nickel (Ni), copper (Cu), and Pb associated with sulfide ores such as chalcopyrite ($CuFeS_2$), PbS, and ZnS, and also from other minerals [13, 87, 93].

The generation of AMD depends upon the material's physical, chemical, and biological properties [13], in addition to the composition of metal sulfides (mostly unknown and could be highly variable) and metal sulfides' inherent properties [14, 50]. Other important factors are rate of oxidants supply, typically as O_2 and Fe^{3+} [6, 84], pH, exposed area of metal sulfides, chemical activation energy, and bacterial activity [3]. Another dominant factor for AMD generation is the wetting and drying cycles. Periodic variations in water content may expose reduced mine waste materials to oxidizing conditions conducive to oxidative dissolution of metal sulfides. Thus, metal sulfides in anoxic subsurface or near-surface soils can undergo oxidative dissolution during drying periods due to lowering of the water table. The increased drying event increases oxidation products that tend to accumulate in the system, and the increased wetting event will flush accumulated contaminants out of the system. In general, the contaminant load is increased with heavy precipitation, particularly for those areas having a wet season [16, 118, 125]. The acidic mine water, rich in metals, poses a substantial risk to water resources, plant productivity, the ecosystem, and human health [90, 95]. However, the quality of drainage released from the mine waste as surface runoff or entering into the ground water depends upon reactions occurring with minerals capable of neutralizing the acidic water as it passes through the waste [99, 105].

Acid Mine Drainage Formation and Its Controlling Factors

The reactions of AMD generation are very commonly observed by examining the oxidation of FeS_2 as given below:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

Equation 1 shows oxidation of the pyrite mineral into dissolved ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and hydrogen, which further lowers the pH and increases total dissolved solids. However, Fe^{2+} oxidation by O_2 at low pH is slower and thus may limit further reactions generating AMD.

$$14Fe^{2+} + 3.5O_2 + 14H^+ \rightarrow 14Fe^{3+} + 7H_2O \quad (2)$$

Equation 2 indicates Fe^{2+} is further oxidized to Fe^{3+} on a sufficiently available O_2 concentration.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (3)$$

In the range between pH 2.3 and 3.5, Fe^{3+} precipitates as $Fe(OH)_3$, reacts spontaneously with the pyrite surface, and leads to more pyrite oxidation via an autocatalytic process, which is shown in Eq. 4.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

Net acidity in AMD is offset primarily from the dissolution of a basic mineral such as calcium carbonate, especially if the parent material consists of a higher percentage of carbonate minerals [56]. Under this scenario, AMD might not occur due to sufficient buffering via dissolution of carbonate minerals (calcite or dolomite); instead, alkaline drainages may persist that are more common in underground mines and less environmentally damaging when compared to AMD, e.g., several active and abandoned mines in the Ivo River Basin Area of Southeastern Nigeria [34]. Regardless of alkaline pH, the potential risk of AMD may occur as presence of high Fe^{2+} ion concentrations could lower the pH via oxidation and hydrolysis, and may render an acidic effluent containing elevated concentrations of trace metals [3]. Therefore, the extent of acid neutralization and porewater pH acts as a main driver to control the mobility of sulfide oxidation products [68].

Environmental Impacts From Abandoned Mine Waste

Impact from abandoned mine waste materials in the form of AMD generation is a serious environmental problem and highly prioritized ecological concern around the globe ([1, 18, 39]; [84]; [101]). More than 10,000 km of streams, and > 72,000 ha of lakes and reservoirs in the eastern USA [109], and up to 160,000 km of streams in the western USA have been affected by AMD [12, 61]. The current data indicates that the total cost of environmental remediation of mining is very high. For example, the environmental remediation cost of the Saxony areas in Germany has already reached 65 billion Euros, and the project to relocate and confine the uranium mining waste in Colorado is budgeted at 1 billion dollars [19, 80]. Discharge of untreated mine water after flooding can lead to surface water pollution, pollution of overlying aquifers, high-sediment deposition in stream channels, localized flooding, and overloading and clogging of sewers [3, 22]. Acid mine drainage effects can be loosely categorized as chemical, physical, biological, and ecological [3, 41]. However, these effects have an overall impact on the community structure via habitat alteration, niche loss, elimination of species, nutrient cycle alteration, and food chain modification, as well as bioaccumulation within the food chain resulting in decreased primary productivity and ecological stability [4, 72, 84]. Another imminent concern is that AMD production may continue for several years after mining operations are closed [54]. Therefore, biology of a stream is the most significant factor ultimately determining true health of the stream, both before and after AMD recovery efforts [96].

Mitigation of the Environmental Impact of Mine Waste

Selection of an appropriate remedial option for the mitigation of mine waste material depends upon its mineralogical composition, reactivity, and potential risk to human health and the environment. In addition, site geology, hydrology, land-use planning, and cost-and-benefit analysis are other factors considered during the decision-making process [66, 87].

Conventional Technologies

Conventional technologies for handling solid mine waste are focused most often on physical and chemical stabilization, such as variety of excavation, landscape adjustment, covering of waste piles, water diversion practices, and in some cases vegetation. However, these techniques are less permanent and less cost-effective as well [3, 77].

Capping

This technique includes capping mine waste materials with non-toxic materials such as gravel, topsoil, clay, layers of plastic, compost, and waste rocks from mining operations. The purpose of using these cappings is to reduce wind- and water-driven erosion of the mine waste materials; however, these treatment options are often considered temporary due to unstable capping processes [77, 116]. Unstable capping may result because of cracking of clays during the wetting-drying cycle, and poor consolidation of mine tailings due to high salinity [83, 113]. While capping may be a reasonable option to reduce potential environmental impacts of abandoned mine waste materials, it generally does not reduce toxicity or volume of the waste [3, 91].

Addition of Alkaline Materials

Addition of alkaline materials such as lime (calcium oxide), slaked lime, calcium carbonate, sodium hydroxide, sodium carbonate, and magnesium oxide/hydroxide are sometimes used in handling AMD, depending on the chemistry of mining water [23, 54, 103]. This technique is used to offset the acid-producing potential of metalliferous mine waste materials, potentially preventing AMD formation. Increased pH with the addition of alkaline materials further reduces the release of acid, Fe, and other heavy metals. However, the addition of alkaline materials during surface mining and reclamation has shown variable results in the reduction of AMD generation [76, 108]. Since abandoned surface mines comprise huge volumes of waste materials with unknown composition and hydrology, the cost of handling and adding alkaline materials is extremely high, and regular monitoring adds more limitations to its use as well [93, 109, 116].

Phytostabilization as a Remediation Strategy

Long-term rehabilitation of metalliferous mine waste materials can be achieved by using phytostabilization. A plant canopy can reduce dispersion by wind and plant roots can be effective in providing required surface stability, as well as in reducing water pollution, and immobilizing metals via accumulation or adsorption within the rhizosphere [40, 77]. High metal concentration, macronutrient deficiencies, and poor substrate structure of mine waste may limit vegetation establishments at mining sites. Much research has been conducted in the past to overcome these limitations for vegetation establishments. Nevertheless, their widespread application is limited due to great variation in physical, chemical, and biological factors across mine waste materials from different geographical settings. A detailed site assessment of geology, climate, and toxicity levels is essential prior to implementing any successful phytostabilization strategy [20, 24, 77].

Innovative Technologies

Innovative technologies include chemical encapsulation of wastes (use of chemicals such as sulfur polymer, chemically bonded phosphate ceramic, polyethylene, and others to encapsulate hazardous waste) [94] and a variety of passive treatments (those that utilize enhanced natural processes, are in situ, and require minimal upkeep such as subsurface submergence) as well. Permeable reactive barriers (PRBs), bioreactors, and constructed wetland technologies are other examples of innovative technologies that are highly utilized [3, 131].

Subsurface Submergence as a Remediation Strategy and Its Associated Challenges

Historically, disposal of mine waste materials involves returning them back to the mine (in-storage pit or backfilling) [102]. Controlling atmospheric O_2 entry into the tailings is an ultimate requirement to avoid oxidation of sulfidic minerals. Water covers offer an alternative approach to dry covers for managing sulfide-mineral oxidation. Subaqueous tailings deposition also has the potential to limit sulfide-mineral oxidation and associated environmental impacts [52, 70, 122, 123] as diffusive flux of O_2 to water-covered tailings may decrease by up to 10,000 times relative to uncovered tailings [5]. Furthermore, anoxic conditions inhibit the microbial catalysis associated with the oxidation process [60, 122]. Several laboratory- and field-based studies on short-term storage of tailings under shallow water covers have been conducted [31, 78, 100], but only a few studies have considered the reactivity of tailings that have been submerged over long time periods [52, 122, 123]. Chemical characteristics, in particular the pH and reduction-oxidation (redox) potential, may change in response to water-level change, influencing the chemistry involved in metal immobilization [3]. This technique has been considered highly cost-effective compared to dry cover, depyritization, and buffering alternatives. For subaqueous submergence of mine tailings, even on-site waste rocks can be used as borrow materials. However, application of subaqueous disposal is strongly limited by site-specific variables. Site geology and hydrology are required to be feasible to allow construction of an impoundment to be flooded indefinitely and maintain a sufficient water cover [17, 117].

In the past decade, research efforts have identified both natural and constructed wetlands as environmentally sound and cost-effective remediation techniques for mine waste materials and mining-influenced water, as they offer an efficient treatment technology with minimum inputs, low investment costs, low operating costs, and no external energy input [28, 48, 75, 89, 130]. Wetlands offer metals remediation via certain processes such as adsorption and ion exchange, bioaccumulation, bacterial and abiotic oxidation, sedimentation, neutralization, reduction, and dissolution of carbonate minerals [28, 75, 86]. The extent of these reactions is determined by the substrate composition and sediment pH. In general, the overall effect of submergence is to make pH values of acid soils (except those low in Fe) and alkaline soils converge to pH 7. The pH can be increased from around 4 to more than 7 [30, 36]. Change in pH value can profoundly influence hydroxides, carbonates, sulfides, phosphates, and silicate equilibria that control the precipitation and dissolution of solids, and sorption and desorption of ions such as Al^{3+}, Fe^{2+}, H_2S, H_2CO_3, and amino acids [92]. Redox processes are another important component in controlling metal (loids) mobility [68, 124]. Constructed wetlands, mostly with vertical flow systems, primarily rely on microbial activity (especially sulfur-reducing bacteria or SRB) and may utilize organic matter to stimulate sulfate-to-sulfide reduction, generate alkalinity, and precipitate metal sulfides along with adsorption and exchange reactions with organic matter [36, 38, 81, 132]. The microbes will remain active as long as the system remains anaerobic and contains an adequate supply of sulfate and small chain organics [30, 104]. In general, metal sulfides precipitate out of solution in an order of $CuS < PbS < CdS < ZnS < NiS < FeS < MnS$ [112, 131]. Most metal sulfides have a lower solubility compared to their hydroxide counterpart (except Al, Fe, and Mn) and can precipitate over a broad pH range [29, 35, 37]. Therefore, constructed wetlands are considered a viable alternative to chemical precipitation for metal removal (up to 90%) [30, 36, 112].

Despite higher efficiency of metal remediation, the major drawback of anaerobic wetlands is the decrease in efficiency over time if conditions change [54]. Based on past studies, the estimated lifetime of a wetland is about 20 years; however, the lifetime of each system depends upon the types of chemical processes involved in the metal removal. An additional organic material must be added periodically in order to maintain acceptable treatment, or the total metal and acid load to the system may need to be reduced substantially [110, 111]. Moreover, sulfide phases of metals would only be an effective means of metal immobilization under static anoxic conditions [65, 107], particularly ZnS, as mineral species of Zn are readily altered in response to changes in environmental conditions [15, 71].

Potential Unintended Consequences Associated with Subsurface Submergence

Metal sulfide precipitates are highly resistant to oxidation; however, the newly precipitated, colloidal metal sulfide clusters may significantly enhance the metals' mobilities under reduced conditions [46, 128], and may persist in water bodies due to their kinetic stability [2, 14, 46]. Colloidal material is defined as sub-micro-meter mineral particles or bacterial cells that have at least one dimension between 1 nm and 1 μm, and are too small to withstand gravitational settings [21, 64, 128]. Due to its higher surface area, and a large number of potentially reactive functional groups exposed to the solution, the colloidal fraction can sorb a large fraction of trace components, and thereby act as potential carrier of poorly soluble contaminants in the subsurface environment [64, 114, 128]. The basic mechanism involved in association of contaminants with colloidal particles is surface complexation, ion exchange, and hydrophobic partitioning [63]. Therefore, the fate of contaminants and their impact on ground water quality depends on the nature and behavior of these potentially mobile colloids that further depend upon the size and connectivity of pores, and stability of the colloids [25]. Colloidal-assisted transport has been highly observed in river basins and flood plains [46, 126]; however, only a handful of studies have been conducted in the reduced environment [62, 128]. In a recent laboratory-based column study, we attempted to measure colloidal-bound trace elements' mobility in mine waste materials treated with S and organic C (OC) under reduced conditions. More details of this case study are presented in the upcoming section, "Case Studies."

Case Studies

In this review article, we are attempting to present case studies focused on subsurface submergence as a remediation technique for mitigating impacts from mine waste materials specifically containing Pb and Zn. We have included studies that evaluated water chemistry, solid phases, association of trace elements, and geochemical changes in sulfidic minerals. We have also addressed utilization of surface amendments of submerged mine tailings for predicting their interactions within sediments and overlying waters.

Coeur d'Alene Lake, Idaho

The sediment of Coeur d'Alene (CDA) Lake, Idaho, is heavily contaminated from mining and mineral processing on the south fork of the CDA Lake. Sediment quality of this lake has been classified as severely affected by arsenic (As), Cd, Pb, and Zn. Moreover, trace element concentrations in the porewater are identified to be acutely toxic to freshwater biota [129]. Harrington et al. [42] conducted a study along the CDA Lake to understand the phases and associations of trace elements in the lake's sediments, in order to predict their interactions within the sediments and overlying waters. Analyses of gravity cores were focused on redox and pH measurements, sequential dissolution analyses, estimates of bacterial densities, and trace element measurements. Results showed these sediments to be highly reduced. A large fraction of both Pb (49.3%) and Zn (63.3%) was associated with sulfides under prevailing redox conditions, whereas the rest of Pb and Zn fractions appeared to be sequestered in the amorphous (hydr)oxide phase. Metals that are associated with the amorphous (hydr)oxide phase may become mobilized, and this explained why some Pb and Zn were released into the overlying waters. In contrast, a larger redistribution of Pb and Zn in sulfide phases indicated microbial sulfate reduction as an important mechanism for metal sequestration. Low redox potential, relatively high pH values (pH 6.3), as well as most probable number (MPN) estimates also provided more evidence for the prevailing sulfate reduction mechanism [32, 97]. The presence of cultivable SRB further indicated a positive influence of flooding on metal immobilization via sulfide formations. The fraction of trace elements, particularly with respect to Pb and Zn bound by organic matter, was significant as well.

In another instance, West Page Swamp is an 11-ha naturally occurring wetland located in the CDA River basin near Pinehurst, Idaho. The depth of mine tailings in the Page swamp ranges from 45 cm to > 3 m with Cd (16 to 249 mg kg^{-1}), Zn (1740 to 18,400 mg kg^{-1}), Pb (4670 to 20,700 mg kg^{-1}), and OC of 1.06%. The swamp maintained a constant water depth over the exposed tailings; however, the wetland was excavated to accommodate the treatment plant effluent. On excavation, accumulated OM was removed, and pure mine tailings that had been buried for more than 50 years were exposed as well. The surface amendment of biosolids, compost, and wood ash, with and without sulfate, was applied under greenhouse conditions in order to restore vegetation and reduce the bioavailable metal concentration in the mine tailings. These amendments were expected to not only stabilize sediment pH but also create a sulfate-reducing environment by providing a food source and sulfate as an electron donor. This type of reducing environment could support organotrophic anaerobes such as *Desulfomonas and Desulfovibrio*, potentially favoring highly insoluble PbS and sphalerite (ZnS) to precipitate [103, 106]. Results from this study indicated surface application of compost + ash + sulfate, at both low and high levels, was especially effective in promoting the PbS proportion in the underlying sediments, indicating metal sulfide formation via sulfate reduction (Table 1). On the other hand, compost + wood ash without sulfate addition promoted vigorous plant growth and reduced the Pb content in plant tissue compared to the control, probably due to the favorable rooting medium provided [26].

Table 1 Lead L_{III}–X-ray absorption near edge structure (XANES) spectroscopy fitting results showing the relative proportions (mole percentages) of PbS, PbCO3, and PbSO4 standards yielding the best fits to the soil XANES data in binary (or ternary) linear combination fitting. (Source: [26])

Treatment	PbS	$PbCO_3$	$PbSO_4$	Goodness of fit (χ^2)	Remarks
Control, 99 days	35 ± 3	66 ± 3		0.0048	The occurrence of PbS in control and compost added samples suggests that PbS was present in the original mine tailing and remained unaltered. However, $PbCO_3$ was a primary dominant mineral in the lack of supplementary sulfate addition. In contrast, PbS formed to a greater extent in both low and high sulfate-treated sediments over longer incubation indicates that sulfate additions need to be adjusted to avoid negative effect on plant growth. Similar results were observed in other studies with and without treatments [42, 58, 78].
Control, 207 days	49 ± 2	51 ± 2		0.0025	
Compost, 99 days	33 ± 2	67 ± 2		0.0042	
Compost, 207 days	40 ± 1	60 ± 2		0.0024	
Low sulfate, 99 days	62 ± 2	38 ± 2		0.0013	
Low sulfate, 207 days‡	87 ± 1 (88.3 ± 0.4)	13 ± 1	11.0 ± 0.3	0.0025 (0.0026)	
High sulfate, 99 days	62 ± 2	38 ± 2		0.0015	
High sulfate, 207 days	80 ± 0.8		20.0 ± 0.4	0.0053	

† Mole percentages reported means ± standard deviations of results for three fittings ranges of XANES spectra: 13,030 to 13,130; 13,030 to 13,090; and 13,030 to 13,075 eV. The χ^2 parameters is the mean for the three fitting results

‡ Fitting using standards PbS + $PbCO_3$ versus PbS + $PbSO_4$ yielded nearly equivalent goodness of fit, with each standard combination giving a better fitting different portions of the sample spectrum

Cu/Zn Mine Located Near Val d'Or, QueÂbec, Canada

A study was conducted by Vigneault et al. [122] on the geochemical changes in sulfidic mine tailings obtained from an underground Cu/Zn mine located near Val d'Or, QueÂbec, Canada. The mineralogy of tailings indicated the presence of silicates (quartz, muscovite, ferroan clinochlore, plagioclase, and K-feldspar), sulfide (trace amounts of chalcopyrite, sphalerite, and galena), carbonate (magnesian siderite and ankerite, or ferroan dolomite), and oxide minerals. This study was conducted to investigate the effectiveness of a shallow water cover (0.3 m) in a man-made reservoir to inhibit the oxidation of sulfidic mine tailings, and to evaluate physical and chemical interactions within the deposited tailings. The experimental measurements were primarily focused on the interstitial water to obtain more evidence on aqueous-phase sensitivity to diagenetic reactions. Measurements were conducted to determine the diffusion of dissolved oxygen from the water cover into the sediments, diffusion of dissolved metals and anions across the tailings-water interface, and interaction between the aqueous and solid phases. Solid-phase porewater and water-column geochemical data were used to interpret controls on the chemical behavior of the submerged tailings. After the fresh tailings were submerged under a 0.3-m water cover, the chemistry of interstitial water near the tailings' overlying water interface was measured using in situ dialysis, and the pH and dissolved oxygen across the tailings' water interface was measured using micro-electrodes for 2 years (1996–1998). Results indicated that penetration of dissolved oxygen into the tailings was limited to 57 mm, despite the dissolved oxygen produced by benthic periphyton. Presence of $\sum H_2S$, Fe, and Mn in porewater sampled at > 1.5 cm below the tailings' water interface was consistent, and reflected the existence of anoxic conditions at these depths. However, there was clear evidence of surface oxidation of the mine tailings at the millimeter scale, supported by dissolved oxygen depletion coupled with a localized increase in concentrations of (H^+) and (SO_4^{2-}). Early data collected from 1996 to 1997 indicated lower Cu, Cd, and Zn concentrations in interstitial water close to the interface; however, most Cd and Zn peaks appeared just below the interface at 0.5 cm in the samples collected during 1998. This clearly indicated some mobilization of these metals, and their diffusion occurred toward the overlying water with time. This result was further supported by sequential extraction results that indicated change in their solid-phase partitioning from refractory to more labile fractions. In contrast to Cd and Zn, mobilization of Cu from the tailings was less evident. Unlike previous reports, which had suggested submerged tailings were effectively inert, this study showed an alteration of the superficial layer over time.

Stekenjokk Copper-Zinc Mine, Northern Sweden

The Stekenjokk mine is located 800 m above sea level in the Lapland Mountains in northern Sweden and has an average annual temperature of 0 °C. This facility mined and processed 8 Mton of the pyritic Zn, Cu, and silver (Ag) ores, and 4.4 Mton of tailings were deposited until mining ceased in 1988. The pond tailings were found to be net acid-producing, with high sulfide and relatively high metal concentrations [33]. Tailings were composed of about 35% sulfides, and 5 to 15% buffering material by weight [47]. Metal concentrations in the tailings were 0.65% zinc, 0.23% copper, 0.15% lead, and 0.14% arsenic by weight [69]. Among carefully evaluated alternatives, the flooding alternative was found to be safer, more efficient, and cost-effective [17]. Additional constructions were done to facilitate a permanent water cover for subaqueous disposal. After the Stekenjokk tailings were flooded in 1991, the most complete geochemical field study was performed in 1995 with results presented by Ljungberg et al. [69], whose work focused on studying the mineralogy of the mine waste materials, concentration of the metals released into porewater, and possible diffusion of the released elements to the water column in the dam. The mineralogical characterization was conducted using common microscopy and scanning electron microscopy energy-dispersive X-ray. Samples were collected from several stations to minimize variation that may occur due to different depths and different occasions to cover seasonal variations at the mining site. Sulfidic waste rocks were used to construct the dykes and break water system in order to measure possible effects from oxidation of sulfides. Moreover, local background conditions were also studied by analyzing samples from the tributaries and the Stekenjokk stream, which has no connection with the tailings pond. Results indicated higher concentrations of Ca, S (as sulfate), Zn, and Cd in the mining-affected water compared with local background metal concentrations, whereas low Cu was detected. Porewater samples had higher Ca and S concentrations than the water column; however, Zn and Cd concentrations were similar except in the tailings that were already oxidized and weathered prior to flooding. Dissolution of gypsum in the oxidized tailings resulted in higher Ca and S concentrations in the porewater. Overall, water discharged from the impoundment in 1988 revealed an annual concentration of SO_4^{2-}, Zn, Pb, and Cu as 293, 0.18, 0.015, and 0.25 mg L^{-1}, respectively. Sulfate concentration was decreased to 60 mg L^{-1}, and Zn concentration was decreased by 90% after the pond surface water was largely drained and re-flooded as a part of closure (Erikkson 2001; [47]). Sulfide surfaces were less reactive with time due to coating them with Fe-oxy(hydroxides); this was attributed to prevailing high pH conditions in the Stekenjokk dam. Weathering of sulfide-bearing waste rock used in dyke construction, along with runoff waters draining the areas surrounding the dam, were identified as safe. Reintegration of the site into the local environment was considered successful utilizing the technique of subaqueous disposal; however, continuous monitoring and maintenance were needed [11]. The reclaimed mining site is an integrated part of the landscape at present [51].

Tri-State Mining District (Kansas, Missouri, Oklahoma)

The Tri-State Mining District located in southeast Kansas, southwest Missouri, and northeast Oklahoma, covers an area of 6475 km^2. It had been mined mainly for sulfide forms of Pb (galena) and Zn (sphalerite), and to a lesser extent for Zn carbonate (smithsonite), Pb carbonate, Pb phosphate, and other less abundant ores [10]. Mining in the district ceased in 1967, but for 100 years (1850–1950), the Tri-State produced 50% of the Zn and 10% of the Pb in the USA. The process of mining PbS and ZnS generated some smelter slag, and plenty of chat and mine tailings that were discarded and typically stored on the site. Ground water flood control ended when pumpage declined in 1950s and 1960s, and contaminated runoff became a threat to the quality of neighboring ground and surface water [82]. With lack of efficient milling and mining, residual Pb and Zn remained in chat and tailings. The US EPA proposed six plans for remediation of toxic metals present in the mine waste materials in the Tri-State Mining District: (1) no action; (2) source consolidation, containment, and revegetation using biosolids; (3) source consolidation, and containment and revegetation using simple soil cover; (4) source removal and disposal in mine subsidence pits; (5a) source removal and disposal in centralized aboveground repositories; and (5b) source removal and disposal in centralized aboveground repositories, and water treatment [90]. Among these proposed alternatives, US EPA's highly preferred alternative 4 was based on the hypothesis that upon submergence, metals present in the mine waste materials will transform back to their sulfide forms, limiting their mobility and toxicity.

The idea of source removal and disposal of mine tailings in subsidence pits has not been used on a large scale; however, the pilot-scale study was conducted by Newfields [82] in order to reduce metal loadings in surface water. The demonstration site selected for this remedial option was a subsidence pit in the Waco subdistrict of the Tri-State Mining District near Waco, Missouri. At the experiment site, a subsidence pit was backfilled with 4.4×10^4 m^3 of mine tailings. For post-backfill monitoring, water samples were collected from nearby ponds, shallow aquifer wells, and a central well placed at full depth in the center of the backfilled pit. Chemical analysis of the collected samples indicated no increase in water quality parameters compared with targeted detection limits at the demonstration site, except a short-term spike in Zn concentration was observed (Table 2) at one site but stabilized around 0.01 mg L^{-1}, and that could have happened due to recharge of the pond via periodic flooding. No further metal transport was predicted once the reducing conditions were established and had persisted [82].

As a follow-up of the study conducted by Newfields in 2003, a series of lab-based column experiments were conducted utilizing mine waste materials collected from the Tri-State Mining District to test the efficacy of the most-preferred alternative provided by US EPA [57]; Ph. D. Dissertation. Several challenges were associated with this strategy such as inherently low dissolved organic carbon (DOC) present in the mine waste material, which could slow down reduction-influencing redox processes [14, 43, 133], and low S that might limit sulfide formations. Higher carbonate concentration-emanating alkaline pH may favor carbonate precipitation that is not as stable as sulfide minerals [27, 59, 67, 115]. Taking

Table 2 Water quality parameters measurements collected from the subsidence pit in the Waco subdistrict of the Tri-State Mining District near Waco, Missouri. (Source: [82])

Analytes	Target detection limit[a] mg L^{-1}	Remarks
Alkalinity, total[b]	5	Chemical analysis of the collected samples indicated no increase in water quality parameters compared with targeted detection limits in the demonstration site except only a short-term spike in Zn concentration was observed at one site but stabilized around 0.01 mg L^{-1}. In contrast, the water chemistry results along with mineralogical results indicated that synergistic effect of organic carbon and sulfur may be more promising option for mitigating environmental impacts from mine waste materials in the Tri-State mining site [58].
Chloride, total[c]	5	
Hardness, total[b]	5	
Sulfate, total[c]	5	
Total dissolved solids[b]	10	
Total Suspended solids[b]	5	
Cadmium[c,d]	0.0005	
Calcium[c,d]	0.4	
Iron[c,d]	0.2	
Lead[c,d]	0.002	
Manganese[c,d]	0.005	
Zinc[c,d]	0.01	

[a] Detection limits are highly matrix dependent. The detection limits listed are provided for guidance and may not always be achieved

[b] Standard methods for examination of water and waste waters

[c] Methods for Chemical Analysis of Water and Wastes

[d] Dissolved and total recoverable

into account the above challenges, three series of short- (32-day), medium- (119-day), and long-term (252-day) saturated column experiments were conducted under anaerobic conditions inside the glovebox, using a completely randomized design with a two-way factorial combination of treatments (Factor 1: OC) with two levels, 0 and 10.7 mM L^{-1}; Factor 2: S (Na_2SO_4), with two levels, 0 and 252.7 mg kg^{-1}). Hardly, any of the studies conducted provided a complete understanding of the biogeochemical transformation of elements present in the mine waste materials treated with OC and S under reduced conditions. Detailed wet chemistry measurements were collected, and transformation of minerals/solids upon OC and/or S treatments were identified

Table 3 Summary of aqueous data collected at different time points. (Source: [58])

Sample[†]	Zn µg L^{-1}	Cd[€]	Pb[€]	Fe$_{Total}$	pH	DOC[‡] mg L^{-1}	Sulfate-S	Mn
C0S0 7-day	1377 ± 8	264 ± 3	247 ± 19	14 ± 0.06	8.4 ± 0.1	26 ± 5	627 ± 5	9.6 ± 1.5
C0S0 28-day	828 ± 12	585 ± 39	193 ± 32	360 ± 36	8.5 ± 0.06	15 ± 0.5	505.67 ± 1	16 ± 0.4
C0S0 119-day	723 ± 41	432 ± 11	< DL	31 ± 2	7.6 ± 0.02	5 ± 0.03	474 ± 10	1.8 ± 0.3
C0S0 252-day	517 ± 31	28 ± 1	< DL	85 ± 6	8.4 ± 0.03	62 ± 2.6	571 ± 5	< DL
C0S1 7-day	311 ± 3	48 ± 0.5	84 ± 0.09	19.0	8.2 ± 0.03	28 ± 0.3	732 ± 2	2.3 ± 0.1
C0S1 32-day	104 ± 18	40 ± 15	3 ± 0.15	329 ± 4	8.2 ± 0.12	13.4 ± 0.9	508 ± 1	4 ± 0.01
C0S1 119-day	30 ± 2	2 ± 0.01	< DL	197 ± 24	8.00 ± 0.02	4 ± 0.1	468 ± 6	4 ± 0.06
C0S1 252-day	< DL	1 ± 0.006	36 ± 1.6	25 ± 5	6.4 ± 0.005	65 ± 0.8	¶	< DL
C1S0 7-day	734 ± 13	334 ± 0.2	251 ± 9	166 ± 5	8.2 ± 0.03	190.6 ± 0.9	637 ± 1	6 ± 2
C1S0 32-day	22 ± 1	235 ± 54	< DL	4165 ± 605	7.9 ± 0.03	307.2 ± 4.9	577 ± 2	14 ± 5
C1S0 119-day	< DL	1 ± 0.004	< DL	257 ± 3	8.2 ± 0.01	5 ± 0.02	503 ± 7	< DL
C1S0 252-day	< DL	< DL	< DL	108.0	7.6 ± 0.01	< DL	474 ± 3	< DL
C1S1 7-day	139 ± 7		11 ± 0.2	20 ± 0.5	8.2 ± 0.00	270.4 ± 4.0	723 ± 7	1 ± 0.02
C1S1 32-day	< DL	6. ± 0.1	< DL	26 ± 0.5	8.1 ± 0.01	232.9 ± 1.8	543 ± 2	2 ± 0.02
C1S1 119-day	< DL	1 ± 0.004	< DL	1087.0	7.4 ± 0.01	4 ± 0.1	437 ± 10	< DL
C1S1 252-day	< DL	< DL	< DL	149.0	7.02 ± 0.01	< DL	288 ± 8	< DL

[†] C0S0, control (no treatment); C0S1, only S treated; C1S0, only organic C treated; C1S1, organic C plus S treated

[‡] Dissolved organic C

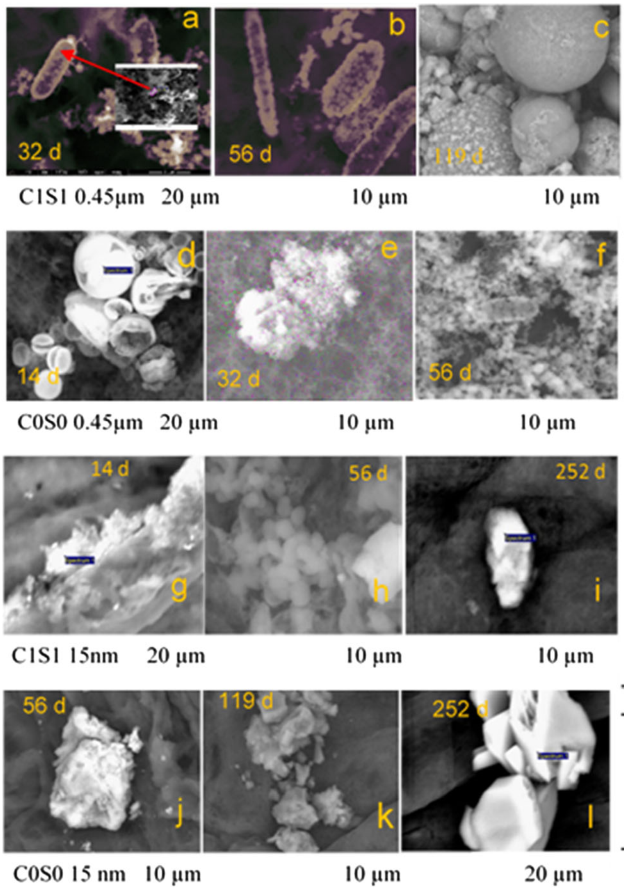
[€] Detection limit of 0.6 for Cd, and 0.7 µg L^{-1} for Pb were determined

[¶] Data not collected

using micro- and bulk-X-ray absorption spectroscopy (XAS) methods. GeoChip 4.2 was used to identify genes involved in redox-processes leading to metal sulfide formations. To trace the colloidal bound trace elements' mobility, possibly due to sulfide precipitates, a scanning electron microscopy energy-dispersive X-ray was conducted on the residues retained on the 0.45-μm nylon membrane and 15-nm polycarbonate membrane at sampling points of 14, 32, 56, 119, and 252 days of submergence. As supportive evidence, effluent filtered through 0.45-μm and 15 nm membranes was also analyzed using inductively coupled, plasma optical emission spectroscopy and graphite furnace atomic absorption spectroscopy. Details of each approach can be obtained from Karna ([57], Ph. D. Dissertation; [58]).

Effluent chemistry analyses indicated that alkaline pH prevailed throughout the submergence due to a parent material with high-carbonate content in the Tri-State Mining District. A decrease in DOC, sulfate, and soluble trace element concentrations, including Fe, indicated that metals were effectively immobilized under submergence under all short-, medium-, and long-term submergences (Table 3). Mineralogical identification via bulk-XAS analysis indicated both OC and S to be more effective in metal sulfide formation, and sulfides detected in this treatment exceeded the sum of each individual treatment (62% for Pb, 33% for Zn, and 39% for Cd under 252-day submergence). However, the addition of OC, with or without S, promoted similar amounts of PbS formation in the long-term (under 252-day submergence). In contrast, metal carbonates dominated in the non-amended flooded mine waste materials and mine waste materials only amended with S [58]. Detection of increased SRB genes, dsrA/ B in both OC- and S-treated samples, appeared to be key players in forming metal sulfides over 252-day submergence ([57], Ph. D. Dissertation).

Colloidal-bound trace metal mobility was observed via scanning electron microscopy, energy-dispersive X-ray conducted on residues collected on 0.45-μm and ~15-nm nylon membranes at different time points. Images



Element	14 d	32 d	56 d	119 d
Fe	1214	1187	751	118
S	6	31	56	175
Zn	44	-	15	27
Cd	20	19	6	-
Pb	7	-	-	4

Element	14 d	32 d	56 d	119 d
Fe		340	1656	1176
S	53	25	31	
Zn	361	477	265	123
Cd	122	93	4	14
Pb	48	14	1.5	2

Element	14 d	32 d	56 d	119d	252 d
Fe	1542	11	93	-	5
S	143	2991	365	384	19
Zn	50	3	17	8	-
Cd	3	-	-	-	3
Pb	12	-	-	-	2

Element	14 d	32 d	56 d	119d	252 d
Fe	40	-	2547	69	19
S	6	-	319	-	3925
Zn	3	-	-	15	-
Cd	-	2	-	2	-
Pb	1	-	15	3	15

Fig. 1 Scanning electron microscopy energy dispersive X-ray showing bacterial associated and freely dispersed colloidal bound trace elements mobility observed on residue retained on 0.45-μm and 15-nm pore size membranes at different time points. The images for each data points are not presented; elemental analyses are presented in the attached table. The letter "d" in the attached table represents for day. Nova NanoSEM 430 (FEI, Hillsboro, OR) equipped with energy dispersive spectroscopy (EDS) silicon drift detector (SDD: 80 mm^2). For EDS, the primary electron beam energy was 15 KeV, the spot size was 4, and data were collected over 120 s for minimum three spots per sample under vacuum of 0.45 Torr to obtain good quality image. Copper was used for quant optimization of the EDS. The weight % were converted into millimolar for better comparison of elements with different molecular weights

exhibited both bacterial associated, and/or dispersed colloidal-bound trace elements' mobility was most often observed in control (C0S0) compared to treated (C1S1) (Fig. 1). Larger size colloid ($> 0.45\ \mu m$) appeared to be highly involved in Cd and Pb mobility compared with smaller colloids (< 15 nm) (Fig. 1). This was further supported by concentrations of trace elements in effluent samples filtered through 0.45-μm and 15-nm membranes. Pb and Cd mobility detected was about 1% of the total concentration. However, considering the percentage of metal escape, it may not be a concern as escaped metals could get diluted once mixed with groundwater over time. In any case, a retention filter and other engineering controls may be needed to meet the US EPA groundwater MCL for Cd ($< 5\ \mu g\ L^{-1}$) and Pb ($< 10\ \mu g\ L^{-1}$).

Based on the above case studies, it can be inferred that subsurface disposal of mine waste materials in the subsidence pit is a viable option when applied with some agronomic and engineering control. Furthermore, increased nutrient availability can facilitate microbial activities involved in the sulfate-reduction process and enhance metal sulfide precipitation processes. Since, redox-based reactions and associated complexities are involved with subsurface submergence, it is important to have a better physical, chemical, biological, and mineralogical understanding of mine waste materials prior to and after disposing of the materials in the subsidence pits, or any natural or constructed wetlands. However, the "one-fits-all" approach for remediating mine waste materials may have more potentially damaging consequences if natural water resources such as lakes, or man-made water reservoirs, are used for this purpose. In addition to continual development of this technique with more engineering controls, an integrated remedial option should also be tested, along with subsurface submergence of mine waste materials to mitigate any unintended consequences that may occur over time. Results obtained from the studies conducted by Öhlander et al. [87] and Vigneault et al. [122] also substantiate to take this approach, where selection of an appropriate remedial option for the mitigation of mine waste material depends upon its mineralogical composition, reactivity, and potential risk to human health and the environment; since only a few studies have considered the reactivity of tailings that have been submerged over long time periods. In addition, site geology, hydrology, land-use planning, and cost-and-benefit analysis are other factors considered during the decision-making process.

Funding This work was supported by the USDA National Institute of Food and Agriculture, Hatch/Multi-State project 1005397, and K-State Research and Extension. RKs time is currently supported in part by an appointment to the Internship/Research Participation Program at the (National Risk Management Research Laboratory, Cincinnati, OH), US Environmental Protection Agency, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and EPA.

Compliance with Ethical Standards

Conflict of Interest The authors declare no conflict of interest.

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