GUIDELINES FOR

CONDUCTING A

MERCURY BALANCE

May 1999

AN INTERNAL GUIDANCE DOCUMENT

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1. INTRODUCTION

1.1 PURPOSE

The Mercury Balance Task Group has prepared these voluntary guidelines for producers who wish to conduct a balance to account for mercury use in the mercury cell operation. As used in this guidance document, a mercury balance is an accounting of mercury that enters and leaves a system (a chlor-alkali facility) during a specified time.

The task group prepared this document for the following reasons:

The industry and the Chlorine Institute are committed to the principles of Responsible Care™. The Chlor-Alkali industry is responsible and accountable for the safe use of mercury in our plants and the safe use of our products. While we believe the release of mercury from the chlor-alkali industry is a very low percentage of anthropogenic and natural releases of mercury to the environment, our vision and objective is to ensure our actions do not cause harm to human health or the environment and to surpass environmental standards now and in the future. The Institute's Board of Directors has approved measures to monitor the progress towards reduction of mercury use by the industry and has specifically requested the Mercury Balance Task Group to insure these measures are adequately defined.

Conducting periodic mercury balances is one method to better understand mercury use and releases. The document does not describe reduction methods but may help the plant to target where reduction is most beneficial. Plants that utilize this information and follow these guidelines will have consistency in approaches to the balance and the data reported will be on the same basis.

1.2 RESPONSIBLE CARE

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

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

1.3 DISCLAIMER

The information in this guidance document is drawn from sources believed to be reliable. The Institute and its members, jointly and severally, make no guarantee, and assume no liability, in connection with any of this information. Moreover, it should not be assumed that every acceptable procedure is included, or that special circumstances may not warrant modified or additional procedures. The user should be aware that changing technology or regulations may require a change in the recommendations herein. Appropriate steps should be taken to assure that the information is current. These suggestions should not be confused with federal, state, provincial, or municipal regulations nor with national safety codes or insurance requirements.

1.4 APPROVAL

The Board Committee on Mercury Issues approved this guidance document on May 13, 1999.

1.5 REVISIONS

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

1.6 REPRODUCTION

2. MERCURY BALANCE PHILOSOPHY

Prior to conducting a mercury balance, the facility needs to understand what is required to make the undertaking successful. While there can be a variety of approaches to the balance, we believe there are three key ingredients that lead to any successful approach. These are commitment, time, and resources.

Total Commitment

A successful mercury balance requires commitment from people at all levels. A mercury balance requires a unified approach in the way mercury is viewed and treated in the plant. It may include but is not limited to purchasing, stores inventory, process use, identification of point sources, emissions, accumulation areas, identification of measurement points, conducting mercury inventory and mercury balance, analyzing samples, calculating and interpreting results, and troubleshooting mercury losses in the process.

Time

A balance is a snap shot based on years of data. A successful balance program requires ongoing sampling, repeated inspections, and detailed record keeping.

Resources

Sufficient resources should be allotted for mercury accounting and cell inventory purposes. Depending on the complexity of the facility, a dedicated person may be needed to coordinate the balance activities. Alternatively, the facility may use a “Mercury Balance Team” to coordinate the balance as well as reduction efforts. The team may include cross-functional disciplines including but not limited to the following:

- Site Coordinator-Team Leader
- Production Engineering
- Plant Operator

- Process Engineering
- Process Technology
- Analytical
- Responsible Care Representative
- Plant Hygienist
- Safety Engineer
- Plant Management

The balance can be useful toward reducing mercury use. The approach to the identification of losses and reduction of mercury use should include the following:

- Reliable Measurement Techniques
- Representative Sampling
- Process Surveys to identify losses
- Prioritization of areas for improvement
- Defining and implementation of removal technologies

3. COMMUNICATION STRATEGY

Communication is a cornerstone of a successful Mercury Balance. It provides the continuity to many moving pieces of the balance. **Informed people are more willing to participate cooperatively.**

A communication strategy should consider a broad audience which may include facility personnel, division and/or corporate staff, immediate community around the plant site, and environmental regulators. Implementation of the strategy should begin within the facility and be well established before expanding to external audiences.

The communication strategy should be defined and "championed" by the mercury balance team or coordinator. It may be more effective to have a separate communications team if the scope of the balance work and mercury reduction program is large.

Some companies have developed a formal "Communications Blueprint" which is especially effective in the launch phase of mercury balance and reduction programs. Appendix 9.1 provides an example of a communication blueprint.

4. RESPONSIBILITIES AND EXPECTATIONS

Because of the magnitude of the task and the number of variables involved it is desirable to have involvement from as many employees as possible. Everyone connected to the operation is responsible, to some extent, for the success of the mercury balance.

Awareness is key to the involvement of employees. Keeping people informed will help keep them involved. Many ideas and suggestions are generated outside the mercury balance team (or

coordinator). A mechanism should be in place to insure proper evaluation of all such ideas and suggestions.

Spreading out the responsibilities will also help keep people involved. Analyze the long and short term goals and assign specific tasks or action items needed to accomplish the short term goals. Set dates when the person(s) are expected to complete the items and stick to the dates. The action items as well as the short term goals should be specific and attainable. This may require periodic reassessment of priorities and short term goals.

The team leader should be a good motivator and keep the team focused by clearly stating responsibilities and expectations. Keeping a log of meeting minutes and action items can help facilitate an organized approach to the task. If the team is held accountable to well specified tasks and can readily see results then progress toward the long term goal(s) will continue.

Tracking progress is a useful tool. Keeping management and other personnel in the facility informed about how the group is advancing is important.

5. GOALS AND OBJECTIVES

It is essential to have a plan or strategy to construct a successful mercury balance. Achieving a successful mercury balance will take time. It is important to have long term goals (e.g., achieving a 100% accountable mercury balance), but it is also important to determine short term goals. A mass balance of this magnitude is not simply solved, but evolves. A key component of a successful mercury material balance is to outline goals and objectives and anticipate what is needed to reach those goals.

Although approaches will differ with the specific challenges of each site, there are four basic steps to outlining a mercury balance strategy. These are as follows:

1. List the Mercury Balance "Streams"

Establish the boundary of the system for the mass balance. Then assess operations within that boundary to determine how mercury enters the system, where it is contained in the system, where it is accumulating in the system and where mercury can escape the system. This assessment can be done by an individual who is knowledgeable of plant operations or by a diverse group knowledgeable of different aspects of the operation.

2. Determine the Known Variables

Determine what is known about each of the items on the above list. Do you have a mass value for the item? How accurate is the value? Is it a measured or estimated value? Is it supported by analyses? What is the relative size of the value? How accurate does it need to be? For example, when evaluating the hydrogen by product one might determine:

- The mass rate of the hydrogen is a measured value by an accurate flowmeter in ft^3/min.

- The mercury concentration in the hydrogen (mg/m^3) is determined monthly by an accurate test method.
- Hydrogen accounts for a significant amount of mercury leaving the system.
- It is important to be precise when determining hydrogen emissions for the mass balance.

On the other hand if you are trying to determine how much mercury leaves the system through fugitive emissions from brine clarifiers:

- The mass rate of the fumes is an estimated value in ft^3/day.
- The concentration of mercury in the fumes (mg/m^3) is determined once a year (e.g., by using an instrument such as Jerome meter).
- These fugitives account for a very small portion of mercury leaving the system.
- It is not as important to be accurate when determining these fugitive emissions for the mass balance.

3. Prioritize

Prioritize the "streams" or variables into categories. Criteria for prioritization will vary but may include the following:

- Impact on balance (largest values may have higher priority)
- Ease of data collection (some streams may be easily measured or analyzed)
- Cost (some items may be very high cost and have minimal impact on balance).

4. Set Goals

Set appropriate long and short term goals. This should be done by the entire team if appropriate. The process of achieving the long term goals may take several years. It is important to set realistic, achievable short term goals to keep focused. Short term goals should lead directly to the long term goals.

6. DIFFERENT APPROACHES

When performing a mercury balance it is important to choose the appropriate time frame to collect data. Some data can be readily obtained on a daily or weekly basis while other data can only be obtained when equipment can be made available. Some data can only be obtained once or twice a year. Some data may need to be obtained even less frequently if shown to be relatively constant and have little impact on the overall balance.

It is useful to convert all of the data to the same basis. For example, loss of mercury to the hydrogen system might be measured in pounds per week while loss to the product sodium hydroxide might be measured in grams per ton. Converting all data to the same basis will help compare relative sizes of the "streams" and help reduce errors in bookkeeping.

It is also important to choose the time frame over which the balance is performed. Establishing a basis for the data will help keep this time period flexible. Three typical time frames are monthly, semi-annually, and annually. Individual facilities need to decide the frequency for conducting mercury balances which will best meet their needs.

Monthly Balance

This type of balance may be useful as an early indicator of balance problems. Each inventory and use category is calculated except for the cell inventory. The mass balance calculations are performed and any unaccounted use is reflected in the unknown cell inventory or as a difference to balance. The cell inventory value becoming unrealistic or the difference to balance becoming large indicates an area for further investigation.

Semi-Annual Balance

When performed, this type of balance can be used to accelerate the learning process. After the mercury balance is established, the semi-annual may not be needed. This type of balance should coincide with a measurement of the cell inventory. The mass balance calculations are performed and, if all mercury is accounted for correctly, the accountability will be near 100%.

Annual Balance

An annual balance should coincide with the measurement of the cell inventory. It is essentially the same as a semi-annual balance and can be used a good marker of progress towards a complete mercury balance.

7. MERCURY BALANCE COMPONENTS

A mercury balance is an accounting of mercury entering and leaving a system during a specified period of time. A mercury balance identifies where mercury is within the system at the beginning and end of the period , where mercury leaves the system irretrievably, and compares the inventory change with the known losses.

7.1 INVENTORY

Inventory calculations appear to be the easiest and most straightforward portion of a mercury balance, but actually hold some pitfalls which are not obvious. Inventory calculations include not only the easily counted virgin mercury in the storeroom or vault, but also the actual volume of mercury contained in the cells at the beginning and end of the balance period; mercury contained in wastes which have not yet been disposed; mercury collected in sumps, traps, and portable containers; and in-process accumulations of mercury in pipes and other systems which are not

regularly cleaned or replaced. An inventory worksheet (See Appendix 9.6) is often helpful to define all areas which contribute to the total inventory and ensure that all are considered when preparing a mercury balance.

One of the most important parts of the inventory calculation is the mercury inventory in the cells themselves. As total use of mercury is decreased due to process improvements, losses become ever-smaller in comparison to the total inventory. Because the cell inventory is both the largest portion of the total inventory and one of the most difficult to accurately measure, errors in measuring the cell inventory of only a few per cent will dwarf the total losses with which they are being compared.

The utilization of radioactive mercury to measure the actual inventory of mercury in a cell is believed to be one of the more practical ways to determine the quantity of mercury in a cell or a group of cells. There are various physical methods of measuring the mercury in the cells, but accuracy is difficult to obtain unless the plant is shut down and all cells are drained.

There are some precautions which must be taken to ensure the accuracy of the radioactive tracer survey. Personnel performing the survey should be knowledgeable and skilled in tracer techniques. Complete mixing of the spike sample within each cell is vital. The point of addition and the point where subsequent mercury samples are collected must be chosen with care so that adequate mixing can occur. Operational conditions which lead to excessive amalgam or "butter" formation can trap the radioactive mercury before it can mix. Also, the physical addition of the spike samples must be done carefully to make sure that all of the spike is added and none is left behind in the vial. Leaks on cells which occur shortly after addition can cause the loss of a portion of the radioactive spike before complete mixing. Appendix 9.2 describes the methodology in more detail.

In calculating the total inventory of other parts of the system (portable tanks, waste awaiting disposal, etc.), it is important to try to measure all the factors at the same time (within a few days), so that a snapshot of the entire inventory can be constructed. When this is impossible, then extrapolation of one or a few factors to a particular date can be used. However, this should be minimized as much as possible, since it introduces a known error into the calculations.

Some facilities calculate accumulation rates for specific sub-systems, such as the wash water system or brine system, based on data collected over several instances of complete cleaning of the system. For example, the wash water system may be shut down, the lines cleaned, and all mercury from the system collected and measured. If this is done on other than an annual basis, an annualized accumulation rate can be calculated to use during those years that the system is not shut down and cleaned. Accumulation rates for in-process systems are unique and should not be extrapolated from another facility.

7.2 USE

Mercury use is the amount of mercury leaving the system during the time period of the balance. Use includes air emissions, solid and hazardous wastes, water emissions, and products and intermediates. For many facilities, most of this information will already be calculated for other reasons (e.g., Toxic Release Inventory reports, water discharge monitoring reports, product QA/QC analyses). Mercury that is added to the process and can be accounted for is not considered a use.

In reality, when a facility conducts a balance, the mercury added to a system during the time period of the balance may not equal the mercury leaving the system even after making the required adjustments for known system accumulations. The differences between these two values is called the difference to balance. One goal of conducting mercury balances is to get the difference value to approach zero.

If a facility ships material off-site for recovery, the recovered mercury should be considered a transfer to another facility unless it is physically returned. Thus, the use of mercury accounted for in that waste will only equal the amount of mercury remaining in the residue which is subsequently disposed. If a facility operates a treatment unit which accepts waste from off-site for recovery, then the recovered mercury should be considered a transfer from another facility unless it is physically returned. When doing the accounting this transfer would be handled the same way as a purchase of mercury. Sending and receiving plants should use the same number for the amount transferred.

7.3 ACCOUNTABILITY

Mercury can enter a system in only a few ways. It can be purchased, it can be transferred from another facility, or it can be returned from wastes sent off-site for recovery. There are more ways for mercury to leave. These include air emissions, water emissions, wastes sent off-site for recovery or disposal, and in products or intermediates sent off-site.

Mercury which is collected on-site from lines, temporary holding tanks, sumps, or other in-process areas is important to be measured for an accurate total inventory. It is important not to double count mercury. For example, mercury which is added to a cell from inventory, leaks into a sump, and is subsequently collected from the sump and returned into the cell is not being added twice from inventory.

7.4 CALCULATIONS AND ASSUMPTIONS

Appendix 11.3 presents a typical mercury balance form along with definitions and work sheets which can be modified for use at any facility. For example, if a facility does not send wastes off-site for mercury recovery, then those line items dealing with such wastes can be omitted.

The basic assumption of the balance form is that all mercury which leaves the facility (through emissions, products, or wastes) can be accounted for as losses. Losses plus the change in total system inventory (storage, cells, etc.) should equal the amount of mercury received into the facility. Typical calculations necessary to complete a mercury balance are presented in Appendix 9.3.

8. DATA COLLECTION

When a facility undertakes a mercury balance, the reliability and confidence of the numbers developed will depend upon the quality of the data. Although initially many assumptions may be necessary, the repeatability factor will only be improved by replacing the assumptions with collected data. The validity of data collected is dependent on critical factors such as sampling and analytical techniques. The accuracy of the analytical techniques is crucial in obtaining precise estimates of the

mercury that might be contained in relatively large volumes of material. For example, if products are recorded as being less than the specification limits, rather than an average of actual results, the amount of mercury in products could be overstated. The sampling techniques and frequency are also extremely important in obtaining representative results. For example, one grab sample from a solid waste shipment may not represent the entire shipment. Statistical methods may be used to set up a sampling program.

8.1 Analytical Procedures And Equipment

Appendix 9.4 summarizes the analytical procedures and some of the necessary equipment needed to conduct the necessary chemical analyses. Methods are summarized for liquids, solids and sludges, and gases. As noted in this appendix, some of the methods are not approved by EPA.

8.2 Data Collection Points

8.2.1 Inventory

Mercury inventory can be considered to have three components. These are storage inventory, working inventory, and inventory at accumulation points.

Storage inventory is the physical inventory of the mercury purchased, but not contained in the cells. Storage inventory includes metallic mercury in temporary storage containers and flasks. Typically storage inventory can be measured easily and accurately.

Working inventory includes all mercury in the cells, decomposers, and associated mercury piping. Properly accounting for working inventory is one of the most difficult areas to obtain repeatable quantities; for a gain or loss of several tons in this inventory may be hard to detect due to the large mass of mercury being used.

One of the major problem areas with providing a credible material balance is mercury moving through the process and collecting at accumulation points. To predict what quantities might be found in different pieces of equipment, a history of the specific quantities found should be kept and the time frame between cleaning or measurements determined. The purpose for this record is to develop an estimated rate of mercury accumulation for different process equipment unique to each facility. Experience will show where drains, cone bottom tanks and other methods of trapping mercury for recovery can successfully be utilized.

Examples of equipment where mercury can accumulate include the following:

- Cell Water System - (e.g., inlet end box piping and tanks, outlet end box piping and tanks, decomposer makeup and, soft water head tank)
- Hydrogen System - (e.g., water seal pots, piping, Adsorption carbon or other reagent)
- Caustic System - (e.g., receiver, recovery tank, piping, filters, and storage)
- Cell Room Sump - (e.g., collection tanks, sumps, and trenches)
- Fume System - (e.g., piping and adsorbing carbon or other reagent)

As data are collected, it may be found that in some systems, e.g., piping, mercury only accumulates to a certain capacity and then it moves to the next accumulation spot. This is a site specific determination based upon piping configuration, drain points, etc. For example, consider a section of pipe which slopes or bends allows only 400 pounds of mercury to accumulate before it is passed through. If the accumulation rate is found to be 0.50 pounds/day then after 800 days (800 x 0.5 = 400) the accumulation rate goes to zero. A tank, however, may hold 6,000 pounds or more before it reaches a bottom drain to be collected. At an accumulation rate of, say, 2.5 pounds/day, then 2400 days would elapse before enough mercury accumulates to be collected at the drain. In many cases it may be appropriate to leave the heel in place once the quantity is determined.

Accumulation quantities are needed only on equipment that can not be drained of mercury at the time of a material balance. Even after draining, many vessels may have a substantial heel that should be taken into account.

A site specific assessment should be made to determine the scope of piping and equipment that would be included in accumulation data. Once the scope is determined, a plan can be made on how each section of piping or accumulation point will be safely drained and weighed.

Some or most of the equipment can only be cleaned when taken out of service or during facility outages. A list should be developed so that a cleaning rotation can be followed, assuring some recovery or measurement over an appropriate time frame.

When a material balance is undertaken, all site specific equipment with its accumulated mercury becomes a part of the material balance and can influence the mercury usage calculations. In one facility's experience, with the exception of tanks, the accumulation in piping systems reaches capacity rather quickly and inventories do not change much from year to year. However, if process changes, such as tank or piping replacement, occur, they could affect the accumulation rate within the facility.

8.2.2 Wastes

Wastes are both collection and use points. For the purpose of collection, this category refers to accumulated wastes that have been weighed and sampled and are waiting recovery or shipment to proper landfill. These wastes include all of the waste as discussed in Appendix 9.3. Wastes are transferred from this collection (inventory) category to use category when shipped to disposal or retorted for recovery. Each facility should determine if there are other areas which have mercury bearing streams that were not previously accounted as a usage.

8.2.3 Use

Mercury that is not collected internally and is lost from the system because it is contained in products or lost through air, water, or solid waste streams is considered a use.

The determination of mercury in products is a relatively simple process and should be determined on a periodic basis if individual shipments are not measured. Depending on the system boundary, the measurements can be made of products going to storage or shipments from storage. It should be recognized that if the storage tanks are outside the balance, then any collected mercury from tank

cleaning should be applied to reduce usage as it has previously been charged as a loss. If the tank sludges are not recovered, then the disposed material should not be added back to usage for the same reason.

Losses to air should be reflected in the TRI data and typically include periodic analyses for hydrogen, end box ventilation, thermal treatment vents, and other monitored point source air emissions. For the cell room emissions two options are currently available. The EPA permitted housekeeping standard allowance may be used if the facility chooses this option. If the facility has developed an alternative method of determining cell room emissions, then that number can be used.

A program to determine losses in solid wastes should include all of the solid wastes generated. They are listed in Appendix 9.3. Proper sampling of non-homogeneous solids is critical for the measurement of the mercury content.

Mercury to surface water should be calculated based on discharge monitoring report data.

9. APPENDICES

9.1 COMMUNICATIONS BLUEPRINT

(This is an example of a formal communications blue print that as been formatted to be effective particularly in the launch phase of mercury balance and reduction programs.)

PROJECT NAME: MERCURY BALANCE

Communications Objectives

What do you want to accomplish?

Examples:

Create an understanding of what a mercury balance is and why it is important.

Change the culture from one of compliance to one of prevention.

Inform employees of the "who, what, when, and how" in regards to mercury balance.

Target Audiences

Describe the audience(s) you want to reach in as much detail as possible.

Examples:

Primary - Facility employees and their families

Secondary – Division and corporate employees and their families

Tertiary – External audiences such as local community and regulatory groups

Audience Needs/Wants

Explain what each target audience is most interested in learning about your project

Example:

Why is this important and why I should actively engage and support all efforts

Communication Strategy

Define the main message to be communicated.

Communication will (verb-convince, persuade, etc.) the (target audience) that (mercury balance, mercury reduction) will provide (statement of objective or benefit).

Example:

Communication will convince the division population that mercury accountability and mercury reduction is necessary for the future of our business and a condition of employment.

Tone

Describe the tone and or feeling of the communication using words such as exciting, new and innovative, serious, urgent etc.

Examples:

Serious commitment

Emotionally engaging

Create a sense of responsibility

Support

List all supporting details to your communication strategy

Examples:

Public perception and regulatory agencies are demanding change

Chlorine Institute has formed a Mercury Issues Management Subcommittee.

Desired Result/Response

After reading/hearing/seeing this what do you want me to do or how do you want me to feel?

Examples:

Understanding and commitment

Enthusiastic support

Direct participation

Mind set change

Level Of Commitment

Describe the outcome you are seeking (enthusiastic compliance, compliance, by the book, forced compliance etc.)

Example:

Enthusiastic Engagement: We are willing to extend the outage to collect mercury data. We establish an open policy on information.

Suggested Format For Communication

Brochure, video, CD ROM, team meetings, Internet, Intranet, E-mail etc.

Examples:

E-mail

Newsletter

Linked to critical numbers

Posters

CD ROM

Team meetings

Project Timing/Milestones/Budget

Key dates, key events, and financial and human resources allocated

Examples:

July 1, xxxx - Complete briefings for employees and their families

January 1, xxxx - Complete radioactive isotope measurement of the cells

9.2 ESTABLISHING MERCURY INVENTORIES AT CHLOR-ALKALI PLANTS BY ISOTOPIC DILUTION OF RADIOACTIVE ^{203}HG

This appendix was prepared by RadChem Services, Inc.. The Institute and the mercury cell producers acknowledge with our appreciation this voluntary contribution by RadChem. By including this methodology in this guidance document, the Institute is not endorsing the preparer. Individual facilities that wish to utilize contractors with radioactive measurement expertise should determine which can best fill the needs.

9.2.1 Establishing Mercury Inventories in Process Cells

Mercury-203 is used for conducting mercury inventory studies of electrolytic cells. A millicurie (or mCi) is a measure of radioactivity; it is that amount of radioactive material that chlor-alkali plants based on isotopic dilution. The overall procedure contains the following major steps:

^{203}Hg is produced in a nuclear reactor, typically by irradiation of HgO; radioactive mercury is converted into elemental mercury metal, diluted to the desired concentration, and made up into spikes containing 3-4 millicuries[a] of ^{203}Hg in 60-100 grams of Hg;
the radioactive mercury spikes are added to each process cell of the chlor-alkali plant during a period of stable operations in which no (or at least minimal) additions or losses of mercury occur; each spike is allowed to mix with the mercury in each cell and to equilibrate with all of its chemical and physical forms, after which samples are collected at approximately 24 hours and 48 hours; the radioactivity of the diluted sample is measured and compared to a background sample pulled just before the spiking to determine the dilution that occurred; the amount of mercury that was required to produce the observed diminution in net radioactivity is the amount of mercury in each cell; the amount of mercury is calculated and reported with an uncertainty based on radioactivity counting statistics; the specification for the method is ± 0.5% per cell measurement, but the actual uncertainty in the measurement is calculated and is usually less than ± 0.3% (this would yield an uncertainty of 15-25 lb. for a 5,000 lb. cell). Since the uncertainty is randomly positive or negative, overall plant total is probably ± 0.1% or better.

The radioactivity dilution procedure thus provides a "snap shot" of the amount of mercury in each cell for a one- or two-day period only because these are active processes during which various amounts of mercury can be lost to process streams and these amounts are replenished periodically. The 1-2 day dilution procedure is thus a compromise between the time that the plant can be expected to maintain stable operations and an assured mixing time. Although recent studies have shown that thorough mixing usually occurs in a few hours, anomalies may occur in one or more cells in which thorough mixing may not be achieved for a few days and it is necessary to collect an additional sample several days later. The 48-hour sample has provided very reliable data for many years as long as plant operations were stable, and the 24-hour sample has provided a reliable backup for checking the measurement. Once the "snap shot" inventory is established, the amount of mercury on hand is maintained by inventory control of new mercury added to processes, losses to waste management, etc.

9.2.2 Plant and Service Laboratory Roles

Close cooperation between the service laboratory and senior plant management is essential for a good inventory study. The laboratory must prepare accurate spikes and perform precise measurements both of which are checked with quality controls. And since plant operations are dynamic processes even during the period of the dilution study, the plant needs to stabilize operations as much as practicable because even the best laboratory measurement cannot overcome plant conditions that significantly affect and/or alter dilution of the radioactive spike once it is added to the cells. The service laboratory will, by a series of standard dilutions of the stock material, check and recheck that the laboratory technique is better than ± 0.5% and that the only difference in the samples from the mercury cells and that of the standard dilutions performed in the laboratory is the amount of dilution that occurred in the cell over the sampling period. In order to assure that the collected sample best represents dilution in the cell it is essential that the plant be stabilized and operated carefully during the study period by collecting all residual mercury and topping off all cells just prior to the spiking; to the extent practicable, no mercury should be added to the cells and losses

[a] A millicurie (or mCi) is a measure of radioactivity; it is that amount of radioactive material that undergoes 3.7×10^7 transformations per second, yielding emitted radiation in each transformation.

to process streams should be minimized for at least 48 hours and preferably for 5-10 days following the spiking; if mercury is added, however, it should only be done for essential plant operations, and it should only be new mercury, or at least from stock accumulated prior to the spiking; i.e., no radioactive mercury should be added for the 5-10 day study period; any mercury collected from wastes or process streams for 5-10 days after spiking should be carefully inventoried and records kept of changes in these accumulations; records should be kept of any additions to or losses from each cell individually in case it is necessary to resample a cell(s) after the 48-hour period to address any anomalies; and plant personnel need to be prepared to collect an additional follow up sample to assess identified anomalies for 4-10 days after spiking occurs.

Achievement of these conditions for a plant requires senior management attention by both the plant and the service laboratory to assure that good results are obtained and/or any anomalies are addressed. Mixing studies have shown that the radioactive mercury mixes in a few hours. However, anomalous conditions occasionally arise that indicate uncertain mixing. These situations require a follow up sample to resolve, and for this reason, it is important to understand as much as practicable the performance of each individual cell in the intervening period. The service laboratory and plant personnel can identify the anomaly, but resolving such situations may either require maintaining stable plant conditions and detailed records for a few days until laboratory results are obtained or on-site measurements.

9.2.3 Procedure

Each mercury spike contains about 200 grams of mercury and has about 3-4 millicuries of ^{203}Hg in it and a similar but variable amount of ^{197}Hg contaminant, depending on the amount of decay prior to shipment. Since ^{197}Hg, an electron-capture nuclide, has a lower gamma energy of 77 keV that occurs in 18.7% of transformations, its hazard is well controlled by the procedure for ^{203}Hg. Mercury-203 emits a 279 keV gamma ray which allows it to be counted to establish the amount of radioactivity in prepared spikes and diluted samples; the 279 keV gamma ray is, however, of relatively low energy making it easy to shield and self absorption by dense stable mercury means that radiation levels are minimal once it is diluted in process cells. The radiation exposure level of each spike vials is about 250 mR[b] /hr at contact and less than 2 mR/hr at one meter.

A radioactive materials license is required for conducting mercury inventory studies at each plant since a several hundred mCi[c] of ^{203}Hg are used. The license is issued by the State if it is an agreement state for the Nuclear Regulatory Commission; if not the license must be obtained from one of the Regional Offices of the U.S. Nuclear Regulatory Commission. The license-authorization for a given plant can be issued to the plant owner but is typically held by the investigator providing and processing the radioactive mercury spikes and samples. The license mainly governs the receipt and spiking operations, which generally require less than half a day each time spiking occurs. Once the ^{203}Hg is in the process cells, the radiation exposure rate is non-detectable outside the mercury cells and there is no radiological hazard to workers or the public. The dilution in stable mercury is such that the radioactivity concentration will be below exempt concentration limits (Code of Federal Regulations {10CFR30.70 - Schedule A}) in about 90-100 days.

[b] mR is an abbreviation for milliroentgen and is roughly equivalent to a millirem of radiation dose (see note e).

[c] mCi is an abbreviation for millicurie (see note a).

Investigators who conduct such studies are required by regulations to demonstrate expertise to handle and control the radioactive mercury; they also require expertise in measuring radioactive and stable mercury in a variety of samples, including ^{203}Hg spikes in order to provide accurate and reliable inventory data. These requirements are best met by professionals in chemistry, radiochemistry, health physics, and neutron irradiation procedures. Since such practices are highly regulated it is especially important that investigators have expertise in radiation control, licensing and inspection, and transportation of radioactive and hazardous materials.

The mercury cell spikes are made up in the supplier laboratory and placed into rigid polycarbonate vials, each of which is sealed in a plastic bag, and shipped in a DOT-approved wood and metal case. The package is received and opened by a formal procedure which, according to the radioactive materials license, is required to be done by a person that has received training in the procedures. A wipe test of the exterior surface of the box is first done to verify there has been no release of radioactivity during shipment. This is done by reading the swipe test with a Geiger-Muller (GM) counter equipped with a thin-window pancake probe to assure that the count rate is less than 2,200 dpm per 100 cm^2. If contamination is detected, the project person will determine, in consultation with the radiation safety officer designated in the license, whether to perform decontamination or arrange for other spikes to be supplied. This procedure has been followed at chlor-alkali plants for some 20 years now with no measurable release of radioactivity.

The spiking of the mercury process cells is performed by a trained investigator, again in accordance with formal procedures submitted with the license application. After verifying that it is appropriate to open the box, it is then opened and each plastic bag is inspected to assure that no leakage has occurred. The spike vials are then removed from the plastic bags, reinspected, and replaced in the shipping box (which provides radiation shielding) and taken to the process cells. Cell spikes are required to be in the view of and under the control of the trained investigator at all times from the time the box is opened until the final spike is added to the cell. In essence, the ^{203}Hg spike material only exists outside of the shipping container in the plant in concentrated form for a few (2-6) hours for each inventory study.

A representative sample is taken from each cell at 24 and 48 hours after spiking at a location where good mixing is assured. On occasion, samples may also be collected at intermediate times for a few cells to determine the mixing pattern for cell types at a given plant. These samples are collected and prepared for shipment, along with the spent spiking vials, to the laboratory in the shipping box which was used to transport the samples to the plant. At this time the radioactivity in the mercury is less than 1.0 nanocuries per gram; i.e., about half the limiting concentrations in transportation regulations (Code of Federal Regulations {(10CFR71.10}) and can be shipped without regard to its radioactivity.

9.2.4 Radiation Exposure

As a precaution, dosimetry is provided to the person doing the spiking. This consists of a personal dosimeter[d] worn at the shirt collar; however, experience has shown no detectable exposure for this procedure. A ring badge is also worn by the person doing the spiking because hand exposure is the

[d] Personal dosimeter is a thermoluminescent dosimeter (TLD), film badge, or ring badge worn by a person to measure radiation dose received; it is an integrating device that records radiation received.

most likely; experience has demonstrated that exposure of the hands is less than 25 mrem[e] (0.05% of the annual limit) for the total procedure. Based on this, a plant employee may, from time to time, assist by removing spikes from the shielded container and handing them to the person doing the spiking. He, too, would wear a ring badge. From a safety point of view, this is desirable as it eliminates some maneuvering between the cart and the spiking point while holding onto the spikes, and also reduces the total time spikes are handled. Such helpers have received minimal exposure. The plant employee is given on-the-job instruction, and handles the sealed ^{203}Hg spikes only under the supervision of the trained investigator doing the study. The plant person is of course already skilled in working with mercury and recovering any spills so s/he contributes significantly to the overall control of mercury in the plant. No other employee comes into contact with the radioactive material during the process of spiking the cells.

It is not necessary to establish a restricted area for spiking operations although a buffer area is established to provide efficient access to the cells during spiking operations, a procedure that also optimizes control of any spills that might occur. Such housekeeping details do not interfere with plant operations since they exist for only a few minutes at any given cell. Airborne radioactivity concentrations are orders of magnitude below regulated levels because plant controls on stable mercury ensure that any ^{203}Hg entrained in airborne mercury is rapidly diluted to minimal levels. Radiation levels for shipment containers will always comply with Part 71 transportation and package requirements, and when spikes are outside of packaging the radiation levels are well within Code of Federal Regulations {10CFR20} criteria for unrestricted areas.

Radiation dosimeters are often provided to document radiation doses employees might receive from the radioactive mercury after it has mixed in the cells. These dosimeters might be worn by a principal operator (or other person selected by plant employees) or posted for several weeks in an area of concern (an assembly or rest area, for example). All such measurements have yielded non-detectable exposures, but are believed to be appropriate for providing employees with information on potential radiation exposure.

9.2.5 Laboratory Measurements

Two types of laboratory measurements are required. First, it is necessary to assure that prepared spikes contain the requisite activity for reliable measurement once diluted in the mercury cells. The radioactive mercury received from the reactor irradiation is purified, diluted in stable mercury, and mixed for several hours to obtain a mass of mercury with uniform radioactivity concentration. The ^{203}Hg spikes are weighed out from this stock in amounts (or spikes) that contain 3-4 millicuries of ^{203}Hg. It is essential that each spike contain same amount of ^{203}Hg; i.e., that uniformity exists between spikes. The degree of uniformity is determined by diluting several (usually 5 to 10) random extractions from the mixed stock with carefully determined amounts of non-radioactive mercury. These precise dilutions constitute “standards” that are used to assess that each spike is uniform by measuring the activity of each standard and determining the standard deviation of the measurements; if it exceeds ± 0.5%, the batch is rejected and the stock is remixed before spikes are prepared. This process aggregates all the uncertainties that could occur due to laboratory technique and assures that

[e] mrem (for millirem) is a unit of radiation dose; one mrem is 0.001 rem, which is 100 ergs of deposited energy in a gram of tissue by gamma rays and beta particles. The dose to a person from natural background is about 100 mrem per year.

the only difference that exists in measurements of the sample taken from the mercury cells is the dilution that occurred in the cell.

The second type of laboratory measurement occurs for samples taken after the radioactive spike has mixed in the mercury cells. These samples are measured in the laboratory by weighing out a standard amount for counting in a sodium-iodide well with associated electronics. Counts are measured for a region-of-interest that encompasses the primary gamma energy emitted by ^{203}Hg for 10-20 minutes to obtain good counting statistics. These carefully determined measurements are then compared to the diluted standards of the same stock material used to prepare the spikes, thus establishing the amount of dilution in each process cell and the amount of mercury. Counting statistics are computed for each measurement, the background activity is subtracted, the total amount of mercury is summed, and the overall uncertainty in the plant inventory is calculated. These data are reported to the plant in draft form to identify any anomalies that indicate samples that should be recounted, or any cells that should be resampled or re-spiked for a follow up measurement. The detailed measurement data are also provided to the plant for statistical analyses, etc.

9.2.6 Radiation Safety Program - Mercury Inventory Studies

An on-site radiation protection program is carried out while performing mercury inventory determinations to preclude any spills of the radioactive cell spike that may pose potential exposure to persons or the environment. No special handling facilities are required at the plant since the ^{203}Hg spikes are received already prepared. Packages are surveyed and opened in a clean area with appropriate considerations for preventing radioactivity contamination should upset conditions exist due to shipping and handling. The amount of ^{203}Hg handled at any one time is kept to a minimum, and each ^{203}Hg spike exists outside of shielded containers for only a few minutes. The radiation level outside the spiked cells is non-detectable because the ^{203}Hg added to each cell is rapidly diluted in about 10-12,000 pounds of mercury and is thus below 1 nCi^f/g soon after spiking occurs. Since mercury is a dense element, it provides considerable self shielding of the 279 keV gamma rays emitted by ^{203}Hg (or 77 keV from ^{197}Hg). The activity is allowed to decay in the cells where it reaches concentrations exempt from regulation in about 90 days.

Controls imposed by the plant for stable mercury assure control of any potential radiological conditions for both routine and non-routine operations. The mercury spikes are packaged in 50-ml polycarbonate centrifuge tubes which are resistant to breakage. However, if a spill occurs (either due to breakage or dropping an open tube) during the spiking operation, the first concern would be to contain and absorb the mercury itself, and meeting guidelines for stable mercury also controls the diluted ^{203}Hg. Chlor-alkali plants are quite well prepared to deal with mercury spills since they typically have spill kits, specially designed vacuum cleaners, and specialized procedures for recovering mercury. After containing and recovering the mercury by a vacuuming and washing procedure, the spilled area would be surveyed for radioactive contamination. If the contaminated area yields more than 550 counts per minute (based on NRC guidelines and the detector efficiency and geometry of the GM used), then another cleanup would be done. The recovered ^{203}Hg and accompanying mercury is returned to the system. The mercury vacuum is also surveyed to be certain that there is no exposure due to residual ^{203}Hg still in the machine.

9.2.7 Radioactivity Contamination of Products

Based on typical mercury content in products, radioactive contamination of products due to the use of this procedure would be below any regulated concentration or any potential concentration of concern for consumers, and is virtually unmeasurable.

9.2.8 Radioactivity in Waste

No radioactive waste is directly generated by the work. However, as a result of normal operations of the chlor-alkali process, small amounts of mercury become chemically contaminated, and these are removed for recycling or disposal. This material will contain some radioactivity. However, the activity of ^{203}Hg in waste generated at the time of highest activity (right after a spiking event) should be below the exempt concentration (2×10^{-4} μCi/g) as stated in 10CFR30.70 - Schedule A.

9.3 MERCURY BALANCE FORM

Calendar Year _____

Mercury in Hydrogen
Sold Off-Site _____
Burned to Make HCl _____

Burned in Boilers _____
Vented to Atmosphere _____
Other _____ _____

Mercury in Products
Caustic Products _____
Chlorine _____
Spent H_2SO_4 _____
Bleach _____
Sodium Hydrosulfite _____
Other _____ _____

Mercury to Air
Cell Room Fugitives _____
Fume System Vent or Outlet End box Vent _____
Thermal Treatment Vent _____
Other _____ _____

Mercury to Water
Treatment Effluent _____
Non-Treated Effluent or Other Monitored Streams _____
Rainwater Runoff _____

Mercury to Solids (Generated On-Site:)
Thermal Treatment Ash (total) _____
D009 Debris _____
Hazardous and Non-Hazardous Solids to Landfill _____
Solids to Off-Site Treatment and Recovery _____

Usage
Total Mercury Accounted for Leaving Process _____

If You Recover Mercury from Off-Site Wastes:
Less Thermal Treatment Ash (from external sources) _____
Less Recovered Mercury (from external sources) _____

If You Send Wastes Off-Site for Recovery:
Less Mercury Recovered from Wastes Sent Off-Site _____

Total Annual Usage Accounted For _____

Summary
New Mercury Added to Process _____
Total Annual Purchased _____
Inventory Increase (Decrease) (see worksheet) _____

Unaccounted for Losses / Gain _____
(Difference to Balance)

9.4 DEFINITIONS / DESCRIPTIONS FOR THE MERCURY BALANCE FORM (APPENDIX 9.3)

Mercury Use = New mercury purchases +/- changes in storage inventory

+/- Identifiable process inventory changes

+/- Transferred mercury from/to another facility

+/- Recovered mercury (in a thermal treatment unit) from solid wastes from another site

Note - for the last two items, the same figures should be used by the sending and receiving facilities.

Mercury in Hydrogen:

Sold Off-Site – Mercury in hydrogen which is sold and shipped off-site as a product. The customer may use the hydrogen as a fuel or as a feedstock to another process.

Burned to Make HCl – Some facilities use their hydrogen to manufacture HCl at a co-located site or another unit on-site. This is the amount of mercury in the hydrogen which is used to manufacture HCl.

Burned in Boilers – Mercury in hydrogen used as a combustion fuel on-site.

Vented to Atmosphere – Mercury in hydrogen which is directly vented to the atmosphere.

Other – Mercury in hydrogen used in some other manner not covered above.

Mercury in Products:

Caustic Products – Sodium or potassium hydroxide which is sold and shipped off-site as a product. Do not include internal use here.

Chlorine – Product chlorine shipped off-site.

Spent H_2SO_4 – Spent sulfuric acid which is shipped off-site for use by a customer as a feedstock, neutralizing agent, etc. Do not include spent sulfuric which is used internally for neutralization, etc.; this will end up double counting mercury. Note - some sulfuric acid that is purchased for use in the process may contain mercury. Facilities should determine whether this source of mercury is significant enough to be accounted for in doing the mercury balance. If so, this mercury should be considered an addition to the process when doing the mercury balance.
Bleach – Bleach shipped off-site to a customer. Do not include bleach which is treated and discharged as waste water; this will double count the mercury.

Sodium Hydrosulfite – Product shipped off-site to a customer.

Other – Other products, such as brine, which may be shipped off-site to a customer. Do not include product hydrogen or HCl; these are included in the hydrogen category. Do not double count any mercury.

Mercury to Air:

Cell Room Fugitives – Mercury loss assumed based on NESHAP standards equal to 1,045 pounds per year or a calculated number based upon measurements using air flows or cell room turnover calculations.

Fume System Vent or Outlet Endbox Vent – Total reported mercury lost to atmosphere as a result of operating a cell room vacuum scrubbing system or outlet endbox vent system.

Thermal Treatment Vent – Total reported mercury lost to the atmosphere due to operating a scrubber system for a permitted thermal treatment unit.

Other – Other losses to air not included in the above listings that may be specific to a plant. Includes the neutralizer vent. May also be a centralized vacuum vent if not otherwise captured.

Mercury to Water:

Treatment Effluent – Final effluent discharge; includes treated effluent from process wastewater and other discharge streams from the mercury cell plant; does not include stormwater discharge or discharge streams from co-located plants.

Non-Treated Effluent or Other Monitored Streams – Other streams which may contain mercury, but are not final effluent discharges from the mercury cell plant; does not include stormwater discharge; may include a discharge stream from a co-located plant which may contain mercury. Do not double count any mercury; if an internal stream is monitored, but it flows into a final effluent stream which is counted above, do not count the internal stream.

Rainwater Runoff – Stormwater discharge, final effluent; includes stormwater which is discharged under an individual industrial NPDES permit; also includes stormwater which is discharged under a general permit or discharges exempted from permitting (sheet flow, as opposed to point flow). If this stream is not monitored, this value may need to be estimated.

Mercury to Solids (Generated On-Site):

General Assumptions – This is mercury included in solid wastes which are generated on your plant site. This includes all solid wastes which are generated on-site and treated on-site, wastes which are generated on-site and shipped off-site for disposal or for recovery, and residue from on-site treatment of wastes which are generated both on-site and off-site.

Thermal Treatment Ash (total) – This is the mercury contained in the residue from a thermal treatment unit. This residue comes from treatment of wastes generated on-site as well as wastes generated off-site, either from a sister plant of the same company or from another company. This will not double count mercury; see the usage section below.

D009 Debris – Mercury contained in contaminated debris under the debris rules; usually disposed in a landfill either on-site or off-site. This will probably have to be estimated, as it is very difficult to analyze debris.

Hazardous and Non-Hazardous Solids to Landfill – Solid wastes, usually fairly homogeneous, which are disposed in a landfill, either on-site or off-site. They may be either hazardous or non-hazardous under RCRA. Includes landfilled residue from alternate K106 treatment.

Solids to Off-Site Treatment and Recovery – Solid wastes sent off-site to a facility for recovery of mercury. This is included in the total mercury accounted for leaving the process, but a usage credit can be claimed for the amount of mercury which is recovered; see the usage section below.

Solids Checklist – Attached is a list of solid wastes which should be considered when collecting the information for the Mercury to Solids section.

Usage:

General Assumptions – Usage calculations will fall into one of 3 categories, depending on whether your facility sends material off-site for mercury recovery, accepts material from off-site for mercury recovery on-site, or does neither. If your facility does neither, then the total usage accounted for will equal the total mercury accounted for leaving the process (the sum of the individual sections at the top of the survey form). If your facility ships material off-site for recovery, then the usage accounted for includes the total mercury shipped off-site in the waste, less a credit for the amount of mercury recovered. Thus, your usage will only equal the amount of mercury remaining in the residue which is subsequently disposed. If your facility operates a treatment unit which accepts waste from off-site for recovery, then your consumption will include the mercury accounted for leaving the process (including mercury in the thermal treatment ash for all wastes), less the mercury recovered from off-site wastes and less the mercury in the ash from external wastes. This separates mercury from internal wastes and mercury from external wastes. Sending and receiving plants should use the same number for the amount recovered.

Total Mercury Accounted For Leaving the Process – Sum of individual sections listed in top portion of questionnaire.

Thermal Treatment Ash (from external sources) – Mercury in residue from recovery operations on wastes received from off-site. This includes wastes from another facility in the same company.

Recovered Mercury (from external sources) – Mercury recovered from wastes received from off-site and reintroduced into your own process.

Mercury Recovered from Wastes Sent Off-Site – A usage credit taken for mercury which is recovered from your wastes by another facility; the mercury itself is not returned to your facility. This is a "paper" credit to avoid double counting of the same mercury by two facilities.

Total Annual Usage Accounted For – Calculated usage on based on whether your facility sends material off-site or receives material from off-site for mercury recovery.

Summary Section:

New Mercury Added to Process – Mercury removed from storage (vault or storeroom) and added to cells; does not include mercury recycled or collected from other portions of the process (this has been counted already when it was originally removed from storage and added to the process).

Total Annual Purchased – Mercury purchased or received from off-site; includes mercury received from a sister plant which has closed, even if the mercury is not purchased.

Inventory Change – Change in total inventory of mercury on-site. (See inventory worksheet for details.) Inventory includes:

- Cells
- Storeroom or vault (virgin)
- Accumulation tanks (temporary holding tanks or other vessels)
  Working inventory
  In process (must have a basis for calculating – assume no process inventory change if not doing process inventory calculations)
- Accumulated wastes (awaiting disposal)

Unaccounted for Losses/Gain – Difference between accounted for usage + inventory change and the amount purchased or received. This value is referred to as the difference to balance.

9.5 SOLIDS CHECKLIST FOR THE MERCURY BALANCE FORM (APPENDIX 9.3)

BRINE TREATMENT SOLIDS - Solid material that results from brine treatment. Should include carbonate and hydroxide sludge formed from chemical treatment and precipitation of brine impurities. Filter aid or media (sand, gravel, etc.) should also be included. Waste from dissolution of rock salt should be included if it comes in contact with mercury contaminated brine.

PIPE, TANKS, VALVES (PROCESS EQUIPMENT) - Process equipment that has been removed from service for disposal and has come into contact with mercury or mercury contaminated fluids. Consideration should be given to equipment that had been rubber-lined, even if the rubber has been removed. Equipment that has been thermally treated for mercury removal should be included in the "Thermal Treatment Solids" category.

EXCAVATION MATERIALS (SOILS) - Any material that comes from an excavation in a potentially mercury contaminated area. This includes concrete that may have been removed from the site.

GLOVES, BOOTS, ETC. - Expendable maintenance materials that may be contaminated with mercury. (Not associated with process equipment.)

UNTREATED K106 - Solid material that comes from treatment of wastewater to remove mercury. This includes filter aid associated with the removal of these solids from the waste stream.

ALTERNATE K106 TREATMENT SOLIDS - Solids remaining after removal of mercury from K106 material by any means other than thermal treatment.

CONCRETE - Concrete material that comes from a structure demolition at a potentially mercury contaminated site.

EXPENDABLE CELL MATERIALS, RUBBERLINING, ETC. - Solid material to be disposed resulting from the cell renewal and cell maintenance activities. Items such as cell covers, copper stem gaskets and O-rings, old rubber lining removed from lined steel cell parts, and any other expendable cell parts removed for disposal.

DENUDER GRAPHITE - Packing material from the cell denuder or decomposer removed for disposal. (Normally, this material is treated to remove mercury.)

ACTIVATED CARBON - Spent activated carbon material that is used to remove mercury from wastewater, from ventilation air, from hydrogen, or any other activated carbon that could potentially be contaminated with mercury.

CAUSTIC FILTER SOLIDS - Solid material that comes from the operation of filters in the product caustic stream. This includes any precoat material used in normal operation of the filters. Note - broken filter elements and other pieces of equipment removed for disposal would be considered "process equipment".

MOLECULAR SIEVE MATERIAL - Would include material used to dry mercury contaminated hydrogen or used in contact with mercury containing liquid streams.

SAND - Recovered from sump; used as filter media for mercury containing liquids used as surface blasting or mercury contaminated surfaces or otherwise known to have been contaminated.

DEMINERALIZER RESIN - Material used in mercury removal or in contact with mercury contaminated liquids.

TANK CLEANING - Solids removed when cleaning tanks that have contained mercury cell products or process materials. Liquids are assumed to be treated for mercury removal and will be collected under other categories.

TOWER PACKING - Packing materials (rings, saddles, mesh, etc.) of plastic, ceramic, metal that has been in contact with mercury containing gases or liquids.

SUMP CLEANING - Solids removed from sumps containing or exposed to mercury contaminated materials.

OIL & ABSORBENT - Material that has been in contact with mercury contaminated surfaces.

FIBERGLASS & WOOD - Material that has been in cell rooms or allowed to be contaminated by contact with mercury containing liquids.

USED MERCURY FLASKS - Only those flasks being disposed of. Empty flasks returned to vendor can be disregarded as long as empty.

SANDBLASTING MEDIA (SPENT) - Sand, talc, walnut shells, glass beads, etc. that have been used to clean mercury contaminated material and equipment.

CENTRAL VACUUM SYSTEM SOLIDS - Material generated by cell room vacuum systems. It would include filters.

FLOOR SWEEPINGS - Cell room floor sweepings or areas where mercury containing liquids could spill and later evaporate.

9.6 INVENTORY WORKSHEET

	Beginning Inventory	Ending Inventory	Inventory Gain / (Loss)
I. Cells	_____	_____	_____
II. Mercury Storage			
III. Misc. Collection & Accumulation			
A. Traps, Sumps, Tanks			
B. Portable Tanks or Containers			
C. Fume System or Outlet Endbox Vent System			
D. Hydrogen System			
E. Hypo System			
F. Wash Water System			
G. NaOH or KOH System			
Subtotal Miscellaneous			
IV. In Process			
A. Brine System			
B. Wastes for Retort			
C. Retort			
V. Accumulated Wastes			
A. K106			
B. D009			
C. K071			
D. In Recycle Process			
Subtotal Stored Wastes			
TOTAL INVENTORY	_____	_____	_____

9.7 Analytical Procedures And Equipment

Liquid Samples

- Flameless Atomic Absorption: EPA Method #245.1

The sample is digested with acidic $KMnO_4$ to oxidize all mercury to the +2 state and minimize interferents in the cold-vapor detection system. Persulfate is added to the solution to ensure oxidation of organic compound that may interfere with the analysis and to oxidize any organo-mercury compounds that may be present. After the digestion, excess $KMnO_4$ is reduced by the addition of hydroxylamine hydrochloride in the solution is discharged. The digested sample is transferred to a BOD bottle, a solution of stannous chloride is added to reduce the mercury to elemental mercury, and the solution sparged with argon or nitrogen. The sparged gas is passed into a precalibrated atomic absorption detector, which measures the amount of light of wavelength 253.7 nmb absorbed by the vapor.

If the mercury content of the solution is high, a measured aliquot of the solution may be injected into a mixing vessel containing a solution of stannous chloride. This mixing vessel is then sparged with argon or nitrogen and the gas passed into the cold vapor detector described above. ***The injection method is not approved by the EPA***.

The actual detection limit of either method can be varied by sample size, detector path length, adjustments of detector sensitivity, and recorder expansion. Using a 100 ml sample, the detection limit cited by the EPA is 0.2 ug/1 (ppb). Potential interferents include chlorine, organic compounds which can absorb at 253.7 mm, sulfides, and copper.

- Atomic Fluorescence Detection ***This method is not currently approved by the EPA for analyses, but is under evaluation.***

The sample is acidified, oxidized, and digested in the same fashion as described above. The sample is then sparged into a mixing vessel, where it is mixed with stannous chloride and the gas phase passed into a precalibrated detector where the mercury vapor is excited by light of 253.7 nm

The fluorescent light is analyzed at 90^0 to the gas flow. The detection limit is defined by sample size. Using a 100 ml sample, it is 1 ng/1 (1ppt) under clean room conditions. It is estimated to be 10 ng/1 (10ppt) in routine analytical applications. Potential interferents include chorine and sulfur dioxide, both of which absorb the fluorescent radiation at 253.7 nm.

Solids and sludges

- EPA Method #245.5

A weighed portion of the solid or sludge is dissolved in aqua regia. The resulting

solution is treated as in Method 245.1 for the analysis of the mercury in the solid.

- Drying of the sample is recommended, but must be done with caution to avoid loss of mercury.
- This method applies only to mercury compounds which are soluble during the dissolution step.
- The detection limit is subject to the same parameters as in Method 245.12.

- X-Ray Fluorescence Analysis ***This method is not approved by the EPA for effluent or solids analyses.***

The solid is analyzed directly by a precalibrated X-Ray fluorescence spectrometer. There is no sample pretreatment.

- This analysis is limited to the surface of the material. Penetrating power of the x-rays will be on the order of microns in most solids. This means that multiple analyses should be conducted on any given sample. The exact number of analyses will be a function of sample size and/or homogeneity.
- Commercial analyzers are either bench analyzers, which are limited to samples which will fit into the sample container (approximately 100 cm in diameter), or portable, which will analyze samples of any shape or size.
- The detection limit is approximately 4 ppm using any energy-dispersive analyzer.
- There are not interferents if multiple X-Ray emission lines are used for the analysis.

<u>Gases</u>

There are no specific EPA methods for the analysis of mercury in gases. The preferred method is dissolution of the mercury in an acidified solution of oxidant.

- Absorption

A measured volume of the gas is passed through absorbers which will dissolve or absorb the mercury present in the vapor. Accepted absorbers are acidified $KMnO_4$ solutions, silver wool, or a gold foil. The acidified $KMnO_4$ solution is then treated in accordance with EPA Method 245.1 for solutions. If silver wool or gold foil is utilized, it is heated to 400^0 and the vapors analyzed by either atomic absorption or atomic fluorescence.

- The detection limit is subject to the same parameters as described above. As fluorescence detectors are 100-1000x more sensitive than the atomic absorption, much less sample is required.
- Silver wool and gold foil are limited to analysis for elemental mercury.

- Impingers

A measured volume of gas may be passed through precalibrated impingers containing absorbent solution. The analysis is based on color changes within the solution.

- The detection limit is much higher for this type of analyzer and dependent on the indicator solution used.

- Electrochemical Measurements

A measured volume of gas may be passed over a gold film. As mercury is absorbed on the gold film, the electrical resistance of the film is quantitatively increased. This method of analysis is valid only for elemental mercury. Information on specific interferences should be obtained from the instrument manufacturer.