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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 Frances Semida Chikanda

学 位 論 文 題 名

Behavior of Fe colloids in mine drainages of circumneutral and acidic pH: Implications from
geochemical trends and Fe isotopes

(酸性および中性 pH の鉱山廃水における鉄コロイドの挙動: 地球化学的傾向と Fe 同位体からの
示唆)

Mine drainages are increasingly attracting attention with regards to their contribution to toxic elements in river systems. Fe commonly exists in abundance in most mine drainages, resulting in Fe minerals that form through the life of the drainage, and aid in mine remediation due to the dynamics of Fe. Abundant and as a precursor of the Fe minerals in general are Fe nanoparticles, which are a very common form of Fe. Fe nanoparticles are remarkably abundant, and studies have widely reported their increased reactivity that is attributed to their increased surface area, but also, high mobility. These nanoparticles have been reported to sequester toxic elements in mine drainages, and act as transport vectors for Fe and the other elements, thereby affecting the elements' cycles. This therefore makes mine drainages significant players in contributing to global element cycles. Despite their significance, very few field studies have been carried to elucidate the detailed behavior of the nanoparticles in mine drainages. Therefore, this study was focused on highlighting the behavior of the nanoparticles in mine drainages, to clarify their impact on other toxic elements in the drainage and their contribution to element cycles.

The study was carried out at two mine drainages, Ainai mine drainage and Shojin river because mine drainages vary significantly in their geochemical characteristics. Dissolved and colloidal fractions of wastewater were used to understand the water chemistry, supported by iron isotopic fractionations and geochemical modelling to further explore the formation, behavior and transportation of the Fe nanoparticles.

Ainai mine drainage is a near-neutral pH drainage (avg 7.1), that utilizes aeration to treat, Fe, As and Zn by releasing wastewater from an abandoned underground mine, through a 1 km drain, before being disposed off in a nearby river. The ferrous Fe-rich type water, is quickly oxidized, resulting in ferric Fe, which then forms ferrihydrite colloids. The colloids are aggregated to over 300 nm when they begin to settle from the drainage towards the downstream. Fe colloids form as the primary colloids, while As colloids form as pseudo colloids and are incorporated into the Fe colloids, thereby being removed together with the Fe colloids. A variation in behaviors with seasons exists in that, in the rainy season, the colloids aggregate quickly due to increased interactions and are removed faster than in dry season when their aggregation is slower, then the colloids remain longer in the drainage.

On the other hand, Shojin river is an acidic drainage (avg 3.1), whose waste water is released with abundant ferric Fe. Wastewater (pH 3.1) containing Fe, As, Pb, Cd and other toxic elements is released, which then mixes with natural river water (pH 6.9), therefore resulting in an increase in pH after

mixing. The dilution of the wastewater by river water plays a significant role in reducing the toxic elements to about a fourth of the original concentrations. Following dilution, an increase in pH occurs, which initiates hydrolysis of the ferric Fe, and due to the presence of sulphate in the wastewater, schwertmannite colloids are formed, also sorbing As during the process. Unlike at Ainaí, the colloids at Shojin display a dissolution behavior that is displayed, that results in a release of Fe and As. However, further downstream, the colloid formation picks up due to increase in pH, thereby effectively removing the toxic elements from the drainage, through aggregation and deposition. The different formation processes of the colloids are seen as a trigger for the variations in the processes occurring in the drainage and one that is highly affected is the aggregation rate. Quantitative calculations showed a faster aggregation rate at Ainaí, compared to Shojin and this was due to the quicker formation kinetics at Ainaí, compared to those of Shojin, given the low pH, which slows down reaction kinetics.

A novel approach of utilizing Fe isotopic fractionations of the water fractions is reported. At Ainaí, the redox related, oxidative precipitation of the Fe colloids resulted in notable fractionations between the dissolved and colloidal fractions. The dissolved fraction had significantly lighter Fe isotope ratios, compared to the colloidal fraction, which had relatively heavier values. Seasonal variation showed a difference in the oxidation rate, but which was, in either case, a difference that highlights the oxidative precipitation at Ainaí mine drainage. When compared to Rayleigh fractionation model, a misfit was observed, which was attributed to colloids unaccounted for in the model, and hence reflected the colloids that were transported from the upstream of the drainage. The misfit was estimated quantitatively to reflect the number of colloids transported at the given distance. Finally, from the Fe isotopes, it was evident that the major phase of Fe being transported was in form of Fe colloids and remained the same unless extreme changes occurred. At Shojin on the other hand, minimal fractionations were observed in the Fe isotope ratio, because of the non-redox associated processes at Shojin river, during the formation of the colloids. Minor fractionations were however observed which reflected the dissolution of the colloids.

My findings can be implemented to increase the efficiency of mine drainage designs since appropriate pH, seasonal variations, aggregation, and deposition behavior are highlighted. Furthermore, Fe colloids are stable at neutral pH and minor instability is observed at low pH, therefore, close monitoring at low pH is required to avoid re-release of toxic elements to the water. At a larger scale, I confirm the abundance of Fe colloids in mine drainage systems and show that the transportation of the colloids may be a route through which Fe is supplied to rivers. This highlights why the rivers are high suppliers of Fe to oceans, and more importantly, the size fraction that is transported should always be in check to avoid mis estimations of the amount of Fe supplied to oceans by rivers, that is transported from mine drainage systems.