



INDUSTRIAL WASTE STUDY MERCURY--USING INDUSTRIES

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MERCURY-USING INDUSTRIES

By

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ENVIRONMENTAL PROTECTION AGENCY

ABSTRACT

This study discusses information obtained from a literature survey, mail survey, telephone contact phase, and field trip pertaining to industrial wastes of mercury-using industries. The main topics presented for each industrial group are: (1) uses of mercury; (2) reasons for industry's use of mercury; (3) alternatives to use of mercury in the industry; and (4) best available level of treatment and control. Research needs are also recommended for future studies.

In general, it was found that under present technology mercury cannot be fully replaced in dentistry, the electrical industry (lamps, batteries), production of chemicals (pharmaceuticals, laboratory reagents), catalysis, and industrial and control instrumentation. Substitution is technologically possible but probably not warranted because of minimal hazard from mercury use in switches and in some industrial and control instrumentation. Substitution is possible and highly desirable (in the absence of fully effective treatment and control methods) in the chlor-alkali and plastics industries. Use of mercury has come or is coming to an end in agriculture, paints, and pulp and paper production.

The best present and proposed treatment and control methods can reduce typical mercury concentrations in industrial waste waters to levels of 1 to 5 ppb. However, very few facilities control their mercury discharges to this extent.

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SECTION I

INTRODUCTION

Mercury contamination of the environment from industrial sources is not a recent phenomenon. Beginning in the 1950's, Japan experienced the effects of methyl mercury chloride pollution from a vinyl chloride and acetaldehyde plant which was discharging into Minamata Bay. The seafood taken from this bay was highly contaminated with mercury; and over a period of years, numerous persons became ill and some died from consuming mercury-laden seafood. In Europe, the Swedish government imposed a ban in 1968 on seed dressings containing alkyl mercurials, following the discovery of high mercury levels in wildlife; and it continues to conduct detailed investigations of other industrial sources of mercury contamination. Finally, in 1970 the attention of the world was focused on the problem of mercury pollution when a Norwegian graduate student at the University of Western Ontario, after studying the pesticide problems that involve wildlife from 1967 to 1970, reported high concentrations of mercury in fish from Lake St. Clair.

The Federal Government has held extensive hearings, called enforcement conferences, and begun litigation against several companies for discharging mercury and its compounds into the sewerage systems and watercourses of this country. Results of these Government actions have been a notable reduction in mercury discharges and industrial reassessment of the need to use mercury and/or its compounds in production and manufacturing. At the same time, a broad program of studies has been initiated to define the environmental impact of mercury on air, water, and land. The scope of the industrial aspects of the problem is suggested by the fact that in 1970 industrial uses consumed over 4½ million pounds of mercury.

As a part of this Federal study program, this report defines the state-of-the-art of the best level of treatment and control currently available to the industries using mercury or its compounds in production or processing. This study discusses by industrial category the following topics:

- 1) mercury use
- 2) reason that the industry uses mercury
- 3) alternatives available to the industry instead of using mercury
- 4) best level of treatment and control currently available

Furthermore, research needs are indicated when currently available treatment and control technology is insufficient to meet effluent criteria for mercury. The optimum effluent criterion is no discharge. On the whole, significant and useful information is

available on uses of mercury, reasons for these uses, alternatives to these uses, and the nature of treatment and control methods; but data on effectiveness of these methods (i.e., on the mercury concentrations in final effluents) are relatively scarce.

To accomplish the objectives of this study, an in-depth literature survey was begun using Dow Chemical's extensive bibliography on mercury. During this same period, 194 companies were contacted by letter for information pertinent to this study, as were numerous trade and manufacturer associations. A response of 46% was received from the company survey, with one third of the answers being "no longer use" or "do not use" mercury. Among the industries no longer using mercury are electroplating, jewelry casting, hat making, and explosives manufacture. Fifteen associations answered a similar inquiry. Where the answers were unclear or incomplete, telephone contact was made to acquire the desired information. Further contacts were made with State and Federal agencies to secure information. Following the literature and mail surveys and telephone contact phase, a field trip was made to visit companies using mercury in production and manufacturing, as well as to meet persons knowledgeable in the treatment and control of industrial effluents containing mercury. After the field trip, all information obtained was reviewed and assimilated. Much of the information gathered by direct inquiry from industrial sources is presented in this report without reference to avoid individual company identification.

Finally, as a result of this investigation it has become clear to the researchers that mercury is a widespread contaminant in many commonly used industrial and household chemicals and products. In this sense, very few people are not involved in a "mercury-using industry" of some sort. The scope of the potential problem in this situation requires definitive study.

SECTION II

MERCURY-USING INDUSTRIES

Mining

Mercury is commonly found in nature, primarily as cinnabar (HgS); but major ore deposits of economical quality are relatively few. In the first quarter of 1971, 11 mines producing over 100 flasks each (a flask contains 76 pounds of mercury) accounted for over 87% of U. S. production (1). (Figures for individual mines are considered proprietary information.) Total U. S. mine production in 1970 was 27,281 flasks (1), down slightly from 1969 and 1968 totals of 29,360 and 28,874 flasks, respectively (2).

In recent years, the average U. S. mine recovered approximately 5 pounds of mercury per ton of ore mined (2). The principal recovery method is by rotary kiln which heats the ore to as high as 1500°F. The mercury vaporizes and is collected by air-cooled condensers. A detailed process diagram (Figure 1) is shown on the following page.

The following treatment and control method is used at a major mercury mine which was visited for this study. All the water required in the processing of ore, such as that from a hoeing table and from washdown of the mill floor, comes to a common drain which then takes the water (50 gpm) through two counter-current traps. Then the water is pumped to a tailings pond and allowed to pass through the soil. When tested, mercury was undetectable in the water six miles downstream of this tailings pond. However, the background concentrations of Hg in the area are high. Ground water has a mercury content of 8 ppb. Since geological characteristics of mercury ore deposits are basically the same from area to area, this information is probably applicable to mercury mining in general.

Mercury has in the past been used also in gold mining to extract finely divided gold from its ore. The mercury was amalgamated with the gold, the amalgam physically separated from the ore, and the mercury distilled off in retort furnaces to leave a gold residue. This process was in use in recent years at only one mine and has been completely replaced there by a cyanide process. The change was prompted by high mercury levels in the mine's effluent streams. Quantitative data are not available.

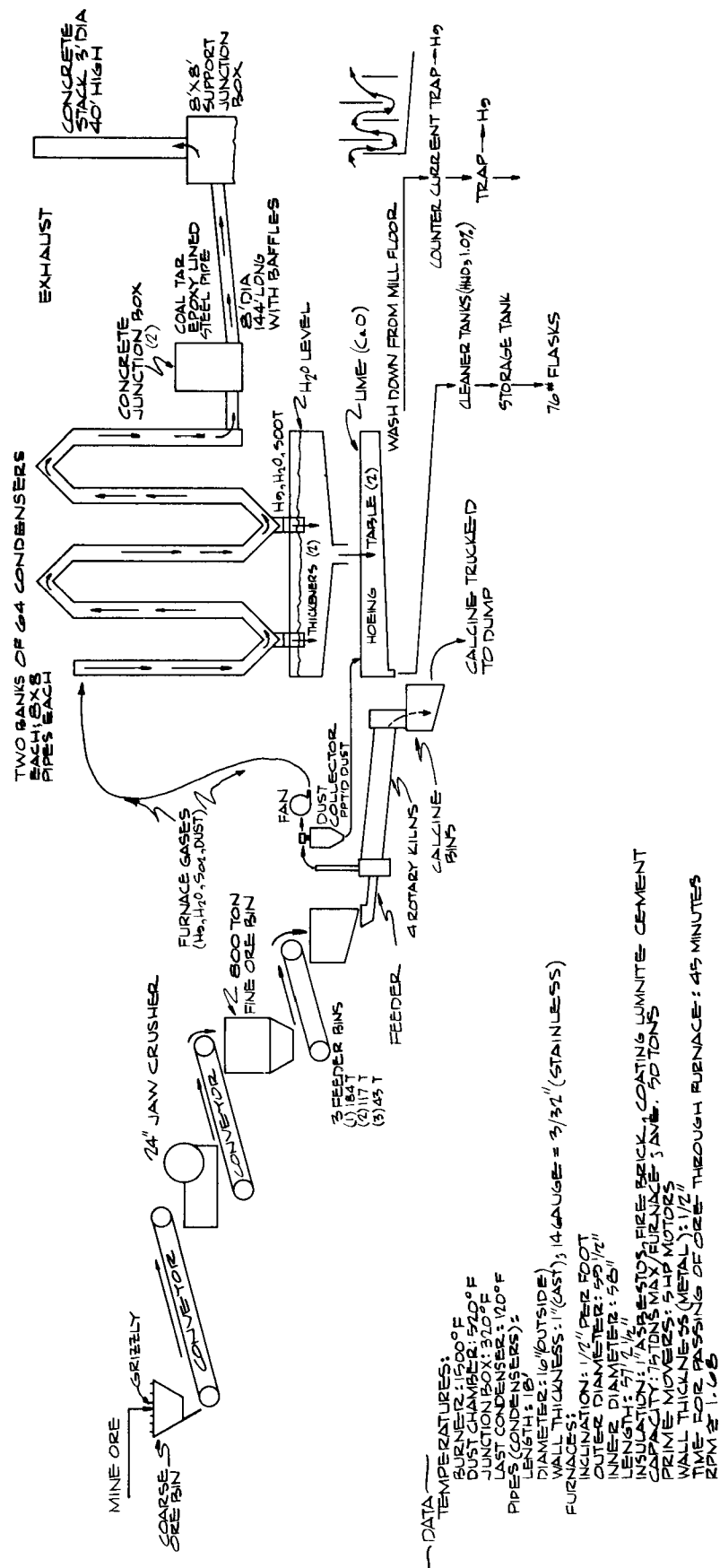


Figure 1. Flow Diagram of Mercury Mining

Chemical Production

The production of industrial chemicals includes a large number of organic and inorganic mercury compounds. In various forms and formulations these chemicals become catalysts, finished products, and raw and intermediate products for other industrial processes, including the production of agricultural chemicals, paints, and pharmaceuticals. The production of mercurials, however, is basically a single category of industrial activity independent of the diversity of end uses to which the products are put. Table 1 depicts the quantitative distribution of mercury consumed by chemical production over the last five years.

TABLE 1. MERCURY CONSUMED IN U.S. FOR CHEMICAL PRODUCTION (1,2)
(76-pound flasks)

Use	1966	1967	1968	1969	1970
Agriculture ¹	2,374	3,732	3,430	2,689	1,811
Catalysts	1,932	2,489	1,914	2,958	2,238
Paint	8,420	7,178	10,566	9,730	10,347
Pharmaceuticals	232	283	424	724	690
TOTAL	12,958	13,682	16,334	16,101	15,086

1. Includes fungicides and bactericides for industrial purposes.

By definition, there are no alternatives to the use of mercury in the production of mercury compounds as a whole. In specific instances, of course, a non-mercurial may be a suitable substitute for a mercury compound. For the producer of mercury compounds, however, this may mean merely that production of the mercurial will end, since he may not be equipped to produce the substitute. Specific alternatives are applicable to end uses of the mercurials and are discussed under individual uses in this section.

As a single industrial category, the production of industrial chemicals, and specifically of mercurials, presents most of the water pollution problems experienced in other mercury-using industries. Reduced to its simplest terms, the basic problem is to remove organic and inorganic, suspended and dissolved mercury and mercury compounds in various initial concentrations from effluents with a wide variety of characteristics. All aspects of

this problem are represented to some extent in the treatment of effluents from chemical production plants. It is useful, therefore, to consider at this point the best methods of treatment and control applicable to this industry, and to discuss variations and exceptions in these methods where applicable under the specific industrial activities involved.

Best Available Level of Treatment and Control for Chemical Production

In general, treatment and control techniques for mercury in liquid wastes consist of chemical reactions and physical separation methods. Among the chemical means are conversion (e.g., organic to inorganic compounds), chelation, ion exchange, and precipitation; the physical means consist of filtration, centrifugal separation, and gravitational settling. The chemical means are generally applicable to dissolved compounds and the physical means to suspended particles. Surface-chemical effects can also be used to remove mercury from waste streams, with flocculation being effective for suspended solids and activated adsorption for dissolved solids. Various combinations of these individual techniques can be used to provide the best available treatment methods for characteristic effluents of different mercury-using industries. Table 2 summarizes the four best available treatment methods and their applicability and effectiveness.

Sodium Borohydride and Chelating Resin Treatment Process

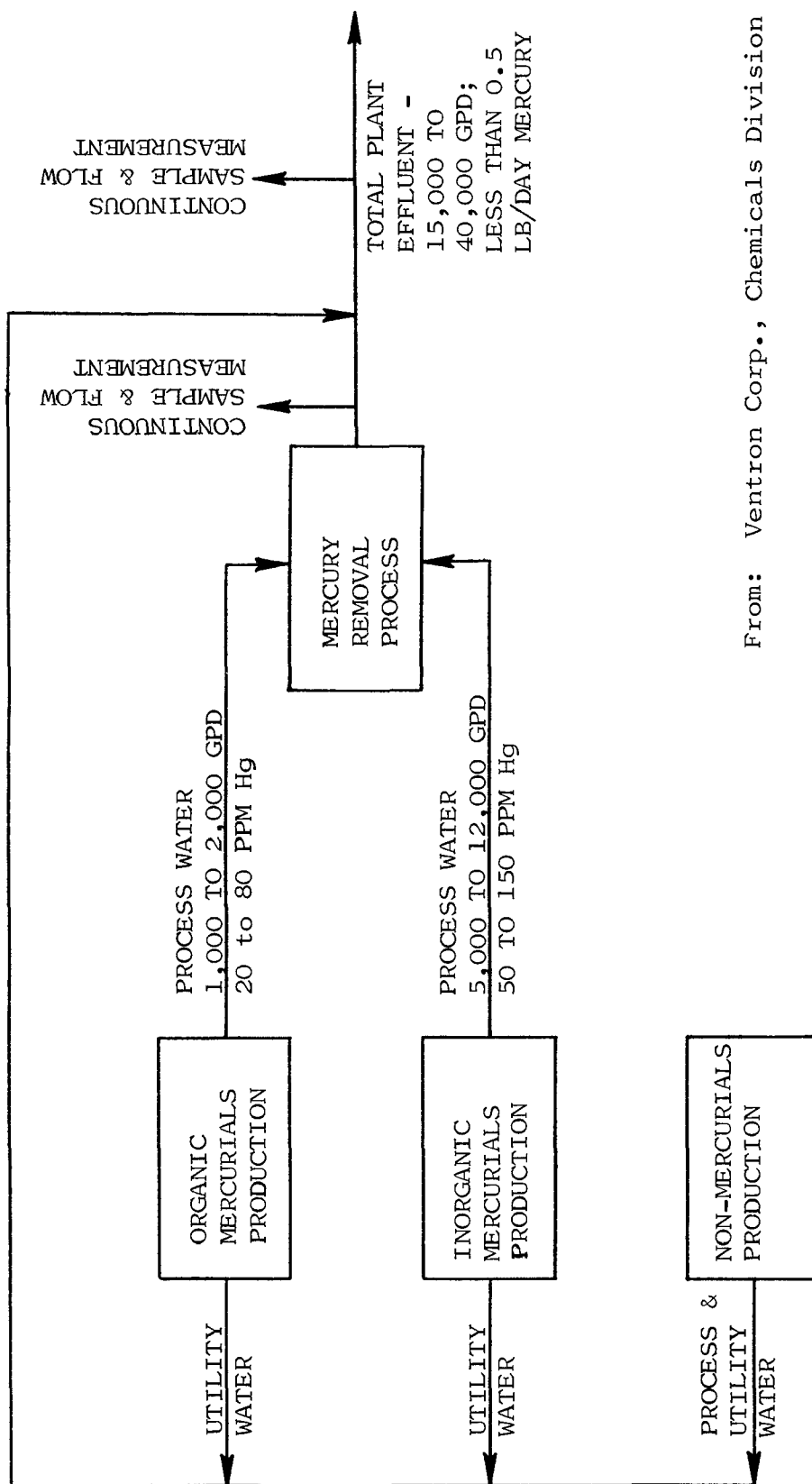
This method of treatment and control of mercury in chemical production effluents is a recently developed process in limited field use and is based on mercury reduction with sodium borohydride. Figure 2 is a diagram of the waste water flow from the production of mercurial and non-mercurial chemicals. Description of the "mercury removal process" indicated in Figure 2 is depicted in detail in Figure 3. This removal process is the primary treatment system used by its developer, the Ventron Corporation.

Mercury-bearing waste waters resulting from production of purified mercury and mercury-based chemicals are treated to limit mercury discharges to an average of less than 0.5 lbs/day (three shifts) in aqueous effluent. Since the plant effluent flow rate varies between 15,000 and 40,000 gpd, the effluent contains mercury in the range of 1.5 to 4 ppm (mg/l). Before mercury removal in the primary treating system, the processing discharge from production of inorganic compounds contains 50 to 150 ppm mercury, and that from production of phenyl organic compounds contains 10 to 80 ppm (after chemical pre-treatment).

The primary treatment method involves a proprietary combination of chemical conversion of organic to inorganic mercury compounds, precipitation with sodium borohydride, and physical separation. The effluent from the primary treatment process is secondarily passed through a chelating resin bed for further reduction of mercury

TABLE 2. SUMMARY OF BEST AVAILABLE TREATMENT METHODS FOR CHEMICAL PRODUCTION

Type of Process	Industries Where Applicable	Effluent Data-- Mercury Concentration	Removal
Sodium borohy- dride plus chelating resin	chemical, others	potentially 1 to 5 ppb	-----
Osaka Soda (ion exchange after pH adjust- ment)	pulp and paper, electrical, instru- ment, chemical, ¹ and pharmaceutical	2 to 5 ppb	-----
Cationic polymer flocculation	paint, pulp and paper, chemical	2.5 to 15 ppb	99% suspended solids 60% chemical oxygen demand (COD) 75% phenyl mercurials
Proprietary-- Terraneers, Limited	chemical, others	10 ppb	-----
1. Chlor-alkali to be included under chemical.			



From: Ventron Corp., Chemicals Division

Figure 2. Waste Water Flow Diagram - Ventron Corp.

From: Chemical and Engineering News,
December 14, 1970, p. 48

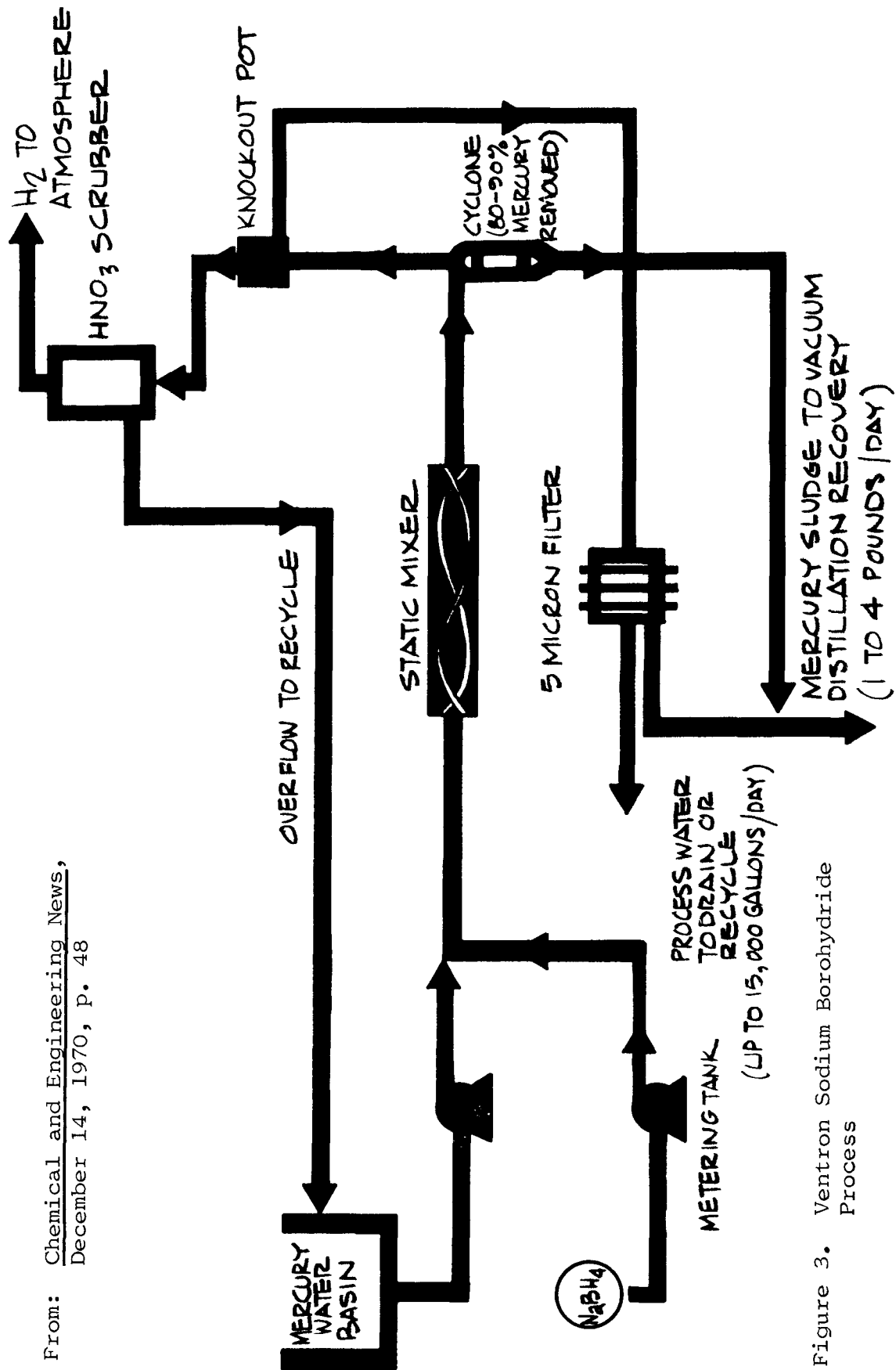


Figure 3. Ventron Sodium Borohydride Process

content. Use of the chelating resin as a secondary treatment process is still under investigation by Ventron. Ultimately, the Ventron Corporation expects to achieve mercury levels of 1 to 5 ppb by combining sodium borohydride reduction with secondary treatment of a chelating ion exchange resin.

Osaka Soda Mercury Recovery Process

The Osaka Soda (OS) Process, as seen in Figure 4, was developed over a ten-year period in Japan and has been used commercially in four Japanese chlor-alkali plants for up to five years. It is also claimed to be applicable to waste streams from pulp and paper, electrical, instrument, chemical, and pharmaceutical industries (4).

Solutions are treated by adjusting to a free chlorine content and then filtering. At this point, the Hg concentration has been reduced from an initial value of about 20 ppm to about 5-7 ppm (5). The filtrate is then passed over ion exchange resin (reducing mercury level to about 150 ppb (5)) and then through a tower containing Osaka Soda's MR resin. The MR resin reduces mercury content to a typical level of 2 ppb and a maximum level of 5 ppb. Mercury is then recovered from the primary ion exchange resin; the MR resin is discarded several times a year (4).

Cationic Polymer Flocculation

Another treatment process has been developed to keep the effluent concentration of mercury down to the concentrations of 2.5 ppb to 15 ppb by employing a cationic polymer for flocculation of the waste water effluent stream containing mercury. The flocculant removes approximately 99% suspended solids and 60% of the chemical oxygen demand (COD) from the waste stream. In addition, approximately 95% of the phenyl mercurials are removed from the waste by this flocculant step so as to produce a treated effluent stream appreciably devoid of mercury, suspended solids, and COD (6). This process is presently being used in treating a paint manufacturer's effluents.

Proprietary Process--Terraneers, Limited

Terraneers, Limited has developed a mercury-removal system which brings waste waters down to levels of 10 ppb. The exact nature of the process has not been revealed to date because of patent considerations. The waste has to be neutralized (pH 8), dechlorinated, and filtered prior to reprocessing in this system (7).

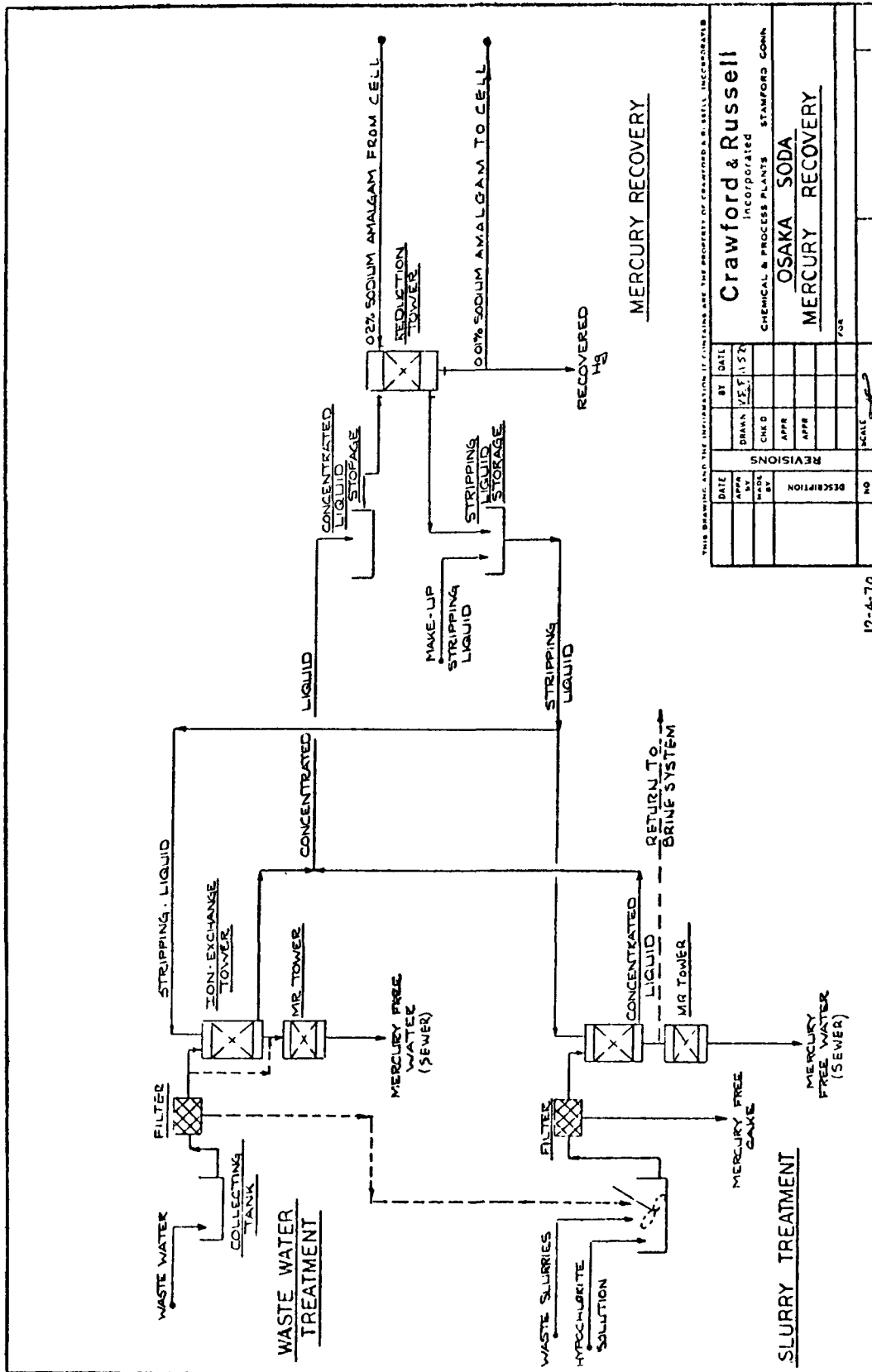


Figure 4. Osaka Soda Mercury Recovery Process

Agricultural Chemicals

Accurate figures for the consumption of mercury for agricultural chemicals are not available, since the standard Bureau of Mines statistics include fungicides and bactericides used for industrial purposes under the Agriculture use category. With this qualification, agricultural consumption of mercury in 1970 amounted to 1811 flasks, a significant reduction from an average level of about 3000 flasks in previous years (1,2). This reduction can be fairly confidently attributed to the Department of Agriculture's cancellation of registrations of alkyl mercurials, which did not become officially binding until late in the year but which clearly indicated the limited future in mercury pesticides. The first quarter of 1971 shows the use of 338 flasks, up from 150 in the last quarter of 1970. Quarterly figures for the past two years, however, show similarly large fluctuations (8), so that no special significance can be attached to this statistic.

Alternatives to the mercurial pesticides have long been available but have been little used because they have drawbacks in terms of cost, effectiveness, or ease of application. The cancellation of registration for alkyl mercury pesticides, however, is forcing the adoption of existing substitutes and the development of new ones. Major producers have already discontinued lines of agricultural mercurials and are marketing substitute products.

Specifically, non-mercurial fungicides being produced for small grains include thiram, maneb, and captan. For cottonseed, the same three are available, as well as Terracoat L21, Busan 72, and chlorothalonil-Dexon. Use of a systemic fungicide like chloroneb or carboxin in conjunction with one of the others has resulted in levels of effectiveness equal to or greater than those of mercurials (9). These combinations and others tend to approach the broad spectrum of activity of the mercurials, which none of the substitute products individually possess (10). Chemical compositions and other data on specific products are presented in Appendix A.

Since agricultural chemicals are generally marketed directly by the chemical producers, the treatment methods described on pages 6-10 are directly applicable.

Catalysts

According to Bureau of Mines reports (1,2), the yearly average of mercury consumption in catalytic use was 2,300 flasks for the period of 1966 to 1970. No appreciable trend in increased or decreased consumption is evident during this period.

Mercury catalysts have been tried as esterification, hydration, reduction, oxidation, dehydration, chlorination, fluoridation, sulfurization, sulfonation, isomerization, polymerization, and disproportionation catalysts.

The important mercury compounds that are used industrially or experimentally as catalysts are:

Mercury	Mercuric oxide
Mercuric acetate	Mercuric phosphate
Mercuric chloride	Mercuric sulfate

These compounds have been used extensively in the manufacturing of acetaldehyde, vinyl acetate, vinyl chloride (plastics), and sulfonated anthraquinone (vat dyes) (11). Information on the relative quantities of these different mercury catalysts used was not found.

Organic mercurial salts are used in urethane elastomers for casting, sheeting, and sealant applications. Another use of organic mercury catalysts is in a urethane resin, molded into a nearly indestructible automobile bumper. Approximately three parts of commercial mercury catalyst are employed in each 100 parts of resin. Active content of mercury in the catalyst is about 5%. A low-cost sealant, whose production is in the multi-million pound range, also employs PMA (phenyl mercuric acetate) catalyst. In this case, about 0.1 per cent of the PMA dissolved in a solvent is used for each 100 parts of resin. Active content of mercury in the catalyst is again 5 percent. Cellulosic sheeting is backed by these kinds of urethane elastomers and is the subject of U. S. and foreign patents (12).

Vinyl chloride ($\text{CH}_2=\text{CHCl}$) monomer is produced by the reaction of HCl with acetylene in the presence of a catalyst, mercuric chloride. About 0.074 pound of mercury used as a mercuric chloride catalyst is consumed per thousand pounds of vinyl chloride monomer in the acetylene process (12). Further data describing the percentage of consumed mercury that would be released in waste water were not available.

All mono- and disulfonic acids (except the 2-anthraquinone sulfonic acid) of anthraquinone require use of a mercury-salt catalyst for sulfonation (11). These acids are produced by the sulfonation of anthraquinone with oleum, the orientation of the entering group being determined by whether or not mercury is used as a catalyst (13).

Another catalytic use of mercury is the process of making acetaldehyde by hydration of acetylene. Vinyl acetate, also, is made by the condensation of polyhydric alcohols, with mercuric chloride catalyzing this reaction.

Vinyl chloride monomer production (used in plastics) is shifting from the requirement of acetylene plus mercurial catalyst to oxychlorination of ethylene to make ethylene chloride, which is subsequently cracked to vinyl chloride (11). Substitutes for organic mercurial salts used in production of urethane elastomers are amines and stannous soap and salts (12). Dehydrogenation and air oxidation of ethyl alcohol are production methods now being used to manufacture large quantities of acetaldehyde (11).

Effluents from catalytic reactions can be treated by the methods described on pp. 6-10 to remove mercury and both organic and inorganic mercury compounds.

Paint Industry

The principal use of paint in general is for protection of surfaces from environmental exposure. Many categories of paint compose this industry's product market. The two basic types used are solvent-thinned and water-thinned (latex) paints. Special antifouling paints are applicable to protection of underwater marine surfaces. The principal use of mercury in paints is as a can preservative and mildewcide (fungicide) for latex paints and as a mildewcide in many solvent-thinned paints. Phenyl mercury compounds are the most widely used additives. Depending on the climate, 3.5 to 10 pounds of phenyl mercuric acetate (PMA), which is 18% mercury by weight, are required per hundred gallons of both types of paint for effective protection (14). In 1970, 10,149 flasks of mercury were used in the formulation of mildew-proofing (fungicide) and preservative compounds for paints (1). Previously, an average of 8,630 flasks/yr were consumed for these purposes in the years 1965 - 1969 (2). By contrast, for the last five years, the use of mercurials in antifouling paints has been kept to a minimum, ranging from a consumption of 140 flasks in 1966 to a high of 392 flasks in 1968 (2). In 1970, 198 flasks were required to produce antifouling compounds in paints (1). It must be realized that, generally, the paint companies do not manufacture mildewcides or antifoulants but purchase these compounds as additives to their paint products.

Phenyl mercurials are a general protoplasmic poison when they come in contact with molds, mildew, and bacteria. Phenyl mercurials prevent the growth of mildew on exterior paint systems applied over bare wood through long-term protection of the wood surface. Fungicidal mercury compounds are securely bound, in an undetermined manner, in the wood surface beneath the paint film (15).

Alternatives to the Use of Mercury

Cuprous oxide and tributyltin oxide have already generally replaced mercuric oxide in antifouling paints, although mercuric oxide is still registered for use under the Federal Insecticide, Fungicide, and Rodenticide Act.

A recently published list (16) of paint biocides (including phenyl mercurials) contains a number of possible substitutes for mercurials. Among the apparently most widely applicable are modified barium metaborate, parachlorometacresol, dodecylguanidines, thiocyanates, chlorophenols, and salicylanilides. All of these are suggested by the manufacturer as candidates for use as fungicides and preservatives in both solvent-thinned and water-emulsion paints. The complete list appears in Appendix A.

However, toxicities of these compounds have not been completely determined, nor have their fungicidal or bactericidal qualities been finalized. These products are presently being evaluated by their manufacturers and by paint companies, and further definitive research and long-term evaluation are clearly needed to assess the suitability, effectiveness, and safety of these and other potential substitutes for mercurials in paints. The paint industry has estimated that two years of research will be required for discovery and testing of substitutes as fungicides on exterior surfaces (17).

Best Available Level of Treatment and Control

The best available method of control presently used for latex paint production is the retention and subsequent recycling of wash water into a new batch of paint. This process also is applicable to solvent-thinned paint production in that the solvent sludge from vat cleaning can be similarly reused. Therefore, the best level of control exercised is the ideal one of no discharge. The cleanup procedure after manufacturing a batch of paint is to scrub the mixer and wash down with water or solvent for latex or solvent-thinned paint, respectively. This wash water or solvent, which may contain fungicide and preservative, is then pumped into a holding or storage tank. The water or solvent stays in the tank until it can be pumped back into a new batch mix. However, the closed recycling system is not applicable to all paint manufacturers. The smaller production facilities cannot afford this system, and they do not always have the available space for the storage tanks which are required. The reason for a number of storage tanks is that each type of paint is of a specific formulation and contains different ingredients; therefore, the blending of the retained wash water or solvent sludge must be matched and must not interfere with the ingredients in the new batch being manufactured.

This process of holding the wash water or solvent sludge has further complications in that the size of the manufactured batch, and consequently the entire process, varies at each company. The recirculation ratio of hold wash water or solvent sludge to new make-up ingredients also varies from company to company. Furthermore, the mercury content of the wash water or sludge is dependent on the type of paint being produced and the amount of mercury additive used.

Solvent-thinned paint wastes can be settled and filtered and the waste solids incinerated. No water pollution results from this process since the solvent is not discharged into a water-course or sewage system. Some paint companies incinerate this type of waste on their premises. Others send their wastes to a separate company whose business is to dispose of industrial

wastes. The solvent-thinned paint wastes are then incinerated on the waste disposal company's premises (18).

Paint companies not employing these methods of treatment and control can use those methods described under Chemical Production, pp. 6-10.

Pharmaceuticals

According to Bureau of Mines statistics (1), 690 flasks of mercury were consumed by the pharmaceutical industry in 1970. This level of usage indicates an apparent return to a downward trend in mercury consumption for pharmaceuticals evident between 1950 (5996 flasks) and 1966 (232 flasks), after a three-year upswing to 724 flasks in 1969 (2,8).

Mercurials are used in a number of pharmaceutical and cosmetic preparations. Organic mercury compounds are used in diuretics and antiseptics; inorganic mercury salts are used in solutions for sterilization of instruments; ammoniated mercury, oxides of mercury, and metallic mercury are used in skin preparations; phenyl mercury compounds are used as preservatives in cosmetics and soaps (12).

For all uses except diuretics, the antimicrobial properties of mercurials are the essential reasons for the use of these compounds in pharmaceuticals, cosmetics, and soaps. "The inactivation of bacteria by mercurials may be caused by a blocking of cellular enzymatic thiol receptors with formation of mercaptide bonds, and without any other demonstrable cell injury" (19). Another suggestion is that the mercurial interferes with essential sulfhydryl groups of organisms (20).

Effective nonmercurials are available for use as diuretics, and substitutions are possible in antiseptics, sterilization solutions, skin preparations, and preservatives (12). Hexachlorophene, for example, is a nonmercurial disinfectant and is commonly used in germicidal soaps (21). It is also used in the treatment of burns (although mercurochrome appears to promote more rapid healing) (22). Bithionol compounds are nonmercurials effective as topical antiseptics (21). Iodine and iodine compounds are, of course, also still widely used as nonmercurial antiseptics. Thiazide compounds (e.g., benzthiazide, chlorothiazide) and other nonmercurials (e.g., chlorazanyl, acetazolamide, theobromine) are already reducing the importance of mercurials as diuretics (11,21).

One general factor in opposition to development of nonmercurial substitute pharmaceuticals is the need for recertification by the FDA. Aside from the costs of development and testing, there is a significant time lag in the processing of new drug applications.

Best Available Level of Treatment and Control

Limited information was obtained on the treatment and control methods used by pharmaceutical manufacturers using mercury and its compounds. Information obtained indicates that the amount of mercury-containing

residues resulting from the production of certain pharmaceuticals is 0.1% of the quantity of mercury used in the end product. For example, if 10 mg of phenyl mercuric acetate (PMA) is used as a preservative in a tube of topical cream, 0.01 mg of PMA per tube would be the residue resulting from the production of this pharmaceutical. These mercury-containing residues are discarded by a State-approved system of dry-fill burial, with no residues discharged into or reaching any stream. Insufficient information is available to rule out the possibility of groundwater contamination, however,

In general, the treatment methods described on pp. 6-10 are applicable to effluents contaminated by pharmaceutical mercury compounds.

Pulp And Paper Industry

Mercurial compounds (mostly phenyl mercuries) played an important part for many years in slime control applications in the pulp and paper industry. Their use, however, had been steadily declining even before the mercury controversy of 1970, which resulted in their complete discontinuance (23). This trend is evident in Bureau of Mines consumption figures (1,8), which show an almost uninterrupted decline in usage from 3,481 flasks in 1960 to 226 flasks in 1970 (most of which were used in the first quarter). Consumption for the first quarter of 1971 has dropped to zero (1).

As in agricultural, paint, and pharmaceutical uses, the biocidal properties of mercurials made them useful compounds in pulping and paper manufacturing processes. They are effective over a broad pH range and against a wide variety of microorganisms (23).

Alternatives to the Use of Mercury

The pulp and paper industry now uses only nonmercurials for slime control. In general, however, these alternative products are more specialized either in pH range or in microorganism activity. By using products in proper combinations, however, the effectiveness of the mercurials should be attainable (23).

Four main areas of application can be defined, with particular products most suitable to each area (23):

1. Bacteria control at pH's below 7.0. Methylene bithiocyanate-based products are the most common in this area, and they include Nalco 270, 271, 272 and 273 and Betz's Slime-Trol Rx 30, Rx 31, Rx 32 and Rx 38. In some instances, better performance can be obtained with an organo-sulfur by itself or alternated with a methylene bithiocyanate product. Examples of these cases are where pink slime is a potential problem or where the aerobic, nonsporeforming bacteria Pseudomonas is the chief cause of trouble. Such organo-sulfurs include Nalco 243, 244 and 246.
2. Fungi Control. The chlorinated phenols are the usual alternates in this area, although the amines are good also. Some examples in the chlorinated phenol category are Nalco 21-M, Nalco 21-S and Nalco 201 and Betz Rx 12, 17, 23 and 26. Nalco 236 is a popular amine-based material.
3. Bacteria Control at pH's above 7.0. The organo-sulfurs and the amines are most favored in this area, while methylene bithiocyanate products can be used with special feeding techniques.

4. Preservatives. In general, the organo-sulfurs and chlorinated phenols have shown the best performance and are covered in the Betz-Nalco range. The organo-sulfur is generally preferred because of its broad pH range and FDA clearance for coatings applications.

Of the various organo-sulfurs available, apart from the above products, R. T. Vanderbilt's Vancide 51Z has proved effective as a mold-proofing agent, preservative and slimicide. It is a compound of zinc dimethyldithiocarbamate (87 per cent), zinc 2-mercaptobenzothiazole (7.5 per cent) and having total zinc as a metallic of 19.8 per cent. As far as mold-proofing is concerned, it is as effective as mercury. For mold resistance in some applications requiring FDA clearance, Vancide P-75 has also proved effective. Its composition: N-trichloromethyl-mercapto-4-cyclohexene-1 2-dicarboximide (75 per cent) and inert ingredients 25 per cent (23).

Best Available Level of Treatment and Control

Although mercury is no longer being used in the pulp and paper industry, it still appears to be a possible heavy metal in the plants' effluent streams (24). The explanation of this phenomenon is that the caustic soda (produced by mercury cells) used in processing the pulp and paper contains a certain amount of mercury contamination. Since this industry uses considerable amounts of chlorine and caustic, mercury contamination would be very possible. The manufacturing processes where this contamination would appear are:

Kraft Bleaching:	Semi-Bleach
	High Bleach
	Dissolving Grades (Soft Wood)
	Dissolving Grades (Hard Wood)

Sulfite Pulp Bleaching:	Paper Grade
	Dissolving Grade

If mercury-free caustic and chlorine cannot be obtained for pulp and paper processing, the industry may have to adopt one or more of the treatment methods described on pp. 6-10 to eliminate mercury discharges entirely.

Chlor-Alkali Industry

Production of chlorine and alkali is one of the largest industrial consumers of mercury in the United States. According to Bureau of Mines reports, 15,011 flasks of mercury were used in 1970 for the electrolytic preparation of chlorine and alkali (1). Previously, 20,720 flasks were consumed for production in 1969 and 17,453 flasks in 1968 (1,2). However, prior to 1968 the production use of mercury averaged 11,533 flasks for 1965 to 1968 (2). Reasons for the 27% decrease in mercury consumption from 1969 to 1970 were economic conditions in the country, and the strict control measures imposed by the government on the discharge of mercury to the environment.

Mercury has a unique combination of properties enabling it to be liquid, electrically conducting, and chemically amalgamative during the production of chlorine and caustic. In the mercury cell method, mercury is used as a flowing cathode for the electrolysis of sodium chloride. Chloride ion is oxidized at the anode to form a fluid sodium amalgam. Amalgamation serves to transport the reduced sodium from the electrolytic reaction to the caustic-producing regeneration compartment, where it is catalytically reacted with water to form caustic soda and hydrogen. Mercury is then recycled to the electrolyzer section (25). This entire process is depicted in Figure 5. Appendix B contains another diagram of the process, showing in detail the points of mercury discharge.

Alternatives to the Use of Mercury

Alternatives to the use of the mercury cell for chlor-alkali production are the diaphragm cell and the Downs cell. The diaphragm cell is used by 54% of the chlor-alkali manufacturers, as compared to 40% of the manufacturers operating a mercury cell and 6% operating a Downs cell.

In a diaphragm cell, the electrolytic reaction products are kept separate by an asbestos diaphragm. When an electric current is applied to a salt solution within the cell, chlorine is generated at the positively charged anode on one side of the diaphragm. Meanwhile, the negatively charged cathode on the other side of the barrier attracts dissolved sodium ions, ultimately producing caustic soda and hydrogen gas (26).

The Downs cell involves an electrolytic process which takes place in a closed, rectangular, refractory lined steel box. The anode is made of carbon and the cathode of iron. Anode and cathode are arranged in separate compartments to facilitate

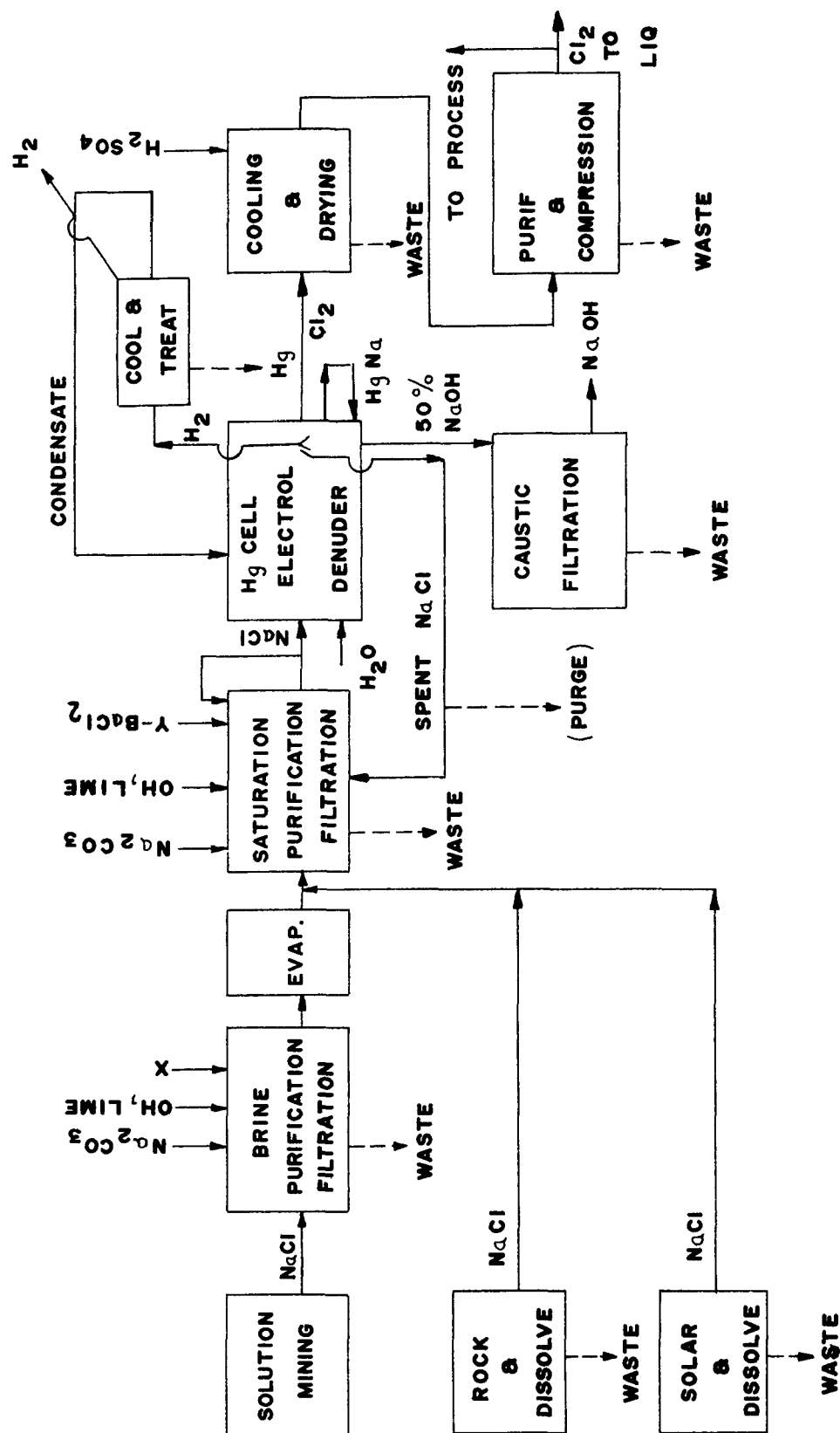


Figure 5. Chlorine - Caustic Soda Flow Diagram -- Mercury Cell (29)

the recovery of the sodium and chlorine. The electrolyte is a eutectic of 33.2% sodium chloride and 66.8% calcium chloride. The relatively low operating temperature increases the life of the refractory lining of the cell, makes it easier to collect the chlorine, and prevents the sodium from forming a difficultly recoverable fog (27).

However, the Downs cell and the diaphragm cell do not produce caustic soda which is sufficiently pure for many important applications. Mercury-cell-grade caustic is the preferred material for most applications when available at the equivalent price of diaphragm-cell caustic. The Chlorine Institute states that the diaphragm-cell caustic, no matter how it might be later purified, is still technically inferior in meeting the needs of the rayon, cellophane, and pulp and paper industries as well as being unsatisfactory as food stock for a number of specialty chemicals (28).

Best Available Level of Treatment and Control

Mercury is emitted from three main areas during the manufacturing of caustic and chlorine. They are: 1) the hydrogen stream, 2) the brine mixtures leaving the cell, and 3) the suspended elemental mercury in the product alkali (7,19). The concern in this study is the liquid mercury and mercury compounds leaving with the process waste waters from the brine treatment sludge handling (see Figure 6) and the suspended elemental mercury in the product alkali.

Plant Waste Water Treatment

Currently, the best treatment method of these process waste waters is a combination of precipitation with sodium hydrosulfide (NaHS) or ferrous chloride (FeCl_2), and the employment of activated carbon as a cleanup bed, the precipitate being collected as solid waste. A treatment scheme employing NaHS is shown in Figure 7.

Activated carbon, as shown in Figure 7, is a secondary treatment process following the precipitation by NaHS . The concentration of Hg in the effluents from the precipitation process is approximately 100 ppb. Employment of the activated carbon as a cleanup bed results in mercury levels of 10-20 ppb (7). The efficiency of this mercury removal process is about 99.7% since the mercury is reduced from approximately 40 lb/100 tons Cl_2 produced to a range of 0.05 to 0.25 lb Hg/100 tons (25).

Caustic Purification Treatment

Further treatment of the caustic end product can generally be recommended since the caustic will normally contain up to 10 ppm mercury. This mercury content can be reduced to 1 ppm with

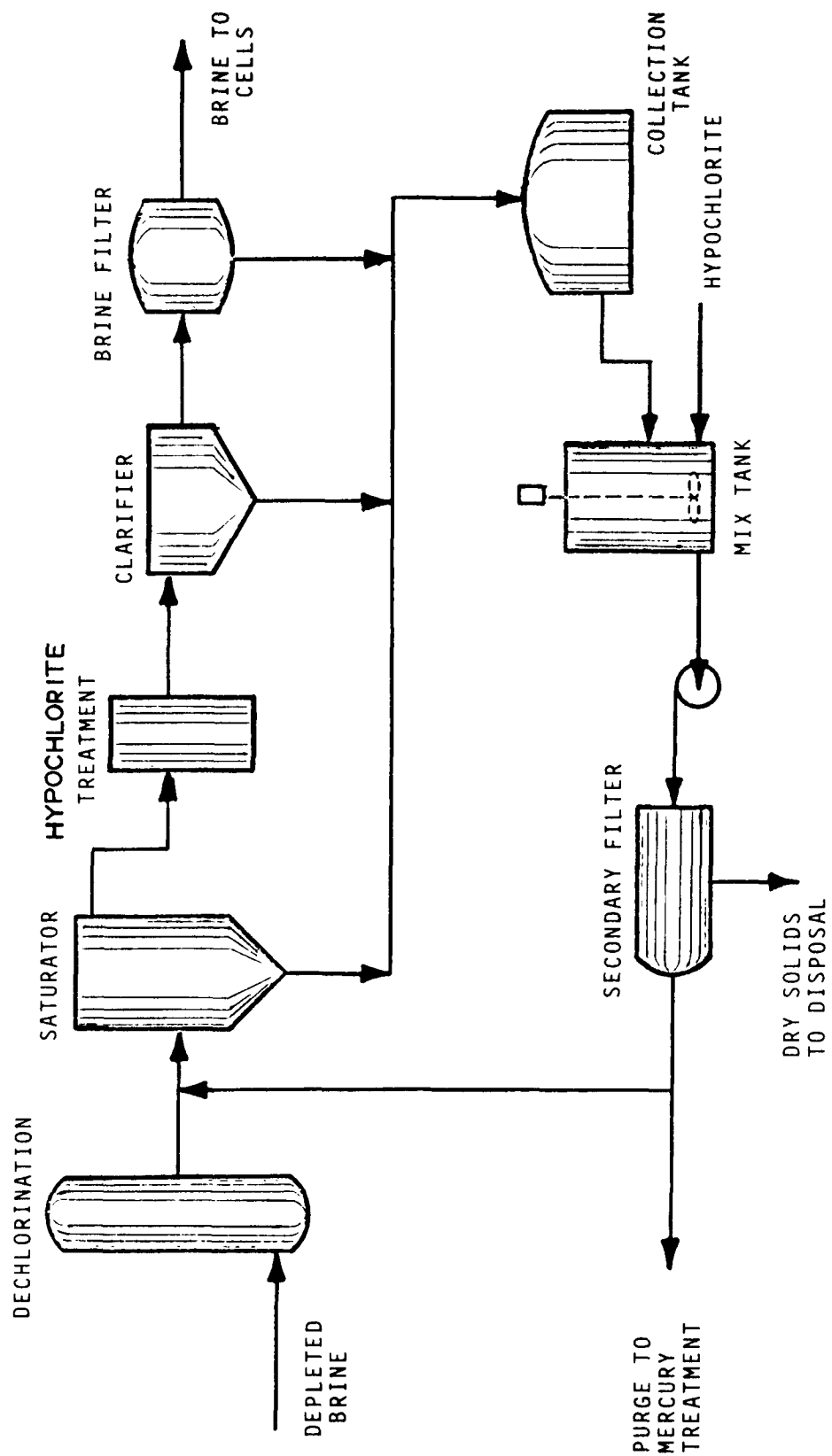


Figure 6. Brine Treatment Sludge Handling (7)

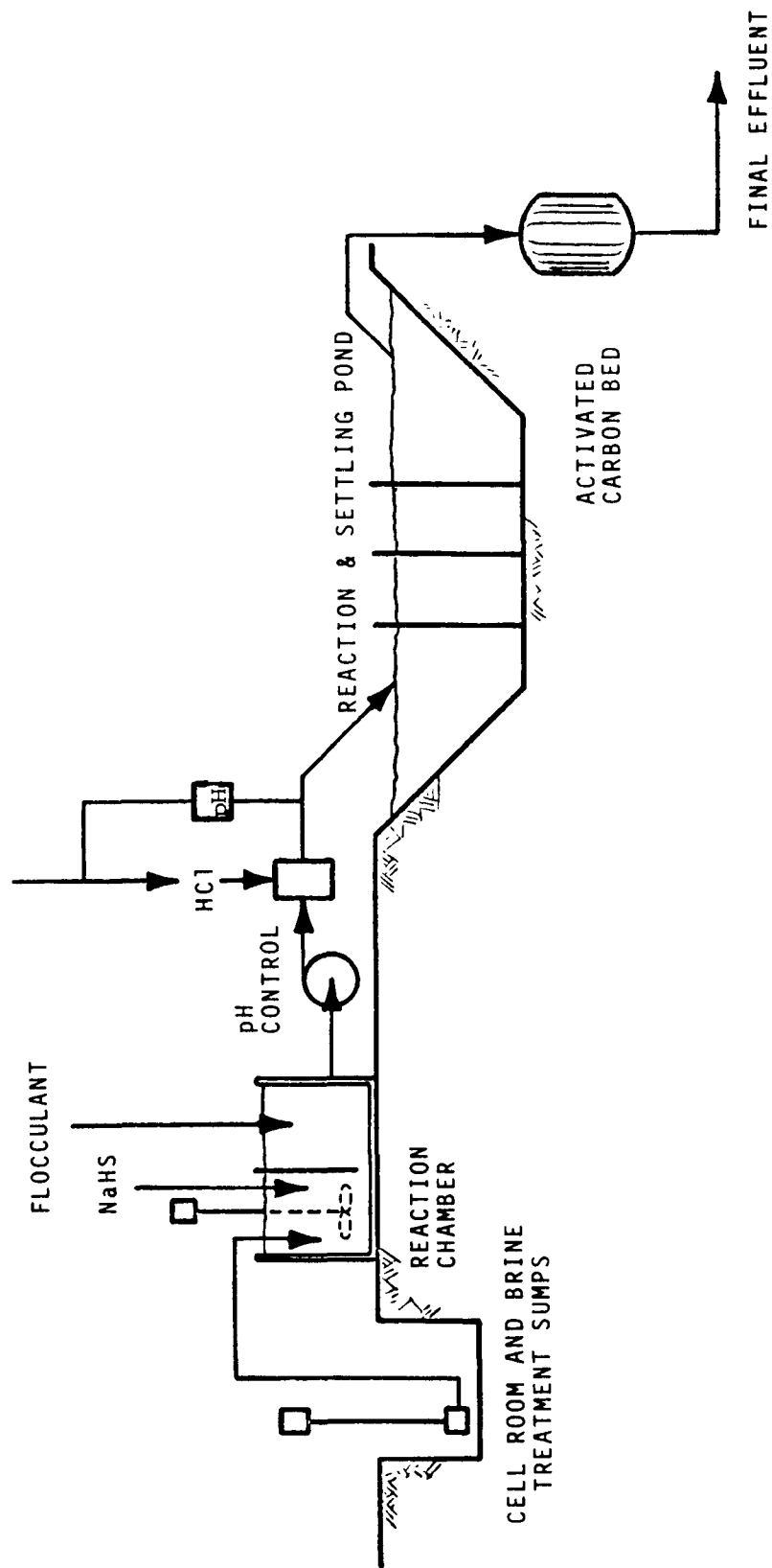


Figure 7. Sodium Hydrosulfide Treatment Process (7)

filtering without precoat, and to 0.05 ppm with use of precoat (preliminary application of certain substances to filter material to improve filtering capabilities). Both cellulose and carbon are used for precoat, with the performance of the carbon better than that of the cellulose. The sludge from this filtration is agitated, settled, and decanted, whereupon 85% of the contained sludge is recovered as metallic mercury. The remaining sludge is subjected to secondary filtration, and the filtrate is returned into the product stream. Recovery of mercury from this secondary sludge can be achieved via distillation or retorting. This entire process of mercury recovery from caustic filter is shown in Figure 8 (7).

Other best levels of treatment applicable to chlor-alkali production are discussed under Chemical Production, pp. 6-10.

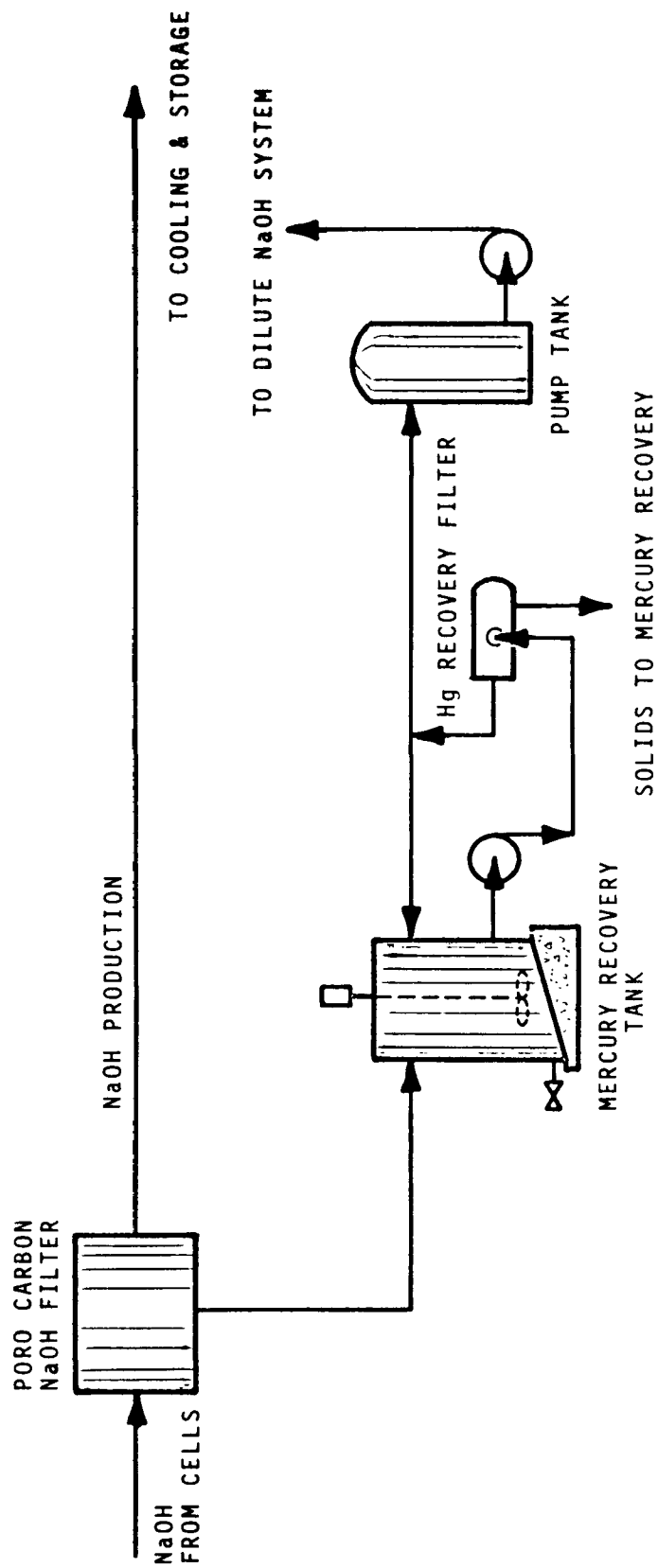


Figure 8. Mercury Recovery From Caustic Filter (7)

Electrical Industry

Battery, lamp, switch, and rectifier manufacturers comprise the categories of mercury-using companies in the electrical field. According to Bureau of Mines reports (1,2), 15,952 flasks of mercury were consumed in 1970 for electrical apparatuses. Previously, 18,650 flasks were used for production in 1969 and 17,484 flasks in 1968. A level of consumption above 14,500 flasks of mercury was maintained through the years 1965 to 1967. The following discussion is divided into sections on batteries, lamps, and switches and rectifiers.

Batteries

Mercury cells are used in lighting devices, photographic equipment, medical electronic equipment, transistor radios and other transistorized devices, missiles and satellites, instruments and computers, and clocks and watches (30). For example, mercury batteries are used in 75 to 80 per cent of all hearing aids. They are also used for high-demand, high-reliability applications such as power sources for sono-buoys, marine devices, and air-sea rescue radios and beacons.

The major advantage of mercury cells over other batteries is their small size. Mercury batteries deliver the same electrical energy in cells one-third to one-fourth as large as comparable zinc-carbon batteries (14). They also have a longer shelf life. Furthermore, they lose less voltage with either steady or intermittent use; other batteries start to fade appreciably after only partial use (31). Mercury is used in both the mercury cell and the alkaline energy cell, where it is amalgamated with zinc to reduce hydrogen over-voltage at the anode (12). In the mercury cell, the positive electrode also includes mercury as a mixture of graphite and mercuric oxide. In this cell, the anode and cathode are separated by a composite shield that contains an electrolyte of potassium hydroxide and zinc oxide (11).

The determination of alternatives to mercury batteries concerns three types of batteries. Two of these alternative batteries (magnesium-alkaline and zinc-carbon) have a small quantity of mercury used in their manufacture. The third battery, nickel-cadmium, does not require mercury and is rechargeable. Size of the battery and rate of energy drain from the battery are important parameters in the selection of the proper battery for a given use.

Mercury batteries generally have an energy density of 45 watt-hours/lb, while zinc-carbon batteries have a range of 10 to 67 watt-hours/lb with an average density of 15 watt-hours/lb.

Therefore it would take about three average zinc-carbon batteries to replace an average mercury battery. Five nickel-cadmium batteries would be required to replace the average mercury battery, since the energy density of nickel-cadmium batteries ranges from 4 to 20 watt-hours/lb, with an average battery being rated at 10 watt-hours/lb (32).

Best Available Level of Treatment and Control

Two types of battery manufacturing processes affect the best level of treatment and control. In one process, where virgin mercury is chemically compounded into a dough-like material and extruded into battery casings, there is no discharge of mercury in the effluent. However, in the second process, the use of process water in the production of mercuric oxide and zinc amalgam creates two points of discharge into plant effluent (33,34).

The treatment for soluble mercury in mercuric oxide production is to adjust the pH to 7, add sodium sulfite, and allow the mercury to precipitate out of solution as an insoluble compound. Mercury concentration in this effluent is less than 2.5 ppm. Treatment method for the mercury in the zinc amalgam production is to weir out heavy particles through several holding sections and treat with scrap zinc. This zinc is periodically changed as the mercury is amalgamated with the zinc. The concentration of mercury in this effluent is less than 0.5 ppm. For further reduction of mercury content, the methods described on pp. 6-10 could be used (33).

Lamps

Mercury is used as a basic or supplementary light source in most types of gas discharge (as opposed to incandescent) lamps. In the common fluorescent tube, mercury is vaporized by an electrical discharge and excited to emit ultraviolet radiation, which in turn stimulates the emission of visible light from phosphors coating the inside of the tube. In the high-pressure mercury lamp, mercury vapor at a pressure of about two atmospheres emits visible light directly, without an intermediate phosphor stage. Mercury lamps are also produced with various additives (metals and metal halides) for improved electrical and/or color characteristics (35).

Compared to other industrial uses, the lighting industry uses only a minute portion of the over 6 million pounds of mercury used in the United States in 1969. It is estimated that about 48,000 pounds of mercury were used in the manufacture of 6.2 million mercury and metal halide lamps and 268.2 million fluorescent lamps by the lighting industry in 1969. This usage accounts for only about 0.8% of the 6 million pounds total

mercury used and 3.5% of the 1.382 million pounds used in electrical apparatus (36). In addition, lamp production involves no use of process waters which could result in mercury-contaminated plant effluents.

The relatively low amount of mercury used by the lighting industry for making lamps is due to the small amount of mercury required in each lamp. For example 50 milligrams (mg) or 0.00011 pounds of mercury are used to manufacture a standard 40 watt fluorescent lamp, 68 milligrams for a 400 watt mercury lamp and 51 milligrams for a 400 watt metal halide lamp (36).

Mercury lamps are used extensively for street and highway lighting, in high-ceilinged rooms, and where intensive lighting is needed for motion picture projection, in photography, for examination of teeth, in heat lamps, and for water sterilization (11).

Mercury is used in the manufacture of high-intensity discharge lamps (mercury, metal-halide, and sodium-mercury lamps) and fluorescent lamps because it has the unique physical and electrical properties responsible for the high energy conversion efficiencies of these light sources. These lamps deliver more lumens per watt of energy consumed than any other commercial light source. Incandescent tungsten lamps and some noble gas (neon and helium) lamps could be alternatives to using mercury lamps, but they are low in efficiency and therefore require greater amounts of power. Total conversion to low-efficiency lighting would require more electrical power than the present generating capacity of the power industry.

Best Available Level of Treatment and Control

Since no process discharges take place, routine precautions in handling and storing of mercury apply. Mercury is received in flasks. For use, it is placed in dispensers and sealed. A hypodermic-type needle is then used to inject a single drop of mercury into each lamp. Control is further exercised by having sumps under floor drains to contain any spilled mercury. These sumps are periodically cleaned. Mercury vacuum cleaners, equipped with dust and charcoal filters, are used to clean the manufacturing area (37).

Mercury flow diagrams of two fluorescent lamp plants and one high-intensity lamp plant are shown in Appendix B. Losses of mercury (1% to 6%) are indicated in these diagrams. These losses may be attributed to evaporation.

Switches and Rectifiers

Power rectifiers account for most of the mercury used in electron tubes. Mercury is also used in producing silent, smooth, frictionless, and durable switches, for which it provides a self-replenishing contact material. The mercury provides a low contact resistance with very stable repeatability from operation to operation, as well as over long life of billions of operations (12).

Mercury rectifiers have to a large extent been replaced by silicon and/or selenium rectifiers. For many applications, alternatives are also available to substitute for mercury switches, but they are not as reliable or economical. Mechanical switches, for example, will serve as well as mercury switches in many cases, but they are much less durable under heavy use. Solid-state switches, such as those based on bi-metallic thermostatic elements or on capacitive effects (touch-plate switches), are also potential replacements for mercury switches (12).

Best Available Level of Treatment and Control

No treatment is required in the manufacturing of mercury switches and rectifiers. Mercury does not enter any waste water streams in the manufacturing plant. Therefore, control consists of precautions in the handling and storage of mercury to avoid accidental discharges. One procedure in use involves storage of mercury in sealed plastic bottles. The mercury is withdrawn from the bottles by a vacuum system and inserted into switch capsules by a pressure system. All mercury-contaminated scrap is transported in closed plastic containers to be refined for mercury salvage by a vendor (38).

Industrial and Control Instrumentation

Mercury is used as an indicator in instrumentation because of its liquid state at normal temperatures, because of its stable physical characteristics, and because of its uniform responsiveness to changes in environmental parameters. The items in the following list of control apparatuses and instrumentation all commonly use a certain amount of virgin mercury in their operation (11).

Thermometers	Vacuum gauges
Hygrometers (measurement of dew point)	Tank gauges
Manometers (pressure gauges for all gases)	Flowmeters (water, sewage, steam, compressed air, high-pressure gases)
Compensating clock pendulums	Gyroscopes
Barometers (a type of manometer)	High-vacuum diffusion pumps
Weightometers	Electric-motor clutches and seals

According to Bureau of Mines reports, there was a 31% decrease from 1969 (6,981 flasks) to 1970 (4,832 flasks) in the consumption of mercury for use in industrial and control instrumentation (1,2). Prior to 1969 the average yearly consumption of mercury for this manufacturing area was 4,131 flasks. No trend in mercury usage is apparent during the period of 1965 through 1968 (2).

For many applications, no alternatives are presently available to using mercury in industrial and control instruments. In some cases, however, substitutions can be made. For example, mechanical gauges and aneroid instrumentation can replace some types of mercury instruments.

Best Available Level of Treatment and Control

Essentially, there is no mercury discharged to the plant's sewerage system in the manufacture of instruments. Any elemental mercury collected in the cleaning of the filling areas is sent to a refiner.

Particulate mercury is collected in a central vacuum system that contains traps for liquid mercury, which is filtered, re-distilled, and reused. Further control is practiced by transferring spilled or dirty mercury to shipping containers and sending it to a

refiner for reprocessing. Cleaning the floor areas in the mercury-filling sections with U. S. Government approved "HGX" Powder is a recommended practice. This compound changes mercury to non-volatile, insoluble sulfide. Sweepings are collected in plastic rubbish bags and deposited with trash in approved land fill areas. There is some possibility of water contamination from mercury in solid wastes deposited in land fills.

Dentistry

According to Bureau of Mines reports (1,2) 2,286 flasks of mercury were used for dental preparations in 1970, as compared with 3,053 flasks in 1969. In 1968, the dental profession consumed 2,089 flasks; and prior to 1968 consumption fluctuated around a relatively constant rate of about 1,500 flasks annually. No explanation for the apparently anomalous 1969 usage rate has been found; however, the decline in 1970 can be at least partially accounted for by concern over mercury pollution and by a general economic slowdown (40). Consumption for the first quarter of 1971 was almost identical with that for the last quarter of 1970 (1).

Written evidence of the use of amalgam (an alloy of mercury with another metal) in dentistry dates back to 1528, and today it remains the most common therapeutic agent used for restoring decayed teeth, accounting for three out of four restorations of individual teeth. Dental amalgam consists of mercury combined variously with silver, zinc, tin, and copper. The current American Dental Association (ADA) specification for dental alloy (before final amalgamation with mercury) lists the following standard requirements for chemical composition (39):

Silver	Min. wt.	65%
Tin	Max. wt	29%
Copper	Max. wt.	6%
Zinc	Max. wt.	2%
Mercury	Max. wt.	3%

To make the final amalgam, this "pre-alloy" is triturerated with an approximately equal amount of mercury. Excess mercury is squeezed out in a condensation operation, leaving a usable amalgam usually containing about 50% mercury but sometimes containing as little as 40%. The proportion of mercury remaining in the amalgam after squeezing is inversely proportional to the logarithm of the pressure employed (41) and is also affected by the presence of mercury in the pre-alloy (39).

Amalgams possess a number of physical properties that make them particularly well-suited to use as dental restorative material. Ease of preparation in the dentist's office is assured by the readiness with which mercury amalgamates with other metals. Amalgams are easy to work and shape, since they are plastic at body temperature for a few minutes before they harden. Once in the tooth, they are stable and secure, since the hardening process

involves little or no change in volume. Once hardened, properly condensed amalgams exhibit compressive strength as high as some cast irons. They also withstand the corrosive environment of the mouth and are bland to the host (39).

Acceptable alternatives to the use of amalgams are: alloys of gold (with small amounts of platinum, palladium, silver, copper, and zinc), silicate cements, unreinforced acrylic resin; and reinforced or composite resins. The resins, however, are not applicable or approved for all dental uses; and the ADA has taken the position that amalgam and gold are still the best restoration materials to use (39).

Gold (alloy) has been and is being used as filling material in dentistry, usually in one of three forms: gold foil, crystalline or mat gold, and powdered or sintered gold. Powdered gold is not as easily used or worked as amalgam, but its edge strength is more than twice that of amalgam (and half that of gold foil)(39). The high cost of gold is actually the most significant limitation on its use as a complete substitute for amalgam.

For fillings where aesthetic considerations require matching the appearance of the natural tooth, silicate cements have long been used. Powders used for silicate cements are pulverized complex glasses consisting essentially of alumino-silicates containing magnesium, fluorine, calcium, sodium, and phosphorus. Modern silicate cements have sufficient compressive strength to resist masticatory forces and offer versatility in matching the opacity and shading of natural teeth. A major weakness of silicate cements is their tendency to dissolve and disintegrate in the mouth, especially in areas of the restoration which are not self-cleansing (39).

Restorative resins are also in limited but growing use in dentistry where aesthetic considerations are involved. Conventional acrylic resin (methyl methacrylate) has been used but has drawbacks such as shrinkage on polymerization, high coefficient of thermal expansion compared with tooth material, lack of color suitability, and recurrent decay around and under the filling. Newer composite resins, which contain inorganic fillers--e.g., glass beads, rods, quartz, or lithium aluminum silicate--to reinforce the resin, are now replacing the conventional resins. They have advantages in compressive strength, higher modulus of elasticity, higher hardness and resistance to abrasion, lower polymerization shrinkage, and a coefficient of thermal expansion much more nearly comparable to that of the natural tooth material. Possible disadvantages which are still under investigation are gradual color changes, surface roughness and difficulty of finishing, and lack of chemical adhesion to natural tooth tissues (39). The Council on Dental Materials and Devices of the ADA has recognized the effectiveness of these

resins for certain types of restorations, but approval for wider use awaits further clinical investigation (42). Further developments in this field promise to make restorative resins true alternatives to both amalgam and gold.

Best Level of Treatment and Control

Each time a dentist places an amalgam restoration, he must prepare an excess to ensure sufficient amalgam to construct the restoration properly. This excess amalgam becomes waste. Similarly, the amalgam removed from the filling during shaping is usually rinsed from the mouth or aspirated and becomes waste which can be caught in a strainer or trap in the drain. Such scrap can be recovered from waste traps on cuspidors, aspirators, and evacuators and placed in a covered container along with the excess unused amalgam. Since about 50% of the scrap is mercury and 25% or more is silver, reclamation is economically worthwhile. Under the best level of control, no soluble mercury should be discharged if a properly designed waste trap is used. Although the use of waste traps is common among dentists, no data or estimates of amounts of recovered and discharged mercury are available (43).

Laboratory and Hospital Uses

According to Bureau of Mines reports (1,2), the consumptive use of mercury in laboratories decreased by 11.5% from 1969 (2,041 flasks) to 1970 (1,806 flasks). However, no trend in laboratory use of mercury is evident in the years 1965 through 1968. The average number of flasks of mercury consumed per year during this time period (1965-1968) was 1,265 flasks.

Mercury and mercurials are standard laboratory items used as reagents and indicators, for calibration and sealing, and in instruments and vacuum pumps. Since for many research applications the unique properties of mercury make it indispensable, the emphasis in this area must be on treatment and control.

Medical diagnosis and operations use mercury for specific applications. Radioactive mercury plays an important part in the area of diagnosis. The antiseptic qualities of mercury also are utilized in hospital operating room practices.

Radioactive mercury (^{197}Hg , ^{203}Hg) can be used for brain scans for tumors, and for renal scanning. Neohydrin (^{203}Hg) is used in brain scanning since it is more accurate in the demonstration of metastatic lesions, and it seems to obtain clear delineation of lesions in parasagittal sinus, brain bases, and posterior fossa (44). Renal uptake of mercury (^{197}Hg) depends on renal function. The uptake value of ^{197}Hg , measured by external counting, allows the quantitative estimation of the functional value of each kidney (45).

Mercuric chloride, 0.2% (1:500) has been used in the prevention of suture line recurrences in anterior resection for colonic cancer (46).

Alternatives to the Use of Mercury

Laboratory

No respondent using mercury or mercurials for laboratory purposes suggested any available alternatives to such use. It is likely that particular mercury compounds used as chemical reagents can be replaced by non-mercurials, but no specific examples can be cited.

Hospital

Technetium ($^{99\text{m}}\text{Tc}$), radioactive potassium carbonate (^{42}K), and diiodofluorescein (^{131}I), may be used in place of radioactive mercury for brain scans (21,47). An alternative to mercuric

chloride could be centrimide (1% solution). It has been shown to be effective in preventing growth of tumor cells in experimental wounds (46).

Medical considerations must govern in this area, and recommendations can be made only by medically qualified investigators.

Best Available Level of Treatment and Control

Because of the nature of laboratory and hospital operations, there is almost no danger of continuous large effluent flow containing unacceptable concentrations of mercury. The danger is in careless or accidental disposition of relatively small amounts of expended mercurials down the drain and in careless handling of spilled metallic mercury. In a laboratory and hospital context, the best available level of treatment and control consists of conscientious practice of routine methods such as:

- a. Precipitation of dissolved mercury compounds for recovery or safe disposal as solid waste.
- b. Separation of suspended mercury compounds for recovery or safe disposal as solid waste.
- c. Chemical treatment or fixation of spilled metallic mercury before vacuuming or washing, with subsequent precipitation or separation of mercury for recovery or safe disposal as solid waste.

Mercury Reclamation

Many companies process mercury-containing substances (especially dental amalgam and contaminated metal) for the recovery of elemental mercury. A typical process is the operation of one-liter stills under vacuum to recover the mercury. The still is heated to temperatures allowing the mercury to vaporize and to be carried through a condenser to recovery.

The recovery process involves washing stages using acid and/or water. Acid wash is reused, but wash water is discharged to sewers. Although this water may contain up to 25 ppm dissolved mercury, the amount discharged is relatively insignificant. Recovery of mercury from an operation processing two to three tons of amalgam and metal annually involves discharge of less than 1000 gallons of wash water per year.

Best Available Level of Treatment and Control

Physical control is exerted in the reclamation of mercury by having no drains in the building and having sinks equipped with traps which are cleaned once a week. The sludge remaining from the distillation of the mercury-laden substances is dumped into containers and reprocessed. Cleanup of the refining area is performed with a vacuum after washing with an inorganic sulfide. The material generated from this cleanup operation is also sent out for further mercury reclamation.

SECTION III

OTHER TREATMENT AND CONTROL METHODS

This section includes actual or possible methods of treatment and control that were either reported by industry, but not equivalent to the best available methods, or reported in the literature and generally applicable to more than one industry. Tables 3 and 4 summarize those treatment methods for which sufficient information is available.

Chemical Production

1. An experimental metal reduction process for removing mercury from industrial waste water has been tested by Merck Sharp and Dohme Research Laboratories (48). The addition of powdered zinc to effluent from a plant producing organic and inorganic mercurials resulted in the removal of over 99% of the mercury by the formation of filterable zinc-mercury complex. A mean effluent level of 0.021 lb/day (estimated by the present writers from tabulated data as a mean concentration of 0.6 mg/l) was obtained by using 3.8 pounds of zinc per pound of mercury. On an experimental scale, the method appears to be both effective and economical. Further research is being conducted on the nature of the reaction mechanism, on modifications required to adapt the method to large volume flows having a low initial mercury level, and on alternative metals (e.g., aluminum) to use in place of zinc.
2. One example of claimed total control was found, but its applicability is extremely limited. A producer of English Vermilion pigment (49), which is mercuric sulfide, uses a process as shown in Figure 9.

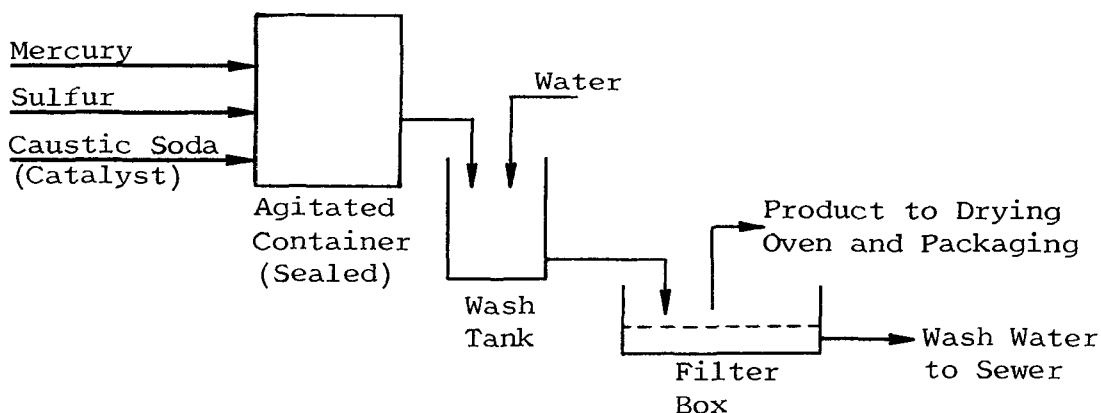


Figure 9. Mercury Control in Production of English Vermilion

TABLE 3. SUMMARY OF OTHER TREATMENT METHODS BY INDUSTRY

Industry	Treatment Process	Effluent Data-- Mercury Concentration
Chemical Production	Metal (zinc) reduction	0.021 lb/day (99% removal)
Manufacture of mercuric sulfide	Filtration and stoich- iometric proportioning	No discharge
Use of catalysts	Chemical precipitation	-----
Chlor-Alkali	Sodium hydrosulfide plus/or Ferrous chloride	0.3 to 0.5 lb Hg/day; 0.025 lb Hg/100 tons Cl ₂
	Ion exchange (brine treatment)	0.3 ppm
	Treatment of brine with formaldehyde	1 ppm

TABLE 4. SUMMARY OF OTHER TREATMENT METHODS BY TREATMENT PROCESS

Treatment Process	Applicable Industry	Effluent Data-- Mercury Concentration
<u>Chemical Processes</u>		
Metal (zinc) reduction	Chemical Production	0.021 lb/day (99% removal)
Chemical pre- cipitation	Catalytic wastes	-----
Sodium hydrosul- fide plus/or Ferrous chloride	Chlor-Alkali	0.3 to 0.5 lb Hg/day; 0.025 lb Hg/100 tons Cl ₂
Ion exchange	Chlor-Alkali (brine treatment)	0.3 ppm
Treatment with formaldehyde	Chlor-Alkali (brine treatment)	1 ppm
<u>Physical Process</u>		
Filtration and stoichiometric proportioning	Chemical Production (Manufacture of mercuric sulfide)	No discharge

Since HgS is the most insoluble form of mercury, with specific gravity of 8.0, it is completely separated from the wash water by the 36 x 34 twill fabric filter medium. No unreacted mercury is involved, since the raw materials are reacted in stoichiometric proportions and fully recovered as product.

Paint Industry

Paint companies can reduce the amount of mercury in the effluent streams by reducing the number of washings of tanks in which paints are manufactured.

Treatment of Catalyst Wastes

An effective method for purifying waste waters involves heating them with KClO_3 (converting all Hg to HgCl_2) and subsequent precipitation of Hg^{++} as HgS . A residue obtained from treatment of sulfonic acids with iron shavings of Na_2S contained HgS , Hg , anthraquinone, and its sulfonic acids. The residue was boiled with a mixture consisting of KClO_3 , NaCl , and H_2SO_4 , which resulted in conversion of Hg and HgS to HgCl_2 and precipitation of organic impurities which were then filtered off and washed free of HgCl_2 . Practically pure HgS , suitable for processing in Hg factories, was precipitated (with Na_2S) from the mixture of filtrate and wash water (50).

Chlor-Alkali Industry

1. A flow diagram showing an effluent treatment commonly used in the chlor-alkali industry is depicted in Figure 10. This method results in a discharge of 0.3 to 0.5 pounds of mercury per day. Since the total effluent flow was not given, the Hg concentration in the final effluent discharge could not be calculated.

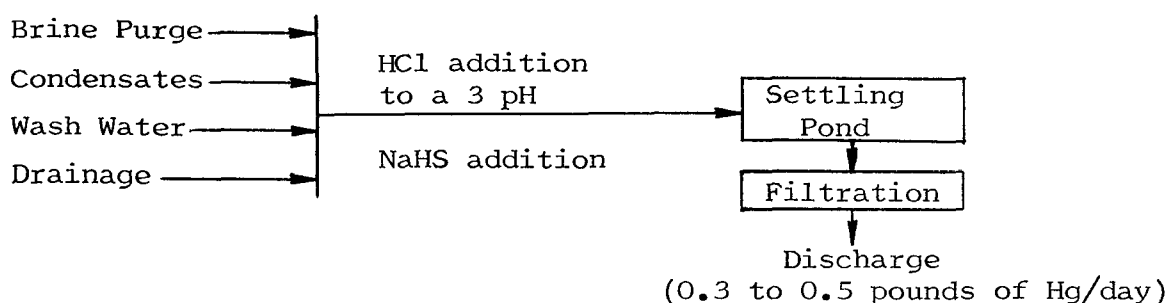


Figure 10. Treatment of Chlor-Alkali Effluents

2. A manufacturer of mercury cells (Hoechst-Uhde Corp.) discussed a process flow sheet of mercury emissions from a mercury cell at a symposium on chlorine at Buck Hill Falls, Pennsylvania, on May 21-22, 1970 (51). However, a discussion with Mr. Edmund Laubusch, Technical Manager of the Chlorine Institute, revealed that the claims made in the following discussion should be viewed with caution. Judicious judgment of the data presented is needed because the amount of mercury wasted per 100 tons of chlorine produced is reported to be 0.025 pounds. (This figure was calculated from the given information that the described Hoechst-Uhde process had a mercury loss in the waste water of 0.14 grams/metric ton of Cl_2 produced.) This value (0.025 lb) is far lower than previously reported values (0.10 lb Hg discharged/100 tons Cl_2 produced) by General Technology Corporation's EPA-WQO Interim Report (29).

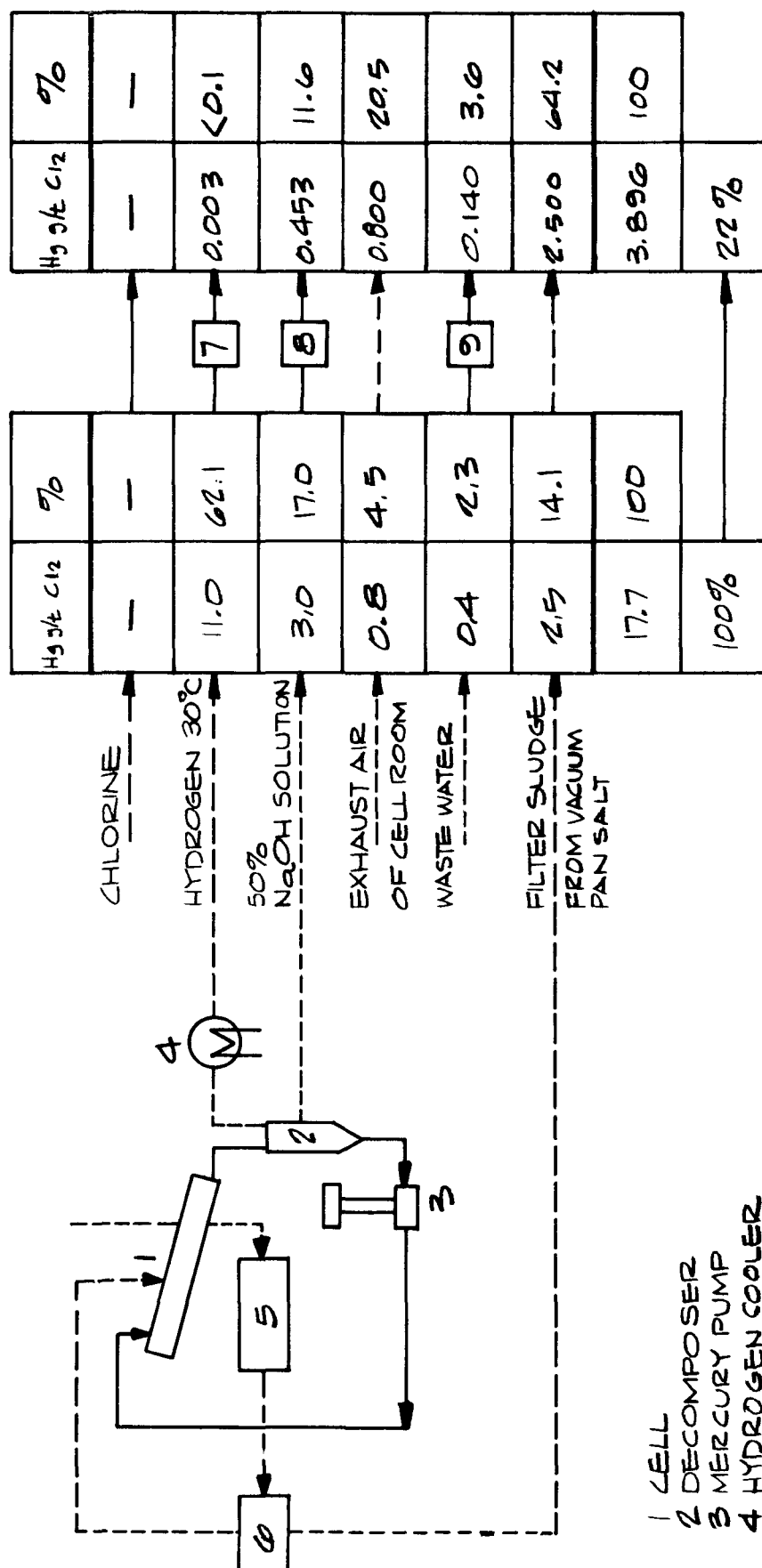
The following discussion is from a paper (52) by Dr. Bernd Strasser, presented at the symposium:

"The total quantity of technological mercury losses encountered in the Hoechst-Uhde mercury cell process is normally less than 20 grams of mercury per metric ton of chlorine. Figure 11 shows the distribution of these losses. It will be noted that the major portion, that is about 62%, is entrained by the hydrogen whose temperature has been reduced to 30°C. This cooling step should preferably take place at the decomposer exit which eliminates losses due to mechanical handling and because the mercury inventory in the cell can be controlled more efficiently.

"The hydrogen cooler is part of the standard equipment of the Hoechst-Uhde cell. A further reduction of the mercury quantity entrained by the hydrogen is achieved by cooling the hydrogen to a lower temperature or by a combined compression and cooling step. Through adsorption by activated carbon or chemisorption by iodine-activated carbon, the mercury content of the hydrogen can be reduced to 3 milligrams per ton of chlorine and 6 milligrams per ton of chlorine, respectively. When using a catalyst developed by Farbenfabriken Bayer AG, a residual content of only 3 milligrams of mercury per ton of chlorine can be achieved.

"The mercury content of the 50% caustic soda solution can be reduced from 3 grams to about 0.45 grams per ton of chlorine or less by means of precoat filters.

"The exit brine from the cells contains certain quantities of mercury in the form of a complex solution. The mercury content of the inlet brine is lower by the mercury quantity which is precipitated during alkalization and entrained by the filter sludge from the brine system.



- 1 CELL
- 2 DECOMPOSER
- 3 MERCURY PUMP
- 4 HYDROGEN COOLER
- 5 BRINE DECHLORINATION
- 6 BRINE RESATURATION, PURIFICATION & PRECIPITATION
- 7 COOLING TO 41°F AND ADSORPTION WITH ACTIVATED CARBON
- 8 FILTRATION
- 9 PRECOAT FILTER

Figure 11. Process Flowsheet Showing the Hg Emission from a Mercury Cell (52)

"The difference in mercury content before and after precipitation, that is the mercury lost together with the filter sludge, depends on the mode of operation of the brine system; empirical figures range from 2.5 to 100 grams of mercury per ton of chlorine. The mercury can be recovered, indeed, from the filter sludge by various methods which are, however, relatively complex and fairly expensive. It is possible, nevertheless, to reduce mercury losses in the brine system to a minimum without having to apply said complex procedures for demercurizing the sludge and brine. The specific procedures used by Farbwerke Hoechst AG are based on maintaining oxidizing characteristics of the brine even during precipitation and filtration to prevent the precipitation of mercury. In this way, the amount of mercury going into the sludge of the brine purification will not exceed the portion that corresponds to the percentage of brine in the sludge. The mercury losses can be reduced from 2.5 grams additionally theoretically to zero by washing the sludge and additional chemical treatment of the waste water containing iogenic mercury.

"A small percentage of mercury is lost in the waste water which comprises:

"The condensate from the hydrogen cooling systems, wash water from the filters, end boxes and feed boxes, flushing water from the cells, from the cell room floor, etc.

"For reducing these losses it is possible, for example, to backwash the filters with brine and to return to the process at least part of the condensate from the end boxes and feed boxes. Other water streams can be freed of metallic mercury by means of precoat filters and from ionic mercury as already mentioned in the recovery of the brine sludge.

"Modern cells have practically eliminated mercury losses caused by the discharge of ventilation air. The exhaust air from the end boxes can be considered as being free of mercury. The latest design of the Hoechst-Uhde cell has eliminated any mercury loss in the exhaust air from the feed boxes. The feed box is of the totally closed design and is connected to the hydrogen system.

"These are the main aspects of mercury losses. If procedures are used as in discussed here, mercury losses can be held in the order of about 4 grams per ton of chlorine or less.

"Engineering advances made in recent years have also drastically reduced the mercury losses previously encountered through the mechanical handling of mercury, that is through daily routine operations performed in the electrolysis plant (for

example filling and refilling cells with mercury, cleaning of cells, and so on). Today, mercury losses in new plants can be reduced to 5 to 10% of the figures encountered in 1960."

3. Dechlorinated spent brine is sent through a column of quaternary ammonium ion exchange resin, where mercury is adsorbed as HgCl_4^- . Treatment with Na_2S forms sulfide and polysulfides of mercury, which can be oxidized to Hg(II) sulfate by chlorine-containing brine. The sulfate can be returned to the electrolytic cell, where it is reduced to Hg metal at the cathode (53).

4. Mercuric ions have been removed experimentally from brine by contacting the brine with certain glycine copolymers which act as selective ion exchange resins. A synthetic brine containing 15 ppm mercuric ions was treated, with a reduction of Hg^{++} ions to 0.3 ppm (54).

5. Dissolved mercury compounds can be removed from solution by reduction to the metallic state. Reducing agents that can be used in brine include aldehydes and carboxylic acids (55). Experimental treatment with formaldehyde of brine containing 69 ppm mercury reduced the mercury content to less than 1 ppm (56).

6. Methods of Waste Water Control in Operation of a Mercury Cell (7)

Cells

- a. Endbox periodic flushing. Control by recycling as much of flushings as possible. Send purge to final treatment system.
- b. Sloppings or spilling of brine during cell start-up. Start up cells with alkaline brine and remove metallic impurities in brine filtering system.
- c. Cell washout water to clean out cell during cell maintenance. Recycle wash water as much as possible. Send "spent" washout water to final treatment system.

Hydrogen Stream

- a. Cooling water in direct contact coolers. Use condensate to cool hydrogen and recycle condensate to decomposer chamber or convert to indirect cooling.
- b. Condensate drips in indirect coolers. Recycle condensate drips to decomposer.

Caustic Stream

- a. Backwash from caustic filters. Impound solids for mercury recovery. Send clear liquor to final treatment system.
- b. Caustic tank cleanouts including storages and tank cars. Wash waters having useful alkali values returned to plant. Dilute wash waters recycled as much as possible, then send to final treatment system.

Brine System

- a. Purge brine. Send necessary brine purges to final treatment system.
- b. Brine filter backwash. Impound solids for possible mercury recovery or send solids-liquor mixture to final treatment system. Conversion from sand filters to leaf filters may be justified as a means of reducing volume to be treated.

Cell Room

- a. Cell maintenance area. Collect solid refuse such as spent anodes, etc. for possible mercury recovery. If mercury recovery is not possible, permanently impound.
- b. General wash water. Curtail and recycle as much as possible, install tanks or weirs to settle out recoverable mercury and send water to final treatment system.

Switches and Rectifiers

The following procedure is in use to control mercury. The mercury coming from the distributor goes into an "oxifier"* for 5 to 6 hours for exposure to air which is pumped in. Baffles in the "oxifier" help mix the mercury. From the "oxifier," the mercury is placed into settling jars. The fines (mercury oxides) come to the top and the mercury is drawn off the bottom, leaving a 1½" mercury layer (containing the fines) on the bottom of settlers. Fines are placed in a separate jar and emptied into a larger jar every month. Finally, every 6 months these jars are recycled back to the "oxifier" for reprocessing.

When the mercury is drawn off the bottom of the settling jars, it passes through a gold adhesion filter into a dispenser bottle. The filter removes all contaminants except noble metals. The dispenser is then used to hand-fill the glass switch. After filling, the

*Oxifier manufactured by Bethlehem Apparatus Company, Hellertown, Pennsylvania.

switch is sealed and is checked for leaks. The mercury from any leaky switch is reprocessed as is the mercury picked up by the vacuum cleaner used to clean the troughs at the edges of the manufacturing benches. Vacuuming is performed once a week.

Another procedure is to use stainless steel drip trays to catch spillage. The surface of the caught mercury is flooded with water to minimize evaporation. Waste mercury is returned for refining.

Generally, no mercury leaves either of these production areas such that it could enter a sewer or pollute a stream.

General Treatment Methods

General treatment methods which are applicable to mercury-bearing waste streams but are not in themselves the best available methods are discussed below.

1. One of the most common, simplest, and most effective methods to remove mercury from solution is precipitation of an insoluble mercury compound (57). Sodium sulfide (Na_2S) and sodium hydrosulfide (NaHS) are effective in forming the extremely insoluble HgS . This method is not favored, however, when recovery of mercury is desired, since offensive and poisonous hydrogen sulfide (H_2S) gas is formed in the reduction process.
2. Another treatment system developed by Aktiebolaget Billingsfors-Langed is based on a special ion-exchange resin, Q 13, which possesses an affinity for mercury, even in the presence of sodium chloride. Metallic mercury content is oxidized with chlorine, the pH controlled to 5-7, and the waste then dechlorinated prior to ion-exchange with Q 13. Two ion-exchangers in series are recommended, with the final effluent at 0.1-0.2 ppm mercury. Regeneration is acidified brine, recovering mercury to the brine circuit. A final absorption filter of their design should drop the mercury content to 0.01-0.02 ppm mercury (7).
3. Cellulose ion-exchange fibers have been used to purify mercury-containing waters, absorbing 4.3 equivalents Hg per kilogram (58).
4. Flocculation can be effective, in conjunction with a precipitation method, for control and recovery of mercury from solution. After precipitation, dispersed HgS can be scavenged with gelatinous $\text{Fe}(\text{OH})_3$, which is formed by the addition of FeCl_3 and starch with pH adjusted to 10 with NaOH . In effluent containing appreciable amounts of Fe^{+3} ion, $\text{Fe}(\text{OH})_3$ can be formed by addition of $\text{Ca}(\text{OH})_2$ or CaO (59,60).
5. A possible generally applicable method for waste water treatment is to precipitate mercury with an alkali sulfide with simultaneous or subsequent addition of iron or zinc salts for floccu-

lation (61). The iron or zinc salts also prevent the formation of soluble mercury-sulfide complexes (e.g., Na_2HgS_2). An experiment with industrial waste containing 15 to 25 mg Hg/l involved precipitating HgS with NaHS in the presence of ZnCl_2 or FeSO_4 , leaving a residual Hg concentration of 0.003 to 0.01 mg/l (62).

6. Filtration with adsorptive compounds can be used to remove mercury from solution. Some of the compounds found to be effective in experiments are: activated carbon (63), graphite powder (64), graphite dust plus serpentine-asbestos dust additive (for alkaline solutions) (65), and wool fiber (66).

7. For mercuric ion in acidic solutions, hydrazine hydrate can be used to reduce more than 99% of the mercury to the metallic form (67).

SECTION IV

RESEARCH NEEDS

Many treatment processes have been described in the literature and have been tried by several companies in attempting to meet tentative water quality standards for mercury. We recommend an extensive research program for those industries where no alternative for the use of mercury is available. This research and development program should have its emphasis on examining the merits of the following treatment methods for implementation in the field.

1. Sodium Hydrosulfide plus Activated Carbon Process
2. Osaka Soda Process
3. Aktiebolaget Billingsfors-Langed Process
4. Terraneers, Limited Process
5. Ventron Corporation Process
6. Zinc Dust Process

Outline of Approach

This program of comparative studies on these different treatment methods of mercury-bearing effluents can be accomplished by Federal financial and technical assistance for pilot plant and demonstrational projects. These types of Federal programs allow industry and government to share equally the burden of the costs of research and development for solving the complex problem of mercury in waste water effluents.

Specific companies to be contacted for this research program are detailed below in conjunction with further steps in the research program.

- A. Select a paint company, a chemical manufacturer, a chlor-alkali producer (mercury cell), and a company using mercury as a catalyst to test these methods on a pilot plant scale.
- B. Determine reaction-limiting conditions with respect to each treatment process. Several of these processes may be affected by physical and/or chemical conditions present during the treatment of the plant's wastes. For example, pH or chelating agents may determine whether the efficiency of removal is 50% or 90%.

- C. Compile results of pilot plant scale study and implement the one treatment process or combination of processes suitable for the entire industry.

SECTION V

CONCLUSIONS

1. Many treatment methods for industrial waste water effluents, typically containing more than 1 ppm mercury, can remove up to 99% of the mercury. However these methods individually are not efficient enough to produce a condition where no mercury is discharged. It appears that treatment of effluents with combinations of methods will be necessary to approach or achieve this condition. The best currently available treatment methods for industrial effluents can reduce mercury content to less than 5 ppb. No actual or proposed method appears capable of achieving levels below 1 ppb. See Table 5 for a summation of treatment methods by industry.
2. The actual and foreseeable banning of all (or nearly all) mercury compounds for use in agricultural chemicals has already caused major reductions in the amounts of these products on the market. Except in specialized instances, nonmercurial alternatives are being used with equal or better effect.
3. The catalytic use of mercurials in the production of vinyl chloride monomer, sulfonated anthraquinone, and certain urethanes generally can be eliminated. Present technology has produced less environmentally damaging processes replacing mercury catalysts in the production of these three materials.
4. Research is presently being conducted to find alternatives to using mercurial additives to paint. The paint industry says two years will be required before fully tested substitutes will be available.
5. Mercuric oxide has been eliminated from use as a biocide in antifouling paints, and replaced by cuprous oxide and tributyltin oxide. It is, however, still registered under the Federal Insecticide, Fungicide, and Rodenticide Act.
6. Nonmercurial substitutes exist for the most common pharmaceutical and cosmetic mercurials. However, medical consideration (e.g., side effects, toxicity, site and specificity of activity) rather than environmental effects must ultimately dictate the product choices. Treatment and control must be emphasized.
7. The pulp and paper industry has stopped using phenyl mercury slimicides. These compounds have been replaced by an array of different compounds such as organo-sulfurs, thiocyanates, and chlorinated phenols. However, some of the chemicals this industry is using in its processing of paper are contaminated with trace quantities of mercury.

TABLE 5. SUMMARY OF BEST AVAILABLE
TREATMENT METHODS FOR EACH INDUSTRY

Industry	Treatment Process	Effluent Data-- Mercury Concentration	Removal
Mining	Soil Filtration	No Hg detected downstream	-----
Chemical Production Agricultural Chemicals	1. Cationic polymer floccu- lation	2.5 to 15 ppb	99% suspended solids 60% COD 75% phenyl mercurials
	2. Osaka Soda (ion exchange)	2 to 5 ppb	-----
	3. Sodium boro- hydride plus che- lating resin	Potentially 1 to 5 ppb	-----
	4. Proprietary-- Terraneers, Lim- ited	10 ppb	-----
Catalytic Wastes	1, 2, 3, 4 (as above)	-----	-----
Paint	Holding and re- cycling wash waters or solvent sludge; 1, 2, 3, 4 (as above)	None	-----
Pharmaceutical	1, 2, 3, 4 (as above)	-----	-----
Pulp and Paper	1, 2, 3, 4 (as above)	-----	-----
Chlor-Alkali	1, 2, 3, 4 (as above)	-----	-----
Plant waste water	Sodium hydro- sulfide and/or ferrous chloride plus activated carbon bed	10 to 20 ppb 0.05 to 0.25 lb Hg/100 tons Cl ₂	99.7% mercury
Caustic Purification	Filtration	0.05 ppm	-----
Electrical			
Batteries	Extruded dough process: no dis- charge	-----	-----
	Mercuric oxide production: treat with sodium sulfite	2.5 ppm	-----
	Zinc amalgam production: set- tling and zinc amalgamation	0.5 ppm	-----
Lamps	No discharge	-----	-----
Switches and Rectifiers	No discharge	-----	-----
Industrial and Control Instrumentation	No discharge	-----	-----
Dentistry	Waste traps	-----	-----
Laboratory and Hospital Uses	Routine precautions	-----	-----

8. Although the mercury cell can technically be replaced by the diaphragm or the Downs cell in the chlor-alkali industry, the caustic produced by the latter two types is not suitable for some industries. Unless quality of caustic produced by the diaphragm or Downs cell process can be improved, the emphasis in this industry must be on treatment and control of mercury discharges rather than substitution for the mercury cell.
9. Lamp manufacturers do not discharge mercury into water, but they do dispose of rejects in sanitary landfills. Process losses of mercury appear to be confined to evaporation.
10. In the manufacturing of mercury switches and rectifiers, no discharge of mercury is made to the sewerage system. Mechanical or solid state switches can be used as substitutes, but the minimal hazards associated with the production of mercury switches do not warrant their replacement. Mercury rectifiers can be replaced by selenium or silicon rectifiers.
11. Industrial and control instrumentation manufacturers have few alternatives to using mercury except to substitute mechanical gauges and aneroid instrumentation. However, the substitutions may not be warranted since there are no mercury discharges from these manufacturers.
12. Present dental research on the replacement of amalgams as restoratives should in the near future produce substances capable of replacing mercury successfully for most dental applications.
13. The laboratory and hospital uses of mercury can not be avoided, but the judicious use and disposal of mercury and its compounds will help to avoid the introduction of mercury into the sewerage system.
14. The industries of electroplating, jewelry casting, hat making, and explosives manufacture have abandoned products or processes involving mercury.

SECTION VI

RECOMMENDATIONS

1. Study of economic considerations for the alternatives to using mercury and its compounds in individual industries is recommended.
2. Serious consideration should be given to requirements for accounting of all elemental mercury purchases, uses, and disposal by every user.
3. An in-depth study should be performed to evaluate the trace contamination of mercury in chemicals used in the production of consumer products.
4. In the paint industry, the control method of holding the wash water used in cleaning equipment after a batch paint mix is recommended since no mercury will be discharged.
5. Battery manufacturers should evaluate the process of chemically handling mercury in a dough-like material before placement in the battery casings, since this method does not produce any concentration of mercury in the final effluent.
6. Recycling and recovery of mercury in electrical products should be investigated and encouraged.
7. The American Dental Association should establish specifications or standard procedures for installation and use of traps in dental office sinks to capture the excess amalgam from tooth fillings.
8. All laboratory personnel should be trained in the proper use, treatment, and disposal of mercury and its compounds. The hazardous nature of these materials should be continuously and prominently emphasized (e.g., by posters) in the actual working areas.
9. Hospitals should be studied for the number of hazardous materials, such as mercury, which they discharge into municipal sewerage systems.
10. A medical committee should be established to assess the need to use mercury and its compounds in treatment and diagnosis.

SECTION VII

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APPENDIX A

PAINT BIOCIDES GUIDE

From: Paint and Varnish Production,
March 1971, reprinted by
permission.

BRAND NAME	GENERIC DESIGNATION	MANUFACTURER	FUNGICIDE	PRESERVATIVE	MERCURIAL	NON-MERCURIAL	FOR OIL BASE PAINTS	FOR EMULSION PAINTS
Advacide ATO	tributyltin oxide	5	•	•	•	•	•	•
Advacide FC	tributyltin oxide complex	5	•	•	•	•	•	•
Advacide N-628	tri-alkyl organotin	5	•	•	•	•	•	•
Advacide PMA 18	phenyl mercury acetate liquid	5	•	•	•	•	•	•
Advacide PMO 11	phenyl mercury oleate liquid	5	•	•	•	•	•	•
Advacide TMP	(n-trichloromethyl) thio phthalimide	5	•	•	•	•	•	•
Advacide 60	phenyl mercury acetate powder	5	•	•	•	•	•	•
Advacide 340-A	tributyltin oxide	5	•	•	•	•	•	•
Bairskin A	methylethylketoxime	3	•	•	•	•	•	•
bioMet TBTF	tributyltin fluoride	12	•	•	•	•	•	•
bioMet TBTO	bis tributyltin oxide	12	•	•	•	•	•	•
Busan 11-M1	modified barium metaborate	4	•	•	•	•	•	•
Busan 74	proprietary	4	•	•	•	•	•	•
CB-111	copper borate	10	•	•	•	•	•	•
CNC	copper naph. 8%	20	•	•	•	•	•	•
Cosan P	N-trichloromethyl thiophthalimide	6	•	•	•	•	•	•
Cosan PCMC	parachlorometacresol	6	•	•	•	•	•	•
Cosan PMA-30	phenyl mercury acetate solubilized	6	•	•	•	•	•	•
Cosan PMA-100 (Bulk)	phenyl mercury acetate	6	•	•	•	•	•	•
Cosan PMA-100-WSB	phenyl mercury acetate in water soluble bags	6	•	•	•	•	•	•
Cosan PMO-30	phenyl mercury oleate	6	•	•	•	•	•	•
Cosan S	3, 5-dimethyltetrahydro 1, 3, 5, 2H-thiadiazine-2-thione	6	•	•	•	•	•	•
Cosan 171-S	phenyl mercury 2-ethylhexylmaleate	6	•	•	•	•	•	•
Cosan 340	organotin/organomercurial	6	•	•	•	•	•	•
Cosan 635-W	complexed alkyl amine	6	•	•	•	•	•	•
Cytox 2013	dodecylguanidine hydrochloride	2	•	•	•	•	•	•
Cytox 2160	dodecylguanidine acetate	2	•	•	•	•	•	•
Cytox 3522	methylenebisithiocyanate	2	•	•	•	•	•	•
Cytox 3810	chloroethylene bisithiocyanate	2	•	•	•	•	•	•
Diaphene	3,4'5 tribromosalicylanilide	17	•	•	•	•	•	•
Dioxin	dimethoxane	9	•	•	•	•	•	•
Dowicide A Antimicrobial Agent	O-phenylphenol, sodium salt, tetrahydrate	8	•	•	•	•	•	•
Dowicide G Antimicrobial Agent	sodium pentachlorophenate	8	•	•	•	•	•	•
Dowicide 6 Antimicrobial Agent	2, 3, 4, 6-tetrachlorophenol	8	•	•	•	•	•	•
Dowicide 7 Antimicrobial Agent	pentachlorophenol	8	•	•	•	•	•	•
Dowicil 100 Antimicrobial Agent	1-(3-chloroallyl)-3,5, 7, triaza-1-azonia-adamantane chloride	8	•	•	•	•	•	•
Dowicil S13 Antimicrobial Agent	2, 3, 5, 6-tetrachloro-4-(methyl sulfonyl)-pyridine	8	•	•	•	•	•	•
DS 2787 Industrial Biocide	tetrachloroisophthalonitrile	7	•	•	•	•	•	•
DS 4018 Industrial Biocide	3, 4, 5-trichloro-2, 6-dicyanopyridine	7	•	•	•	•	•	•
Fundex CQ	copper 8-quinolinalate	1	•	•	•	•	•	•
Fundex DO	m-dodecylguanidine acetate	1	•	•	•	•	•	•
Fundex DT	3, 5 dimethyl tetrahydro 1,3, 5 2H-thiadiazine 2-thione	1	•	•	•	•	•	•
Fundex TMT	n-trichloromethyl thiophthalimide	1	•	•	•	•	•	•
Fundex TO	tributyltin oxide	1	•	•	•	•	•	•
Fundex ZO	zinc dimethyl dithiocarbamate	1	•	•	•	•	•	•
Fungitrol 11	N(trichloromethylthio) phthalimide	21	•	•	•	•	•	•
G4 Tech.	dichlorophene	9	•	•	•	•	•	•
G4-40-Tech.	dichlorophene solution	9	•	•	•	•	•	•
Giv-Gard BNS	bromonitrostyrene	9	•	•	•	•	•	•
Keycide X-10	stabilized form of tributyltin oxide	25	•	•	•	•	•	•
Merbac-35	benzyl bromoacetate	13	•	•	•	•	•	•
Mersolite 88	phenyl mercuric acetate	24	•	•	•	•	•	•
Mersolite 90	phenyl mercuric borate	24	•	•	•	•	•	•
Mersolite 430	phenyl mercuric oleate	24	•	•	•	•	•	•
Mersolite 810	phenyl mercuric acetate	24	•	•	•	•	•	•
Mersolite 830	phenyl mercuric acetate	24	•	•	•	•	•	•
Metasol D3T	tetrahydro-3, 5 dimethyl-2H-1, 3, 5-thiadiazine-2-thione	13	•	•	•	•	•	•
Metasol TK-100	2-(4-thiazolyl) benzimidazole	13	•	•	•	•	•	•
Metasol 57	phenyl mercuric propionate	13	•	•	•	•	•	•
Nildew AC30	phenyl mercuric acetate	14	•	•	•	•	•	•
Nildew CMK	p-chloro-m-cresol	14	•	•	•	•	•	•
Nildew D1	acetal	14	•	•	•	•	•	•
Nildew D2	acetal	14	•	•	•	•	•	•
Nildew OL30	phenyl mercuric oleate	14	•	•	•	•	•	•

BRAND NAME	GENERIC DESIGNATION	MANUFACTURER	FUNGICIDE	PRESERVATIVE	MERCURIAL	NON-MERCURIAL	FOR OIL BASE PAINTS	FOR EMULSION PAINTS
Omacide-2	sodium pyridinethione-N-oxide plus sodium tetra borate pentahydrate	15	•	•	•	•	•	•
Omacide-12C	sodium pyridinethione-N-oxide plus sodium chromate	15	•	•	•	•	•	•
Omacide-645	zinc pyridinethione-N-oxide and a polybrominated salicylanilide	15	•	•	•	•	•	•
Omadine solution (40% sodium)	40% solution of sodium pyridinethione-N-oxide	15	•	•	•	•	•	•
Onyxide 172	alkyl dimethyl ethylbenzyl ammonium cyclohexylsulfamate	16	•	•	•	•	•	•
Organoarse	phenarsazine chloride	1	•	•	•	•	•	•
Organoarse	phenarsazine dimethyl dithiocarbamate	1	•	•	•	•	•	•
Organoarse	triphenarsazine chloride	1	•	•	•	•	•	•
PMA-18	phenyl mercury acetate	21	•	•	•	•	•	•
PMO-10	phenyl mercury oleate	21	•	•	•	•	•	•
Proxel CRL	benzisothiazolone	11	•	•	•	•	•	•
RCI	O-phenylphenol	18	•	•	•	•	•	•
RCI 49-135, 136	O-benzyl P-chlorophenol	18	•	•	•	•	•	•
RCI 49-162	pentachlorophenol	18	•	•	•	•	•	•
Salicylanilide	salicylanilide	17	•	•	•	•	•	•
Sherstat SLN	salicylanilide	19	•	•	•	•	•	•
Sherstat TBS	3, 4, 5-tribromosalicylanilide	19	•	•	•	•	•	•
Super Ad-It	phenyl mercury dodecenyl succinate	21	•	•	•	•	•	•
Troysan CMP Acetate	chlormethoxypropyl/mercury compound	22	•	•	•	•	•	•
Troysan PMA-10SEP	phenyl mercury compound	22	•	•	•	•	•	•
Troysan PMA-20SEP	phenyl mercury compound	22	•	•	•	•	•	•
Troysan PMA-30	phenyl mercury compound	22	•	•	•	•	•	•
Troysan PMA-100	phenyl mercury compound	22	•	•	•	•	•	•
Troysan PMO-30	phenyl mercury compound	22	•	•	•	•	•	•
Troysan 142	heterocyclic sulfur compound	22	•	•	•	•	•	•
Troysan 174	aminoethanol compound	22	•	•	•	•	•	•
Troysan 269	alkyl tin compound	22	•	•	•	•	•	•
Vancide PA	ethene type	23	•	•	•	•	•	•
Vancide TH	triazine type	23	•	•	•	•	•	•
Vancide 51Z	dithiocarbamate type	23	•	•	•	•	•	•
Vancide 89	substituted hydrophthalimide	23	•	•	•	•	•	•
ZB-112, ZB-237	zinc borate	10	•	•	•	•	•	•
ZB-325	zinc borate	10	•	•	•	•	•	•
ZNC	zinc naph.	20	•	•	•	•	•	•

- ACETO CHEMICAL CO., INC.
126-02 Northern Blvd.
Flushing, N.Y. 11368
- AMERICAN CYANAMID CO.
Industrial Chemical Division
1937 West Main St.
Stamford, Conn. 06904
- BAIRD CHEMICAL INDUSTRIES, INC.
22-10 Route 208
Fair Lawn, N.J. 07410
- BUCKMAN LABORATORIES, INC.
1256 North McLean Blvd.
Memphis, Tenn. 38108
- CINCINNATI MILACRON CHEMICALS, INC.
500 Jersey Ave.
New Brunswick, N.J. 08903
- COSAN CHEMICAL CORP.
481 River Road
Clifton, N.J. 07014
- DIAMOND SHAMROCK CORP.
300 Union Commerce Blvd.
Cleveland, Ohio 44115
- DOW CHEMICAL CO.
Midland, Mich. 48640
- GIVAUDAN CORP.
321 West 44th St.
New York, N.Y. 10036
- HUMPHREY CHEMICAL CORP.
P.O. Box 2
Edgewater Arsenal, Md. 21010
- ICI AMERICA, INC.
151 South St
Stamford, Conn. 06904
- M & T CHEMICALS, INC.
Subsidiary of American Can Co.
Rahway, N.J. 07065
- MERCK & CO., INC.
Merck Chemical Division
Rahway, N.J. 07065
- NAFTONE, INC.
425 Park Ave.
New York, N.Y. 10022
- OLIN CHEMICALS
120 Long Ridge Rd.
Stamford, Conn. 06904
- ONYX CHEMICAL CO.
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Jersey City, N.J. 07302
- PFISTER CHEMICAL WORKS, INC.
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RCI Building
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- SHERWIN-WILLIAMS CHEMICALS
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Cleveland, Ohio 44101
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SUBSIDIARY INTERNATIONAL MINERALS
& CHEMICALS CORP.
400 West Roosevelt Ave.
Bensenville, Ill. 60106
- TENNECO CHEMICALS, INC.
Intermediates Division
P.O. Box 2
Piscataway, N.J. 08854
- TROY CHEMICAL CORP.
One Avenue L
Newark, N.J. 07105
- R.T. VANDERBILT CO., INC.
230 Park Ave.
New York, N.Y. 10017
- VENTRON CORP.
Congress Street
Beverly, Mass. 01915
- WITCO CHEMICAL CORP.
Organics Division
277 Park Ave.
New York, N.Y. 10017

Agricultural Chemicals

The following tables represent some of the current technical and quantitative data available on seed treatment fungicides.

Table 1. Seed Treatment Fungicides Used on Cottonseed

Common or Trade Name	Form Applied	Chemical Composition
<u>Mercurial fungicides:</u>		
Ceresan M	Slurry	7.7% <u>N</u> -(ethylmercury)- <u>p</u> -toluenesulfonanilide
Ceresan L	Liquid	2.89% methylmercury 2,3-dihydroxy-propylmercaptide and 0.62% methylmercury acetate
Panogen 15	Liquid	2.2% cyano(methylmercuri)-guanidine
PMA	Liquid	7% phenylmercury acetate
<u>Non-Mercurial fungicides:</u>		
Busan 72	Liquid	60% 2-(thiocyanomethylthio)-benzothiazole
captan	Slurry	75% <u>N</u> -((trichloromethyl)thio)-4-cyclohexene-1,2-dicarboximide
chloroneb	Slurry	65% 1,4-dichloro-2,5-dimethoxybenzene
chlorothalonil-Dexon	Slurry	40% tetrachloroisophthalonitrile and 32% sodium- <u>p</u> -(dimethylamino)-benzene-diazosulfonate
Terracoat L21	Liquid	23.2% pentachloronitrobenzene and 11.3% 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole
thiram	Slurry	70% bis(dimethylthiocarbamoyl)-disulfide
carboxin	Slurry	75% 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide

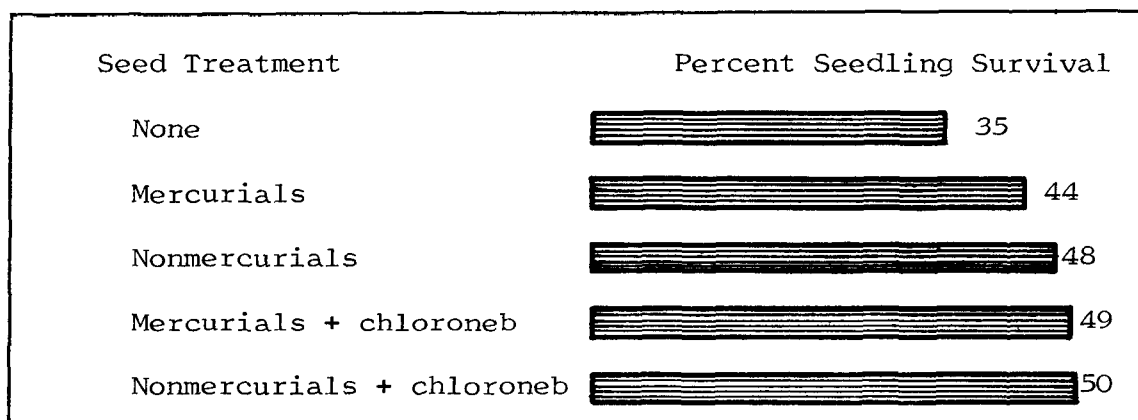
From: C. D. Ranney, "Effective Substitutes for Alkyl Mercury Seed Treatments for Cottonseed," Plant Disease Reporter, March 1971.

Table 2. Comparative Amounts of Active Ingredients Required for Treatment

<u>Non-Mercurials</u>				Ounces Active per bu. or cwt.*	Ounces Active "Ceresan" L (Mercurial)*
Common Name	Product Name	Manufacturer	Crop		
Thiram	"Arasan" 75	Du Pont	Cotton	2.25 cwt.	.105
			Small Grain	1.0 bu.	.0175
			Flax	1.5 bu.	.0525
Captan	"Captan" 75	Stauffer		Same	
	"Orthocide" 75	Chevron		Same	
Maneb	"Manzate"	Du Pont	Small		
			Grain	1.5 bu	.0175
	"Dithane"	Rohm & Haas	Flax	2.0 bu.	.0525
PCNB + Terrazole	"Terra-Coat" L-205 Olin (under development)		Cotton	4.8 bu.	.105
			Small		
			Grain	.6 bu.	.0175
Carboxin	"Vitavax"	UniRoyal	Cotton	6.0 bu.	.105
			Small		
			Grain	2.25 bu.	.0175
-	"Busan" 72	Buckman Lab.		2.1 bu.	.105

* At Average Rate of Application.

From: Dr. T. C. Ryker (Du Pont Company), private communication,
May 18, 1971.



From: C. D. Ranney, Plant Disease Reporter, March 1971.

Figure 1. Pictorial Summary of Data from Table 4

Table 3. Effectiveness and Costs of Wheat Seed Fungicides

<u>Wheat Seed Fungicide</u>	<u>More Plants Per 100 Kernels</u>	<u>Stinking Smut (bunt) Control*</u>	<u>Cost Treat Bushel**</u>
methyl mercury	12	B	10¢
phenyl mercury	6	B	8
thiram	14	S	15
maneb	14	S	20
captan	16	MS	20
captan HCB	16	S	15
Vitavax	12	S	40

*B = best, S = satisfactory, MS = satisfactory if bunt spores are not on the seed.

**Maneb and captan may cost less in large quantities.

From: Claude L. King (Kansas State University), "Mercuries Gone -- What for Seed Treatment?"

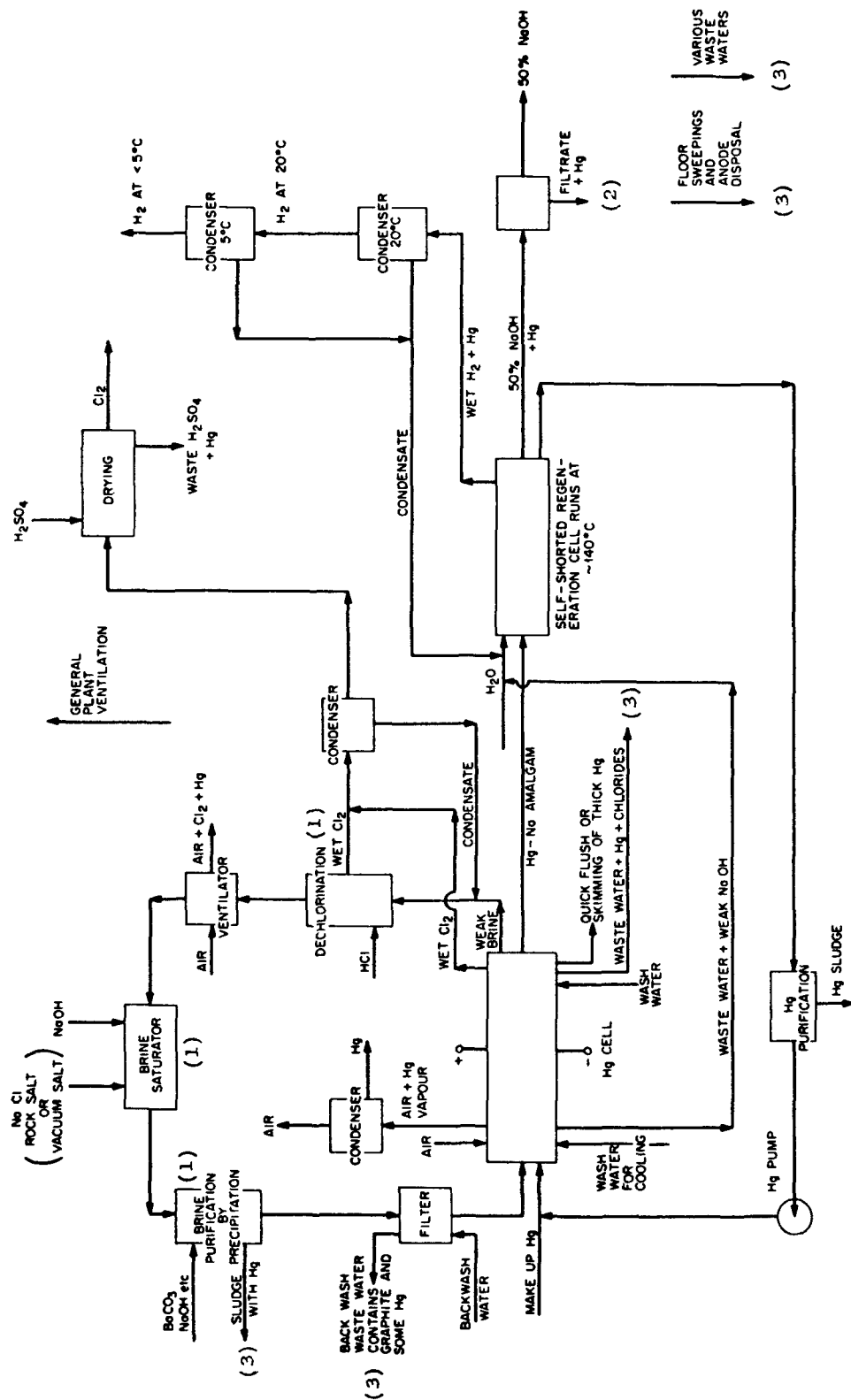
Table 4. Summary of Regional Cottonseed Treatment Tests
1968 - 1970

<u>Seed Treatment</u>	<u>Percent Seedling Survival</u>		
	<u>1968</u>	<u>1969</u>	<u>1970</u>
Number of tests*	<u>14</u>	<u>21</u>	<u>19</u>
Check (no treatment)	34.0	26.4	43.4
Ceresan M	48.1	38.4	55.4
Panogen 15	45.1	36.9	--
Ceresan L	47.4	39.3	46.7
Ceresan L + chloroneb	53.8	46.4	--
Busan 72	46.3	38.8	52.1
Busan 72 + chloroneb	--	44.2	59.6
chlorothalonil - Dexon	49.7	41.7	--
chlorothalonil - Dexon + chloroneb	54.2	44.2	64.1
Terracoat L21	52.3	46.7	57.8

* Conducted in the Cotton Belt by the Cotton Disease Council.

From: C. D. Ranney, Plant Disease Reporter, March 1971.

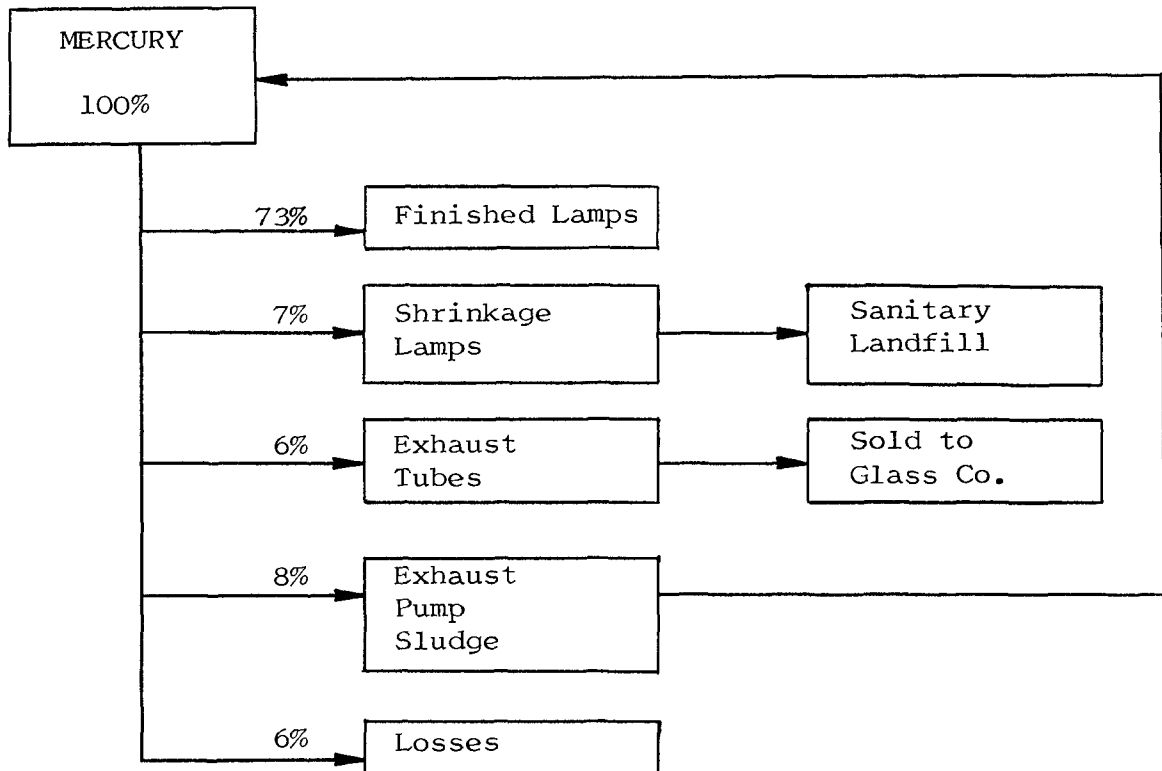
APPENDIX B



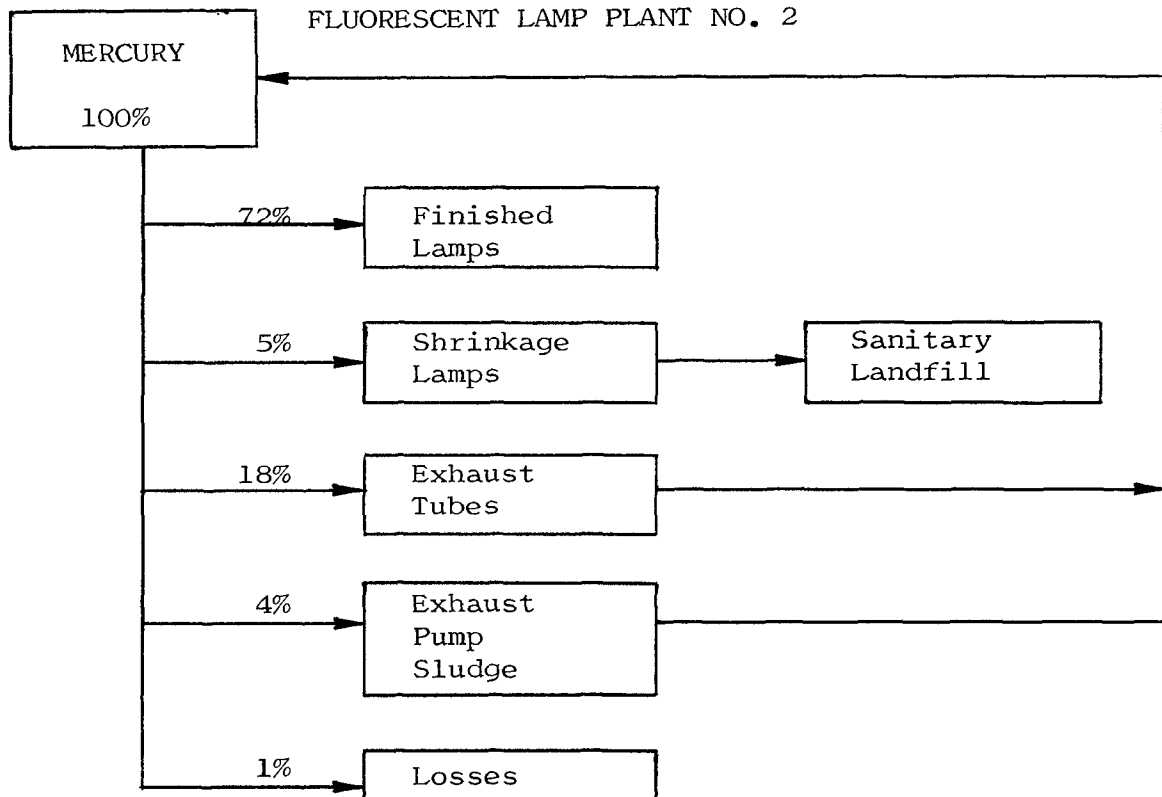
Flow Diagram for the Chlor-Alkali Mercury Cell Showing Potential Sources of Mercury Effluents

- (1) See Figure 6, p. 25 From: Wallace, R.A., et al. Mercury in the Environment, Oak Ridge National Laboratory, ORNL NSF-EP-1, January, 1971
- (2) See Figure 7, p. 26
- (3) See Figure 8, p. 28

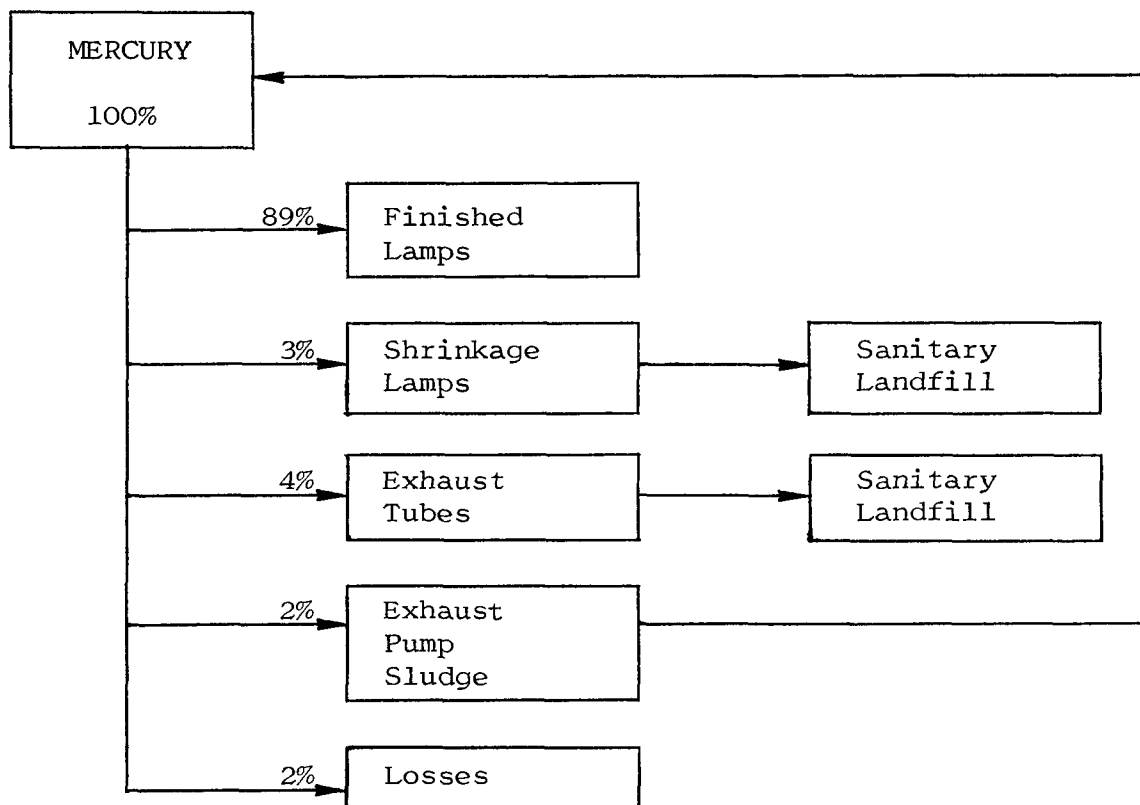
FLUORESCENT LAMP PLANT NO. 1



FLUORESCENT LAMP PLANT NO. 2



HIGH-INTENSITY DISCHARGE LAMP PLANT



1	Accession Number	2	Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W		05G		

5	Organization
	Litton Systems, Inc., Camarillo, California Environmental Systems Division

6	Title
	INDUSTRIAL WASTE STUDY -- MERCURY-USING INDUSTRIES

10	Author(s)	16	Project Designation
	Shilesky, D. M.		EPA, OWP - Project No. 805/25-18000 HIP
	Krause, K.W.	21	Note

22	Citation

23	Descriptors (Starred First)
	*Abatement, *Industrial Waste Water Treatment, *Heavy Metal, *Waste Water Disposal, Effluents, Liquid Wastes, Waste Disposal, Wastes Water Pollution Sources

25	Identifiers (Starred First)
	*Water Pollution Sources, *Waste Treatment, *Heavy Metal, Chemical Precipitation, Activated Carbon, Pollution Abatement, Landfills

27	Abstract
	<p>This study discusses information obtained from a literature survey, mail survey, telephone contact phase, and field trip pertaining to industrial wastes of mercury-using industries. The main topics presented for each industrial group are: (1) uses of mercury; (2) reasons for industry's use of mercury; (3) alternatives to use of mercury in the industry; and (4) best available level of treatment and control. Research needs are also recommended for future studies. In general, it was found that under present technology mercury cannot be fully replaced in dentistry, the electrical industry (lamps, batteries), production of chemicals (pharmaceuticals, laboratory reagents), catalysis, and industrial and control instrumentation. Substitution is technologically possible but probably not warranted because of minimal hazard from mercury use in switches and in some industrial and control instrumentation. Substitution is possible and highly desirable (in the absence of fully effective treatment and control methods) in the chlor-alkali and plastics industries. Use if mercury has come or is coming to an end in agriculture, paints, and pulp and paper production. The best present and proposed treatment and control methods can reduce typical mercury concentrations in industrial waste waters to levels of 1 to 5 ppb. However, very few facilities control their mercury discharges to this extent.</p> <p>(Shilesky - Litton)</p>

Abstractor	Institution
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