

0. Executive Summary

Placing sulfide-bearing Minnesota mine wastes under water (subaqueous disposal) might provide a method of secure, permanent disposal by reducing the rate of sulfide mineral oxidation and the consequent release of acid and heavy metals. Addition of alkalinity or oxygen-consuming material might provide additional mitigative benefit. The project described below quantified reactions controlling release of acid and heavy metals from Minnesota rock for different subaqueous disposal strategies. Reactions at the rock-water interface suggested these releases would be initially reduced and indicated they would decrease with time.

Experiments were conducted for four to six years on Virginia Formation hornfels rock containing 12 - 14 weight percent pyrrhotite ($\text{Fe}_{0.9}\text{S}$). They evaluated the mitigative potential of 1) subaqueous disposal (238-week period of record); 2) subaqueous disposal augmented by addition of alkalinity to the water cover (230 weeks); and 3) incorporation of an oxygen consuming compost layer at the water/rock interface (324 weeks with leached solids from aforementioned experiment; 265 weeks with fresh solids). Thin layers of rock (~11 mm) were used to more precisely describe reactions at the water-rock interface.

Under subaerial conditions (562 weeks, simulating disposal on the land surface), rates of sulfide mineral oxidation increased by roughly a factor of five after 120 weeks of reaction. The initial rates were likely abiotic and the increase was attributed to microbial mediation of the reaction. Associated with this increase, pH decreased from the upper threes to near 3.0, and trace metals concentrations increased by as much as a factor of 30. Drainage pH values reached a minimum near 2.5 after about 200 weeks. After about 300 weeks of reaction, oxidation rates declined (and pH increased) due to depletion of 70 to 100 percent of the sulfide minerals initially present.

Initial sulfide oxidation rates from all subaqueous disposal conditions approximated initial subaerial rates, but oxidation rates did not increase as did the subaerial environment. In contrast, rates of sulfide mineral oxidation under unmodified subaqueous conditions declined by roughly 50 to 70 percent after 100 to 200 weeks of reaction. The decline was influenced by both sulfide mineral depletion and inhibition of oxygen transport due to iron oxyhydroxide precipitates. At this time 70 to 90 percent of the sulfide minerals present remained to oxidize at the slower rate. The minimum pH for subaqueous disposal with no modification was 3.3. Maximum release rates for copper, nickel, cobalt, and zinc from the subaqueous rock were 0.001 to 0.01 times those from the subaerial rock but did respond to pH changes in the water covers.

Removing residual soluble components from the rock surface prior to immersion, adding alkalinity to the overlying water during oxidation, and amending the waste rock (leached and fresh) with compost provided no further reduction in oxidation rates. Furthermore, the decline in oxidation rates in experiments using small additions of alkalinity or compost (3-4 mm) did not occur until 300 to 400 weeks of dissolution. This lag was roughly twice that for the unmodified subaqueous disposal. Both additions generally maintained circumneutral pH and, consequently, reduced copper, nickel, cobalt, and zinc release rates.

The results demonstrate the promise of subaqueous disposal and also infer cautions to be exercised. Because acid is contributed by both subaqueous iron sulfide mineral oxidation and residual acidic salts on the mine waste, these contributions must be quantified so that requirements to neutralize these inputs can be determined. Potential sources of neutralization include alkaline water inputs to the mine (e.g. with groundwater), dissolution of acid neutralizing minerals in the mine (e.g. mine walls, residual rock), and intentional addition of alkaline amendments.