

THE RECOVERY AND RECYCLE OF MERCURY FROM CHLOR-ALKALI PLANT WASTEWATER SLUDGE

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ABSTRACT

Universal Dynamics and Montana Tech of the University of Montana have developed a hydrometallurgical process for the recovery and recycle of mercury from chlorine plant wastewater sludge materials (EPA hazardous waste classification K106). The hydrometallurgical process is also applicable for the treatment of mercury contaminated soils (EPA hazardous waste classification D009) and other mercury bearing waste materials. The process is capable of lowering the mercury content in the K106 solids from 10% to <50 mg/kg Hg. The treated solids pass the U.S. EPA Toxicity Characteristic Leach Procedure for Hg of <25 µg/liter. The process has been commercialized and utilized at three U.S. Chlor-Alkali plants.

This paper describes the fundamental chemistry of the process, the flowsheet being used industrially (2-stage hypochlorite leach with subsequent recovery of mercury by iron cementation or electrowinning), and operating plant case histories.

INTRODUCTION

Universal Dynamics, Ltd and Montana Tech of the University of Montana have developed a hydrometallurgical process for the recovery and recycle of mercury from caustic plant wastewater sludge materials (United States Environmental Protection Agency, EPA, hazardous waste classification K106)^(1, 2). The hydrometallurgical process is also applicable for the treatment of mercury contaminated soils and other mercury bearing waste (EPA hazardous waste classification D009). The process is capable of lowering the mercury content in K106 solids from 10% to < 50 mg/kg Hg. The treated solid materials pass the EPA Toxicity Characterization Leach Procedure, TCLP, (Hg < 25 µg/liter, ppb) which means that the solids are deemed nonhazardous. This hydrometallurgical process has been accepted by the EPA as an alternative Best Demonstrated Available Technology (BDAT). Universal Dynamics has commercialized the process under the name REMERC. The REMERC hydrometallurgical process has been installed at three U.S. Chlor-Alkali plants (Georgia-Pacific, Bellingham, Washington; Westlake C&D Corporation, Calvert City, Kentucky; and Pioneer Chlor-Alkali, St. Gabriel, Louisiana).

The following presentation describes the fundamental chemistry of the REMERC process and the process flowsheet.

WASTE SOURCE

Most of the discussion in this presentation relates to K106 waste material. Many Chlor-Alkali plants clean up their wastewater by sulfide precipitation, i.e., mercury sulfide is precipitated as the K106 waste material. The K106 waste sludge generally contains 3-10% mercury, primarily as mercuric sulfide. The quantity of waste generated by individual facilities that utilize the REMERC

process is presented in Table I.

Table I. K106 Waste Generation by Chlor-Alkali Plants in the United States that Utilize the REMERC Technology

<u>Facility</u>	<u>Waste Generation, tons/yr</u>	<u>Mercury Content, %</u>
Georgia-Pacific, Bellingham, Washington	110	3-4
Westlake Chemicals, Calvert City, Kentucky	180	8-10
Pioneer Chlor-Alkali, St. Gabriel, Louisiana	180	5-6

These waste materials cannot be disposed in U.S. landfills without prior pretreatment (EPA requirement since May 1994).

EPA ENVIRONMENTAL REQUIREMENTS

The environmental requirements for various mercury bearing waste materials are presented in Table II. The EPA designated BDAT for K106 waste sludge (containing ≥ 260 ppm mercury) is thermal treatment by retorting or roasting. The hypochlorite leach process is a competitive technology that has been designated by the EPA as an acceptable treatment technology for K106 category waste sludge materials.

Table II. United States Environmental Requirements for Mercury Bearing Nonwastewaters

<u>Category</u> ¹	<u>Total Hg in original sludge, ppm</u>	<u>TCLP Hg on treated waste, ppb</u> ²	<u>BDAT applied to original sludge</u> ³
K106	≥ 260	≤ 200	Thermal Recovery (Retort/Roast)
K106	≤ 260	≤ 25	Acid Leach/Oxidize/Dewater
K071	Not specified	≤ 200	Thermal Recovery
K071	Not specified	≤ 25	Acid Leach/Oxidize/Dewater
D009	≥ 260	≤ 200	Thermal Recovery
D009	≤ 260	≤ 25	Acid Leach/Oxidize/Dewater

1 K106 is sludge produced by sulfide precipitation from mercury cell chlor-alkali wastewater; K071 is mercury cell chlor-alkali brine purification muds; D009 is mercury bearing sludge from generic sources.

2 TCLP is the maximum leachable mercury allowed by EPA for sludge treated for land disposal.

3 The EPA required treatment technology.

LEACH CHEMISTRY

The REMERC process is based on leaching mercury and mercury compounds in an oxidizing chloride bearing environment (hypochlorite) with subsequent recovery of mercury from the leach solution via either cementation on iron or by aqueous phase electrolysis.

The dissolution of mercury or mercury sulfide is not effective without the presence of the chloride ligand (Figure 1) except under oxidizing/acidic conditions, i.e., note in Figure 1 that the E_H/pH leach conditions necessary to solubilize mercury must be chosen to lie within the region marked as $HgSO_4(a)$. However, note in Figure 2 that the dissolution of elemental mercury and mercury solids is thermodynamically favorable over a wide range of solution potentials and pH values in a chloride environment. An example of the influence of solution potential on mercury solubility at pH 6 is presented in Figure 3. Note the relatively high mercury solubility at E_H potentials >500 millivolts.

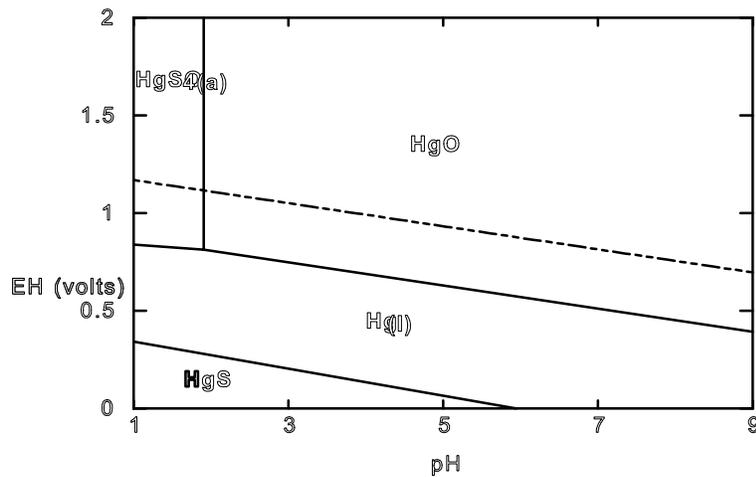


Figure 1. E_H/pH diagram for the Hg-S-H₂O system

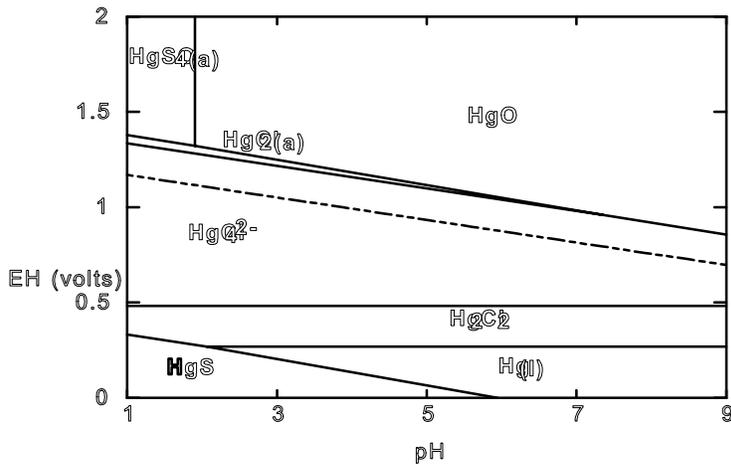


Figure 2. E_H/pH diagram for the Hg-Cl-S-H₂O system

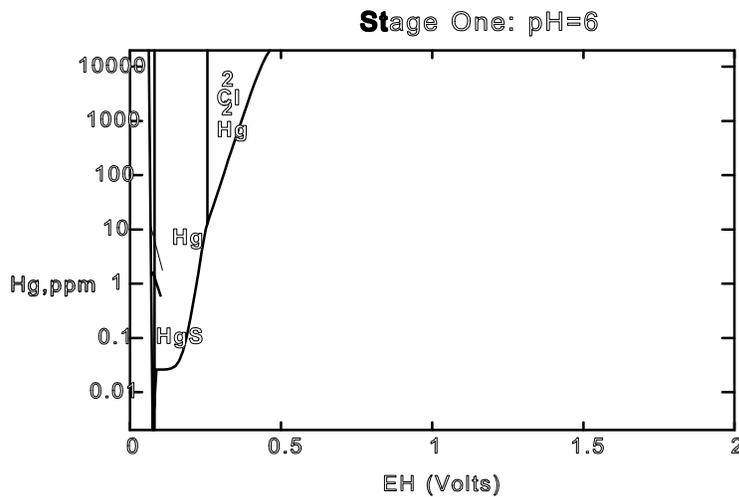
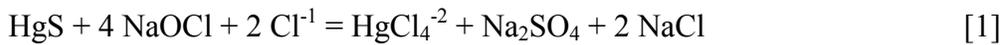


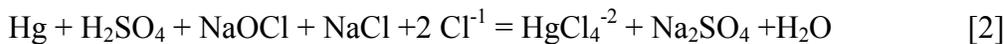
Figure 3. The influence of E_H on mercury solubility at pH=6 (stage one leach)

The leach reactions in a chloride environment are presented below:

For mercury sulfide,



For mercury,



The leach process can be performed in simple stirred reactors. The leach is normally conducted in two stages. Typical conditions utilized in commercial operations for leaching are Stage One: pH=6, 5-27% sodium chloride, E_H~1100 mv, T°C=20-100, 30 minutes to 1 hour residence time; Stage Two: pH=2, 5-27% sodium chloride, E_H~1100 mv, T=20-100°C, 15 minute residence time.

Typical leach results achieved at operating commercial facilities are presented in Table III.

Table III. Typical Mercury Recovery Leach Results Achieved by Commercial Facilities

<u>Facility/Location/Date Adopted</u>	<u>Initial Hg, ppm</u>	<u>Residual Hg, ppm*</u>
Georgia-Pacific/Bellingham, Washington/1993	60,000	150
Westlake Chemicals/Calvert City, Kentucky/1994	110,000	220
Pioneer Chlor-Alkali/St. Gabriel, Louisiana/1996	55,000	50

*EPA Regulatory Requirement: the hypochlorite leach residue must contain <260 ppm mercury and the treated product must leach mercury in the TCLP test to < 25 ppb.

MERCURY RECOVERY

Mercury recovery from the leach solution can be accomplished by one of two approaches: Cementation (displacement from solution by metallic iron) or Electrolytic recovery by recycling the leach solutions to the chlor-alkali cells. The approach presently chosen by the Georgia Pacific and Pioneer operating commercial facilities is recovery by cementation; the approach chosen by Westlake is recycle of the loaded mercury brine to their mercury amalgam electrolytic cells.

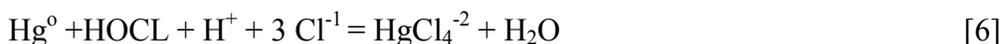
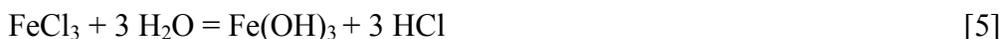
The basic chemistry for cementation of mercury by an iron substrate is electrochemical deposition. Elemental iron lowers the solution potential so that mercuric chloride is reduced to elemental mercury. The reaction that controls the formation of elemental mercury is:

Primary Reaction



Secondary reactions also occur in the presence of hypochlorite. These reactions are undesirable because they produce ferric hydroxide and redissolve elemental mercury.

Secondary Reactions



Therefore, the hypochlorite must be destroyed by pretreating the solution entering the cementation reactor. The usual reagent utilized for the destruction of hypochlorite is sodium bisulfite.

The cementation reaction can be performed in a simple mix tank or rotating mill. A three-phase system is present in the cementation reactor, i.e., a lower mercury pool, an aqueous phase containing the aqueous mercuric chloride and a coarse iron particulate phase. Iron scrap or iron powder floats on a mercury pool which is maintained in the bottom of the reactor. Iron is always

in contact with the liquid mercury and with the mercury bearing solution phase. Globules of mercury form on the iron as the cementation reaction occurs. The globules of mercury coalesce into the mercury pool. It is therefore possible to remove solution from the reactor containing ferrous chloride but essentially no mercury. Elemental mercury can be extracted from the bottom of the vessel. The mercury product is equivalent in purity to triple distilled mercury. The mercury free ferrous chloride solution is treated by hypochlorite oxidation to produce a ferric hydroxide product (which passes the EPA TCLP test) and the cleaned brine solution is recycled to the chlor-alkali process plant water.

INDUSTRIAL FLOWSHEETS

Three mercury amalgam facilities have used the REMERC process and the other facilities use retorting for the treatment of K106 waste. The Georgia Pacific and the Pioneer facilities utilize a continuous treatment system; Westlake Chemicals use a batch treatment system. The generalized flowsheet (Figure 4) used by all three of these facilities consist of the following unit operations:

- C Stage One Leach (pH=6, 5-27% sodium chloride, sodium hypochlorite to maintain an $E_H \sim 1100$ mv, $T^\circ C = 20-100$, 30 minutes to 1 hour residence time).
- C Solid/Liquid separation and solids washing. Solids are passed on to stage two leach; the solution phase is recycled to the caustic plant process water.
- C Stage Two Leach (pH=2, 5-27% sodium chloride, sodium hypochlorite to maintain an $E_H \sim 1200$ mv, $T = 20-100^\circ C$, 15 minute residence time).
- C Solid/Liquid separation and solids washing; cleaned solids are passed on to disposal; the solution phase is recycled to the stage one leach.
- C Mercury recovery from the solution phase by cementation (except BFG recycles their solution to the mercury amalgam electrolytic cells). The conditions for the cementation are; -38/+65 mesh iron, 15-30 minutes residence time, and $pH < 3$. Liquid mercury is recovered periodically from the cementation cell. Iron consumption is minimal, e.g., approximately 25 pounds/day.

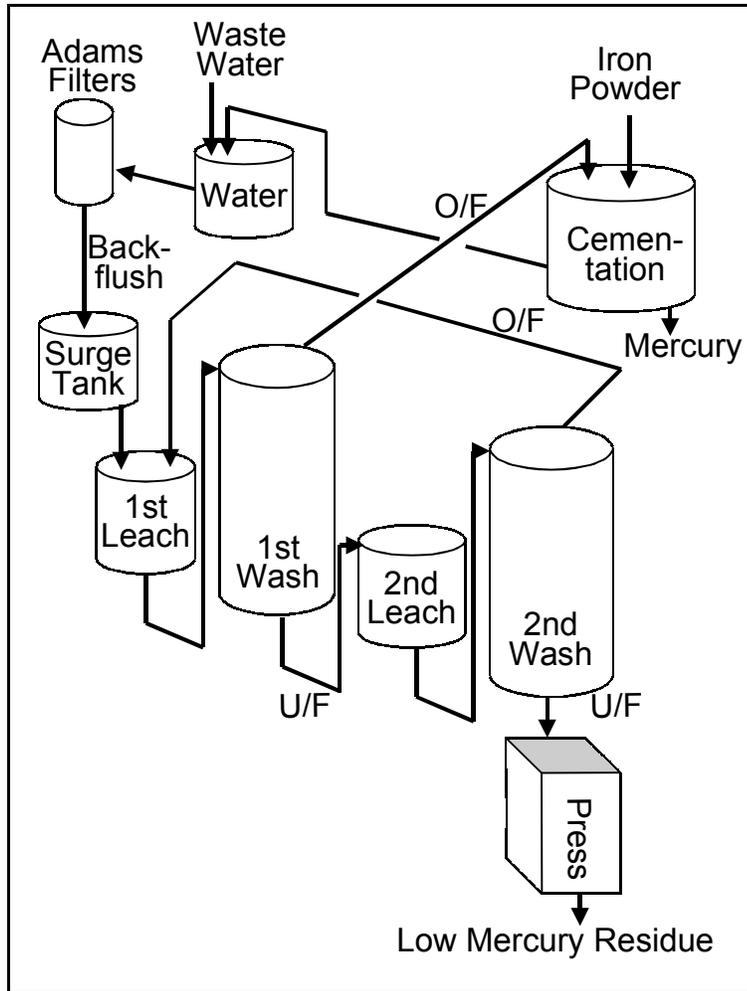


Figure 4. Generalized industrial flowsheet

PROCESS COST

The capital cost for the hydrometallurgical REMERC process is approximately 1.5 million U.S. dollars for a plant that has a treatment capacity of 2000-3000 pounds/day. This cost is less than one-half the capital cost of a retorting system, e.g., 3 to 5 million dollars for the same treatment capacity.

Operating costs are very site specific and are presently unavailable. It is noted, however, that this process utilizes excess plant hypochlorite and excess acid so that the reagent costs are minimal. The only reagent that must be purchased is the elemental iron used in the cementation process. Typical reagent requirements are presented in Table IV. Operating labor cost are approximately \$20,000/year, i.e., the process is highly automated and requires only occasional oversight (0.3-0.5 man-hours/day) by operating personnel.

Table IV. Typical Process Data for the Georgia Pacific Plant

	<u>Pounds/ton</u>	<u>Pounds/day</u>	<u>Tons/year</u>
K106		1,100	110
Reagents			
Sulfuric Acid	300	150	15
Hypochlorite	120	60	120
Iron	80	40	4
Mercury Produced	60	35	3.5

Plant operates 200 days/year

SUMMARY

A hydrometallurgical process for treating mercury bearing wastes and by-products has been developed and has progressed to commercial application. The process features include:

- C Acceptance by the EPA as an alternative BDAT for treating K106 waste. Greater than ninety-eight percent mercury recovery is achieved; treated residues contain only 50-100 mg/kg of mercury; and the residues pass the required EPA TCLP, i.e., the mercury content of the TCLP extraction fluid is <25 µg/liter.
- C Relatively simply hydrometallurgical reactors and solid/liquid separation devices are required, i.e., conventional, readily available industrial equipment are utilized. Leach reactors and thickeners are constructed of commonly available materials, e.g., fiberglass reinforced plastic (except the rakes in the thickeners are made of Hastelloy C).
- C Mercury (equivalent to triply distilled) is recovered for market or it is recycled to the chlor-alkali plant electrolytic amalgam process.
- C Effluent brine water is recycled to the chlor-alkali plant process water.
- C There are no atmospheric emissions.
- C The process utilizes spent and waste chemicals from the chlor-alkali process as reagents.
- C The process can be used on many mercury bearing waste materials, i.e., EPA D009 waste.
- C The process shows an economic advantage when compared to retorting, e.g., the capital costs for the hydrometallurgical process are only about 25% of the cost for retorting.

REFERENCES

1. M.A. Rockandel, L.G. Twidwell, "Hydrometallurgical Process for Treating Mercury Contaminated Muds", *United States Patent 5,209,774*, (1993), 8 p.
2. M.A. Rockandel, L.G. Twidwell, "Mercury Contaminated Mud Treatment", *United States Patent 5,314,527*, (1994), 18 p.

List of Figure Titles

Figure 1. E_H/pH diagram for the Hg-S-H₂O system

Figure 2. E_H/pH diagram for the Hg-Cl-S-H₂O system

Figure 3. The influence of E_H on mercury solubility at pH=6 (stage one leach)

Figure 4. Generalized industrial flowsheet