X-ray microprobe studies of Tc and Cr adsorption in Hanford sediments

PNC-CAT

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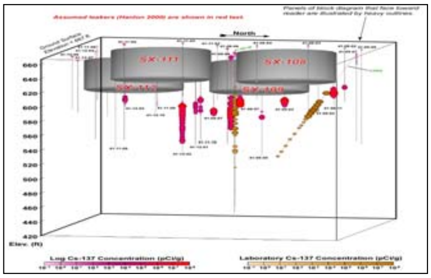
Cr and ^{99}Tc are a major component of leaking tanks

Cr is a major non-radioactive component. Cr in the form of chromate is highly toxic and mobile. XMP measurements are aimed at looking at the conversion of chromate to less mobile and toxic Cr(III) by interactions with the sediment. The potential for remobilization of the Cr is an important issue.

Radioactive Tc is present in the tanks mainly as pertechnetate. The chemistry of pertechnetate is similar to chromate. The goal current work is to examine the potential for enhancement of abiotic reduction of pertechnetate by the action of bacteria.

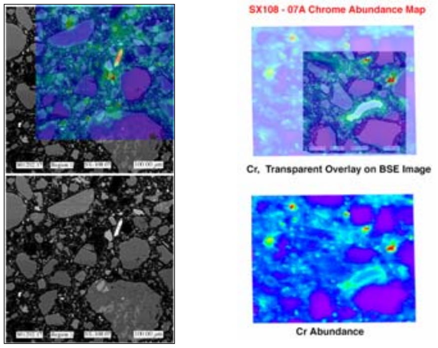
Double shelled tanks under construction showing the scale of the problem. (156 tanks of similar size)



Boreholes near SX-108 and SX-109. The Cr samples were from the slant borehole under SX-108.

Cr results

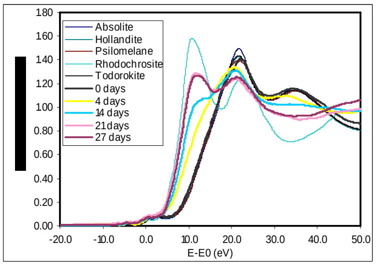
Samples obtained at various depths from an SX-108 borehole were compared. To look at the Cr correlation with different minerals, Cr abundance maps obtained by the x-ray microprobe are overlayed with backscattered electron images. Correlations with magnetite and mica are found. These may help reduce soluble chromate to less soluble Cr^{3+}.

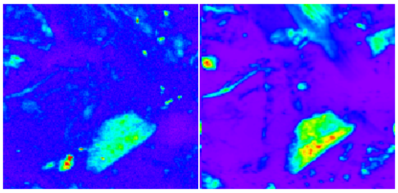


Tc results

Pertechnetate can be reduced by ferrous iron present in the sediments. Reduction of pertechnetate is desirable to reduce is mobility in the sediment. Relatively oxidizing Mn(IV) can interfere with this process. Bacteria can reduce Mn and Fe to facilitate the reduction of pertechnetate. In the current study Hanford sediments were exposed to Shewanella p. for varying time. After the bacteria were killed and removed by washing, the sediments were exposed to pertechnetate solution. Bulk and micro-XAFS was used to monitor the reduction of Tc, Mn, and Fe. Imaging was used to look at the correlation of the Tc adsorption with the minerals present.

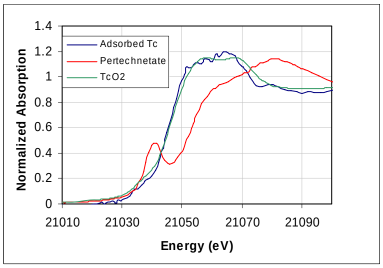
Left: Comparison of the Mn XAFS for bacteria treated sediments treated with some Mn minerals. Rhodochrosite is Mn(II) while rest are Mn(IV)





Tc Fe

Element specific images for Tc and Fe in the sediments. The Fe containing grain has accumulated Tc. Image size 900 x 900 microns

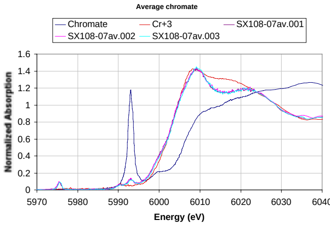


MicroXANES of the adsorbed Tc compared to some Tc standards. All of the adsorbed Tc was found to be Tc(IV)

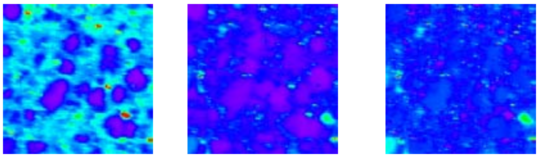
Summary: Reduction of Mn by bacteria enhanced the reduction and precipitation of pertechnetate. In all cases the adsorbed Tc was similar to TcO_2. Micro-XANES showed the progressive reduction of Mn over time by Shewanella p., and the formation of discrete precipitates of TcO_2 in sediments where all Mn was bioreduced. It is likely the Tc was reduced by ferrous Fe on the surface of the Fe containing minerals, since most of the Fe remained ferric. The ferrous Fe could be pre-existing or bioreduced.

Chromate imaging

The Chromate form of Cr has a distinct pre-edge peak. As shown below, this can be used to identify the amount of chromate present. With a large beam (1x3mm) the average chromate for an SX-108 sample from a depth with maximum radioactive Cs contamination is only about 5% of the total chromium.

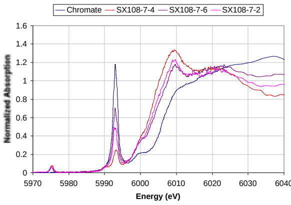


To identify regions with high chromate fractions, images were taken at high energy (total Cr), and at the chromate peak (5993 eV). The difference gives a chromate map.



Total Cr Cr(5993 eV) Chromate

Confirmation that chromate hotspots contain higher levels of chromate is obtained by near edge scans:



Acknowledgements

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