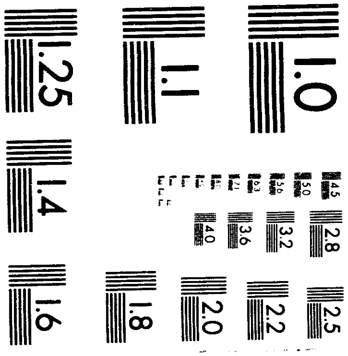
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Y/DZ-1043

AQUEOUS MERCURY TREATMENT TECHNOLOGY REVIEW FOR NPDES OUTFALL 49 Y-12 PLANT

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CONTENTS

EXECUTIVE SUMMARY

During 1950 to 1955, Building 9201-2 at the Oak Ridge Y-12 Plant* was used to house development facilities for processes that employed elemental mercury to separate lithium isotopes as part of the thermonuclear weapons production operations. As a result of several spills, this building area and several other areas associated with the separation process were contaminated with mercury and became a source of continuing contamination of the Y-12 Plant discharge water to East Fork Poplar Creek (EFPC). Mercury concentrations in the outfalls south of Building 9201-2 have ranged up to 80 ppb, with the highest concentrations being experienced at Outfall 49. As a result, this outfall was chosen as a test site for future mercury treatment technology evaluation and development at the Oak Ridge Y-12 Plant.

A literature review and vendor survey has identified several promising materials and technologies that may be applicable to mercury removal at the Outfall 49 site. This document summarizes those findings.

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INTRODUCTION

Elemental mercury in large quantities was used in the Colex process to separate lithium isotopes at the Y-12 Plant between 1950 and 1966. Several significant spills of mercury occurred during that time period. All buildings except Building 9201-4 were stripped, decontaminated, and converted to other uses by 1966. Building 9201-4 was subsequently decommissioned, and the mercury was drained from the process equipment. The equipment has not been removed from the building.

An investigation of sources and discharges of mercury into the Y-12 Plant drainage water was conducted. Results of the investigation, presented in June 1985 in a paper titled *Sources and Discharges of Mercury in Drainage Waters at the Oak Ridge Y-12 Plant*, Y/TS-90, indicated that the largest discharges were associated with Buildings 9204-4 (55 g/d), 9201-5 (40 g/d), 81-10 area (30 g/d), and 9201-4 (25 g/d). Building 9201-2 contributed an additional 10 g/d with all other areas yielding another 10 g/d. New Hope Pond acts as an effective trap for mercury transported by the plant drainage waters with an overall average mercury removal efficiency of 50%.

Building 9201-2 was used in 1950 and 1951 as a process development facility for the Elex process and was subsequently used from 1952 to 1955 as a major Colex process development facility. Upon shutdown of the Colex facilities, the mercury was transferred to other isotope-separation facilities with a balance of 135,157 lb of unaccounted-for mercury. Efforts made to recover the mercury were not very successful. A heavy layer of sulfur was finally added to the top of the dirt basement floor to contain mercury vapor.

Mercury concentrations in outfalls south of Building 9201-2 have ranged up to 80 μg/L, with the highest concentrations in Outfall 49. This outfall has been chosen as a test site for future mercury treatment technology at the Oak Ridge Y-12 Plant.

WASTE CHARACTERIZATION

Elemental mercury is only sparingly soluble in pure water. The equilibrium value is 60 μg/L. The following three reactions are likely to be altering the solubility of the mercury in the Y-12 Plant drainage system.

1. Oxidation by hypochlorite: hypochlorite, a by-product of one operation at the Y-12 Plant, has entered drainage waters. Dilute hypochlorite oxidizes elemental mercury to Hg^{2+}, increasing the solubility of the mercury.

2. Complexation by hydroxide and chloride ion: salts increase the solubility of mercury as a result of the strong complexation by chloride, forming $HgCl_4^{2-}$.

3. Particulate matter adsorption: mercury, especially ionic, has a tendency to be adsorbed on any available surface.

This fact suggests that mercury can enter the Y-12 Plant drainage water by dissolution of metallic mercury trapped in sumps, catch basins, and pipes and by erosion/resuspension of mercury-contaminated particulate matter.

The Y-12 Plant Laboratory currently uses SW846 Method 7470A and EPA Method 245.1 for mercury detection. The lower reporting limit for mercury in water is 0.2 μg/L. EPA Method 245.1 states that by sacrificing range and using 200-mL portions instead of 100-mL portions, with special conditions, 0.025 μg/L can be detected with an uncertainty of 0.004 μg/L.

Samples from Outfall 49 show an average daily loading of 10 g/d of mercury with concentrations reaching 80 μg/L and a flow of 20 to 40 gpm. Other main constituents in the outfall are chlorine (Cl) at 7 mg/L (Cl_2 at 2 mg/L), calcium at 25 mg/L, magnesium at 7.5 mg/L, aluminum at 0.1 mg/L, phosphorus at 0.3 mg/L, zinc at 0.1 mg/L, sodium at 5 mg/L, and potassium at 2 mg/L. Total dissolved solids (TDS) for Outfall 49 is 180 mg/L, and total suspended solids (TSS) is 9 mg/L.

Removing solids from an Outfall 49 water sample using a 0.45-μm filter failed to remove any appreciable amounts of mercury from the stream. Therefore, most of the mercury is in an ionic form, primarily complexed with the chloride ion, with some mercury present in the Hg^{2+} ionic form being attached to suspended particulate matter.

The chloride present in Outfall 49, complexing with the mercury, suggests that once-through cooling water is being discharged at Outfall 49. A project is under way to determine if this discharge water can be removed from the outfall. Should this effort be successful, the mercury loading of the stream will be decreased by removing chloride that is complexing with the mercury, decreasing the flow in Outfall 49, and eliminating flow through mercury-contaminated piping at Building 9201-2.

TREATMENT TECHNOLOGIES OVERVIEW

This section evaluates treatment technologies as an option to reduce the mercury concentration in Outfall 49 from 40 to 80 μg/L to less than 0.3 μg/L. Heavy metals are responsive to practical treatment methods developed and used for water purification and metal-recovery operations. The technology selected will be aimed primarily at polishing because of the low levels of mercury in the stream. With the direct discharge into EFPC, selection will be biased against technologies that generate secondary waste streams.

ADSORPTIVE FILTRATION

The most common adsorption filter for contamination reduction is granular-activated carbon (GAC). These filters reduce some turbidity, residual chlorine, and many organic contaminants with varying degrees of efficiency.

The use of impregnated carbon for mercury removal is proven technology. It is able to treat solutions in the range of from 40 to 100 μg/L down to 1 to 5 μg/L consistently. Iodine-impregnated carbon has an adsorption capacity between 6 and 8 wt % with a removal efficiency >99.0%. In 1972, Sinha and Walker introduced sulfur-impregnated carbon, which demonstrated an adsorption capacity between 18% and 20% with a removal efficiency >99.0%.

The University of Washington has developed a technology in which ferrihydrite is applied to the surface of sand. Once the ferrihydrite-coated sand is loaded to removal capacity, the metals are stripped and concentrated by using a pH-induced desorption process. The process has the following advantages:

1. it acts as a filter to remove both dissolved and suspended contaminants,
2. it removes a variety of complex metals,
3. it works in the presence of a high concentration of background ions, and
4. it removes anions within a wide pH band.

Treatment efficiencies remain constant even after several regeneration cycles.

BIOLOGICAL ION EXCHANGE

Biological ion exchange processes involve the preparation of a resin that binds both metallic cations and oxoanions, excluding chlorides or sulfides. One example of this technology is AlgaSORB. AlgaSORB is a proprietary, nonliving, immobilized biomass with an affinity for heavy metals that was developed by Bio-Recovery Systems, Inc. (BRS). A treatability study on discharge water from Building 9201-2 sumps (Outfall 49) by Howard D. Feiler of Science Applications International Corporation (SAIC) and Dennis W. Darnall of BRS offered the following recommendation and arguments for AlgaSORB:

1. AlgaSORB can produce effluents in the μg/L range for metal ions;

2. precipitation technology produces a large volume of sludge and has effluents in the mg/L range;

3. although reverse osmosis is capable, in theory, of producing effluents in the μg/L range, it is expensive, particularly with metal ions in the μg/L range; and

4. the use of ion exchange resins is a possible method for treatment of the water, but it becomes expensive when the total dissolved mercury content is over 50 mg/L. The algal-based resin is less expensive than commercially available selective ion resins.

Whereas the elutant will require additional treatment, the side stream will be more concentrated and more amenable to traditional treatment.

For Outfall 49, the recommended material is AlgaSORB AZ-601, which will treat 15,000 gal from 30 to 2 μg/L mercury per cubic foot of resin, a total capacity of 0.06 mercury g/L. Regeneration of the column is accomplished by the passage of 10 bed volumes of 1.0 M thiourea in 0.1 M hydrogen chloride. Doulite GT-73 tested at the Savannah River Site has a theoretical capacity of 30 mercury g/L. Extrapolating the flow to 20 gpm with a mercury concentration of 70 μg/L, treatment of 15,000 gal will require 2.43 ft^3 of AlgaSORB to treat to 2 μg/L and will produce an elutant flow of 0.24 gpm of 5.6 mg/L mercury concentration level.

CHEMICAL PRECIPITATION

The most generally applied treatment, lime precipitation, removes metals as a hydroxide precipitate. For mercury, hydroxide precipitation tends to be incomplete; therefore, mercury is usually removed as metal salt by sulfide precipitation. Sulfide precipitation offers the advantages of concentrated mercury products, inexpensive chemicals, and minimum environmental impact. However, precipitation is seldom complete, resulting in heavy metal effluents levels of 0.5 to 1 mg/L; therefore, the process is used for initial treatments rather than for polishing.

Polythiocarbonates, organic polysulfurs, are more effective when low metal concentrations are required. Sufficient reaction time is required for the carbamate reaction to go to completion, or it is almost impossible to remove the resulting precipitate by conventional sedimentation. The advantages of this process over ferrous sulfide precipitation is that 93% less sludge is produced, overall treatment cost is lower, and discharge compliance is more consistent.

CHEMICAL REDUCTION

Chemical reduction of metals involves the lowering of the oxidation state of a metal by the addition of electrons to the atom. The reduction is pH-dependent. Depending on how well the pH is controlled, the reduction can be selective. Reducing agents include alkali metals, sulfur dioxide, sulfite salts, and ferrous sulfate. Reduction is more commonly applied to metals than to organics and is primarily used for reduction of hexavalent chromium, mercury, hexavalent selenium, and lead. Removal is seldom complete, producing effluent levels of from 0.5 to 1 mg/L, and the process is used for initial treatments rather than for polishing. However, two chemical reduction schemes, the Ventron sodium borohydride process and the use of zinc dusts, appear to be able to improve wastewaters to low μg/L mercury limits.

The Ventron Process

Twelve percent sodium borohydride in 40% sodium hydroxide is fed with the wastewater into a static mixer. The solution pH is held to between 9 and 11 because the process is not critically pH dependent. Reduction of the mercury compounds yields metallic mercury and hydrogen gas. What mercury is removed in the sludge is recovered from the effluent by vacuum distillation. A New Jersey mercury chemicals manufacturing facility reported treating 15,000 gpd of a 100-mg/L soluble mercury wastewater stream. After polishing with activated carbon followed by treatment with a chelating resin, the effluents contained less than 5 μg/L mercury.

Zinc Reduction

Metallic mercury forms an alloy with powdered zinc. The zinc is later recovered by heating the alloy and condensing the mercury vapors. In an investigation by New Jersey Zinc Company, solutions containing 10,000 μg/L of mercury were purified to 20 μg/L in 13 s and to 5 μg/L in 110 s by passing them through a 4.7-in.-deep bed of granular zinc particles with average diameters of 2 mm. A problem with this method is the presence of residual zinc in the effluent. Some method of removing zinc will be required, adding to the cost and complexity of the system.

ELECTROCOAGULATION

A continuous wastewater treatment, the CURE electrocoagulation process, electrolytically treats wastewater, resulting in the precipitation of suspended solids and certain metals and organics. The CURE process has achieved the following removal efficiencies on contaminants in wastewater: arsenic, >37%; cadmium, 97% to 99.8%; and TSS, 94% to 99.8%. Capital and operating costs range from $0.25 to $0.50/1000 gal.

Electro-Pure Systems has developed an electrocoagulation process that uses an alternating current to separate stable aqueous suspension containing <5% oil. The treatment increases the mean particle size of soil suspensions and improves their filtration properties. The technology is effective at removing certain metals and other soluble pollutants in the polishing step of effluent treatment. Reported removal efficiencies are as follows: lead, 56%; copper, 96%; zinc, 91%; and fluoride, 56%. The clays to which the metals have adsorbed are removed and the metals are reduced.

ION EXCHANGE

Ion exchange, a widely used, proven technology consistently treating 40 to 100 μg/L mercury-contaminated streams to 1 to 5 μg/L final mercury levels, is a reversible reaction in which anions and cations electrostatically attach to a solid resin material. The resins are usually regenerable synthetic organic materials that hold up under a wide range of temperature and pH conditions and exhibit a selectivity toward specific ions. The selection of resin depends on the type of mercury compounds present in the water. In most cases, chloride complexes will be found; therefore, an anion exchange resin will be used.

The resins that have been considered for use in mercury removal are as follows.

RESIN: IONAC C-249, Sybron Chemicals
Strongly acidic cationic resin
Sulfonate functional group

Cationic mercury HG2+
By-product H+

Because affinity of mercury is similar to other divalent cations, there will be many interferences.

RESIN: IONAC CC, Sybron Chemicals
Weakly acidic cationic resin
RCOOH functional group
Mercuric salt from slightly alkaline solution
By-product H+

The same interference problems exist for this resin as for IONAC C-249. Both of these resins strip well with acids.

RESIN: IONAC SR-4, Sybron Chemicals
Chelating resin, cationic
CH_2SH functional group
Cationic mercury Hg2+, HgCl-
By-product H+

This resin forms a stable complex that is difficult to regenerate, requiring high concentrations of acid, such as 35% HCl. The calculated capacity of this resin is 240 g/L. This loading is unlikely to be achieved in practice and decreases linearly with decreasing feed concentration. With a 70-μg/L stream, one could expect a loading of 4.5 g/L. This resin is the most selective for mercury, but it is necessary to avoid oxidants that will convert it to a strongly acidic cation exchanger. Radian Corporation recommended this resin along with GAC for Outfall 49.

RESIN: IONAC SR-3, Sybron Chemicals
Polythiouronium ion exchanger
HgC14--
By-product H+

The loading for this resin is similar to IONAC SR-4, but the resin is less selective. Effective for mercury removal at low pH, the resin can be regenerated using 5% thiourea acidified with hydrochloric acid.

RESIN: IONAC SR-5, Sybron Chemicals
Iminodiacetate ion exchanger
Cationic mercury, Hg2+
By-product Na+

Selective for mercury, copper, nickel, and cobalt, this resin can be regenerated with sulfuric and hydrochloric acids. It is similar to IONAC SR-5 and should remove cationic mercury, HG2+.

RESIN: IONAC ASB-1P, Sybron Chemicals
Strongly basic anion exchange resin

Chloride complexes, HgC14--
By-product Cl-

This resin requires high concentrations of sulfuric acid or hydrochloric acids for regeneration.

RESIN: IONAC AFB-329, Sybron Chemicals
Weakly basic anion exchange resins
Chloride complexes, HGC14--

AFB-329 is easy to regenerate with alkaline salt solutions, but care must be taken to avoid precipitation.

Rohm & Haas Co. produces a resin, Amberlite IRC-7189, that has a high affinity for heavy metals cations over alkaline earth metals. Selectivity is achieved by an iminodiatic acid functional group chemically bonded to the resin matrix.

Westinghouse Savannah River Company uses Rohm & Haas Doulite GT-73 routinely to reduce mercury content to from 1 to 5 μg/L from a varying influent waste stream containing from 0.2 to 70 mg/L mercury. The GT-73 resin is a weakly acidic, polystyrene/divinylbenzene, cation resin with thiol functional groups. This is the same mechanism by which IONAC SR-4 functions.

MEMBRANE SEPARATIONS

Membrane technologies separate solutes or contaminants from liquids by using semipermeable membranes. The membranes function by selectively rejecting contaminants based on pore size, ion valence, or coprecipitation. Membrane technologies can be used for volume reduction, purification, concentration, and/or recovery of the contaminants. The types of membrane separation technologies include reverse osmosis, ultrafiltration, and electrodialysis.

Reverse Osmosis

The reverse osmosis (RO) system allows a solvent to be removed from a solution containing solutes by a pressure-driven membrane. The solvent molecules are forced through microscopic pores by achieving enough hydrostatic pressure to overcome the concentrate osmotic pressure. Typical operating pressures range from 200 to 800 psi.

Separate RO performance is based on the type of semipermeable membrane in the module. Cellulose acetate and polyamide-type membranes are now used extensively. The RO systems normally consist of a particulate filter followed by an optional activated carbon filter (if a chlorine-sensitive membrane is used), an RO module, and a water reservoir.

Initial contacts with RO vendors showed that it will take two staged units working at 90% efficiency at a cost of $7000 each to treat a 20-gpm stream from 70 μg/L to 2 μg/L mercury at an operating cost of $1.00/1000 gal, not including labor. Each unit generates a waste stream volume equivalent to 25% of the influent flow volume. The waste stream of the second unit is recycled back to the first unit. The 5-gpm waste stream of the first unit is discharged at approximately 0.3 mg/L mercury for further treatment. Up to 60% of the first waste stream can be recycled, and the system will still meet the 2-μg/L mercury discharge limit, resulting in a waste stream of 2 gpm and containing 0.5 to 0.6 mg/L mercury.

The use of RO as a separate technology or in conjunction with the packed media should be tested on a bench-scale level. The bench-scale level may demonstrate mercury removal efficiencies only up to 70% compared with the possible 95% removal efficiency of larger

RECOMMENDED TECHNICAL OPTIONS

Based on the results of this literature review and vendor survey, the author recommends that the treatability studies for Outfall 49 include batch and column tests to evaluate the following packed media for removal of mercury to low $\mu g/L$ levels:

1. Adsorptive filtration media: standard GAC, along with sulfur-impregnated GAC, and

2. Ion exchange media: Thio group chelating resin, IONAC SR-4.

Polythiocarbonate precipitation should be investigated as a means of removing the mercury from the concentrated regenerate or the waste flow from the primary treatment.

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