

# Achieving Low Mercury Concentrations in Chlor-Alkali Wastewaters

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*In the early 1980s, EPA established production-based effluent limitation guidelines for mercury in wastewater discharges from mercury cell chlor-alkali plants based on the application of best available technology economically achievable (BAT). The principal process for achieving the BAT guidelines has been chemical precipitation with sulfide compounds, followed by filtration to remove the mercury as insoluble mercury sulfide. This treatment process typically results in effluent mercury concentrations ranging from 10 to 50 µg/kg (ppb).*

*In response to changes in environmental laws in Maine in 1997, HoltraChem Manufacturing Company in Orrington, Maine, began searching for new technologies to reduce mercury in its effluent. Working with suppliers, an onsite pilot plant test with sulfur-impregnated, activated carbon, MERSORB® LW mercury adsorbent, indicated it was feasible to achieve effluent mercury levels of < 100 ng/kg (ppt). A full-scale treatment system was designed and installed after the existing primary sulfide treatment process to treat 100 gpm of wastewater. Mercury concentrations after initial start-up of the secondary adsorption process were one to two orders of magnitude higher than expected. After optimization of the sulfide treatment process, optimizing pH of the influent and the addition of 0.5 micron filters prior to the adsorption trains, mercury concentrations averaging < 100 ppt and as low as 20 ppt have been achieved.*

## INTRODUCTION

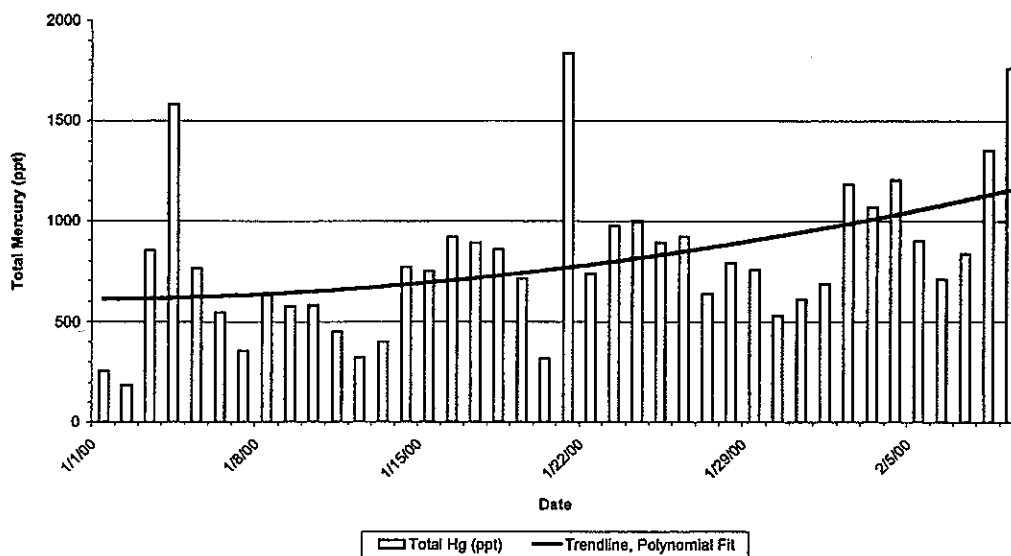
From 1967 through 2000, HoltraChem Manufacturing Company and its predecessors operated a mercury cell chlor-alkali manufacturing process at a facility located in Orrington, Maine. The mercury cell chlor-alkali process utilizes elemental mercury as the cathode in an electrolytic process producing chlorine and caustic soda from saturated salt solutions (brine). Wastewaters generated by the process are contaminat-

ed with mercury. Typical mercury concentrations are 10,000 to 70,000 ppb by weight total mercury.

In the early 1980s, EPA established national effluent limitation guidelines for mercury discharges from the chlor-alkali industry under sections 301 and 304 of the Clean Water Act [1]. By June 29, 1985, all existing mercury cell facilities were required to be in compliance with the effluent guidelines by application of the best available technology (BAT) economically achievable. The technology equivalent to BAT has been to react mercury-bearing wastewaters with sulfide compounds to form insoluble mercury sulfide, followed by filtration to remove the precipitate.

In June 1999, Maine enacted legislation reducing allowable mercury discharges from chlor-alkali facilities, and requiring mercury in effluent to be reduced two orders of magnitude lower than the federal BAT limits by January 1, 2002 [2]. New mercury removal technologies were evaluated. Adsorption technology utilizing sulfur-impregnated, activated carbon was selected for pilot testing as a post-sulfide treatment (secondary treatment) process to achieve the new mercury discharge limits. The results of pilot testing using effluent from the sulfide treatment process suggested that adsorption technology could achieve the mercury reductions required to meet the new discharge limits. A full-scale system was designed and installed in the fall of 1999.

Initial mercury removal efficiencies during pre-commissioning start up in November 1999 were similar to those observed during pilot testing, however, performance deteriorated very quickly. Investigation of the potential causes over the next several months led to changes in operating conditions in both the Primary and Secondary Treatment processes to optimize performance. Unfortunately, the adsorbent media was damaged early in the process and was replaced.



**Figure 4.** Total mercury in effluent after adsorption, secondary treatment start-up, after influent pH was increased to 9.5 - 10.

adsorption trains to trap any solids carried over from the sulfide precipitation (Primary Treatment) process.

Flow meters were installed on the inlet to each train to adjust and balance the flows, and pH control systems were installed to adjust the pH prior to and after adsorption.

#### Process Start-Up

Qualification trials began in November 1999 with random batches of wastewater from the Primary Treatment process being run through the adsorption trains (Secondary Treatment). The trials continued until January 2000 when the Secondary Treatment system was put online and began processing all of the effluent from Primary Treatment. Figure 3 shows the trend in mercury concentration during the qualification trials.

During the trial period, the pH prior to adsorption was 7.5-8.5, and the mercury concentration trended downward, leveling off at about 500-600 ppt.

Based on their experience with treating other mercury containing wastewaters using MERSORB LW, SAA and NUCON recommended increasing the pH prior to adsorption to increase adsorption efficiency. The pH was increased to 9.5-10 when the Secondary Treatment system was brought on line in January, and operated at this pH until early March 2000. The impact of the pH change is shown in Figure 4.

Effluent mercury concentrations trended steadily upward, more than doubling within a month. The presence of sulfur in the effluent and the increasing trend in mercury concentration indicated degradation of the adsorbent. Samples of the MERSORB mercury adsorbent were taken from each train and sent to NUCON for analysis. The results of their analysis showed that the sulfur content of the adsorbent had decreased from 13.5% by weight to 1-6% by weight. Further investigation of this phenomenon indicated that the combination of excess sulfide in the effluent from the Primary Treatment system, combined with high chloride content and alkaline pH, caused the sul-

fur to be stripped from the carbon. Further degradation was halted by reducing the pH prior to adsorption to 6.0 to 8.0 in early March.

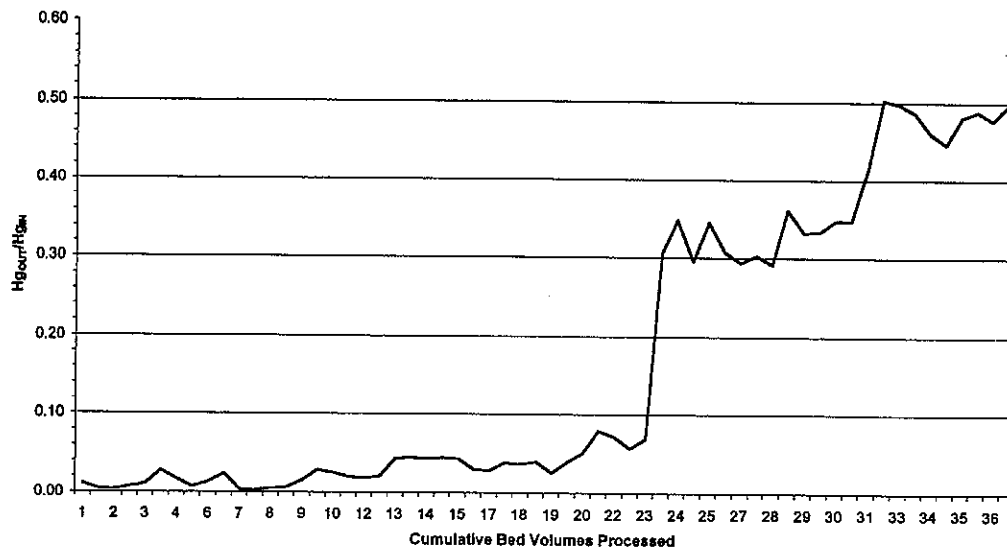
In addition, samples of wastewater taken at the inlet and outlet of both the pre-adsorption filters and the adsorption train were tested for total and dissolved mercury. The analytical results showed that significant concentrations of particulate mercury were passing through the Secondary Treatment system and contributing to higher than expected effluent mercury concentrations. Particle size analysis of effluent samples from the Primary Treatment system showed significant concentrations of small particulate matter in the < 2 µm diameter range.

#### Process Optimization

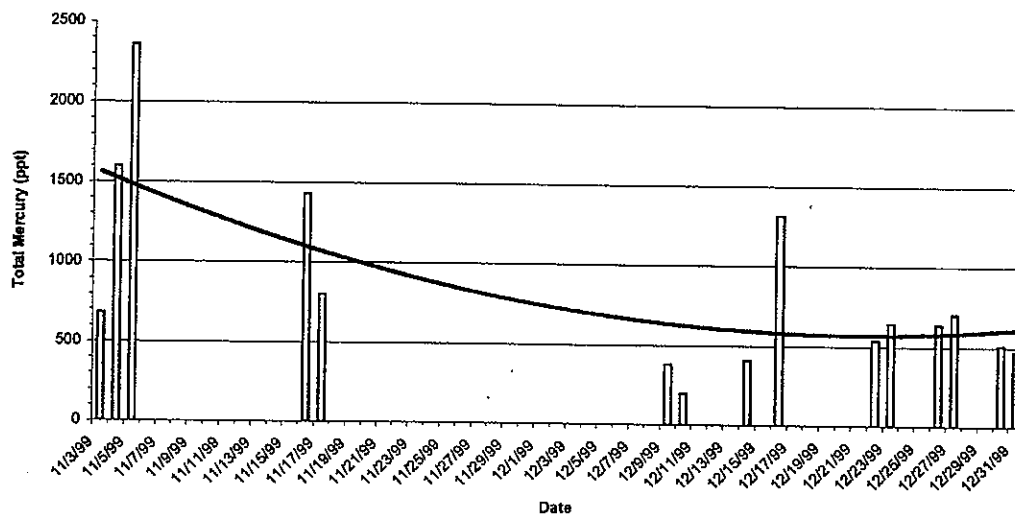
From March through August 2000, HoltraChem made a number of process changes intended to improve the overall performance of the Primary and Secondary Treatment systems. These changes included:

- A reduction in pH in the Primary Treatment system to 4.7-4.9 prior to addition of the sulfide to improve crystal growth, increase particle size, and reduce mercury in wastewater sent to the Secondary Treatment system;
- The addition of ferric chloride (~ 2 mg/kg as FeCl<sub>3</sub>) and reduction in pH to about 3.5 prior to the Secondary Treatment system pre-filters to coagulate and remove colloidal mercury;
- Additional filtration after the 0.5 µm Secondary pre-filters using 0.1 and 0.02 µm filter elements; and
- Reducing the influent flow rate to increase adsorption contact time (EBCT) to a minimum of about 90 minutes.

With the exception of the smaller pore size filter elements, all of the changes resulted in improved mercury removal efficiency. The smaller pore size filters did not improve mercury removal. As shown in Figure 5, the average mercury concentration achieved with the damaged adsorbent decreased



**Figure 2.** Pilot test results of mercury breakthrough curve, plotting mercury concentration ratio vs. bed volumes processed.



**Figure 3.** Total mercury in effluent after adsorption, secondary treatment start-up, influent pH 7.5 - 8.5.

The pilot unit was run until mercury breakthrough occurred, indicating that the adsorbent had been exhausted. Mercury removal efficiency was plotted against total volume processed to generate a "breakthrough curve" to be used to estimate the minimum contact time required to achieve the desired removal rates.

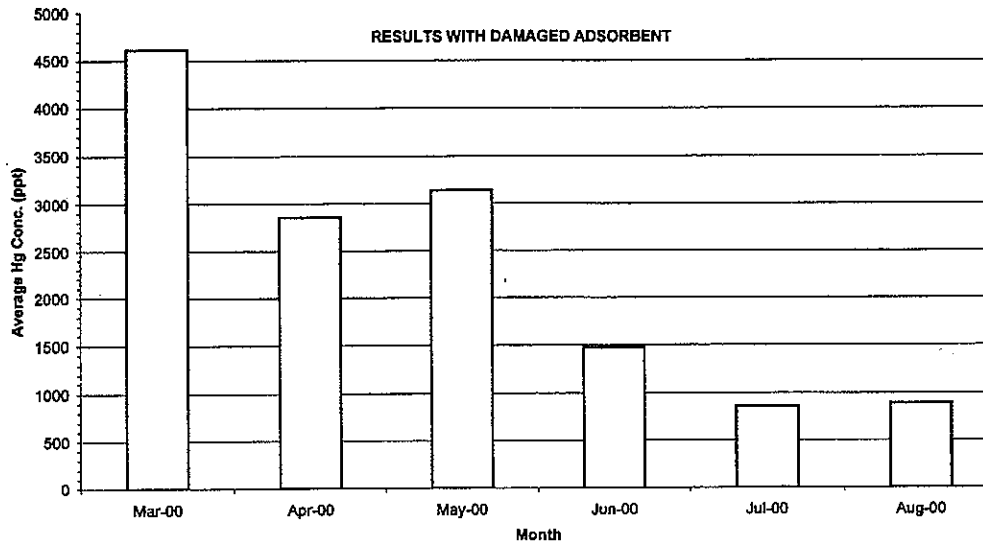
### Experimental Results

Prior to breakthrough, a median outlet mercury concentration of 112 ppt was achieved, with results ranging from 25-413 ppt. The average mercury removal efficiency was 98.64%. As shown by the breakthrough curve in Figure 2, the pilot data showed a significant reduction in removal efficiency after the total volume processed exceeded 20 bed volumes, indicating that the adsorbent had been exhausted.

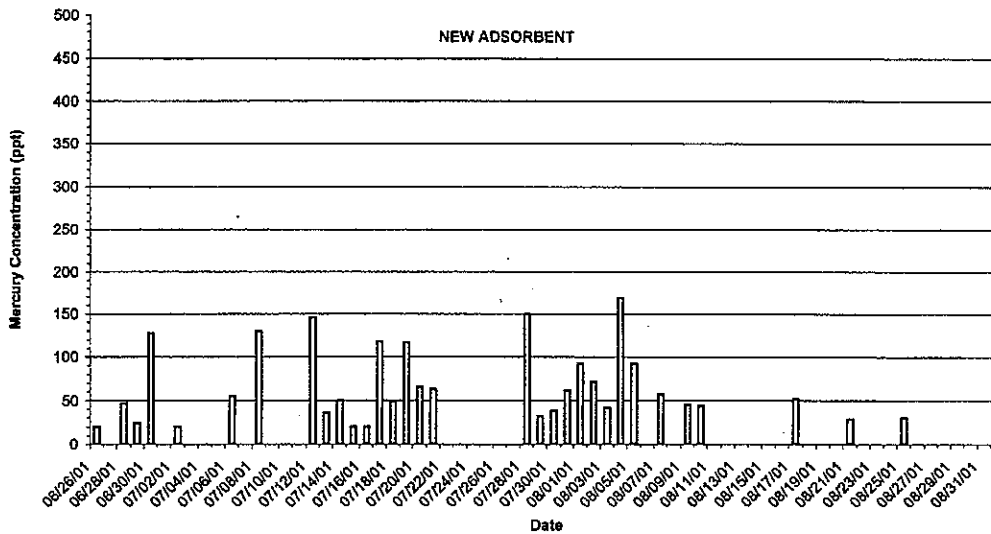
The results of the pilot test confirmed that MER-SORB LW was capable of achieving the mercury concentrations in treated effluent required, and sufficient data was generated to determine the minimum contact time required for the full-scale system.

### Process Design

The full-scale system was designed with four parallel adsorption trains, each containing three adsorption vessels, and each capable of processing up to 25 gpm of wastewater. Using 4 trains allowed standard-sized, 48-inch diameter by 48-inch high fiberglass reinforced (FRP) vessels to be used. The adsorption vessels were made to ASME Code 10 for durability and corrosion resistance. Total adsorbent volume was 603 ft<sup>3</sup>, providing a minimum contact time of 45 minutes at the maximum design flow rate. Cartridge type filters with 0.5 µm filter elements were installed prior to the



**Figure 5.** Effect of process optimization trials. Total mercury in effluent from secondary treatment system, March to August 2000.



**Figure 6.** Total mercury after adsorption, June to August 2001, influent pH 3.3 - 3.7.

from about 4,600 ppt to just under 900 ppt, more than an 80% improvement in mercury removal.

#### Additional Process Changes

In September 2000, HoltraChem idled all manufacturing operations at the Orrington facility. The cessation of operations caused major changes in the characteristics of the wastewater being processed. Mercury and silica contaminated groundwater became a major component of the wastewater stream and could not be processed through the Primary Treatment system without pretreatment to remove the silica. Wastewater was bypassed around the Primary and Secondary Treatment systems until a silica removal system could be designed and installed in June 2001.

Silica, in the form of sodium silicate, is removed from the wastewater by precipitation as insoluble calcium silicate. The wastewater pH is adjusted to pH 11.0, and calcium chloride is added and allowed to react forming calcium silicate. The precipitated solids are allowed to settle out and the supernate is pumped to the Primary Treatment process for mercury removal.

In addition to installation of the silica removal system, the damaged adsorbent was replaced prior to restarting the Secondary Treatment system in June 2001.

Figure 6 shows the trend in mercury concentration after Secondary Treatment for the period from June 26 through September 1, 2001. Total mercury in the effluent ranged from 20-169 ppt, averaging 66 ppt for the period.

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#### CONCLUSIONS

1. Adsorption utilizing sulfur-impregnated, activated carbon as a post-sulfide treatment process can be used to reduce mercury in chlor-alkali wastewaters.
2. Effluent mercury concentrations of less than 100 ppt are achievable.
3. Adding ferric chloride to the effluent from the sulfide treatment process, and filtering prior to adsorption improves overall mercury removal efficiency.
4. Operating results suggest that optimal conditions for removing mercury from chlor-alkali wastewaters by adsorption occur at an influent pH of about 3.5.

#### LITERATURE CITED

1. "Federal Water Pollution Control Act Amendments of 1972, Public Law 92-500 as amended by the Clean Water Act of 1977, Public Law 95-217," *Federal Register*, 44, p 32948, June 7, 1979, as amended at *Federal Register*, 45, p 33512, May 9, 1980.
  2. Maine Statute, "Waste Discharge Licenses," Title 38: Waters of Navigation, Chapter 3: Protection and Improvement of Waters, Subsection 413, paragraph 11, E, 1999.
  3. *Kirk-Othmer-Encyclopedia of Chemical Technology, Fourth Edition*, 1, p 958, John Wiley & Sons, Inc., New York, NY, 1991.
  4. "National Effluent Limitation Guidelines," Code of Federal Regulations, Title 40-Protection of the Environment, Part 415-Inorganic Chemicals Manufacturing Point Source Category, Subpart F-Chlor-Alkali Subcategory.
  5. **Raviguandran, M., et al.**, "Inhibition of Precipitation and Aggregation of Metacinnabar (Mercuric Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades," *Environmental Science & Technology*, 33, 9, pp 1418-1423, 1999.
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