Removal of Selenium from Refinery Wastewater Using Sulfur-Modified Iron (SMI)

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Background/Objectives. Effluent from sour water strippers and other wastewater from oil refineries is often impacted with selenium due to the presence of selenium in sour crude oil that is carried through the refining process. Selenium concentrations in the wastewaters can reach over 1 milligram per liter (mg/L). The California maximum contaminant level for selenium is 0.05 mg/L. Existing removal technologies include iron co-precipitation and biological removal under anoxic conditions, but these are often expensive or difficult to operate, produce large amounts of sludge, or require a large footprint. Sulfur-modified iron (SMI) is a granular media known to remove a variety of contaminants from water including arsenic, mercury, Cr(VI), and nitrate. Removal occurs through adsorption (in the case of arsenic and metals) and through chemical reduction (in the case of nitrate). Laboratory and field pilot testing was conducted to evaluate the ability of SMI to remove selenium from wastewaters from several refineries.

Approach/Activities. Small-scale (1 inch diameter) screening-level column tests were conducted to determine whether SMI could remove selenium from wastewater from various refineries located in the Western United States. The empty bed contact time (EBCT) ranged from 10 to 20 minutes. Water was used as received, pre-treated with polymer to remove solids or oil, or adjusted to pH 6 prior to contact with SMI. Based on the results, larger-scale (2-inch diameter) field pilot column tests were conducted.

Results/Lessons Learned.
Small-scale tests demonstrated that SMI can remove selenium from sour water stripper effluent or effluent mixed with other waste streams, but that pre-treatment may be needed. For effluent free of oil or phenolic compounds (Sites A and B), SMI decreased selenium from 0.64-0.92 mg/L to less than 0.01 mg/L with 10 min EBCT and no pre-treatment. For one water containing oil and phenolic compounds, SMI decreased selenium from 1.5 mg/L to 0.43 mg/L when the EBCT was 10 minutes and oil was first removed. For a second source containing oil and phenolics, SMI removed 64% of the selenium when the EBCT was 10 minutes and 86% when EBCT was 20 minutes.

Based on results of small-scale tests, field pilot tests were conducted at Sites A and B. At Site A, the test ran for 6 months and decreased selenium concentrations from variable influent levels (0.6-1.8 mg/L) to less than 0.002 mg/L using no pre-treatment and 10 minute EBCT. The pilot test at Site B ran for 30 days and decreased selenium from influent levels of 0.64-1.2 mg/L to less than 0.004 mg/L, also with no pre-treatment and 10 minute EBCT. Additional field pilot tests, including one to assess both selenium and arsenic removal, are planned. Two large systems (150-300 gpm) are expected to be installed in 2018.