

Technology Evaluation for Waterborne Mercury Removal from Contaminated Source Waters

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Abstract

Despite decades of efforts to reduce mercury (Hg) contamination, low levels of mercury continue being discharged into the East Fork Poplar Creek (EFPC) from the Y-12 National Security Complex (NSC), Oak Ridge, Tennessee. This study has been carried out to address how to remove waterborne mercury at concentrations ranging from <1 to ~40 microgram/L ($\mu\text{g/L}$). To protect the ecosystem of EFPC, significant mercury removal has to be achieved before the discharge at the headwater of EFPC (Outfall 200). However, the high flow rate (1,300 gpm) presents a great challenge for mercury removal using traditional treatment technologies.

Two alternative methods were evaluated. One was using SnCl_2 to reduce Hg(II) in the enclosed storm drain network to dissolved gaseous mercury (DGM) prior to discharge at Outfall 200. Field tests conducted in 2009 using ascorbic acid as dechlorinating agent achieved an overall conversion rate of Hg(II) to Hg(0) of 92% at a molar ratios of Sn:Hg of 25 (Southworth et al., 2010, *ORNL/TM-2009*). Engineering calculation suggested that it is feasible to construct an air-stripping system to remove Hg from 1300 gpm flow at the Y-12 headwater.

A pilot test is being designed and implemented by Y-12 NSC to address key questions such as Hg-removal efficiency, and the fate of tin in the environment. Extensive mercury data collected in the past decades show that the mercury flux at the EFPC headwater is mainly from a small number of relatively short sections of storm drains. Laboratory testing has been conducted to evaluate the efficiency of mercury removal by 10 different sorbents, including carbon-based materials (granular activated carbon (GAC) and Nanomyte), S-based resins, and self-assembled monolayers on mesoporous supports (SAMMS) (Chen et al., 1999, *Sep. Sci. Technol.* 34, 1121). The experimental results show that the thiol-functionalized resins and SAMMS have faster mercury sorption rates and potentially higher Hg sorption capacity than GAC. Therefore, the use of these materials can reduce the size of sorption vessel and the frequency of sorbent replacement, as well as minimize the generation of secondary waste.

Background

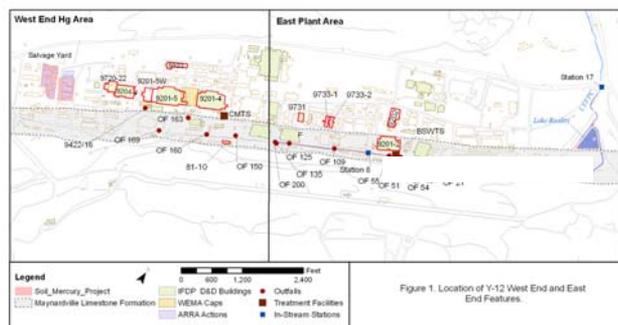


Figure 1. Major historical mercury-use infrastructure, treatments systems, and outfalls within the Y-12 Complex (Peterson et al., 2011, *ORNL/TM-2011/75*).

SnCl_2 treatment technology evaluation

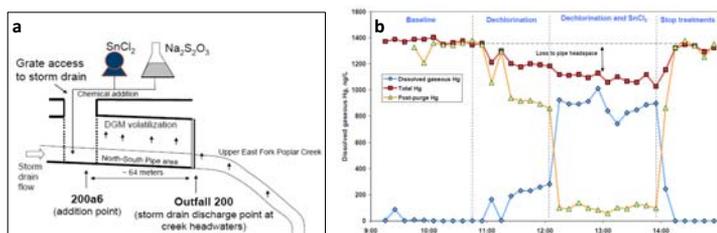


Figure 2. (a) Schematic of the SnCl_2 chemical reduction field test (2008) in Y-12 storm drain system entering upper EFPC, (b) Concentrations of total mercury, dissolved gaseous mercury, and post-purge mercury concentrations in Outfall 200 water versus time during the 2009 in-stream mercury reduction experiment in upper EFPC.

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- $\text{Na}_2\text{S}_2\text{O}_3$ and ascorbic acid were used as dechlorinating agents (chlorine consumes SnCl_2) in 2008 and 2009 field tests, respectively. $\text{Na}_2\text{S}_2\text{O}_3$ mobilized sorbed mercury in the storm drain while ascorbic acid was as effective as $\text{Na}_2\text{S}_2\text{O}_3$ in dechlorination but did not mobilize mercury.
- During the 2009 field test, ascorbic acid was added at a location 250 m upstream of 200a6 (Fig. 2(a)) at OF 150 while SnCl_2 was added at 200a6.
- At the molar ratio of Sn/Hg = ~25, conversion of Hg(II) to Hg(0) was > 92% at OF 200 during the 2009 field study.
- The tested dechlorinating and reducing agents did not significantly affect the dissolved oxygen and pH of the stream water and exhibited low toxicity.
- Ascorbic acid partially converted Hg(II) to Hg(0) in the field study (no reduction was observed in lab studies).
- Natural evasion of Hg(0) from the turbulent flow of EFPC downstream from OF 200 was not effective at purging the Hg(0) from the water.
- Reoxidation of Hg(0) during air stripping was minimal.

Sorption technology evaluation

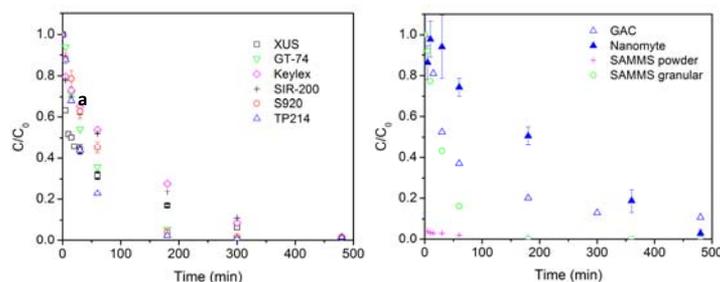


Figure 3. Sorption kinetics of Hg(II) by thiol- or sulfur-based resins (a) and other sorbents (b). Tap water was used as the surrogate wastewater with mercury concentration of 40 $\mu\text{g/L}$ and pH of 8.0. The solid to water ratio was 1:2860 for all batches.

- Macropore sulfur-based resins (XUS, GT-74, Keylex, SIR-200, S920, TP214) and SAMMS performed better than carbon-based sorbents (GAC and Nanomyte (sulfur-impregnated)).
- Pore diffusion coefficients of the sorbents control the sorption kinetics. The removal of Hg(II) by powder SAMMS was much faster than that by granular SAMMS due to the removal of pore diffusion.

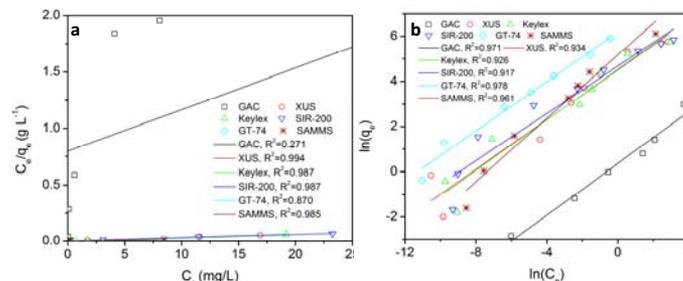


Figure 4. 5-day sorption isotherm of Hg(II) by selected sorbents (a) Langmuir modeling and (b) Freundlich modeling.

- The sorption isotherm of Hg(II) by thiol-based resins (except GT-74) is better described by Langmuir than Freundlich modeling, indicating that the extent of mercury binding is a function of specific binding sites (i.e., thiol), a finite number of which are located on the surface.
- The sorption isotherm of Hg(II) by GAC and GT-74, however, is better described by Freundlich modeling, indicating multiple types of binding sites in both materials.
- The Hg(II) sorption capacities of thiol-based resins Keylex, XUS, and SIR-200 are very similar, which are much higher than that of GAC but lower than that of GT-74 and SAMMS.

Conclusions

- Both SnCl_2 /air stripping and adsorption technologies can be applied to remove low concentration of Hg(II) from the Y-12 headwater or source water.
- The SnCl_2 technology can treat large flow of water but pose environmental uncertainties with discharge of tin into the environment, while adsorption can treat low flow of water at upgradient source zones with proven reliability.