GUIDELINES FOR TECHNOLOGIES TO REDUCE MERCURY IN SODIUM HYDROXIDE

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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 appropr0iate.

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^2), 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 140ºF 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^2 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^2 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^2 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/Ft^2 filter area. The activated carbon application rate varies between 0.005-0.27 Lbs/Ft^2 filter area. The diatomaceous earth application rate is approximately 0.15 -0.20 Lbs/Ft^2 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 140-175ºF.

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^2 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