

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

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THE CHLORINE INSTITUTE, INC.

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1. 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/Ft²), 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.

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/Ft² 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 25-50 μ . 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/Ft² 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/Ft² 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 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/Ft² filter area. The activated carbon application rate varies between 0.005-0.27 Lbs/Ft² filter area. The diatomaceous earth application rate is approximately 0.15 -0.20 Lbs/Ft² 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/Ft² 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.

3. **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 -10 μ . Pilot studies suggest that pore sizes less than 0.45 μ do not improve mercury removal and that the 0.45 μ 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.

3.2.3 Pleated Cartridges

Pleated cartridges have a large surface area, typically 7-8 ft²/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 1ft²/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-ft² 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 0.45μ 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.

4. 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 – 1st Stage Adams Filtration
- Step 2 – 2nd Stage Adams Filtration
- Step 3 – Cooling
- Step 4 – 1st Stage Microfiltration
- Step 5 – Storage
- Step 6 – 2nd Stage Microfiltration

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

Outlet Mercury Concentration (PPM)

Sodium Receiver	1st Stage Adams	2nd Stage Adams	1st Stage Microfiltration	2nd Stage Microfiltration
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.

5. 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.

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:

- Chem Abstracts (Chemical Abstract Service)
- World Patent Index (Derwent)
- Pollution Abstracts (Cambridge Scientific Abstracts)
- Compendex (Engineering Information, Inc.)
- 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)
 - Activated carbon
 - Graphite
 - Polyolefins
 - Nickel gauze
 - Asbestos
 - PTFE
 - 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)

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% KMnO₄ / 10% H₂SO₄ 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

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- 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**.
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- 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.
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Phone: (716) 877-2608
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- 6.2.5 Votator/Schenk Filters, c/o Chemetron Process Equipment, PO Box 35600, Louisville, KY 40232
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- 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
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