GUIDELINES FOR THE OPTIMIZATION OF MERCURY WASTEWATER TREATMENT (SULFIDE PRECIPITATION PROCESS) SYSTEMS

INTERNAL DOCUMENT

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THE CHLORINE INSTITUTE, INC.

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1. INTRODUCTION

Mercury discharges to aquatic ecosystems have been targeted for reduction since the 1970s. In the mid-1970s, mercury cell chlor-alkali facilities in the USA installed mercury sulfide precipitation wastewater treatment systems to remove mercury before discharge. Typical treated effluent concentrations are in the range of 5 to 25 ppb (ug/L or parts per billion) versus ppm (mg/L or parts per million) concentrations in untreated wastewaters. Sulfide precipitation is very effective in removing divalent inorganic mercury from water and is still considered by the United States Environmental Protection Agency as Best Available Technology (BAT). The discharge reductions associated with use of sulfide treatment have normally been deemed sufficient to protect aquatic ecosystems and humans.

EPA and state agencies have continued to implement measures to protect human health and the environment. More stringent water quality standards for bioaccumulative substances, including mercury, were promulgated in the late 1990s. The most stringent water quality based standard for mercury in the Great Lakes was established as 1.3 ppt (ng/L or parts per trillion). Water quality standards for other areas of the USA range from 12 ppt to 120 ppt total mercury.

At about the same time that ppt concentrations for mercury discharge were being established, EPA promulgated a new analytical method that allows measurement at these low concentrations. Because mercury is a ubiquitous pollutant many effluents will likely have to be treated to low ppt concentrations to attain new water quality based permit limits. There is currently no known technology to treat wastewater effluent to less than 12 ppt mercury.

1.1 Purpose and Scope

Given the increasing need to meet more stringent water discharge permit limits that can not be attained using BAT technology (e.g. sulfide precipitation), Chlorine Institute member companies decided to evaluate potential improvements to their existing sulfide precipitation technology. If this technology could be optimized, then it was felt that treated effluent goals of 5 ppb or below might be attainable on a consistent basis. Although no member company was achieving this level of performance with existing systems, there are numerous process variables and added post-treatment technologies (e.g. filtration to remove residual solids) that might be optimized or tried in combination.

This guidance document describes process and operational variables, as well as opportunities that could now be evaluated at each chlor-alkali facility, taking into consideration site-specific factors, to improve effluent quality. Actual real-world treatment systems may deviate from the theoretical optimum configuration. Site-specific conditions which may affect the treatment system configuration include various additional wastewater components, the design of specific installed equipment, and/or results of site-specific process optimization studies.

Chlorine Institute members familiar with the operation of sulfide treatment systems and chlor-alkali plant engineering and operational issues met in a 3-day workshop in early 2002 to review potential opportunities for improvement. Participants reviewed the chemistry of the sulfide treatment process, as well as engineering aspects of each existing treatment system. Ideas were freely shared and suggestions for optimization were formulated.

Note that only the sulfide precipitation process that is used at most mercury cell chlor-alkali facilities was evaluated by workshop participants. Other technologies, such as ion exchange or activated carbon were specifically excluded. These technologies might be evaluated by Chlorine Institute members in the future once sulfide treatment systems have been optimized.

1.2 Responsible Care

The Institute is an American Chemistry Council (ACC) Responsible Care® Partnership Association. In this capacity, the Institute is committed to: Fostering the adoption by its members of the Codes of Management Practices; facilitating their implementation; and encouraging members to join the Responsible Care® initiative directly.

Chlorine Institute members who are not ACC members are encouraged to follow the elements of similar responsible care programs through other associations such as the National Association of Chemical Distributors (NACD) Responsible Distribution Program or the Canadian Chemical Manufacturers Association's Responsible Care® program.

1.3 Abbreviations and Definitions

BAT	Best Available Technology
Brine	A solution of water and salt (typically sodium chloride***)***
CFR	Code of Federal Regulations (United States)
CWA	Clean Water Act
DE	Diatomaceous Earth
D/P	Differential Pressure
EPA	Environmental Protection Agency (United States)
Mercury (0)	Elemental mercury; mercury
Mercury (I)	Mercurous; mercury ion with a valence of +1
Mercury (II)	Mercuric; mercury ion with a valence of +2
mg/L	milligrams per liter (for water this is equal to ppm)
ng/L	nanograms per liter (for water this is equal to ppt)
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
TMDL	Total maximum daily load

ug/L	micrograms per liter (for water this is equal to ppb)

1.4 Disclaimer

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1.5 Approval

The Mercury Issues Management Steering Committee approved this guidance document on October 28, 2003.

1.6 Revisions

Suggestions for revisions should be directed to the Secretary of the Institute.

1.7 Reproduction

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2. PROCESS CHEMISTRY

2.1 Simplified View of the Process Chemistry

The mercury containing wastewater treatment process is viewed as being the simple reaction of mercury (II) with sulfide ion according the following reaction:

$$Hg^{+2} + S^{=} \leftarrow\!\!===\!\!\rightarrow HgS$$

The mercuric sulfide is then precipitated out of solution and filtered. This process has resulted in wastewater that was reduced sufficiently in mercury content to meet discharge requirements. Under ever tightening regulatory pressure the industry may need to lower the discharge levels of mercury by a factor of as much as 10 to 100. To do this, the sulfide treatment removal step needs to be optimized and in control to allow future, more sophisticated removal technologies to augment the sulfide treatment process.

2.1.1 pH Dependency

The first step in learning how to optimize the mercury treatment system is to take a more in depth look at the chemistry involved in the treatment process. Independent of the chemical form of sulfide addition, the form of sulfide present in solution will be controlled by pH as seen in the following reactions:

$$H_2S \leftarrow\!\!=\!=\!=\!\!\rightarrow HS^- + H^+$$
$$HS^- \leftarrow\!\!=\!=\!=\!\!\rightarrow S^= + H^+$$

Table 2.1 illustrates the concentrations of the various forms of sulfide as the pH is varied holding the concentration of hydrogen sulfide constant at 0.1M. Barnes, et al., 1967, demonstrated that the maximum amount of mercury is precipitated at a pH of 4 using sulfide (Figure 2.1). According to the following table, virtually all of the sulfide is in the hydrogen sulfide form. At this pH, the following reaction takes place:

$$Hg^{+2} + H_2S \leftarrow\!\!=\!=\!=\!\!\rightarrow HgS + 2H^+$$

The Effect of pH on a 105 ppm Sulfide Solution

pH	S= ppm	HS- ppm	H2S ppm
1	0.000	0.000	105.400
2	0.000	0.000	105.400
3	0.000	0.002	105.398
4	0.000	0.019	105.380
5	0.000	0.194	105.200
6	0.000	1.907	103.435
7	0.000	16.334	88.571
8	0.000	67.024	36.345
9	0.000	97.185	5.270
10	0.001	101.763	0.552
11	0.012	102.234	0.055
12	0.119	102.172	0.006
13	1.176	101.086	0.001
14	10.629	91.339	0.000

Table 2.1 (Reference 7.1.1)

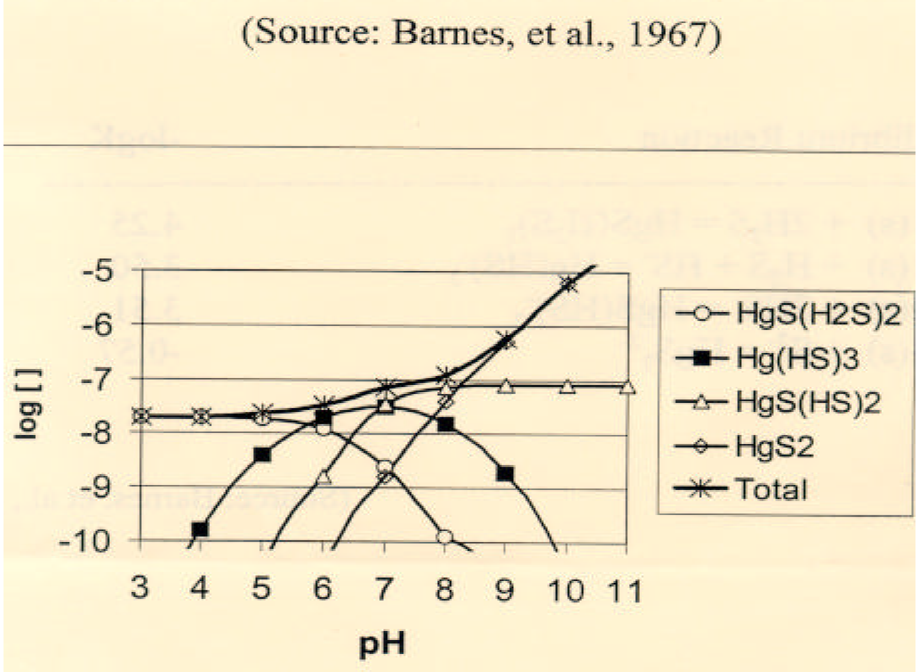

(Source: Barnes, et al., 1967)

Figure 2.1 (Reference 7.1.2)

At a pH of 4 or lower, the negative sulfide ion no longer exists. Therefore, there can be no attraction to the positive mercury ion. The pH of the wastewater also has an impact on the form of mercury present in solution. Mercury exists in three distinct forms:

mercury (I),

mercury (II), and

elemental mercury (0).

These three forms are interchangeable and are in equilibrium according to the following reaction:

$$\mathrm{Hg}^{+2}_{2} \leftarrow\!=\!=\!=\!\rightarrow \mathrm{Hg}^{+2} + \mathrm{Hg}^{0}$$

[mercury (I) ←===→ mercury (II) + elemental mercury (0)]

This equilibrium can be rapid and can be complete in the time of mixing. Mercury (I) is not stable under alkaline conditions, forcing the equilibrium to the right.

2.1.2 Hg^{0} Solubility in Water

Elemental mercury (0) is also soluble in water at a concentration of 60 ppb at 23 degrees C (Reference 7.1.3). The solubility will increase with temperature, but is depressed by the presence of salts in the wastewater. Since some process water will contact elemental mercury in the cell room, soluble mercury (0) should always be expected in the wastewater. Elemental mercury (0) will not be removed in a sulfide precipitation process.

2.1.3 Expected Reaction

Wastewater treatment under alkaline conditions has two distinct advantages: there should be very little mercury (I) since it is not alkaline stable and the concentration of free sulfide ion will be eight orders of magnitude greater at pH 8 than at pH 4. Under alkaline conditions the positively charged mercury (II) is reacting with the negatively charged free sulfide ion. Keep in mind that mercury (0) will not react under these conditions. The reaction of sulfide with mercury (II) in wastewater by the following reaction can be easily demonstrated by the titration of wastewater with a dilute solution of sodium sulfide.

$$Hg^{+2} + S^{=} \leftarrow\!\!=\!=\!=\!\!\rightarrow HgS$$

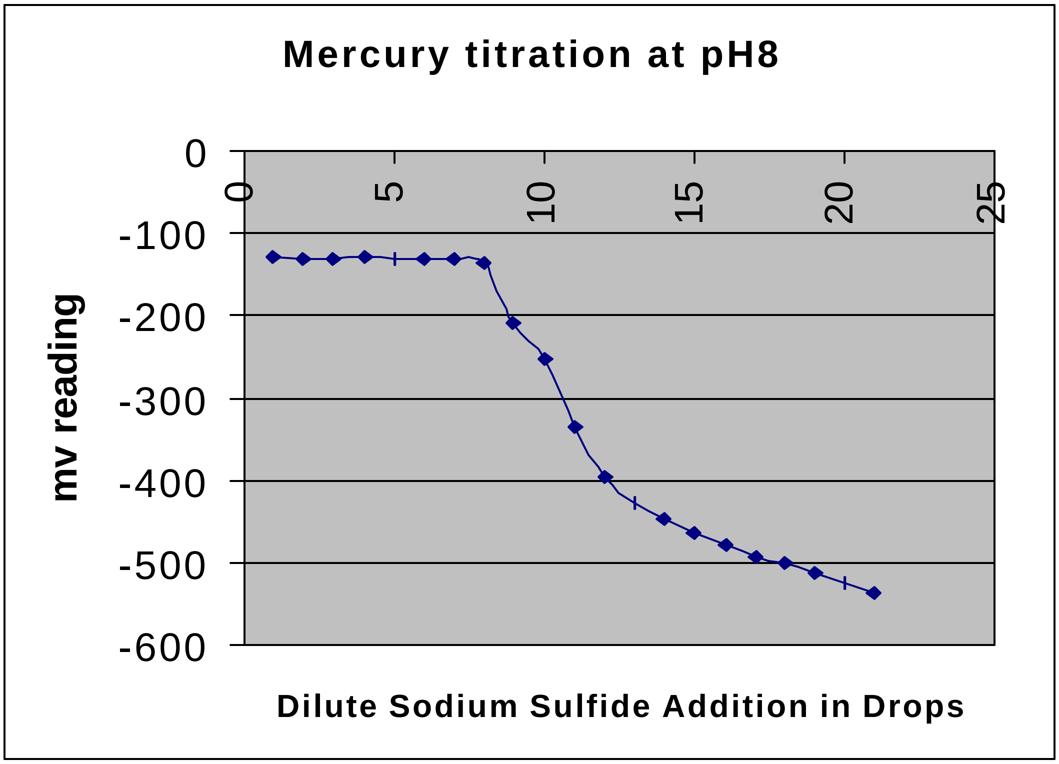


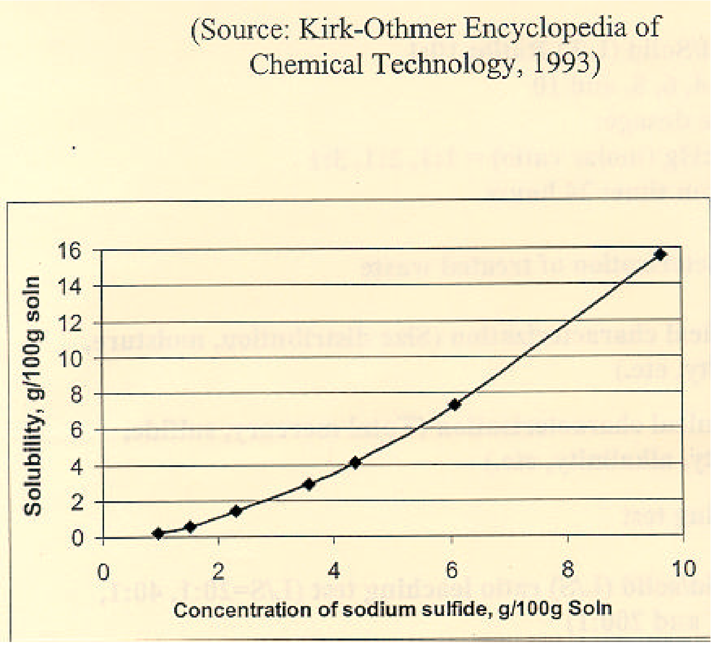
Figure 2.2 (Reference 7.1.1)

The reaction in the above figure was monitored by using an ion specific electrode for sulfide ion. This electrode only responds to the free concentration of the sulfide ion in solution-not to the total concentration of all of the sulfide forms present. As the titrant is added to the wastewater, the sulfide ion added to the solution is consumed by the mercury (II) and the ion electrode reading remains constant. At the point in the addition where the sulfide ion is in excess in the solution, the ion electrode reading increases. This is clear evidence that the expected reaction is in fact taking place.

2.1.4 Unexpected Reaction

In addition to the expected reaction an additional reaction is also taking place when excess sulfide is added to the wastewater. Mercury (II) is capable of adding a second sulfide ion and again becoming a water soluble ionic species as seen in the following equation:

$$Hg^{+2} + 2S^{=} \leftarrow\!=\!=\!=\!\rightarrow HgS_2^{=}$$



(Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1993)

Figure 2.3 (Reference 7.1.4)

As seen in the above figure the addition of excess sulfide increases the mercury solubility in the treated wastewater. The addition of extra sulfide will actually reduce the efficiency of the process.

2.1.5 Sulfide Species pH Dependency

To further complicate the above chemistry, this interaction between mercury (II) and sulfide is also pH dependent, according to the following reactions:

$$Hg^{+2} + S^{=} \leftarrow\!=\!=\!=\!\rightarrow HgS$$

$$HgS + 2H_2S \leftarrow\!=\!=\!=\!\rightarrow HgS(H_2S)_2$$

$$HgS + H_2S + HS^{-} \leftarrow\!=\!=\!=\!\rightarrow Hg(HS)_3^{-}$$

$$HgS + 2HS^{-} \leftarrow\!=\!=\!=\!\rightarrow HgS(HS)_2^{-}$$

$$HgS + S^{=} \leftarrow\!=\!=\!=\!\rightarrow HgS_2^{=}$$

Figure 2.1 illustrates the concentrations of the various mercury (II) sulfide species as a function of pH. Note, the line on the graph representing the mercury concentration in solution is a minimum between a pH of 3 to 4.

2.1.6 Hg^{+2}_2 pH Dependency

As Figure 2.1 indicates, sulfide treatment should be done between pH 3 and 4 to maximize the amount of mercury removal from wastewater. **CAUTION:** if the pH is further lowered, hydrogen sulfide gas generation increases, creating a potential safety hazard. Since the optimized reaction occurs under acidic conditions, all three forms of mercury will need to be addressed. Keep in mind that these forms have the ability to shift back and forth depending on the other ions in solution and the pH as shown in the following equation.

$$Hg^{+2}_2 \leftarrow\!\!=\!=\!=\!\!\rightarrow Hg^{+2} + Hg^0$$

2.1.7 Wastewater Composition

The discussion thus far has centered on the chemistry of mercury, sulfide and the effect of pH. There are many other ionic species in wastewater that interact with mercury. At a minimum, the wastewater will contain percent levels of chloride and sulfate in addition to brine sludge and iron compounds.

2.1.8 Chloride and Hg^{+2}

Mercury forms an extremely strong complex with chloride. Mercury will add chloride ions stepwise to form a tetrachloro anion as seen in the following reactions:

$$Hg^{+2} + Cl^- \leftarrow\!\!=\!=\!=\!\!\rightarrow HgCl^+$$

$$HgCl^+ + Cl^- \leftarrow\!\!=\!=\!=\!\!\rightarrow HgCl_2$$

$$HgCl_2 + Cl^- \leftarrow\!\!=\!=\!=\!\!\rightarrow HgCl_3^-$$

$$HgCl_3^- + Cl^- \leftarrow\!\!=\!=\!=\!\!\rightarrow HgCl_4^=$$

The formation constant for this series of reactions is almost as large as it is for sulfide and has a direct impact on the ability of sulfide to remove mercury(II) from the wastewater as shown in the following graph.

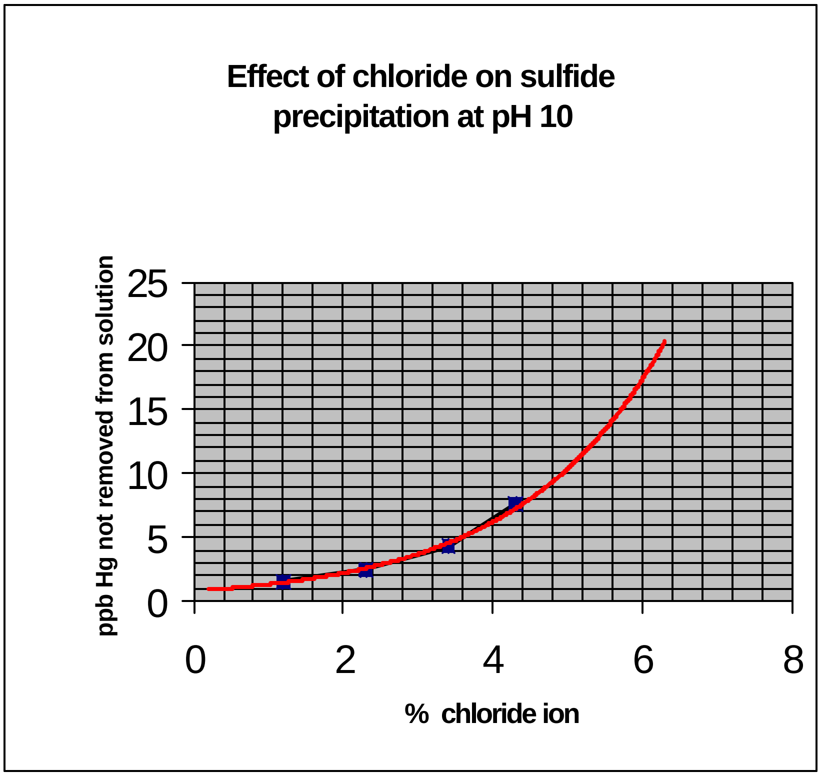


Figure 2.4 (Reference 7.1.1)

As the above figure indicates, increasing concentrations of chlorides will decrease the removal of mercury from the wastewater. Every effort should be made to minimize the amount of brine in the wastewater.

2.1.9 Chloride and Hg^{+2}_2

Mercury(I) forms very strong complexes with low chloride concentrations, affecting the equilibrium between its three forms as shown in the following equations:

$$Hg^{+2}_2 + Cl^- \leftarrow\!\!===\!\!\rightarrow Hg_2Cl^+$$

$$Hg_2Cl^+ + Cl^- \leftarrow\!\!===\!\!\rightarrow Hg_2Cl_2$$

$$Hg^{+2} + Hg^0 \leftarrow\!\!===\!\!\rightarrow Hg^{+2}_2$$

As long as mercury (I) remains in solution, mercury(0) will always be present. The quantity of mercury (0) in solution can easily be measured in a non-reducing analysis. As an increasing quantity of chloride is added to the solution, mercury(I) is precipitated, shifting the equilibrium and resulting in the removal the available mercury(0) from solution.

The following figure represents the amount of mercury (0) in solution aerated by gas purging in a non-reducing analysis. As the chloride concentration is increased, all of the mercury (I) is converted into the chloride form and becomes an insoluble crystal. The presence of as little as 1×10^{-4} molar chloride effectively stops the interchange of the three forms of mercury.

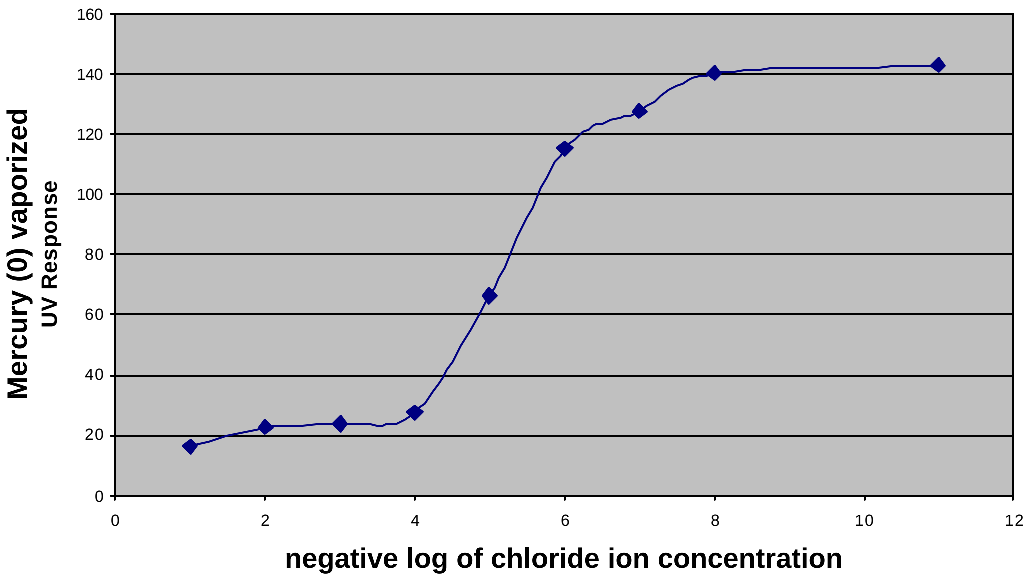

Mercury (0) Vaporized from Mercury (I) Solution as a Function of Chloride ion Concentration

Figure 2.5 (Re-drawn from Reference 7.1.3)

As seen in the following figure, the rate of crystal growth can be measured using the same non-reducing analysis method by monitoring a solution over time. The crystal growth has progressed to the size that effectively stopped the interchange of mercury forms after 25 minutes at room temperature (25° C).

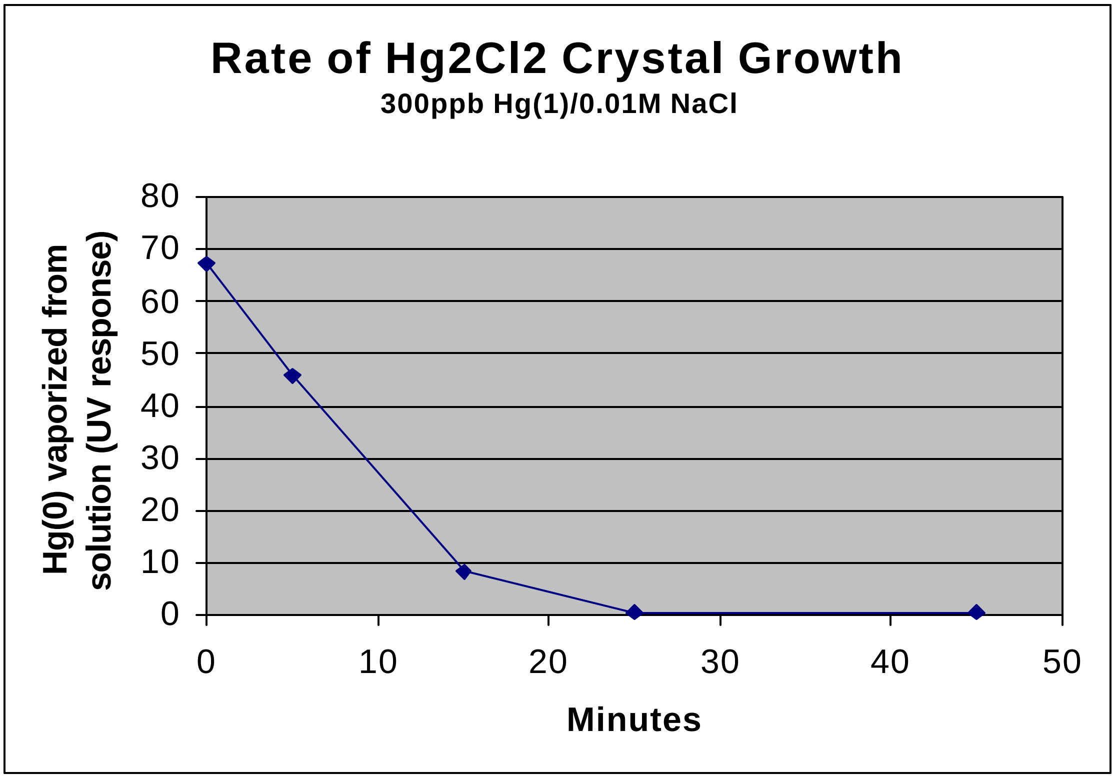


Figure 2.6 (Data taken from Reference 7.1.3, p 153)

2.1.10 Expected Reaction

The reaction between mercury (II) and sulfide is expected to be the following:

$$HgCl_4^{=} + H_2S \leftarrow\!\!===\!\!\rightarrow HgS \quad + \quad 2HCl \quad + \quad 2Cl^{-}$$

Although sodium sulfide (or other sulfide salts) is added to the treatment process, at pH 3 to 4, the sulfide will be converted to hydrogen sulfide. While this reaction takes place, instead of a one step reaction, a seven-step process that may be kinetically limited occurs. Laboratory studies have indicated that reaction times of 1 to 2 hours are needed to complete the reaction and grow large enough mercury (II) sulfide crystals to be filterable.

So far, no provisions have been made to remove mercury (0) or the mercury (I) chloride from the wastewater. Larger droplets of mercury (0) will filter out of the wastewater provided that the pressure differential across the filter is kept below about 15 psi. If the differential gets too high, the mercury (0) liquid can be extruded through the filter. Filtration will have no effect on the amount of mercury (0) dissolved in the wastewater. At short reaction times (less than one to two hours), the mercury (I) chloride crystal size may be too small to be filterable.

2.1.11 Sodium Molybdate Interference

Laboratory work has shown that the presence of sodium molybdate will prevent the formation of mercury (II) sulfide. Mercury (II) forms the following complex:

$$[Hg^{+2}Mo_6O_{24}]^{-10}$$

This complex is an anion that is water soluble and prevents mercury precipitation with the sulfide. Every effort should be made to exclude molybdate from the wastewater.

2.2 Proposed Treatment System Based on the Chemistry

Given the above information about the chemistry of mercury and the other ions in the wastewater and their interactions with the different forms of mercury, it should be possible to design a wastewater treatment process that will consistently remove the maximum amount of mercury from the wastewater.

2.2.1 **Step 1:** Use a Large Holding Tank to Time Average the Wastewater Streams.

Depending on what is occurring in production units, the composition of the wastewater is continually changing. The use of a large holding tank that is continually mixed with a 48 hour residence time will reduce the variation in the concentrations of all of the components in the wastewater, allowing better control of the treatment process. For example, reducing spikes in chloride concentration will allow more effective precipitation of mercury (II).

2.2.2 **Step 2:** Settle and/or Filter at pH 10-11 to Remove Mercury (0) and Mercury (I) Chloride.

Some of the mercury in wastewater is present in solid form or adhering to other solids present in the stream including mercury (0) in the liquid form. Settling and filtering at alkaline pH will remove all of the solids including brine sludge, iron compounds and liquid mercury (0) allowing only clear solution to be transferred on the next step of the treatment process.

2.2.3 **Step 3:** Reduce pH to 3-4 and Oxidize the Dissolved Mercury (0).

At this point in the treatment process the pH is reduced to between 3 and 4 with hydrochloric acid to oxidize mercury with free chlorine. The use of sulfuric acid in this step is not recommended as shown in Figure 2.7. Sulfuric acid adversely affects the ability of sulfide to precipitate mercury (II) from solution. It is thought that the crystals of mercury (II) sulfate are too fine to be filtered.

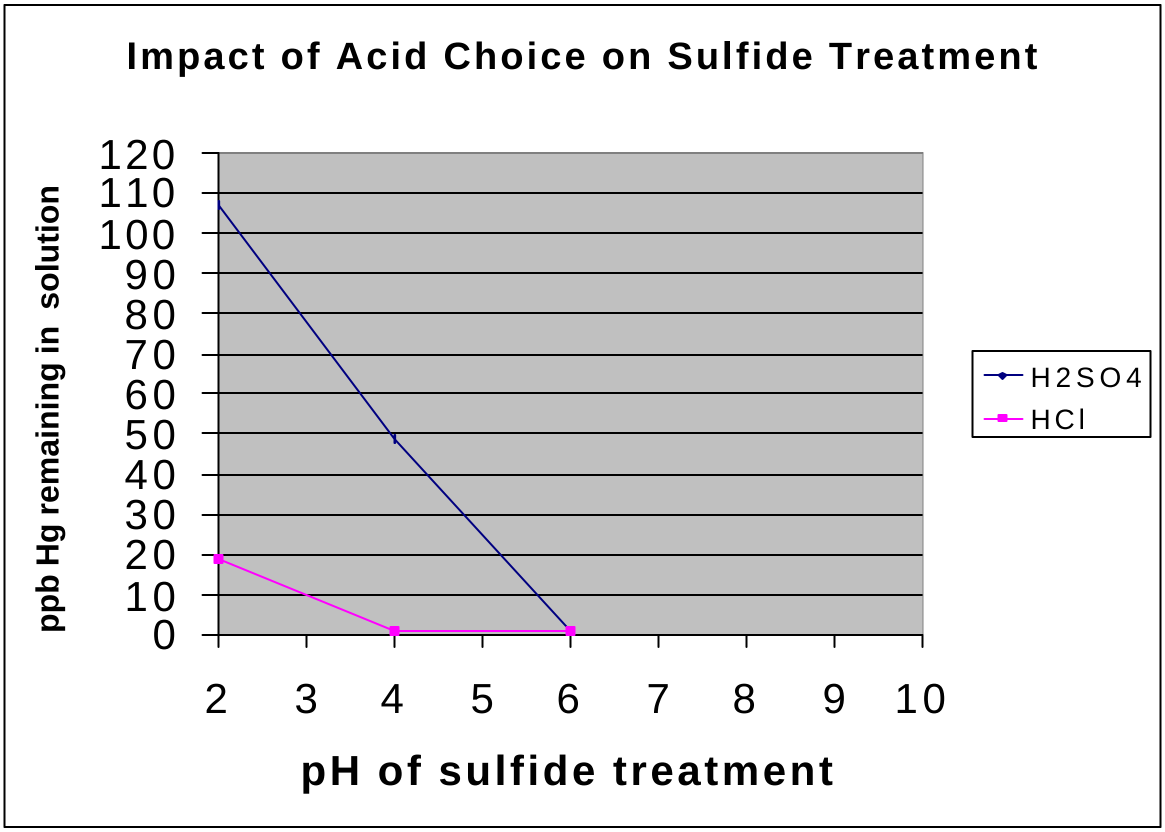


Figure 2.7 (Reference 7.1.2)

Bleach or free chlorine is added to the treatment solution to oxidize all of the mercury forms to mercury (II). By removing all of the solids and the droplets of mercury (0) in the previous step, the free chlorine is only oxidizing the soluble mercury (0), converting it to mercury (II) needed to react with the sulfide. Laboratory studies have indicated that oxidation times of 1 to 2 hours are needed in wastewater saturated with free chlorine. **CAUTION:** Chlorine emissions from this treatment step must be contained.

2.2.4 **Step 4:** Add Sulfide to Remove Excess Oxidant and Precipitate the Mercury (II) as the Sulfide.

After the oxidation is complete, the excess free chlorine is consumed with sodium sulfide. Sodium sulfide dosage should be controlled such that excess sulfide residual is between 1 and 5 ppm. **CAUTION:** Too large of an excess of sulfide will re-solubilize the mercury (II) sulfide precipitate. The use of other sulfur compounds to consume the free chlorine will adversely affect the filtration step.

As seen in the photograph below (Figure 2.8), sodium sulfide produced the least amount of colloidal sulfur upon consuming the free chlorine in the wastewater. Note there is a stirring bar in the bottom of each of the test jars and it is only visible in the bottom of the sodium sulfide jar. Colloidal sulfur plugs filters very quickly, increasing the difficulty of filtration.

Figure 2.8 (Reference 7.1.5)

2.2.5 **Step 5:** Allow Mercury (II) Sulfide Crystal Growth for 1-3 Hours at pH 3 to 4.

Laboratory studies have shown that a 1 hour reaction time is adequate in the majority of wastewater samples. In a limited number of cases, an incremental improvement was seen with a second hour of reaction time. This improvement may be dependent on the other ions that are present in some of the batches of wastewater. This is additional evidence of the benefit of the large mixed holding tank at the beginning of the process, producing more consistent reaction times between batches. The longer the wastewater is allowed to mix before filtration the larger the mercury (II) sulfide crystals will grow and the easier the solution will filter.

The use of pH 3 to 4 will minimize the presence of soluble mercury (II) sulfide forms and maximize mercury removal from the wastewater.

2.2.6 **Step 6:** Filter Mercury (II) Sulfide Crystals.

Filter the mercury (II) sulfide using a precoat filter. Filtration is discussed in Section 5.

3. PROCESS FLOW STREAMS

3.1 General

In general, a knowledge of the characteristics and components of the process streams flowing to treatment for mercury is important to properly treat those flows. Segregation of streams to treatment is needed for those flows which are not amenable to sulfide treatment. Consideration should also be given to methods of reducing the total amount of wastewater to be treated.

3.2 Components

For most facilities, process flows to treatment originate mainly from:

- Cell room sump (primarily wash down water)
- Brine purge
- Outlet end box water
- Chlorine condensate
- Thermal recovery unit (if present at facility)
- Process area rain water (for some facilities)

3.3 Segregation of Streams

Segregation of streams should be considered carefully when designing or reviewing the operation of the wastewater treatment system. The advantages of routing some streams away from treatment include lower cost of treatment, more efficient operation of the treatment system, more consistent treatment of the wastewater, and reducing or eliminating certain treatment problems. Disadvantages may include difficulty in meeting permit limits if certain streams are not treated.

The following concerns should be considered In deciding whether a stream should go to sulfide treatment:

- Mercury concentration in the stream – in general, lower mercury concentration streams can be routed away from sulfide treatment. An alternative treatment may need to be considered if permit limits do not allow these streams to be discharged totally untreated, such as routing through a carbon bed or ultra filtration to remove particulates.

- Form of mercury species present in stream – mercury will be present as mercury (0), mercury (I) or mercury (II). Only mercury (II) is precipitated by sulfide treatment to form mercury (II) sulfide. The other species must be either removed and handled separately or converted to mercury (II) for sulfide precipitation. A stream containing significant concentrations of mercury (0) and mercury (I) may need to be segregated and treated separately or pretreated before routing to sulfide treatment.

- Problem components – several facilities have encountered difficulties with specific compounds found in certain sub streams. See Section 3.4 for more detail. Streams containing components known to interfere with operation of the sulfide treatment system may need to be segregated for pretreatment or separate treatment.

- Intermittent streams – intermittent streams may be created in two ways: from events which do not occur continuously, such as rainfall or equipment washouts; or from streams which are collected and then routed to sulfide treatment batch-wise (see discussion below). Intermittent streams may require the use of an equalization tank to ensure blending with the continuous influent to the sulfide treatment system.

- Streams with varying characteristics – streams such as storm water may have widely differing characteristics at various times. For example, the first flush of storm water in process areas may have relatively higher concentrations of mercury, which quickly decrease as areas are flushed by the storm water. These streams may be good candidates for partial segregation, where the stream is initially routed to sulfide treatment, then routed away when concentrations have declined.

Some streams may be individually collected and subsequently routed to the treatment system, resulting in an intermittent stream. One advantage to this practice is the ability to determine the characteristics of the stream before adding it into the sulfide treatment system. If components known to cause problems with the treatment system are found, then pretreatment of only the sub stream can be performed, avoiding an upset of the entire treatment system. One disadvantage of this process is the creation of an intermittent stream of a volume which may be sufficient to change the characteristics of the flow into the treatment system and upsetting the normal operation of the system. An equalization tank may be helpful in this case.

3.4 Difficult to Treat Components

Several streams or components within streams can be difficult to treat or cause problems with the sulfide treatment system. Some of these are listed below.

- Hypochlorite or chlorinated brine streams - high concentrations of free chlorine will affect the sulfide addition/precipitation steps of sulfide treatment because of rapidly changing sulfide demand. The presence of free chlorine is an excellent oxidizer, and is used by some facilities to convert mercury (0) and mercury (I) to the treatable mercury (II) form at the beginning of the treatment train, even to the point of intentionally adding hypochlorite or chlorinated brine to accomplish this step. Once that is accomplished, the free chlorine is neutralized by the addition of sodium sulfide, sodium thiosulfate, sodium bisulfite, hydrazine, or similar reducing agent. As noted in Section 2.2.4, sodium sulfide may be the best choice.

- Silica - caustic in contact with sand can create silica compounds which blind the filters. This can be caused by deionization regeneration water if silica is present in the well water (silica ions removed from well water contacting caustic during the caustic regeneration cycle of the ion exchange resin). Sand blasting operations in the area can also result in silica problems. Concentrations greater than 100 ppm can interfere with the filtration step of sulfide treatment. Silica can be removed from the treatment system influent by precipitating it out as calcium silicate ($CaSiO_2$) at high pH, i.e., above 12.

- Cooling tower and boiler treatment chemicals - blowdown from cooling towers often contain treatment chemicals designed to dissolve or suspend scale particles. These chemicals can have a similar effect on the precipitated mercury (II) sulfide, preventing settling of the precipitate and causing carry-over of the suspended mercury (II) sulfide particles. Cooling tower and boiler blowdown streams are usually segregated from sulfide treatment.

- Sodium molybdate - this compound reacts with mercury to form mercury molybdate, which is soluble (See Section 2.1.11). Although a very useful compound in extending the life of decomposer graphite, care must be taken to ensure no molybdate enters the influent to sulfide treatment.

- Iron - iron hydroxide is very hard to filter. If an influent stream of pH about 9 or greater contains iron, one solution is to reduce the pH to 2 using acid to dissolve the iron, then raise the pH back up to 3 to 4 before introducing the stream to the sulfide treatment system. As discussed in Section 2.1.9, increasing concentrations of chlorides or sulfates may adversely affect sulfide treatment.

- Aluminum - black slag blasting media is high in aluminum, which causes problems with sulfide treatment.

- Carbon particles - carbon can adsorb mercury (0). Streams with carbon in them can deposit the carbon and mercury (0) onto the filter, and subsequently slowly release mercury (0) back into the wastewater.

- Organics - organics (including some detergents and cleaners) in wastewater streams can form complexes with mercury which are soluble or do not settle well and are thus difficult to filter.

4. PROCESS FLOW

4.1 General

Throughout most of the mercury-cell chlor-alkali industry in the United States, the prevalent technology for wastewater treatment is sulfide removal of mercury. However, there are many differences between individual facilities in the exact components, their order, the specific chemicals used in the process, batch vs. continuous process, etc. Some of these variations will be highlighted below.

4.2 Process Type

Several facilities use batch processes, usually (but not always) smaller facilities. This allows greater control over each step of the treatment system. The majority of the facilities use continuous systems, especially the largest facilities with too great a volume of wastewater to be treated in a batch process. Continuous systems also have the advantage of only needing occasional adjustment once lined out, rather than each batch having to be individually adjusted for each step of the process.

4.3 Process Components

Nearly all facilities use at least one holding or equalization tank to reduce variability of the influent stream. Some facilities use a separate tank for fluctuating streams (components or flow), such as the cell room sump, which is then fed at a consistent rate to sulfide treatment. Some facilities have additional pretreatment steps for some or all of their influent streams. These may include settling, oxidation/reduction, or filtration.

Then the common treatment steps of pH adjustment, sulfide addition, and settling and/or filtration occur. Some facilities adjust the pH to different pH levels and at different points in this process. At various facilities, pH adjustment is performed before sulfide addition, after sulfide addition but before filtration, or after filtration, or some combination. Some facilities also use a stepwise sulfide addition with pH adjustment between the two stages.

Some facilities use a carbon bed as a final polishing filter prior to discharge. Others have not found the carbon filter to be especially useful.

4.4 Process Chemicals

Many facilities use sodium hydrosulfide (NaHS) as the sulfide agent. Others use sodium sulfide (Na_2S) instead. While some have indicated that field tests show no differences in these two sulfide agents, as discussed in Section 2.2.4, sodium sulfide appears to produce the least amount of colloidal sulfur after consuming any free chlorine in the wastewater. Colloidal sulfur plugs filters very quickly increasing the difficulty of filtration.

Facilities also differ in the acid used for pH adjustment, some using hydrochloric and some using sulfuric acid. As discussed in Section 2.2.3, sulfuric acid inhibits the ability of sulfide to precipitate mercury (II) from solution, and its use for pH adjustment in this step of the process is not recommended.

4.5 Process Control Variables

The most commonly controlled process variable is pH at various stages of the sulfide treatment system. pH adjustment prior to sulfide addition generally falls into 3 ranges: 2 to 4, 5.5 to 6, or alkaline conditions. When sulfiding under alkaline conditions, the pH after sulfide addition is dropped to either 2 to 4 or neutral before filtration. When sulfiding under acid conditions, either the wastewater is filtered at that pH before neutralization for discharge, or the wastewater is neutralized and then filtered.

4.6 Process Monitoring and Analytical

Monitoring of the sulfide treatment process with continuous instruments, or periodic sampling for analysis is often conducted at several points within the process to assess the performance of the system and allow adjustments to be made. In addition to the pH mentioned in the section above, monitoring or sampling is usually performed for mercury and flow rates. ***The most critical items for monitoring are the mercury content of the water downstream of the last process step (typically the filtration system) and the flow rate at this point. These two measurements determine the quantity of mercury being discharged in the effluent.*** Some facilities may also monitor or sample for oxidation-reduction potential (ORP), residual chlorine, or excess sulfide levels. On-stream analyzers or ion-specific probes are available for all of these parameters, although some facilities may prefer to periodically sample for some of the parameters due to cost, maintenance, or reliability issues.

5. PRECIPITATE FILTRATION

5.1 General

The solids removal step (filtration) is critical in the removal of the bulk of mercury from the wastewater stream as part of the sulfide treatment processing. There are a number of considerations within the filtration step. The filtration process can be broken down into three distinct types or categories. They are cake filtration, depth filtration, and surface filtration.

In the cake filtration process, the solids are removed from the liquid streams by passing the liquid through a porous media. For depth filtration the solids are trapped in the depths of the filter media. Surface filtration is the process of solids removal at the matrix interface and flow reductions begin to occur before any significant cake is formed. All three types of filtration have been used in the sulfide treatment process.

In general in the sulfide treatment process step, the recovery and recycle of the resultant mercury by chemical or thermal means is desired. Therefore, a type of filtration process that allows for the recovery of the mercury is generally preferred.

5.2 Filter Equipment Process Types

There exist a variety of filter types available for the solids removal application. The types noted are:

- Horizontal leaf (generally considered cake filtration)
- Back pulse (surface filtration)
- Depth (depth filtration)
- Vertical leaf (or sometimes called a filter press-cake filtration)

Each of the various types has advantages and disadvantages. As part of the examination for selection of a specific type of filter, the following should be considered:

- Quality of Filtered Water - what is the desired or required mercury concentration in the filtered water?
- Blinding - how quickly does the filter’s flow begin to be reduced?
- Ease of Cleaning - how difficult is the filter to clean/clear and be ready to return to service?
- Characteristics of Removed Solids - what are the difficulties in the handling of the resultant solids from the filter?
- Recycle/Disposal of Filtered Solids - how will the solids be processed?

In general, there must be an understanding of cake filtration basics for the specific process stream and laboratory scale evaluations may be required.

5.2.1 Cake Filtration Basics

5.2.1.1 Cake Formation

Filter cake builds up on the cloth (or other suitable substrate) over time. With the startup of any filter the solids formed in the reaction step will be filtered from the solution stream (usually a large quantity of water with some solids content). Since the filter removes the solids on the filter media surface at the start of the cycle, the initial effectiveness of the filtration step depends on the porosity (micron rating) of the filter media. Once a cake has been formed, the cake actually does the filtration, not the cloth or other substrate.

5.2.1.2 Characteristics of Solids to be Filtered

The solids formed during the reaction step (addition of sulfide ions at the proper pH) of the process will exhibit specific characteristics. These characteristics are described by the solids porosity and compressibility.

- Porosity - amount of open flow path.
- Compressibility - solids compaction.

In most cases the typical solids have a low porosity and are compressible. The results of these two variables are:

- Filter cake tends to blind off quickly.
- Low porosity retards flow through the cake.
- Filter gets blinded - cloth becomes fouled.
- Solids can bleed through cloth.

Therefore, for effective solids removal and for longer filter life, filter aid materials may be used. In addition, through the use of filter aids the removed mercury solids can be recycled utilizing a chemical or thermal recovery process.

5.2.2 Specific Filter Types

5.2.2.1 Horizontal Leaf

This type of filter has leaves mounted in the horizontal plane with flow passing through the leaves from the top and collected at the outside. The advantages with this type of filter are the reduction in floor space and simplified operation. The disadvantage is the difficulty in cleaning the filter to recover the solids.

5.2.2.2 Back Pulse

The principle of the back pulse is to shock the surface of the bag to release the accumulated solids. The advantages of the filter are (1) reduced leakage; (2) better or tighter micron rating initially set by the bag selection; and (3) reduction in the quantity of water in the solids discharged from the unit. The disadvantages of this filter type are (1) potential for solids invading the bag causing blinding; (2) inadequate solids release from the bags (resulting in a loss of effectiveness); and (3) the requirement for adequate air pressure for the release.

5.2.2.3 Depth

In this application, depth filtration usually means cartridges that are spiral wound configurations. The advantages of this type of filtration are (1) relatively inexpensive installation cost; (2) standard vessel sizing for various micron rated cartridges; and (3) ease of operation. The disadvantages of the depth type of filtration are (1) cost for replacement of the cartridges; (2) depending on the solids loading, operations can be inconsistent; and (3) bypassing of cartridges can be a problem with repeated change outs.

5.2.2.4 Vertical Leaf

The vertical leaf is similar to the horizontal leaf filter. Specifically, flow of solution passes through the leaves for collection to an outlet manifold. The advantages of the vertical leaf are: 1) easy to clean; 2) the precipitated solids are recoverable; and 3) removal is generally very effective. The disadvantages of this type of filter are: 1) filter occasionally leaks to the outside; 2) care has to be exercised to establish and maintain flow rates for both the process stream and the precoat; and 3) filter usually must be precoated to aid in filtration.

5.3 Filter Aids

5.3.1 General

Filter aid materials (commonly called precoat materials) are typically materials with a high porosity and low compressibility. Through the use of a filter aid, the filter life is usually extended and adds flow paths through the filter cake. Certain filter aids can add BTU value to any recovered solids and may affect the performance of the recovery unit and its regulatory status.

5.3.2 Types

A precoat-type filter can use a variety of precoats. All of the precoat types have been used in this application (mercury solids removal from the wastewater). The types mentioned are:

- Diatomaceous earth
- Perlite
- Cellulose
- Rice Hulls

5.3.2.1 Diatomaceous Earth (DE)

In general, this type of filter aid is derived from fossils of plants containing silica. Several companies have tested and used this type of precoat. For mercury solids removal, this filter aid exhibits a number of traits. These include:

- Susceptibility to blinding.
- Difficulty of maintaining the aid on the filter. (DE seems to fall off the filter cloth easily during a flow interruption).
- DE does not provide fuel value to the solids but may create other disposal issues (e.g., quantity of solids).

5.3.2.2 Perlite

Perlite is a generic term for naturally occurring silica mineral. This type of precoat is less likely to slough off the filter. This type of filter aid exhibits three significant characteristics:

- Does not provide any fuel value to the solids.
- Precoat is light and easier to handle.
- Perlite expands like popcorn upon heating in a thermal recovery system.

5.3.2.3 Cellulose

Cellulose is the chief constituent of the cell walls of plants. This type of filter aid exhibits the following significant characteristics:

- Provides fuel value to the solids.
- Provides the maximum volumetric reduction when placed in a thermal recovery unit as the cellulose is combusted.
- Cleans off the filter cloth better during back washing.
- Produces less blinding because of the swelling properties.
- Likely to slough off the filter cloth if the flow is disrupted.

5.3.2.4 Rice Hulls

Two facilities have tested this type of filter aid. The results were poor and rice hulls are not recommended for this application.

5.3.3 Use of Filter Aid Materials

Filter aid materials can be used as

- Precoat at the beginning of the filter cycle.

- Body feed during the filter cycle.
- Both precoat and body feed material.

5.3.4 Precoat

5.3.4.1 General

The precoat performs three vital functions within the filter:

- Provides an initial layer of filter aid on the cloth.
- Protects cloth from fouling by the filtered solids.
- Bridges the cloth for finer filtration.

Since the precoat serves such an important function, the selection of the filter aid should be made considering the following:

- Type and criteria for selection.
- Size and criteria for selection.
- Compatibility with material used for the body feed (if applicable).
- Amount of precoat that should be used for the filter.

An understanding of the following should determine the size and amount for precoating the filter:

- Size of the precoat should match median size (particle distribution needed) of the filtered particles. A smaller size will increase tendency to blind and a larger size will reduce effluent quality (mercury concentration may be higher).
- Depth of the precoat can be critical to effective filtering operations. If too much precoat is used, the precoat fills available cake space prematurely. If too little precoat is used, the filter has incomplete coverage with potential fouling of the filter cloth.

5.3.4.2 Precoating the Filter

As part of the development of the protocol for precoating, a detailed examination of the procedure is needed. Some questions to address are:

- What liquid to use for precoating the filter?
- Should the flow rate be controlled while precoating?
- How to determine the proper flow for precoating?
- How is the precoat to be added? Before or during circulation through the filter?

- How should flow be maintained through the filter **AFTER** it is precoated?

In addressing these very important questions the following are suggested as starting points:

- Use a constant flow rate between 0.25 and 1.0 gpm/ft^2 of filter area. Optimum flow should be determined by field trials.
- Establish recirculation flow through the filter before adding the precoat.
- Once the precoat is applied, flow should be maintained at **ALL** times throughout the rest of the filter life. Maintaining flow is particularly important for vertical leaf filters. In general, the consequence of flow interruptions is poor precoat, lack of coverage, and possibly total loss of precoat.

5.3.4.3 Filter Cloths for Precoated Filters

For most applications, the filter uses a cloth as a substrate for the precoat. Consider the following in the selection and installation of the cloth:

- Materials, porosity, weave, and yarn all affect flow rate, retention, cake release, and resistance to blinding.
- Selection is based on either laboratory testing or empirically (trial and error).
- Filter cloth installation can affect the cake release characteristics. The cloth should be either flat or hanging straight in the filter without wrinkling. For proper cloth installation, consult the filter supplier and the cloth manufacturer.

5.3.5 Body Feed Addition

Body feed is sometimes used to assist in filter operations. Body feed is filter aid material that is added to the liquid being filtered. This kind of addition keeps the porosity of the filter cake high. In addition, the body feed should be continuously added to the filtered liquid; otherwise a layer of lower porosity is formed.

As with filter aid used for the precoat, the quantity of body feed is very important. Body feed considerations are:

- Too much body feed fills available cake space prematurely and generates higher amounts of solid for subsequent processing.
- Too little body feed could cause blinding of filter due to a layer of low porosity solids.

Consideration should be given to the following:

- How much body feed is added?
- How is body feed added?

The following are suggested as starting points:

- Use between 0.1 and 2.0 times the amount of solids (by weight) being filtered.
- Use more body feed at lower solids concentration in wastewater.
- Ensure that all the liquid to be filtered contains some body feed. A pre-mix in a batch tank and continuous addition of a small amount to the filter feed is recommended.

The body feed rate is typically derived by empirical means (trial and error).

5.4 Operating Parameters/Recommendations

For most filter applications, some type of laboratory testing is recommended to establish the type and quantity of precoat to use along with filter sizing. For good filter operations, there are several operating parameters to consider.

5.4.1 Flow

Control of flow (both precoat and process fluid) through the filter should be considered. Poor control of flow can cause filtration problems.

- Low flow could lead to the precoat sloughing off.
- High flow can lead to compressing the precoat causing short filter cycle (from high differential pressure).
- Sudden changes in flow can cause uneven precoat and poor solids removal.
- Minimum and maximum limits should be established for flow.

5.4.2 Differential Pressure (D/P)

A pressure drop across the filter is necessary for it to be operated as an effective solids removal system. Consider the following:

- D/P can help to hold cake on the cloth at lower flow rates.
- High D/P (above15 psi) may cause metallic mercury to be extruded through the filter cake.
- Minimum and maximum limits should be established for D/P.

5.4.3 Recommendations

The following recommendations for operating precoat filters are based on the collective experience of Chlorine Institute member companies. There is limited experience in the operation of other types of filters.

- The maximum precoat depth for sulfide treatment filters should be 1/16 to 1/8 inch. Ten to 25 lbs of the selected filter aid per 100 ft^2 of filter surface area has been shown to produce this depth of filter cake.
- Water used for the precoat should be clean filtered water.
- A flow rate of 0.25 to 1.0 gpm/ft^2 of filter surface area is recommended for precoating the filter.
- A flow rate of 0.1 to 1.0 gpm/ft^2 of filter surface area is recommended for operating the filter. Best results are achieved through empirical testing considering precoat type, filter construction, solids loading, flow requirement, and control approach.
- Particle size analysis of the solids formed may be of benefit in understanding the loading on the filter.
- Recirculation flow through the filter should be established **BEFORE** adding the precoat.
- The flow must be maintained after the precoat has been applied.
- D/P above 15 psi may cause metallic mercury to be extruded through the filter cake. High differential pressure with low flow would suggest filter plugging. Correspondingly, low differential pressure with high flow rates would suggest poor precoating or a hole in the precoat.
- A controlled flow rate through the filter is desirable. Flow meters and control valves provide a standard means to maintain a constant flow to the filter.
- Due to turbulence at the inlet neck of the inlet plates, lower precoat rates and/or different types of filter cloths may be needed to reduce scouring, especially during periods of flow transition. The scouring leads to delays in getting a good filter discharge (acceptable mercury concentrations).

5.5 Maintenance and Troubleshooting of Different Types of Filters

5.5.1 Precoat Type Filter

5.5.1.1 Cleaning

Cleaning frequency depends on (1) throughput of process fluids and control of flow rate; (2) solids loading to the filter (including the precoat and the body feed); (3) surface area of the filter; (4) filter cloth type (generally polypropylene cloth is used in the filter as the base medium); (5) release characteristics of the cloth including the cloth orientation; and (6) filter orientation (vertical or horizontal).

The cake produced by the filtration process is blown down by air to remove as much water as possible. Water removal will result in a drier cake facilitating the handling of the cake and possibly improving the performance of any thermal treatment unit used for subsequent recovery of the mercury from the solids.

Consideration should be given to the technique to remove the cake. Is the cake removal before or after the filter is opened? It is generally difficult to clear the leaves of solids completely before a filter is opened and it should be anticipated that leaf washing (usually with water) would be a part of the cleaning process. In some cases, water washing does not remove all of the residual cake and acid washing may be needed.

Since cloth clearing is so critical, consideration should be given to changing the cloth on a regular basis as determined by plant operating experience.

5.5.1.2 Assembly

For the leaf type filter with cloth insertion, leakage to the outside is a typical concern that needs to be addressed. In general, a vertical leaf precoat filter can be assembled with a minimum of problems. During process operations, containment of any wastewater leakage may be required.

Materials of construction of the various components of a filter play a critical role in its performance and operational life. Most filters are constructed of plastic (e.g., polyvinyl chloride, polypropylene, fiberglass reinforced polyester) or rubber lined components. Some units are constructed using corrosion resistant metals (e.g. titanium).

The following are some key items that need to be addressed during the filter assembly to insure good filter performance:

- Gasket placement.
- Cloth placement /integrity/orientation to flow.
- Clamping forces.
- Alignment of the leaves.
- Checking for warped frames/leaves.

5.5.1.3 Troubleshooting -Loss of Precoat Layer

If the precoat layer has been compromised (e.g., thinning or hole in the precoat) and body feed is being used, the body feed will slowly, preferentially recoat the affected areas, which will re-establish mercury removal. Using body feed will not re-establish a clean precoat layer and may result in some mercury (II) sulfide against the cloth. This cloth contamination increases the potential for bleed through of the mercury (II) sulfide. Using body feed as the means to solve thin areas of precoat may improve effluent quality, but there may be insufficient body feed, shortening filter life.

5.5.1.4 Sludge Quantity

The quantity (solids plus liquid) of sludge (assuming a complete backwash is accomplished each time) is directly related to:

- Rate and concentration of body feed (if used).
- The initial quantity of precoat used.
- The quantity of precipitate in the water being filtered.

Using the precoated type filters allows the recovery of the mercury from the sludge in a recovery (e.g., thermal treatment) unit back into the process.

5.5.2 Depth Type Filter

5.5.2.1 Cleaning

For most depth filter applications, the cleaning operation is the replacement of the cartridges with new cartridges. Mercury-contaminated cartridges must be disposed in accordance with the applicable regulatory requirements.

5.5.2.2 Assembly

For cartridge change out, the factors to consider are:

- Cartridge O-ring seals are in place.
- Cartridges are installed properly according to filter/cartridges supplier recommendations.
- Gaskets are in place, are not cut or distorted, and of the proper materials of construction.

5.5.2.3 Sludge Quantity

The quantity of generated solids using the depth filters is directly related to the cartridge, cartridge type, and the quantity of sludge from the process. In general, most of the solids are comprised of the cartridge volumes.

6. POST [FILTRATION] TREATMENT

6.1 General

As previously discussed, the removal of the bulk of the mercury occurs in the precipitate filtration step (Section 5 of this guidance document). In general, with proper operations, one can expect to obtain effluent mercury concentrations from the precipitate filtration step in the 5 to 25 ppb range.

Post treatment (sometimes called a post filtration step) may produce lower concentrations of mercury in the discharge. For post treatment to be effective, it is necessary to have the precipitate filtration system operating optimally. If the requirement is to consistently achieve a mercury concentration less than 5 ppb, a post treatment step is necessary.

There are two potential processes that are currently available. These are:

- Activated carbon bed treatment
- Post cartridge filter system (may include multiple stages of mechanical filtration).

While there have been references to ion exchange resins as a viable post treatment option, the data that the Institute has seen would indicate that effluent from an ion exchange based treatment system is comparable to a well run sulfide treatment system as described in earlier sections of this document.

6.2 Activated Carbon Bed Treatment

Within the member companies, there is a wide range of experience under the general category of carbon filtration or adsorption. Data from a number of sources indicate that activated carbon can be an effective tool for removal of mercury from sulfide treated wastewater. The key parameter for good mercury removal is low suspended or colloidal solids feed to the carbon unit.

6.2.1 Activated Carbon

Granular carbon is used for mercury removal at several chlor-alkali facilities. Commercially available liquid-phase carbons include those derived from sawdust, lignite, fly ash, charcoal, bituminous coal, and petroleum coke. Liquid-phase carbons can also be impregnated with one or more active ingredients to enhance performance. An example of this type is the Mersorb® carbon which contains more than 10% sulfur content by weight.

Liquid-phase carbons are available in two forms - powdered and granular. Granular activated carbon in a packed bed form seems to be preferred for most chlor-alkali applications. Control of pressure drop (head loss) in down flow beds and the bed expansion during backwashing are of primary importance. Since head loss and bed expansion can vary significantly for the various types of carbon, the manufacturers or suppliers should be able to supply this information as part of a design data package.

6.2.2 Application

When this technology is used at chlor-alkali plants, the activated carbon is normally in a packed bed configuration. Effluent flow through the carbon adsorption bed is typically down flow. Flow exits the bottom of the bed and flows up through a seal loop to maintain a level in the packed bed. The seal loops are equipped with vacuum breakers, which should be left open.

Since the carbon bed may eventually plug with solids generated from the precipitate filtration step, provisions to backwash the bed is a design requirement. In order to maintain continuous, consistent treatment, facilities will usually have the ability to switch to a standby bed when the operating bed becomes exhausted. The degree of exhaustion is typically determined by the effluent mercury concentration, pressure drop across the bed, or insufficient flow rate through the bed. Backwashing is up flow through the bed. Excessively high backwash flow rates will fluidize the entire carbon bed which is not desirable. However, too low a flow rate will not properly flush out the solids. The correct backwashing flow rate must be determined and is dependent on the configuration of the carbon bed.

A crust may form on the surface of the carbon bed if there is a high total solids content in the stream entering the bed. The crust formation will cause excessive pressure drop and must be dissolved or broken up during backwashing of the carbon.

Spent carbon (carbon may lose its effectiveness over time) from the beds can be chemically or thermally treated in a mercury recovery system. Recycling of the carbon has not proven to be cost effective.

6.2.3 Mersorb® Carbon (Reference 7.1.7)

The Mersorb® type of carbon has been tested for chlor-alkali effluent for a limited period of time at a facility now closed. The limited available data indicated that the Mersorb® carbon was capable of reducing the mercury content to below 100 ppt when used in conjunction with a 0.5-micron depth cartridge filter ahead of the Mersorb®. Cartridge filtration has demonstrated a 50% reduction if the influent is less than 10 ppb Hg and less than 50 ppm silica. A finer pore size (< 0.5 micron) has not been shown to remove any additional mercury. However, the system was not operated sufficiently long to determine whether the technology could consistently reduce the mercury content to these levels. Currently this technology is being used to treat contaminated groundwater. This type of carbon is different from standard or granular carbon in that Mersorb® is impregnated with sulfur. The sulfur content is about 13.5 % by weight.

The limited operating experience indicates that the performance of this type of carbon is highly sensitive to influent wastewater characteristics. The following items comprise an initial list of reported critical characteristics (Note - there may be others.):

- Silica (must be consistently less than 50 ppm);
- Elevated chlorides in the feed stream to the carbon has a tendency to strip the sulfur out of the carbon;
- Recommended pH in the feed is approximately 3.5 (Reference 7.1.8).

6.3 Post Filter Cartridge Systems

The cartridge-type system installed after the precipitate filtration step can be used as a polishing step and as a short-term back-up if the upstream mercury sulfide filter fails. Cartridges are typically used only once. After use, they must be disposed of according to regulatory requirements. Member companies report that no improvement is noted at filtration ratings < 0.5 micron.

Cartridges for the application generally fall into three types. These are (1) bag filters of varying micron ratings; (2) pleated cartridge units of varying micron ratings; and, (3) depth cartridge units of varying micron ratings.

6.3.1 Cartridge Types

6.3.1.1 Bag Type

Bag filters are typically installed in a metal or plastic housing. The bag can be of various micron pore sizes and materials of construction.

Only one facility is believed to use bags as the filter media. From this experience, the following information is noted:

- The maximum differential pressure is 35 psi (above this pressure there is a possibility of damaging the bag).
- Bag filter micron pore size can go down to as low as 0.5 micron.
- The bag filter is reported to be polypropylene with EPDM “O” rings for the housing.

6.3.1.2 Pleated Type

Pleated filters are usually constructed as a cartridge to fit within a housing. As with all filters, the pleated type has a wide variety of micron pore sizes available.

Feedback from member companies notes the following for the use of pleated filters:

- The filters are not considered durable for the service.
- The material of construction is the same as the bag filters (polypropylene with gaskets of EPDM).

6.3.1.3 Depth Type

As with pleated filters, the depth filters in use for mercury removal are also a cartridge or a number of cartridges that fit within a housing. Generally, depth cartridges provide optimum solids removal in the 0.5 micron range. The flux rate for this type of cartridge is between 0.125 gpm/ft^2 and 0.250 gpm/ft^2. As with all of the cartridges, the application is a single use. Once the mercury leaches through the filter media the cartridge has to be changed and disposed of properly. The cartridges are generally very effective in mercury removal depending on the micron pore size used. Typically, the recommended materials of construction are polypropylene filter media with EPDM gaskets or “O” rings.

6.4 <u>Comparison of the Different Technologies</u>

6.4.1 Carbon

6.4.1.1 Advantages – Carbon

- The carbon usually is amenable to backwashing and therefore service life before change outs is extended.
- Whether the removal is via adsorption or filtration, carbon units tend to produce low mercury discharge concentrations (on the order of < 5 ppb Hg).

- The carbon is commercially available and the design parameters for carbon application are well known.
- The mercury removed by the carbon can be recovered via various processes (e.g., thermal treatment or retorting).
- The operation of the carbon system tends to be less complex than other forms of removal.
- The cost of operation of the carbon tends to be relatively low after the initial equipment installation.
- The carbon system is better suited for higher flow rates.
- A carbon system is better understood by the regulatory community and is recognized as proven technology.

6.4.1.2 Disadvantages - Carbon

- The system unit tends to occupy a larger “foot print” for vessels plus piping and therefore has a higher installation cost.
- If a retort operation is unavailable, the cost of disposal for the mercury contaminated carbon may be excessive.
- To backwash the carbon, additional pumps, piping, and holding tanks are required.
- For a carbon system, there seems to be a “threshold” below which carbon can not remove mercury either by adsorption or filtration (the lower limit reported by several members is in the range of 2 ppb Hg).
- Retorted carbon is unsuitable for reuse.
- Particulate mercury is not irreversibly retained. Under certain conditions, the mercury can be released back into the effluent.

6.4.2 Mersorb® System

6.4.2.1 Advantages - Mersorb® System

- The system appears to have the capability to achieve very low mercury discharge concentrations under optimal conditions.
- The removal rates appear to be in the range of 95% removal of the inlet mercury.

6.4.2.2 Disadvantages - Mersorb® System

- The cost of the system can be significant (both the original installation plus the ongoing cost of material change outs).

- The system's operating characteristics need to be fully understood before a system is installed (specifically, extensive and long duration pilot testing should be considered a prerequisite for such an installation).

6.4.3 Cartridge Filters

6.4.3.1 Advantages - Cartridge Filters

- Simple to operate.
- Material of construction and corrosion resistance is not an issue.
- Cartridges generally are readily available from numerous vendors depending on the housing configuration being used.
- Depending on flux rate and micron pore size, effective removal of mercury to a level of less than 5ppb Hg is achievable.
- Cartridges generally have good loading and retention characteristics.

6.4.3.2 Disadvantages - Cartridge Filters

- The cost of cartridge change-out could be high if the solids or mercury loading is excessive.
- Filter operations can be labor intensive depending on the loading of the cartridges (both for cartridge change out and monitoring).
- The cartridge filter housing "foot print" can be large depending on the flow rates.
- Cartridges are a single use item and with large filter systems, they constitute a large volume of waste materials.

7. REFERENCES

7.1 References

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7.1.2 *Figure 2.3, "Solubility of Mercuric Sulfide in Sulfide Solutions"* Barnes, H. L.; Romberger, S. B.; Stemprok, M. (Pennsylvania State Univ. University Park) Econ. Geol. 1967, 62(7), 957-82(Eng).

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7.1.4 *Kirk-Othmer Encyclopedia of Chemical Technology*, 1993, John Wiley & Sons, Hoboken, NJ 07030.

7.1.5 *Figure 2.8, "Personal Communication"*, David Hildebrand, Vulcan Chemicals, July 2002

7.1.6 *Handbook of Separation Techniques for Chemical Engineers*; Philip Schweitzer, Editor-in-Chief, McGraw-Hill Book Company, Copyright © 1979, Section 4.1, Filtration Theory, page 4-3.

7.1.7 Mersorb® Carbon is available from Selective Absorption Associates, 534 Gables Court, Langhorne, PA 19047 (phone: 215-702-0323).

7.1.8 *Achieving Low Mercury Concentrations in Chlor-Alkali Wastes*, David R. Tonini, et al, Environmental Progress, October 2003 (Vol. 22, No. 3).