Recovery of Mercury from Contaminated Liquid Wastes

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SUMMARY

Mercury was widely used in U.S. Department of Energy (DOE) weapons facilities, resulting in a broad range of mercury-contaminated wastes and wastewaters. Some of the mercury contamination has escaped to the local environment, particularly at the Y-12 Plant in Oak Ridge, Tennessee, where approximately 330 metric tons of mercury were discharged to the environment between 1953 and 1963 (TN & Associates, 1998).

Effective removal of mercury contamination from water is a complex and difficult problem. In particular, mercury treatment of natural waters is difficult because of the low regulatory standards. For example, the Environmental Protection Agency has established a national ambient water quality standard of 12 parts-per-trillion (ppt), whereas the standard is 1.8 ppt in the Great Lakes Region. In addition, mercury in the environment is typically present in several different forms, but sorption processes are rarely effective with more than one or two of these forms. To meet the low regulatory discharge limits, an effective sorption process must be able to address all forms of mercury present in the water. One approach is to apply different sorbents in series depending on the mercury speciation and the regulatory discharge limits.

ADA Technologies, Inc. has developed four new sorbents to address the variety of mercury species present in industrial discharges and natural waters. Three of these sorbents have been field tested on contaminated creek water at the Y-12 Plant. Two of these sorbents have been successfully demonstrated very high removal efficiencies for soluble mercury species, reducing mercury concentrations at the outlet of a pilot-scale system to less than 12 ppt for as long as six months. The other sorbent tested at the Y-12 Plant targeted colloidal mercury not removed by standard sorption or filtration processes. At the Y-12 Plant, colloidal mercury appears to be associated with iron, so a sorbent that removes mercury-iron complexes in the presence of a magnetic field was evaluated. Field results indicated good removal of this mercury fraction from the Y-12 waters. In addition, this sorbent is easily regenerated by simply removing the magnetic field and flushing the columns with water.

The fourth sorbent is still undergoing laboratory development, but results to date indicate exceptionally high mercury sorption capacity. The sorbent is capable of removing all forms of mercury typically present in natural and industrial waters, including Hg^{2+}, elemental mercury, methyl mercury, and colloidal mercury. The process possesses very fast kinetics, which allows for higher flow rates and smaller treatment units.

These sorbent technologies, used in tandem or individually depending on the treatment needs, can provide DOE sites with a cost-effective method for reducing mercury concentrations to very low levels mandated by the regulatory community. In addition, the technologies do not generate significant amounts of secondary wastes for disposal.
Furthermore, the need for improved water treatment technologies is not unique to the DOE. The new, stringent requirements on mercury concentrations impact other government agencies as well as the private sector. Some of the private-sector industries needing improved methods for removing mercury from water include mining, chlor-alkali production, chemical processing, and medical waste treatment.

The next logical step is to deploy one or more of these sorbents at a contaminated DOE site or at a commercial facility needing improved mercury treatment technologies. A full-scale deployment is planned in fiscal year 2000.
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SCOPE OF WORK

The objective of this Option I project is to develop and demonstrate improved processes for removing mercury contamination from liquid wastes. The project is focused on mercury-contaminated wastes that are already in the DOE’s inventory as well as the secondary wastes resulting from many of the processes planned for treating mercury-contaminated soils, debris, and sludges.

Under the base contract, ADA developed a new sorbent based on the highly selective sorption of mercury onto noble metals. This work was an extension of a similar process demonstrated by ADA for removing mercury vapors from off-gas streams. Base contract accomplishments included laboratory testing of the new sorbent, scale-up of the sorbent fabrication process, testing of the sorption process at a DOE site, and determining the regeneration conditions of a small field unit. These results are documented in the base contract Topical Report (1).

The current project concentrated on the development of lower cost and improved capacity sorbents. Thermal regeneration of the spent sorbent from the Y-12 tests was also demonstrated, and the desorbed mercury was captured as a stable sulfur compound. Two of the new sorbents were tested at the Y-12 unit, and an economic analysis of the most promising new sorbent was completed.

This report provides background information on the mercury-in-water problem and presents the rationale behind the sorbent development strategy. Each of the sorbents evaluated in this project is described, followed by a discussion of laboratory and field test results. The economic analysis of the most promising sorbent is provided, followed by a summary of significant and results and recommendations for future work.
BACKGROUND

Mercury was widely used in U.S. Department of Energy (DOE) weapons facilities, resulting in a broad range of mercury-contaminated wastes and wastewaters. Some of the mercury contamination has escaped to the local environment, particularly at the Y-12 Plant in Oak Ridge, Tennessee, where approximately 330 metric tons of mercury were discharged to the environment between 1953 and 1963 (TN & Associates, 1998).

Effective removal of mercury contamination from water is a complex and difficult problem. In particular, mercury treatment of natural waters is difficult because of the low regulatory standards. For example, the Environmental Protection Agency has established a national ambient water quality standard of 12 parts-per-trillion (ppt), whereas the standard is 1.8 ppt in the Great Lakes Region. In addition, mercury in the environment is typically present in several different forms.

Mercury speciation at the headwaters of the Upper East Fork Poplar Creek at the Y-12 Plant is summarized in Table 1. Mercury speciation is significantly different downstream of this point. Near Lake Reality, more than 80% of the mercury is particulate-bound (Bostick, 1998).

Table 1. Mercury Speciation at the Headwaters of Upper East Fork Poplar Creek, Y-12 Plant, Oak Ridge, Tennessee

<table>
<thead>
<tr>
<th>Form of Mercury</th>
<th>Percent of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate-bound mercury</td>
<td>10 - 20%</td>
</tr>
<tr>
<td>Methyl mercury</td>
<td>10 - 40%</td>
</tr>
<tr>
<td>Elemental mercury</td>
<td>0 - 20%</td>
</tr>
<tr>
<td>Mercury 2+</td>
<td>up to 80%</td>
</tr>
</tbody>
</table>

Although process wastewater streams typically do not contain all of the mercury species seen at Outfall 200, different streams are likely to have different problems. Depending on the waste stream composition, process wastewater streams are likely to contain mostly elemental mercury, ionized mercury (Hg$^{2+}$), or particulate-bound mercury. Methyl mercury does not appear to be a problem in DOE process wastewaters.

To effectively remove mercury from natural systems or process wastewaters, a sorbent must be highly selective for the mercury species present in the process stream.
Table 2 summarizes the mercury species targeted by some commercially available types of mercury sorbents.

**Table 2. Mercury species removed by commercially available sorbents (3, 4)**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Mercury species targeted</th>
<th>Mercury species not removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>Methyl Hg, Hg$^{2+}$</td>
<td>Hg$^{0}$, particulate-bound mercury</td>
</tr>
<tr>
<td>Ion-exchange resins</td>
<td>Hg$^{2+}$</td>
<td>Hg$^{0}$, particulate-bound mercury, methyl mercury</td>
</tr>
<tr>
<td>Thiol-based sorbents</td>
<td>Hg$^{2+}$</td>
<td>Hg$^{0}$, particulate-bound mercury, methyl mercury</td>
</tr>
<tr>
<td>(iso) thiuronium resins</td>
<td>Hg$^{2+}$, methyl mercury</td>
<td>Hg$^{0}$, particulate-bound mercury</td>
</tr>
</tbody>
</table>

A sorption process intended to treat water from a natural system must treat all forms of soluble mercury, plus particulate-bound mercury, to meet mercury discharge limits. However, as Table 2 illustrates, sorption processes are rarely effective with more than one or two of these forms.

Discharge standards at the Oak Ridge Y-12 site are still being negotiated. Limits of 12 ppt, 51 ppt, and 200 ppt are being discussed. A final decision on the discharge standard is expected in 2000. If the lower limits are imposed, commercially available sorbents are likely to be inadequate to meet the need. Thus, ADA focused its development activities on identifying sorbents with the potential to treat all of the forms of mercury likely to be a problem in industrial discharges and natural waters.
TECHNOLOGY DESCRIPTION

Under the Option I program, ADA has developed four new sorbents to address the various mercury species present in industrial discharges and natural waters. These four sorbents are listed below:

- Noble metals
- Biochemically active sorbent
- Metal chalcogenides
- Magnetic sorbent

Each of these sorbents is described in the following sections.

**Noble Metal Sorbents**

This sorbent is based on the highly selective amalgamation of mercury onto metals such as gold, silver, or zinc. Noble metal sorbents have a high affinity for elemental mercury, although work conducted at ADA indicates that noble metals also take up gas-phase speciated forms of mercury (i.e. mercuric chloride) [Roberts, 1998]. In streams containing elemental mercury, noble metal sorbents have a very high theoretical maximum capacity of 175 mg Hg/gm sorbent. For comparison, the theoretical maximum loading for activation carbon sorbents is 1-3 mg Hg/g sorbent.

In water treatment, ADA typically uses activated carbon as a base for the noble metal to enhance the uptake of methyl mercury and ionized forms of mercury. Although the noble metal sorbents are expensive compared to carbon, for the appropriate application, the higher sorption capacity, longer life, and thermal regenerability of the sorbent offset higher noble metal sorbent costs compared to activated carbon.

**Biochemically Active Sorbent**

To improve the sorption of ionized forms of mercury, ADA investigated an approach that was based on the incorporation of chelating agents onto long polymer chains attached to various supports. This work had mixed success, but led to a variety of new approaches. The work culminated in the development of a sorbent in which a polymerized biomolecule is attached to an activated carbon substrate. Two variations of this sorbent were prepared (NCC-1 and NCC-2), and NCC-2 exhibited performance roughly an order of magnitude above that of either the base activated carbon (Norit ROX) or the original formulation. The new NCC-2 sorbent has several positive attributes:

- It can take up speciated, elemental, and organic forms of mercury
- It has a very high theoretical maximum loading (150 mg Hg/g sorbent)
- It is simple to make
- It is inexpensive
- It chemically binds the mercury to the sorbent
The sorbent is expected to be active toward speciated (Hg\(^{2+}\)), elemental (Hg\(^0\)), and organic (methylated) forms of mercury. The affinity for elemental and organic forms primarily comes from the activated carbon portion of the sorbent, and the speciated affinity for Hg\(^{2+}\) is due to the biochemical polymer. This allows the sorbent to treat a wide range of target mercury species, which is unique to this sorbent compared to other commercially available high-capacity sorbents.

The high theoretical loading of 150 mg Hg/g sorbent is essentially due to the biochemical polymer present on the carbon. The carbon contributes only about 1-3 mg Hg/g sorbent to this number. A review of the literature suggests that while the biochemical polymer primarily takes up speciated (Hg\(^{2+}\)) mercury, it may also have the ability to oxidize elemental mercury to some extent, allowing elemental mercury to be taken up by the polymer as well. Therefore, the actual capacity of the sorbent may be dependent on the speciation of the mercury present.

**Metal Chalcogenides**

A research group at Colorado State University (CSU) has a material that takes advantage of redox and ion-exchange chemistry to effectively remove mercury (II) ions from aqueous systems (Gash, 1998). This material uses a process known as intercalation to insert metal atoms between the layers of the transition metal chalcogenide host.

To date, prototype metal chalcogenide sorbents using sodium and lithium intercalating atoms have been prepared. These sorbents are effective in capturing mercury (II) ions by exchanging with the intercalating ions in the host material. During the ion-exchange process, water molecules are reduced and hydrogen gas is generated. The rapid formation of hydrogen gas spreads apart the layers of the transition metal host. This increase in distance between the chalcogenide layers appears to facilitate the mercury ion-exchange process. The mercury capacity for this class of sorbents is extraordinary – 580 mg Hg/g sorbent compared to 1-3 gm Hg/g sorbent for activated carbon.

**Magnetic Sorption**

Analysis of data collected at the Y-12 site indicated that a significant fraction of the mercury in Upper East Fork Poplar Creek – between 20 and 40% – is present as colloidal mercury. This mercury fraction passes through a 1-micron filter and is inactive to sorption on both activated carbon and noble metal sorbents. Because of the high levels of naturally occurring iron in the soils and water in the Oak Ridge areas, it is postulated that this colloidal mercury might be associated with iron.
Jim Navratil of the Idaho National Environmental and Engineering Laboratory (INEEL) suggested demonstrating a new magnetic field-enhanced process that uses inexpensive magnetite in a supported mode to remove contaminants from water. In the presence of an external magnetic field, Navratil and his coworkers observed a synergistic effect in using supported magnetite in a fixed bed for removal of plutonium and americium from water (Kochen, 1997). Although mercury is not magnetic, it readily associates with iron, and so is a good candidate for removal by magnetic separation.

Two major advantages of the magnetic separation process are its low cost and its ease of regeneration. Elution of the contaminant from the sorbent material is accomplished by simply cycling the electromagnetic field.
LABORATORY RESULTS

Laboratory evaluation of the noble metal sorbent, the biochemically active sorbent, and the metal chalcogenides were conducted at ADA’s facilities using surrogate wastewaters. Surrogate tests were not conducted on the magnetic sorbent because of difficulties in preparing a representative waste.

In the laboratory, samples of each sorbent were placed in an Erlenmeyer flask with solutions of mercuric chloride. Sorbents were tested in various mercury concentrations under isothermal conditions. Flasks were placed on a shaker table and agitated for 1 hour to 24 hours. Solutions were analyzed by an EPA-approved laboratory, and the resulting data was used to generate a sorption isotherm for each sorbent.

**Noble Metal Sorbents**

Extensive testing of the Alpha-1 noble metal sorbent was completed under the base contract; those results were documented in the base contract Topical Report (ADA, 1998). Under the Option I program, other lower cost metals were tested to determine if cost savings could be achieved without compromising sorption capacity.

One issue investigated was the exchange capacity of some of the metals. Silver, for example, will exchange with HgCl$_2$ to form insoluble AgCl and a Hg-Ag amalgam. This exchange capacity could increase the mercury capacity, but the concern was whether unacceptable amounts of the exchanging metal would leach into solution.

The University of North Dakota Energy and Environmental Research Center (EERC) perform sorption isotherm tests on activated carbon (Norit ROX), carbon coated with silver, and carbon coated with zinc. The surrogate waste contained 5-ppm mercury as HgCl$_2$.

Results are summarized in Figure 1. Both silver and zinc showed significantly higher mercury uptake than the base carbon. However, high concentrations of silver and zinc were detected in the solutions, which renders sorbents with these metals useless for application to any waste streams that contain chlorides. The Alpha-1 sorbent does not leach into solution in the presence of chlorides.
**Biochemically Enhanced Sorbent**

The NCC-2 sorbent was evaluated at ADA’s facilities using a 5-ppm surrogate wastewater containing mercury in the form of mercuric chloride. A series of isotherm tests were run at room temperature for 24 hours to create a basic sorption isotherm plot, which is shown in Figure 2. Simultaneous tests were run with the base Norit ROX carbon to ensure both test series would represent data taken under identical conditions. As can be seen in the plot, the NCC-2 sorbent clearly outperforms the base activated carbon.
Rinse tests were also performed with used sorbent from the isotherm tests, to verify that no mercury is released from the sorbent. This involved adding several grams of used sorbent to 100 ml of clean deionized water and agitating for 1 hour. No mercury was released during these rinse tests.

It should be possible to increase the loading by incorporating more polymer into the carbon with a modified preparation method. This would allow the sorbent loading to approach the theoretical maximum for the polymer, which is over 800 mg Hg/g sorbent. Second, a more inexpensive carbon substrate could likely be found; the base carbon is a significant portion of the finished sorbent cost. The current base material is an extruded carbon that is twice as expensive as a granular activated carbon. Other substrates could be investigated as well.

**Metal Chalcogenides**

ADA, in conjunction with researchers at Colorado State University (CSU), conducted a series of isotherm tests to evaluate the sorption potential of intercalated chalcogenides. The first set of experiments was designed to determine the low-end
removal capabilities of three regenerable ion-exchange materials synthesized by CSU. Three materials were evaluated:

- Lithium-intercalated molybdenum disulfide (Li$_{1.3}$MoS$_2$)
- Proton-intercalated MoS$_2$
- A layered zirconium-sulfide compound

Sorption isotherms were conducted for one hour using starting concentrations of 1 and 100 ppb as mercuric nitrate. The pH of the solution was set at 1 using 0.1 M HNO$_3$. Previously reported mercury removal experiments with the Li$_{1.3}$MoS$_2$ material were performed under oxygen-free conditions.

Results are summarized in Table 3. The Li$_{1.3}$MoS$_2$ material showed excellent removal of mercury (II) from aqueous solutions. Results using the zirconium-sulfide material were promising, but not nearly as successful as the Li$_{1.3}$MoS$_2$. To generate a non-pyrophoric form of the MoS$_2$ sorbent, a prototype sorbent was prepared using a proton-based intercalated MoS$_2$. However, the proton-intercalated MoS$_2$ was unsuccessful.

<table>
<thead>
<tr>
<th>Sorbent Material</th>
<th>Initial concentration (ppt)</th>
<th>Final concentration (ppt)</th>
<th>Standard Deviation (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_{1.3}$MoS$_2$</td>
<td>1,000</td>
<td>7.42</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>100,000</td>
<td>21.8</td>
<td>0.53</td>
</tr>
<tr>
<td>Zr-S</td>
<td>1,000</td>
<td>81.5</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>100,000</td>
<td>726</td>
<td>346</td>
</tr>
<tr>
<td>H$_x$MoS$_2$</td>
<td>1,000</td>
<td>1,460</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>100,000</td>
<td>71,220</td>
<td>7,390</td>
</tr>
</tbody>
</table>

A second set of experiments was conducted to determine the effectiveness of the Li$_{1.3}$MoS$_2$ sorbent under neutral pH experiments. A similar compound – sodium intercalated MoS$_2$ was also tested. In addition, mercury removal was monitored over a two-hour time frame to investigate the time dependency of the redox-recyclable ion-exchange materials.

As before, starting mercury concentrations were 1 and 100 ppb as mercuric nitrate. After on hour of agitation in this solution, the Li$_{1.3}$MoS$_2$ material had exfoliated to a much larger degree than it had at a pH of 1. Because of filtration problems, no meaningful data was generated. The sodium compounds did not exfoliate as much as the
lithium material, but the data generated did not show substantial mercury removal capabilities. After one hour, mercury concentrations dropped from 100 ppb to 63.9 ppb ($\sigma = 9.9$ ppb). After two hours, the mercury concentration dropped to 21.9 ppb ($\sigma = 7.4$ ppb).

The final set of experiments was conducted to evaluate the effectiveness of deactivated Li$_{1.3}$MoS$_2$ at neutral pH and compare its performance to plain activated carbon. Samples were deactivated by exposing them to air for one week. All other test conditions were the same as before. Results indicate that the layers had not expanded as much as in the previous series of tests. As a result, mercury removal efficiencies were significantly diminished. The 1 ppb samples were only reduced by a factor of two to 547 ppt ($\sigma = 46.7$ ppt), while the 100 ppb samples were reduced to 1.19 ppb ($\sigma = 0.3$ ppb). Activated carbon reduced the 1 ppb samples to 57 ppt ($\sigma = 5.3$ ppt) and the 100 ppb samples to 75 ppt ($\sigma = 48$ ppt).

Results indicate that the CSU sorbents rely on lithium atoms to remove mercury (II) ions. After exposure to air, the intercalated lithium atoms react with airborne water molecules to form LiOH and hydrogen gas. Without the lithium atoms, very little mercury (II) ions were removed from solution.

The LiMoS$_2$ sorbent developed by CSU has a very high theoretical maximum sorption capacity of 580 mg Hg/g sorbent. The sorption process appears to have incredibly fast kinetics. This is apparent from the very low equilibrium mercury concentrations established after one hour. If so, these sorbents could tolerate higher than usual flow rates, thus reducing the size of the treatment unit. The sorbent is also thermally regenerable using a two-step process.

However, the CSU sorbent has some severe drawbacks. In its current state, its use is limited to acidic wastes. The exchange of the lithium into solution is likely to be a problem, plus the sorbent fabrication process is costly and hazardous. Moreover, the sorbent is pyrophoric, which is a fundamental difficulty for water treatment applications.

ADA has developed an approach to retain much of the sorption capacity of the intercalated MoS$_2$ without depending on lithium atoms for the redox ion-exchange reaction. In addition, ADA is incorporating the MoS$_2$ in an extruded activated carbon filter to enhance the removal of particulate-bound and methyl mercury. While the overall sorption capacity is reduced, cost and safety improvements in addition to the ability to remove multiple mercury species greatly enhance the usefulness of the sorbent.

Unfortunately, the enhanced sorbents could not be completed and tested at the Y-12 field unit before the end of the project. Because the sorbents hold promise for both gas-phase and aqueous-phase mercury treatment, ADA plans to continue development of this sorbent.
FIELD RESULTS

Three sorbents were tested at Outfall 200 on Upper East Fork Poplar Creek at the Y-12 Plant during the Option I program:

- Alpha-1 noble metal sorbent
- NCC-2 biochemically active sorbent
- Magnetic sorbent

The field-scale sorption-regeneration unit was built by EERC and consists of three beds of sorbent. A photograph of the unit is provided in Figure 2. Two beds are used in series at all times, while the third bed is being held in reserve or undergoing regeneration. The sorbent columns are 28-inch-long stainless steel tubes with a 4-inch inner diameter. The sorbent bed depth is 24 inches. A diaphragm pump draws the water from the outfall stream through a one-micron filter and into the sorption unit. The flow of water is upwards through the sorbent beds at a rate of six bed volumes per hour. The valve configuration allows the operator to switch the flow of liquid through different beds. When the first column shows breakthrough of mercury, the flow is switched so that the second and third columns treat the water while the first column is being regenerated.

In addition to the sorption tests, regeneration of the spent Alpha-1 sorbent was performed at ADA’s facilities. Results are summarized in the following text.

Figure 2. Field sorption skid at the Y-12 Plant
**Noble Metal Sorbent**

ADA began field testing the Alpha-1 noble-metal-based sorbent in September 1997. Results are summarized in Figure 3. Soluble mercury concentrations at the outlet of the pilot-scale unit remained below 12 ppt for six months at an inlet concentration of 800-1,000 ppt. Soluble mercury concentration remained below 51 ppt for 15 months, at which point the sorbent in the first column was replaced with fresh sorbent.

![Figure 4. Soluble Mercury Removal ADA Outfall 200 Field Tests](image)

**Regeneration of Noble Metal Sorbent**

The spent sorbent from the Y-12 pilot-scale unit was transferred to ADA’s facilities in Colorado for regeneration. The original plan was to perform the pilot-scale regeneration at the field site to best simulate full-scale conditions. However, ADA determined that a centralized regeneration facility would be significantly more cost effective than building a separate regeneration skid for each full-scale field sorption unit. Therefore, the spent sorbent from the field sorption tests was transferred to ADA’s facilities in Englewood, Colorado for regeneration.
ADA’s Carbon Regeneration System is a skid-mounted unit designed to remove water and mercury compounds from carbonaceous and alumina sorbents. Mercury compounds volatilized from the sorbent are captured in a gas scrubber. Additional mixing and filtration equipment is available to stabilize the mercury compounds in the scrubber liquor. A photo of the skid is shown in Figure 1. The main components seen in the photo are two NEMA-type enclosures to house the electrical components and a portion of the gas handling equipment, a horizontal nitrogen heater, a regeneration vessel, and a gas scrubber packed column.

![Figure 1 – Carbon Regeneration Skid](image)

The freestanding enclosure next to the electrical enclosure houses some the necessary gas handling equipment. Inside, there is a Perma-Pure gas dryer system, equipment for generating instrument quality air used for Perma-Pure gas dryer, and a
mass flow controller and power supply needed to regulate nitrogen gas through the carbon regeneration vessel.

On the left edge of the skid is a horizontal nitrogen gas heater. The heater is rated for 2 kWatts and is capable of heating 2 standard cubic feet per minute (scfm) to a temperature of 1000°F. Next to the heater is the regeneration vessel where the carbon is heated to remove water and mercury compounds. Temperature of the carbon bed is monitored with six thermocouples.

Nitrogen gas and volatile vapors leaving the regeneration vessel enter the freestanding enclosure where the gas mixture is processed through the Perma-Pure Dryer. In the Perma-Pure Dryer, a majority of the water is removed from the gas stream using a micro-tubular polypropylene membrane. The wet gas flows on the tube-side of the membrane while instrument quality air (-20°F dew point) passes counter current on the outside of the tube. Because of temperature and moisture differences between the two gas streams, moisture migrates through the tube towards the drier, cooler instrument air. Roughly 80% of the moisture in the wet nitrogen gas is removed in the dryer. The dried gas then passes to a gas scrubber. Water removed from the nitrogen gas stream is condensed in a stainless steel coil immersed in an ice bath and collected in a gas-liquid separator.

The gas scrubber is a packed column with a 2-foot high section of Teflon packing. Packing material is made from 3/8” Teflon tubing cut length-wise and cross-wise to yield ½” long “U” shape elements. Scrubber liquid is a solution used to solubilize elemental as well as speciated mercury compounds. The scrubber liquid flows counter-current to the gas flow at a rate of 0.5 to 3 gallons per minute (gpm). Gases leaving the scrubber pass through a gas-liquid separator to remove entrained liquid droplets before being vented to the atmosphere. Captured liquids are re-admitted to the reservoir of the scrubber through a valve on the bottom of the separator.

Gases entering the scrubber and leaving the gas-liquid separator are analyzed for mercury content. An ADA Mercury Analyzer is used during the carbon regeneration tests. Mercury capture efficiency was determined for different gas and liquid flow rates. Laboratory tests have shown the scrubber removed more than 95% of the mercury in the gas stream.

Mercury compounds in the scrubber liquids are stabilized using a liquid sulfur compound. The sulfur chemical is added to the scrubber liquids and mixed for several hours to convert the solubilized mercury compounds into mercuric sulfide. The resulting precipitate is then filtered from the supernate liquid.

In regards to safety concerns, the carbon regeneration equipment was pressure checked for gas leaks prior to use. In the leak check procedure, the equipment was pressurized to 30 psig with nitrogen gas. An operator monitored system pressure using a pressure gauge to ensure that no leakage occurred. Process gas from the regeneration skid and mercury analyzer was vented outside of the test facility. During the
regeneration tests, a Jerome hand-held mercury monitor was used to test the air around the skid for mercury compounds. On a scaled-up version of the regeneration skid, added protection would be realized by operating the system under a slight vacuum. This approach was not adopted by the Project Team for the regeneration skid since the equipment was originally intended for outdoor use.

The method for capturing mercury in the regeneration off-gas was thoroughly evaluated and successfully demonstrated before the spent sorbent from the Y-12 field unit was regenerated. Test variables considered in the demonstration included packing diameter, packing style, liquid-to-gas ratio, mercury species, mercury concentration, scrubber liquid temperature, and additive-to-water ratio. An example of the scrubber performance as a function of addition concentration using elemental mercury in the gas stream is provided in Figure 6.

Once the development tests were completed and the regeneration equipment was built, the system was tested with surrogate samples (carbon doped with mercuric chloride). After successful completion of these tests, the spent sorbent from the Y-12 unit was treated in two batches. All of the equipment performed properly, and good recovery of the mercury from the sorbent was observed. Scrubber performance efficiencies were in all cases better than 90% and most cases were greater than 96%. At no point in the operation did the mercury concentration in the vicinity of the skid approach the Occupation Safety and Health Administration (OSHA) time limited value (TLV) of 50 µg/m³.
Scrubber liquids were treated with sulfur-containing liquids and flocculants to precipitate the mercury as a sulfide compound. The amount of mercury-containing precipitate captured during a regeneration run was on the order of 1,000 grams per 2.2 kg of treated carbon. This amount of solids for disposal is minor compared to the 8,420 gallons of water treated by the 2.2 kg of carbon. In addition, the solids passed the Toxicity Characteristic Leaching Procedure (TCLP).

**Biochemically Enhanced Sorbent**

Following the successful laboratory tests, 4 kg of the NCC-2 sorbent was prepared for testing in the water-treatment skid at Outfall 200. The sorbent was placed in service on August 4, 1999. During these tests, water was directed through only one column containing the NCC-2 sorbent. Water samples were taken at the inlet and outlet of the test column on a weekly basis. Test data received to date is presented in Table 4. The NCC-2 sorbent is showing excellent mercury removal capabilities, removing soluble mercury down to as low as 5 ppt.

**Table 4. NCC-2 sorbent performance at Outfall 200**

<table>
<thead>
<tr>
<th>Date</th>
<th>Inlet Total Mercury (ppt)</th>
<th>Outlet Total Mercury (ppt)</th>
<th>Inlet Soluble Mercury (ppt)</th>
<th>Outlet Soluble Mercury (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/9/99</td>
<td>195.7</td>
<td>-</td>
<td>184.3</td>
<td>6.51</td>
</tr>
<tr>
<td>8/13/99</td>
<td>293</td>
<td>39.3</td>
<td>270</td>
<td>5.27</td>
</tr>
<tr>
<td>8/20/99</td>
<td>244</td>
<td>26.1</td>
<td>201</td>
<td>5.40</td>
</tr>
<tr>
<td>8/28/99</td>
<td>244</td>
<td>166</td>
<td>162</td>
<td>44.5</td>
</tr>
<tr>
<td>9/2/99</td>
<td>281</td>
<td>29.9</td>
<td>222</td>
<td>10.4</td>
</tr>
</tbody>
</table>

**Magnetic Sorbent**

ADA prepared a variant of the Navratil magnetite sorbent by supporting fine magnetite particles in a silica matrix. The larger diameter particles were needed to allow high flows through the sorption column while minimizing the pressure drop. This sorbent was placed in two 1” diameter by 14” long Teflon columns in a parallel arrangement. The sorbent bed was 10”. Flow was in an upflow direction at a rate of 50 cc/min. One column was operated in a magnetic field by placing permanent magnets on opposite sides of the column. The minimum magnetic field was 0.4 Tesla at the center of the column, with 1 Tesla at the face of the magnets. The second column contained magnetite but no magnets.
In the first series of tests, the magnetite sorbent was used at the backend of the pilot-scale unit treating the effluent from two columns of noble metal sorbent. Three samples were collected over a three-week period. Results are plotted in Figure 7. Major storm events during the sampling period significantly changed the amount of colloidal mercury in the creek water. Since September 1997, ADA has typically observed 20% to 40% of the total mercury in the creek was in a colloidal form. However, samples taken during June and July 1999 showed that colloidal mercury was only a tiny fraction of the total mercury concentration. Nonetheless, the magnetite column operating in the magnetic field increased the amount of mercury, effectively eliminating the colloidal mercury fraction and passing only the soluble fraction. In contrast, the magnetite column operating without an external magnetic field did not remove a significant amount of mercury. Data from the two columns were analyzed for mean and standard deviation differences, which showed a statistically significant difference between the two data sets.

Although the results from the Outfall 200 tests demonstrate the feasibility of the magnetic sorption concept, the amount of colloidal mercury at this location is not likely to be significant enough to warrant such specific treatment. However, downstream of Outfall 200 near Reality Lake, the colloidal mercury concentration is about 80% of the total mercury in the creek (2). At this location where significant fractions of colloidal mercury are present, the magnetic sorption process appears to be a viable treatment option.
ECONOMIC ANALYSIS

An economic evaluation was performed comparing annualized operating cost for a water treatment system using untreated Norit carbon and a proprietary carbon-based sorbent developed by ADA Technologies, Inc. The NCC-2 biochemically active sorbent was selected for the cost analysis because it is the most appropriate of the ADA sorbents for application at Outfall 200 and should have wider application to wastewater treatment in general.

Elements of the cost estimate included sorbent cost, process equipment costs for the water treatment, annual operating costs, and disposal and stabilization costs of the spent sorbent. The estimate was based on a process treating 20 gallons of water per minute from an industrial source. The sorbent is expected to reduce the wastewater mercury concentration from 2,000 ppb to 200 ppt.

**Sorbent Costs**

Loading capacity for the untreated carbon is roughly 6 times less the capacity for the NCC-2 biochemically active sorbent, which requires the untreated carbon be changed out 6 times more often. To meet the discharge mercury concentration, untreated carbon in the lead column is replaced after the first 134 days and every 67 days thereafter. With the NCC-2 sorbent, the material in the lead column would need to be changed after the first 740 days of operation and then on an annual basis.

Based on this analysis, it is anticipated that approximately 1,775 pounds of Norit carbon are needed on an annual basis, which has a bulk cost of $4 per pound. In addition to the carbon cost, there will also be treatment and disposal costs for the spent carbon material. To landfill the material, it will cost $400 annually based on a cost of $6/ft$^3$ of sorbent. Treatment of the carbon is expected to stabilize the mercury adsorbed on the carbon. For the purpose of this cost comparison, treatment of the carbon was based on $57/ft^3$. Annual expense to stabilize the carbon is $3,200.

In contrast, only 350 pounds of the ADA sorbent are needed annually. Manufacturing cost for the sorbent have been estimated at $28 per pound, which includes materials, labor, disposal of waste stream generated in the process, as well as overhead and G&A to cover administrative costs. Disposal cost for the spent sorbent is less than $100 per year. Because the mercury is chemically bond to the sorbent material, the spent ADA sorbent is expected to pass the TCLP for mercury and therefore will not require stabilization.

**Process Description**

In the process, water is passed through a filter to remove particulate matter and then through two columns to remove elemental and speciated mercury. Water is moved through the treatment system using a centrifugal pump with a maximum flow rate of 50 gallons per minute. Water flow is controlled using a diaphragm control valve. A signal from a paddle wheel flow element positions the valve for proper flow.
Suspended solids in the water stream are removed using a bag filter. Two filter housings in parallel are provided so that water can be diverted through a clean bag filter while the used bag is replaced. Particles greater than 1 µm should be removed from the water to prevent accumulation of particulate matter in the carbon columns.

The carbon columns were sized using the Rosen adsorption model. Dimensions of the vessels were changed to satisfy both residence time and liquid loading requirements. Design of the columns were based on a minimum residence time of 7.5 minutes and a liquid loading less than 10 gpm/ft². The final size of the columns was 18” diameter and 7’ high. Vessels are constructed from schedule 80 PVC piping. Several reducers are used to interface the 18” diameter columns with the 11/2” diameter schedule 80 PVC piping used throughout the system. Several ball valves are needed to direct the water into and out of the various carbon vessels. The estimated total installed cost for the process equipment is $29,500.

Instrumentation for the system is minimal. Only flow rate, total flow, pump discharge pressure and carbon vessel inlet pressures are monitored. Electrical requirements for the systems are also minimal, driven mainly by the 5-hp motor on the circulation pump. At a cost of $31 per megawatt-hr, it will cost $0.10 to treat 1,000 gallons of water.

The annual operating cost, which includes maintenance, was also estimated. Perry et. al. recommends estimating the maintenance cost based on a fixed percentage of the new equipment investment cost. In general, a 4% per year of the new investment should be used as a minimum maintenance cost for chemical processing equipment. This cost would include the materials, cost to install new equipment, and the overhead costs. For a capital equipment investment of $14,250, the annual maintenance cost is estimated at $600.

**Treatment Cost Comparison**

The treatment cost comparison between untreated Norit carbon and ADA’s proprietary sorbent was done on an annualized cost basis over a 15-year period. The annualized cost was calculated using an interest rate of 8% and an escalation rate of 3.5% per year. Treatment costs for a system using Norit carbon and ADA’s proprietary sorbent are $2.21 and $1.82 per 1,000 gallons of water treated, respectively. The table below summarizes the various cost elements. Although the ADA sorbent cost is more than the untreated carbon on a weight basis, significant savings are realized because the ADA sorbent has a higher mercury loading, so it needs to be changed out less often, and it is not expected to incur stabilization costs prior to disposal.
### Table 5. Comparison of Annualized Water Treatment Costs

<table>
<thead>
<tr>
<th>Cost Elements ($$/yr)</th>
<th>NCC-2 Sorbent Costs ($$/yr)</th>
<th>Norit Carbon Costs ($$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent Cost</td>
<td>$8,200</td>
<td>$7,100</td>
</tr>
<tr>
<td>Operating Cost</td>
<td>$2,900</td>
<td>$3,200</td>
</tr>
<tr>
<td>Stabilization Cost</td>
<td>- -</td>
<td>$3,200</td>
</tr>
<tr>
<td>Disposal Cost</td>
<td>$100</td>
<td>$400</td>
</tr>
<tr>
<td>Indirect Cost</td>
<td>$1,600</td>
<td>$2,300</td>
</tr>
<tr>
<td>Total Cost</td>
<td>$12,800</td>
<td>$16,200</td>
</tr>
<tr>
<td>Life-cycle Cost</td>
<td>$163,400</td>
<td>$199,200</td>
</tr>
<tr>
<td>Annualized Cost</td>
<td>$19,100</td>
<td>$23,270</td>
</tr>
<tr>
<td>Treatment Cost</td>
<td>$1.82 per 1,000 gallons</td>
<td>$2.21 per 1,000 gallons</td>
</tr>
</tbody>
</table>
CONCLUSIONS

ADA has developed four new mercury sorbents to address the variety of mercury species found in natural systems and industrial wastewaters. Individually or in tandem, these sorbents can effectively remove all mercury species present to the very low levels being imposed by the regulatory agencies. Three of these technologies are ready for deployment, while the fourth needs additional development. Table 6 summarizes by sorbent type the maximum mercury sorption capacity and the mercury species targeted.

Table 6. Summary of ADA’s Novel Sorbents for Removal of Mercury from Aqueous Streams

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Maximum Mercury Sorption Capacity</th>
<th>Mercury Species Targeted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha-1 Noble Metal</td>
<td>175 mg Hg/g sorbent</td>
<td>Hg^0, methyl mercury, Hg^{2+}</td>
</tr>
<tr>
<td>NCC-2 Biochemically Active</td>
<td>150 mg Hg/g sorbent</td>
<td>Hg^{2+}, Hg^0, methyl mercury</td>
</tr>
<tr>
<td>Metal chalcogenides</td>
<td>580 mg Hg/g sorbent</td>
<td>Hg^{2+}, methyl mercury, particulate-bound mercury, Hg^0</td>
</tr>
<tr>
<td>Magnetic sorbent</td>
<td>Not determined</td>
<td>Particulate-bound mercury</td>
</tr>
</tbody>
</table>

The most promising of the sorbents for application at the Outfall 200 site is the NCC-2 biochemically active sorbent. This sorbent has a theoretical maximum capacity of 150 mg Hg/g sorbent and removes all mercury species except colloidal mercury. It has a special affinity for mercury (II) species. The sorbent is easily made from widely available materials, which helps make the most cost-effective option for the Outfall 200 site.

The Alpha-1 noble metal sorbent also showed very high mercury removal capabilities at the Y-12 site. Its theoretical maximum capacity is 330 mg Hg/g sorbent.
It removes all species of mercury except colloidal, and it has a special affinity for elemental mercury. Relatively high materials costs render this sorbent less attractive than the NCC-2 sorbent for application at Outfall 200. However, this sorbent is an excellent candidate for treating chlor-alkali and dental industry wastes containing high concentrations of elemental mercury. Under separate contracts, ADA is currently field testing a variant of this sorbent at a chlor-alkali plant and in dental offices.

The magnetic sorption process is a niche technology that has special affinity for colloidal mercury associated with iron. It is a cheap, easy-to-deploy technology for streams containing a large fraction of colloidal mercury that is inactive to other sorption processes.

The metal chalcogenide sorbent has an extremely high theoretical maximum sorption capacity of 580 mg Hg/g sorbent, but the technology needs additional development before it can used for water treatment applications. This sorbent also shows good promise for gas-phase applications.

These sorbent technologies, used in tandem or individually depending on the treatment needs, can provide DOE sites with a cost-effective method for removing mercury concentrations to the very low levels being mandated by the regulatory community. In addition, the technologies do not generate significant amounts of secondary wastes for disposal.

A economic evaluation was performed comparing the life cycle cost (15-yr life) for a water treatment system using untreated Norit carbon and ADA’s biochemically active carbon based sorbent (NCC-2). Elements of the cost analysis included sorbent cost, process equipment costs, operating costs, and disposal and stabilization costs for the spent sorbent. The treatment system was sized to treat 20 gallons of water per minute. The cost of these two systems is summarized in Table 7.

Table 7. Life cycle cost comparison for water treatment systems using ADA NCC-2 sorbent and Norit carbon.

<table>
<thead>
<tr>
<th>Sorbent Used in Treatment System</th>
<th>Life Cycle Cost, $K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit Carbon</td>
<td>199.2</td>
</tr>
<tr>
<td>ADA NCC-2 Sorbent</td>
<td>163.4</td>
</tr>
</tbody>
</table>

As indicated in Table 7, the life cycle cost for the ADA sorbent compares favorably with the cost of the Norit-based system. Although the ADA sorbent costs more
on a unit weight basis, significant savings are realized because the ADA sorbent has a higher mercury capacity and will not incur stabilization costs that the Norit material requires prior to disposal.

The need for improved water treatment technologies is not unique to the DOE. The new, stringent requirements on mercury concentrations impact other government agencies as well as the private sector. Some of the private-sector companies needing improved methods for removing mercury from water include mining, chlor-alkali production, chemical processing, and medical waste treatment.

The chlor-alkali industry and dental offices have shown particular interest applying ADA’s sorbents to remove mercury from their wastewaters. Under separate projects, both industries have started testing variants of ADA’s noble metal sorbent on actual wastewater streams. A chlor-alkali company is also considering applying the NCC-2 sorbent and the magnetic sorbent to some problematic waste streams.

The next logical step is to a treatment system at a contaminated DOE site or at a commercial facility that currently or may in the future need improved mercury treatment technologies. The mercury in water issue is difficult due the stringent treatment goals and the separation complexity associated with mercury speciation (Hg\(^0\), Hg\(^{2+}\), organic mercury, and particulate mercury). The deployed system must address these issues for the specific waste to be treated. The choice of sorbent is a key variable that influences (and is influenced by) selection of other system components.

After a site is selected, the waste stream should be thoroughly characterized to determine which sorbent (or sorbents) and other unit processes are most appropriate for removing the mercury species present in the waste stream. ADA will then conduct comparison tests to isotherms on actual wastewater using novel ADA sorbents, baseline carbon, and one or more innovative sorbents selected by the user along with evaluation of other required treatment steps. In conjunction with the user, ADA will select the best sorbent and system components for deployment. ADA will then build and deploy a treatment skid for processing all (or a significant fraction) of a problematic waste stream.
REFERENCES


