

VALORIZATION OF RESIDUAL MATERIALS IN THE PREVENTION AND TREATMENT OF CONTAMINATED MINE WATER AND AIR

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ABSTRACT – Valorization of residual materials, close to mine sites, reduces the environmental footprint and helps balance the ratio of rentability to responsible management of natural resources. Relevant case studies using raw vs modified, organic vs inorganic residual materials for contaminated mine water prevention and efficient treatment, using active and passive treatment processes are presented. Main findings show: 1) mono- and multi-layer solid covers installed on top of fresh or weathered mine tailings have beneficial role in limiting oxygen and water ingress to reactive minerals and mine drainage generation; 2) reactive mixtures composed of natural and residual materials are efficient in (semi)-passive treatment of contaminated mine drainage from covered tailings; 3) contaminated residues from active and passive treatment of mine water can efficiently be used in the revegetation of rehabilitated mine sites; 4) modified materials (efficiency enhancement) with porous structure and basic character (functional groups connected to their surface) are effective for the capture of acid gases such as SO₂ emitted from mining and metallurgical industries, and water contaminants from forestry lumber and mining. Valorization of raw and modified materials for the prevention and treatment of contaminated mine water and air is promising for circular economy development in remote regions as well as the reduction of the environmental footprint.

Keywords: Residuals valorization, Prevention and treatment, Mine sites rehabilitation.

INTRODUCTION

Mixed contamination of mine water is entailed by the exploitation of low-grade ores that require more aggressive metallurgical separation. However, efficient mine water treatment and responsible management of sludge is imperative for mining industry and governments. Metastable characteristics of some species, changes related to the mine life cycle and mixing processes occurring at various scales lead to evolutive behavior of contaminants. In cold climate, water treatment requires adaptation to site conditions such as high flow rates, salinity, low temperatures, remoteness, and high sensitivity of receiving streams [1]. Contaminants of emerging concern (CEC) are a newer challenge in mine water, including species such as: new (rare earth and radioactive elements, Mn, Se), of emerging interest (salinity, sulfate), for which environmental issues were not fully comprehended earlier, and “well-documented” (flotation collectors, As, S- and N-

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compounds), with persistent but unknown aquatic toxicity [1]. Consistently, atmospheric contaminants increasingly become another critical environmental issue.

At the same time, several natural and residual materials are available close to mine sites: wood waste [2-4], desulfurized tailings [5], activated biochar [6-9], food waste and zeolites [10], peat [3], ash [11], dolomite [7], and mine water treatment residues [12-14]. These materials can be used as amendments or covers for tailings [12], for mine water treatment and mine site rehabilitation and, thus, limit the transportation costs, environmental footprints, and related impacts. They can be used as raw, modified or activated products. Several relevant examples of case studies, at laboratory vs field-scale are presented and discussed, for materials' performance and overall implications.

FUNDAMENTALS

Mine water and air treatment and mine sites rehabilitation require high quantities of products and materials, most of each are transported from outside the mine sites. To limit contamination and long-term water treatment, prevention and mitigation of porewater quality in mine tailings are necessary. Acid mine drainage (AMD) prevention is facilitated when done on fresh vs severely weathered acid-generating tailings. The leaching front of AMD in the porewater of highly oxidized tailings may take at least 20 years to wash out [15], depending on the properties of tailings and climate.

The mechanisms within amendments and covers made of organic or mineral, natural or residual materials can lead to geochemical and geotechnical stability of amended or covered tailings [16]: 1) Anoxic/anaerobic environment creation, for metal sulfides precipitation; 2) pH and alkalinity increase by neutralizing materials or by mineralized organic carbon; 3) Contaminated porewater dilution and improved efficiency of passive treatment; 4) Formation of a hardpan of secondary minerals playing a protecting role to prevent unoxidized tailings; 5) Limitation of water infiltration in tailings by favoring horizontal runoff; 6) Improvement of geochemical and mechanical properties of tailings and development of a protective layer favorable to tailings revegetation.

Laboratory vs field case studies from Canada are detailed in the next chapter.

CASE STUDIES

Laboratory scale

Case I: Wood residues from sawmills and reconstituted wood panels were converted into activated biochar (AC) through a two-step thermochemical process: (i) a pilot scale fast pyrolysis at 250 kg/h and 450°C; and (ii) a physical activation at up to 950°C using an activation furnace (1 kg/h). A laboratory dispositive for evaluating the SO₂ retention performance of all materials was developed, and their adsorption capacities were the following: up to 77 mg/g (AC from wood residues) [6]; up to 2140 mg/g (AC from wood panels residues) [17] as well as up to 65 mg/g for a commercial activated carbon. These results could be explained by the high specific surface area of AC, the presence of nitrogen to a basic material' surface, efficient for the SO₂ capture, as well as a great microporosity developed. This study could help the Canadian residual materials

management policies through the valorization of wood residues for the creation of a green economy reducing the carbon footprint through their transport.

Case II: A biochar pellet made from sawmills wood residues rich in ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, by the conversion of N-NH_3 from a mine effluent, was developed as a soil substrate in laboratory scale [13]. Greenhouse tests were carried out using combinations of substrates for black spruce growth such as (i) peat; (ii) peat and bulk biochar; (iii) peat and $(\text{NH}_4)_2\text{SO}_4$ -bulk biochar; (iv) peat and wet biochar pellets; (v) peat and $(\text{NH}_4)_2\text{SO}_4$ -biochar pellets; and (vi) peat, $(\text{NH}_4)_2\text{SO}_4$ -biochar pellets and perlite. The results showed that a quarter of peat could be replaced by biochar to obtain similar or better biomass yield (27% higher vs peat as control). This approach could benefit the carbon capture and storage in soil, and be applied for other fields such as golf courses, forestry producers and horticultural nurseries with the aim of replacing conventional fertilizers and peat.

Case III: N-rich residues (saturated zeolites and biomass from 50-280 mg/L $\text{NH}_3\text{-N}$ treatment in synthetic and real mine effluents) were tested as substitute of commercial fertilizers for the vegetation of non-acid generating tailings [14]. Tests were conducted over a 3-month period in pots with agronomic herbaceous plants. Unamended vs amended tailings with a mineral NPK fertilizer, and a commercial topsoil were used as controls. The comparison used were above-/below-ground biomass production, leaf area, root length/diameter, and leaf NPK concentration. Transfer of contaminants to leaves and runoff was assessed. The results showed low biomass with the N-rich zeolite amendment, whereas plants in MBBR biomass amended tailings had similar biomass to those in the tailings amended with the NPK mineral fertilizer and commercial topsoil. Leaf nitrogen in amended treatments were higher vs the unamended control. A concentration 6-9 times higher in Na was found in the leaves of plants in the zeolite treatments vs other treatments. Transfer of Cr from amended tailings to the plants and a Se bioaccumulation in plants in the MBBR biomass treatments were found. Surface runoff did not show metal contamination. The findings showed promising potential valorization of MBBR biomass as amendments to non-acid-generating mine tailings.

Case IV: Biochar and activated biochar made from wood residues from sawmills were also applied for the removal of phenol from synthetic (up to 1500 mg/L) and real effluents (0.54 mg/L) [8]. The sorption capacity of AC for phenol was more than twice compared to biochar (303 vs 159 mg/g). This is probably due to their improved textural properties having micropores and high proportion of oxygenated carbonyl groups connected to their surface. Up to 95% of phenol removal from leachates in a lumber industry site was found to below Québec's discharge criteria (0.05 mg/L). Activated biochar was also efficiently thermally regenerated after 5 cycles adsorption-desorption.

Case V: Physically (CO_2 vs steam) and chemically (KOH) activated biochar was developed from sawmills wood residues by a two-step process: fast pyrolysis using a pilot scale furnace (250 kg/h); activation using an in-house activation furnace [9]. The CO_2 -activated biochar was the most efficient material for Cu removal (99%), at concentrations up to 200 mg/L, whereas KOH-activated biochar was the most efficient material for Cu removal at 1 g/L Cu and a real effluent (AMD). The latter was attained to below the authorized monthly mean allowed by Canadian law (0.3 mg/L). Both materials presented

improved physicochemical characteristics (high surface area and porosity, oxygenated functional groups connected to the materials' surface). However, the KOH material presented the highest oxygenated functional groups that favored the chemisorption of Cu ions. Moreover, the ion competition in multi-metal acid mine drainage probably lowered metal adsorption capacities of all modified materials.

Case VI: Low-cost materials including biochar (B), Fe-loaded biochar (BF), activated biochar (BC), Fe-loaded activated biochar (BCF and BFC), thermally modified dolomite (MD), wood ash (WA), and modified wood ash (MWA) were evaluated as adsorbents for As removal from synthetic vs real mining effluents, in batch and column tests [7]. The most performing material for As(V) removal was MD followed by WA, BCF, BF, BFC, MWA, BC and B. Biochar-derived materials were not the most performant materials probably because of the low As(V) concentration from synthetic and real effluents (850 vs 300 µg/L). Thus, modified dolomite was the most efficient material for the As(V) removal in batch (99.9%) and column testing (99.6%) after more than 112 days. However, the only parameter that must be adjusted is its final pH that was above the Canadian criteria.

Field scale

Case VII: The East-Sullivan mine extracted Au, As, Cu, and Zn (1949-1966) from a sulfide orebody (50% pyrite and pyrrhotite) and produced 15 Mt of tailings covering 228 ha (2.1-13.5 m) [18, 19]. After decades of site abandonment, AMD had pH 2, and up to 18 g/L Fe and 37 g/L sulfate. The mine site rehabilitation started with an experimental wood waste cover (in 1980s) to prevent sulfides oxidation. Wood residuals (barks, logs, sawdust of coniferous and deciduous species) covered the tailings, overlined by biosolids [18, 19]. A seepage collection system around the covered tailings and the passive treatment in constructed wetlands was implemented in 1990. As passive treatment was inefficient, water recirculation (1998-2005) collected from the covered tailings back through the organic cover, which served both as barrier for AMD prevention and as biofilter, was necessary. This approach was successful, and water in wetlands surrounding the covered tailings was then deemed of satisfactory quality. A recent study using 25-year monitoring data (2000-2025) shows compliance with regulation [19]. A previous study showed no associated risks for the avian fauna from the wetlands [18]. Maintaining high moisture conditions in such a wood-waste cover and the replenishment of old by more recent wood-waste were highlighted as main lessons learned from this case study. New research is needed to confirm whether the maintenance of a high degree of saturation in tailings is enough or the AMD recirculation through the cover is still necessary.

Case VIII: The Wood-Cadillac site, a former Au and Ag mine (1939-1949), extracted from ores with As, generated 3.5×10^5 t of tailings over 21 ha up to a depth of 3 m, and around 10^5 t of tailings spreading over 3 km along the Creek Pandora, in Abitibi region of Quebec's Province. The monitoring of As concentrations started in 1995 and showed up to 0.3 mg/L in natural underground and surface water, originating from As-NMD [3, 4]. In 1999, a sand monolayer cover was applied on top of tailings, and a wood-waste based biofilter was constructed for As-NMD passive treatment. The long-term monitoring data

(1999-2022), coupled to newest analysis (isotopic, microbiological, mineralogical) showed the immobilization of As in stable mineral precipitates, with 80% As immobilized by sorption and the 20% left as As sulfides [3, 4].

Case IX: Lorraine mine site. A former Au, Ag, Cu and Ni mine (1964-1968) left behind around 6×10^5 t of acid generating tailings, disposed in a 15.5 ha pond [15]. In 1998, a rehabilitation program was initiated, consisting of a multi-layer dry cover (CCBE) and four passive treatment units using three dolomite drains to prevent further AMD generation. Reclamation strategy proved effective, but the Fe-rich AMD in the tailings pore water was progressively and slowly leached out over time. Total Fe concentrations decreased from approximately 11 g/L, before the construction of the cover, to around 2.5 g/L in 2015, while the pH increased from < 3 to 5-6 over a 12-year period [15]. The efficiency of one of the three dolomitic drains drastically deteriorated over time due to the built-up of Fe precipitates, which clogged the pore spaces, and limited the flow. In 2011, the replacement of the clogged dolomite drain by a three-unit passive biochemical treatment system (train), consisting of two biofilters separated by a wood ash unit was done. The monitoring of the treatment system performed at sampling points in the first 60 months of operation showed significant improvement of AMD. The loss of efficiency over time was observed, due to porosity clogging by Fe precipitates. A stabler long-term performance would be achieved by using a multi-step system of calcite-/dolomite-DAS (dispersed alkaline substrate, a mixture of coarse material, such as wood chips, and neutralizing agents) and passive biochemical reactors [20].

CONCLUSION

The valorization of natural and residual materials available in the proximity of mine sites for mine water and air treatment and mine site rehabilitation reduces the transportation costs, environmental footprint, and contributes to a circular economy. Case studies were detailed as examples of successful application of these materials, combining prevention measures and passive treatment. New studies are necessary for a better understanding of mechanisms and processes explaining the successes obtained, and to adapt to other potential applications.

ACKNOWLEDGEMENT

This study was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canada Research Chairs.

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