ANALYSIS OF SELENIUM SPECIATION IN DIFFICULT MATRICES SUCH AS SOUR WATER AND FGD WASTEWATER

Amy L. Dahl and Monica Garcia-Strickland
Frontier GeoSciences, Inc.
414 Pontius Avenue North
Seattle, WA 98109

ABSTRACT

Frontier GeoSciences has had several recent inquiries for analysis of selenium in industrial wastewaters. One client was investigating selenium removal from sour water produced during removal of sulfur from high-sulfur crude oil. Another client was treating wastewater from a flue gas desulfurization (FGD) process at a coal burning utility. Both types of wastewaters have high sulfide content and other unique chemical properties making removal of selenium challenging. When such treatment difficulties are encountered, measurements of selenium at various points in the process are necessary. Characterization of selenium species provides valuable information for identifying better treatment options. However, accurate measurements of selenium species can be challenging due to the unique chemistry of these wastewaters.

Initial selenium analysis of sour waters did not provide an accurate mass balance suggesting that the digestion or analytical method was not performing well. Appropriate methods were identified by comparing several digestion and analytical methods. Due to similar chemical characteristics, the method comparison included analysis of FGD wastewaters as well. The following digestion methods were investigated: (1) acidic persulfate digest, (2) closed vessel oven digest with nitric acid, (3) alkaline peroxide digest, and (4) aqua regia oven bomb digest. Digests were analyzed by inductively coupled plasma mass spectrometry with dynamic reaction cell technology (ICP-DRC-MS) and hydride generation atomic fluorescence spectrometry (HG-AFS). Selenium speciation was also characterized by liquid chromatography ICP-MS (LC-ICP-MS).

For dissolved Se, the persulfate digest was the simplest and most effective. For total Se, the aqua regia bomb digest was required. Analysis by ICP-DRC-MS was not optimal due to significant interferences present in the samples. Analysis by HG-AFS worked well for all samples. Speciation analysis by LC-ICP-MS indicated that the predominant species in most samples were Se(IV), Se(VI), and SeCN in varying ratios at different points in the facility. Additional Se species were detected in sour water samples but have not been identified at this time.

Accurate measurement of selenium species is critical for selecting the most cost-effective selenium treatment technology for industrial wastewaters. While the methods identified here were successful for these particular samples, wastewaters from different facilities will have different chemistries. Sufficient investment identifying the most appropriate methods up-front will likely reduce further expense and time down the line.

KEYWORDS

Selenium, speciation, sour water, FGD wastewater, refinery, coal-burning utility, ICP-MS, dynamic reaction cell, HG-AFS