

Appendix L

Investigation of Stability of Manganese Slurry at Various pHs

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As part of the nickel/cobalt extraction/recovery process, an acidic waste solution containing elevated dissolved manganese is produced. This solution has been treated with lime on an experimental basis to neutralize the acidity (to a pH greater than 10) and to precipitate the manganese, thus reducing the manganese concentration in solution. The issue of long-term stability of the manganese-containing precipitate and the manganese concentrations in the liquid component of the slurry was raised in view of the fact that ambient saturated- and vadose-zone groundwaters and surface waters exhibit near-neutral pHs. Because re-solubilization of the manganese is anticipated at lower pHs (i.e., less than 10), a small experiment was designed to evaluate the extent of re-solubilization of the slurry solid. Data from this experiment is given in Table 1.

One one-gram, one two-gram and eight 10 g aliquots of the pH 10 homogenized, as-provided manganese slurry were withdrawn, diluted 50 mL de-ionized water and titrated with 0.2 N sulfuric acid to pHs ranging from pH 4 to pH 9. The resulting solution pHs obtained in this way proved to be unstable. After 24 hours of agitation the (final) pH was measured and recorded. Initially high pHs tended to decrease after 24 hours and low pHs increased (see Fig. 1). The final range was between pH 4.99 and pH 7.6 with an apparent tendency toward equilibrium at about pH 7. acid consumed is shown in Fig. 2. The continued reaction over 24 hours is indicative of a relatively sluggish heterogeneous (solid- / aqueous-phase) reactions that continued and only tends toward equilibrium with time. The fact that initially high and low pHs respond oppositely over time suggests the presence of multiple solids or reaction paths.

Fig. 3 shows the observed manganese concentrations in the final solutions as a function of the final solution pH. The observed concentrations for pHs in the range of 6.5 to 5.0 appear to represent the exhaustion of those manganese bearing solid(s) present in the slurry and soluble in that pH range. In other words the observed concentrations do not represent solubilities, merely the available manganese in the aliquot. Fig. 4 confirms that the manganese leached per gram of slurry is the same for each sample in that pH range.

Manganese concentrations in the 24-hour-equilibrated fluids with pH above 6.5 do appear to represent actual solubilities and suggest that $\text{Mn}(\text{OH})_2$ is likely not controlling the solubility of manganese when the pH is lowered from the original pH = 10. Fig. 5 shows the observed manganese concentrations as a function of final pHs and the predicted solubility of $\text{Mn}(\text{OH})_2$. Note that observed manganese concentrations are several hundred times lower than would be predicted for $\text{Mn}(\text{OH})_2$ at a given pH. It was suggested by Jim Reynolds that the solubility may be controlled by a manganese oxyhydroxide rather than $\text{Mn}(\text{OH})_2$.

In the case of each solubility test, a muddy-gray precipitate remained in the bottle following equilibration to the final observed pH. Addition of an excess of sulfuric acid dissolved this material and increased manganese concentrations confirmed that the material was manganese-bearing. It is likely that this residual material is a manganese oxide or oxyhydroxide that is only soluble at very low pHs and is probably present in the slurry along with the $\text{Mn}(\text{OH})_2$.

The data indicates that the manganese concentrations in the slurry will rise quickly if the pH is lowered. The probability that in-pit available acidity will be sufficient to actually cause such a lowering of the pH can be decreased by the addition of an excess of alkalinity during the neutralization. The likelihood of manganese release is further mitigated by the fact that acidities of local natural waters are probably quite low, even if their pH is near-neutral.