

Natural metal nanoparticles and disassociation buffering in circumneutral mine drainage

JEFF B. LANGMAN^{1*} AND JAMES G. MOBERLY²

¹Dept. of Geological Sciences, University of Idaho, Moscow, Idaho, 83844 USA (*correspondence: jlangman@uidaho.edu)

²Dept. of Chemical & Materials Engineering, University of Idaho, Moscow, Idaho, 83844 USA (jgmoberly@uidaho.edu)

The formation and transport of geogenic metal nanoparticles because of the hydrologic flux of mining-impacted environments is a developing concern because of their potential for greater distribution compared to larger particles. The mining-impacted Silvery Valley of Idaho, USA, is producing transportable metal nanoparticles. This legacy mining area contains an ore of galena [PbS], sphalerite [(Zn,Fe)S], pyrite [FeS₂], tetrahedrite [(Cu,Fe,Zn,Ag₃)₁₂Sb₄S₁₃], siderite [FeCO₃], and ankerite [Ca(Fe,Mg,Mn)(CO₃)₂] emplaced in argillite of the Belt Supergroup. Analysis of circumneutral (pH of 6.5–7.7) drainage from the abandoned Gem Mine that discharges to the Canyon Creek floodplain and shallow alluvial aquifer indicate acid-buffering metal nanoparticles containing Fe, Mn, and Zn, whose concentrations and stability did not vary with seasonal changes.

The circumneutral mine drainage contained average mg/L concentrations of $1 \pm 0.3(1\sigma)$ of Fe, 4 ± 0.2 of Mn, and 16 ± 1.8 of Zn. Mixing of the mine drainage metal nanoparticles with groundwater may allow additional buffering of acidity in the shallow aquifer (upgradient pH range of 5.9–6.3). Acid titrations of 0.45- μ m filtered, mine drainage indicate disassociation of the nanoparticles frees additional buffering capacity of up to 0.8 meq/L (median of 0.4 meq/L). The additional buffering capacity was visible with addition of 0.16 N H₂SO₄ as the titrant and subsequent increase in pH followed by an eventual return to the initial pH. This buffering capacity by metal nanoparticle dissociation constituted a median 27% of additional alkalinity compared to the non-disassociation buffering capacity after the return of pH to the initial value. The masked buffering capacity of the water is attributed to the metal nanoparticles because there was no statistical difference between alkalinity of filtered samples and that of unfiltered samples. This masked buffering primarily is contained in Zn nanoparticles and is likely a result of the formation of smithsonite [ZnCO₃] nanoparticles in the mine with entrance of oxygenated water and weathering of sphalerite and siderite. The stability (ζ potential) of the nanoparticles did not substantially change with season—range of -5.8 to -7.8 mV—but differed significantly from the groundwater ζ potential values. The mine discharge ζ potential values indicate a potential for nanoparticle transport, but conditions in the groundwater environment likely will cause some disassociation or aggregation.