

A novel remediation learnt from natural attenuation process for copper and zinc bearing wastewater

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Generally, the removal of copper and zinc from wastewater by using antalkaline to increase pH around 7-10 will produce copper and zinc hydroxides after treatment. However, this method has some disadvantages such as dewaterability and disposal of alkali sludge, so we have to develop more efficient treatment. On the other hand, natural attenuation process for copper and zinc at Dougamaru abandoned mine is achieved at neutral pH 6 and can provide insight on how to develop more efficient and safety treatment by applying this natural attenuation process. Therefore, the objective of this study is to understand and apply the natural attenuation process of copper and zinc in the Dougamaru abandoned mine for real wastewater treatment.

In the copper-zinc-sulphide mining district of Dougamaru in Japan, blue-green precipitate is generated from the drainage. The result of X-ray and chemical analyses revealed that the main mineral component of precipitate was Hydrowoodwardite with average chemical formula of $\text{Cu}_{0.66}\text{Zn}_{0.09}\text{Fe}_{0.01}\text{Al}_{0.23}(\text{SO}_4)_{0.15}(\text{OH})_2$. This mineral is composed of positively charged copper and aluminum hydroxide layers and intercalated with sulfate anion and water molecules. Hence, it can be classified as hydrotalcite-like compounds. The results also confirmed that the reduction of copper and zinc concentrations was due to dilution by river water and natural attenuation process caused by the formation of Hydrowoodwardite at lower pH (6.0).

For understanding of the condition to form the Hydrowoodwardite, five synthesis wastewaters, each containing 1.5 g of copper sulfate and aluminum sulfate in 150ml of distilled water, were prepared. The atomic Cu/Al ratios used were 1:0, 9:1, 4:1, 2:1, and 1:1, respectively. After mixing the solution, 0.1M NaOH were added to adjust the pH to 6.0. The dried precipitates were characterized by XRD, while the filtrate solutions were analyzed by ICP-AES. From the XRD data, the peak of Hydrowoodwardite was identified in three samples with Cu/Al ratio of 4, 2 and 1. This result also suggested that the optimum Cu/Al ratio in order to form Hydrowoodardite was 4. Moreover, a similar experiment was conducted for zinc, and resulted into an optimum Zn/Al ratio of 9 to form hydrotalcite-like compounds. From the result of ICP-AES measurements, most of copper in all samples was distributed in the solid phase. Meanwhile, distribution amount for solid phase of zinc depend on the presence of aluminum in which the samples containing aluminum showed the removal efficiency from 42.4 to 58.7 %, but the sample without aluminum showed 12.7 %. Therefore, the remediation of zinc can be achieved at lower pH 6 by adding aluminum to wastewater. Moreover the interlayer anion of hydrotalcite-like compounds can be exchanged for another anion, as revealed batch adsorption experiment in which the interlayer SO_4^{2-} can be exchange for another hazardous anion. Therefore, Hydrowoodawrdite and zinc hydrotalcite-like compounds can also play a role of adsorbent for toxic anions when the drainage contains spontaneously some anions such as As, Se and Sb.

Keywords: wastewater treatment, copper, zinc, natural attenuation, Hydrowoodwardite, anion sorption