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# Project Summary

# Waste Minimization Audit Report: Case Studies of Minimization of Mercury-Bearing Wastes at a Mercury Cell Chloralkali Plant

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The U.S. Environmental Protection Agency (EPA) is encouraging hazardous waste generators to develop programs in order to reduce the generation of hazardous waste. To foster such programs, the Agency's Office of Research and Development Hazardous Waste Engineering Research Laboratory (ORD/HWERL) is supporting the development and evaluation of a model hazardous waste minimization audit (WMA) procedure using the EPA hierarchy of waste minimizations (WM) options, with source reduction being more desirable and recycle/reuse less desirable. Treatment options, although not considered WM, are evaluated if neither of the former alternatives is available. The WMA procedure was tested initially in several facilities in 1986. WMAs were conducted at generators of a number of generic hazardous wastes, including corrosives, heavy metals, spent solvents, and cyanides.

In 1987, the HWERL WMA program concentrated on ORD's top priority RCRA K and F waste list. Audits were conducted at generators of K071 and K106 wastes (mercury cell chloralkali plants), K048-K052 wastes (sludges and solids from petroleum refining), F002-F004 wastes (spent solvents), and F006 wastes (wastewater treatment sludges from electroplating operations). This Project Summary covers WMAs carried out at two mercury cell chloralkali plants. These audits were aimed at developing WM options for K071 and K106 wastes generated at these plants (referred to as Plant No. 1 and Plant No. 2 in this study).

During the WMAs at Plant No. 1 and Plant No. 2, the audit team determined that the mercury level in the high volume K071 waste (brine treatment sludge) was too low to permit economical recovery and recycle of this pollutant to the process. However, retorting of the K106 waste (mercury-bearing wastewater treatment sludge) for mercury recovery and recycle is technically feasible and may be economically viable from Plant No. 2.

A total of six source reduction options for K071 waste were studied by the audit team at Plant No. 1. All but one were ruled out because of technical and/or economic considerations. Only one source reduction option (replacement of mercury cells with the newer membrane cell technology) is technically feasible and showed an attractive payback (approximately 2 years) when applied at Plant No. 1. However, this option is highly capital intensive (requiring an approximately $20 million investment at Plant No. 1), even though the K071 waste is eliminated if this option were implemented.

Treatment options, while not considered WM, were considered by the audit team for detoxification of K071 waste at Plant No. 1. A total of three treatment options were considered, two of which appeared to be both technically and economically feasible. It is believed

**that implementation of these two options would enable the treated waste to be delisted with resulting saving in disposal costs ranging from $325,000 to $380,000 and payback period ranging from 2 to 2.3 years. Plant No. 2 had already decided to install a treatment option to detoxify K071 waste.**

***This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

The national policy objectives established under the 1984 Hazardous and Solid Waste Amendments to the Resource Conversation and Recovery Act of 1976 include the goal of reducing or eliminating hazardous waste as expeditiously as possible. Further, the EPA Report to Congress on minimization of hazardous waste (issued in 1986) provided recommendations for private industry on waste minimization approaches. To promote waste minimization activities, the HWERL of the EPA, ORD, has undertaken a project to develop and test a WMA procedure. It is envisioned that such a procedure would be useful to generators of hazardous waste as they search for waste minimization alternatives. The present HWERL project expands on an audit procedure developed and tested in 1986 by conducting additional WMAs in cooperating industrial and government facilities. This project is one of several current audit efforts being supported by HWERL.

This study presents the elements of a WM program, of which the audit procedure is a central component and includes details of the WMA procedure, its development, and its final recommended form. A case study is presented using this WMA procedure and covers audits performed at two mercury cell chloralkali plants that generate listed wastes K071 and K106. Findings and conclusions resulting from these audits are presented below.

## *Description of the WMA Procedure*

The function of the WMA procedure is to force the use of an orderly step-by-step procedure for conducting an audit at a host site. The initial WMA procedure was developed in earlier work, and was further refined during the course of the present EPA-sponsored audit effort. This procedure is applicable to the development of both categories of WM options (source reduction and recycling/reuse) as well as the development of treatment options.

The team employed in carrying out the audit described in the full report was composed entirely of employees of an outside consulting/engineering firm. Following selection of the host facility there were eight sequential steps executed by the audit team:

1. Preparation for the audit.
2. Host site pre-audit visit.
3. Waste stream selection.
4. Host site waste minimization audit visit.
5. Generation of WM options.
6. Preliminary WM options evaluation (including preparation of preliminary cost estimates) and ranking of options in three categories (effectiveness, extent of current use, and potential for future application).
7. Presentation, discussion, and joint review of options with plant personnel.
8. Final report preparation and presentation to host site management.

This procedure was followed in carrying out the WMAs summarized below.

## *Results of the WMAs Conducted at Generators of K071 Waste: Audits at Two Mercury Cell Chloralkali Plants*

Mercury cell chloralkali plants produce chlorine, with sodium hydroxide (NaOH) and potassium hydroxide (KOH) as co-products depending on whether sodium chloride (NaCl) or potassium chloride (KCl) brine is used as feed to the mercury electrolytic cells employed in the process. Listed waste K071 generated by these plants is defined in 40CFR 261.32 as follows:

- K071: Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used.

The results of the WMA on K071 waste are presented below.

The two mercury cell plants which acted as the host sites in this case study are both located in the Southeast and designated as Plant No. 1 and Plant No. 2. Plant No. 1 has a nameplate capacity of 138,000 metric tons of chlorine per year. This plant operates two parallel production lines—one producing 310 metric tons per day of NaOH and the other producing 246 metric tons per day of KOH as co-products. Louisiana rock salt received by barge is the raw material used. The plant generates approximately 5,000 tons per year of K071 waste (mercury-bearing brine saturator insolubles and brine purification wastes). All of these wastes are currently sent offsite to a hazardous waste landfill. Figures 1 and 2 are typical schematics of the plant and brine purification operations respectively, for the NaCl-based process.

Plant No. 2 has a nameplate capacity of 116,000 metric tons per year of chlorine. The plant operates one production line which also has a capacity of 354 metric tons per day of NaOH as a co-product. Plant No. 2 uses Louisiana rock salt as feedstock for this process. This plant generates approximately 5,400 tons per year of K071 waste which is currently sent offsite to hazardous waste landfills.*

While K071 is a large-volume waste, the audit team determined that the mercury level (typically in the 25 ppm range) was too low to permit economic recovery and recycle of this pollutant thus ruling out recycle/reuse as a WM option. Prepurification of the NaCl brine feed to the electrolytic cells at Plant No. 1 (in order to eliminate the main sources of this waste—the brine saturator insolubles and brine purification sludge) proved to be an uneconomical source reduction option. A total of seven source reduction options for this waste were considered by the audit team. Six of these had to be ruled out because of unfavorable economics and/or unproven technical feasibility of the process. The seventh option (replacement of the mercury electrolytic cells with the newer

*This plant is currently undergoing a revamp in its brine purification operations in order to achieve a delistable K071 waste, i.e., reduce mercury levels in this waste low enough (as a result of the revised plant treatment) to attain a level of <12 ppb for this pollutant in EP-tox leachate thus enabling EPA to delist this waste.

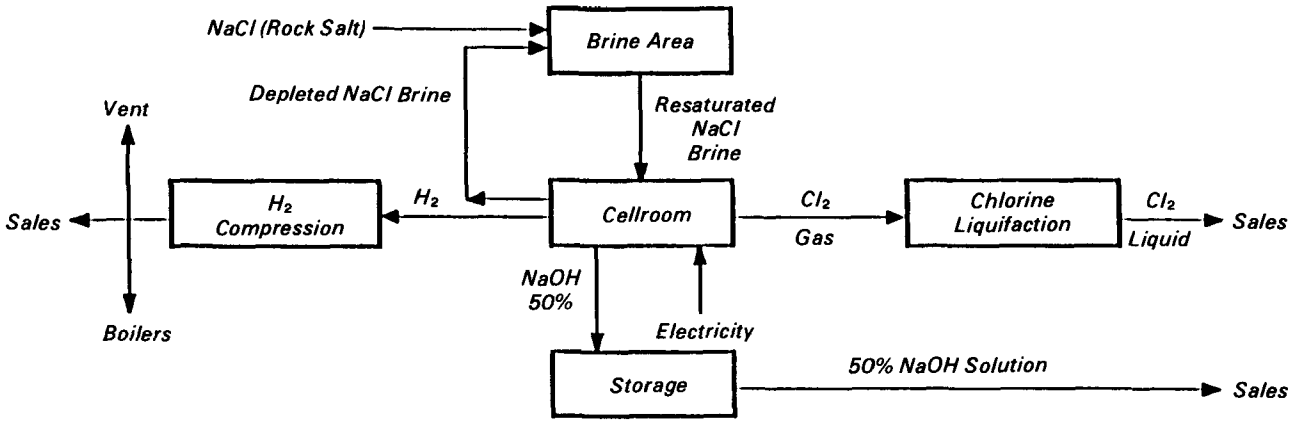


*Figure 1. NaOH/chlorine production process.*

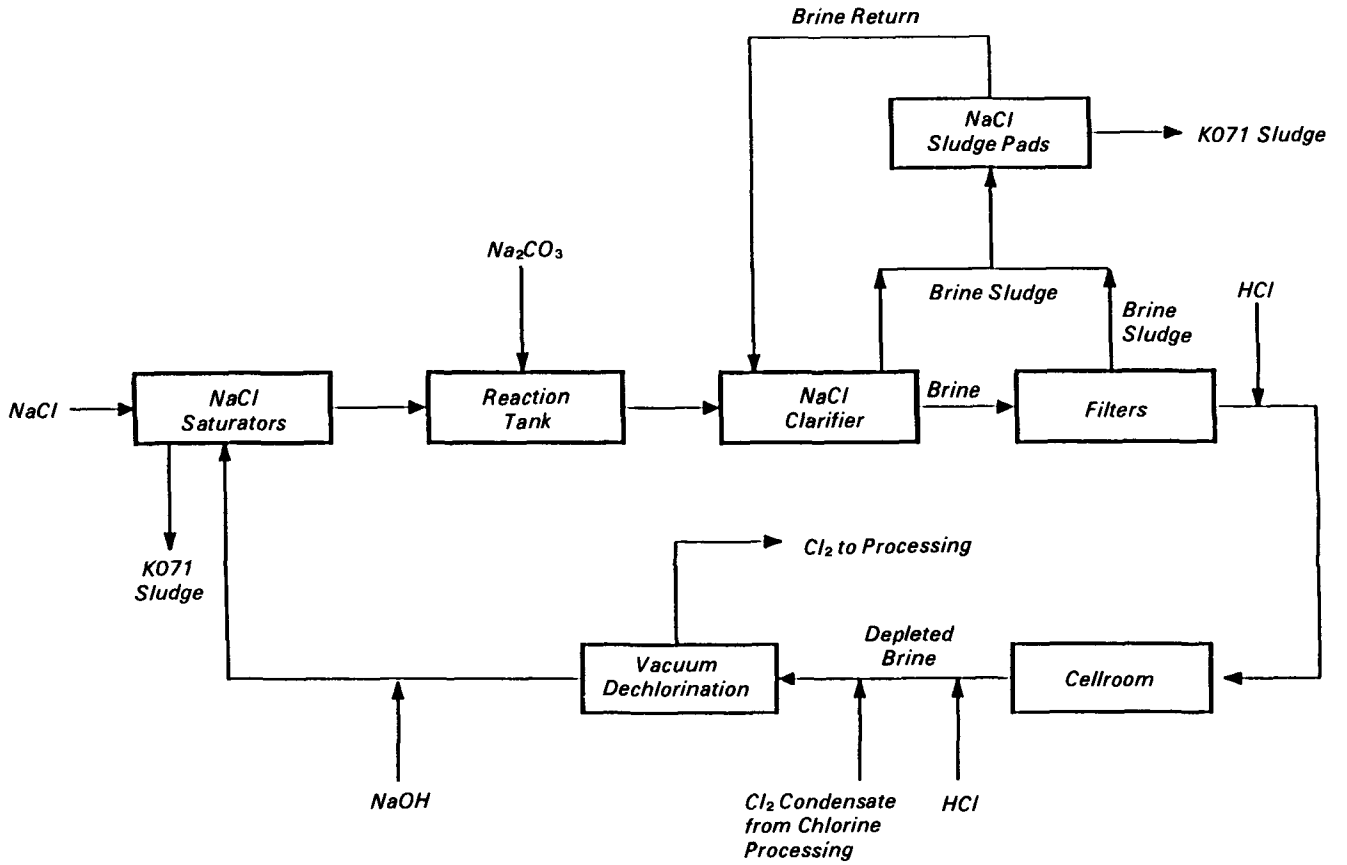


*Figure 2. NaCl brine treatment system.*

membrane cell technology—the industry's process of choice currently) appeared to have an attractive payback period (approximately 2 years) primarily due to significantly more economical chlorine production technology and to a much smaller extent, due to elimination of the K071 hazardous waste disposal cost. However, a retrofit of membrane cell technology requires Plant No. 1 to invest approximately $20 million for installation of this option. An investment of this magnitude is unlikely to be considered at this time because of the current depressed economics of the chloralkali industry.

While K071 waste treatment is not considered a WM option, the audit team determined that Plant No. 1 has several technically viable treatment options with reasonable payback periods available for K071 waste detoxification. One or more of these options, if implemented, has the potential for detoxifying the K071 waste thus allowing it to be delisted by EPA with the resulting non-hazardous waste being able to be placed in a local sanitary

landfill. The plant is studying these alternatives at the present time. Figures 3 and 4 depict two K071 treatment options evaluated by the audit team which appear to be technically feasible and have attractive payback periods (<3 years).

Table 1 summarizes all of the K071 waste reduction and treatment options studied by the audit team for potential application at Plant No. 1. One source reduction option (highly capital intensive) and two treatment options meet the criteria for technicca1 and economic feasibility (at the preliminary evaluation stage) at this time. The plant is giving serious consideration to a significant revision in the present K071 waste treatment and disposal operation (as must all of the 14 mercury cell chloralkali plants faced with this problem) due to the pending imposition of EPA Best Demonstrated Available Technology (BDAT) requirements for disposal in hazardous waste landfills by the summer of 1988.

## *Results of the WMA Conducted at Generators of K106 Waste: Audits at Two Mercury Cell Chloralkali Plants*

The two mercury cell chloralkali plants that acted as host sites for WMAs on minimization of K071 waste, were audited for listed waste K106, defined in 40CFR 261.32 as follows:

- K106: Wastewater treatment sludge from the mercury cell process in chlorine production.

The results of the WMA on K106 waste are presented below.

The K106 waste is a low volume waste being generated at Plant No. 1 at the rate of about 20 tons per year and at Plant No. 2 at the rate of about 75 tons per year. This material (a wastewater treatment sludge in the form of a 0.5 to 1.5 percent mercury content filter cake) is presently being sent offsite together with K071 waste to hazardous waste landfills.

The audit team determined that source reduction options were not available to reduce or eliminate the wastewaters that are the source of this waste since generation of these wastewaters is unavoidable at mercury cell chloralkali plants. A recycle/reuse option to recover and recycle the mercury pollutant from the wastewater is commercially proven but not economically feasible at either of these plants. A recycle/reuse option is available to recover the elemental mercury from the wastewater treatment sludge using a retorting process. This process is technically feasible and small-scale tests on Plant No. 1 filter cake have determined that the retorted residue is low enough in mercury so that EP-tox leachate can pass EPA delisting requirements. However, the cost of recovering the relatively small amount of mercury (<0.2 tons per year) from Plant No. 1 K106 waste appears to make this option economically unattractive. The recoverable mercury from Plant No. 2 K106 waste (approximately 1.5 tons per year) may make the retorting option econom-

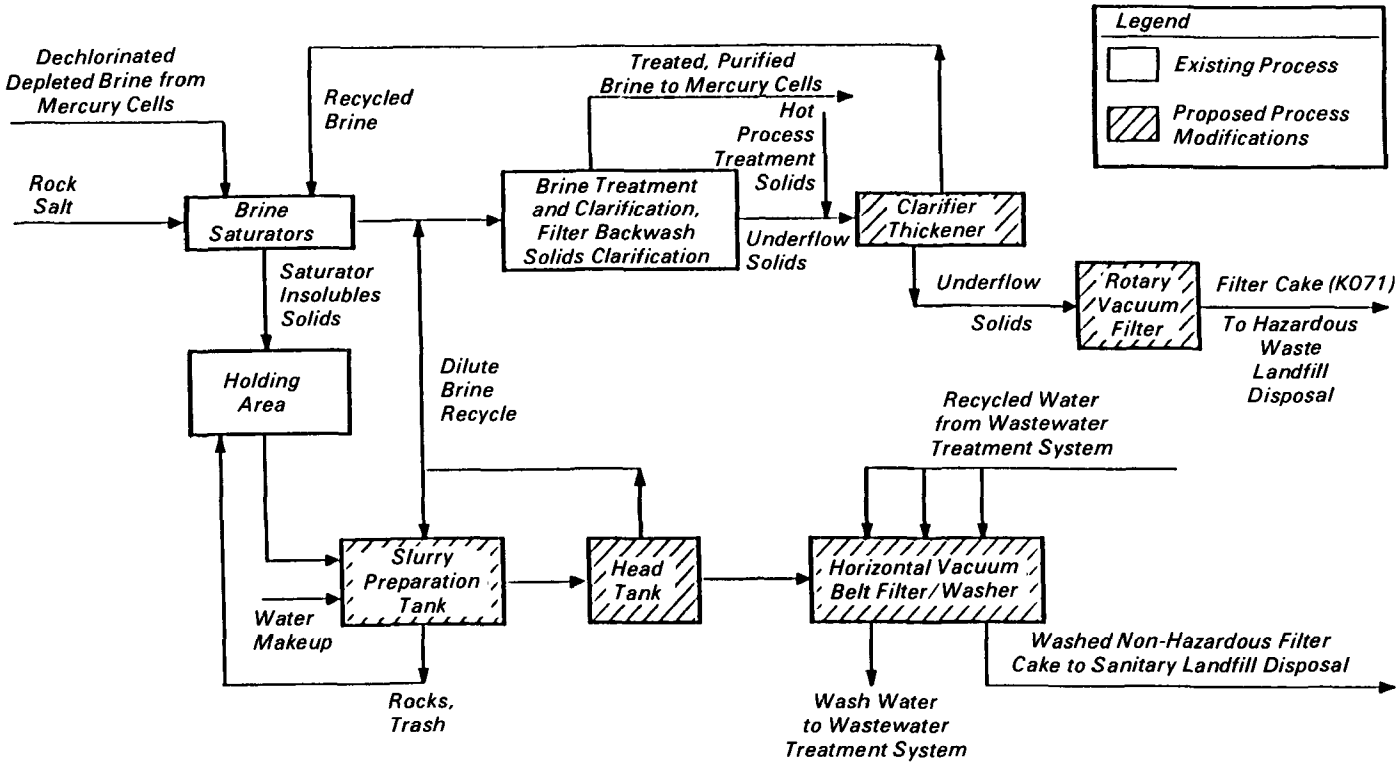


*Figure 3. Proposed water washing process for NaCl saturator insolubles.*

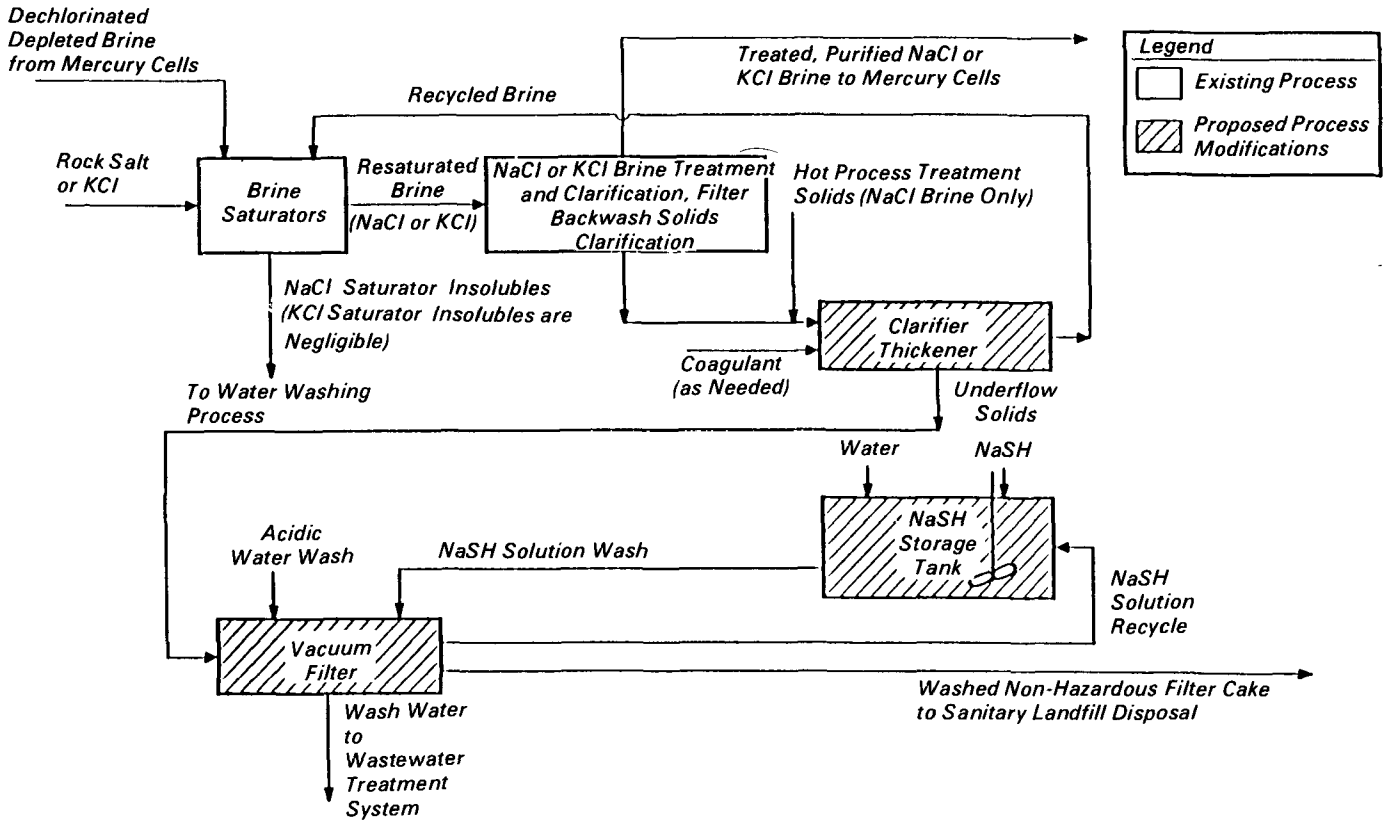


***Figure 4.*** *Proposed sulfide precipitation option for removal of entrained mercury from the K071 brine purification wastes.*

***Table 1.*** *Summary of Postulated Options for Minimization of Listed Waste K071 at Plant No. 1*

| Option | Description | Type of Option | Advantages | Disadvantages | Potential Savings ($/yr) |
|---|---|---|---|---|---|
| A | Reduction of depleted brine dissolved sulfate level to minimize saturator insolubles generation. | Source reduction | Reduce generation rate of saturator insolubles portion of K071 waste by as much as one-third. Save significant labor cost currently involved in periodic cleanout of saturators. | Depleted brine side stream treatment needed to reduce dissolved sulfate results in excessive precipitant cost as well as large additional generation of mercury-contaminated wastes. | -- |
| B | Use of prepurified salt feed stock. | Source reduction | Essentially complete elimination of mercury-contaminated K071 waste generation in NaOH production. | Unacceptable economics. | -- |
| C | Use of solar salt as a feed stock. | Source reduction | Significant reduction of mercury-contaminated K071 generation in NaOH production. | Unacceptable economics. | -- |
| D(1)(a) | Removal of mercury from depleted brine prior to brine resaturation, using sulfide precipitation with disposal of mercury sulfide waste. | Source reduction | Essentially complete elimination of mercury-contaminated K071 waste generation in NaOH production. | Commercially unproven process; creation of another K071 waste; unacceptable economics. | -- |

*Table 1. Continued*

| Option | Description | Type of Option | Advantages | Disadvantages | Potential Savings ($/yr) |
|---|---|---|---|---|---|
| D(1)(b) | Removal of mercury from depleted brine prior to brine resaturation using sulfide precipitation, followed by mercury retorting and recovery from mercuric sulfide waste. | Source reduction | Same as D(1)(a). | Commercially unproved process; unacceptable economics. | -- |
| D(2) | Removal of mercury from depleted brine prior to brine resaturation using ion exchange resin. | Source reduciton | Same as D(1)(a). | No commercially available resin available for handling harsh depleted brine environment without extensive pretreatment for chlorine removal; limited resin capacity and allowable brine flow rate require very large resin beds (unacceptable economics). | -- |
| E | Conversion of mercury electrolytic cells to membrane electrolytic cells. | Source reduction | Complete elimination of all mercury-bearing streams results in elimination of K071 and K106 wastes; preliminary economics indicate acceptable payback period (~2 years). Membrane technology commercially proven. | Detailed feasibility study using definitive base costs may show much worse payback than preliminary estimate. Space requirements for auxiliary equipment may be unavailable. | 600,000 |
| (1) | Use of a washing process to reduce the level of mercury in the K071 saturated insolubles below 12 ppb, enabling this waste to be delisted. | Treatment | Simple, commercially proven process that would allow delisting of a large portion of K071 waste. Favorable payback period (~2 years). Space availability at plant is not a problem. | Potential delay in achieving EPA delisting because of lengthy procedure involved. | 380,000 |
| (2) | Same as (1) for saturator insolubles coupled with NaSH treatment process for brine purification muds, enabling delisting of the entire K071 waste stream. | Treatment | Same as (1) for saturator insolubles; additon of process for brine muds still shows favorable payback period (2.3 years). Space availability at the plant for a combined treatment process is not a problem. | Sulfide treatment step for brine purification muds is commercially unproven. Lack of proven treatment process could delay EPA delisting of the entire stream until adequate body of process data is available. | 325,000 |
| (3) | Same as (1) for saturator insolubles coupled with Vulcan Treatment Process for brine purification muds, enabling delisting of the entire K071 waste stream. | Treatment | Same as (1) for saturator insolubles. Vulcan process is commercially proven and is expected to be BDAT for K071 waste. Space availability at plant for combined treatment process is no problem. | Economics of Vulcan process for combined NaCl and KCl brine stream purification muds appears unfavorable at this time. Vulcan process may also generate higher TDS in effluent from Plant No. 1 than State will allow. | -- |

ically feasible with a payback period (based on a preliminary estimate) of about 3 years and savings of about $60,000 annually in waste disposal cost.

While treatment is not considered as WM, the audit team studied a treated option (still in the experimental stage) for solidification/stabilization of the K106 waste at either Plant No. 1 or Plant No. 2 using lime kiln or cement kiln dust. Preliminary results of tests on the solidified product indicate that this material may be able to pass the EPA delisting requirement for mercury (<12 ppb in the EP-tox leachate). Payback period for the stabilization equipment involved would be less than 6 months and savings in waste disposal costs would be $4,500 and $55,000 per year for Plant No. 1 and Plant No. 2, respectively.

Table 2 summarizes the K106 waste MW and treatment options evaluated by the audit team at Plant No. 1 and Plant No. 2. There appears to be only one technically feasible WM option (recycle/reuse) for this waste involving retorting of the K106 filter cake for elemental mercury recovery. This option appears uneconomical at Plant No. 1 and marginally economical at Plant No. 2 in terms of incremental investment payback period.

**Table 2.** *Summary of Postulated Options for Minimization of Listed Waste K106 at Plants No. 1 and No. 2*

| Option | Description | Type of Option | Advantages | Disadvantages | Potential Savings ($/yr) |
|---|---|---|---|---|---|
| (a) | Ion exchange treatment of raw wastewater for removal and recovery of mercury (applicable to both Plants No.1 and No. 2). | Recycle/ reuse | Process demonstrated commercially. Capable of achieving necessary mercury level in effluent discharged under NPDES. Mercury can be recycled to mercury cell system in ionic form without having to reclaim the metal. | Extensive pretreatment of brine required in order to safeguard resins capacity to remove mercury. Unacceptable economics. | -- |
| (b) | Retorting of K106 waste to recover metallic mercury for recycle to mercury cells at Plant No. 1. | Recycle/ reuse | Process demonstrated commercially for hydrazine-based wastewater treatment sludge. Capable of producing residue low enough in mercury to allow delisting by EPA. Metallic mercury recovered by retorting can be recycled to mercury cells. | Unacceptable economics unless recovery process throughput can be increased substantially. Plant No. 1 is applying for conditional delisting of this waste in spite of negative economics. | -- |
| (c) | Solidification/stabilization of K106 waste in an insoluble matrix followed by disposal by Plant No. 1 as a nonhazardous waste (once delisted by EPA). | Treatment | Simple, inexpensive process to install and operate (favorable payback period). Once waste is delisted by EPA, can be placed in a nearby sanitary landfill. | Process not commercially proven. Will require a large body of operational data to obtain EPA approval for delisting. | 4,500 |
| (d) | Same as (b) for Plant No. 2. | Recycle/ reuse | Process has been in commercial use in several mercury cell chloralkali plants for sulfide-based wastewater treatment sludge. Recovered metallic mercury can be recycled to mercury cells. Capable of producing residue low enough in mercury to allow delisting by EPA. Could have favorable economics (payback period) due to potentially high cost of K106 disposal once it cannot be combined with K071 waste (when the latter is delisted at Plant No. 2) for shipment to the hazardous waste landfill. | May require extensive stack emissions monitoring system for mercury and $SO_2$ emissions. | 60,000 |
| (e) | Same as (c) for Plant No. 2. | Treatment | Same as (c). | Same as (c). | 55,000 |

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***Harry F. Freeman** is the EPA Project Officer (see below).*
*The complete report, entitled "Waste Minimization Audit Report: Case Studies of Minimization of Mercury-Bearing Wastes at a Mercury Cell Chloralkali Plant," (Order No. PB 88-166 798/AS; Cost: $19.95, subject to change) will be available only from:*
*National Technical Information Service*
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