

# 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<sup>®</sup> 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.

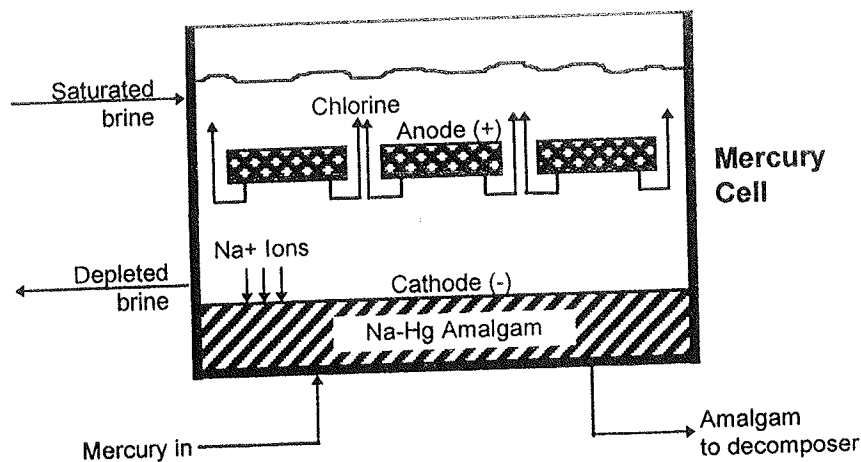


Figure 1. Schematic of the mercury cell process [3].

Additional difficulties were encountered when HoltraChem shut down the manufacturing operation in September 2000. The wastewater being treated changed from primarily mercury-contaminated process wastewaters to predominantly mercury and silica-contaminated groundwater and storm water requiring pretreatment to remove the silica and other dissolved solids before being treated to remove mercury. After adsorbent replacement and installation, and start-up of the pretreatment system, effluent mercury concentrations of < 100 ppt were achieved.

#### PROCESS OVERVIEW

##### The Mercury Cell Process

In the mercury cell chlor-alkali process, chlorine and sodium hydroxide are co-products produced by electrolysis of sodium chloride in a saturated aqueous solution (saturated brine). Saturated brine is produced by dissolving salt in depleted brine returned from the process. The saturated brine is treated to remove impurities, and then flows to a series of electrolytic cells. In the cells, a portion of the dissolved salt undergoes an electro-chemical reaction (electrolysis) forming chlorine gas at the anode, and a sodium-mercury amalgam at the cathode. The cathode is a flowing layer of elemental mercury running over a steel bedplate (cell bottom). Brine flows over the mercury, and metal elements suspended in the brine solution above the mercury form the anode. Low voltage, high amperage, direct current applied across the anode and cathode drives the electro-chemical reaction. Chlorine evolves as a gas at the anode, and is collected, cooled, dried, compressed, and liquefied. The sodium atoms amalgamate with a portion of the flowing mercury cathode, and the amalgam flows to a decomposer, another electrolytic cell, where the sodium-mercury amalgam reacts (decomposes) in the presence of deionized water to form a sodium hydroxide solution, generating hydrogen gas as a by-product. A schematic diagram of the process is shown in Figure 1 [3].

##### Wastewater Characteristics

Wastewaters generated by the mercury cell process typically include process brine purge, wash waters associated with process equipment maintenance and cell room housekeeping procedures, and contaminated storm water and groundwater. Typical properties are summarized below.

- pH: 4-11
- Available chlorine: 5-50 mg/L
- Chloride content: 80-260 g/L
- Total Hg: 6,000-70,000 ppb

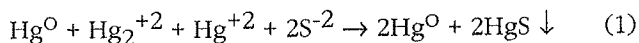
##### Effluent Treatment Guidelines

Under authority of sections 301 and 304 of the Clean Water Act, EPA promulgated production-based effluent limitations for wastewater discharges from mercury cell chlor-alkali facilities. By June 29, 1985, existing facilities were required to be in compliance with effluent limitations representing the degree of effluent reduction attainable by the application of BAT [4]. The limitations established for total mercury were a maximum daily discharge of 0.00023 lb. Hg/1000 lb. chlorine, and an average monthly discharge not to exceed 0.00010 lb. Hg/1,000 lb. chlorine. Based on rated production volume and average wastewater flows, the maximum mercury concentration in wastewater from the facility equivalent to the BAT limit is 202 ppb (202,000 ppt), and an average monthly concentration of about 88 ppb (88,000 ppt).

In June 1999, Maine enacted legislation placing further restrictions on mercury discharges. Licensed discharges of mercury were limited to less than 1.0 lb./year after January 1, 2000, and less than 0.1 lb./year after January 1, 2002 [2]. Compliance with the new limits required maximum and average mercury concentrations in wastewater of approximately 5.5 ppb (5,500 ppt) and 0.55 ppb (550 ppt) respectively, two orders of magnitude lower than the technology based BAT standards.

### Conventional Treatment Process—Sulfide Precipitation

The conventional treatment process for removing mercury from wastewater in the chlor-alkali industry is by reaction with sulfide to produce insoluble mercuric sulfide, followed by filtration to remove the precipitate. The sulfide precipitation reaction is shown in Equation 1.



In the presence of sulfide, and depending upon pH, mercury forms both soluble and insoluble compounds. The formation of insoluble mercuric sulfide is favored at low pH and low sulfide concentrations. At low excess sulfide concentrations and at a pH of 4-8, Raviguandran, *et al.* [5] observed the rapid formation of mercuric sulfide crystals in the laboratory, forming particles > 0.1  $\mu\text{m}$ . At a pH above 10, they found that 90% of the mercury was soluble, passing through a 0.1  $\mu\text{m}$  filter.

The sulfide treatment process at the HoltraChem facility is a multi-stage, batch process as follows.

1. Dechlorination with sodium thiosulfate to remove free chlorine.
2. pH adjustment to 5.5-6.5
3. The addition of approximately 40 mg/kg of sulfide as NaHS (sodium hydrogen sulfide), followed by 2 hours of circulation and reaction time.
4. Filtration to remove precipitated solids.

Typical mercury removal efficiencies are 99.9%, yielding average effluent concentrations of 20-30 ppb (20,000-30,000 ppt).

### EVALUATION OF TREATMENT TECHNOLOGIES

In searching for new mercury removal technologies, HoltraChem found that there were a number of emerging technologies that had shown the promise of being able to attain mercury reductions of the order of magnitude required to meet the new discharge limits. However, most of them were still experimental and a long way from being proven or commercially available. Based on evaluation of the available options, and discussions with various technology vendors, HoltraChem elected to pursue adsorption as a post-sulfide treatment process, and began working with Selective Adsorption Associates, Inc. (SAA), and NUCON International, Inc. (NUCON), to develop a treatment system.

SAA and NUCON recommended adsorption as the technology of choice because of its ability, in general, to reduce contaminant concentrations in gases and liquids by several orders of magnitude. However, an ordinary carbon adsorbent would not work, as ordinary carbons have been shown to have little capacity or efficiency for mercury removal. Sulfur-impregnated, activated carbon was suggested for evaluation. Activated carbon has an extremely large internal surface area of 1,000 square meters per gram of carbon, which gives it the potential to adsorb low concentrations of mercury in water. With elemental sulfur impregnated or dispersed onto the surface inside the carbon, it has the added ability to chemically react the mercury with the sulfur, forming insoluble mercury sulfide. Sulfur-impregnated carbon can pro-

duce extremely low mercury concentrations given sufficient contact time between the water and the adsorbent.

An adsorption system typically consists of one or more carbon tanks, or vessels, piped in series or parallel flow configurations. The adsorption media is loaded into the vertical cylindrical tanks, or vessels, which are also often called beds or adsorbers. The water to be treated is pumped through the carbon beds. Prior to this stage, a pH adjustment may be necessary, and pre- and post-filtration are also often part of the system. The adsorption beds are designed with an inside diameter to match the water flow rate, so that the desired minimum level of turbulence for efficient mass transfer of the mercury to the carbon can be achieved. The height and the number of adsorption beds in series is selected to provide sufficient contact time between the water and the adsorption media for the adsorbent to do its job of removing the contaminant, in this case, mercury atoms.

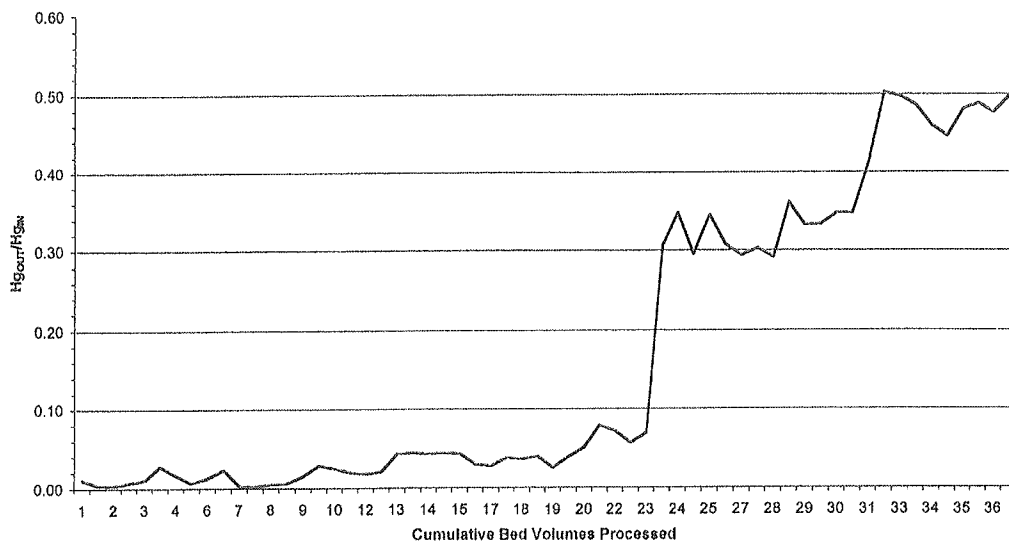
### Adsorption Media

MERSORB<sup>®</sup> LW Mercury Adsorbent had already demonstrated its ability to reduce mercury concentrations in the treatment of condensate from the retorting of mercury-bearing waste materials, and treatment of blow-down water from an air scrubber that treated off-gas from a medical waste incinerator. Mercury concentrations were typically reduced from 5,000,000 ppt to less than 500 ppt, the same order of magnitude reduction required for HoltraChem to meet the new mercury discharge limits. However, no system had yet been designed or operated for treating typical chlor-alkali wastewaters to mercury concentrations of 500 ppt or less in the effluent.

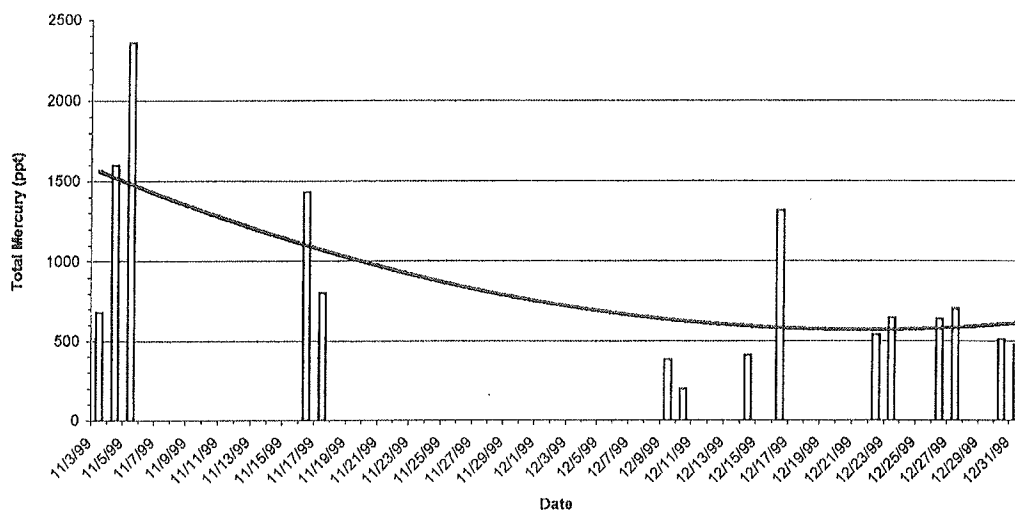
### Process Evaluation—Pilot Study

HoltraChem, SAA, and NUCON agreed to collaborate on a pilot test on the effluent from HoltraChem's sulfide treatment process. The objectives of the testing were to demonstrate the capability of MERSORB LW mercury adsorbent to achieve effluent concentrations sufficient to meet the discharge limits, and to determine the minimum contact time required for this level of mercury removal efficiency. The results of the test would be used to design a full-scale system with the capacity to treat up to 100 gpm of wastewater from HoltraChem's Primary Treatment system.

The pilot test utilized four packed columns arranged in series with a total bed volume of about 4.9 gallons. Cartridge filters with 0.5  $\mu\text{m}$  filter elements were installed before and after the adsorption train. Effluent from the Primary Treatment system was processed through the pilot unit in 15-gallon batches at a flow rate of 0.14 gpm, yielding a total adsorption, empty bed, contact time (EBCT) of about 35 minutes. The pH of the wastewater was adjusted to 10.0-11.0 prior to adsorption. Fourteen separate runs were made over a period of a month utilizing effluent from four different batches of wastewater with influent mercury concentrations ranging from 4.5-86 ppb (4,500-86,000 ppt). Five samples of adsorber effluent were collected at equal time intervals from each run and analyzed for total mercury.



**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.

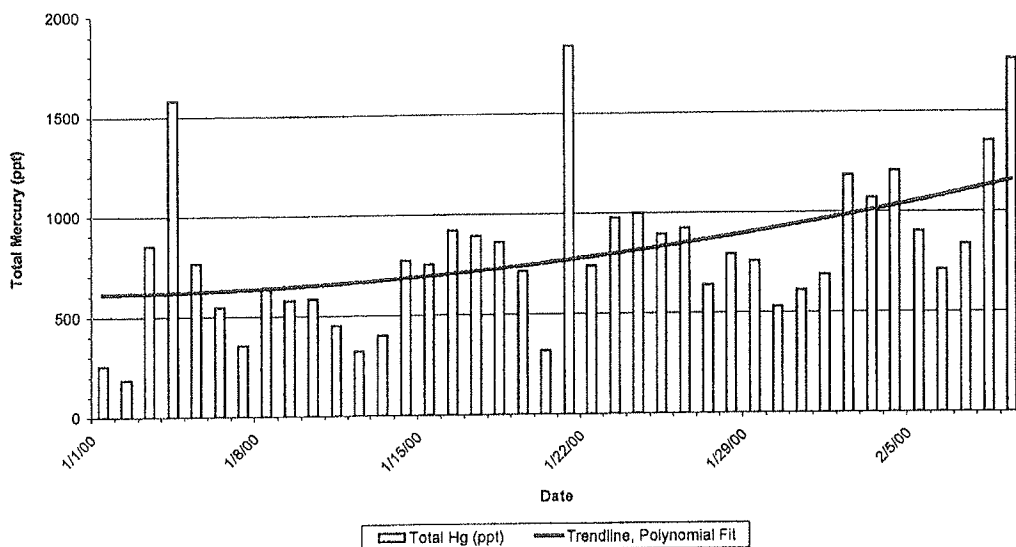
### Experimental Results

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 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.

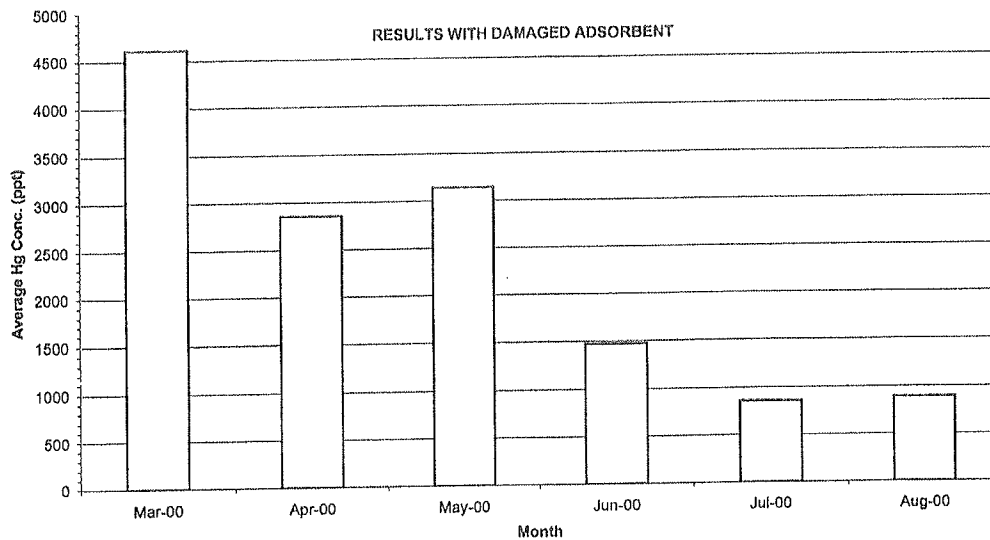
In addition, samples of wastewater taken at the inlet and outlet of both the pre-adsorption filters and the adsorption train were tested for total and dissolved mercury. The analytical results showed that significant concentrations of particulate mercury were passing through the Secondary Treatment system 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

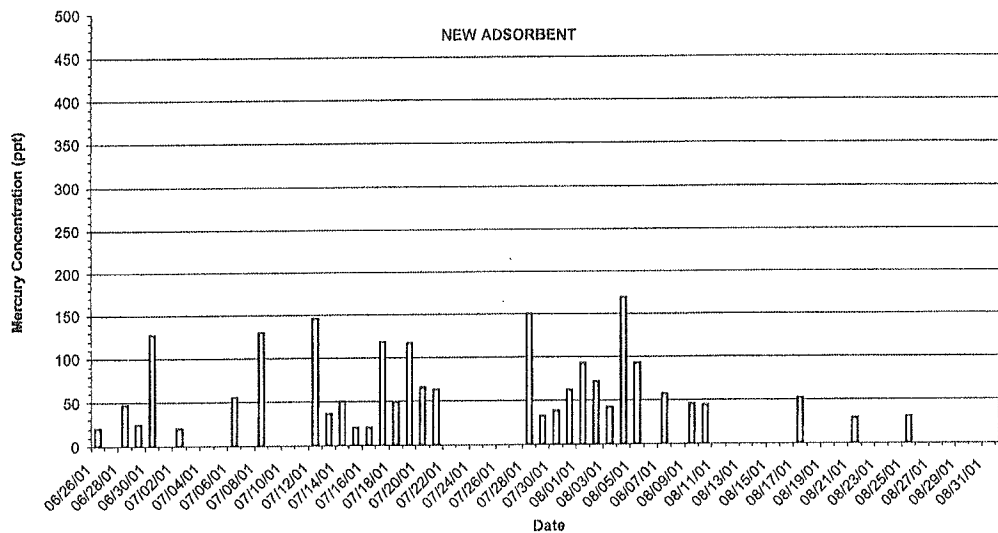
From March through August 2000, HoltraChem made a number of process changes intended to improve the overall performance of the Primary and Secondary Treatment systems. These changes included:

- 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 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

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