Development of Chemical Reduction and Air Stripping Processes to Remove Mercury from Wastewater

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19

20   Abstract

21   This study evaluates the removal of mercury from wastewater using chemical reduction and air stripping

22   using a full-scale treatment system at the Savannah River Site. The existing water treatment system

23   utilizes air stripping as the unit operation to remove organic compounds from groundwater that also

24   contains mercury (C ~ 250 ng/L). The baseline air stripping process was ineffective in removing

25   mercury and the water exceeded a proposed limit of 51 ng/L. To test an enhancement to the existing

26   treatment modality a continuous dose of reducing agent was injected for 6-hours at the inlet of the air

27   stripper. This action resulted in the chemical reduction of mercury to Hg(0), a species that is removable

28   with the existing unit operation. During the injection period a 94% decrease in concentration was

29   observed and the effluent satisfied proposed limits. The process was optimized over a 2-day period by

30   sequentially evaluating dose rates ranging from 0.64X to 297X stoichiometry. A minimum dose of 16X

31   stoichiometry was necessary to initiate the reduction reaction that facilitated the mercury removal.

1   Competing electron acceptors likely inhibited the reaction at the lower doses, which prevented removal

2   by air stripping. These results indicate that chemical reduction coupled with air stripping can effectively

3   treat large-volumes of water to emerging part per trillion regulatory standards for mercury.

4

5   Headings: Mercury; Pollutants; Permits; Waste Treatment Plants; Chemical treatment; Volatilization;

6   Oxidation.

7

Introduction

9   In recent years policies have been formulated and modified to decrease mercury discharges to the

10   environment. The overall objective of these decreases is to reduce mercury exposure to the general

11   population from fish consumption. An illustration involves the Great Lakes Initiative (US EPA 1995 &

12   2000) where water quality criteria for total mercury were established for both the protection of human

13   activities and for the protection of aquatic life (12 to 50 ng/L) for all discharges to the Great Lakes

14   Basin. Subsequently the Methylmercury Fish Tissue Criterion (US EPA 2001) supported a compound

15   specific ambient water quality criteria (AWQC) for methylmercury (0.3 mg/kg) based upon fish tissue

16   wet weight rather than traditionally used ambient water column value (US EPA 1994). Later specific

17   guidance (US EPA 2010) was provided for adoption of water quality standards incorporating water

18   column criteria, monitoring and assessment through water column analysis, and achievement using total

19   maximum daily loads (TMDL) that incorporate water column conditions. These dynamic policies

20   regarding mercury have direct impact to industry, municipalities, and federal agencies. Liquid effluents

21   from these entities are subjected to discharge criteria that are derived from current water quality

22   standards.

23

24   For industrial effluents the National Pollutant Discharge Elimination System (NPDES) establishes

25   discharge specific criteria necessary to meet water quality standards. As directed by the Clean Water Act

26   the NPDES permit program controls water pollution by regulating point sources that discharge

27   pollutants into waters of the United States. As discharge criteria change new water treatment

28   approaches are needed to support reasonable implementation of the reduction programs. For industrial

29   viability, these approaches must have the capacity to treat large volumes of water containing trace levels

30   of the target constituent in the presence of other ions at unit costs that are below conventional metals

31   removal techniques.

1

2   A 2007 synopsis on the state of treating mercury in environmental media (US EPA, 2007) identifies

3   several baseline technology classes for the treatment of mercury in water/wastewater. This summation

4   also provides information on the number of case study deployments. The baseline technology classes

5   include: 1) precipitation/co-precipitation (11 deployments), 2) adsorption (6 deployments), 3) membrane

6   filtration (1 deployment) and 4) biological treatment (2 deployments). For full-scale applications,

7   precipitation/co-precipitation was the most frequently used treatment process identified. When selected,

8   adsorption based systems were generally used as a polishing technology utilizing activated carbon based

9   media. Membrane filtration and bioremediation were the least frequently used technologies, with

10   bioremediation limited to pilot-scale investigations. In a review of heavy metal removal methods, Fu and

11   Wang (2011) extended the list of baseline technology classes to include electrochemical treatment.

12

13   US EPA (2007) identified innovative and emerging technologies, highlighting the results of Looney and

14   others (2003) on chemical reduction and air stripping. The investigation by Looney et al. (2003)

15   documented air stripping as a simple "alternative" treatment method for the removal of mercury from

16   water and wastewater. The basis of the process involves the chemical reduction of dissolved phase

17   mercury, Hg(II), to elemental mercury, Hg(0), using a reducing agent. In the elemental state mercury is

18   volatile and can be effectively removed from water using air stripping. Chemical reduction and sparging

19   of mercury is an integral component of Method 1631E (US EPA 2002). This method is for the

20   determination of total mercury in aqueous samples in the range of 0.5 – 100 ng/L. Under this method

21   aqueous samples are first oxidized with bromine monochloride to destroy organic mercury complexes,

22   then sequentially reduced with hydroxylamine hydrochloride to destroy free halogens, and finally

23   reduced using stannous chloride. The final reduction step converts inorganic Hg(II) to volatile elemental

24   mercury, Hg(0). Under Method 1631E the Hg(0) is separated from the solution using either a bubbler or

25   flow-injection system with an inert gas to collect the mercury onto a gold trap. The analysis involves the

26   thermal desorption of mercury from the gold trap using a cold-vapor atomic fluorescence spectrometer.

27   With three reagent treatments prior to separation from the water phase, the complexity and efficacy of

28   implementing air stripping for treatment is highly dependent upon the mercury species present within

29   the wastewater.

30

1   The work of Looney and others (2003) expanded upon earlier work that evaluated the use of stannous

2   chloride to remove mercury from a spring-fed source (Outfall 51) within the Y-12 Complex at Oak

3   Ridge (Lockhead Martin Inc., 1996). This investigation used a pilot scale (10 gpm) air stripper to

4   evaluate the stannous chloride treatment scheme. The investigation determined that approximately 80%

5   of the mercury in the source water was reactive with stannous chloride. The study explored various

6   oxidants to convert the balance of the mercury to a tin reduceable form. The investigators concluded that

7   none of the conventional oxidizing agents examined were effective at environmentally acceptable

8   concentrations. A subsequent investigation (Klasson et al. 2003) reports the use of ozone/UV systems as

9   a precursor to convert the mercury in this water so that it will readily react with the stannous chloride.

10

11   The Y-12 pilot test (Lockhead Martin Inc., 1996) demonstrated that a 3-4X stoichiometric excess of

12   stannous chloride was effective in removing nearly 100% of the reactive mercury at air to water ratios

13   greater than 13X. The study indicated that stannous chloride solutions in the feed reservoir were

14   unstable in the presence of sunlight and oxygen. Ascorbic acid (Vitamin C) was identified as an

15   effective preservative and proposed a concentrated (> 1 g/L) stock solution prepared with oxygen-free

16   water to increase stability. Southworth (2009) postulates on the role photochemical reactions may have

17   in the stannous chloride treatment scheme. These observations are based upon effective applications in

18   enclosed groundwater systems (Outfall 51) versus ineffective applications in open, exposed surface

19   water (Outfall 200) sources within the Y-12 Complex. To further investigate this aspect stannous

20   chloride was introduced along with sodium thiosulfate to the subterranean piping system immediately

21   upstream of the where the Outfall 200 water emerges into an open channel. The sodium thiosulfate was

22   incorporated to remove latent total residual chlorine. This test relied upon turbulent flow to provide

23   mixing and resulted in a 33% conversion of the baseflow Hg(II) (Southworth et al. 2009). Subsequent

24   experiments targeting Outfall 200 investigated potential enhancements including the use of alternate

25   dechlorinating reagents, alternate stabilizing agents for the stannous chloride solution, and alternate

26   reducing agents other than stannous chloride (Southworth et al. 2010).

27

28   Looney and others (2003) performed a series of experiments to determine the efficacy of stannous

29   chloride reduction alone for water treatment applications. Looney performed a series of batch tests

30   (vessel size = 500ml) using raw and "conditioned" groundwater from the Savannah River Site to

31   evaluate the dose of stannous chloride on various sample matrices (wastewater feed stocks). This study

1   evaluated mercury removal in stoichiometric ratios up to 5,040,000X and determined that stoichiometric

2   doses in the range of 5 to 25X were sufficient for relatively complete removal. A kinetic evaluation was

3   also performed (Looney et al. 2003) to assess sparging rate on removal effectiveness. The kinetic study

4   concluded that the air to water ratio controlled the removal rate and that the reduction-oxidation reaction

5   kinetics were not the rate-limiting step.

6

7   The previous investigations at both Savannah River and Oak Ridge provided critical information on

8   technical viability, information on stoichiometric ranges, insight on rate-limiting processes, and the role

9   that competing electron acceptors can have. Additional demonstration and testing is required for full-

10   scale implementation and regulatory acceptance. Included within this is full-scale testing using

11   conventional treatment equipment.

12   **Groundwater Treatment System**

13   The Savannah River Site (SRS) operates an air stripper that is permitted as a Clean Water Act

14   wastewater treatment plant (SCDHEC Wastewater Construction/Operation Permit #10,253). Discharge

15   of treated wastewater from this system is regulated through NPDES (SCDHEC Permit #SC0000175).

16   The groundwater treatment system consists of a network of groundwater recovery wells and an air

17   stripper. This system has been in operation since 1985 as part of a RCRA corrective action to remove

18   chlorinated solvents, primarily PCE and TCE, from groundwater. In addition to contaminated

19   groundwater the treatment system receives wastewater from an *in-situ* thermal treatment system that

20   targets a DNAPL source zone.

21

22   The inlet groundwater to the air stripper contains mercury on the order of 250 ng/L. This level exceeds a

23   proposed NPDES limit of 51 ng/L (monthly average) and 140 ng/L (daily maximum) for the receiving

24   outfall. Currently air stripping alone is ineffective in removing mercury from the treated effluent. The

25   nominal wastewater flow to the air stripper is 1,609 lpm (425 gpm) that increases to 1,968 lpm

26   (520 gpm) with contributions from the thermal treatment system. Airflow is maintained at a constant

27   rate of 56,634 lpm (2,000 cfm), providing a nominal air to water ratio of 31:1.

28

29   The air stripper is a counter-current, packed column configuration (Kavanaugh and Trussell 1980;

30   Treybal 1980; Montgomery 1985) with an internal volume of 23,280 liters (6,150 gallons). The design

31   incorporates upper and lower beds 5.8-m (19-ft) and 5.2-m (17-ft) long, respectively, that contain loose,

1 random packed plastic saddles. Wastewater sample ports are located at the inlet, the top of the first

2 packed bed, between the two packed beds, and at the discharge of the second packed bed. Figure 1

3 provides a schematic of the system illustrating sample locations and relevant water quality parameters.

4

5 During normal operations mercury at the inlet is on the order of 250 ng/L and increases with episodic

6 contributions from the thermal treatment system. While mercury has not been explicitly identified as a

7 known contaminant, historical releases of small quantities from process operations were likely. When

8 small quantities of mercury were released with large quantities of traditional DNAPLs, non-traditional

9 transport and release mechanisms are likely (Jackson et al. 2006). As DNAPL source zones are removed

10 the mercury, which was partitioned within the non-aqueous phase prior to remediation, becomes

11 available for recovery via the existing pump & treat system.

Mercury Removal Process

13 Mercury removal from the wastewater involves the chemical reduction of Hg(II) to Hg(0) followed by

14 volatilization to the air phase. Chemical reduction is promoted by the addition of stannous chloride that

15 acts as a reducing agent. For describing this treatment modality the following half-reactions are used to

16 develop the oxidation-reduction equation (Lide, 2000):

17

18 (1a) $Hg^{+2} + 2e^- = Hg^0$ $E_0 = +0.851$

19 (1b) $Sn^{+4} + 2e^- = Sn^{+2}$ $E_0 = +0.151$
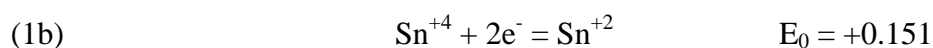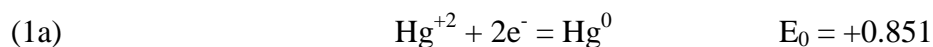
20

21 These half-reactions are combined to develop the following equation that governs the treatment process:

22

23 (1) $Hg^{+2} + Sn^{+2} = Hg^0 + Sn^{+4}$ $E_0 = +0.700$
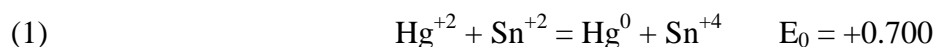
24

25 As written the reaction is spontaneous and under ideal conditions a 1:1 stoichiometric ratio exists

26 between the reducing agent and the oxidized species. Stannous chloride dihydrate [CAS #10025-69-1] is

27 soluble in water and is used as a reducing agent in laboratory (US EPA 2002) and industrial process

28 (Hozalski et al. 2005). When this compound is introduced into the wastewater as a source of Sn(II) the

29 following chemical equation describes the process chemistry:

30

31 (2) $HgCl_2{}^0 + SnCl_2 \cdot 2H_2O = Hg(0) + SnO_2(s) + 4Cl^- + 2H_2O$

1

2   In this equation mercury chloride is identified as the mercury source based upon the thermodynamically

3   favored species in wastewater.

4

5   Inherit in the treatment process is the ability to readily remove the elemental mercury during the air

6   stripping process. Henry's constant provides information on the partitioning of a compound between the

7   air and water phase (Schwarzenbach at.al, 1993). Air stripping is considered a practicable treatment

8   process for compounds having a Henry's constant greater than 10 atm-L/mol (FTRT, 2002). Henry's

9   constant for mercury was determined based upon the relationship between vapor pressure and aqueous

10   solubility (Schwarzenbach et al., 1993) and is presented in Table 1. As shown the Henry's constant for

11   mercury is determined to be 8.7 atm-L/mol and is at the lower end of the applicable range based upon

12   the guidance document. The treatment method does introduce inorganic tin and chloride to the effluent.

13   However when modest doses of reagent are applied the levels of these compounds are below AWQC

14   thresholds.

Experimental Methods

16   The full-scale effectiveness of the treatment process was evaluated as a "Technical Demonstration"

17   under the existing wastewater permit for the air stripper described earlier. A feasibility test was first

18   performed to determine full-scale viability and was followed by a variable dose-response test. These

19   results are used to evaluate the effectiveness of each dose and will serve as a basis for identification of

20   operating conditions for full-scale implementation.

Feasibility Testing

22   Feasibility testing consisted of injecting a reducing agent at the inlet of the air stripper for a period of 6-

23   hours. Previous batch tests (Looney, et al. 2003) had demonstrated stoichiometric ratios in the range of 5

24   to 25X as sufficient for relatively complete mercury removal. Based upon these observations a 25X dose

25   of reducing agent was selected. This level would reduce uncertainties related to potential inadequate

26   mixing, incomplete chemical reduction (contact time), and competing electron acceptors that were

27   considered as possibilities with full-scale implementation. Prior to, during, and following injection

28   wastewater samples were collected for analysis from the inlet, mid-column, and discharge of the air

29   stripper. The reducing agent consisted of an acidified solution of tin(II) chloride dihydrate (MW =

1   225.65). The solution was prepared by dissolving 5.86 grams of reagent grade tin(II) chloride dihydrate

2   [CAS #10025-69-1] in 10-ml of reagent grade hydrochloric acid [CAS #7647-01-0] and diluting to

3   11 liters using 10-18 MΩ-cm Type 1 reagent grade water. Prior to dilution the reagent water was

4   sparged with mercury-free nitrogen to remove dissolved oxygen as described in EPA Method 1631E.

5   This solution was injected using a high-pressure peristaltic pump (Masterflex L/S Pump Drive (Model

6   7523-50) and High Performance Pump Head (Model 77250-62) equipped with L/S 16HP PharMed

7   tubing. To provide adequate mixing the injection point utilized an injection quill (Primary Fluid

8   Systems Model IQ-58-PVDF) installed in a downstream static pressure port of a flow-restricting orifice.

9

10   Prior to injection three wastewater samples were collected, including one sample that was collected

11   approximately 24-hours prior to injection. Six wastewater samples were collected at hourly intervals

12   during injection, and three samples were collected after injection, including one sample that was

13   collected 24-hours after injection. Wastewater samples were collected using ambient water quality trace

14   metals sampling techniques (EPA Method 1669). A certified contract laboratory provided total mercury

15   analysis (EPA Method 1631E).

16   **Dose-Response Testing**

17   Dose-response testing was performed to determine the necessary dose to promote chemical reduction

18   and removal of mercury. During this test an acidic solution of stannous chloride dihydrate [CAS

19   #10025-69-1] was injected into the inlet of the air stripper. The concentration and the injection rate of

20   the reagent were systematically adjusted to evaluate effectiveness at various dose rates. A total of nine

21   dose rates were evaluated between 0.27 and 133 mg/min of reagent. The minimum dose rate is below

22   the ideal stoichiometry described by Equation (2) and the maximum is an order of magnitude greater

23   than that used during the feasibility test. The dose rate and injection parameters are presented in Table 2.

24   As illustrated in this table the dose rate for each subsequent run was approximately twice that of the

25   previous run. The stannous chloride solution was prepared by dissolving an appropriate mass of reagent

26   grade tin(II) chloride dihydrate in concentrated hydrochloric acid and diluting to 7.5 liters (1.98 gallons)

27   with mercury-free water as described earlier. For Runs #1 through #8 this provided sufficient stock to

28   support two treatment levels per reagent batch by simply changing the injection flow rate. The injection

29   flow rate was controlled using the high-pressure peristaltic pump, pump head and tubing previously

30   described. The pump system is capable of delivering flow rates in the range from 0.9 ml/min to 90

31   ml/min with discharge pressure of 100 psig.

1

2 Testing for each dose factor consisted of applying the prescribed dose rate (Table 2) for an equilibrium

3 period of approximately 90 minutes followed by sample collection. Assuming a conservative residence

4 time distribution of 12.3 minutes (based upon a flooded column volume of 6,150 gallons) the

5 equilibrium period corresponds to a minimum of 4 residence times. Following the equilibrium period

6 three sets of wastewater samples were collected (EPA Method 1669) at 10 to 15 minute intervals from

7 the inlet, top, mid-column, and discharge of the air-stripper and analyzed for total mercury (EPA

8 Method 1631E). Following sample collection the dose factor was increased and the equilibrium period

9 and sampling activities repeated for all treatment levels.

10 Results

11 Feasibility Testing

12 During the feasibility test 7.2 liters (1.9 gallons) of tin(II) chloride dihydrate (2.36 mM/L) was injected

13 as a reducing reagent for 325 minutes. This corresponds to an applied dose rate of 11.8 mg/min of

14 reagent, 25X the stoichiometric amount. During the injection period steady-state flow conditions were

15 maintained (Q_{water} = 1,741 lpm (460 gpm), Q_{air} = 56,685 lpm (2001.8 cfm), air:water = 32.6:1). The

16 system variables (Figure 1) were maintained during testing by receiving wastewater only from the

17 groundwater recovery wells. A total of 36 wastewater samples were collected and analyzed for total

18 mercury. During the test the concentration of mercury (mean ± 95% confidence interval) at the inlet

19 (pre + injection + post) was C_0 = 233 ± 12.2 ng/L (n=12). During the injection period total mercury

20 decreased from 248 ± 13.5 ng/L (n=5) at the inlet to 14.1 ± 1.9 ng/L (n=5) at the outlet, a decrease of

21 94%. Following the injection period, mercury in the effluent increased to 190 ± 31.1 ng/L (n=3), within

22 15% of the observed inlet value during the sampling event. The concentration at the mid-column

23 increased to 116 ± 22.5 ng/L (n=3).

24

25 Figure 2 provides insight on the kinetics of the chemical reactions by examining the concentration of

26 mercury at the inlet, mid-column, and outlet as a function of time. Injection of the reducing agent began

27 at t = 00:00, 10-minutes after injection the concentration at the mid-column had decreased 86% to

28 31.5 ng/L while the concentration at the outlet had only decreased 19% to 186 ng/L. After 70 minutes of

29 injection, the concentration at both the mid-column and outlet reached steady state and remained

1   constant for the injection period, mid-column = 3.6 ± 0.50 ng/L (n=5) and outlet =14.1 ± 1.91 ng/L

2   (n=5). These results indicate that the system reaches steady state approximately one hour after injection

3   begins.

4

5   During the collection of samples from the mid-column particulate matter was identified. The particulate

6   matter is associated with precipitation and dislocation of minerals to/from the packing material of the air

7   stripper. Previous sampling at the discharge targeted particulate material and indicated that the material

8   contained mercury on the order of 1-3 mg/kg. Upon discovery the analytical laboratory was requested to

9   filter all samples associated with the mid-column location upon arrival. The laboratory was able to filter

10 eleven of the twelve samples. The one unfiltered sample was collected during the pre-injection period

11 (t = -24:10) and had a total mercury concentration of 603 ng/L. The value was rejected at the 99%

12 confidence level ($r_{11} = 0.814$, $r_{crit} = 0.677$) from the pre-injection population (n=9) using Dixon's "Q"

13 parameter (Rorabacher, 1991).

Dose-Response Testing

15 Dose response testing was performed over a two-day period under constant operational conditions

16 (Q_{water} = 1,613 lpm (426 gpm), Q_{air} = 56,662 lpm (2001 cfm), air:water = 35.1:1). Dose-response testing

17 was performed with wastewater only from the groundwater recovery wells. A total of 108 wastewater

18 samples were collected and analyzed for total mercury using the identified methods. During this test the

19 dose rate of the reagent was incrementally increased from 0.27 mg/min to 133 mg/min. A total of nine

20 different dose rates were investigated. For each treatment level three wastewater samples were collected

21 from four locations: inlet, top of the column, middle of the column, and the outlet/discharge. Previous

22 sampling activities at the mid-column had identified particulate matter associated with the samples. To

23 minimize the amount of particulate material, samples at the top- and mid-column were collected using a

24 500-ml polypropylene filter flask (Fisher P/N 10-182-50A with Teflon FEP tubing) to remove solid

25 particles. A dedicated sampling system was used for each location.

26

27 The results (mean $\pm$ 95% confidence interval) from the sampling are presented in Figure 3 as a function

28 of the stoichiometric dose factor, defined as the molar ratio of reducing agent to total mercury. During

29 the dose-response test total mercury at the inlet was $C_0 = 238.9 \pm 2.47$ ng/L (n=27). As indicated in

30 Figure 3, treatment levels below a dose factor of 10X had minimal effect on the concentration of

31 mercury in the system. Treatment levels above a 10X dose factor exhibited sizeable decreases in total

1   mercury at both the mid-column and the discharge positions. Observations indicate that a minimum dose

2   of 6.65 mg/min (16X stoichiometry) is necessary to promote the removal of mercury from the system

3   (91%). A dose rate of 13.3 mg/min (30X stoichiometry) resulted in removal of 95% of the mercury.

4   Subsequent increases in dose above 30X stoichiometry did not further decrease effluent concentration.

5   **Discussion**

6   During the feasibility test a 25X stoichiometric dose of stannous chloride was demonstrated to be

7   effective in removing mercury from the wastewater. During the injection period the concentration of

8   mercury decreased 94.3% across the column of the air stripper. The difference in concentration observed

9   between the inlet and outlet during the injection period was determined to be statistically significant

10   ($p = 10^{-5.98}$). The decrease in concentration is judged to be from the chemical reduction and

11   volatilization of the mercury from the wastewater. Once injection of stannous chloride was terminated

12   the concentration of mercury increased at both the mid-column and outlet locations.

13

14   The results from the inlet and outlet demonstrate the effectiveness of the treatment modality from a unit

15   operation perspective. Results from the mid-column provide insight on internal processes and the role

16   that the packing has as both a source and a sink within the system. The following observations from

17   Figure 2 are identified as indicators that demonstrate this role: 1) During the injection period the

18   concentration of mercury at the outlet is significantly greater at the mid-column (14.1 ng/L > 3.6 ng/L,

19   n=5, $p = 10^{-3.84}$), 2) following the injection period the concentration of mercury at the mid-column is

20   significantly less than the inlet (116 ng/L < 224 ng/L, n=3, $p = 10^{-3.04}$), and 3) also following the

21   injection period the concentration of mercury at the outlet is significantly greater than at mid-column

22   (190 ng/L > 116 ng/L, n=3, $p = 10^{-2.16}$). These observations illustrate the complex and dynamic

23   processes internal to the system that integrate redox reactions and partitioning coefficients. While this

24   internal integration results in the effective removal of mercury by the unit operation, understanding these

25   processes and the role of chemical partitioning in the vapor, aqueous, and solid phase provides

26   information necessary for predictable and reliable operation.

27

28   Under baseline operations (prior to feasibility testing), mercury enters and exits the system in the

29   wastewater as an aqueous species, $Hg(II)_{aq}$. Under these conditions mercury species are driven towards

30   equilibrium between the aqueous and the solid phases, specifically the internal packing. This chemical

1   driving force results in the mass transfer of mercury from the wastewater to the packing and

2   accumulated coatings resulting in an accumulation of mercury within the system. This is demonstrated

3   from the chemical analysis (EPA Method 7471) of packing material collected prior to testing but after

4   several years of operation. This analysis identified the mercury content of the packing and internal

5   coatings to be 1.54 mg/kg.

6

7   During the injection period the reducing agent, $Sn(II)_{aq}$, promotes the rapid chemical reduction of

8    $Hg(II)_{aq}$ species in the inlet wastewater. Once reduced to $Hg(0)$, air to water partitioning (Henry's Law)

9   results in removal of mercury from the system in vapor phase. This was demonstrated previously

10   (Looney et al. 2003) and is supported by the observations currently presented. The first indicator of the

11   internal dynamics unique to the full-scale system relates to the increase in concentration observed

12   between the mid-column and the outlet during reagent injection. A mass balance between these stations

13   indicates that the loading rate of mercury to the wastewater is 18.3 µg/min from the lower bed during the

14   injection period. This loading is considered to be associated with desorption of mercury that

15   accumulated in the packing material prior to testing.

16

17   Also present during the injection period of the feasibility test is an excess amount of $Sn(II)_{aq}$ and the

18   oxidized $Sn(IV)_s$ species. While both species exit the system in the aqueous phase there is also a driving

19   force for these species to equilibrate with the packing material. We postulate that during reagent

20   injection, some amount of the excess $Sn(II)_{aq}$ accumulates within the system. Evidence of this

21   accumulation is suggested by the response in mercury following the injection period.

22

23   Following the injection of $Sn(II)_{aq}$ recovery to baseline conditions begin. During the transitional period

24   internal processes associated with the packing material result in different responses at the inlet, the mid-

25   column, and outlet positions. The differentials observed between positions demonstrate the internal

26   dynamic transition as the system returns to baseline conditions. This transition period includes a

27   reversal of mass transfer such that the packing acts as a reservoir for the compounds present. The second

28   indicator of the complex internal processes is observed with the incomplete recovery of mercury at the

29   mid-column. Based on the rebound data (Figure 2), mercury is removed from the wastewater by the

30   upper bed at the rate of 188 µg/min following the injection period. Based upon previous observations of

31   mercury accumulation in the packing a fraction of this removal can be attributed to solid phase

1   partitioning. We also support the concept that excess Sn(II) also accumulates in the packing during

2   injection and then desorbs to reduce a portion of the $Hg(II)_{aq}$ entering the system.

3

4   The third indicator of the complex internal processes relates to the significant increase in mercury

5   observed across the lower bed (between the mid-column and the outlet) and definitively demonstrates

6   that a latent source of mercury remained following the feasibility test. Based upon average

7   concentrations following the injection period, the flux from the lower bed to the wastewater is

8   129 μg/min.

9

10   There are several internal variables that were not quantified in this investigation that preclude a more

11   detailed analysis of the internal processes of the system, the most significant relates to concentrations of

12   mercury and tin in solid phase during the injection and recovery periods. Detailed information on these

13   variables and sorption kinetics of the packing material would provide important data for long-term

14   operations. It is very likely that excess reagent during injection partially removed latent mercury from

15   the system under injection. Logically this removal would have occurred first in the upper bed and then in

16   the lower bed. Future research efforts should focus on the packing material and accumulation rates of

17   compounds during operation. We note that in the six weeks between the feasibility test and the dose-

18   response test the system returned to baseline conditions.

19

20   During the dose-response test, the difference in means between the inlet and outlet for each treatment

21   were significantly heterogeneous (one-way anova, $F_{8, 18} = 2,523.5$, $P = 10^{-25.1}$). Pairwise comparison

22   within groups (Tukey–Kramer, MSD = 11.48, $p < 0.05$) was used to distinguish effective and ineffective

23   treatments (Figure 4). Ineffective treatment occurred at dose rate of 6.3X and below and effective

24   treatments occurred at a dose rate of 16X and above. The threshold in effective dose is associated with

25   competing electron acceptors in the wastewater, including dissolved oxygen and possibly volatile

26   organic compounds. Dissolved oxygen is present in the inlet wastewater (DO = 6.6 mg/l) and is also

27   introduced during the stripping process and organic constituents TCE and PCE are present in the inlet

28   wastewater in excess of 2.0 mg/L (Figure 1). Historical removal rates of the volatile constituents exceed

29   99.95% for this system. During dose response testing the removal rate exceeded this threshold with rates

30   generally greater than 99.99% for both TCE and PCE. Effluent results were generally at or below the

31   detection limit for the organic constituents. The low organic concentrations (< 1 μg/L) in the effluent

1 precludes a rigorous analysis of any organic + reagent reactions during dose-response testing. While

2 alternate gases (i.e. nitrogen, carbon dioxide, or inert gas) are viable to reduce interferences from

3 oxygen, for most applications the use of atmospheric air has the lowest long-term operations and

4 maintenance costs. It is noted that when dose-rates at or above 16X were applied, mercury in ng/L

5 range were effectively removed in the presence of known (dissolved oxygen) and potential (TCE and

6 PCE) electron acceptors in concentrations several orders of magnitude higher. These observations are

7 consistent with those from the previous investigation (Looney et al., 2003).

8

9 During the dose-response test concentrations observed at the mid-column and outlet locations were

10 consistent with each other. The agreement in concentration is attributed to the use of increasingly higher

11 dose-rates that likely resulted in the removal of any latent mercury within the system. As indicated in

12 Figure 3, as the dose rate is increased in Treatments #6 through #9, no differential in concentration

13 between the mid-column and the outlet are observed. It is likely that a short application of stannous

14 chloride at a high dose would remove any latent mercury internal to the system.

15

16 Based upon the observations presented a reagent dose rate of 12 – 14 mg/min is recommended for initial

17 operations of this system. This dose rate represents 25-30X the amount of reagent required based upon

18 the observed inlet parameters (Q = 425 gpm, C_0 = 240 ng/L) and conditions. The recommended dose

19 should provide sufficient reagent to overcome competing electron acceptors and remove mercury from

20 the wastewater examined. When this process is considered for other wastewater sources laboratory

21 studies are recommended prior to full-scale implementation. EPA Method 1631E identifies three

22 sequential chemical treatments prior to sparging to assure complete recovery of all mercury species prior

23 to quantification. During an earlier investigation (Southworth 1996) found that stannous chloride alone

24 was only effective at removing 80% of the total mercury from the water, which was attributed to the

25 presence of other "refractory" species. For our application a sufficient dose can be delivered to promote

26 removal so that the effluent wastewater is below current regulatory thresholds.

27 ## Conclusions

28 The feasibility test demonstrated that stannous chloride injection is effective in removing mercury using

29 conventional air stripping processes. An applied dose of 25X stoichiometry caused the chemical

30 reduction of mercury and subsequent removal via air stripping. Dose response testing determined that

1   dose requirements are dependent upon competing electron acceptors and that a dose of 16X

2   stoichiometry or greater is needed to facilitate removal within the system investigated. The results

3   demonstrated that the treatment modality is effective in decreasing mercury to the 5-15 ng/L range that

4   is below discharge requirements for this system.

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4

1

2 **Table 1: Reported Values of Vapor Pressure and Solubility used to Calculate Henry's Constant.**

3

At T = 300K	Hg(0)
Vapor Pressure (atm)	2.63e-06 (1)
Solubility (moles/L)	3.01e-07 (2)
K_H (atm L mole^{-1})	8.7
K'_H (-)	0.36

4   Sources: (1) Vapor Pressure Mercury, (Gokel 2003)

5   (2) Mercury in Water, (Clever 1987)

6

7

8 **Table 2: Dose Rate and Injection Parameters applied during Dose-Response Test.**

Run	Dose Rate (mg/min)	$SnCl_2$ H_2O (mg/L)	Inj. Flow (ml/min)	Dose Factor[1]
#1	0.27	10	26.6	0.64
#2	0.53	10	53.2	1.2
#3	1.33	50	26.6	3.0
#4	2.66	50	53.2	6.3
#5	6.65	250	26.6	16
#6	13.3	250	53.2	30
#7	26.6	1000	26.6	60
#8	53.2	1000	53.2	124
#9	133	2500	53.2	297

9

10   (1) Dose factor based upon observed inlet wastewater conditions. Average wastewater flow

11   rate 1,613 lpm (426 gpm) and mercury concentration C_0 =238.9 $\pm$ 2.47 ng/L (n=27).

12

List of Figures

1

2

3   Figure 1: Air Stripper Schematic, Operational Parameters, and Sample Location Key: inlet (□ square),

4   top of column/inlet to first packed bed (Δ delta), middle of column/between packed beds (○ circle), and

5   bottom of column/discharge of second packed bed (∇ gradient).

6

7   Figure 2: Results from a 6-hour feasibility test to evaluate the removal of mercury using chemical

8   reduction and air stripping. Test Parameters: Average Inlet Concentration = 233 ng/L, Wastewater

9   Flow= 460 gpm, Air Flow = 2000 cfm, Stannous Chloride Dose = 11.8 mg/min.

10

11   Figure 3: Effect of stannous chloride dose rate on promoting the removal of mercury using air stripping.

12   Test Parameters: Average Inlet Concentration = 239 ng/L, Wastewater Flow= 426 gpm, Air Flow =

13   2000 cfm.

14

15   Figure 4: Difference in Concentration for nine dose factors. Tukey-Kramer minimum significant

16   difference is 11.48. Shown is the Mean ± 95% Confidence Intervals.

17

18

Typical Wastewater Parameters

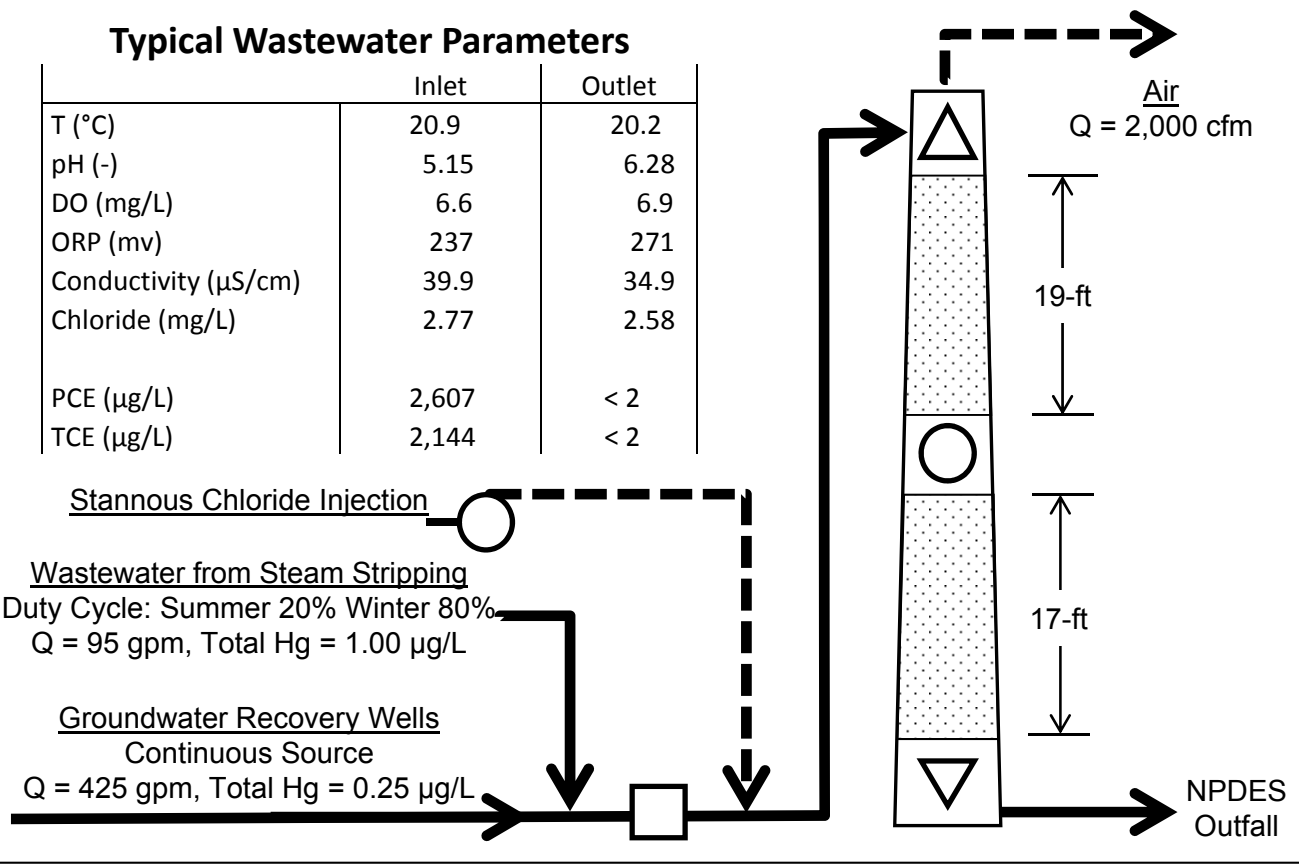|	Inlet	Outlet
T (°C)	20.9	20.2
pH (-)	5.15	6.28
DO (mg/L)	6.6	6.9
ORP (mv)	237	271
Conductivity (µS/cm)	39.9	34.9
Chloride (mg/L)	2.77	2.58
PCE (µg/L)	2,607	< 2
TCE (µg/L)	2,144	< 2

Stannous Chloride Injection

Wastewater from Steam Stripping
Duty Cycle: Summer 20% Winter 80%
Q = 95 gpm, Total Hg = 1.00 µg/L

Groundwater Recovery Wells
Continuous Source
Q = 425 gpm, Total Hg = 0.25 µg/L

Air
Q = 2,000 cfm

19-ft

17-ft

NPDES
Outfall

Total Mercury During the Injection of
Stannous Chloride During Air Stripping