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**REMEDIATION OF ACID MINE DRAINAGE USING MAGNESITE
AND ITS BENTONITE CLAY COMPOSITE**

By

Vhahangwele Masindi (*Pr. Sci. Nat.*)

Senior Researcher

Council for Scientific and Industrial Research (CSIR)

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Promoter: Prof. Mugeru Wilson Gitari

Co-promoters: Prof. Hlanganani Tutu

Dr. Marinda De Beer

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ABSTRACT

Wastewaters originating from mining activities are usually acidic and often contain high concentrations of Fe, Mn, Al and SO_4^{2-} in addition to traces of Pb, Co, Ni, Cu, Zn, Mg, Ca and Na. This wastewater impacts surface and subsurface water resources negatively and has to be treated before release to receiving aquatic ecosystems. Numerous wastewater treatment technologies have been developed and implemented. However, cost implications, ineffectiveness, selective treatment capabilities and generation of secondary sludge that is toxic and expensive to dispose-off to the environment due to stringent environmental regulations often limit their application. As such, mining companies are in a search for cheaper, brine free, effective and efficient mine water treatment technology. This study assessed the potential of applying mechanochemically modified cryptocrystalline magnesite-bentonite clay composite for acid mine drainage (AMD) treatment. To accomplish this, neutralization of acidity and removal of inorganic contaminants from mine effluents were studied using batch laboratory experiments and precipitation of chemical species was determined using pH Redox Equilibrium (in C language) (PHREEQC) geochemical modelling. The present study was divided into three parts which includes: (1) the application of magnesite for remediation of AMD, (2) the application of ball milled bentonite clay for remediation of AMD and (3) the application of magnesite-bentonite clay composite for remediation of AMD.

In the first part of the study, AMD was reacted with cryptocrystalline magnesite. The reaction of AMD with magnesite at an optimum solid: liquid ratio of 1:100 and contact time of 60 min led to an increase in pH, reaching a maximum pH of 10, resulting in significant precipitation of most metal species. Increase of pH in solution with contact time caused the removal of the metal ions mainly by precipitation, co-precipitation and adsorption. SO_4^{2-} concentration was lowered from 4640 to 1910 mg/L. Fe was mainly removed as $\text{Fe}(\text{OH})_3$, goethite, and jarosite, Al as basaluminite, boehmite and jurbanite, $\text{Al}(\text{OH})_3$ and as gibbsite and diaspore. Al and Fe precipitated as iron (oxy)-hydroxides and aluminium (oxy)-hydroxides. Mn precipitated as rhodochrosite and manganite. Ca was removed as gypsum. Sulphate was removed as gypsum, and Fe, Al hydroxyl sulphate minerals. Mg was removed as brucite and dolomite. These would explain the decrease in the metal species and SO_4^{2-} concentration in the product water. Cryptocrystalline magnesite effectively neutralized AMD and attenuated concentration of

inorganic species to within Department of Water and Sanitation (DWS) water quality guidelines for 1997. Though $> 60\%$ SO_4^{2-} removal was achieved, a polishing technology will be required to remove alkali and alkaline earth metal species and remaining SO_4^{2-} from the aqueous system.

In the second part of this study, AMD was reacted with ball milled bentonite clay. The contact of AMD with bentonite clay led to an increase in pH and a significant reduction in concentrations of metal species. At constant agitation time of 30 mins, the pH increased with the increase in dosage of bentonite clay. Removal of Mn^{2+} , Al^{3+} , and Fe^{3+} was greatest after 30 min of agitation. The adsorption affinity obeyed the sequence: $\text{Fe} > \text{Al} > \text{Mn} > \text{SO}_4^{2-}$. The pH of reacted AMD was > 6 . Bentonite clay showed high adsorption capacities for Al and Fe at concentration < 500 mg/L, while the capacity for Mn was lower. Adsorption efficiency for SO_4^{2-} was $> 50\%$. Adsorption kinetics revealed that the suitable kinetic model describing data was pseudo-second-order hence confirming chemisorption. Adsorption isotherms indicated that removal of metals fitted the Langmuir adsorption isotherm for Fe and SO_4^{2-} and the Freundlich adsorption isotherm for Al and Mn, respectively. Gibbs free energy model predicted that the reaction is not spontaneous in nature for Al, Fe and Mn except for SO_4^{2-} . Ball-milled bentonite clay showed an excellent capacity in neutralising acidity and lowering the levels of inorganic contaminants in acidic mine effluents. A polishing technology will be required to remove alkali and alkaline earth metal species and remaining SO_4^{2-} from the aqueous system.

The third part of the study evaluated the reaction of magnesite-bentonite clay composite in neutralisation of the acidity and attenuates levels of inorganic contaminants in metalliferous effluents. The interaction of the composite with AMD led to an increase in pH ($\text{pH} > 11$) and lowering of metal concentrations. The removal of Al^{3+} , $\text{Fe}^{3+/2+}$, Mn^{2+} and SO_4^{2-} was optimum at 20 min of equilibration and 1g of adsorbent dosage. The composite removed $\approx 99\%$ (Al^{3+} , Fe^{3+} , and Mn^{2+}) and $\approx 90\%$ (SO_4^{2-}) from raw mine effluent. Minor elements such as Co, Cu, Zn, Ni and Pb were also removed significantly. The synthesized composite showed a significantly better heavy metals and SO_4^{2-} removal ability of from highly acidic solutions as compared to that obtained by cryptocrystalline magnesite and bentonite clay when used individually. Adsorption kinetics fitted better to pseudo-second-order kinetic than pseudo-first-order kinetic and intra-particle diffusion model hence confirming chemisorption. Adsorption data fitted better to Freundlich adsorption isotherm than Langmuir hence

confirming multisite adsorption. Gibbs free energy model predicted that the reaction is spontaneous in nature for Al, Fe and SO_4^{2-} except for Mn. Geochemical model indicated that Fe was removed as $\text{Fe}(\text{OH})_3$, goethite, and jarosite, Al as basaluminite, boehmite and jurbanite, $\text{Al}(\text{OH})_3$ and as gibbsite and diaspore. Al and Fe precipitated as iron (oxy)-hydroxides and aluminium (oxy)-hydroxides. Mn precipitated as rhodochrosite and manganite. Ca was removed as gypsum. Sulphate (SO_4^{2-}) was removed as gypsum, and Fe, Al hydroxyl sulphate minerals. Mg was removed as brucite and dolomite. This would explain the decrease in the metal species and SO_4^{2-} concentration in the product water. The composite removed the contaminants to below South African legal requirements for water use. It was concluded that the composite has the potential to neutralize acidity and attenuate potentially toxic chemical species from acidic and metalliferous mine drainage as compared to cryptocrystalline magnesite and bentonite clay when used individually. As such, it can be concluded that the new synthesized composite has a synergetic potential in wastewater treatment.

Keywords: Acid mine drainage; cryptocrystalline magnesite; bentonite clay; cryptocrystalline magnesite-bentonite clay composite; chemical species; batch experiments; adsorption; precipitation; geochemical modelling