

Thermally activated minerals and waste for mine water treatment

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Abstract

Mine drainage results from the interaction between the run-off and the bedrock, mine waste or tailings. Its passive treatment is a challenge due to the variable charge in metals, metalloids, sulphate, also variable concentrations range and season impacted flow. Moreover, environmental impacts of mine drainage may persist hundreds to thousands of years after mine closure. Accordingly, mine drainage treatment is mandatory, in order to limit the discharge of contaminants into environment. Mining companies are continuously searching for treatment technologies to reduce their environmental footprint and the cost of water treatment. Therefore, the utilization of waste materials in water remediation is attracting more attention. Moreover, physicochemical and mineralogical modification of waste materials prior to their use enhance their metal removal capacity and their mechanical and chemical stability. Consequently, modified waste becomes an interesting option, for both active and passive treatment of the mine drainage.

Several underutilized natural, or various waste materials resulting from diverse human activities can be modified for water treatment through simple procedures: chemical activation with oxidants, acids, or bases; coating; grafting of metal or organic functional groups; thermal activation (calcination, pyrolysis, alkaline fusion, hydrothermal treatment). Among these, thermal activation by calcination can highly improve materials' performance for water treatment by mean of a simple procedure involving a relatively low cost. Calcination modifies chemical composition and mineralogy, as well as surface charge and oxidation-reduction potential; enhances neutralizing capacity and alkalinity generation, as well as specific surface and porosity; reduces grain size. In our studies, dolomite [$\text{CaMg}(\text{CO}_3)_2$] was partially decomposed in calcite (CaCO_3) and periclase (MgO) by calcination 1h at 750°C . The new material showed improved efficiency for Mn treatment, which was reduced from 0.65 to 0.05 mg/L in a contaminated neutral mine drainage (CND) and also for As treatment, reduced from 196 to 2 $\mu\text{g/L}$ in a CND. Moreover, eggshells calcined 1h at 900°C and employed in a 0.3% solid: liquid ratio increased the pH of an acid mine drainage

(AMD) from 2.5 to 6.9 at 20°C and to 9.2 at 4°C, respectively. Various contaminants concentrations were reduced as follows: As <0.0005 mg/L, Cd 0.00022 and 0.00009 mg/L, Cu 0.0061 and 0.0091 mg/L, Co 0.0338 and 0.0016 mg/L, Cr 0.0015 and 0.0022 mg/L, Fe <0.01 mg/L, Ni 0.0291 and 0.0024 mg/L, Se 0.0033 and 0.0044 mg/L, Zn 0.007 and 0.022 mg/L, at 20°C and 4°C respectively. Eggshells mineralogy changed from 99.43% calcite (CaCO₃) before calcination, to 51.4% calcite (CaCO₃) and 48.6% portlandite [Ca(OH)₂] after calcination. Finally, paper sludge was employed to treat Zn from a CND (pH 7.72). While the raw material reduced Zn from 9.72 mg/L to 1.99 mg/L, calcined material (6h at 700°C) reduced Zn below 0.01 mg/L. To conclude, thermal activation by calcination for different underutilized materials or waste locally available (to reduce transport costs) can be considered and optimized for mine drainage treatment.

Introduction

Mine drainage is unique among contaminated waters, given its mechanism of generation, charge and flow, and environmental impacts, which may persist hundreds to thousands of years after mine closure (Sapsford, 2013; Kučerová et al., 2014; Frau et al., 2015). Mine drainage can be acidic (acid mine drainage; AMD; pH<6), circumneutral (contaminated neutral drainage; CND; 6<pH<9), basic (pH>9), diluted, mineralized, or saline (Nordstrom et al., 2015). The AMD is characterized by the presence of elevated concentrations of various inorganic contaminants such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), nickel (Ni), mercury (Hg), manganese (Mn), iron (Fe), selenium (Se), copper (Cu), vanadium (V), and zinc (Zn) (Nordstrom et al., 2015). The CND contains significant concentrations of metals and metalloids that are soluble at near-neutral pH (As, Sb, Se, Ni, Zn, Mn), being increasingly recognized as an environmental concern (Stantec, 2004; Bright and Sandys, 2015). The above contaminants are harmful to humans and environment, their treatment being mandatory (Etteieb et al., 2021).

Mine waters treatment methods include the following processes: chemical precipitation, coagulation-flocculation, flotation, filtration, solvent extraction, electrochemical treatment, ion exchange, complexation, evaporation, distillation, crystallization, oxidation, reduction, phytoremediation, and adsorption (O'Connell et al., 2008; Sandy and DiSante, 2010). However, treatment is challenging as mine waters contain mixes of contaminants, while optimal treatment conditions can be contaminant-specific (Calugaru et al., 2018). Water pH and Eh (redox potential) are important parameters as they influence elemental speciation and solubility, and thus treatment options (Calugaru et al., 2021b). Other significant issues are the potential for metals recovery (Rakotonimaro et al., 2017) and water recovery and reuse (limited but reusable resource). Finally, site-specific, regulatory, economic, environmental, and social factors represent additional constraints for the selection of a remediation system. As the global commitment to sustainable development and sustainable remediation have increased, mine industry searches for

treatment technologies that reduce the environmental footprint of water treatment, considering, among other factors, the utilization of waste and underused materials in water remediation (Favara and Gamlin, 2017; Hengen et al., 2014). Moreover, modification of readily available materials enables the reutilization and stabilization of residues (Vadapalli et al., 2010), decreases manufacturing and transportation costs (Hengen et al., 2014), offers flexibility in terms of treated pollutants (and to flow and charge variations), and allows metal recovery and sorbent regeneration (O'Connell et al., 2008).

Several mineral and organic materials can be easily modified for application in wastewater treatment. Chemical and mineralogical modification can be performed: by calcination of seashells, eggshells, dolomite, sewage sludge, paper sludge; by alkaline fusion and hydrothermal treatment of coal, bagasse, and waste incineration fly ashes, for zeolite fabrication; pyrolysis of various organic waste for biochar production (Calugaru et al., 2018). Chemical activation can be performed by: oxidation (e.g. of peanut hull biochar and cellulose), alkali activation (e.g. of switchgrass biochar and wood residues), Fe (III) impregnation (e.g. of activated carbon, biochar, peat, agricultural residues, sand, cellulose, zeolite), acid hydrolysis (e.g. of wood residues, chitin, seashells), grafting of metal-binding functions (e.g. on cellulose, wood residue, chitosan, bacterial and fungal biomass) (Calugaru et al., 2018).

The aim of this paper is to present the improved performance by calcination for three largely and readily available materials: dolomite, eggshells and paper sludge, for mine drainage treatment.

Methodology

The dolomite was supplied at Temiska Silice (Saint-Bruno-de-Guigues, Quebec). Its thermal activation (half-calcination) was carried out in a furnace (Thermolyne Furnace type 30400, Barnstead International), at 750°C, for 1 hour (Calugaru et al., 2016).

The eggshells were recovered from a local cafeteria, washed with deionized water and dried at 100°C in an oven (Heratherm, Thermo Scientific). Then, they were crushed for 30 seconds in a ring grinder (SRM type, model C+RC, Rocklabs). Afterwards, eggshell powder was calcined in the oven (Thermolyne Furnace type 30400, Barnstead International), for 1h, at 800°C, 850°C, and 900°C (Calugaru et al., 2022).

The paper sludge was sampled at the pulp mill Nordic Kraft (Lebel-sur-Quevillon, Québec). Its calcination was carried out in a four (Lindberg Blue M), for 6h, at 500, 600, 700, 800, and 900°C.

Characterisation of solids was performed by X-ray diffraction (XRD) using a Bruker AXS D8 advance X-ray diffractometer. The DiffracPlus EVA software was used to identify mineral species and the TOPAS software implementing Rietveld refinement was used to quantify the abundance of all identified mineral species (Calugaru et al., 2016; Calugaru et al., 2022). The loss of ignition was evaluated by 16h calcination at 375°C in a Thermolyne Furnace (type 30400 from Barnstead International), according to standard Method MA. 1010-PAF 1.0. The organic matter was evaluated by charring at 550°C in an oven

(Thermolyne Furnace type 30400, Barnstead International). Thermogravimetry analysis (TGA/DSC, model STA449FS, Netzsch) was performed to evaluate the thermal decomposition. Granulometry was evaluated (Microtrac) and the specific surface was measured (model vacprep061, Micro metrics) as the particle size is supposed to decrease and the specific surface is supposed to increase after calcination. Paste pH was measured (Hach HQ30d Flexi multimeter) after 1 h of contact in ratio solid: liquid (deionized water) of 1:10 (Method D 4972-95a, 1995, ASTM). Then, PZC pH (the pH for the material which has a zero electrical surface charge) was determined by the salt (solid) addition method (Bakatula et al., 2018). Acid digestion followed by elemental qualitative and quantitative analysis was performed using microwave plasma atomic emission spectrometer (Agilent Technologies Spectrometer 4200 Series, Santa Clara, CA, USA) (Calugaru et al., 2016; Calugaru et al., 2022).

Mine effluents were sampled on sites of gold and zinc active mines in the Abitibi-Temiscamingue region of Quebec, Canada. The effluents were preserved at 4°C prior to analysis and testing. Qualitative and quantitative elemental analysis of the mine effluents before and after treatment was performed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800). The Eh and pH were measured with Hach HQ30d Flexi multi-meter.

Results and discussion

Half-calcination at 750°C, for 1 hour, of dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), lead to its decomposition in a mixture of calcite (CaCO_3) and periclase (MgO) (Calugaru et al., 2016).

Half-calcined dolomite was found effective for the treatment of Mn in a gold mine CND (pH 4.8÷8.1) during 6 months of column testing, for 6h or hydraulic residence time (HRT). Previously, the efficiency of raw dolomite vs. half-calcined dolomite was evaluated in batch testing with synthetic DNC and Mn removal by raw dolomite was found very poor: 11,9% Mn removal (Table 1, Calugaru et al., 2021a).

Half-calcined dolomite was also found effective for the treatment of As (V) (Table 1, Braghiroli et al., 2020). Synthetic CND of pH 7 containing 850 mg As (V) / L was put into contact with half-calcined dolomite in a solid: liquid ratio of 1% in batch testing. After 8h, the As concentration was below the detection limit (BLD), whereas the maximum As removal of half-calcined dolomite was found 820 µg As/g. For column testing, a gold mine CND (pH≈7) was employed. For an HRT of 2h, the As concentration was decreased from 196 µg/L to 0.5÷1.9 µg/L. When test was ended (after 112 days), the half-calcined dolomite was still efficient.

Calcination of eggshells (CaCO_3), at 800°C, 850°C, and 900°C, for 1 hour, lead to mixtures of calcite (CaCO_3) and portlandite [$\text{Ca}(\text{OH})_2$] in the ratios : 80% calcite to 20% portlandite; 66% calcite to 34% portlandite; and 50% calcite to 50% portlandite, respectively (Calugaru et al., 2022).

Table 1: Performance of raw and calcined materials for mine effluent's treatment

Material	Effluent characteristics	Treatment conditions	Results
Raw dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$	Synthetic CND, pH 7.2 49.6 mg Mn/L	Batch testing, 48h Solid: liquid ratio 0.75% 25°C, 300 rpm	11,9% Mn removal pH 7.0
Half-calcined dolomite $\text{CaCO}_3 \cdot \text{MgO}$	Synthetic CND, pH 6.1÷7.2 49.6 ÷ 892 mg Mn/L		≥ 97.2% Mn removal pH 9.7÷10.6
Half-calcined dolomite $\text{CaCO}_3 \cdot \text{MgO}$	Real CND, pH 4.8÷8.1 Mn ≈ 0.645 mg/L	Column testing, 6 months 203g material 20°C, 18mL/h, HRT=6h	≥ 90% Mn removal pH 6.7÷9.82 Mn ≈ 0.052 mg/L
Half-calcined dolomite $\text{CaCO}_3 \cdot \text{MgO}$	Synthetic CND, pH 7 850 µg As (V)/L	Batch testing, 48h Solid: liquid ratio 1% 20°C, 500 rpm	[As] BDL after 8h $Q_{\max} = 820 \mu\text{g As/g}$
Half-calcined dolomite $\text{CaCO}_3 \cdot \text{MgO}$	Real CND, pH 6.5÷7.8 196 µg As/L	Column testing, 112 days 120g material 20°C, 0.5mL/min, HRT=2h	0.5÷1.9 µg As/L
Raw eggshells CaCO_3	Real AMD, pH 2.25÷2.62	Batch testing, 2h Solid: liquid ratio 1% 20°C, 300 rpm	pH 5.92 Fe 85.6 mg/L Cu 0.108 mg/L Zn 3.18 mg/L
Calcined eggshells, 800°C 80% CaCO_3 , 20% Ca(OH)_2	Fe 219 mg/L Zn 1.61 mg/L Cu 0.7141 mg/L	Batch testing, 2h Solid: liquid ratio 0.5% 4°C, 20°C, 300 rpm	pH 6.66÷6.84 Fe ≤0.12 mg/L Zn ≤0.367 mg/L Cu 0.0109 mg/L
Calcined eggshells, 900°C 50% CaCO_3 , 50% Ca(OH)_2		Batch testing, 2h Solid: liquid ratio 0.3% 4°C, 20°C, 300 rpm	pH 6.89÷9.22 Fe <0.01 Zn ≤0.022 mg/L Cu ≤0.0091 mg/L
Raw paper sludge	Real CND, pH 7.3÷7.7 Zn 9.72÷13.42 mg/L	Batch testing, 24h Solid: liquid ratio 1%, 20°C, 300 rpm	pH 7.4 Pb 0.0924 mg/L Zn 1.99 mg/L
Calcined paper sludge		Pilot testing 18L, 0.5h Solid: liquid ratio 0.05%, 20°C	pH 8.8 Pb <0.01 mg/L Zn <0.01 mg/L

To comparatively evaluate the efficiency of raw vs. calcined eggshells, a gold mine AMD (pH 2.25÷2.62) was employed. The AMD contained significant concentrations of Fe (219 mg/L), Zn (1.61 mg/L) and Cu (0.7141 mg/L). The raw eggshells raised the pH of the effluent, and significantly (60%) reduced the concentration of Fe. However, the treated effluent was not conforming with Québec and Canadian regulations. In contrast, calcined eggshells succeeded to produce an effluent conform with

Québec and Canadian regulations, after 2h of contact time, at 4°C and 20°C (Table 1). Moreover, calcined eggshells were characterized by XRD after the treatment of the AMD, and gypsum was identified and quantified in significant amount (Table 2). Therefore, sulfate (SO_4^{2-}) was also treated.

Table 2: Post characterization XRD analysis of eggshells effective for AMD treatment

	Crystalline phase, %			Amorphous phase, %
	Total	CaCO_3 , %	$\text{CaSO}_4 \cdot \text{H}_2\text{O}$, %	
Calcined eggshells, 800°C, 0.5%	71.1	40.4	59.6	28.9
Calcined eggshells, 900°C, 0.3%	69.7	45.2	54.8	30.3

Paper sludge was calcined at 500°C, 600°C, 700°C, 800°C and 900°C, for 6 hours (Jha et al., 2006). Thereafter, to comparatively evaluate the efficiency of raw vs. calcined paper sludge, a Zinc mine AMD (pH 7.3÷7.7) was employed. It was noticed that although the raw paper sludge significantly (80%) reduced the concentration of Zn, the final effluent was not conforming with Québec and Canadian regulations. Moreover, for the solid: liquid ratio of 1%, a non-negligible concentration of Pb was measured in the final effluent (0.0924 mg/L). Consequently, increasing the solid: liquid ratio was not considered for enhancing Zn removal (to achieve the effluent conformity). In contrast, paper sludge calcined 6h at 700°C succeeded to produce an effluent conform with Québec and Canadian regulations, after 30 minutes of contact time, in pilot testing (18 L), for a solid: liquid ratio of 0.05% (Table 1).

It can be observed that all materials presented in this paper show significant improvement of their efficiency for mine drainage treatment, by calcination, compared to raw materials.

For the case of dolomite, conversion of MgCO_3 in MgO enhance its neutralizing capacity and increase the effluent's pH, which is an important parameter for Mn removal (Calugaru et al., 2021a). Moreover, CO_2 elimination enhance porosity and specific surface (Calugaru et al., 2016), calcite availability, and therefore the As removal (Salameh et al., 2015; Braghiroli et al., 2020). It is also to note that for dynamic (column) testing, dolomite rocks (diameter 0.5 cm) were employed, which is interesting for a passive treatment, whereas for batch testing, dolomite was use as fine powder.

For the case of the eggshells, 1h of calcination at 800°C led to the decomposition of 20% of the calcite (CaCO_3). Therefore 20% of CO_2 were liberated in the atmosphere, which is inferior when compared to the CO_2 liberated in the complete decomposition of the calcite. The resulting material was able to treat the AMD in both cold and mild temperature conditions. Moreover, a waste was used. Also, for use in dynamic regime, crushing of eggshells is not necessary as it can reduce hydraulic conductivity.

Paper sludge underwent the most important mass loss by calcination, among the materials evaluated in this study. Its calcination at 700°C produced only 1.78% ash, because paper sludge had 70% humidity and contained 86% organic matter. Therefore, $\approx 7\%$ ash could be obtained, if 2 weeks of air drying are

allowed before calcination of the paper sludge. The ash produced showed a good adsorption for Zn while the solid: liquid ratio employed (0.05%) led to a very low amount of treatment sludge, which settled fast. Moreover, a waste generated in high amounts and having few opportunities for recovery was used.

Conclusion

Calcination can highly improve the efficiency of different waste and underused materials for mine drainage treatment. However, field scale testing as well as technical-economic analysis still have to be done, considering transport cost, calcination cost, mine water treatment cost, and sludge management. The global ecological footprint of employing calcined waste for mine water treatment should be compared with the one of engineered materials. Moreover, calcination enhance the mechanical and chemical stability of waste, while products are safe to handle. Employing readily available waste also reduce natural resources exploitation. Therefore, calcined waste and underused materials could be considered as green alternatives for mine water treatment in batch or in dynamic regime, for active or passive treatment, post-closure and restoration, in multistep treatment, or included in a multicomponent/multistep treatment system like biofilter, barrier, drain, etc.

Currently, a project is ongoing at CTRI. Passive treatment solutions including thermally activated minerals and waste are being evaluated for the treatment of an exfiltration AMD issued from the passive treatment system already in place. Filters and sulfate-reducing passive biofilters composed of various materials at various proportions are being evaluated at laboratory scale (batch and column testing), to determine their hydraulic residence time and life time. Technical-economic analysis will be performed, then the best option will be applied at field scale.

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References

- Bakatula EN, Richard D, Neculita CM, Zagury GJ. 2018. Determination of Point of Zero Charge of Natural Organic Materials. *Environ. Sci. Pollut. Res. Int.* 25:7823–7833.
- Braghiroli FL, Calugaru IL, Gonzalez-Merchan C, Neculita CM, Bouafif H, Koubaa A. 2020. Efficiency of eight modified materials for As (V) removal from synthetic and real mine effluents. *Miner Eng.* 151:106310.
- Bright DA, Sandys N. 2015. Beyond ML/ARD: the many faces of neutral mine drainage in the context of mine closure. Mine Closure, June 1-3, 2015, Vancouver, BC, Canada, 10p.

- Calugaru IL, Neculita CM, Genty T, Bussière B, Potvin R. 2016. Performance of thermally activated dolomite for the treatment of Ni and Zn in contaminated neutral mine drainage. *J Hazard Mater.* 310:48-55.
- Calugaru IL, Neculita CM, Genty T, Zagury GJ. 2018. Metals and metalloids treatment in contaminated neutral effluents using modified materials. *J Environ Manage.* 212:142–159.
- Calugaru IL, Neculita CM, Genty T. 2021a. Treatment of manganese in the presence or absence of iron in acid and neutral mine drainage using raw vs half-calcined dolomite. *Miner Eng.* 160:106666.
- Calugaru IL, Etteieb S, Magdouli S, Genty T. 2021b. Selenium-rich mine effluents treatment using zero-valent iron: Mechanism and removal efficiency in the cold climate of Québec, Canada. *Environ Adv.* 5:100099.
- Calugaru IL, Etteieb S, Magdouli S, Brar KK. 2022. Efficiency of thermally activated eggshells for acid mine drainage treatment in cold climate. *J Environ Sci Health – Toxic/Hazard.*
DOI:10.1080/10934529.2022.2027699
- Etteieb S, Zolfaghari M, Magdouli S, Brar KK, Brar SK. 2021. Performance of constructed wetland for selenium, nutrient and heavy metals removal from mine effluents. *Chemosphere* 281, 130921.
- Favara P, Gamlin J. 2017. Utilization of waste materials, non-refined materials, and renewable energy in in situ remediation and their sustainability benefits. *J Environ Manage.* 204, 730-737.
- Frau F, Medas D, Da Pelo S, Wanty, RB, Cidu R. 2015. Environmental effects on the aquatic system and metal discharge to the Mediterranean Sea from a near-neutral zinc-ferrous sulfate mine drainage. *Water Air Soil Pollut.* 226:55.
- Kučerová G, Majzlan J, Lalinská-Voleková B, Radková A, Bačík P, Michňová J, Šottník P, Jurkovič L, Klimko T, Steininger R, Göttlicher J. 2014. Mineralogy of neutral mine drainage in the tailings of siderite-Cu ores in Eastern Slovakia. *Can Mineral.* 52, 779-798.
- Jha VK, Kameshima Y, Nakajima A, Okada K, MacKenzie KJD. 2006. Effect of grinding and heating on Ni²⁺ uptake properties of waste paper sludge. *J. Environ. Manage.* 80, 363-371.
- Nordstrom K, Blowes DW, Ptacek CJ. 2015. Hydrogeochemistry and microbiology of mine drainage: An update. *Appl Geochem.* 57, 3-16.
- O’Connell DW, Birkinshaw C, O’Dwyer TF. 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresour Technol.* 99, 6709-6724.
- Rakotonimaro T, Neculita CM, Bussiere B, Benzaazoua M, Zagury GJ. 2017. Recovery and reuse of sludge from active and passive treatment of mine drainage-impacted waters: a review. *Environ Sci Pollut Res.* 24, 73-91.
- Salameh Y, Albadarin AB, Allen S, Walker G, Ahmad MNM. 2015. Arsenic (III, V) adsorption onto charred dolomite: charring optimization and batch studies. *Chem. Eng. J.* 259, 663–671.
- Sandy T, DiSante C. 2010. Review of available technologies for the removal of selenium from water, prepared for North American Metals Council.

Sapsford DJ. 2013. New perspectives on the passive treatment of ferruginous circumneutral mine waters in the UK. *Environ Sci Pollut Res.* 20, 7827-7836.

Stantec Consulting Ltd. 2004. Review of water quality issues in neutral pH drainage: examples and emerging priorities for the mining industry in Canada. MEND Report 10.1, prepared by Stantec Consulting Ltd., Brampton, ON, Canada, 58p.

Vadapalli VRK, Gitari WM, Ellendt A, Petrik LF, Balfour G. 2010. Synthesis of zeolite-P from coal fly ash derivative and its utilization in mine-water remediation. *S. Afr. J. Sci.* 106, 7p.