

**GUIDELINES FOR  
TECHNOLOGIES TO REDUCE  
MERCURY IN SODIUM  
HYDROXIDE**

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**April 2000**



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**THE CHLORINE INSTITUTE, INC.**

**INTERNAL DOCUMENT**

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## 7. INTRODUCTION

### 1.1 Purpose

The Mercury in Sodium Hydroxide Task Group has prepared these voluntary guidelines for producers who wish to assess technologies to reduce further the levels of mercury in sodium hydroxide. The information developed in these guidelines are also believed to be applicable to potassium hydroxide produced in mercury cell chlor-alkali facilities. Levels of mercury in sodium hydroxide are already quite low. A survey taken by the Institute in 1995 indicated an average level of mercury in product sodium and potassium hydroxide at 0.1 part per million.

If sodium or potassium hydroxide produced by the mercury cell process becomes a waste or comes in contact with a waste, such waste may be covered by the hazardous waste regulations within the United States. For waste containing mercury, it is considered to be hazardous if the leachable mercury concentration as measured by the Toxicity Characterization Leaching Procedure (TCLP), is greater than or equal to 0.2 mg/l [Reference 6.2.1]. In the United States, such waste must be handled according to regulations developed for the Resource Conservation and Recovery Act [Reference 6.2.2]

If all the mercury contained in sodium and potassium hydroxide entered the environment, it would amount to less than **0.2%** of the anthropogenic emissions of mercury to the environment. (Reference 6.2.3) Nevertheless, concerns have been raised by some governmental and non governmental agencies and officials about the levels of mercury contained in this product. These concerns coupled with the industry's and the Chlorine Institute's commitment to the principles of Responsible Care™ have led the task group to review technologies available and to develop new and/or enhanced technologies that would allow the reduction of mercury in sodium hydroxide.

In these guidelines, current technology is assumed to be conventional filtration as employed using filters manufactured by the R. P. Adams Company (Reference: \_\_\_\_\_). In the United States, Adams filters are the predominant filters used in mercury cell chlor-alkali facilities to filter sodium hydroxide. However, a few facilities in the United States, and numerous ones throughout the world, use different types of filters. Because the work group preparing these guidelines had no information on other types of filters, they are not discussed in this pamphlet.

The Chlorine Institute publishes and distributes several pamphlets related to the safe handling and use of sodium hydroxide. They are listed in the reference section. [References 6.1.1-6.1.5]. The reader should consult such pamphlets as appropriate.

### 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 April 27, 2000.

### 1.5 Revisions

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

### 1.6 Reproduction

The contents of this guidance document are not to be copied for publication, in whole or in part, without prior Institute permission.

## 2. **CONVENTIONAL FILTRATION**

In the United States, filters made by the R.P. Adams Company are the predominant equipment used to filter sodium hydroxide. However, many facilities throughout the world use equipment manufactured by Votator Schenk (Reference 6.2.5) or Funda (Reference 6.2.6). All three filters operate at similar conditions and efficiencies. Performance by each filter is affected by the same parameters. The remainder of this discussion is directed specifically to the R. P. Adams filters.

### 2.1 Process Overview - Operating Principles

The R.P. Adams filters are well suited for high temperature sodium hydroxide with inlet mercury concentrations of 1-10 PPM, or higher, depending on the operating flux rate and type of precoat material used. The mercury removal efficiency is a function of sodium hydroxide flux rate through the filter (or flow rate/unit area, normally expressed as gallons per minute per square foot of filter surface area, or GPM/Ft<sup>2</sup>), as well as operating conditions. Other than flux rate the operating conditions most affecting the performance are the sodium hydroxide temperature, and the pressure drop across the filter elements.

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The R.P. Adams filters have multiple reusable filter elements contained in a filter vessel. The normal process configuration utilizes two or more filter units in parallel. The filter elements are precoated to improve filtration efficiency and prevent fouling of filter elements. The precoat can also be used as a means to reduce the effective pore size of the filter elements. The filter elements are periodically backwashed and re-coated with fresh filter aid to remove filterable solids and mercury to maintain filtration efficiency. Filter cycle lengths of two to three weeks is typical. Cycle length is affected by such factors as flux rate, levels of incoming mercury, levels of incoming solids, etc. In 1998 Olin Chlor Alkali Products Division conducted a survey of filtration practices in the Chlor Alkali industry. The report containing the survey results appears in Appendix 7.3. The general experience of the industry is that filters for 50% caustic are constructed with all of the wetted parts made of nickel. Once the temperature is below 140°F stainless steels may be considered as an alternative.

## 2.2 Factors Affecting Filtration Efficiency

Primary factors affecting the filtration efficiency can be placed into two categories. First are the factors that are controlled by the design and the physical arrangement of the equipment. These factors include sodium hydroxide flux rate (GPM/Ft<sup>2</sup> filter area); selection of single or multiple stage filtration in the design; the filter element porosity; the system operating pressure; and, proper assembly of the filter tube-nest when installing new media. To some extent the temperature of the sodium hydroxide is also determined by the design of the cooling system. Proper design of the sodium hydroxide cooling system is critical to avoid plugging, and still provide sufficient cooling due to the influences of varying product recycle and seasonal temperature differences.

Secondary factors are those that are controllable process variables or influenced by operating procedures. These include the instrumentation and controls to provide the proper sodium hydroxide temperature to the filter over a range of production loading and recycle conditions. Also included are the type(s) and quantity of filter aid used, and controls necessary to ensure that the maximum differential pressure across the filter is not exceeded. Backwashing when the maximum differential pressure is reached and strict adherence to the proper operating procedure can be particularly important.

Backwashing is necessary if the mercury breaks through the filter before the pressure drop target is attained. In many installations the sampling and analytical procedure can result in significant lag between sampling and analytical results. Consequently, product may have to be refiltered to get Hg to acceptable levels. On-line instrumentation can address this issue. One supplier with equipment in this service is P S Analytical Ltd. (Reference 6.2.7)

When these factors have been properly considered in the design of the equipment, the equipment is well maintained and operated correctly, these conventional filter systems typically achieve mercury removal efficiencies between 98-99%. This level of removal has been achieved over a range of inlet mercury concentrations of 1-10 PPM. For outlet concentrations consistently below 0.030 PPM, cooling of the sodium hydroxide and multiple filters operating in series may be required.

### 2.2.1 Filter Elements

The R.P. Adams filters contain multiple tubular filter elements in a single housing arranged in a circular array. These filter elements are constructed of a porous carbon substrate with a typical pore size range of 25-50F. Most plants are currently using elements sold as Poro-Carbon™ 200.

### 2.2.2 Filter Aids

The filter elements are precoated with filter aid to improve filtration efficiency and prevent fouling of filter elements. The filter precoat can be single or multiple layers of fibrous, granular or mixed material exhibiting very different characteristics. Some filter aids, particularly fine powdered activated carbon, reduce the effective pore size of the filter elements to 0.5-2m. The filter elements are periodically backwashed and precoated with fresh filter aid to remove filtered solids (from decomposed packing etc.) and mercury to maintain filtration efficiency. Trapped solids are removed during the filter backwashing by flushing them out of the filter vessel along with the used filter aid. The filter elements are recoated with fresh filter aid prior to returning the filter to service.

#### 2.2.2.1 Precoating Materials (*Filter Aids*)

There are a variety of materials used as filter aids. The three materials most often used are bleached chemical wood pulp (alpha cellulose), powdered activated carbon, and diatomaceous earth (DE). Cellulose, used alone and in conjunction with both of the other materials, can leave a trace residual of soluble cellulose in the sodium hydroxide product. This residual, though insignificant from the standpoint of product or precoat performance, may be sufficient to blind and greatly diminish the performance of downstream micro filtration methods. Cellulose is often used as the base layer coating the filter element and frequently, but not always, topped with a layer of activated carbon. Activated carbon is also used as the sole precoat and in combination with other materials. Diatomaceous earth is used in combination with other materials. In some cases all three of the above materials are mixed and fed as an un-layered precoat composite material. Some forms of diatomaceous earth are soluble in hot sodium hydroxide and caution is warranted. It has been suggested that marine based diatomaceous earth may be better for filtering sodium hydroxide than fresh water based material.

#### 2.2.2.2 Precoat Application

Precoat materials are applied as a slurry in clean sodium hydroxide or deionized water. The concentration of the precoat in the slurry is typically 2-5% by weight. The precoat is fed by pumping the slurry into an empty filter. The filter is "topped" off with clean caustic (preferably) or water, if necessary. Once the filter is completely filled, the slurry should be recirculated until the precoat tank is clear. The precoat recirculation rate through the filter should be 0.65-0.75 GPM/Ft<sup>2</sup> when using 50% sodium hydroxide as the suspension medium. When precoating with water the recirculation rate through the filter should be in the 0.9-1.0 GPM/Ft<sup>2</sup> range. It is important that the transition from recirculation to on-line be made without flow interruption through the filter. Any pressure surge, change in flow, or reverse flow can disturb the integrity of the precoat layer and greatly alter the filtration efficiency and cycle time.

The recommended preferred filter aid thickness is approximately 1/8" cake on the outside of the filter elements, though the thickness in practice probably varies greatly. Only one

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filter should be precoated at a time to assure proper application of the precoat to the filter elements. The cellulose application rate varies between 0.13-0.25 Lbs/Ft<sup>2</sup> filter area. The activated carbon application rate varies between 0.005-0.27 Lbs/Ft<sup>2</sup> filter area. The diatomaceous earth application rate is approximately 0.15 -0.20 Lbs/Ft<sup>2</sup> filter area.

The filter manufacturer recommends that the precoat slurry and backwash fluid be maintained at a temperature no more than 100° F below the normal filtration operating temperature. Minimizing the differential pressure serves to maintain the integrity of the tubenest assembly, and limits the possibility of precipitation fouling the media, and wets the filter aids quicker.

### 2.2.3 Operating Variables

Sodium hydroxide temperature, flux rate and the product recycle rate through the filter are the major variables affecting R. P. Adams filter performance. (See Appendix 7.4.) The system pressure, though a factor in the amount of mercury vapor dissolved in the sodium hydroxide, has a greater impact on the precoat cake stability via abrupt changes in flux rate when switching from recirculation to on-line and visa versa during plant upsets. Differential pressure across the filter is clearly a factor in filter efficiency from an operating perspective. The manufacturer's recommended maximum for differential pressure is 25 PSI. The amount of filter recycle can affect the filter performance by maintaining a consistent minimum flow through the filter and thus greatly enhance the precoat cake stability.

#### 2.2.3.1 Temperature

Cooling the sodium hydroxide significantly improves mercury removal. The lower the temperature the greater the surface tension, resulting in less mercury exuding through the precoat cake at a constant differential pressure. Lower temperature also lowers the amount of dissolved mercury passing through the filter at a constant system pressure. For optimal results, the preferred temperature for the mechanical filtration of suspended elemental mercury particles from 50% sodium hydroxide is between 140-175°F.

#### 2.2.3.2 Pressure/ Differential pressure

Inlet pressures range from 15-80 PSIG. Pressure drops across the filter typically range between 3-20 PSI and are highly dependent on the time online and the type of precoat employed. Pressure drop across filter should not exceed 25 PSI for optimal results.

#### 2.2.3.3 Flux Rate

Optimal results are obtained at flux rates of 0.15-0.25 GPM/Ft<sup>2</sup> filter area for single stage filtration using the R.P. Adams filter. Flux rates may be increased slightly for subsequent stages of R.P. Adams filtration in series with first stage.

### 2.3 Multiple-Stage Adams Filtration

Single stage filtration is capable of achieving outlet mercury concentrations of 0.020-0.050 PPM. Adding a second stage of R.P. Adams filtration in series can further reduce outlet Hg concentrations to 0.010-0.030 PPM. It appears that 0.010 PPM is the average practical lower limit achievable with multiple-stage R.P. Adams filtration.

Laboratory testing suggests that at levels of 0.010 PPM Hg in sodium hydroxide, approximately 50% of the mercury is in ionic form and the other 50% is a finely divided elemental Hg suspension. Appendix 7.2 provides a discussion of analytical issues inherent in measuring mercury in sodium hydroxide.

## 1. **MICROFILTRATION**

### 3.1 Process Overview

Microfiltration of 50% sodium hydroxide has proven effective in pilot scale tests and limited plant operation in lowering mercury concentrations to concentrations less than 0.005 ppm. The basic configuration of microfiltration operational units consists of circular arrays of single-use filter elements in a filter housing. After the filters are loaded, the accumulated solids are removed by either removing the filter elements or backflushing the filters.

### 3.2 Filter Design

Two basic filter designs are commonly available, depth cartridge filters and pleated cartridge filters. Depth cartridges are made with a conventional filament wound construction using a synthetic fiber and have a total media thickness of at least ½". Pleated cartridge filters are composed of a woven synthetic fabric folded in pleats around a support structure with a maximum media thickness of 1/16".

#### 3.2.1 Pore Size

Filters are available with pore sizes ranging from 0.02 -10F. Pilot studies suggest that pore sizes less than 0.45F do not improve mercury removal and that the 0.45F pore size may be the best size for sodium hydroxide filtration.

#### 3.2.2 Materials of Construction

Filter elements are available in a variety of materials. Polypropylene and polysulfone filters have been tested and found to work well for sodium hydroxide filtration. Not only are these materials durable in 50% sodium hydroxide, but they are also known to have interactions with mercury which may increase the filter's effectiveness. Fluoropolymer membranes have also been tested successfully.

The filter housings may be constructed of either nickel or stainless steel depending on the temperature. Nickel is preferred for temperatures greater than 140°F while stainless steel is adequate for temperatures less than 140°F.



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### 3.2.3 Pleated Cartridges

Pleated cartridges have a large surface area, typically 7-8 ft<sup>2</sup>/ft length. The thin media results in a short filtration path making pleated filters best suited for high flow rates and low inlet mercury concentrations. Large pleated cartridge units are capable of accommodating flow rates of 250 gal/min with clean pressure drops of typically 2-3 psi. Laboratory and pilot testing have shown pleated cartridges to be effective at removing mercury with inlet mercury concentrations of up to 0.80 ppm.

### 3.2.4 Depth Cartridges

Depth cartridge filters have a low surface area, typically about 1ft<sup>2</sup>/ft length. The thick filter media results in a long filtration path making depth cartridge filters best suited for low flow rates and higher inlet mercury concentrations. Depth cartridge units can accommodate inlet flow rates of 50-100 gal/min with clean pressure drops of typically 3-4 psi. Laboratory and pilot testing have shown depth cartridges to be effective at removing mercury with inlet mercury concentrations of up to 0.80 ppm.

## 3.3 Operating Variables

The main operating variables that affect sodium hydroxide filtration are sodium hydroxide temperature, flux rate, inlet operating pressure and differential pressure across the filter.

### 3.3.1 Temperature

Temperatures in the range of 120-150°F are preferred for sodium hydroxide filtration. Lower sodium hydroxide temperatures enhance mercury filtration; however, when the temperature becomes too low, problems may occur in the filtration because of the increased viscosity of the solution.

### 3.3.2 Pressure

The typical inlet pressures run from 15-60 psi and the typical pressure drop across the filter ranges between 3-10 psi.

### 3.3.3 Flux Rate

The standard flux rates for either pleated or cartridge filters is 0.12-0.16 gal/min-ft<sup>2</sup> filter area. As of the completion of this document a correlation has not been developed to predict performance as a function of the temperature, pressure drop and flux rate.

## 3.4 Multiple-Stage Microfiltration

A single stage of microfiltration with a 0.45F pore size is capable of reducing inlet mercury concentrations of 0.020-0.040 PPM to an outlet concentration of 0.003-0.007 PPM. Pilot data suggests that adding a second stage of microfiltration in series after additional holding time or cooling is capable of reducing outlet mercury concentrations to 0.001-0.003 PPM.

## 2. COMBINED MULTIPLE-STAGE FILTRATION

The results of laboratory and pilot plant studies conducted by several member companies, and initial operating data from one facility, demonstrate that high mercury removal rates may be achieved by utilizing microfiltration in concert with conventional Adams filtration. The data suggest that optimal mercury removal may be achieved by combining two (2) stages of Adams filtration with two (2) stages of submicron filtration.

A typical combined multiple-stage arrangement employed by one member company is as follows:

- Step 1 – 1<sup>st</sup> Stage Adams Filtration
- Step 2 – 2<sup>nd</sup> Stage Adams Filtration
- Step 3 – Cooling
- Step 4 – 1<sup>st</sup> Stage Microfiltration
- Step 5 – Storage
- Step 6 – 2<sup>nd</sup> Stage Microfiltration

The table below summarizes typical outlet mercury concentrations observed for this process after each stage of filtration.

**Outlet Mercury Concentration (PPM)**

<b>Sodium Receiver</b>	<b>1<sup>st</sup> Stage Adams</b>	<b>2<sup>nd</sup> Stage Adams</b>	<b>1<sup>st</sup> Stage Microfiltration</b>	<b>2<sup>nd</sup> Stage Microfiltration</b>
2.0-6.0	0.020-0.080	0.015-0.030	0.004-0.010	0.001-0.004

The overall mercury removal efficiency for this process is 99.80-99.98 %. As noted in previous sections, mercury removal from sodium hydroxide is a function of temperature. Additional cooling and/or retention time between filtration stages may enhance the mercury removal efficiency of this process.

When employing combined multiple-stage filtration, it is recommended that operation of the conventional Adams filters be optimized for maximum mercury removal. This will help in reducing mercury loading to the subsequent microfiltration stages and prolong the useful life of the filter cartridges.

## 3. ALTERNATIVE TECHNOLOGIES

At the outset of this project, a literature search was conducted to assess the state of the knowledge of technologies to remove mercury from sodium hydroxide. This section summarizes the results of the literature search and also discusses work initiated by the task group in assessing technologies where little or no information is reported in the literature.

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## 5.1 Literature Search

The attached literature search (Appendix 7.1) attempts to be as comprehensive as possible. It covers several databases from 1967 to the present. Multiple synonyms and search terms were used to redundantly describe what was sought. Overlapping results were sorted manually. The following were the resources used:

C	Chem Abstracts	(Chemical Abstract Service)
C	World Patent Index	(Derwent)
C	Pollution Abstracts	(Cambridge Scientific Abstracts)
C	Compendex	(Engineering Information, Inc.)
C	SciSearch	(Institute for Scientific Information)

The search originally conducted in early 1998, but was re-executed in July 1999 during the preparation of this guidance document.

### 5.1.1 List of Approaches Found

The following approaches to the removal of mercury from mercury cell sodium hydroxide feature in the scientific literature:

1. Filtration (the media discussed are listed below)
  - C Activated carbon
  - C Graphite
  - C Polyolefins
  - C Nickel gauze
  - C Asbestos
  - C PTFE
  - C Sulfur-impregnated carbon
2. Gas Stripping
3. Electro-Coagulation / Electrolytic Reduction
4. Metallic Amalgamation

Filtration, gas stripping, electrolytic coagulation, and metallic amalgamation can be logically combined with the use of reducing agents that insure that the speciation of mercury is shifted in the direction of metallic. Hydrazine, hydroxylamine, and stannous salts are mentioned in the literature.

Oppositely, oxidizing agents may logically be combined with the use of electrolytic reduction and ion exchange or affinity resins to ensure that the speciation of mercury is shifted in the direction of ionic. These being far less commonly investigated approaches, the literature here is sparse.

Literature on the use of ion exchange and "affinity" resins in the removal of Hg from Hg cell sodium hydroxide was not found. This area is seemingly too new. Please refer to Sections 5.2 and 5.3 for discussions of investigations performed by member companies during the preparation of this document.

### 5.1.2 Descriptions

#### a. Filtration

The most common approach found in the literature for the removal of mercury from mercury cell sodium hydroxide is filtration. The reason for this is that it is accepted that the majority of mercury is present as finely divided metal.

The most common filtration media is activated carbon (mostly used in the form of a precoat). Graphite also receives several mentions. Asbestos, polyolefin, and PTFE materials are also discussed in the literature. Activated carbon has been enhanced with sulfur treatments that help in the binding of mercury.

The attractions of filtration lie in its simplicity and efficacy. Optimization within a filtration unit is possible based on filtration media, precoat materials, temperature, flux rate, etc. The simplicity of operation by backwashing is also advantageous.

Despite the extensive literature, the understanding of filtration is poorly documented. It is clear that suspended metallic mercury is collected and coalesced, but it is unclear to what extent various substrates also adsorb ionic mercury. Saturation of filters is a possible problem -- new technologies, such as micron-level filters, as discussed in Section 3, will have to be monitored closely. Disposal of filtration media is also a consideration.

#### b. Gas Stripping

Gas stripping purification of mercury cell sodium hydroxide relies on the high vapor pressure of mercury. Sufficient gas is passed through the sodium hydroxide to volatilize metallic mercury. Ionic mercury is not affected. The use of reducing agents features in the literature.

Since dilute mercury in sodium hydroxide ends up as dilute mercury in a gas, obviously an additional gas treatment step is required.

Air is not preferred as a stripping gas; it can oxidize metallic mercury to ionic mercury, and this will not strip. Hydrogen has received some attention as a stripping gas, in that hydrogen is present in chlor-alkali plants and facilities are already in place to remove mercury from it (it is, after all, evolved from denuders). Hydrogen, however, has a very low molecular weight and large volumes may be required relative to other candidate gases in order to achieve mercury removal targets.

The advantages of gas stripping are that it is possible to achieve any desired level of mercury removal. The variables are clear: temperature, gas-to-liquid ratio, quality of gas/liquid contacting, and residence time.

The disadvantages are that a system is required for the removal of mercury from the gas phase. Process complexity may also be a concern, since existing hydrogen purification systems may not be sized to handle the added gas flow required by a stripping operation. (See Section 5.4)

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c. Electro-Coagulation / Electrolytic Reduction

The concept of electro-coagulation is to take advantage of the charge on suspended microscopic droplets of mercury and draw them to an electrode where they may coagulate to recoverable bulk mercury. The charged droplets move within a high voltage electric field toward a wettable electrode. The effective electro-reduction of ionic mercury would require far larger electrode surface areas than would be employed in electro-coagulation, and, therefore, the reduction of ionic mercury to metallic using a chemical reagent would be important to achieve the maximum possible removal of mercury by electrocoagulation. Little literature was found in this area.

The electrolytic approach to mercury removal relies on the reduction of ionic mercury to metallic mercury on the surface of a cathode. For most complete effectiveness, metallic mercury would have to be oxidized to ionic with an oxidizing agent.

Electrolytic metals removal cells are commonly used in effluent control. These most often use three dimensional high surface area cathodes. Cathodes composed of beds of carbon feature in the commercial literature. [Examples are cells with the following tradenames: Porocell™ (EA Technology Ltd., Capenhurst, U.K.) and Retec™ (U.S. Filter), among many others]. PPG Industries operates a metals removal cell for sodium hydroxide purification that uses a porous graphite tube cathode. The PPG metals removal cell is used for the treatment of *diaphragm* cell sodium hydroxide and mainly targets Fe, Ni, Pb, and Cu-- it can work on ionic mercury, but would be impractical due to surface area requirements.

For electrolytic removal of very low starting concentrations of mercury (such as 100 ppm), the cathode has to be of very high surface area since mass-transfer of ionic mercury to the electrode surface plays a critical role in the efficacy of this technique. Calculations show that very large cathode surface areas are required for treatment to the <0.005 ppm level. Calculations further show a prohibitive pressure drop results from the requirement to pass large flow rates of sodium hydroxide through a series arrangement of three-dimensional cathodes structures. Due to poor mass transfer and the consequent large surface areas required, the required numbers of electrolytic cells, of whatever design, also appears prohibitive.

There are no apparent advantages to electrolytic methods.

d. Metallic Amalgamation

In the amalgamation approach, advantage is taken of the ease with which metallic mercury amalgamates with selected metals. Ionic mercury being unaffected, use of a reducing agent would be necessary in parallel with this approach. Gold appears to be the metal of choice. Literature on this approach is scarce.

5.2 Ion Exchange

A variety of resins, both commercial and experimental, have been considered for reducing the mercury concentration in 50 wt% sodium hydroxide to below 0.002 PPM. The vast majority of the mercury in 50 wt% sodium hydroxide is not present in an ionic form. Therefore, ion exchange alone, without the benefit of an efficient filtration system, will probably not achieve the goal. Many resins capable of capturing the ionic mercury are not stable in 50 wt% sodium hydroxide at practical process temperatures. When these resins breakdown removal efficiency is lost and organic artifacts are left in the sodium hydroxide.

We are unable to predict the operational problems that would result from the presence of these artifacts in the potential recycle streams to the amalgam process. Furthermore, it is impossible to predict the impact of these artifacts on the many processes and products of customers using 50 wt% sodium hydroxide. Once a resin is found that is physically and chemically stable at process conditions, and is able to be regenerated, reevaluation of this unit operation will be warranted.

### 5.2.1 Ion Exchange Resin investigation

Individuals explored a number of ion exchange resins claiming a variety of mechanisms (The starting material for these laboratory trials was between 20-100 ppm mercury.). The following are observations made by member companies conducting the tests.

<u>Source</u>	<u>Resin</u>	<u>Performance</u>
IBC Technologies	SuperLig 117	0.003-0.005 PPM, one time use
Mitsubishi	Diaion CR020A	0.005 PPM, not stable
Mitsubishi	Diaion CR-11	not stable
Purolite	SS-920	0.010 PPM, one time use
Purolite	SS-930	ineffective
Purolite	SS-940	0.008 - 0.009 PPM, one time use
Purolite	SS-950	ineffective
Rohm & Haas	Duolite GT-73	0.010 PPM, one time use
Calgon	MC140	not stable
Perfix		ineffective

No resins were found to be as effective as microfiltration in reducing the mercury levels to 0.003-0.005 PPM.

### 5.3 Selective Adsorption

Selective adsorption of mercury from sodium hydroxide has a variety of hurdles to overcome depending on whether the mechanism is truly adsorption, ion capture, or amalgamation. In the case of adsorption, which in the case of activated carbon is thought to be physical adsorption, desorption is known to occur. Changes in the inlet mercury concentration to a carbon adsorption bed, or changes in the sodium hydroxide concentration, which can greatly effect the bulk physical properties of the sodium hydroxide, can result in desorption of the mercury into the bulk sodium hydroxide solution. Ion capture systems can suffer from many of the same instability problems as ion exchange resins, potentially leading to contamination of the product. Adsorption or chemisorption of mercury to form an amalgam with a precious metal has the challenge of eliminating the mobility of the precious metal. Formation of the amalgam, or regeneration procedures can cause precious-metal amalgam particles to remain in the sodium hydroxide product. As in the case of ion exchange, it is impossible to predict the impact of artifacts on the many processes and products of

customers using sodium hydroxide. Once stable materials or systems that remain fixed and can be practically regenerated are found, reevaluation of this unit operation will be justified. See Appendix 7.5 for additional information.

#### 5.4 Gas Stripping

##### 5.4.1 Concept

Gas stripping of mercury from mercury cell sodium hydroxide relies on the high vapor pressure of mercury. Gas is dispersed through the sodium hydroxide in order to volatilize the metallic mercury that is present. Ionic mercury is not affected. Use of a reducing agent is known to be helpful in maximizing the efficacy of the technique.

Air is not preferred as a stripping gas; it can oxidize metallic mercury to ionic mercury, and ionic mercury will not vaporize. Thus, nitrogen and hydrogen are discussed in the literature. Hydrogen is present in chlor-alkali plants and facilities are already in place to remove mercury from mercury cell hydrogen. Hydrogen, however, has a very low molecular weight and large volumes may be required relative to other candidate gases in order to achieve Hg removal targets.

The concept has its foundations in an analytical method for mercury. Given 100% metallic speciation through the use of a reducing agent and an oxygen-free stripping gas, achieving any level of Hg removal is possible. It is a matter of how much gas is passed. Whether this concept can be economic is another matter.

##### 5.4.2 Experimental Result

To demonstrate feasibility, experiments were performed by a member company with three fresh 350g samples of 50 wt% mercury cell sodium hydroxide contained within Teflon PFA vessels. These were treated with sodium borohydride to reduce ionic mercury to metallic. At 80°C the samples were purged with approximately ten times the equilibrium volume of gas necessary to volatilize the Hg present. The gas was collected in a series of three 4%  $\text{KMnO}_4$  / 10%  $\text{H}_2\text{SO}_4$  scrubbers. The following table presents the results:

Experiment	A	B	C
Initial Hg	15 ppm	10 ppm	10 ppm
Spike with Hg std.	0 ppm	0 ppm	25 ppm
Total Hg present	15 ppm	10 ppm	35 ppm
Hg after gas stripping	1 ppm	1 ppm	7 ppm
Hg balance with scrubber analysis	17%	36%	46%

##### 5.4.3 Modeling

In order to assess practicality of gas stripping, a very preliminary ChemCad model was constructed. The following assumptions were used:

- 100 ppb feed sodium hydroxide

- Hg follows Henry's Law behavior:  $\text{Partial P} = \text{Act. Coeff.} \times \text{VP}_{\text{Hg}} \times \text{Mole Fraction}$ , where  $\text{Act. Coeff.} = 1/\text{solubility in mole fraction} = 1/(20 \text{ ppb estimate})$
- Hg exerts full Henry's Law vapor pressure to gas
- Counter-current #25 IMTP packed column
- 3 times equilibrium gas flow is used
- Liquid mass transfer is controlling

The high viscosity of the sodium hydroxide will inhibit actual performance, but not in a way the model could quantify. The packing performance was estimated on the basis of the manufacturer's (Norton's) experience with liquids of similar viscosity.

#### 5.4.4 Sizing/performance results

For a 220 T NaOH/day plant, the assumption of 380 SCF/hr of hydrogen was used. The depth of #25 IMTP (Norton) packing in a 12 inch diameter column was estimated to strip 0.100 ppm Hg in 50% sodium hydroxide to 0.002 ppm. A 48 foot column height requirement resulted. Thus, the approach may be envisioned as three 12 inch diameter towers of 16 feet height.

#### 5.4.5 Conclusions

It was decided not to pursue gas stripping. The advantages of gas stripping are that it is possible to achieve any desired level of Hg removal. The variables are clear: temperature, gas-to-liquid ratio, quality of gas/liquid contacting, and residence time.

The disadvantages are that a system is required for the removal of Hg from the gas phase. Complexity is also a concern, since existing hydrogen purification systems may not be sized to handle the added gas flow required by an add-on stripping operation.

## 6. REFERENCES

### 6.1 Institute Publications

- 6.1.1 *Recommended Practices for Handling Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic) Barges*, ed. 2; Pamphlet 80; The Chlorine Institute: Washington, DC, **1995**.



- 
- 6.1.2 *Recommended Practices for Handling Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic): Tank Cars, Loading and Unloading*, ed. 1; Pamphlet 87; The Chlorine Institute: Washington, DC, **1999**.
- 6.1.3 *Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic): Tank Motor Vehicle Loading/Unloading*, ed. 1; Pamphlet 88; The Chlorine Institute: Washington, DC, **1994**.
- 6.1.4 *Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic): Storage Equipment and Piping Systems*, ed. 1; Pamphlet 94; The Chlorine Institute: Washington, DC, **1995**.
- 6.1.5 *Standard Methods for Chemical Analysis of Caustic Soda and Caustic Potash*, reapproved; ASTM-E291; The Chlorine Institute: Washington, DC, **1990**.
- 6.2 Other References
- 6.2.1 Test Method 1311 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW-846.
- 6.2.2 *Code of Federal Regulations*. 40 CFR Part 262; Standards Applicable to Generation of Hazardous Waste.
- 6.2.3 Mercury Study Report to Congress, United States Environmental Protection Agency; EPA-452-/R-97-003, December 1997, Volume I, Table 3-1, Page 3-6.
- 6.2.4 R.P. Adams Company, PO Box 963, Buffalo, NY 14240  
Phone: (716) 877-2608  
Website: [www.rpadams.com](http://www.rpadams.com)
- 6.2.5 Votator/Schenk Filters, c/o Chemetron Process Equipment, PO Box 35600, Louisville, KY 40232  
Phone: (502) 491-4310
- 6.2.6 Funda Filters, c/o Steri Technologies, 857 Lincoln Avenue, Bohemia, NY 11716  
Phone: (516) 563-8300  
Contact: Juengen Hochegger
- 6.2.7 P.S. Analytical; Prof. Peter B. Stockwell, Arthur House, Unit 3, Crayfields Industrial Estate, Main Road, St. Paul Cray, Orpington, Kent BR5 3HP UK  
Phone: (01689) 891211  
Fax: (01689) 896009  
Website: [www.psanalytical.demon.co.uk](http://www.psanalytical.demon.co.uk)

## **Addendum to Appendix 7.1**

(This paragraph will be inserted in the beginning of Appendix 7.1 in the final document)

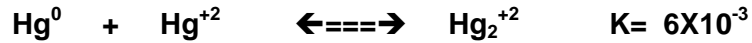
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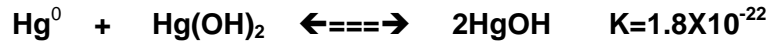
## APPENDIX 7.2

### Analytical Considerations

Mercury exists in three forms that are an equilibrium mixture according to the following equation:



Other anions in solution have a dramatic effect on the position of this equilibrium due to the large variety of strong complexes formed between mercury and the ions.



Due to the very large formation constant between hydroxide and  $\text{Hg}^{+2}$  ( $1.8 \times 10^{-22}$ ),  $\text{Hg}_2^{+2}$  will not exist in the presence of high concentrations of hydroxide ions. Product caustic soda and caustic potash will only contain  $\text{Hg}^0$  and  $\text{Hg}(\text{OH})_2$ .

Mercury is typically analyzed by cold vapor atomic absorption. In this method, a weighed portion of caustic is diluted with water, acidified with a suitable acid and digested at elevated temperatures for time periods of at least one hour in the presence of excess potassium permanganate. This digestion process oxidizes all of the mercury forms present in the sample to  $\text{Hg}^{+2}$ . The excess potassium permanganate is destroyed by the addition of a solution of hydroxyl amine hydrochloride until a clear solution is obtained. This solution is placed into a gas scrubbing bottle along with acidic tin chloride solution to reduce the  $\text{Hg}^{+2}$  to  $\text{Hg}^0$  and scrubbed with an inert gas to transport the elemental mercury from the solution into the gas phase and through the detection cell. The amount of light absorbed in the detection cell is proportional to the amount of mercury removed from solution.

Although the actual detection limit of this method is subject to a number of factors like sample size, detection cell length, volume of scrubbing gas and the volume of the gas scrubbing bottle, this method will generally detect mercury down to about 1-10 parts per billion range. There are practical limits to the sample size used by this method because of the need to dilute and acidify the sample.

ASTM has recently published a new method of mercury analysis in caustic products using cold vapor atomic absorption and an alkaline reducing agent that does not dilute, acidify, or digest the sample. The alkaline tin reducing agent is a much more aggressive and stronger reducing agent than the acidic tin. Since the sample and the reducing agent are both alkaline, the sample size limitation seen in the acidic reducing agent method is removed. Since the alkaline reducing agent is a stronger and more aggressive reducing agent, the need to digest the sample is removed greatly reducing the analysis time of the method. The new method detection limit is easily extended by a factor of ten over the old method to the 0.1-1 parts per billion range. This method is given in test method A of ASTM E 538-98 which first appeared in the 1999 edition of volume E15.05.

The EPA has recently published two methods of mercury analysis in water samples using atomic fluorescence spectrometry: method 1631 and method 245.7. These methods call for the acidification of the sample and oxidation of the mercury species

present in the sample to  $\text{Hg}^{+2}$  with bromine chloride for up to an hour. Excess bromine chloride in the sample is destroyed with a solution of hydroxyl amine hydrochloride. The  $\text{Hg}^{+2}$  is reduced to  $\text{Hg}^0$  with an acidic tin solution and purged from solution into the gas flow followed by detection with atomic fluorescence. In this case the amount of light emitted by the mercury atoms in the gas phase is proportional to the mercury concentration in the sample.

Although each of these methods was written for environmental and wastewater samples, the basic methods and instruments can be adapted to the analysis of caustic samples with great success. The extreme measures taken in the sample handling in each of the methods go far beyond what is required for a normal product analysis.

Atomic fluorescence instruments are about a factor of 1000 times more sensitive than the atomic absorption instruments and detection limits in the 1-10 parts per trillion range can be easily achieved with just moderate controls of the laboratory environment. Be forewarned that with this type of instrument you will find detectable levels of mercury in every thing that is analyzed. This makes control of the instrument blank and having clean reagents and water very important.

As with the earlier methods, these new fluorescence methods use an acidification and oxidation step followed by an acidic tin reducing agent. Each of these reagent additions adds to the amount of mercury background in the blank of the method. By adapting the atomic fluorescence methods to the alkaline tin reducing agent the need for the acidification and oxidation are removed from the method. The sample preparation consists of a 1 to 1 dilution of the 50% caustic in high purity water to simply reduce its viscosity in being pumped into the instrument. This ultimately reduces the instrument blank and lowers the detection limit because of fewer mercury containing reagents being added to the sample and the reduced sample handling out in the room air.

## **APPENDIX 7.3**

# **Survey of Mechanical Filtration From 50% Sodium Hydroxide Solutions**

**Prepared May 13, 1998**

**For Release October 12, 1999**

### **Mechanical Separation Optimization Team**

Butch Carman	Coordinator
Harvey Cochran	Analytical Resource
Jim Heron	Process Resource
Dr. Leonard Scott	Technology Resource
Jorge Vilanova	Process Resource
Edited By	Bob Brooker

# Acknowledgement

We thank our fellow amalgam cell Chlor Alkali manufacturers who participated in making this survey study possible. Without their open and thoughtful disclosures, this effort could not have been successfully completed.

*Mechanical Separation Optimization Team*

## Abstract

The objective of this study was to identify the optimum equipment organization and operating controls necessary to consistently achieve 30 PPB to 50 PPB mercury levels in 50% Sodium Hydroxide product from a amalgam cell Chlor Alkali plant filtration system.

Six amalgam cell Chlor Alkali plants, having seven cell rooms, were visited in order to determine the best operating practices. Individual plant equipment data, and analytical methods were gathered to provide a basis of comparison for the study. It was agreed, prior to the survey, that the data obtained be presented to the Chlorine Institute for public use as deemed appropriate by member companies.

Key features for the caustic filtration system were identified to consistently produce low mercury in caustic product and are as follows.

1. Caustic from the decomposer should be in the 104 °C to 106 °C range.
2. Ensure that a flux rate of 0.30 gallons per minute per square foot through the R. P. Adams filters is not exceeded.
3. Recycle filtered product back to the caustic receiver at a rate equal to or greater than the production rate.
4. Poro-carbon 200 filter elements should be used in the filters.
5. The poro-carbon elements should be “conditioned” prior to their first use. This conditioning should be done with a fine carbon pre-coating material. The particle size of the carbon should be 325 mesh or smaller.
6. Future element pre-coating using only carbon or at least using a carbon base coat is the preferred method.
7. The maximum pressure drop across the filter elements should be 15 pounds per square inch.
8. A constant filter outlet pressure should be maintained. This minimizes down stream pressure changes caused by storage tank changes or valve switching.

The above filtration system recommendations are based solely on a compilation of all sites visited.

## **I. Objective**

The objective of this study was to identify the optimum equipment arrangement and operating controls necessary to consistently achieve 30 PPB to 50 PPB mercury levels in 50% Sodium Hydroxide product from a amalgam cell filtration system. The study approach was to visit Chlor Alkali industry plants that produce 50% Sodium Hydroxide using amalgam cell technology to gather the necessary information. The plants selected have published mercury levels in caustic with the Chlorine Institute, which meet the objective criteria. The conclusions and recommendations will be published through the Chlorine Institute.

## **II. Summary**

A caustic filtration system is detailed that will produce mercury in caustic in the range of 30 PPB to 40 PPB. At the time of this study, the range of 30 PPB to 40 PPB mercury in caustic was believed to be the best sustainable quality in the Chlor Alkali industry using only mechanical separation equipment. The caustic filtration system recommended by this report is a composite system of the plants surveyed.

The final equipment sizing and optimum equipment operating procedures will require an investment in a pilot system. The entire study team recommended the purchase of this verification system.

The composite filtration system involves, first, use of a recycle stream from the discharge of the existing filters back to the caustic surge tank or receiver. This stream is to equal the normal caustic production flow forward to storage. The second part of the recommended system is to achieve a filter area flux rate of 0.25 gallons per minute per square foot. The third process feature is the use of a finely ground carbon pre-coat for the filter tubes. The fourth process optimization reduces the allowable pressure drop to a maximum of 15 PSI. The fifth process enhancement is incorporation of backpressure control on the filter discharge to eliminate the negative impact of switching caustic storage tanks. The sixth process adaptation is a procedure by which fine carbon is body fed to the filter upon elevated or mercury break-through to prolong the filter cycle.

## **III. Background**

One of Olin Chlor Alkali Divisions' goals is to reduce the release of mercury from all sources. It is also a division goal to produce products in a fashion that minimizes mercury discharges from our plants in the air, water, solids, and products so that there is no harm to human health or the environment as a result of emissions or exposure. Specifically, the reduction of mercury in caustic soda has focused on three areas. The first area focuses on the decomposer and its operation. The second area focuses on the mechanical separation of elemental mercury from the 50% caustic soda solution. The

third area is focusing on achieving the next generation of filtration / separation of mercury from the filtered and cooled product.

This report deals only with the second area of mercury removal efforts, namely, mechanical separation. The goal is to achieve the minimum mercury in caustic levels possible by visiting and understanding the techniques used by the industry leaders in caustic filtration. The published literature indicates that 30 to 50 PPB levels are consistently achievable. Levels of 10 PPB have been demonstrated but have not been consistently repeated.

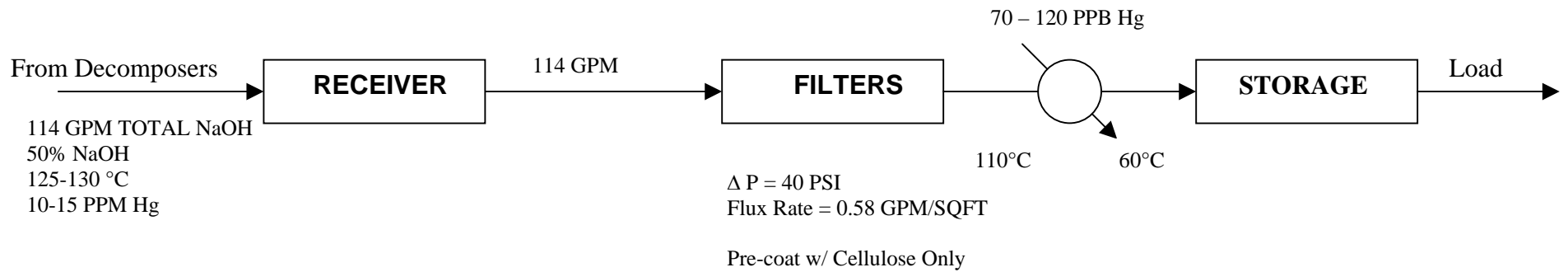
A team of five people was assembled to conduct a study of the current techniques within the Chlor Alkali Industry. The Team's approach was to visit each plant to gather equipment, operating, and analytical data. The data would then be used to formulate the optimum equipment sizing & arrangement, operating procedures, pre-coat material, and analytical procedures. These visits occurred between April 5<sup>th</sup> and April 17<sup>th</sup> of 1998.

## **IV. DATA**

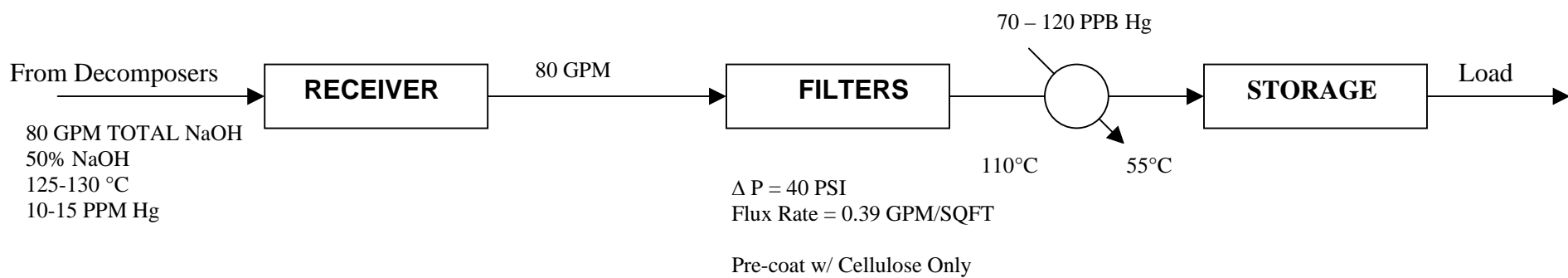
Data collected from five manufacturers forms the basis for the conclusions and recommendations contained within this report. The contained tables compile the data collected. Also included are brief schematic representations of the individual caustic filtration systems studied.



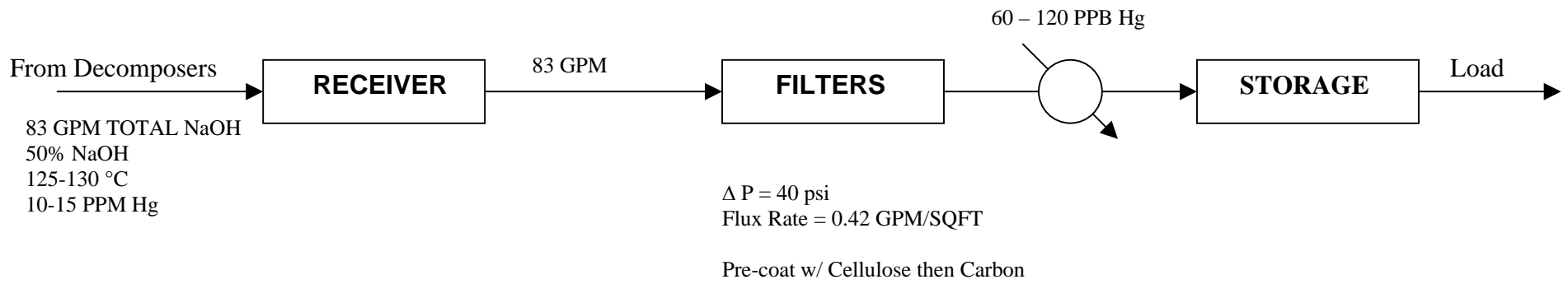
# Plant #1



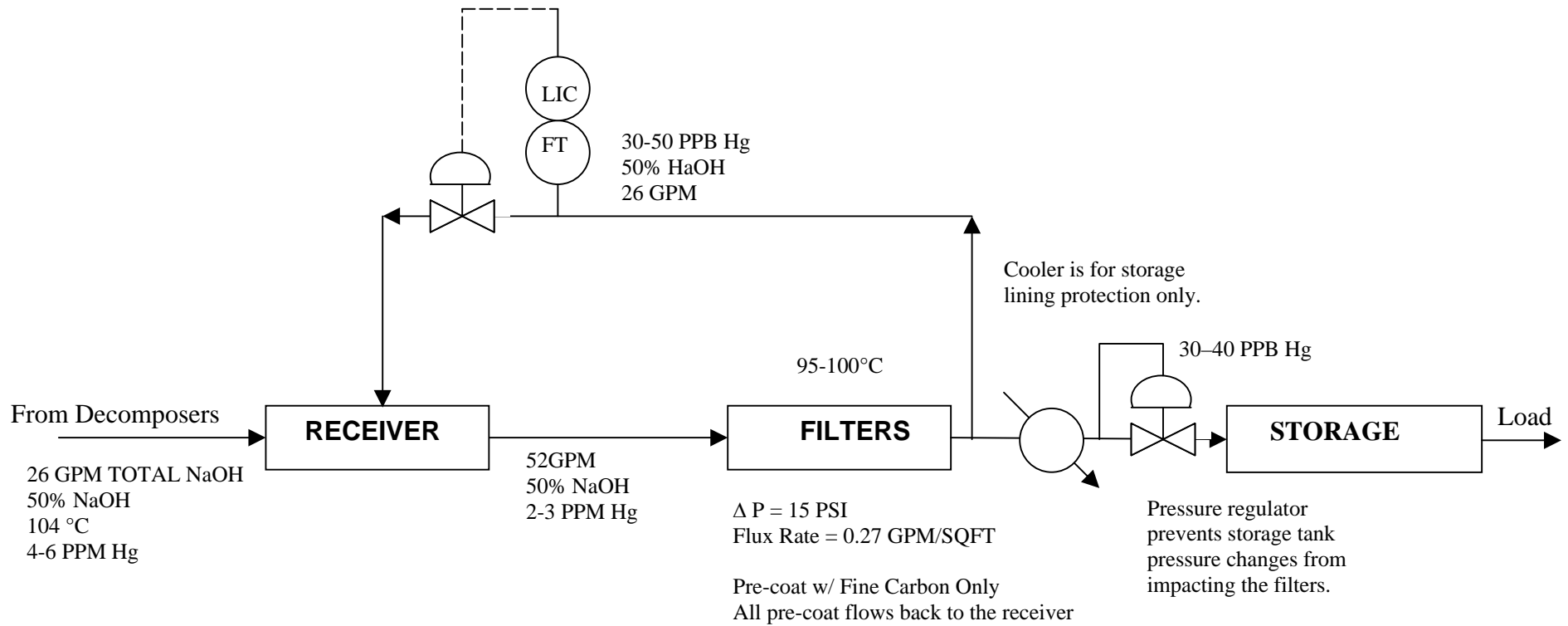
# Plant #2



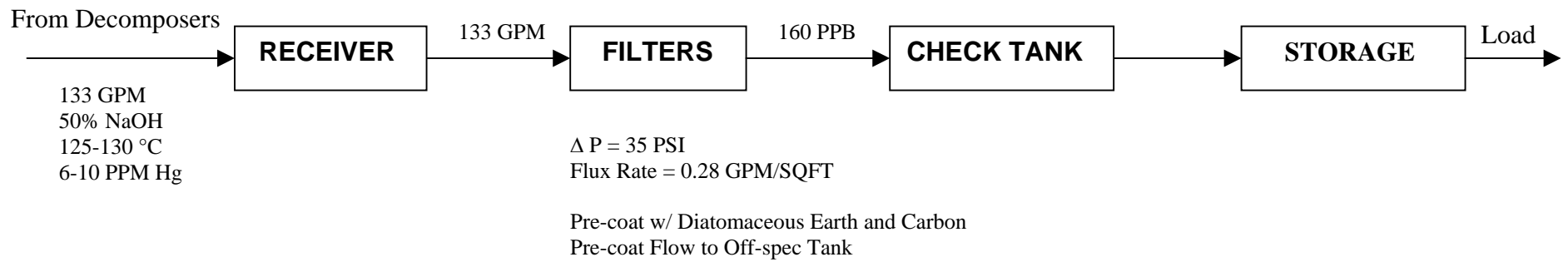
# Plant #3



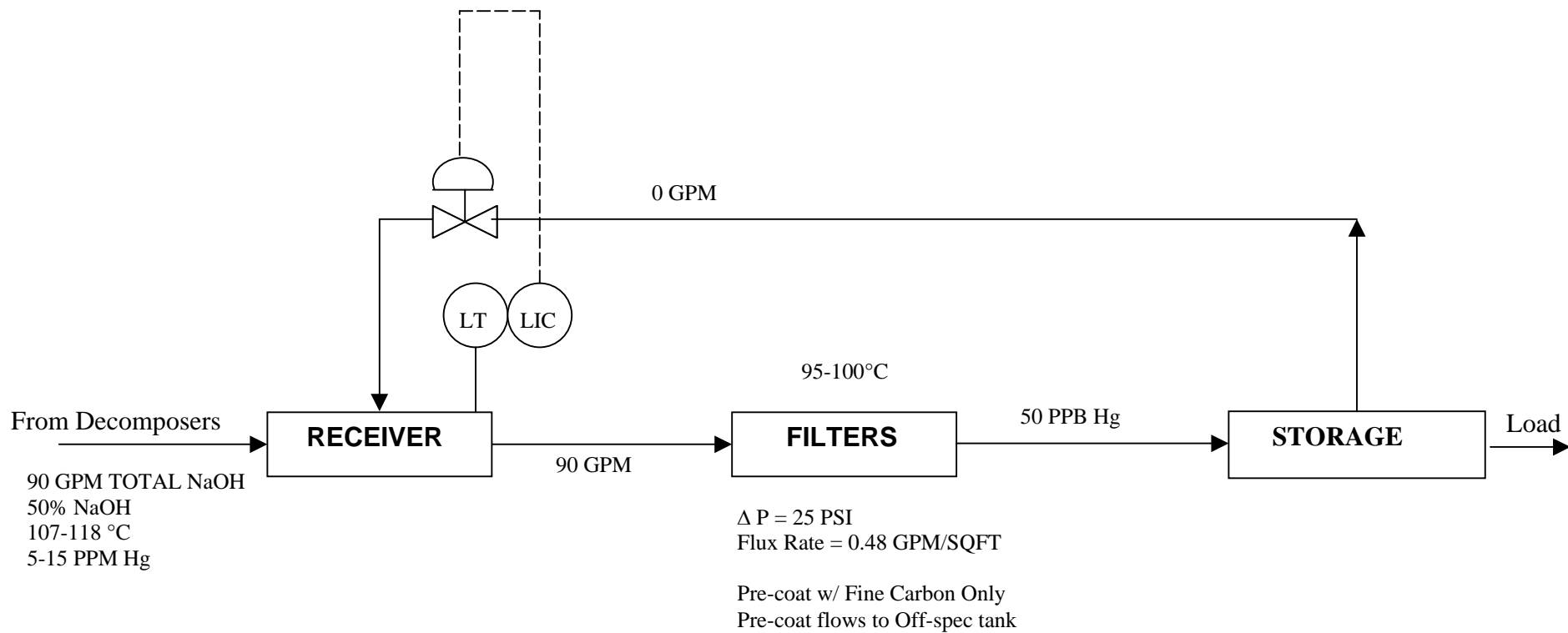
# Plant #4



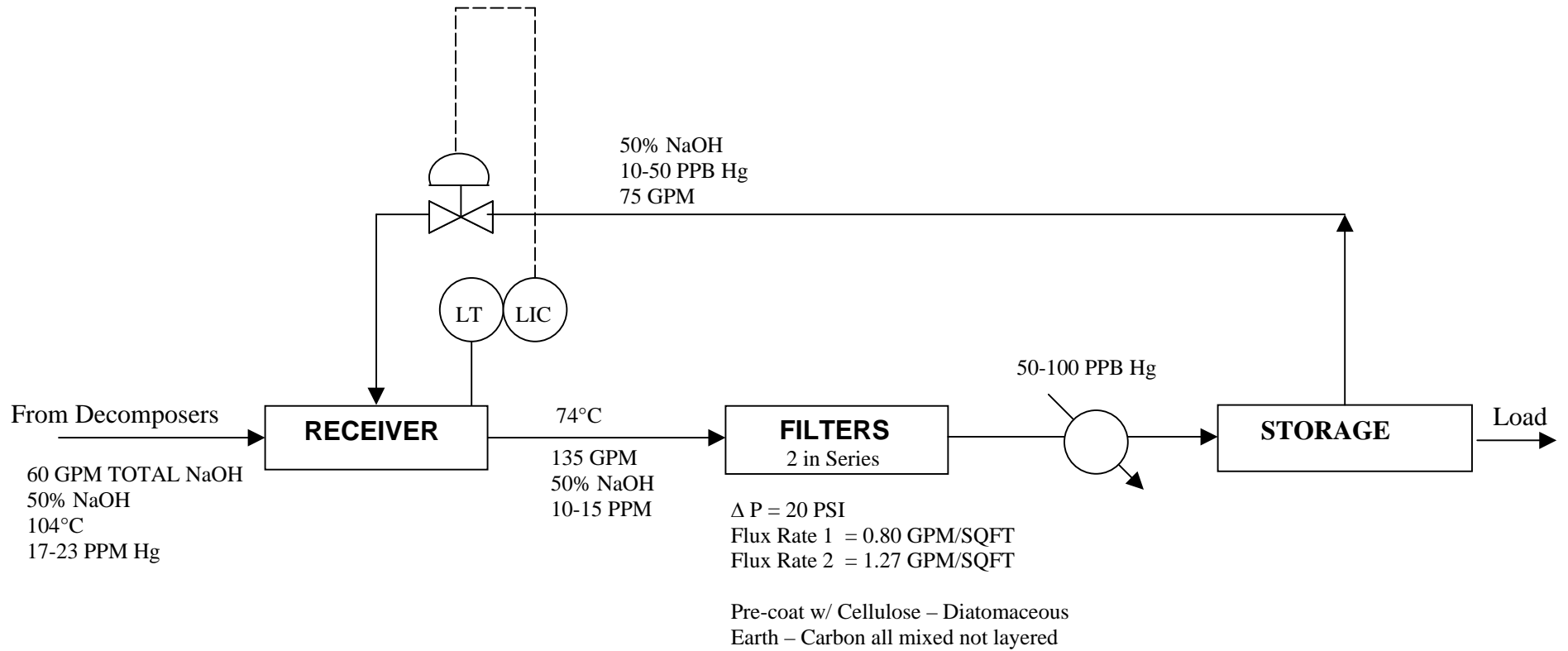
# Plant #5



# Plant #6



# Plant #7



PROCESS INFORMATION	Plant #1	Plant #2	Plant #3	Plant #4	Plant #5	Plant #6	Plant #7
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**GENERAL**

Chlorine Capacity - TPD	455	305	330	99	540	366	250
Cautic Capacity - TPD	513	344	372	113	610	413	275
Cell Type	E-812	E-510	E-510	Denora	UHDE	Denora	Denora
Cell Number	48	58	60	24 11 Na	52	36	32

**DECOMPOSER**

Decomposer NaOH outlet temp.	130 C	130 C	130 C	102-104 C	125-130 C	107-118 C	104 C
Decomposer NaOH flow	114	76	83	26	133	90	60
Outlet NaOH seal leg (Y/N)	No	No	No	Yes	No	No	No
Hydrogen cooling (direct/indirect)	Direct	Direct	Direct	Indirect	Indirect	Indirect	Indirect
Hydrogen condensate temp. (C)	60-80	60-80	60-80	13-27	29	30-60	N/A
Deionized Water Cooling (Y/N)	No	No	No	Yes	No	No	No
Deionized Water Temp. (C)	60-80	60-80	60-80	49	19	N/A	N/A
Hg in NaOH at Decomposer PPM	10 to 15	10 to 15	10 to 15	4 to 6	6 to 10	5 to 15	17 to 23
Hg in NaOH into filters PPM	10 to 15	10 to 15	10 to 15	2 to 3	6 to 10	5 to 15	10 to 15
Hg in NaOH out of filters PPB	<b>70-120</b>	<b>70-120</b>	<b>60-120</b>	<b>30-40</b>	<b>160</b>	<b>50</b>	<b>50-100</b>

**CAUSTIC RECEIVER**

Caustic Receiver Volume - Gal.	2280	2280	1385	1500	4000	4200	2000
Residence Time (min.)	8	9	9	19	15	23	8
Recycle to Receiver (Y/N)	No	No	No	Yes	No	Yes	Yes
Recycle from: (filters / storage)	---	---	---	Filters	---	Storage	Storage
Recycle rate (gpm)	0	0	0	25	0	0	75
Mercury level in recycle - PPM	---	---	---	0.03	---	---	0.03
Operated on level control (Y/N)	Yes	Yes	Yes	Yes	Yes	Yes	Yes
yes - (pump discharge or recycle)	pump flow	pump flow	pump flow	pump flow	pump flow	pump flow	recycle flow

**CAUSTIC TRANSFER PUMP(S)**

Capacity (GPM)	120	80	100	50	133	90	130
Manufacturer	Goulds	Goulds	Goulds	Durco	Durco	Durco	Durco
Type	Mag-drive	Centrif.	Centrif.	Centrif.	Centrif	Centrif	Centrif
Pump Discharge Pressure (PSIG)	85	85	80	72	95	N/A	42
Filter Inlet Pressure (PSIG)	50-80	50-80	50-75	60	78-95	30-60	22



**PROCESS INFORMATION**

Plant #1 Plant #2 Plant #3 Plant #4 Plant #5

**CAUSTIC FILTERS**

Manufacturer	Adams IWF	Adams IWF	Adams IWF	Adams IWF	Adams IWF	Adams IWF	Adams IWF
Filter Element	C200	C200	C200	C200	C200	C200	C200
Primary Filter Area (ft2)	197	197	197	94	238	189	169
Number of Primary Filters	1	1	1	2	2	1	1
Primary Filter Arrangement	Single	Single	Single	Parallel	Parallel	Single	Single
Secondary Filter Area (ft2)	197	197	NA	NA	NA	189	53
Number of Secondary Filters	1	1	---	---	---	1	2
Secondary Filter Arrangement	Single	Single	---	---	---	Single	Parallel
Flux rate on Primary filter- gpm/ft2	0.58	0.39	0.42	0.27	0.28	0.48	0.80
Flux rate-Secondary filter- gpm/ft2	0.58	0.39	NA	NA	NA	0.48	1.27

**FILTER OPERATION**

Precoat Material (1)	Solka-floc BW40	Solka-floc BW40	Solka-floc BW40	Darco Premium	E.P. Diat. FW-60	E.P. PB33	Celite
Precoat Material (2)	---	---	Norit D-10	---	Norit AZO	(Eagle Picher)	Nuchar SA
Precoat Material (3)	---	---	---	---	---	---	E.P. PB33
Loading (1) lb/ft2	0.254	0.254	0.127	0.005	0.084	0.132	0.296
Loading (2) lb/ft2	---	---	0.254	---	0.084	---	0.266
Loading (3) lb/ft2	---	---	---	---	---	---	0.237
Precoat Fluid	Water	Water	50% Hot NaOH	50% Hot NaOH	DI Water	DI Water	DI Water
Precoat Quality Assesment	*1	*1	*1	*2	*3	*1	*1
*1 -- Filter discharge sent to off-spec tank until lab verification of acceptable Hg levels in filtered caustic.							
*2 -- Filter discharge recycled to caustic receiver until lab verification of acceptable Hg levels in filtered caustic.							
*3 -- Filter discharge sent to check tank until lab verification of acceptable Hg levels in filtered caustic.							
Filter Tube Pre-conditioning	No	No	No	.096 lbs/ft2	No	No	Yes
Scheduled Replacement	As needed	As needed	As needed	As needed	24months	18 months	48 months

**BACKWASH CRITERIA**

Hg concentration	>0.25 ppm	>0.25 ppm		Body feed	>0.5 ppm	>0.09 ppm	>0.30 ppm
Pressure drop across filters	40 PSIG	40 PSIG		15 PSIG	35 PSIG	25 PSIG	20 PSIG
Time on-line	5 days	7 days		4 weeks	3 weeks	3 weeks	5-10 days
Backwashes	2 min - 4 max	2 min - 4 max		1	3 pulse/2 wash	3	1
Bodyfeed	No	No	No	High Hg	No	No	No
Amount (lbs)	---	---	---	0.5	---	---	---

PROCESS INFORMATION	Plant #1	Plant #2	Plant #3	Plant #4	Plant #5	Plant #6	Plant #7
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**Misc.**

Off Spec NaOH	Separate	Separate	Separate	Blend/Product	Blend/Product	Blend/Product	Blend/Product
Off Spec Filter at Off Spec Tank	No	No	No	Yes	No	No	No
Check Tank	No	No	No	No	Yes	No	No
Inlet Cooler Temperature (C)	110	110		93	125	110	77
Outlet Cooler Temperature (C)	60	55		54	60	77	60

**LABORATORY ANALYSIS**

Analytical Instrumentation	LDC Milton Roy 920404 & P.S. Analytical	LDC Milton Roy 920404 & P.S. Analytical	LDC Milton Roy 920404 & PSA	Bacharach, Coleman; Model 50D & Leeman Labs PS200	Varian, M-6000A & Perkin-Elmer M 3100	Jerome Model 411	Methods for analysis were not available at time of visit.
Analytical Method	CVAA, & CVAF	CVAA, & CVAF	CVAA, & CVAF	CVAA & CVUV	CVAA & CVUV	Gold Film	
Digestion Sample Size (grams)	10	10	20	5	2	1.5	
Neutralization Acid	Conc. HNO3	Conc. HNO3	Conc. HNO3	1:4 H2SO4	Conc. H2SO4	Conc. HNO3	
Aliquot Sample Size (grams)	0.05	0.05	0.2	5	2	0.3	
Oxidation Solution	5% Acid KMnO4	5% Acid KMnO4	5% Acid KMnO4	5% Acid KMnO4	5% Acid KMnO4	5% Acid KMnO4	
Reduction Solution	SnCl2	SnCl2	SnCl2	SnCl2 or SnSO4	SnCl2 (10%)	SnCl2	
Calibration	Verification Once per Shift & Multi- Point Quarterly.	Verification Once per Shift & Multi- Point Quarterly.	Verification Once per Shift	Multi-Point Calibration Monthly & Verification Daily.	Verification Once per Shift & Multi- Point Monthly.	Multi-Point Calibration Monthly	
Operators Analysis Frequency	N/A	N/A	Hourly	Hourly	Four times/day	Every 4 Hours	
Laboratory Analysis Frequency	Every 4 Hours	Every 4 Hours	Every 8 Hours	Daily 24 hour Composite & 0800 confirmation	Daily 24 hour Composite ,0800 confirmation & Check Tank.	Daily 24 hour Composite ,0800 hrs. confirmation.	

CVAA = Cold Vapor Atomic Adsorption

CVAF = Cold Vapor Atomic Florescence

CVUV = Cold Vapor UV-Vis Spectroscopy

## V. Team Conclusions

1. Cooler decomposers reduce the level of mercury to be removed from the caustic product. Caustic from the decomposer should be in the 104 °C to 106 °C range.
2. Ensure that a flux rate of 0.30 gallons per minute per square foot through the R. P. Adams filters is not exceeded.
3. A recycle from the filter discharge to the caustic receiver should be used and it should equal to or greater than the production flow rate coming to the receiver.
4. The filter elements should be R. P. Adams poro-carbon 200 or equal.
5. The poro-carbon elements should be “conditioned” prior to their first use. This conditioning consists of having fine carbon distributed on the elements until the desired filter quality is achieved.. The particle size of the carbon should be 325 mesh or smaller.
6. Filter element pre-coating using only carbon or at least using a carbon base coat is the preferred method.
7. The pressure drop across the elements should not be allowed to exceed 15 pounds per square inch.
8. A constant filter outlet pressure should be maintained. This minimizes down stream pressure changes caused by storage tank changes or valve switching.

Specific elements of a composite caustic filtration system are detailed that will aid in achieving mercury in caustic in the range of 30 PPB to 40 PPB. At the time of this study, the range of 30 PPB to 40 PPB mercury in caustic was believed to be the best sustainable quality in the Chlor Alkali industry using only mechanical separation equipment. The caustic filtration system recommended by this report is a composite system based upon all of the manufacturing facilities visited.

The final equipment sizing and optimum equipment operating procedures will require an investment in a pilot system. The filtration system involves, first, use of a recycle stream from the discharge of the existing filters back to the caustic surge tank or receiver. This stream is at least equal to the normal caustic production flow forward to storage. The second part of the recommended system is to achieve a filter area flux rate of 0.25 gallons per minute per square foot. The third process feature is the use of a finely ground carbon pre-coat for the filter tubes. This pre-coat is to “fill” the pores of the filter element and not meant to provide the separation medium for the elemental mercury to be removed. This conditioning medium will make the filter elements less porous and thus more efficient. The fourth process optimization reduces the allowable pressure drop to a maximum of 15 PSI. The backwash of the filters would be done first on 15 PSI pressure drop, and second on high mercury. The fifth process enhancement is incorporation of backpressure control on the filter discharge to eliminate the negative impact of switching caustic storage tanks. The sixth process adaptation is a procedure by which fine carbon is body fed to the filter upon elevated or mercury break-through to prolong the filter cycle.

## VI. Team Recommendations

The entire Team recommends purchase of a pilot filter system. The pilot program requires an investment in equipment, and commitment of our development resources to design and interpret the data from the proposed experimental plan. The Team recommends working with the Chlorine Institute to help us share the cost of this effort. However, the Team further believes that we must go forward with a pilot system on our own if necessary.

In addition to pilot testing, our Team makes recommendations in the following areas:

1. Continue to develop approaches to cooling the decomposer operation i.e. cooler caustic inside the decomposer and cooler caustic leaving the decomposer
2. Install 'Sir Galahad' on-line analyzers for final product and pre-coat recycle streams.
3. Optimize filter flux rates and caustic recycle rates.
4. Install filter recycle, pump capacity, and filter surface area capacity to match the results of the pilot testing.
5. Retain current lab techniques for mercury analysis.

A limited testing program with existing production equipment may provide a cost-effective and timely way to verify some of the conclusions drawn in this report. However, due to many factors only a limited amount of testing can be done without interruption of normal production, and would require equipment installation. Therefore, a combination of pilot testing and field-testing at one or both production sites provides the best approach for determining the exact requirements for our caustic filtration systems. The results from these studies would allow more precise capital assessments as well as providing a more thorough knowledge of caustic filter operation that is desperately needed in order to consistently achieve 30-40 PPB mercury, or lower, in caustic product.

## APPENDIX 7.4

# Optimization of R P Adams Filter

Experimental Design  
& Results

Review with Chlorine  
Institute

# Results of Pilot Work



- Defined operating conditions that reliably predict the level of mercury in 50% caustic after filtration.
- Demonstrated the conditions to consistently achieve 30-40 ppb level after filtration.
- Developed statistical model to predict filter performance.

# Design Approach



- Select significant variables
  - Temperature
  - Flux Rate
  - Recycle Rate (Recycle Ratio)
- Utilize Fractional Factorial Design as screening test
- Analyze Variances

# Project Organization

- Schedule- August 1998 - January 1999
- Equipment Cost - \$210K
- Equipment
  - Pilot RP Adams (14 ft<sup>2</sup>)
  - Mercury On-line analyzer
  - Process Control- OMNX



# Fractional Factorial Design



- Intended to be used in early stage of investigation as screening
- Main effects > 2-factor interactions > 3 factor interactions
- Designs can be augmented to resolve ambiguities.
- Can directly go to Evolutionary Optimization

# Fractional Factorial Design

Variable	-	0	+
1. Temperature, °C	80	90	100
2. Flux Rate,gpm/ft <sup>2</sup> min	0.20	0.25	0.30
3. Recycle Rate,ratio	0	0.5	1.0

Constrained Variables	
Pressure Drop, psig	≤ 20
Precoat type	AZO carbon
Precoat amount, lb./ft <sup>2</sup>	0.25

<i>Design</i>				
<i>Run</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>Response ppb Mercury</i>
1	80	.20	0	
2	80	.25	.50	
3	80	.30	1.0	
4	90	.20	.50	
5	90	.25	1.0	
6	90	.30	0	
7	100	.20	1.0	
8	100	.25	0	
9	100	.30	.50	

# Statistical Inference



- ANOVA (Standard Error)
- Coefficients (Algorithm)
- Contour Plot (Surface Response)
- Echip
  - Echip, Inc. 724 Yorklyn Road, Hoeckessin, DE
  - Tel. (302) 239-5429

# Analysis of Variance

## ANOVA

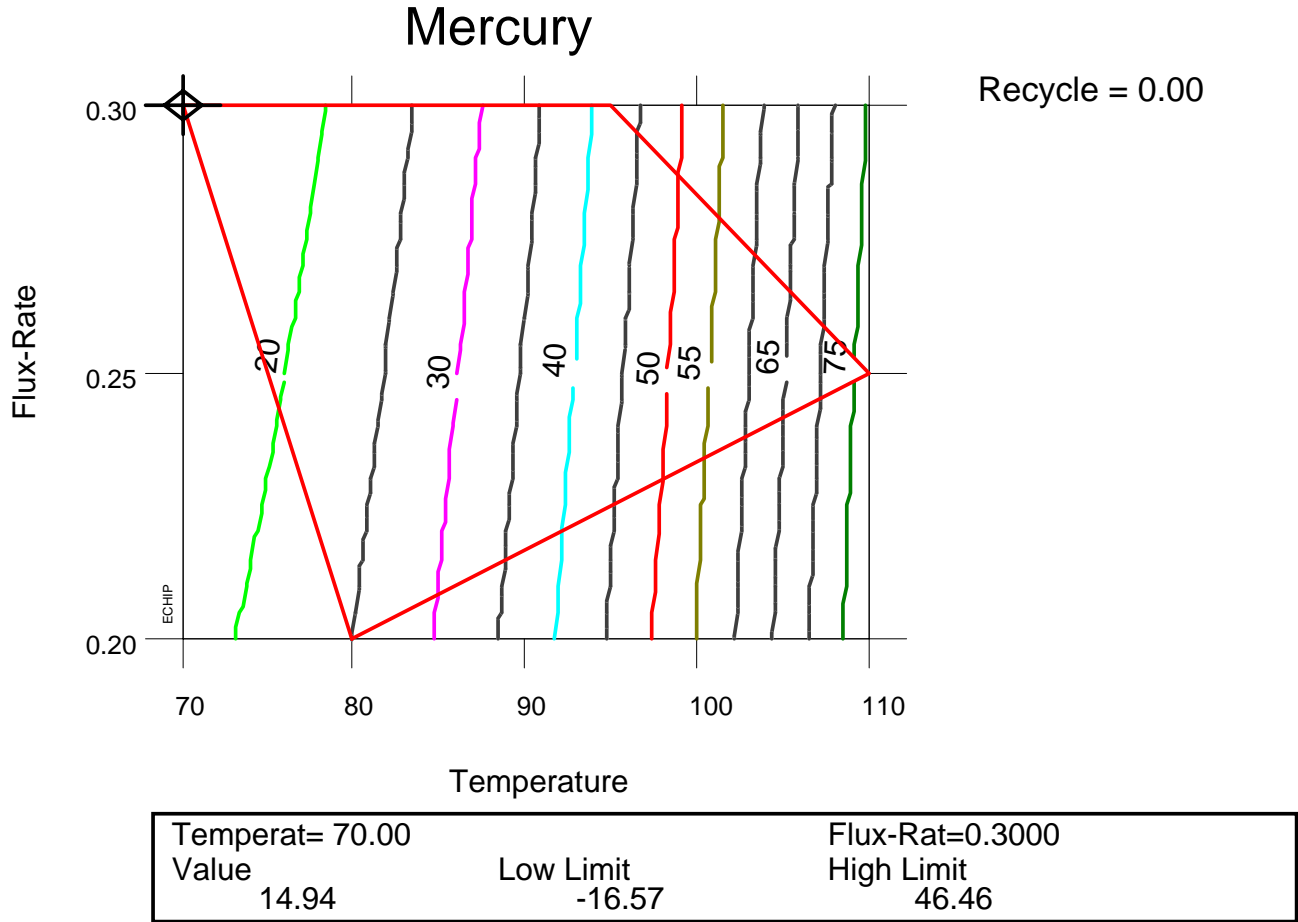
Variable	Mean Squares	Degrees of Freedom	P
Temperature	3257.2	2	0.0001
Flux-Rate	25.258	1	0.6499
Recycle	79.2014	1	.4273
Error	114.6	9	

## Coefficients

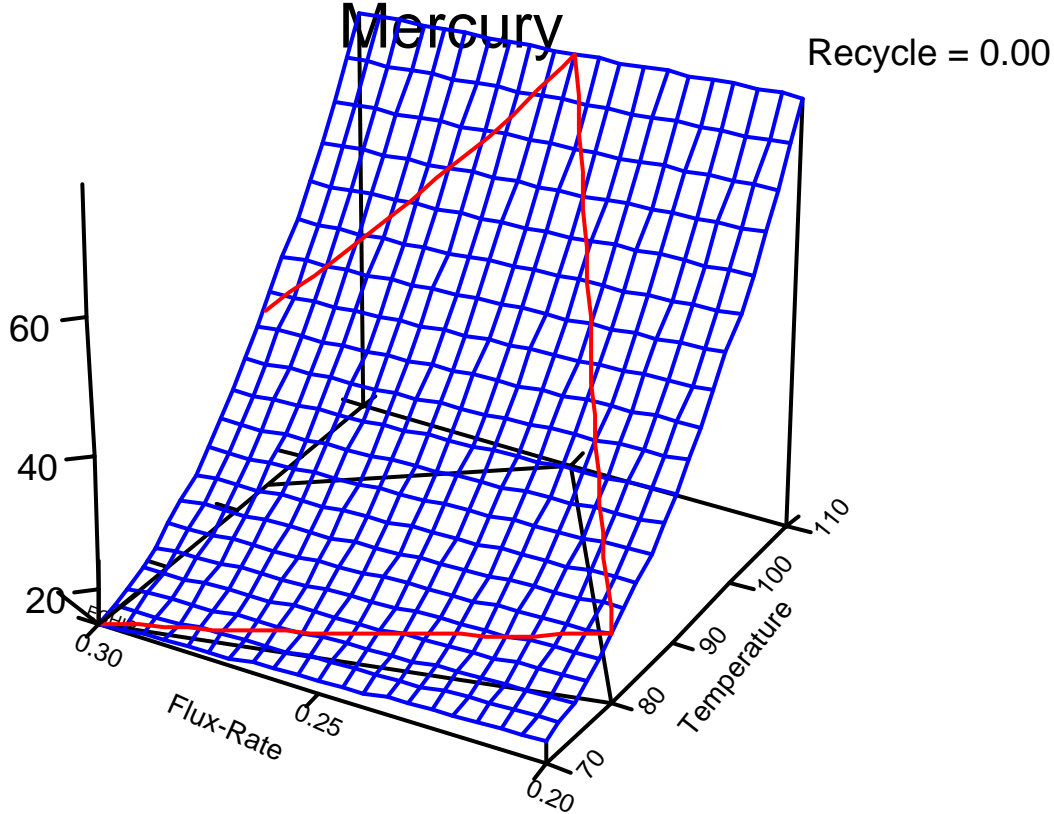
Variable	Coefficients	Standard Deviation	P
Constant	39.0267		
Temperature	1.5047	.256839	.0001
Flux-Rate	-36.6366	78.0385	.6499
Recycle	3.65373	4.39505	.4273
Temperature <sup>2</sup>	.0287338	.0194628	.1740

N TRIALS = 14
N terms = 5
R Squared = 0.982

# Contour Plot



# Contour Plot



# Results of Predictive Model

Prediction Values at 95% Confidence

Temperature	Flux Rate	Recycle	C-Hull	Mercury	Limits
70	.30	0	Inside	15	(-16,46)
80	.30	0	Inside	21	(-5,47)
90	.30	0	Inside	33	(6,61)
100	.30	0	Outside	51	(23,79)
110	.30	0	Outside	75	(46,104)
120	.30	0	Outside	104	(65,143)

# Optimization of R P Adams Filter



Equipment Configuration  
& Reliability  
Review with Chlorine  
Institute



# Equipment Design



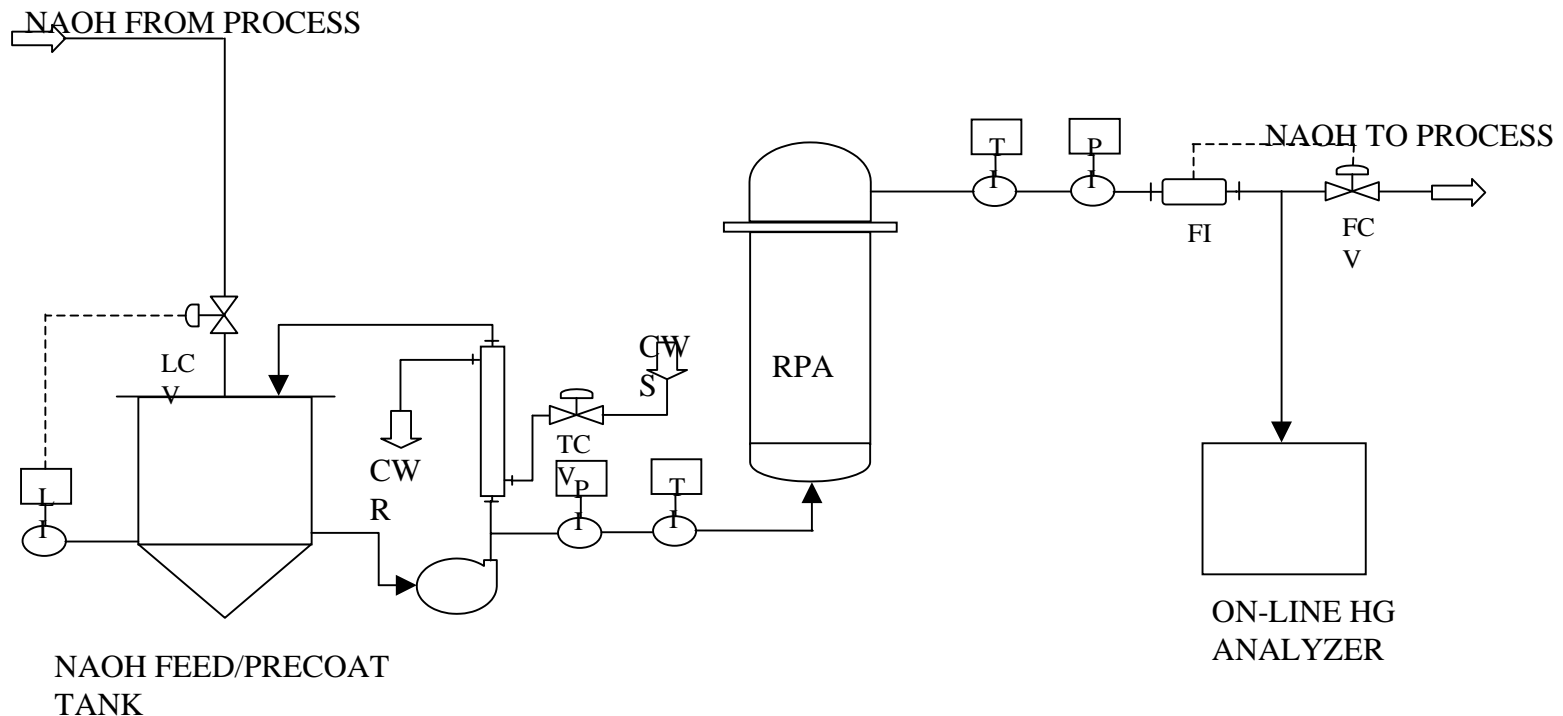
- Test Platform-RP Adams Unit
  - Nickel Lined/Carbon Steel Shell
  - Elements-C-200 Porocarbon Tubes
  - Four Elements in unit-14 ft<sup>2</sup>
- Filtration Media-Norit AZO
- Mercury On-Line Unit-P S Analytical
- Control via OMNX Software Package

# Equipment Reliability



- Up-time for RP Adams @ 100%
- On-line Analyzer
  - Unit requires routine maintenance
  - Unit requires attention to details of operation

# Equipment Configuration



FLOW DIAGRAM - RPA FILTER

## APPENDIX 7.5

### SELECTIVE ABSORPTION TECHNOLOGIES

#### 7.5.1 SAMMS

This technology is based on the attachment of a sulfur ligand to a ceramic bead for immobilization. This technology was developed for the treatment of radioactive nuclear waste. The ceramic beads used in this process are in the 1 to 5 micron size and would be very difficult to work with on an industrial scale. They have been working on method of imbedding the particles into membranes to make them more usable. This technology has not gotten beyond the laboratory testing stage and the material is still being manufactured in gram size batches.

Technical Contact: Jun Liu  
Pacific Northwest National Lab  
509 375 2616

Commercial Contact: Nick Lombardo  
509 375 3644

#### 7.5.2 Thio Crown Ether

Thio crown ethers have been manufactured and used to remove mercury from aqueous solutions even at very low pH. This technology was developed for the removal of mercury from acid solutions. The developer has not yet attached the thio crown ether group to a polymer to immobilize it. So far it has been used as a flocculent followed by filtration. Testing in muriatic acid was found to be ineffective and 50% sodium hydroxide was not tested because the developer felt that the ether would not survive the test.

Technical Contact: John Reynolds  
Lawrence Livermore National Laboratory  
925 423 4289

