学 位 論 文 内 容 の 要 旨

DISSERTATION ABSTRACT

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学 位 論 文 題 名

Title of dissertation submitted for the degree

Long-term acid generation containing heavy metals from the tailings of a closed mine and its countermeasures

(休廃止鉱山における鉱滓からの重金属を含む酸性水の長期溶出とその対策)

Acid mine drainage (AMD) from abandoned mines is a well-known problem all over the world. The AMD is produced by the oxidation of pyrite and metal sulfides. A significant release of heavy metals (*e.g.*, copper (Cu), zinc (Zn), iron (Fe), and others) is generated and could affect the surrounding environment as well as human health when they are ingested through food crop and contaminated water. Numerous researches have been done to solve these problems by neutralizing the AMD (*e.g.*, calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH), etc.). However, it remains unclear when the treatment would stop. To answer this question, leaching behaviors of heavy metals and acid generation from a tailings dam were studied. In this dissertation, an in-depth study of the mechanisms controlling the long-term leaching of heavy metals, such as Cu, Zn, and Fe from the tailings was conducted. First, the tailings dam was characterized and speciation of heavy metals was studied. Second, the column experiments were carried out at a different irrigation rate. Finally, chicken eggshell as a low-cost neutralizer for the AMD was applied. This dissertation contains 5 chapters.

Chapter 1 introduces the background of AMD from the tailings and gives the motivation, importance, and objectives of the study.

Chapter 2 addresses the mechanism of AMD generation in the tailings from a closed mine and predicts the evolution of Cu, Zn, and Fe concentrations. Batch leaching experiments and sequential extractions were conducted to investigate the leaching behaviors of these contaminants from the tailings and to understand their solid-phase partitioning. Acid-base accounting and principal component analysis (PCA) were used to confirm factors affecting Cu, Zn, and Fe leaching and acid formation based on the leaching experiments. There were strong positive correlations between Zn, Fe, or EC and sulfate ion (SO_4^{2-}), indicating that pyrite and sphalerite are the major minerals releasing Zn and Fe. This agreed with the PCA results. In the upper part of the tailings, the water-soluble and sulfide fractions of Cu, Zn, and Fe were almost flushed out, whereas they remained high in the deeper tailings. This implies that the tailings will likely continue to release these contaminants (Zn > Cu > Fe) for a long time unless remedial measures are taken.

After identifying the high content of heavy metals and ions in the deeper tailings samples, Chapter 3 addresses the understanding of the long-term acid generation and leaching behaviors of Cu, Zn, and Fe. The unweathered tailings samples at depths of 1 to 3 m were collected from the tailings dam. The mechanisms of long-term tailings weathering were assessed through leaching of heavy metals by three

column experiments. Mineralogical and chemical constituents, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), sequential extraction of the tailings, and chemical analyses of the effluents were carried out to determine the processes responsible for the leaching of Cu, Zn, Fe, and SO_4^{2-}. The contents of Cu, Zn, and Fe in the tailings were mainly associated with ion exchangeable and sulfide fractions. The pH values of the effluents from the columns were 3.0-3.7 throughout the experiments over 84 weeks, and approximately 15-23% of Cu, 35-45% of Zn, 2.5-4% of Fe and 15-20% of S were leached out. Higher concentrations of Cu, Zn, Fe, and SO_4^{2-} at the beginning of the experiments were observed, which could be attributed to the dissolution of soluble sulfate minerals present in the tailings. This indicates that the formation and dissolution of secondary soluble sulfate minerals contributed to Cu and Zn leaching. The continuous leaching of Cu, Zn, Fe, and SO_4^{2-} suggests the oxidation of pyrite and other sulfide minerals. During these processes, ferrihydrite, goethite, lepidocrocite, and maghemite were formed and these minerals also acted as a sink for Cu and Zn by adsorption, and/or co-precipitation. These results mean the significance of the long-term behaviors of heavy metals released from mine tailings dams.

Chapter 4 focuses on the evaluation of the effectiveness of the chicken eggshell for the neutralization of the AMD and the removal of heavy metals. The eggshell was collected from kitchen wastes, and then washed, dried, ground, and stored in the air-dried container before use. The batch adsorptions were conducted at different contact times, particle sizes, and doses of the eggshell. The morphology of the eggshell before and after batch adsorptions was analyzed by SEM-EDX. The results showed that pH reached 6.7 and the highest removal efficiency of Cu (98%), Zn (60%), Fe (99%), and Mn (20%) were obtained at the contact time of 24 h, the particle size of 75-150 μm, and the dose of 1 g. The removal efficiency of heavy metals was in order Fe > Cu > Zn > Mn. The removal process of Cu and Fe was rapid and reached equilibrium within 30 and 40 min, respectively, while that of Zn and Mn was slow and reached equilibrium at 24 h. This means that the removal of Cu and Fe is due to precipitation whereas that of Zn and Mn is due to adsorption. Based on the results, the chicken eggshell can be used for neutralization and removal of the heavy metals from the actual AMD.

Chapter 5 gives the overall conclusions of the research and suggestions for future study on the AMD as well as heavy metals from the tailings. The results could provide helpful information on the management of tailings dams after mine closure.