Environmental Protection Technology Series

RECOMMENDED METHODS OF

REDUCTION, NEUTRALIZATION, RECOVERY OR

DISPOSAL OF HAZARDOUS WASTE

Volume VI Mercury, Arsenic, Cr, Cadmium

RECOMMENDED METHODS OF

REDUCTION, NEUTRALIZATION, RECOVERY

OR DISPOSAL OF HAZARDOUS WASTE

Volume VI. National Disposal Site Candidate
Waste Stream Constituent Profile Reports -
Mercury, Arsenic, Chromium, and Cadmium Compounds

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and

- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

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1. GENERAL

Introduction

Mercury, commonly called quicksilver, was one of the first metals known to man and has been mined at Almaden, Spain for 27 centuries. In earlier times, mercury has been mainly used as a decorative (in the form of cinnabar), as a medical ointment for skin diseases, and as an amalgam for tin and copper. Introduction of mercury into scientific research occurred in 1643, with the invention of the barometer by Torricelli. This was followed in later years by the invention of the mercury thermometer, the discovery of the use of mercury as a seal for water-soluble gases in gas analysis, and the preparation of mercury fulminate as a detonator for explosives. Because of the relatively small scale use of mercury in the past, mercury and mercury compounds were never considered a real threat to the quality of the environment, although the toxic nature of mercury and its compounds have been known for centuries. Mercury today, however, is used on a substantial scale in chemical industries, in the manufacture of paints and paper, in pesticides for agriculture, and in the electrical industry. With the development of these applications, and the failure to recognize the hazards associated with seemingly harmless levels of mercury and inorganic mercury compounds, came serious problems.

First in 1960, it was reported that 111 persons had died or suffered serious neurological damage near Minamata, Japan, as a result of eating fish and shellfish which had been contaminated by methyl mercury and mercuric chloride discharged into Minamata Bay by a plastics manufacturing plant. In 1965, another poisoning incident was reported in Niigata, Japan,

and in 1966, Swedish studies showed that many species of birds were being poisoned by mercury. Finally, in the spring of 1970, high levels of mercury were discovered in fish in Lake St. Clair, on the Canada-United States border. Canada banned the sale of fish from the lake, and 10 days later Michigan followed suit. In succeeding months, there followed a series of bans on fish and seafood containing excessive mercury, legislations against discharge of mercury into navigable waters, and the cancellations of Federal registrations of numerous mercury compounds for industrial and agricultural uses.

It was these several spectacular reported incidents of mercury poisoning in recent years, and the positive demonstration that inorganic mercury could be biologically methylated in the natural aquatic environment and subsequently concentrated up to 3,000 times in fish and other marine organisms, that finally led to the full realization of the extent of the mercury pollution problem.

The quantity of mercury used each year in the world increased at a rate of about 1,800 flasks* per year for the ten-year period previous to 1968. Most of the increase was due to the U.S. demand, which grew at a rate of 1,600 flasks per year over the same period until in 1968 it represented about 30 percent of the world primary production of 257,000 flasks. Also in 1968, the U.S. supply of mercury came from four sources: 18 percent from recycled material; 36 percent from U.S. mining; 22 percent from net imports; and 24 percent from Government stockpile releases.[2105] Individual statistics for the production and consumption of inorganic mercury compounds are not available, but could be estimated from the consumption figures of mercury by uses (Table 1).

Manufacture

Mercury. The most common metallurgical process for recovering mercury is that of roasting cinnabar (mercuric sulfide) in either mechanical

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*A flask contains 76 lb mercury and is the standard commercial unit of trade.

furnaces or retorts to volatilize the mercury followed by condensation of the vapor. Furnacing is a continuous operation where the mercury bearing materials are directly heated by the gases of combustion, and has the disadvantage of involving large volumes of furnace gas. Retorting, on the other hand, is a batch operation where the material is heated indirectly and consequently the volume of retort gas is small.[1433] Hydrometallurgical processes for extracting mercury include leaching with either sodium hypochlorite or sodium sulfide, but to date both methods have not been commercially employed for the recovery of mercury.[2064] The major U.S. producers of mercury include the following:[0637]

> Decoursey Mountain Mining Company; Anchorage, Alaska
> Harold Braggini; Atascadero, California
> COG Minerals Corp.; Denver, Colorado
> New Idria Mining and Chemical Co.; Guerneville, California
> Holly Minerals Corp.; Albuquerque, New Mexico
> Rare Metals Corp. of America; Salt Lake City, Utah
> Cordero Mining Co.; Palo Alto, California
> Arentz-Comstock Mining Venture; Salt Lake City, Utah
> Bonanza Oil and Mining Corp.; Sutherlin, Oregon

Mercuric Chloride. Mercuric chloride is produced commercially by the direct chlorination of mercury. Older processes, based on the reaction between mercurous sulfate and sodium chloride, are no longer extensively practiced in the United States.[1433]

Mercuric Nitrate. Mercuric nitrate is made by dissolving mercury in an excess of hot concentrated nitric acid, followed by cooling to crystallize the hydrate. Seeding with a small quantity of pure crystals is usually recommended, as there is a strong tendency to form supersaturated solutions.[1433]

Mercuric Sulfate. Mercuric sulfate is prepared by reacting a paste of freshly precipitated and washed yellow mercuric oxide with the calculated amount of sulfuric acid, followed by filtration of the white crystalline sulfate on a nutsch and subsequent drying.[1433] It may also be prepared by heating mercury with an excess of sulfuric acid; the formation is favored at high temperatures.[2039]

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Mercuric Diammonium Chloride. Mercuric chloride diammine is made by dissolving mercuric chloride in a strong aqueous solution of ammonium chloride, and adding ammonia solution. It may also be prepared by treating finely powdered dry mercuric chloride with anhydrous ammonia vapor.[1433] The major U.S. producers of inorganic mercury chemicals include the following:[0637]

> Allied Chemical Corp.; Specialty Chemicals Division; Morristown, New Jersey
>
> City Chemical Corp.; Jersey City, New Jersey
>
> Mallinckrodt Chemical Works, Industrial Chemical Division; Jersey City, New Jersey
>
> Merck & Co., Inc., Merck Chemical Division, Rahway, New Jersey
>
> Troy Chemical Corp.; Newark, New Jersey
>
> Ventron Corp., Alfa Products; Beverly, Massachusetts
>
> Ventron Corp., Chemicals Division; Beverly, Massachusetts

Uses

The U.S. demand for mercury can be broken down into recyclable and dissipative uses, which account for 74 and 26 percent of the total respectively. Recyclable uses are defined as those for which it is technically feasible to recycle, whereas for dissipative uses it is not.[2105]

The major use of mercury is as a cathode in the electrolytic preparation of chlorine and caustic soda. Actual consumption in this manufacturing process is small for each unit, although up until recently large quantities were required for new installations (10 percent of 1968 demand). Because of the many plants now in operation, however, the requirement to replace losses has become a major use (23 percent of 1971 demand). Large quantities of mercury are also used in electrical apparatus, in industrial and control instruments, and in general laboratory applications. These potentially recyclable uses of mercury are for fluorescent and high-pressure mercury lamps, arc rectifiers, mercury battery cells, switches, thermometers, barometers, diffusion pump, vacuum gage, and as a vibration damper.[1433,2105]

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The largest dissipative use of mercury is for mildewproofing paints. (Mercury is no longer used in antifouling paints). Mercury compounds are also widely used in agriculture as a result of their broad antifungal capabilities, for catalytic purposes, and formulated into many of the over-the-counter cosmetics (such as creams and lotions, hair preparations, and facial make-up) and patent medicines (antacids, astringents, eye drops, laxatives, nasal sprays, skin antiseptics, contraceptives). Mercury is used in dental amalgams, and to a decreasing extent, for the control of slime in the paper and pulp mills.[0533,2105]

Individual figures of mercury consumption by use from 1967 to 1971 have been compiled by the Bureau of Mines (Table 1), and indicate that declining levels of consumption were noted for mercury uses in agriculture, catalysts, electrolytic preparation of chlorine and caustic soda, installation and expansion of chlor-alkali plants, and paper and pulp manufacture (Table 2).

An estimate of the current and future use pattern of mercury over the next few years has also been presented (Table 3). Of the eleven major categories represented, decreasing demands are forecasted in five including agriculture, electrolytic preparation of chlorine and soda, installation and expansion of chlor-alkali plants, paints, and paper and pulp manufacture. The other six major uses of mercury are expected to continue at about the same level. These predicted trends in mercury consumption also point toward the direction where future efforts of mercury recovery and pollution control should be aimed.

Of the four inorganic mercury compounds included in this Profile Report, mercuric diammonium chloride is of no commercial significance; whereas mercuric chloride is one of the most industrially important mercury compounds. Mercuric chloride is used for the production of various mercuric compounds, as a catalyst in vinyl chloride manufacture and other organic reactions, and as a preservative for wood. In agriculture, it is used either as a dust or spray for the control of certain fungus diseases on seeds. Solutions

TABLE 1

MERCURY CONSUMED IN THE UNITED STATES BY USES

Use	Consumption, flasks				
	1967	1968	1969	1970	1971
Agriculture (includes fungicides and bactericides for industrial purposes)	3,732	3,430	2,689	1,812	1,477
Amalgamation	219	267	195	216	*
Catalysts	2,689	1,914	2,958	2,041	1,141
Dental preparations	1,359	2,089	3,083	1,799	2,387
Electrical apparatus	14,610	17,484	18,650	15,789	16,938
Electrolytic preparation of chlorine & caustic soda	14,306	17,458	20,720	14,977	12,262
General laboratory uses	1,133	1,246	2,041	1,513	1,809
Industrial & control instruments	3,865	3,935	6,981	4,035	4,871
Paint:					
Antifouling	152	392	244	193	414
Mildew proofing	7,026	10,174	9,486	8,771	8,191
Paper & pulp manufacture	446	417	588	316	*
Pharmaceuticals	283	424	724	571	682
Redistilled †	7,129	8,247	---	---	---
Other ⧺	12,568	7,945	9,689	6,521	2,300
Total known uses	69,517	75,422	78,048	58,554	52,472
Total uses unknown	--	--	1,056	2,936	3
Grand total	69,517	75,422	79,104	61,490	52,475

* Withheld to avoid disclosing individual company confidential data; included with "Other".

† "Redistilled" used in industrial instruments, dental preparations, and electrical apparatus.
   Figures for the Redistilled category are not available after 1969, but have probably been
   broken down and added to the figures of the individual use categories.

⧺ "Other" includes mercury used for installation and expansion of chlor-alkali plants.

TABLE 2

TRENDS IN USES OF MERCURY OVER THE PERIOD 1967 to 1971

| Use | 1971 Consumption | |
	Flasks	Percent of Total
Decreasing Level of Consumption		
Agriculture	1,477	2.8
Catalysts	1,141	2.2
Electrolytic Preparation of Chlorine and Soda	12,262	23.4
Other Uses*	2,300	4.4
Subtotal	17,180	32.8
No Significant Changes in Consumption		
Dental Preparations	2,387	4.5
Electrical Apparatus	16,938	32.3
General Laboratory Uses	1,809	3.4
Industrial and Control Instruments	4,871	9.3
Paints	8,605	16.4
Pharmaceuticals	682	1.3
Subtotal	35,292	67.2
Grand total	52,472	100.0

*Other uses include mercury used for installation and expansion of chlor-alkali plants, amalgamation, and in paper and pulp manufacture.

TABLE 3

ESTIMATED TRENDS IN CONSUMPTION OF MERCURY

Use	Estimated Mercury Consumption, flasks	
	1971	1974-1975
Agriculture	1,477	0
Catalysts	1,141	1,141
Dental Applications	2,387	2,387
Electrical Apparatus	16,938	16,938
Electrolytic Preparation of Chlorine and Soda	12,262	672*
General Laboratory Use	1,809	1,809
Industrial & Control Instruments	4,871	4,871
Paints	8,605	0
Paper and Pulp	10[+]	0
Pharmaceuticals	682	682
Others[‡]	2,290	300
Totals	52,472	28,800

*Based on total mercury loss of 0.02 lb/ton chlorine produced and a chlorine production capacity of 7,000 tons per day.

[+]Estimated

[‡]"Others" include mercury used for installation and expansion of chlor-alkali plants and amalgamation.

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of mercuric chloride are used medicinally as an antiseptic, and in photography to intensify negatives.[1433]

Mercuric nitrate is used in the preparation of other mercury compounds, and in particular, mercury fulminate. It is also used in the manufacture of felt, and for the destruction of phylloxera.[0637]

Mercuric sulfate is mainly used as an electrolyte for primary batteries.[0637] Aside from its occasional use as a catalyst, mercuric sulfate has been employed in conjunction with sodium chloride to extract gold and silver from roasted pyrites.[1433]

Sources and Types of Waste

The wide variety of uses of mercury and mercury compounds by man has resulted in significant mercury pollution of the environment in many parts of the world. By far the single largest source of commercial discharges of mercury during 1968 was derived from inventory losses suffered by the chlor-alkali plants. Approximately 25 percent of the U.S. supply of chlorine comes from mercury cells, which produce a higher grade caustic soda that is highly concentrated and essentially free of chloride impurities, and thus the trend in new construction until recently, has greatly favored the mercury cell. The total chlorine capacity of mercury cells in the United States is about 7,000 tons per day from about 29 installations around the country, with plant capacities ranging from 6 to about 700 tons per day. In the mercury cell process, a circulating sodium chloride solution is electrolyzed in the cell in which mercury serves as the cathode; the anode is usually graphite. Sodium ion reacts with mercury to form an amalgam, and chlorine gas is produced at the anode. The mercury flows through the cell, picking up sodium on the way, and is pumped to a regeneration cell, where the amalgam is mixed with water and forms one-half of a self-shorted electrolytic cell, with iron serving as the other electrode. The regeneration cell removes sodium from the amalgam and produces caustic soda (approximately 50 percent solution) and hydrogen gas. The regenerated mercury is then returned to the mercury cell, and the process is repeated. The brine solution leaves the mercury cell and is vacuum de-chlorinated and then

purged with air to remove the last of the chlorine. The solution is then saturated with salt, and this is followed by a purification step, in which various impurities from the newly added salt are precipitated. The brine is then passed through a filter and back to the mercury cell.

The primary sources of mercury loss in mercury-cell chlor-alkali plants are the hydrogen gas stream, the sludge from the brine purification process, the caustic soda stream, cell room ventilation air, and various waste wash water (Table 4).[0533, 2042, 2062, 2105] The reported values of mercury loss from Swedish and U.S. plants are 55 to 190 gm/ton and 202 to 538 gm/ton of chlorine produced respectively in 1968. As early as 1970, however, it was technically feasible to reduce the total mercury loss from a chlor-alkali plant to only 0.63 to 2.11 gm/ton of chlorine produced.

Based upon 1968 U.S. data, 17,458 flasks of mercury were used in the manufacture of chlorine, which represents an industry average of about 0.5 lb of mercury loss per ton of chlorine produced.[0533] However, this loss can apparently be decreased by one to two orders of magnitude by proper plant management. During the summer of 1970, lawsuit threats and tentative water standards caused many of the chlor-alkali manufacturers to reduce their mercury discharge significantly. As monitored by the Department of Interior, the overall level of mercury emission to receiving waters was found to be dropped 86 percent from 287 lb per day in July to 40 lb per day in September 1970.[2105]

The major mercury problem associated with the chlor-alkali plants at present is the safe disposal of the mercury containing brine sludges. For resaturation of the partly depleted brine from electrolysis, solid salt is required by the mercury cell process. If only brine is available, this must be evaporated first to produce solid salt. Typical sources of salt include shaft mined rock salt vacuum pan salt, solar pond salt, and salt recovered from the cell liquor evaporator in an adjacent diaphragm cell plant. The ideal raw material for the mercury cell process is, of course, highly purified recrystallized salt with a purity of 99.99 + percent NaCl.

If the salt feed is of extremely high purity, the brine need only be filtered before returning it to the cells. If salt recovered from the

TABLE 4

SOURCES OF MERCURY LOSSES
FROM CHLOR-ALKALI PROCESS(0533, 2042, 2062, 2105)*

Source	Sweden (1967)	United States (1968)	Technically feasible (1970)
H_2 gas	27-85	180-230	0.01
NaOH	0.4-20	2-3	0.01-0.5
Brine sludge	2-50	5-125	0.1-1.0
Ventilation	15-25	5-45	0.5
Wash waters	10	5-70	0.01-0.1
Others	-	5-65	-
Total	55-190	202-538	0.63-2.11

*Grams of mercury lost per ton of chlorine produced.

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diaphragm cell caustic evaporators is used, brine purification normally involves the addition of caustic soda followed by filtration, the sludge obtained is mainly graphite, along with some $CaCO_3$, $Mg(OH)_2$, and iron. When either high purity recrystallized salt or recovered salt from the diaphragm cell caustic evaporator is used, smaller quantities of mercury containing brine sludges are generated. These can often be treated and disposed of safely on the property.

If rock salt or solar salt is used, the full brine stream is treated for the removal of Mg, Fe, $CaCl_2$ and $CaSO_4$ equivalent to the pickup from the salt dissolved. Brine purification includes the addition of barium carbonate to remove sulfates, the addition of sodium carbonate or carbon dioxide to precipitate calcium, the addition of caustic soda to remove magnesium and heavy metals, and the addition of flocculents to cause settling of the precipitates. Depending on the impurities initially present in the salt, the constituents of the brine sludge include barium sulfate, calcium carbonate, calcium sulfate, magnesium oxide, magnesium hydroxide, graphite, some iron, aluminum, mud, rocks, and typically 100 ppm mercury in the form of $HgCl_4^=$. Mercury losses through the brine sludges from the mercury cell chlor-alkali plants range from 0.001 to 0.04 lb per ton of chlorine produced. The mercury containing brine sludges are currently being pumped into settling basins awaiting the development and installation of adequate treatment processes. The total mercury loss is estimated to be 16,500 lb per year through 57,000 tons of brine sludges.*

Of the mercury used in 1968 for other potentially recyclable uses, such as electrical equipment, measurement and control apparatus, and general laboratory uses, 520 tons were recycled and 660 tons had an unknown disposition, (in batteries, fluorescent tubes, switches, etc.) and probably ended up mostly in landfills, dumps, and incinerators.[2105]

The dissipative uses of mercury include paints, agriculture, dental fillings, catalysts, paper and pulp manufacture, and pharmaceuticals; a

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*This is discussed in more detail in the volume on Waste Forms and Quantities.

total of 26 percent (745 tons) of the mercury demand in 1968. Mercury from these various uses enter the environment in a variety of ways and at different rates. For example, although mercury-formulated paints constitute a considerable source, their release into the environment is rather slow and probably has a minimal effect. Dental amalgams also apparently have no measurable effect on the user. On the other hand, mercury catalysts employed for acetaldehyde and vinyl chloride manufacture and mercury formulations used as seed dressings have promoted serious consequences, even though such usage represents a small percentage of the total consumption. However, in March 1970, the U.S. Department of Agriculture suspended 42 alkylmercury compounds from interstate commerce. Furthermore, the use of mercury compounds as slimicides in the paper and pulp industry has decreased drastically since the early 1960's so that it now amounts to well less than one percent of the total demand.[2105]

Other man-made sources of environmental mercury include mine tailings and vapor released by the mining and smelting of mercury, and a stack loss of three percent during the refining process would mean that 31 tons were emitted into the atmosphere from smelting during 1968. In addition, ore deposits of heavy metals are generally surrounded by aureoles in which a notable enrichment in mercury has occurred, and considerable mercury generally escapes from stacks during the smelting of tin, zinc, copper, and gold. As an example, zinc concentrates from Tennessee contain an average of 5 to 10 ppm mercury; thus a single smelter handling 500 tons per day might emit as much as 10 lb mercury vapor daily.[2105]

Another major source of airborne mercury is the combustion of paper products and fossil fuel. The actual amounts of mercury in fossil fuels are quite variable, but preliminary values for U.S. coals average from 0.5 to 3.3 ppm mercury.[2100] Since about 550 million tons of coal are burned in the United States every year, a conservative estimate of 1 ppm mercury in coal would correspond to an annual release of 550 tons of mercury to the environment. However, although the general consensus was that fly ash from coal-burning plants contained negligible amounts of mercury so that the mercury present in the coal must be released to the atmosphere during the combustion process, a recent U.S. Bureau of Mines study revealed

that more than 70 percent of the mercury could be trapped by the fly ash (which can be separated out of the stack gases) and thus be more readily amenable to recovery.[2172] No information is available on the mercury released during petroleum processing and oil burning, although it is believed that the enormous amounts of these substances consumed and burned in the United States each year probably contribute a substantial amount to mercury pollution. Samples from California crudes have yielded mercury values in the range of 1.0 to 21 ppm; and related tars which have lost much of their volatile hydrocarbons are known to contain as much as 500 ppm mercury.[2117]

Lastly, because mercury has a tendency to vaporize and is widely distributed, mercury also enters into the environment through natural sources. The air over mercury ore deposits and precious metal or copper ore deposits generally contain elevated levels of mercury. Relatively high concentrations of mercury are also likely to occur in underground waters because of the longer and intimate contact with mineral grains. Oil field brines, hot springs, and geothermal stream fields have been associated with high mercury levels, and hot vapors which stream up through fine-grained muds produce mud volcanoes and deposit considerable quantities of mercury during condensation.[2117]

Physical and Chemical Properties

The physical and chemical properties of mercury and the four inorganic mercury compounds are summarized in the attached worksheets.

2. TOXICOLOGY

Inorganic mercury may enter into the body by adsorption through inhalation of elemental mercury vapor or aerosols of mercuric salts and by oral ingestion. Penetration through the skin, on the other hand, is rather slow.

Inhalation of mercury in concentrations of 1,200 to 8,500 micrograms per cubic meter in air results in acute intoxication, affecting primarily the digestive system and kidneys, and is characterized by a metallic taste,

nausea, abdominal pain, vomiting, diarrhea, headache, and sometimes albuminuria. After a few days, the salivary glands swell, stomatitis and and gingivitis develop, and a dark line of mercuric sulfide forms on the inflamed gums. Furthermore, teeth may loosen and ulcers may appear on the lips and cheeks. Severe exposure to mercury vapor produces tightness and pain in the chest, difficulty in breathing, and coughing. Severe cases of acute poisoning are characterized in later stages by hemolysis, sleeplessness, headache, facial tics, digital tremors, delirium and hallucinations. Death as a result of extreme exhaustion frequently occurs with poisoning of this degree of severity. In milder cases of acute mercury poisoning, some patients recover within 10 to 14 days, but others may develop the chronic symptoms, such as muscular tremors or erethism.[0637]

Chronic poisoning of mercury is more common than the acute form. In the case of chronic poisoning of inorganic mercury, symptoms and signs involving the central nervous system are most commonly seen, the principal features being tremors and psychological disturbances. Symptoms related to the mouth, such as gingivitis, stomatitis, and excessive salivation, may occur along with a number of nonspecific symptoms such as loss of appetite, weight loss, anemia, and muscular weakness. Intoxication from mercury vapor or from absorption of mercuric salts may be due, in both cases, to the action of the mercuric ion. Metallic mercury is able to diffuse much more extensively into the blood cells and various tissues than inorganic mercury, but once distributed, most of it is oxidized to the mercuric form. Numerous cases of industrial exposure to mercurials with resultant toxic symptoms have been reported, mostly involving incidents in the mining of hat-felt industries (which utilizes mercuric nitrate). In most cases, however, symptoms of mercury poisoning were observed only among workers who had been exposed to mercury levels above 100 micrograms per cubic meter in air.[2105]

It has been reported that a 1 gm oral dose of mercuric chloride could cause death in adults whereas a 0.1 gm dose would lead to chronic illness.[2117] The acute oral LD50 of mercuric chloride to rat is 37 mg/kg body weight, and that of mercuric nitrate to mouse is 4 mg/kg body weight.[1312]

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended as Threshold Limit Values (TLV) for 1971 a time-weighed average concentration of 50 micrograms per cubic meter in air for metallic mercury vapor and inorganic mercury compounds.[0225] The new ACGIH TLV for inorganic mercury is probably based on the report of the 1968 International Symposium at the Karolinski Institute, Sweden, which recommended 8-hour Maximum Allowable Concentrations (MAC) of 50 micrograms per cubic meter in air for mercury vapor and 100 micrograms per cubic meter in air for inorganic mercury salts.[2036]

The lethal concentrations of mercury compounds for various aquatic organisms have been summarized in a 1970 U.S. Geological Survey Report.[2117] For mercuric chloride, the lethal concentrations in ppb for aquatic organisms are: Escherichia coli (bacteria), 200; Schenedismus (phytoplankton), 30; Microregma (protozoa), 150; Daphnia magna (zooplankton), 6; Marinogammarus marinus (amphipod), 100; Polycelis nigra (flatworm), 270; Bivalve larve (mollusca), 27; Australorbis glabratus (mollusca), 1,000; Stickleback (fish), 4 to 20; Guppy (fish), 20; Eel (fish) 27; Rainbow trout (fish), 9,200. For mercuric nitrate, the lethal concentrations in ppb for aquatic organisms are: Mesospheroma oregonensis (isopod), 15; Mercierella enigmatica (polychaete), 1,000; Stickleback (fish), 20; Guppy (fish), 20. No aquatic toxicity data are available for mercury, mercuric sulfate, or mercuric diammonium chloride, as mercuric sulfate decomposes in cold water into a yellow insoluble basic sulfate and free sulfuric acid, and both mercury and mercuric diammonium chloride are insoluble in cold water. It must be remembered, however, that mercury and all inorganic mercury compounds discharged into the aquatic environment could eventually be biologically converted into the more toxic methyl mercury by anaerobic microorganisms, [0658, 2099] which can then be concentrated through food chains to fish living in both fresh water and marine environments, thus leading to the present dimensions of the mercury pollution problem.

3. OTHER HAZARDS

All inorganic mercury compounds, with the notable exception of the halides, decompose to give toxic fumes of mercury on heating.

In addition to its toxic properties, mercuric nitrate also possesses some of the properties of nitrates. Acetylene forms a sensitive acetylide when passed into an aqueous solution of mercuric nitrate. Alcohols should not be mixed with mercuric nitrate, as explosive mercury fulminate may be formed. Reactions of mercuric nitrate and phosphine give a yellow precipitate, which explodes when heated or subjected to shock. Mercuric nitrate also reacts with unsaturates and aromatics with violence if given time to generate enough heat, and could lead to explosions in its use for determining sulfur in Ball's reaction.[0096]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Because of the extreme toxicity of mercury and mercury compounds, care must be exercised in their handling to minimize contact with the skin or the inhalation of airborne dust, as well as ingestion. Safety precautions should include adequate ventilation of all work and storage areas, enforcing strict standards of housekeeping and personal cleanliness, and the use of protective equipment. Workers should be examined periodically by competent physicians, and referred to medical treatment after any mishap that might give rise to an abnormally high intake of mercury.

The volatility of mercury and the dangers of airborne inorganic mercury salt dusts have necessitated the storage of mercury and inorganic compounds in tight containers. Mercury, mercuric chloride, and mercuric sulfate are classified as Poison B by the Department of Transportation (DOT), and the rules governing its transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 100 to 199.[0278] Although mercuric nitrate and mercuric diammonium chloride are not on the DOT list of hazardous materials, the same regulations for Class B Poisons should also be applied in the transportation of these compounds because of their toxic nature.

Spilled mercury and inorganic mercury compounds on floors can normally by handled by several of the removal methods available. Sweeping with

special vacuum cleaners can effectively remove large droplets of mercury and the greater portion of inorganic mercury salt in powder or dust form, and this can be followed by flooding with water, collection of the water with suction pumps, and subsequent removal of the mercury from the contaminated water by chemical precipitation, chemical reduction, ion exchange, or solvent extraction methods. For the chemical removal of mercury, a substance is generally applied to react readily with mercury at ambient temperatures forming nearly nonvolatile mercury compounds, which can then be swept up. The chemical agents commonly used are inorganic polysulfides or powdered sulfur.[0533]

Methods suggested for treating water spills of mercury and inorganic mercury compounds include adsorption with activated carbon and ion-exchanger masses such as the Q-13 resin. Results of experiments conducted at the Cornell Aeronautical Laboratory (CAL) has shown that an activated carbon dose of 500 ppm could effect greater than 99 percent removal of mercury from water with an initial mercury concentration (as mercuric chloride) of 100 ppm, and it has been suggested the activated carbon could best be introduced into the stream in water-permeable bags which would allow the pollutant-laden water to pass through the bag material and interact with the contained carbon.[1419] Ion-exchanger masses that could be employed in treating water spills of mercury will be discussed later along with other methods for removing mercury and inorganic mercury compounds from liquids.

Disposal/Reuse

The greater portion of mercury and inorganic mercury compounds present in air and water waste streams can be removed and the mercury recovered for its value. However, although zero mercury discharge is the eventual goal of all concerns, this is not achievable with current technology, especially when economical factors are also considered. For these reasons, the safe disposal of mercury and inorganic mercury compounds must still be defined in terms of recommended provisional limits in the atmosphere and potable water source and/or marine habitat. The provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Mercury	0.0005 mg/M^3	0.01 TLV
Mercuric Chloride	0.0005 mg/M^3 as Hg	0.01 TLV
Mercuric Nitrate	0.0005 mg/M^3 as Hg	0.01 TLV
Mercuric Sulfate	0.0005 mg/M^3 as Hg	0.01 TLV
Mercuric Diammonium Chloride	0.0005 mg/M^3 as Hg	0.01 TLV

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Mercury	0.005 ppm (mg/l)	U. S. Drinking Water Standard
Mercuric Chloride	0.005 ppm (mg/l) as Hg	U. S. Drinking Water Standard
Mercuric Nitrate	0.005 ppm (mg/l) as Hg	U. S. Drinking Water Standard
Mercuric Sulfate	0.005 ppm (mg/l) as Hg	U. S. Drinking Water Standard
Mercuric Diammonium Chloride	0.005 ppm (mg/l) as Hg	U. S. Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Removal from Gases

Removal of mercury from gases usually concerns one of two types of operation. The first is removal of mercury vapor from the hydrogen produced in the mercury-cell chlor-alkali process. The second involves the more general problem of the removal of mercury vapor from gases such as air, incineration effluents, and natural gas.

Hydrogen produced by the electrolysis of brine at a mercury cathode contains substantial quantities of mercury vapor, at times more than 20,000 micrograms of mercury per cubic meter, and is usually saturated with water vapor. It is desirable to substantially lower the mercury concentrations in hydrogen, not only from the environmental standpoint, but also because

the presence of mercury at concentrations higher than 10 micrograms per cubic meter interfere with the use of hydrogen in catalylic reductions of organic compounds.[0537] The common current practice is to remove the greater portion of the mercury present by initially cooling the hot hydrogen gas stream (80-120 C) to 5 C before it is sent through other gas treatment systems.[2047] The equilibrium concentration of mercury in the gas phase changes dramatically with temperature. A reduction in temperature to 5 C from 80 C will bring the equilibrium concentration in the hydrogen gas stream down to 3.7 mg per cubic meter from 565 mg per cubic meter.[2062]

The removal of mercury vapor from air and other gases is obviously desirable for health reasons. Health hazards exist if the concentration of mercury vapor in air rises above the recommended MAC in chemical laboratories where mercury is used or in plants, such as those utilizing mercury boilers and leakage of mercury vapor may possibly occur accidentally. Dangerous concentration may also readily exist in enclosed places due to exposed or spilled liquid mercury as air saturated with mercury vapor at ordinary temperatures may contain around 0.015 gm of mercury per cubic meter, far exceeding the safe level.

The several methods available for the removal of mercury from gas streams are discussed below.

Option No. 1 - Removal with Mist Eliminators. The Brink mist eliminators developed by the Monsanto Enviro-Chem Systems are being used by many U.S. chlorine plants, and have been tested over a period of several months by Georgia-Pacific at its Billingham, Washington plant as part of that company's overall program to cut mercury emissions, with highly successful results.[2047, 2062] The hydrogen gas stream containing an equilibrium mercury concentration of 3.7 mg per cubic meter is sent through the Brink mist eliminators, which are fiber beds packed between two flat parallel screens or between concentric cylindrical screens, and 90 to 95 percent of the particulate mercury are removed in a readily recoverable form. A similar type of filter separators consisting of coalescing filter elements preceding a mist eliminator has also been recently installed in well clusters to extract the major portion of the mercury produced with

Dutch natural gas by NAM, the Netherlands producing company and operator of the giant Groningen gas field.[2049] The mercury content of the Groningen gas at the wellhead is 180 micrograms per cubic meter, and the gas is first cooled by air and then further cooled to -12 C by Joule-Kelvin expansion. Much of the mercury in the gas condenses with the water and hydrocarbons and is drawn off with the condensate, and in the process the mercury content of the gas discharged from the coolers is reduced to about 40 micrograms per cubic meter. The tiny droplets of mercury carried in the gas are then removed efficiently by passing the cooled gas through the coalescing filter separators, so it is insured that the gas entering the transportation network contains no more than 12 micrograms per cubic meter of mercury. Although both the Brink mist eliminator and the NAM coalescing filter separator do not reduce the mercury concentration in the gas stream to the recommended MAC level, a second stage unit could be added to remove the last remaining traces of mercury. For example, Farbenfabriken Bayer has a catalytic approach capable of reducing the mercury level to less than 1 microgram per cubic meter and would be ideally suited for this purpose.[2047]

Option No. 2 - Adsorption with Molecular Sieves. Although the use of molecular sieves for the removal of mercury vapor from hydrogen has been investigated by Logan as early as 1966, it was found that the Union Carbide Type 13X molecular sieve employed in the study had a very low capacity for mercury.[2050] However, a process called PuraSiv Hg that utilizes a new type of proprietary molecular sieves has recently been developed and marketed by Union Carbide's Molecular Sieve Department, and a commercial unit (outside of Union Carbide) is presently being put on-stream at Sobin Chlor-Alkali's Orrington, Maine chlorine plant.[2104] The PuraSiv Hg Process can be applied to any mercury containing gas stream, and consists of three separate skids mounted in tandem: (1) a blower skid; (2) a chiller/demister skid; and (3) an adsorption skid. In a typical PuraSiv Hg unit (Figure 1), the hydrogen gas stream at atmospheric pressure (evolving from the chlorine plant decomposer system) and containing 10 ppmv mercury first enters the PuraSiv Hg blower skid, where its pressure is increased by 4 to 5 psi. The compressed gas next passes through the knock-out pot into the chiller/ demister skid, which consists of a packed chiller unit, a chilled water heat exchanger, and a Petersen separator. As the hydrogen cools, water and
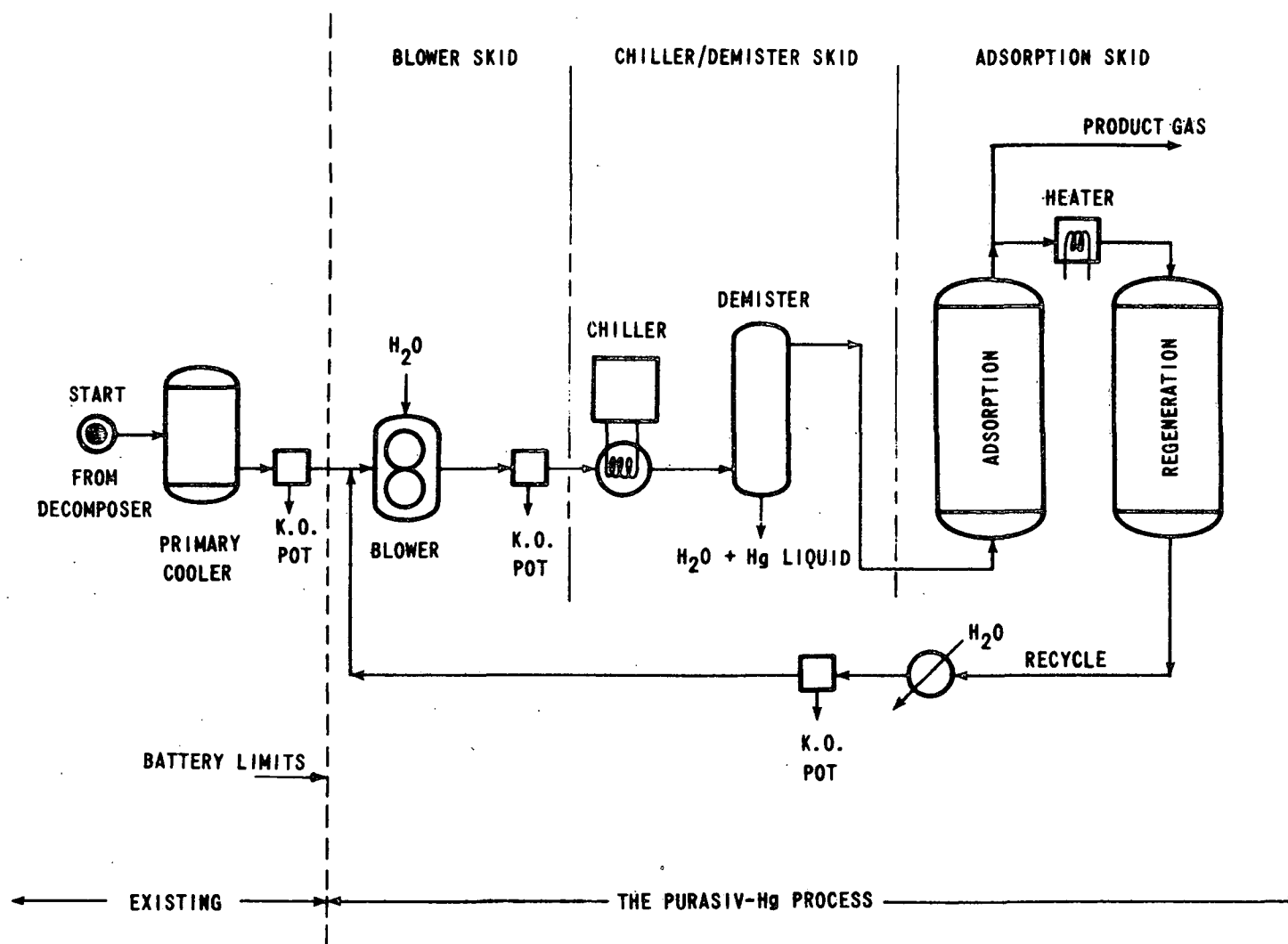
Figure 1.   The Union Carbide PuraSiv Hg Process

elemental mercury mists are formed, and these mists are removed in the
Petersen separator and recycled to the chlorine plant as a liquid stream.
The separator itself consists of stacks (or candles) of ring elements
specially contoured to act as converging-diverging nozzles, and the mist
particles collect on the diverging side of the rings and are washed away
with spray water. The low mist content hydrogen leaves the separator and
enters the adsorption skid, which consists of two adsorber vessels and
auxiliary equipment. Gas enters the "on-line" vessel (while the other bed
is being regenerated) and flows upward through the bed of PuraSiv Hg
adsorbents so that the remaining mercury is trapped. During the first 20
hours of operation, essentially no mercury breaks through the adsorbent bed.
In the remaining 4 hours of the run, however, the effluent concentration
increases gradually to 50 ppbv. Commercial PuraSiv Hg Systems are designed
to be regenerated every 24 hours by heating a portion of the effluent gas
in an electric furnace and passing it downward through the vessel, thus
stripping out the mercury. The relatively concentrated mercury stream is
then recycled through a water cooled heat exchanger, a knock-out pot, and
into the suction of the blower, with final recovery of the stripped-out
mercury occuring in the demister. PuraSiv Hg Systems are guaranteed to
provide effluent mercury levels averaging less than 60 ppbv for 3 years,
so that the total mercury emitted with the effluent hydrogen from a 300
ton per day chlorine plant will be less than 0.1 lb per day and below the
proposed Federal Standards for total mercury emission.* This guaranteed
mercury level of 60 ppbv (540 micrograms per cubic meter), however, is
considerably above the level of any acceptable environmental standard for
mercury in air or the permissible level of mercury in hydrogen for industrial
uses. To render the Union Carbide PuraSiv Hg System useful for a wider
range of applications, it is suggested that either the bed volume of the
adsorption vessels be increased or a shorter on-line time for the adsorption
vessels be instituted (this can be accomplished by installing more adsorption
vessels if a regeneration time of 24 hours is required), so that the level
of mercury in the effluent from the adsorbent bed will remain extremely
low (below 1 ppbv) at all times.

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*Proposed Federal Standards for Chlorine plants allow 1,000 gm (2.2 lb)
per day of mercury in the by-product hydrogen and seal air streams (combined)
total).

Option No. 3 - Adsorption with Activated Carbon. Although activated carbon by itself is a relatively inefficient adsorbent for mercury, its adsorption capacity for mercury can be greatly enhanced by impregnation with silver, potassium iodide, or any other substance that will react with mercury.[2065, 2066, 2068] However, as only in some instances (such as adsorption on silver) can the substrate be regenerated by heating to around 400 C, adsorption with mercury reactant impregnated activated carbon has not received wide acceptance in the industry. In addition to the difficulty of adsorbent regeneration, the process is also too expensive and its efficiency may be drastically reduced by the presence of water.

Option No. 4 - Scrubbing with Oxidizing Solutions. A fourth approach in removing mercury from gases consists of adsorption with a strongly oxidizing aqueous solution so as to bring the mercury into solution in the mercuric state; the mercuric ions can then be removed from solution by methods such as chemical precipitation, chemical reduction, ion exchange, or solvent extraction.[2062] Although an acid permanganate solution can be used for this purpose in the same fashion as is done for the analytical determination of mercury, the introduction of a completely foreign stream into the system and subsequent recovery of the metal from the loaded solution will require an additional processing system. A more attractive alternative, therefore, is to use sodium hypochlorite as the oxidizing agent. Sodium hypochlorite had been used already for a few processes where hydrogen had to be purified for use in the preparation of hydrogenated fats or foodstuffs, or in catalytic reactions where the catalyst was subject to mercury poisoning.[2064, 2069] The hypochlorite system has been installed recently by at least one chlor-alkali plant for mercury removal and found to be highly effective.[2062]

Other processes for the removal of mercury from gas streams that have been investigated include adsorption with chromic acid on silica gel,[2050] adsorption with mercury-wettable materials on extended surfaces,[2085] adsorption with fused alumina oxide containing silver,[2067] and absorption with a suspension of manganese dioxide.[2042] Chromic acid on silica gel has a reasonably high capacity for mercury, but this could be significantly reduced by the presence of water vapor, presumably due to the strong

physical adsorption of water molecules on the gel preventing access to mercury. In the case of adsorption with mercury-wettable materials on extended surfaces (such as fused alumina oxide), the preferred deposited adsorbent metal based on affinity for mercury is silver, which has the disadvantage of being easily poisoned by hydrogen sulfide or chlorine in the atmosphere. Application of the method on the commercial scale also remains to be demonstrated. Bench-scale tests have shown that mercury could be removed from gas streams by adsorption in a suspension of manganese dioxide, but again the process proved unsuitable for scale-up to the size of commercial units.[2049] These processes are therefore considered as inadequate methods for the removal of mercury from gas streams.

Removal from Liquids

Various liquid streams in the mercury-cell chlorine plant contain high concentrations of mercury which must be removed before they could be discharged to public waters. Depleted brine and the brine sludge formed on the subsequent treatment with soda and barium chloride are rich in mercuric ions, mostly in the form of the tetrachloro complex ($HgCl_4^{2-}$), and mercury can enter the aquatic environment when either a small portion of the depleted brine is bled off to prevent continual build-up of sulfate (originally present in the sodium chloride) concentration in the salt solution or through dewatering of the brine sludges. The cell room and caustic wash water and other aqueous solutions that are a part of mercury cell operations also contain soluble or colloidal mercury, primarily in the elemental form.

Other liquid streams containing inorganic mercury requiring treatment include: (1) wastewaters from manufacturers of mercury chemicals, chemcial plants using mercury catalysts, and paper and pulp mills using sodium hydroxide with a trace of mercury; (2) scrubbing solutions for removing mercury from gases; (3) leaching solutions for extracting mercury from ores, sludges and fly ash from combustion of fossil fuels; and possibly (4) sewage treatment plant effluents as a result of breakage of mercury seals used in trickling filters, switches, flow meters, and other instrumentation.

Several methods available for the removal of inorganic mercury from liquids are discussed below.

Option No. 1 - Chemical Precipitation. Inorganic mercury can generally be removed from liquid solution by direct precipitation as an insoluble metal salt either with or without further processing. Raising the pH to the range of 10 to 12 with sodium hydroxide or sodium hypochlorite will render mercuric oxide, which can then be removed by filtration.[2069] Mercury and mercuric ions could also be precipitated as mercuric sulfide by the addition of a soluble sulfide or hydrogen sulfide gas to the liquid solution.[2042, 2069, 2070, 2072] Sodium sulfide is generally used, and the colloidal mercuric sulfide formed could be separated from the liquid stream through flocculation with ferric chloride. Both these methods, however, suffer from the fact that precipitation is seldom complete (effluent often contains 1 ppm mercury) and the fine precipitate formed is difficult to remove.

Option No. 2 - Chemical Reduction. Mercuric ion can be chemically reduced from various liquid solutions with a variety of agents: alkali metals, zinc, antimony, iron, aldehydes, hydrazine hydrate, and sodium borohydride among many others. Direct reduction of mercuric ions by passing the waste stream and an alkali metal amalgam through either an active bed of amalgamated steel turnings and pieces or an inert bed whereby additional amalgam is obtained along with metallic mercury appears to be a unique and clean way of recovering mercury, but tests so far have indicated that a relatively high level of mercuric ions remain in the treated effluent.[2072, 2073] One set of results showed that the mercury content was reduced from 15.4 ppm to 3.3 ppm in the "active-bed" treatment and from 10 ppm to 7.2 ppm in the "inert-bed" treatment. Town described a method of precipitating elemental mercury from an aqueous sodium sulfide-sodium hydroxide solution containing mercury by the addition of elemental antimony,[2080] but an excess of antimony is usually required and the amount of mercury left in solution has not been analyzed. Niepert and Bon suggested the addition of an aldehyde to waste streams containing mercury compounds and the recovery of the reduced metallic mercury by settling.[2071] The method again proves to be unsatisfactory because of the high mercury concentration (approximately 1 ppm) remaining in the waste stream after treatment. However, two other chemical reduction schemes, the Ventron sodium borohydride process and the use of zinc dusts, appear to be able to improve wastewaters to low ppb mercury limits.

The Ventron Process.[1145, 2057, 2058] Sodium borohydride is a powerful reducing agent capable of reducing both mercuric and mercurous ions to the metal almost instantaneously. The reaction also has the advantages of taking place at low temperatures and is not critically pH dependent. In the Ventron flow scheme (Figure 2) wastewater containing inorganic mercury compounds is fed with a 12 percent solution of sodium borohydride (in 40 percent caustic soda) into a static mixer. The pH is held between 9 and 11. The hydride reduces the mercury compounds, yielding metallic mercury precipitate and hydrogen gas. Following separation of the gas, which is scrubbed with a dilute nitric acid solution to eliminate any mercury vapor, the slurry is passed to a cyclone. There 80 to 90 percent of the mercury comes out as a sludge. The clarified effluent is then sent to polishing filters where just about all of the remaining mercury is removed; the recovered metal is purified by vacuum distillation. A Ventron sodium borohydride unit has been onstream since January 1971 at its Woodridge, New Jersey mercury chemicals manufacturing facility. The waste treatment system presently handles 15,000 gallons per day of an effluent averaging 100 ppm soluble mercury. Experience with actual operation has indicated that effluent discharge from the Ventron system, after final polishing with activated carbon followed by chelating resins, contains less than 5 ppb mercury.

Zinc Reduction.[2060, 2074] Removal of mercury compounds from an aqueous solution having a pH between 7 and 11 and containing 1 to 500 ppm of dissolved mercury by contacting a bed of reductor metal (zinc or iron) has been previously described by Gilbert and Rallis. Mercury is recovered as the metal and the typical removal efficiency is 90 percent. More recently, the New Jersey Zinc Company (NJZ) has issued a report discussing the use of zinc to remove mercury from wastewater, including a summary of the results obtained by NJZ researchers. As described by NJZ, the simplest mercury removal method is to add an excess of fine zinc dusts and to keep the dusts suspended in the solution by constant stirring. The tanks and stirring blades should be baffled to avoid the formation of an air vortex, which would result in oxidation and loss of the metallic zinc. The excess zinc will quickly settle to the bottom of the bank when the agitation
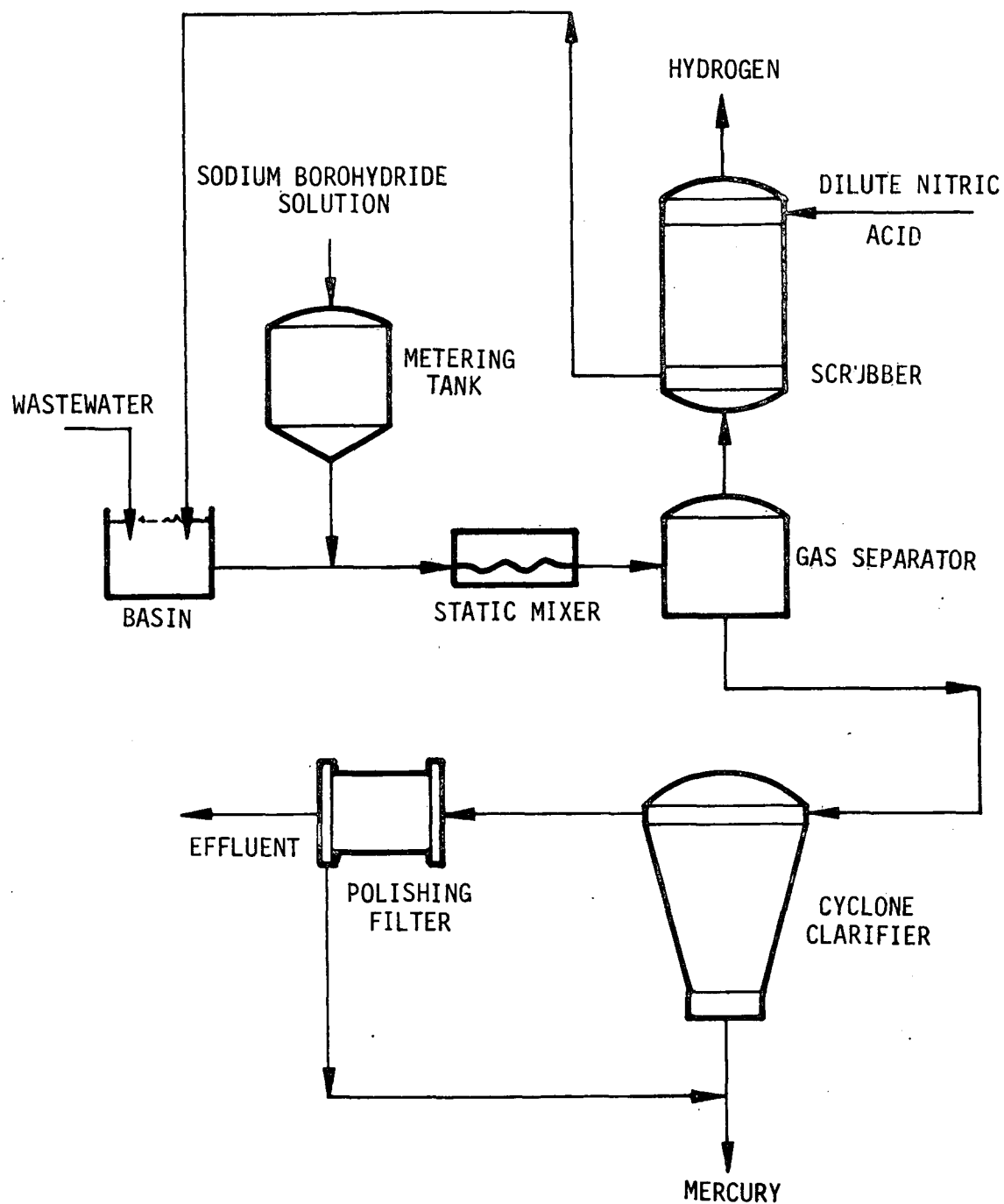
Figure 2. The Ventron Sodium Borohydride Process

stopped. The tank effluent usually still contains a few ppm of zinc, but zinc is much less toxic to aquatic life and may even act as a desirable ecological nutrient. The metallic mercury obtained by zinc reduction could be removed by filtration. A method more applicable to the treatment of industrial wastewater, however, is to pass the streams containing mercuric ions through a bed of coarser commercial zinc powders. The metallic mercury forms an alloy with zinc in the bed, which could be recovered later by heating the crude alloy, distilling off the mercury, then condensing the vapors. In the NJZ laboratory investigations, solutions containing 10,000 ppb of mercury (prepared from either mercuric chloride or phenylmercury acetate) were purified to 20 ppb in 13 seconds, and to 5 ppb in 110 seconds, by passing them through a 4.7 in. deep bed of granular zinc with average particle diameters of 2 mm. A slightly deeper bed lowered the mercury concentration from 10,000 ppb to 2 ppb in 60 seconds. The treatment is generally effective for streams within a pH range of 5 to 10.

Option No. 3 - Ion Exchange. Ion exchange is another effective method for removing mercury from liquids. Through the process of adsorbing mercury on a resin and then eluting it during regeneration, a harmful substance is removed from a waste stream and transferred to another more concentrated solution where it can be easily precipitated by conventional techniques. A few cation exchangers have been reported to be quite successful in extracting ionic mercury, including the Dowex 500W X-8, the Dowex Al, and the Amberlite IRC-50.[2052] Chuveleva et al[2051] made studies with the carboxylic acid resin SG-1 on mercuric nitrate solution, taking advantage of the stability of the acetate - Hg(II) complex. Cation-exchange resins, however, have no application in brines where, because of the high chloride concentration, mercury exists as the $HgCl_4^{2-}$ anion. Most successful ion exchange processes for the removal of mercury from liquid, therefore, employ either anion-exchange or chelating resins. A number of patents exist describing the use of quaternary ammonium cross-linked resins. Calkins et al discussed the selective removal of mercuric ions from brines containing halide ions and metal ions, with an insoluble homopolymer or copolymer prepared from at least one monomer of the group consisting of vinyphenyl aliphatic primary and secondary aminomonocarboxylic acids and mixtures containing a predominant amount by weight of at least one such

aminomonocarboxylic acid and a minor portion of divinylbenzene.[2075] As an example, the effluent brine initially containing 15 ppm of mercuric ions, after passage through a bed of a copolymer of vinylphenyl glycine and N,N-bis (vinylbenzyl) glycine was found to contain 0.3 ppm of mercuric ions, and mercury was recovered from the resin bed by elution with sodium chloride solution at pH7. Both the Schotten and Prielipp patent[2076] and the Crain and Justice patent[2079] discussed the use of a strongly basic anion-exchange resin of insoluble quaternary ammonium composition to remove mercuric ions from liquid solution, with typical effluent mercury concentration less than 0.01 ppm, and regeneration of the ion-exchange resins with aqueous sulfide solution. Of the commercially developed ion-exchange resins, the Amberlite IRA-400 has been shown to adsorb significant quantities of mercury regardless of pH as long as it is present as an anion.[1795] Two other proven processes in commercial operation, however, are applicable to most mercury-bearing streams found in the industry. Both the Osaka Soda Process and the Aktiebolaget Billingsfors-Langed Process also have the ability to reduce the mercury content in wastewater to less than 5 ppb, and are discussed in greater detail below.

The Osaka Soda Process.[1145, 2045, 2061] In the Osaka Soda Process (Figure 3), wastewater is first collected in a storage tank, where any metallic mercury present is allowed to settle out. It is then chemically treated for adjustment of pH and free-chlorine concentration (if necessary), followed by filtering to remove any floating insolubles. The filtered water is passed through a tower packed with Osaka Soda's proprietary ion-exchange resin (IE), and the mercury content of the wastewater is reduced to a range of 100 to 150 ppb. Next, the waste stream passes through a tower packed with another Osaka Soda's proprietary resin, designated "MR". Mercury content is reduced to an undetectable level in the MR tower when a fresh charge is provided, although the effluent concentration gradually builds up to 5 ppb and is typically 2 ppb. Mercury values are recovered from the ion exchanges by periodic stripping. A sodium amalgam or other agent is then added to the pregnant stripping liquid to reduce the mercury to metallic form. Generally, IE resin beds are regenerated approximately once a week, whereas the MR resin is simply discarded several times a year after recovery of the mercury. Five Japanese chlor-alkali plants, ranging in
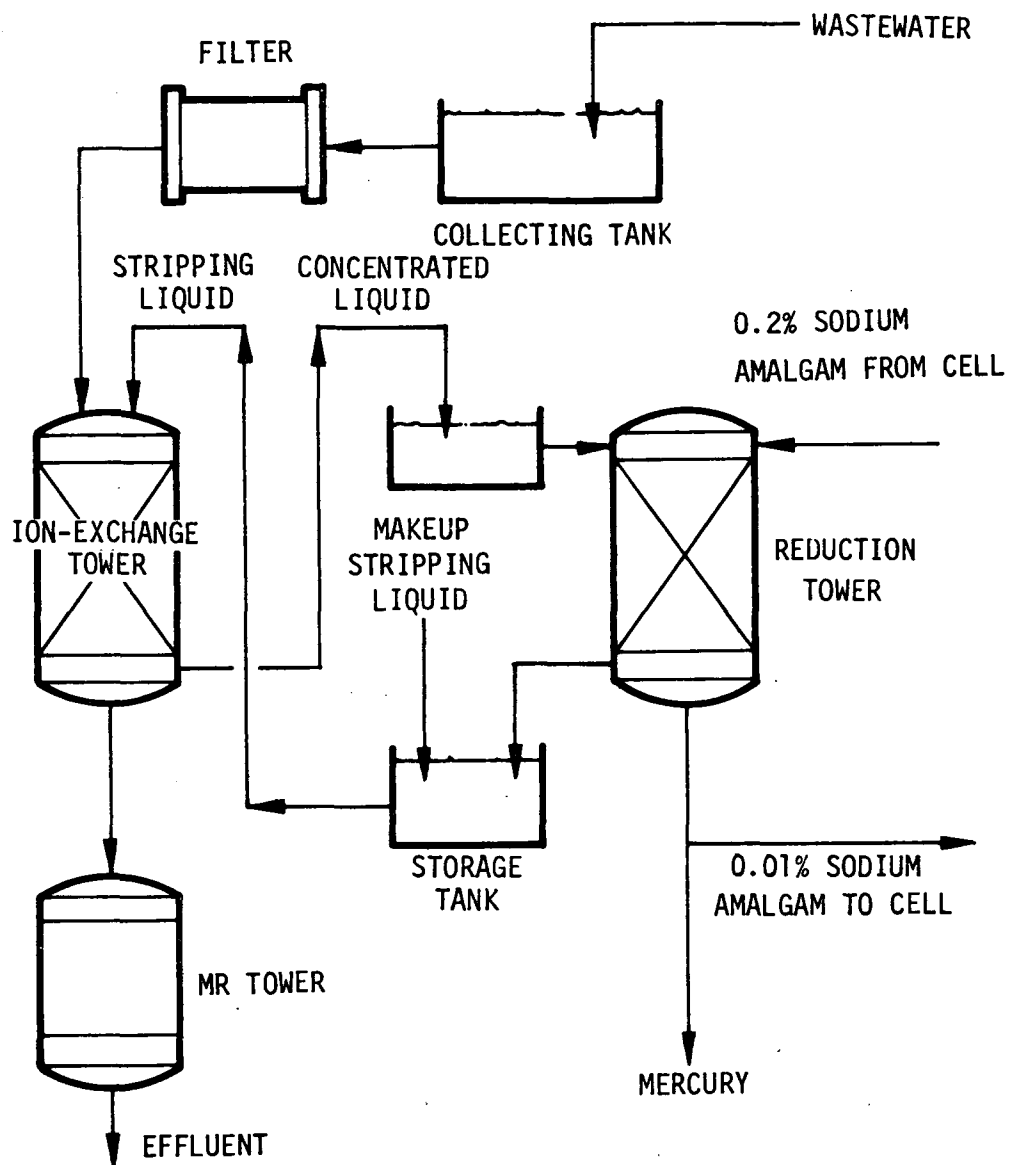
Figure 3. The Osaka Soda Mercury Removal Process

capacity from 70 to 200 tons per day, have been using the Osaka Soda process for six years, treating 18,000 to 32,000 gal per day of wastewater. It should be noted, however, that caustic-soda-bearing streams cannot be treated by this process because of the poisonous effects of the caustic on the IE resin. Also, the IE resin cannot handle sulfides, but since naturally occurring hydrogen sulfide reacts with mercury and precipitates prior to introduction to the treatment plant, this limitation is not expected to be a problem. The process is licensed in the United States by Crawford and Russel.

The Aktiebolaget Billingsfors-Langed Process.[1144] In this Swedish developed process (Figure 4), which has been in operation for two years, wastewater is first passed to a vessel where the pH is adjusted to between 5 and 7 and metallic mercury in colloidal form is oxidized by chlorination. Since the resins subsequently used are sensitive to oxidizers, excess chlorine is removed in a dechlorinator via acitvated-carbon filtration. The water is then piped to a series of ion-exchange towers filled with a special, stable resin, dubbed Q-13. Mercury level is cut to around 100 ppb. No chloride ions are needed for good performance. The mercury level is reduced to a few parts per billion in an absorption tower containing another resin, called Q-Sorb. The Q-13 resin is regenerable, and yields an eluate rich in mercury. This can be passed to an electrolytic circuit for recovery of the metal. The Q-Sorb, however, is not regenerable by stripping. Although the composition of the Q-13 resin is proprietary, it is probable that this is the same ion-exchange resin described by Fuxelius and prepared from the reaction of sulfate pulp black liquor and epichlorohydrin.[2084]

Option No. 4 - Solvent Extraction. Chapman and Caban of the University of Wisconsin have recently developed a solvent extraction process for removing mercury from liquid or solid mercury-containing wastes, as well as crushed mercury ore.[2062] Mercury content in the feed is first converted to mercuric chloride, and the pH of the solution is adjusted to less than 3.0 by the addition of excess hydrochloric acid. The liquid waste stream is then brought into contact with a xylene phase that contains tri-iso-octylamine (TIOA), so that the mercuric chloride reacts with the amine, thus entering the xylene phase. The solubilities of both TIOA and TIOA salts in water
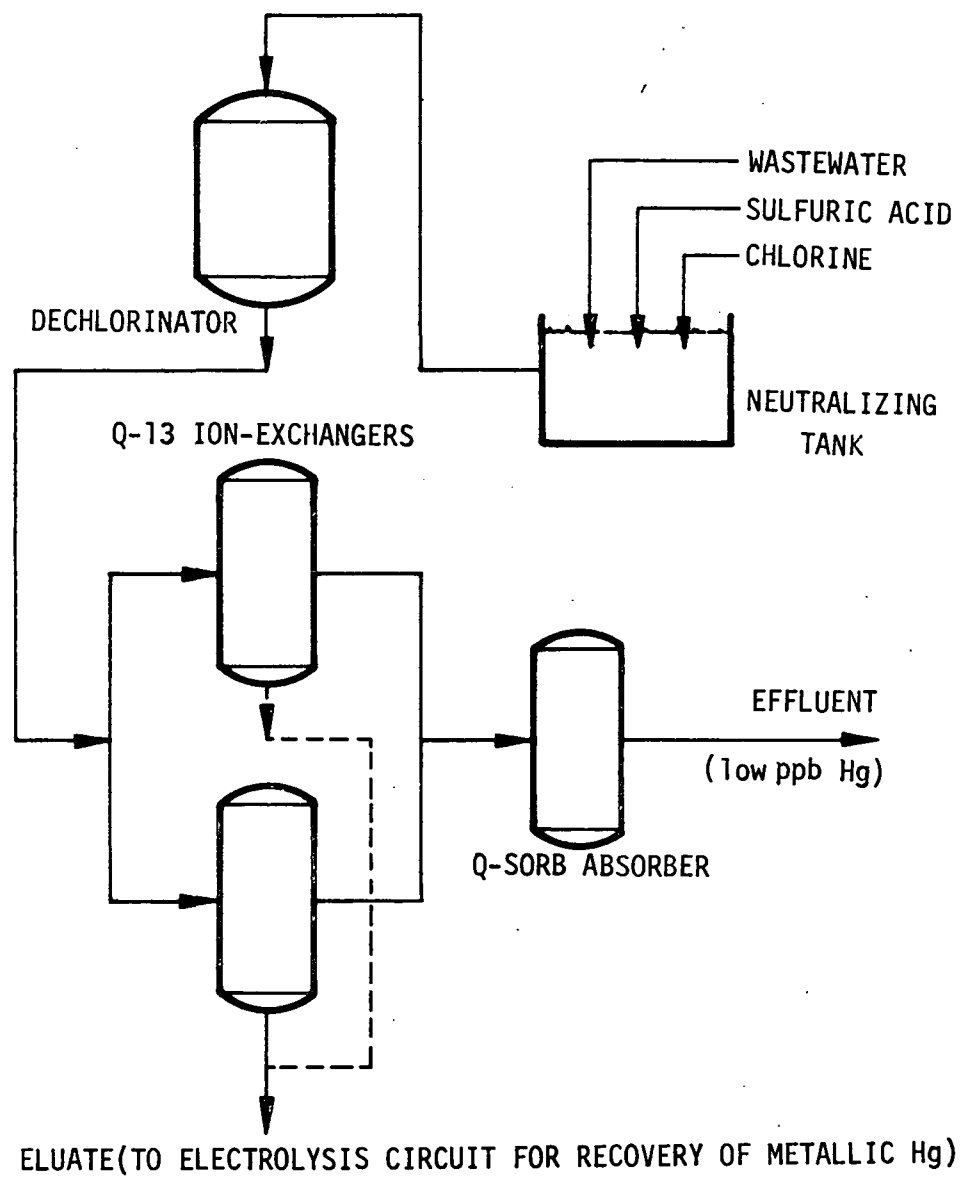
Figure 4. The Aktiebolaget Billingsfors-Langed Mercury Removal Process

are negligible, and a multistage countercurrent contacting system could be designed to remove almost all the mercury from the aqueous waste stream. For example, the mercury level in a depleted brine, originally containing mercuric chloride in concentrations of about 10 ppm Hg, can be reduced to 10 ppb by extraction with 0.1M TIOA in xylene after only six theoretical equilibrium stages. With an organic aqueous volume ratio of 0.01, an organic phase concentration of 1000 micrograms per multiliter mercury is obtained. In turn, the organic phase can be stripped of nearly all its mercury content with a small volume of brine at an equilibrium pH from 9 to 13. Again, this could be accomplished by the addition of enough sodium hydroxide to neutralize the hydrochloric acid in amine and bring the equilibrium pH to the desired value. By using a high organic to aqueous phase volume ratio, a resulting aqueous phase up to 10,000 times more concentrated in mercury can thus be obtained. Such concentrated solutions can undergo further processing more easily, both from a technical and economic viewpoint.

Option No. 5 - Filtration. Diatomite filtration is used to remove the insoluble mercury particulate matter that do not normally settle out by conventional treatment methods, and has reduced the mercury content of certain industrial wastes from a high of 5 ppm to less than 0.5 ppm. If the mercury is soluble, the waste stream is first chemically treated to convert the mercury to an insoluble form, such as elemental mercury, mercuric oxide, or mercuric sulfide.[2048] A more direct approach, however, is the Ecotech process currently under development that employs a filter medium of inorganic mineral containing magnesium.[2041] Mercury in any ionic form is directly reduced to elemental mercury in the filter medium by a replacement reaction, so that removal of soluble inorganic mercury from wastewater could be accomplished in a single step. Preliminary work at Ecotech has shown that: (1) for influent mercury concentration of 5 ppm or less, the removal efficiency in a single pass is typically 85 to 90 percent; (2) typical filtration rates are 2 to 4 gal per sq ft per min; and (3) a minimum bed depth of 36 in. is normally required for single-pass treatment. According to Ecotech, the process is best suited for removing trace elements of mercury from large volumes of wastewater, such as the paper and Kraft mill effluents.

Option No. 6 - Chemical Absorption. The application of chemical absorbents for removing mercury from wastewater has been studied by Environmental Engineering.[1145] Laboratory and pilot plant data with a proprietary absorbent have demonstrated that concentrations of mercury contaminants can be reduced in minutes from 2,000 ppm to 50 ppb, and even lower levels may be possible.

Option No. 7 - Adsorption with Activated Carbon. The use of activated carbon for removing mercury from wastewater has been investigated by Ziegler and Lafornara,[1419] and their experimental results showed that a carbon dose of 500 ppm could effectively reduce the mercury concentration in water from 100 ppm (as mercuric chloride) to less than 1 ppm. MacMillan proposed a mercury removal system comprising of a bed of activated carbon sandwiched between nickel* and mesh pads, and reported that the mercury content of a mercury cell caustic soda liquor was reduced from 0.8 ppm at the beginning to 0.1 ppm after passing through the carbon-nickel bed.[2082] In both cases, however, the mercury concentration in the treated effluent is still considerably above the recommended level.

Removal from Solids

For the extraction of mercury from solids or semi-solids such as brine sludges and mercury catalysts, the general proposed procedure is to use sodium hypochlorite as the leaching solution. Adequate systems based on hypochlorite leaching or any other method to treat brine sludges containing traces of mercury, however, have apparently not been designed and placed into operation. For example, the brine sludges produced at Georgia-Pacific's Bellingham, Washington plant are currently being pumped into a small settling basin awaiting the development and installation of adequate treatment processes. In addition to hypochlorite leaching, another process has been recently proposed for the recovery of mercury from brine sludges or other solids. Yamori et al suggested dissolving the sludge in aqueous acid and then adsorbing the mercury content of the resultant solution on

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*Nickel is wettable by mercury and resistant to attack by caustic soda.

an anion exchange resin, from which the mercury can be eluted, preferably with hydrochloric acid, and recovered from the resultant elute.[2083] No quantitative data, however, was presented to allow evaluation of the process.

To summarize, the adequate methods for removing mercury from gases are: (1) the Brink mist eliminator or the NAM coalescing filter separator, with a second-stage unit such as the Farbenfabriken Bayer catalytic system to remove the last remaining traces; (2) the Union Carbide PuraSiv Hg System; and (3) scrubbing with sodium hypochlorite solution.

The adequate methods for removing mercury from liquids are: (1) the Ventron sodium borohydride process; (2) chemical reduction with a granular zinc bed; (3) the Osaka Soda ion-exchange process; and (4) the Aktiebolaget Bellingsfors-Langed ion-exchange process. In addition, the Chapman-Caban solvent extraction process also shows considerable promise as a near future method for treating mercury containing liquid wastes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Most of the mercury containing wastes generated by the industry, such as wastewaters from mercury-cell chlor-alkali plants, could best be handled and treated at the site of generation. There are, however, other types of mercury wastes where no simple adequate disposal/recovery methods exist, and these are prime candidate waste streams for National Disposal: brine sludges, poisoned mercury catalysts, mercury battery cells, mercury pesticide wastes, mercury paints, and possibly fly ash from coal and other fossil fuel burning power plants. Methods for the treatment of the mercury containing wastes at National Disposal Sites will include incineration and liquid extraction facilities, followed subsequently by recovery/removal of the mercury from the gas and liquid streams. For the recovery/removal of mercury from gases, the recommended processes are:

Process	Order of Preference	Remarks
Union Carbide PuraSiv Hg system	First choice	Demonstrated technology; simplicity in operation; no second-stage unit required for additional treatment of effluent.
Sodium hypochlorite scrubbing	Second choice	Demonstrated technology; insufficient pilot plant and full scale operating data for optimal design of scrubbing system.

For the recovery/removal of mercury from liquids, the recommended processes are:

Process	Order of Preference	Remarks
Aktiebolaget Billingsfors- Langed ion exchange process	First choice	In full scale operation for two years; ability to treat wastewaters containing mercury in any form; ion exchange resins not poisoned by caustic or sulfides.
Ventron sodium borohydride process	Second choice	Demonstrated technology; not critically pH dependent; requires final polishing of effluent with activated carbon or chelating resin; process applicable to wastewaters containing mercury ions rather than elemental mercury.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Mercury (257)___

IUC Name _____

Common Names __quick silver__

Structural Formula

Hg

Molecular Wt. __200.59[1]__   Melting Pt. __-38.9 C[1]__   Boiling Pt. __356.6 C[1]__

Density (Condensed) __13.594__ @ _20 C[1]_ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

__1.2 X 10^{-3}mm@ 20 C[1]__   __1 mm @ 126.2 C[3]__   __10 mm @ 184 C[3]__

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water _20-30 ppm in deaerated_   Hot Water_____   Ethanol_____
Others:_____water._____

Acid, Base Properties_____

Highly Reactive with_halogens, hydrogen, sulfide, sulfur, vapor_____

Compatible with_____

Shipped in_____

ICC Classification__Poison B[2]_____   Coast Guard Classification_____

Comments_____

References (1) 2105
          (2) 278
          (3) 1673

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Mercuric Chloride (253)

IUC Name _____

Common Names corrosive sublimate _____

Structural Formula

$HgCl_2$

Molecular Wt. 271.50[1]   Melting Pt. 276 C[1]   Boiling Pt. 302 C[1]

Density (Condensed) 5.440   @ 25 C[1]   Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

1 mm   @ 136.2 C[2]   10 mm   @ 180.2 C[2]   100 mm   @ 237 C[2]

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water 6.9g/100cc at 20 C[1]   Hot Water 48g/100cc at 100 C[1] Ethanol soluble[1]

Others:_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification Poison B[3]   Coast Guard Classification_____

Comments White crystals or powder. Highly toxic.

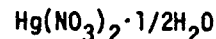References (1) 1570
           (2) 1673
           (3) 0278

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Mercuric Nitrate (255)__

IUC Name _____

Common Names_____

Structural Formula

$Hg(NO_3)_2 \cdot 1/2H_2O$

Molecular Wt. __333.61[1]__   Melting Pt. __79 C[1]__   Boiling Pt.__decomposes[1]__

Density (Condensed)__4.39[1]__ @____ ____ Density (gas)_____ @ ____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water__very soluble[1]__   Hot Water__decomposes[1]__   Ethanol__insoluble[1]__

Others:__visible in HNO_3, NH_3, acetone[1]__

Acid, Base Properties_____

Highly Reactive with__alcohols to form explosive mercury fulminate with acetylene to form__
__a sensitive acetylide, and with unsaturates and aromatics[2]__

Compatible with_____

Shipped in_____

ICC Classification_____   Coast Guard Classification_____

Comments__White yellowish, deliquescent powder. Highly toxic.__

References (1) 1570
           (2) 0096
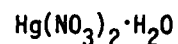
HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Mercuric Nitrate (255)

IUC Name _____

Common Names_____

Structural Formula

$Hg(NO_3)_2 \cdot H_2O$

Molecular Wt. __342.61__   Melting Pt. _____   Boiling Pt._____

Density (Condensed)__4.3__ @____ _____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

    Cold Water__soluble_____   Hot Water_____   Ethanol_insoluble_____

    Others:__soluble in HNO_3_____

Acid Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments __Colorless crystal or white powder, deliquescent_____

_____

_____

References (1) 1570

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Mercuric Sulfate (256)__

IUC Name _____

Common Names_____

Structural Formula

$HgSO_4$

Molecular Wt. __296.65_____   Melting Pt. __decomposes____   Boiling Pt._____

Density (Condensed)___6.47____ @____ ____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water___decomposes_____   Hot Water_____   Ethanol__insoluble____

Others:___soluble in acids_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification___Poison B[2]_____   Coast Guard Classification___Poison B___

Comments___White, crystalline powder. Highly toxic._____

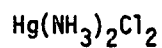References (1) 1570
          (2) 0278

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Mercuric Diammonium Chloride (503)

IUC Name Mercuric Chloride diammine

Common Names Fusible white precipitate

Structural Formula

$$Hg(NH_3)_2Cl_2$$

Molecular Wt. __305.56__ Melting Pt. __300 C__ Boiling Pt._____

Density (Condensed)_____ @____ ____ Density (gas)_____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____ _____@_____ _____@_____

Flash Point _____ Autoignition Temp.____

Flammability Limits in Air (wt %) Lower_____ Upper_____

Explosive Limits in Air (wt. %) Lower_____ Upper_____

Solubility

  Cold Water_insoluble_____ Hot Water___decomposes___ Ethanol_____

  Others:_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification__Poison B[2]_____ Coast Guard Classification_____

Comments_Rhombic crystal_____
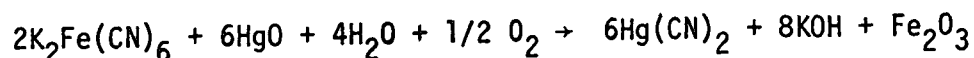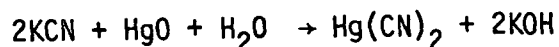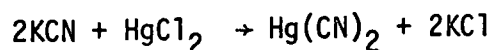
References (1) 1570
           (2) 0278

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PROFILE REPORT

Mercuric Cyanide (254)

1. GENERAL

Mercuric cyanide is one of the most stable of the simple cyanides.
It is formed as colorless or white tetragonal prisms. At 320 C it begins
to decompose and over 400 C it is completely decomposed into mercury and
cyanogen.

Mercuric cyanide is formed when any simple cyanide or ferrocyanide is
heated with a mercuric salt or mercuric oxide.[1433]

$$2KCN + HgCl_2 \rightarrow Hg(CN)_2 + 2KCl$$

$$2KCN + HgO + H_2O \rightarrow Hg(CN)_2 + 2KOH$$

$$2K_2Fe(CN)_6 + 6HgO + 4H_2O + 1/2\ O_2 \rightarrow 6Hg(CN)_2 + 8KOH + Fe_2O_3$$

Mercuric cyanide is used as a substitute for mercuric chloride as
an antiseptic in medicine. Since mercuric cyanide is not ionized, it is
less irritating to the tissues and it does not precipitate proteins or
corrode steel instruments as does the chloride. Dry distillation of
mercuric cyanide is used in the laboratory for the preparation of dry
cyanogen. Patents have been issued, though they are apparently not used,
on the introduction of mercuric cyanide into engine fuels as an "antidetonant"
or antiknock agent.[1433]

2. TOXICOLOGY

When heated to decomposition, or on contact with acid or acid fumes, mercuric cyanide emits highly toxic fumes of cyanide and mercury. The Threshold Limit Value (TLV) for mercury is 0.005 ppm (0.05 mg per cubic meter of air), as recommended by American Conference of Governmental Industrial Hygienists (ACGIH); the TLV is 10 ppm (11 mg per cubic meter) for cyanides. The toxicology for cyanides is documented in Profile Reports on Hydrocyanic Acid (215) and Hydrogen Cyanide (218). Mercury is a general protoplasmic poison. After absorption mercury circulates in the blood and is stored in the liver, kidneys, spleen and bone. In industrial poisoning, the chief effect is upon the central nervous systems and upon the mouth and gums.[0766] Because mercury has been found concentrated in sea life, its discharge is avoided.

3. OTHER HAZARDS

When mercuric cyanide is reacted in aqueous solution with mercuric oxide or chloride, mercuric oxycyanide of varying composition is formed. The approximate composition of mercuric oxycyanide is $3Hg(CN)_2 \cdot HgO$. The mercuric oxycyanide is reacted with various acids to form such compounds as mercuric cyanide nitrate, formate, acetate, oxalate and benzoate. Mercuric oxycyanide in the dry form is known to explode when being transferred from one container to another. Therefore, care must be taken not to form mercuric oxycyanide when mercuric cyanide is being prepared.[1433]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Mercuric cyanide is classed by the Department of Transportation (DOT) as a Class B poison requiring a Poison label. It is shipped in amber glass bottles, wooden kegs and fiber drums.

As with other cyanides, the release of the cyanide ion from mercuric cyanide must be controlled. The permissible level of cyanide ion in an effluent stream is 0.2 mg/l with a desirable criterion of complete absence (Federal Water Pollution Control Administration [FWPCA]).[0536] A goal of complete absence of mercury from effluents is in effect since the recent reported mercury buildup in certain fish.

The safe disposal of mercuric cyanide is described in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Mercuric Cyanide	0.0005 mg/M^3 as Hg	.01 TLV

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Mercuric Cyanide	0.005 ppm (mg/l) as Hg	U.S. Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

With the goal of no mercury in waste streams, two processes were recently described that can be used to destroy mercuric cyanide. These two processes appear equally acceptable and are described briefly in the following paragraphs.

Option No. 1 - Sodium Borohydride Reduction

After alkaline chlorination to destroy the cyanide ion, sodium borohydride is used to reduce mercury ions to the metal.[1145] This is accomplished by adjusting the pH to the 8 to 10 range and adding a solution of sodium borohydride which reduces mercury to the elemental form and liberates hydrogen. The liberated hydrogen is passed through dilute nitric acid to remove mercury vapors. The mercury is collected by filtering, and purified by vacuum distillation. Sodium borohydride cost is $13.00 per lb, but one lb reduces 21 lbs of mercury.[1145]

Option No. 2 - Ion Exchange Collection

After destruction of cyanide by chlorination, mercuric ions are collected on a special ion exchange resin, Q-13 sold by Aktiebolaget Billingsfors-Langed of Billingsfors, Sweden. This resin lowers mercury concentration to the 100 ppb level. Then an absorption tower packed with Q-sorb, sold by the same company as Q-13, reduces the mercury content to a few parts per billion. The Q-13 resin can be regenerated to recover the mercury, but the Q-sorb resin cannot be regenerated which causes a storage/disposal problem that was not discussed.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Mercuric cyanide wastes are candidates for disposal at National Disposal Sites since the goal of no mercury in waste streams requires collection of all mercury wastes. It would be expected that concentrated wastes could be treated commercially as described earlier and remarketed, but mixed wastes would require treatment and storage or burial.

It is recommended that Option No. 1, as described in Section 5 of this Profile Report, be employed for destruction of mercuric cyanide at National Disposal Sites.

7. REFERENCES

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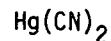
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Mercuric Cyanide (254)__

IUC Name __Mercuric Cyanide__

Common Names_____

Structural Formula

$$Hg(CN)_2$$

Molecular Wt. __252.65__   Melting Pt. __320 C decomposes__ Boiling Pt._____

Density (Condensed)__4.00 g/cc__ @__20 C__. Density (gas)_____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water__9.3g/100ml at 14 C__   Hot Water__53g/100ml at 100 C__ Ethanol__soluble__

Others:__pyridine, acetone, ammonia__

Acid, Base Properties_____

Highly Reactive with__mercuric oxide or chloride__

Compatible with__most materials of construction__

Shipped in __amber glass, bottles, wooden kegs, and fiber drums__

ICC Classification__Class "B" Poison__   Coast Guard Classification__Class "B" Poison__

Comments_____

References (1) 1433

PROFILE REPORT

Organic Mercury (258)

1. GENERAL

Introduction

The organic compounds of mercury comprise a diverse group of
materials distinguished by the presence of atoms of mercury joined to
organic molecular structures through chemical bonds. By contrast to the
long history of use of metallic mercury and its inorganic compounds,
organic mercury compounds have been important articles of commerce for a
relatively brief period of time. The development of many of the most
important members of this group of materials was motivated by the need to
find replacements for inorganic mercurials, particularly for agricultural
use, that would provide greater efficiency and lower toxicity to plants,
animals and man.[1618]

Although the promise of improved efficiency has been, to a great
extent, fulfilled by the organic mercury compounds, their affect on the
environment has been less salutary. Indeed the tragic incident at
Minamata, Japan, the high levels of mercury found in tuna and swordfish
and the discovery of the facile, biological conversion of mercury and its
compounds to methyl mercury have brought into question the wisdom of any
large scale use of mercury and its inorganic and organic compounds.[1951]
Recognition of the extent of the problem of mercury pollution has prompted
a determined effort to define more efficient methods of disposal and con-
trol, and a search for safer substitutes for all current applications of
mercury and mercurials.

Preliminary figures[2190] for organic mercury consumption in the United
States in 1971 are: agricultural (includes fungicide and bactericides for
industrial purposes), 1,477 flasks (one flask equals 76 lb); antifouling
paint, 414 flasks; mildew proofing paint, 8,191 flasks; and pharmaceuti-
cals, 682 flasks. Total consumption of all mercury and mercury compounds
for 1971 is estimated at more than 52,000 flasks.[2190]

Manufacture

<u>Mercury compounds of the aliphatic series</u>[1618] Aliphatic mercury compounds of the general formula (I) are produced by the reaction of a dialkylmercury with the appropriate mercury salts:

$$R_2Hg + Hg(Ac)_2 \rightarrow 2RHgAc$$

$$(I)$$
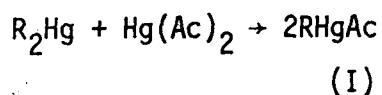
The dialkylmercury necessary for this synthesis is prepared industrially by two methods:

(1) Reaction of alkyl halides with amalgams of the alkali metals (most often sodium amalgam):

$$2RBr + Hg + 2Na \rightarrow R_2Hg + 2NaBr$$
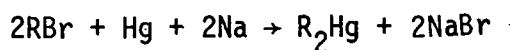
The process is carried out in the presence of catalysts and at low temperatures.

(2) Reaction of the appropriate organomagnesium compounds with mercuric chloride:

$$R + Mg \rightarrow RMg + 2RMgX + HgCl_2 \rightarrow R_2Hg + MgX_2 + MgCl_2$$
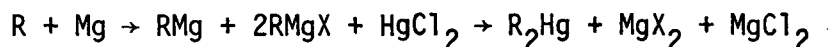
A new method for preparing alkylmercury salts by initiated breakdown of the mercury salts of the carboxylic acids has been suggested by G. A. Razuvaev:

$$(HgOCOCH_3)_2 \rightarrow CH_3HgOCOCH_2 + CO_2$$
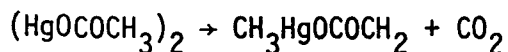
Hydrogen peroxide or inorganic peroxide are used as initiators.

It has also been proposed that ethylmercury salts be prepared from tetraethyllead and mercuric chloride:

$$(C_2H_5)_4Pb + 2HgCl_2 \rightarrow (C_2H_5)_2PbCl_2 + 2C_2H_5HgCl$$

Mercury compounds of the aromatic series[1618]   A number of methods are known for the synthesis of mercury compounds of the aromatic series that are suitable for industrial production.
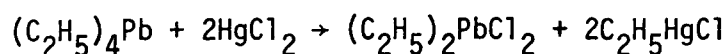
One of the principal methods of producing phenylmercury derivatives is the direct mercuration of benzene which takes place in >90 percent yield when mercuric acetate or other mercury salts of carboxylic acids are heated with benzene.

A second method of synthesizing phenylmercury derivatives is the Nesmeanov reaction, in which the yield of phemymercuric halides amounts to 70 to 85 percent.

Total production of cyclic mercury fungicides for the year 1970 was 1,571 x 10^3 lb, of that amount, 457 x 10^3 lb, or 29 percent, was phenyl-mercuric acetate.[1718]

Uses[0533]

Agriculture.   The primary use of mercury in agriculture has been for seed treatment of cereal grains (phenyl mercuric acetate, methoxyethyl-mercury).   Secondary uses are for disease control of fruits, vegetables, etc.   Mercurial disease control usage has a long history of successful application with the added advantage of being relatively inexpensive.   The major commercial applications are with generally mature products vulnerable to being supplanted by newer and/or more effective materials.   Therefore, the opportunities for increased usage and new applications are either nonexistent or severely limited.

The search for suitable, non-mercurial, substitutes has intensified in recent years.   However, there is general agreement in the industry that there is not currently available a product affording the broad spectrum control provided by mercury compounds.

Catalysts. Organic mercurial salts (mercuric acetate, phenylmercuric oleate) are used in urethane elastomers for casting, sheeting and sealant applications, frequently as a replacement for stannous octoate catalysts. The availability of suitable substitutes for organic mercury-based catalysts varies with the particular process under consideration.

Paints. Organomercurial compounds (e.g., phenyl mercuric acetate) are the most widely used bactericide/fungicide products in the paint industry, accounting for about 80 percent of dollar sales of such protective paints. Efficiency/cost comparisons with other preservatives invariably demonstrate the superiority of mercurials in providing both shelf preservation and exterior protection. However, higher cost non-mercurial substitutes now exist for use in paints and they will probably see increased use in the future. Most of the currently available substitutes are also organic metallic (Zn, Pb) and their long-term effect on the environment is not yet known.

Paper and Pulp. Substantial use of mercury compounds as slimicides in the pulp and paper industry has continued to decline though they have a high degree of effectiveness where other types of products have failed. The decline in use is due to government prohibition of the use of food packaging paper that have come in contact with mercury compounds and tighter pollution controls on pulp mill effluent water. The organic mercury slimicides (principally, aliphatic mercurials) are being replaced by organotin compounds.[1618]

Pharmaceuticals. Mercury is used in a variety of well defined pharmaceutical and cosmetic applications. These include diuretics (mercurin), antiseptics (merthiolate), and preservatives (phenylmercuric acetate). Substitutes exist for many of the pharmaceutical uses of organic mercury compounds.

Sources and Types of Organic Mercury Wastes

Organic mercury wastes may arise from the manufacture of pesticides, pharmaceuticals, slimicides, explosives and paints, as well as their use in hospitals, pulp and paper manufacture, farming, home and ship building, and photographic processing.

Organic mercury wastes can be classified as diluted or concentrated. Dilute organic mercury wastes include those generated in the waste streams of manufacturers, and formulators, as well as contaminated formulations such as pesticides and paints containing small percentages of organic mercury compounds. For example, water based paints usually contain from 0.004 to 0.1 percent mercury in the form of phenyl mercuric acetate, phenyl mercuric oleate or di (phenyl mercuric) dodecenyl succinate. Total organic mercury waste generation in the paint industry is estimated to be 34,500 lb annually. Concentrated wastes include any unused or contaminated organic mercury compound unfit for its intended use.

Chemical and Physical Properties

The number and diversity of the organic mercury compounds now in use precludes the preparation of property worksheets for all of them. However, worksheets have been attached covering the chemical and physical properties of phenyl mercuric acetate because of its position as the organic mercury compound with by far the largest sales volume, and of methyl mercury, believed to be the most widespread and potentially the most dangerous form of organomercury in the environment.

2. TOXICOLOGY

Organic mercury compounds may enter the body by inhalation, skin absorption or ingestion.[2036] There is evidence that inhalation of organic

mercury vapor and aerosols may be more detrimental than the other means of entry since absorption through the respiratory tract leads to a higher rate of accumulation of mercury in the brain.[0533]

The toxicologic effects of organomercurials are strongly influenced by the nature of the organic portion of the molecule. Short chain alkyl mercury compounds (e.g., methyl and ethyl mercury) are relatively stable in the body and may circulate for a long time unchanged in the blood; methyl mercury has a biological half-life in man of about 70 days.[2036] The stability of the alkyl mercurials, particularly methyl mercury, favors their accumulation in the body where they are found principally in the brain. Thus, more than 98 percent of the mercury found in the brain is in the form of methyl mercury.[2036]

Aromatic mercury compounds (e.g., phenyl mercury, phenyl mercuric acetate), methoxyalkyl mercurials (e.g., methoxyethyl mercury) and most other organic mercury compounds are degraded to inorganic mercury in the body. Therefore, the physiological and toxicological behavior of the non-alkyl organomercurials resembles that of inorganic mercury compounds, with preferential accumulation in the kidneys and more rapid excretion than the short chain alkyl analogs.[2306]

Symptoms of methyl and ethyl mercury poisoning may occur weeks to months after an acute exposure to toxic concentrations. The symptomatology of acute and chronic poisoning from both compounds is similar; including numbness and tingling of the lips or hands and feet, ataxia, disturbances of speech, concentric constriction of the visual fields, impairment of hearing, and emotional disturbances. With severe intoxication the symptoms are irreversible. Children born to mothers with exposure to large amounts of methyl mercury exhibited mental retardation and also cerebral palsy with convulsions.[2036]

Because so few cases of toxicity have appeared from phenyl mercurials exposure, even to high levels in air over a period of years, it is apparent that these compounds are low in toxicity relative to other forms of mercury. Clinical and experimental evidence suggests that a similar conclusion is applicable to methoxyethyl compounds.[2036]

The Threshold Limit Values (TLV) of 1971[0225] recommended by the American Conference of Governmental Industrial Hygienists for alkyl mercury compounds on the skin is 0.01 mg/m^3, and 0.05 mg/m^3 for all forms of organic mercury compounds except alkyl.

3. OTHER HAZARDS

The flammability of organic mercury compounds is governed by the nature of the organic portion of the molecule and any other materials (solvents, additives, etc.) with which they are associated in commercial products. The danger of liberated mercury or mercury compounds must always be recognized whenever organic mercury compounds are decomposed by heat or fire.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Since all organic mercury compounds are toxic to man in some degree by inhalation, ingestion, or skin contact, great care must be exercised in their handling. Manufacturers instructions for handling and storage should be closely followed. The use of rubber gloves, goggles, a respirator, and full protective clothing is recommended in the handling of these materials over an extended period of time or in large amounts where the likelihood of exceeding the Threshold Limit Value is present. Shipping of these materials should be commensurate with existing federal regulations.[0278]

Disposal/Reuse

Contaminated, degraded, or surplus organic mercury compounds most probably will not be considered for reprocessing because of the cloudly commercial future for these materials. Suspension of government approval of some products containing alkyl mercury and proceedings to cancel federal registration of the 750 uses of mercury pesticides[2138] might have sufficient impact to shut down production facilities and eliminate the market for recycled materials. Any method of safe disposal of these materials must be defined in terms of recommended provisional limits in the environment. The recommended provisional limits are as follows:

Contaminant and Environment	Provisional Limits	Basis of Recommendation
Alkylmercury compounds in air	0.0001 mg/M^3	0.01 TLV
Alkylmercury compounds in water and soil	0.0005 ppm	Stokinger and Woodward Method
Other organic mercury compounds in air	0.0005 mg/M^3	0.01 TLV
Other organic mercury compounds in water and soil	0.0025 ppm	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Dilute Aqueous Organic Mercury Wastes[2127]

A system for the removal of mercury from plant waste liquors has been developed by the Ventron Corporation. Waste water containing organic mercury compounds is treated with chlorine to convert the organic mercury to inorganic mercury compounds. Then the waste water containing inorganic mercury compounds is fed, along with a 12 percent solution of $NaBH_4$ (in caustic), into a static mixer. The pH is held between 9 and 11. The $NaBH_4$ reduces the mercury compounds, yielding a metallic mercury precipitate and hydrogen gas. Following separation of the gas, which is scrubbed with dilute

nitric acid solution to eliminate any mercury vapor, the slurry is passed
to a cyclone. There, 80 to 90 percent of the Hg comes out as a sludge.
Clarified effluent is then sent to polishing filters where the remaining
mercury is removed.

Option No. 2 - Dilute Organic Mercury in Organic Wastes
and Concentrated Organic Mercury Wastes

Organic materials containing mercury are best disposed of by incinera-
tion with recovery of the metallic mercury using mist eliminators, molecu-
lar sieves, sodium hypochlorite scrubbing, or a combination of the above,
as discussed in detail in the Profile Report on Mercury and Inorganic Mercury
Compounds (p. 23 - 30). Incinerators must be provided with adequate means
of removing other combustion products derived from the organic portion of
the molecules from the gas stream such as chlorine, hydrogen chloride,
sulfur dioxide, NO_x and other compounds considered to be pollutants.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that dilute aqueous organomercury-containing wastes
can be adequately treated at the site of waste generation using Option No.
1 or a similar method. Disposal of dilute and concentrated organic wastes
containing organic mercury compounds may also be handled by manufacturers
and some users at the site of waste generation provided the organization
in question has properly designed and operated incineration facilities.
However, it is likely that many sources of organic mercury-containing wastes
will not be able to support the specialized incineration and recovery faci-
lities needed for their disposal. Therefore, it is recommended that provi-
sion be made at appropriate National Disposal Sites for disposal of organo-
mercury wastes by some variation of Option No. 2.

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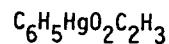
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __ORGANIC MERCURY COMPOUNDS__

IUC Name _____

Common Names __PHENYL MERCURIC ACETATE__

Structural Formula

$C_6H_5HgO_2C_2H_3$

Molecular Wt. __336.75__   Melting Pt.[1] __149 C__   Boiling Pt._____

Density (Condensed)_____ @_____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water __Slightly soluble__   Hot Water __Slightly soluble__   Ethanol __soluble__

Others: __Soluble in glacial acetic acid, acetic acid, benzene__

Acid, Base Properties_____

Highly Reactive with __Dangerous when heated to decomposition_____

Compatible with_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments __High mammalian toxicity,[2] oral LD_{50} for rats 72 mg/Kg[2]__

References (1) 1570
         (2) 0637

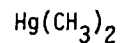# HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name <u>Organic Mercury</u>   (258)

IUC Name <u>Dimethyl Mercury</u>

Common Names <u>Methyl Mercury</u>

Structural Formula

$Hg(CH_3)_2$

Molecular Wt. ___230.66___   Melting Pt. ___-154 C___   Boiling Pt.[1] ___96 C___

Density[1] (Condensed)___3.069___ @ _20/4 C_ Density (gas)_____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility [1]

    Cold Water___insoluable___   Hot Water_____   Ethanol___soluble___

    Others:___ether___

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments_____

_____

_____

References (1) 1570

PROFILE REPORT

Arsenic Trioxide (51)

1. GENERAL

Arsenic trioxide is a highly toxic, solid compound which occurs as a
waste in a number of industrial and agricultural industries. The starting
material occurs in nature as ores containing various arsenic compounds.
These ores are not mined and processed for their arsenic but rather it is
a major byproduct of the copper, lead, zinc and gold smelting industries.
Arsenic is present, in small amounts, in most of the ores that are smelted
about the United States, but the ores processed in the Pacific Northwest
produce greater amounts of As_2O_3. The ores mined from the Pacific Northwest
area also contain higher amounts of arsenic and in addition, high arsenic
containing foreign ores are smelted there. The copper ores from the Pacific
Northwest contain 2 to 4 percent arsenic and these ores, as well as the
foreign ores, are processed by American Smelting and Refining Company (ASARCO)
in their Tacoma, Washington operations. ASARCO is also the only company
that receives arsenic containing flue dusts (nominally 30 % As_2O_3) from
other smelters for the refining of arsenic trioxide and its 1970 arsenic
trioxide production was 14,000 tons.[1559] These arsenic oxides sublime
off the ore into the flue gas stream and are condensed in a series of
brick condensing chambers called kitchens. The dust emerging from the
kitchens (about 90% As_2O_3) is collected on bag filters or electrostatic
precipitators for purification or sale as crude product.[1433] While
awaiting sale and shipment, the arsenic trioxide is stored in large
weatherproof silos at ASARCO's site at Tacoma, Washington. Kennicott
stores their As_2O_3 in railroad hopper cars before shipment to ASARCO for
metals and arsenic recovery. The demand for arsenic trioxide varies
greatly depending upon the demand for arsenical pesticides whose popularity
appears to be cyclical. The fluctuation in the arsenical pesticide market

is generated by the natural buildup of immunities by agricultural pests to the compounds which are applied to control them, thus making it necessary to substitute organics for arsenicals and conversely. At the present time, it is estimated that there are 40,000,000 lb arsenic trioxide in storage at ASARCO's Tacoma site.

It is recognized that the dry filter bag trapping process and electrostatic precipitators are efficient in removing large dust particles but a significant amount of small particulates escape into the air. One smelter plant reported its source testing results as 1.1 tons of particulate emitted per day which contained 34 percent arsenic, 23 percent lead and smaller amounts of copper and zinc. Phelps Dodge, Kennicott and American Smelting did not feel it was to their advantage to reveal exact dust collection efficiencies or emitted flue gas composition and this tends to indicate that the problem is significant.[1549,1550,1565]

The major use for arsenic trioxide is in the production of agricultural pesticides. These include calcium arsenates, arsenic acid, lead arsenate, sodium arsenate, various arsenites, and organic arsenicals. Arsenic trioxide has often been found as a waste stream constituent in the manufacture of arsenic pesticides. Examples of waste streams from the pesticide industry include:

   3 percent by weight of arsenic trioxide with trace of arsenic acid, carbon, filter aid, and 80 percent water; and

   2 percent by weight of arsenic trioxide, 25 percent filter aid, and 73 percent water.

The lagoon system at Rocky Mountain Arsenal, for example, has been used over the years by pesticide manufacturers as well as the military for the discharge of their waste water, and its bottom mud now contains 10 to 100 ppm arsenic (probably mostly in the form of As_2O_3). In addition, there are also still bottom residues from the production of arsenic fungicides. The waste amounts to about 16,000 lb, contains approximately 15 percent arsenic in various chemical forms, and is currently stored in 55-gal. drums.

The arsenic pesticides are applied to foliage or to the ground, and are also used in cattle and sheep dip solutions, as well as being employed for wood preservatives where nonionic arsenates are fixed in the wood by means of an autoclave process.

Arsenic trioxide when used in the manufacture of pesticides applied to plants, such as cotton defoliants, can be expected to occur again as an arsenic trioxide waste product as a result of burning the pesticide containing foliage. Arsenic trioxide or other arsenic compounds are found in the dust particles from cotton gins and the trioxide occurs in the flue gases from the burning of cotton gin trash. The use of bag filters and electrostatic precipitators is reasonably adequate for arsenic control from the ginning operation but the burning of the collected trash is not being adequately controlled. Adverse effects on vegetation in the neighboring areas downwind of cotton gins have been observed and confirmed by laboratory analysis.[0634] About 37 percent of the gins burn their trash with the remainder returning it to the farm land. Devices are available for flue gas cooling and particulate collection for cotton trash burning. They simply require forced implementation by authorities.

The glass industry consumed an estimated 4,100 tons of arsenic trioxide in 1968 for glass processing, friting materials and enamels.[458] The Drakenfield Co., who is the sales agent of As_2O_3 for ASARCO, reported sales of 3,000 tons in 1971. Arsenic trioxide is used as a "fining" agent. Purified As_2O_3 is added to molten glass batches in 0.2 percent to 0.75 percent loadings. The As_2O_3 volatilizes and disperses through the glass batch removing entrained air bubbles while being oxidized to As_2O_5 in the process. The arsenic remains dispersed in the glass and in the absence of waste glass slag, there are no significant waste arsenic oxides produced.[1568]

Coal contains 0.08 to 16 micrograms of arsenic per gram of coal and for this reason the air of most large cities contains a small amount of arsenic, probably as arsenic trioxide. Based upon the range above and a 400 million ton yearly consumption of coal the amount of As_2O_3 emitted

from coal burning lies somewhere between 300 and 6,400 tons per year. The average arsenic concentration in air is estimated to be .020 mg/M^3. The maximum urban concentration of arsenic to which one could expect to be exposed is about 1.4 mg/M^3.[0634]

2. TOXICOLOGY

Human Toxicity

Arsenic trioxide is a powerful poison. The systemic effects are normally caused by ingestion. As little as 0.1 grams ingested can be fatal. It can also be absorbed by inhalation of the dust. Local contact on the skin can cause a variety of dermatitis conditions but normally will not cause systemic symptoms. The acute poisoning symptoms include difficulty in swallowing, severe abdominal pain, vomiting, diarrhea, with pain in the limbs and muscle cramps, cold damp skin, rapid weak pulse, shock, unconsciousness, convulsions and death. The symptoms caused by chronic low level arsenic exposure are difficult to diagnose due to the wide variety of unpredictable symptoms which may arise. The MCA Chemical Safety Data Sheet SD-60 on arsenic trioxide describes in greater detail the symptoms of both acute and chronic exposure to arsenic trioxide.[1557]

Toxicity Towards Other Plans and Animals

Arsenic trioxide is highly toxic to most forms of animal life. Previously mentioned damage to plants has been observed but detailed information on plant effects is not presently available.

3. OTHER HAZARDS

Arsenic trioxide is noncombustible, nonexplosive and as dry solid is noncorrosive to steel. It dissolves slowly in water to form arsenious acid at about 2 percent strength which is also highly toxic. It sublimes at 193 C and as a result the material should be considered a hazard if heated.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Because of the highly toxic nature of the arsenic trioxide, special considerations must be taken to prevent contact with personnel in the storage, handling, transportation and disposal of this material. Arsenic trioxide should be stored in areas away from such items as food products and combustible materials. It should be stored in containers which are considered "siftproof", that is, mild steel drums, silos or hoppers. During unloading, emptying or other handling operations, extreme care must be taken to avoid the generation of dust. Negative pressure pneumatic transfer equipment is recommended for the loading of hopper cars and barrels. Adequate exhaust and dust collection equipment is necessary. Spills of arsenic trioxide should be cleaned up using a vacuum cleaner or by washing down with a hose to a waste sump after a fine spray of water has been laid down to prevent dust generation. Arsenic trioxide is classified by the Department of Transportation (DOT) as a poisonous solid, Class B. When shipped by rail, water or highway it must comply with all DOT regulations regarding loading, handling, and labeling. Normal shipping containers are steel drums, and tight wooden barrels, DOT specification 10A, 10B or 10C. Hopper or bottom outlet steel railroad cars are also commonly used. These should be siftproof, self-clearing and equipped with weatherproof covers. They should not be used for shipping other material. Each railroad car or individual container must bear the DOT "Dangerous" placard. All other DOT regulations must be followed.[1557]

American Smelting and Refining is currently accepting crude As_2O_3 from the smelting industry on a broad scale. Other smelters collect their flue dust and ship it to ASARCO for residual metals recovery and As_2O_3 purification. The As_2O_3 is stored in weatherproof silos while awaiting sale to pesticide manufacturers and glass companies. With the possible exception of ASARCO's own flue dust control which is inadequate but believed to be no worse than other smelters, the arsenic trioxide handling methods at ASARCO appear adequate and are a key link in As_2O_3 waste management.[1547, 1548]

The acceptable criteria for the release of arsenic trioxide into the environment are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Arsenic trioxide	0.005 mg/M^3 as As	0.01 TLV for As

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Arsenic trioxide	0.05 ppm (mg/l) as As	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Arsenic trioxide is highly toxic and this greatly influences the types of waste management techniques to be applied at a National Disposal Site. Especially critical is the problem of reducing the As_2O_3 emission to the air from disposal site stacks.

Management of Arsenic Trioxide Wastes

Option No.1 - Recycling/Reprocessing. The acceptance by American Smelting and refining of flue dust from a large part of the other smelting operations done by other companies is not only adequate but extremely desirable. They represent a vital key in the adequate handling of As_2O_3 waste from sources across the nation. Moreover they are also reclaiming residual copper, lead, zinc and silver from the dust for significant credits via a proprietary process. ASARCO charges the other smelting companies for the treatment of their dust. The value for the recovered metals is returned to the other smelters. The value received for the recovered metals exceeds the treatment charge thereby creating a profit for the firm submitting the dust. The disadvantage of this waste management method is that the demand for As_2O_3 fluctuates wildly resulting in frequent large overstocks at the Tacoma, Washington site. Such a condition exists currently and ASARCO is presently reluctantly receiving outside flue dust. With government subsidies, it is entirely possible that ASARCO represents a National Disposal Site for all As_2O_3 and related arsenic compounds.

Option No.2 - Land Burial. Under proper conditions of encapsulation and burial, As_2O_3 and other arsenic compounds might be accepted for disposal by a few selected landfill sites.[1518] Lacking enough information to determine if landfill is adequate, such a decision cannot be presently made. Two disadvantages are however apparent. It will cost the As_2O_3 producer to have the material shipped and landfilled with expectedly expensive encapsulation. Secondly, for all intents and purposes the material is unrecoverable. This method should be used only in the event that large overstocks of As_2O_3 are present and long term storage of additional amounts is not feasible.

Option No.3 - Long Term Storage. Overstocks of arsenic trioxide, as previously mentioned, are being stored in large weatherproof silos on the site of ASARCO's plant in Tacoma, Washington. No figures were available to determine the cost of storing the material. The storage silos are siftproof and weatherproof and as such they constitute an adequate means of isolating and containing this poisonous material. Other firms that are also generating arsenic trioxide as a waste material are also storing this material in a similar manner by employing railroad hopper cars.

Abatement of As_2O_3 in Flue Streams

The concentration of As_2O_3 in the flue gases being lost to the air despite the use of dust removal equipment was not revealed by the firms contacted, but their refusal to discuss it indicates that the problem is probably significant. Abatement of As_2O_3 in gas streams is a current concern for smelters, cotton gins and other minor As_2O_3 producers. Additionally, improvements in dust removal will be an important and necessary part of any National Disposal Site process design. The following dust abatement options would be used after smelting or cotton gin flue gases were cooled, as required, by passing the flue gases through As_2O_3 condensing "kitchens."

Option No.1 - Multistage Electrostatic Precipitators. Installation of electrostatic precipitators is the most common method for As_2O_3 removal.

They are 70 to 90 percent effective and require rapping or flushing of the grids to remove the dust. The smaller, lighter particles normally escape entrapment. The types of negative responses received from contacts indicate they are doing a less than adequate job for As_2O_3 precipitation.[1549,1550]

Option No.2 - Filter/Bag House. Bag house operations are normally about 99 percent efficient. However, they require 2 to 3 times as much power as the precipitators. The bags are normally cleaned and dust recovered by reversing air flow through them. They are not used as extensively as precipitators and are more costly to acquire. They are expected to be used more as abatement compliance is required.

Option No.3 - TRW Charged Droplet Scrubber. Charged droplet scrubbers employ a stream of electrostatically charged water droplets. They are accelerated through the field between the positive-voltage nozzles and the negative-voltage collector plates on the side of the flue. In transit, the droplets collide with dust particles and carry them to the collector plate where they drain away. Efficiency for a two-stage unit is estimated to be 99 percent. Size and power requirements are smaller than bag houses or precipitators. The system is self-flushing and has no moving parts. The unit is also less expensive to buy or to install.[1566]

Option No.4 - Wet Vacuum Filtering. There is sketchy information regarding a chemical plant in the USSR whereby the efficiency of arsenic removal was greatly improved by using wet vacuum pumps instead of fabric bag filters. When the fabric filters are used the arsenic content in the air frequently reached several 100 micrograms per cubic meter. After the wet scrubbing vacuum pumps were installed, the removal is reported to have been 100 percent effective. This information is obtained from the Survey of the USSR Literature on Air Pollution and Related Occupational Diseases by V. G. Matsak, 1960.[0634]

To summarize, the adequate methods for managing arsenic trioxide wastes include: (1) shipment to ASARCO for reprocessing; and (2) long term storage in siftproof and weatherproof containers.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Arsenic trioxide is considered as a candidate waste stream constituent for National Disposal Sites for the following reasons: (1) the material is highly toxic and nondegradable; (2) the material is present in sizable quantities as a waste; (3) wastes containing arsenic trioxide are widely distributed and are contributed by a number of industries; and (4) the feasibility of the centralized disposal/reprocessing concept has already been demonstrated by the treatment of one particular type of arsenic trioxide waste, the flue dusts from copper, zinc, and lead smelters, on a large scale at ASARCO's Tacoma facility.

For the treatment of arsenic trioxide wastes at a National Disposal Site, the recommended process is:

Process	Order of Preference	Remarks
Long Term Storage	First Choice	Best current method as there is no demand for As_2O_3

An identified need in the reprocessing of arsenic trioxide wastes is improved flue dust abatement equipment. The residual high level of arsenic containing dusts in flue gases downstream of currently used dust removal equipment remains a significant problem in copper, lead and zinc smelting and arsenic trioxide reprocessing. At present, the use of fabric bag filters, although not entirely satisfactory, is the preferred method for controlling airborne arsenic trioxide dusts.

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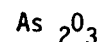
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Arsenic trioxide (51)___

IUC Name _____

Common Names ___White arsenic_____

Structural Formula

As_2O_3

Molecular Wt. ___197.82[1]___ Melting Pt. ___sublimes 193 C[2]___ Boiling Pt. ___457.2 C[2]___

Density (Condensed) _3.738 g/cc_ @_____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

____1 mm___ @ ___212__ C[2]   ___10 mm @ 259.7[2]___ C   ___100 mm @ 332.5[2]___ C

Flash Point __none[2]___   Autoignition Temp. _none_ [2]

Flammability Limits in Air (wt %)   Lower_____   Upper_____
Explosive Limits in Air (wt. %)   Lower_none[2]___   Upper_____

Solubility

^oC[1]

Cold Water _2.04 g/100 cc at 25 C[1]_ Hot Water _11.46 g/100 cc at 100_ Ethanol _sol._

Others: ___alkali and HCl_____

Acid, Base Properties_____

Highly Reactive with ___fluorine, hydrogen fluoride_____

Compatible with ___steel when dry[2]_____

Shipped in ___tight wooden barrels, hopper or bottom outlet steel cars_____

ICC Classification _Poisonous solid, Class B___   Coast Guard Classification_____

Comments _Powerful poison. TLV 0.5 mg/m^3 air [2], volatile_____
          Need eye, head, respiratory, skin protection

References (1) 1570
           (2) 1557

PROFILE REPORT

Cacodylic Acid (80) and Sodium Cacodylate (382)

1. GENERAL

Cacodylic acid and its sodium salt are poisonous compounds that are used in agriculture as post emergent, leaf contact, weed killers and defoliants. The acid is also called dimethylarsinic acid; its formula being $(CH_3)_2 AsOOH$. Either the acid or the salt is used depending on the pH of the solution used for a specific application. For purposes of this Profile Report, the two compounds will be referred to as the cacodylates.

These compounds are normally produced and applied as solutions. The estimated annual production is about 1,200,000 gal.[2215] These solutions generally contain 2 to 3 lb of cacodylates per gallon of solution. The Ansul Chemical Company of Marinette, Wisconsin is responsible for about 80 percent of the cacodylate production. The Vineland Chemical Company produces much of the remaining 20 percent. The cacodylates have EPA registered uses in non-bearing citrus groves, utility rights of way, ornamental turf control under the trees and shrubs, and around industrial sites. Recent or soon-to-be-added registrations include uses in bearing citrus groves and as defoliating agents in cotton fields.[2021,2215] Residues from the fallen leaves or material misdirected to the ground from spraying become tightly bound to soil particles in a form of irreversible adsorption. Representatives of Ansul Chemical Company indicated that studies have confirmed no residual plant toxicity in the soil because these compounds cannot be leached from the soil or taken up by plant root systems. As an example, they cited the Scott Lawn products people who, a number of years ago, marketed a cacodylate base compound which they called "Erase". Erase was applied to ornamental

lawn areas as a contact herbicide, and in three or four days the lawn died.
A new seeding could then be made immediately with no harmful effects on
the new lawn.

Ansul representatives indicated that use of the cacodylates is
heaviest in Texas with smaller amounts being consumed in Arizona and
California. Consumption in the rest of the United States is considered
commercially insignificant.[2215]

Manufacture of Cacodylates

The commercial production of cacodylic acid is a 3-step process.
Arsenic trioxide is reacted with sodium hydroxide to yield sodium arsenite.
Methyl chloride is added to produce methanearsonic acid, $CH_3AsO(OH)_2$. The
mixture is then reduced with SO_2 and methylated to recover the dimethylarsinic
acid.[2215] There is no liquid effluent from this process as all the liquid
streams are recycled for reuse. A number of multiple effect evaporators
are employed in the solution recycling systems. The process does, however,
create a solid waste which is a mixture of sodium chloride and sodium
sulfate containing 1 to 1-1/2 percent cacodylate contaminants.

Market Trends for Cacodylate Compounds

Cacodylic acid production was heavier in the early and mid-sixties
when the Army was buying large amounts of it under the general description
of defoliants. It was used extensively in Vietnam for the destruction of
rice fields, now a discontinued practice. Production dropped significantly
when Army purchases ceased but the trend is again toward increased
consumption of the cacodylates because of new EPA registrations for use
of cacodylates on cotton and bearing citrus groves.

Sources and Types of Waste

The major sources of cacodylate wastes are: (1) manufacturers of
cacodylate pesticides; and (2) pesticide residue left in empty containers.
No surplus cacodylate pesticides have been identified.

As indicated previously, solid wastes containing sodium chloride, sodium sulfate, and 1 to 1.5 percent cacodylate contaminants are generated in the pesticide production process. The rate at which this waste material is produced is not known, but at the present time there are 60,000,000 lb being stored in concrete vaults in the Marinette, Wisconsin area. There are currently no plans for the waste material other than to store it indefinitely.[2214]

Both cacodylic acid and sodium cacodylate are normally formulated as liquid solutions. As such, there are usually 0.5 oz to 1 lb of liquid residue left in the empty containers, depending on the shapes and sizes of the containers. The safe and economical disposal of pesticide contaminated containers remains a serious problem that is still unresolved.

2. TOXICOLOGY

Human Toxicity

Organo-arsenic compounds are highly toxic materials and are very dangerous even in low concentrations.[0766] The American Conference of Government Hygienists (ACGH) has recommended a Threshold Limit Value (TLV) of 0.5 milligrams per cubic meter of air for all arsenic compounds.[0225] This value represents the conditions to which nearly all workers may be repeatedly exposed on an 8-hr period without adverse effect.

Acute arsenic poisoning from ingestion results in corrosive irritation of the stomach and intestines with accompanying nausea, vomiting and diarrhea. In severe cases, collapse and shock can occur with a weak, rapid pulse, cold sweats, coma or death. The diagnosis of latent, chronic arsenic poisoning is difficult since the condition manifests itself with many different and unpredictable symptoms. Included are disturbances of the digestive tract, liver damage resulting in jaundice, blood and kidney disturbances and a variety of skin abnormalities.[0766]

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Toxicity Towards Plant and Animal Life

Since these compounds are used as herbicides and defoliants, it is reasonable to believe that they are harmful to terrestial plant life in general. Arsenic concentrations of 2 to 4 ppm have been found to not interfere with the self purification of streams, however, fish display harmful effects at about 15 ppm.[1752] It is reasonable to assume that toxic levels for terrestial animal life are about the same as levels determined for humans.

3. OTHER HAZARDS

The cacodylates do not exhibit any explosive, flammable, or volatile properties, nor do they present any other hazards.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The cacodylate herbicides because of their toxicities require special consideration for storage, handling, transportation and disposal. Storage areas for these compounds should be isolated from locations where food and animal feed are stored. The waste materials should be stored in the type of containers originally used by the manufacturer. Cacodylate solutions are packed and shipped by Ansul Chemical Company in 30-gal. phenolic-lined metal drums, 5-gal. metal pails and 1-gal. high density polyethylene bottles packed four to a case. Ansul also packs a solid product in a polyethylene lined 100-lb fiber drum.[2215]

Protective clothing, goggles, gloves and dust filtering respirators are recommended for unloading or otherwise handling these herbicides. Similar precautions are recommended for handling any liquid solutions. Spills of the solid materials should be cleaned up using a vacuum cleaner after a fine spray of water has been laid down to prevent dust. The liquid compounds or formulations should be handled in an area such that

if they are spilled they can be contained for easy cleanup or transfer
to a sump where they will not create a hazard.

The cacodylates are classified as Class B poisons. All Department
of Transportation (DOT) regulations should be followed when shipping,
storing, or otherwise handling the cacodylates.

Disposal/Reuse

The wholesale disposal of these materials into the air, water or
soil must be considered completely unacceptable considering their high
toxicities. The U.S. Public Health Service has established a maximum of
0.05 mg/1 arsenic content (50 ppb) for drinking water if no other drinking
water is available. The ideal maximum is 0.01 mg/1 (10 ppb). The
acceptable criteria for the release of cacodylates into the environment
are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Cacodylic acid	0.005 mg/M^3 as As	0.01 TLV
Sodium cacodylate	0.005 mg/M^3 as As	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Cacodylic acid	0.05 ppm (mg/1) as As	Drinking Water Standard
Sodium cacodylate	0.05 ppm (mg/1) as As	Drinking Water Standard

The cacodylates do not cause soil sterility or adverse plant effects
when found in the soil; nevertheless disposal of them by land spreading is
not recommended because intentional loading of soil with material not
naturally found there is environmentally unacceptable when easier, cheaper
options are available.

There are channels by which unused and unopened containers of
cacodylate compounds can be returned to the manufacturer for resale.[2215]
Representatives of Ansul also indicated that they would accept contaminated
or otherwise unwanted material for recycling provided that a process to
remove contaminants was technically and economically feasible.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The cacodylates are not expected to occur as waste products in a reasonably pure or concentrated form. The only identified cacodylate wastes are the salt by-products from cacodylate manufacturing and contaminated empty containers. The waste management options for the cacodylates are presented below.

Option No.1 - Recycle/Reuse

Representatives of Ansul Chemical Co. have stipulated the conditions under which the usable cacodylates can be returned to them for reprocessing or resale.[2215] They will accept unwanted stocks for resale without any reprocessing if the batch had originally been made by Ansul and if the materials were in their original unopened containers. This is a completely adequate waste management technique for these materials if they are in a concentrated form.

Option No.2 - Long-Term Storage

Storage of cacodylates and cacodylate wastes, until they can be used or reprocessed, is a satisfactory waste management option. These materials are stable compounds and require the minimal storage precautions needed for any toxic material. Storage in the original containers is recommended but they should be periodically checked for corrosion or breakage of the containers. Bulk quantities of waste, such as the salt by-products from cacodylate manufacture, can be stored in concrete vaults or weatherproof bins.

Option No.3 - Landfill

The disposal of cacodylate wastes in santitary landfills is generally not acceptable because of the potential danger of ground and surface water pollution, as well as possible occupational hazards resulting from on-site handling. There are, however, certain approved sites located over

nonwater-bearing sediments or with only unusable ground water underlying them and are completely protected from flooding and surface runoff and drainage such as those designated as Class 1 sites in California. The disposal of small stocks of cacodylate wastes or empty containers contaminated with cacodylates in "Class 1" sites is considered as adequate, provided special handling techniques as discussed in the previous section are employed to protect site personnel.

To summarize, the adequate management methods for cacodylate wastes are: (1) recycle/reuse, (2) long-term storage, and (3) landfill in "Class 1" sites.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The cacodylates are considered as candidate waste stream constituents for National Disposal Sites for the following reasons: (1) the high degree of toxicity of the compounds, (2) the nondegradable nature of the toxic arsenic component of the compounds; (3) cacodylate wastes are present in sizable quantities as contaminated empty containers; (4) cacodylate wastes are widely distributed and are often handled by personnel without adequate training, such as farmers; and (5) facilities for treating other arsenic-containing materials such as arsenic trioxide, arsenate, arsenite and other organic arsenical (the mono and di-sodium salts of methane arsonic acid, commonly called MSMA and DSMA) wastes will be required at National Disposal Sites.

The processes recommended for the treatment of cacodylate wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Long-Term Storage	First Choice	Best current method as there is no market demand for As_2O_3; also recommended for the disposal of waste salt by-product from cacodylate manufacture.
Landfill	Second Choice	Disposal sites must meet the criteria for a California "Class 1" site; recommended for the disposal of contaminated empty containers.

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The solid waste salt by-product from cacodylate manufacture contains sodium chloride, sodium sulfate, and 1 to 1.5 percent cacodylate contaminants. The volume of this waste material currently in storage amounts to 60,000,000 lb. There is a definite need for the development of an economical process capable of extracting the cacodylate constituents from the salt waste so that the latter can be readily and safely disposed of in municipal landfills.

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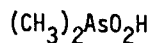J. F. Clausen, TRW Systems, July 28, 1972.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Cacodylic Acid__ (80)

IUC Name __Dimethylarsinic__ acid

Common Names_____Alkargen_____

Structural Formula

$(CH_3)_2AsO_2H$

Molecular Wt. __138.00[1]__ Melting Pt. __200 C[1]__ Boiling Pt._____

Density (Condensed)_____ @____ ____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____ _____@_____ _____@_____

Flash Point _____ Autoignition Temp.____

Flammability Limits in Air (wt %) Lower_____ Upper_____

Explosive Limits in Air (wt. %) Lower_____ Upper_____

Solubility

Cold Water__very soluble__ Hot Water_____ Ethanol__very soluble__

Others:_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification __Poison B, poison label,__ 200 lbs Coast Guard Classification __Poison B, poison__ label

Comments __essentially non-irritating to skin.[2]__   Acute oral LD$_{50}$ for __rats 1,350 mg/kg[2]__

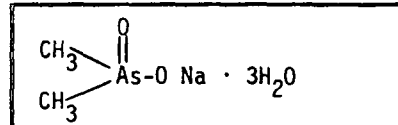References (1) 1570
          (2) 1784

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Sodium cacodylate___ (382)

IUC Name ____Sodium dimethylarsinate___

Common Names_____

Structural Formula

$$CH_3 \diagdown \\ \quad\quad As\text{-}O\ Na \cdot 3H_2O \\ CH_3 \diagup$$

with $\overset{O}{\underset{\|}{}}$ double bond on As

Molecular Wt. ___314.21[1]___   Melting Pt. ___-H_2O 120 C[1]___   Boiling Pt._____

Density (Condensed)_____ @____ ____ Density (gas)_____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water___83 g/100 g[2] decomposes[1]___ Hot Water___decomposes[1]___ Ethanol_____

Others:_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification_Poison B, poison label,_ 200 lbs[3] Coast Guard Classification_Poison B,_ Poison label[3]

Comments ___Relatively non irritating to skin and eyes[2]___

References (1) 1570
           (2) 1784
           (3) 0766

PROFILE REPORT

Calcium Arsenate (87), Copper Arsenate (119), Lead Arsenate (235),
Sodium Arsenate (376), Zinc Arsenate (453), Manganese Arsenate (500)

1. GENERAL

The arsenates are highly poisonous materials, some of which find
commercial uses in agriculture as pesticides, herbicides, and fungicides.
All six materials have toxic properties but only the calcium and lead
compounds are employed as ingredients in various commercial pesticide
formulations.[1433] The remaining arsenates of copper, manganese, sodium
and zinc are not being prepared for agriculture or any other uses in
significant amounts. It is estimated that the consumption for these
other arsenates as laboratory reagents or research curiosities is very
small.[1715,1716] Therefore, the emphasis of this Profile Report is on
the arsenates of calcium and lead, although the available pertinent
information of the remaining compounds is also presented.

Manufacturing Processes

Industrial awareness for the hazardous properties of the arsenic
compounds has an important influence upon the design of industrial pro-
cesses for the manufacture of arsenic pesticide compounds. Batch pro-
cesses are employed in the production of these materials. The plants
that produce these materials can generally be characterized by their
complete containment of any byproducts or contaminated effluents that
result from these processes. The only liquid effluents from any of
these processes are small amounts of contaminated water from equipment
washout and they are held in evaporating ponds at the plant site.[1740]
Water is driven off of the products by means of steam-heated, continuous
drum dryers or spray drying apparatus. Scrubbing equipment treats the

steam effluent from the drying equipment and the scrubbing liquids are recycled for use as makeup solutions for the next batch. Grinding and bagging of the products are performed in a closed area with devices to control the emission of particulates from the operation. Bag filters are in common use and particulates removed from the bags are packaged for sale. There is no washing or purifying of the manufactured arsenates and any aqueous filtrates are recycled for makeup of the next batch.[1708]
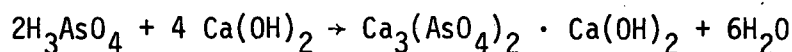
Calcium Arsenate - Calcium arsenate is a white poisonous material which is slightly water soluble and is used to control codling moths and various plant chewing pests. The technical grade product contains a mixture of the calcium salts of arsenic acid, in which it is believed the alkaline salt of the composition $Ca_3(AsO_4)_2 \cdot Ca(OH)_2$ predominates.[1742] Other components of the mixture might include $CaHAsO_4$, $Ca_3(AsO_4)_2 \cdot Ca_5H_2(AsO_4)_4$, $CaCO_3$ and some unreacted $Ca(OH)_2$.

Calcium arsenate is made from reacting arsenic acid or its salts with calcium hydroxide:

(1) Reaction of water soluble salts of arsenic acid with lime.

$$Na_3AsO_4 + 4\ CaOH_2 \rightarrow Ca_3(AsO_4)_2 \cdot Ca(OH)_2 + 6\ NaOH$$
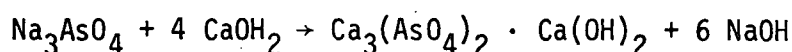
(2) Reaction of arsenic acid with lime.

$$2H_3AsO_4 + 4\ Ca(OH)_2 \rightarrow Ca_3(AsO_4)_2 \cdot Ca(OH)_2 + 6H_2O$$

The product is applied both as a dust and as a sprayable aqueous suspension. It is incorporated in baits for the control of worms, snails and slugs for tree and vegetable crops. It is also used as a selective herbicide on ornamental lawns.[1728]

Calcium arsenate has certain undesirable properties that have limited its general use on most plants. Unless applied with an excess of lime, serious plant damage may result from application on certain crops. Calcium

arsenate is also easily decomposed after application to plant surfaces. Hydrolysis of the calcium arsenate takes place in aqueous suspension and results in the formation of calcium hydroxide and arsenic acid. However, calcium arsenate still finds use as a dust since it is simple to produce the material in a form suitable for dusting on certain plants that are less susceptible to damage. Approximately 2 million lb were consumed in 1969 (little change from 1968).[1738]

Lead Arsenates - There are many mixtures of lead and arsenic that are commonly called lead arsenates.[1570] The chemistry of these various combinations have been exhaustively investigated,[1742] and only two lead arsenates have the physical properties and chemistry which makes them useful as pesticides. Standard lead and basic lead arsenate are the two which will be discussed. The other lead arsenate compounds are apparently found only in the laboratory, if at all. During manufacture, purification of these pesticides is not performed, and they are sold as mixtures of reactants and various products.

Dilead ortho arsenate, $PbHAsO_4$, is commonly called acid lead arsenate and is also known as dibasic lead arsenate, diblumbic hydrogen arsenate, hydrogen arsenate and others. As a pesticide it is called standard lead arsenate, the name to be used in this report. Standard lead arsenate is prepared on a commercial scale by the combination of arsenic trioxide, nitric acid and litharge.

The other lead arsenate used in pesticides is commonly called basic lead arsenate. Various formulas have been suggested for the series of compounds including $Pb_4(PbOH) \cdot (AsO_4)_3 \cdot H_2O$ and $Pb_5(PbOH)_2 \cdot (AsO_4)_4$ but it is difficult to determine which of the above or any other is correct. Undoubtedly, several compounds exist in the commercial preparations that are called basic lead arsenates. It is also apparent that a whole range of compositions is possible depending upon the composition of the reactants as well as time and temperature parameters for each particular preparation.

The lead arsenates are applied to fight various worms, moths and other foliage-destroying insects that occur on fruit trees, grapes, walnuts, grapefruit and oak trees. The 1969 consumption (or domestic disappearance) of lead arsenate was estimated to be 7.7 million lb, which was an increase over the 1968 consumption of 4.7 million lb. The consumption of lead arsenate since 1969 has been generally decreasing and in the spring of 1972 the EPA has lifted the registration which permitted the use of lead arsenate compounds. This effectively will cause the decline of lead arsenate use to the point where it will be insignificant in the future.

Other Arsenate Compounds - The remaining arsenate compounds included in the Profile Report, while having approximately the same toxic properties as those of lead and calcium, are not currently being used as pesticides in the United States. This section will therefore be confined to the discussion of the limited available information concerning these arsenic compounds.

Copper arsenate [$Cu(CuOH)AsO_4$] is a very stable crystalline material that is not easily hydrolyzed by water. This basic copper arsenate is believed to be as toxic as lead arsenate when used as an insecticide. The three current arsenate manufacturers were not aware of any copper arsenate being produced or used in the United States since Sherwin-Williams closed down their plant. The commercial product covered by the patents is prepared from arsenic acid, copper sulfate and lime. The calcium sulfate in the reaction product is not removed and the final mixture contains 41 to 46 percent of the basic copper arsenate.

Manganese arsenates have been prepared for research purposes and have been found to have some merit as insecticides although they have been determined to be less effective than lead arsenate. It appears to have a very high toxic effect on plants and this reduces its appeal as an effective insecticide.

The basic salt of zinc arsenate is reported to have the approximate composition: 5 ZnO · 2 AsO$_5$ · 4H$_2$O. Its toxicity is similar to that of calcium arsenate and the Pesticide Index has indicated its use as an insecticide.[1784]

Sodium arsenate appears to be the common name for disodium arsenate (Na$_2$HAsO$_4$ or Na$_2$HAsO$_4$ · 7H$_2$O). It is a solid which is freely soluble in water and glycerol. It is considered to be highly poisonous. It has been used in the past as an insecticide and a herbicide.

Physical Properties of the Arsenate Compounds - In trying to obtain information of the physical properties of these arsenate compounds, it has become clear that the common name calcium arsenate, lead arsenate, etc., applies to a rather large host of different arsenic/metal compounds. The differences between these compounds involve different oxidation states of the various arsenic and metal ions as well as waters of hydration and crystal structure. It must also be remembered that many of these compounds are still being debated as to their actual structure. In light of this, some of the data which would normally be found on the hazardous properties worksheets are not presented on the worksheets in this profile report.

Market Trends for Arsenates - The inorganic arsenate market has been in broad decline in recent years, as a result of the strict government controls placed on the use of arsenical pesticides. These materials are highly poisonous in all forms and prolonged application of them in agriculture have caused a serious buildup of these materials in the soil. The point has been reached in some areas where the arsenic pesticides or their hydrolyzed products have become so concentrated in the soil that they have made it almost unsuitable for growing anything. Some orchards have had the top 3 ft of soil replaced.[1716] There also is the threat of large amounts of arsenic being leached out of the soil into streams and rivers thus causing serious damages to the aquatic life.

The consumption of lead and calcium arsenate compounds for 1969 was estimated to be approximately 10 million lb. This is in sharp contrast to the production of over 100 million lb several years ago. The number of companies that are producing arsenate compounds have also decreased. Only three exist today for the manufacture of calcium arsenate and lead arsenate. They are Chevron Chemical Company, Niagara Chemical Company, and Los Angeles Chemical Company.

Sources and Types of Wastes

As indicated previously, arsenic pesticide manufacturers are generally characterized by their complete containment of any byproducts or contaminated effluents that result from the production processes. The three major sources of arsenate wastes are therefore: (1) pesticide residue left in empty containers; (2) surplus pesticides stored in Department of Defense (DOD) and state/municipal facilities, Environmental Protection Agency (EPA) regional offices, and formulating plants; and (3) soil contaminated with high levels of arsenates from the repeated use of the pesticides.

Arsenate pesticides are usually formulated as dusts, granules, or wettable powders and packed in siftproof, multiwall paper bags. The amount of pesticide residue left in the containers is therefore considerably less than those for liquid pesticide formulations, and the disposal of arsenate contaminated paper bags also poses a lesser problem than the disposal of liquid pesticide containers such as glass bottles and steel drums.

Surplus arsenate pesticides currently in storage awaiting disposal include the following:

(1) DOD - 1,624 lb of 98 percent lead arsenate in Texas, and 12 lb of 98 percent lead arsenate in Michigan.

(2) State/EPA - 96 lb of 95 percent lead arsenate and 305 lb of 70 percent calcium arsenate in Washington, and 2,460 units of arsenate containing Harris Ant Buttons in Georgia.

(3) Pesticide manufacturers - an estimated 24,000 lb of lead arsenate at South Gate, California.

The extensive use of arsenic pesticides in the past, particularly lead arsenate, has led to soil sterilization and rendered large acreages of farm land unusable for the growth of future crops.

2. TOXICOLOGY

Human Toxicity

The arsenate compounds are highly toxic materials and are dangerous even in very low concentrations.[0766] The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 0.5 mg/M^3 for all arsenic compounds. This value represents the condition to which nearly all workers may be repeatedly exposed without adverse effect.

Acute arsenic poisoning from ingestion results in irritation of the stomach and intestines with accompanying nausea, vomiting and diarrhea. In severe cases, collapse and shock with a weak, rapid pulse, cold sweats, coma or death can occur. The diagnosis of latent chronic arsenic poisoning is difficult since the condition may manifest itself with many different and unpredictable symptoms. Included are disturbances of the digestive tract, liver damage resulting in jaundice, blood and kidney disturbances and a variety of skin abnormalities.[0766]

Toxicity Towards Plant and Animal Life - Each of the arsenates has a somewhat different effect on either plant or animal life. Some of the compounds, calcium arsenate or lead arsenate, can be applied to certain vegetable and fruit foliage without adverse effect, although all the compounds should generally be considered as being toxic to some plant life. The extreme toxicity of these compounds towards human life can be considered the same for animal life as well. All precautions must be taken to prevent run-off from farms and orchards into streams and rivers where the arsenate compounds can adversely affect aquatic plant and animal life.

Emphasis has thus far been placed on the arsenic constituents of the arsenate compounds being discussed but it should not be forgotten that some of the cations involved in the arsenate compounds also have toxic properties. The compounds of copper and lead under general conditions are also very hazardous. The Threshold Limit Values (TLV's) of these materials are also 1 mg/M^3 and below.[0225] Therefore, the toxicity of these cations should be at least considered in the scope of this Profile Report inasmuch as they are themselves hazardous.

3. OTHER HAZARDS

The arsenates do not exhibit any explosive or flammable properties nor do they present any other hazards.

4. DEFINTION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The arsenate pesticides require special consideration in their storage, handling, transportation and disposal. Storage areas for these compounds should be isolated from locations where food and animal feed is stored. Calcium and lead arsenate should be stored in siftproof, multiwall paper bags originally supplied by the manufacturer. The use of protective clothing, goggles, gloves and dust filtering respirators are recommended for unloading or otherwise handling these pesticides. Similar precautions are recommended for handling any liquid solutions. Spills of the solid materials should be cleaned up using a vacuum cleaner after a fine spray of water has been laid down to prevent dust. The liquid compounds or formulations should be handled in an area such that if they are spilled they can be contained for easy cleanup or at least will not create a hazard if they are absorbed by the ground.

Although only some of the arsenical compounds are labeled as
Class B poisons by the Department of Transportation (DOT), it is recom-
mended to treat the others in the same manner. All other DOT regulations
should be followed when shipping, storing or otherwise handling arsenate
compounds.

Disposal/Reuse

The wholesale disposal of arsenate compounds into the air, water, or
soil must be considered completely unacceptable considering their high
toxicities. The U. S. Public Health Service has established a maximum
of 0.05 mg/l arsenic content (50 ppb) for drinking water, if no other
drinking water is available. The ideal maximum is 0.01 mg/l (10 ppb).[1752]
The disposal of these materials is ironically a moot point since it is the
air, water and soil where the arsenic pesticides ultimately end up in
normal cases. The lead and calcium arsenates after application to plant
surfaces, find their way to the ground when the plant drops its leaves or
when rainfall washes them from the plant onto the ground. In a practical
sense, this is where the real waste problem with the arsenates lies. The
pesticides then reside in the soil where they are not easily removed
except by the equally undesirable process of leaching and runoff into
nearby streams and lakes. In some cases, small overstocks of these
pesticides have been spread out on farm land for disposal much in the
same manner as when they are applied to crops. The rather weak rationale
for this is that the soil is already contaminated with these materials
and the addition of a small increment would not make any difference. In
another case, it might be applied to farm land, where arsenical pesticide
application has never been used, with the reasoning that a small amount
in the soil would cause no significant effect. However, it should be
emphasized that the buildup of arsenic compounds in the soil has created
the problem of soil sterilization and the inability of any type of plant
to grow. It is, of course, this very problem of arsenic compound buildup
within the soil that is causing the Environmental Protection Agency to
strongly regulate against the use of these compounds.[1711,1716]

The acceptable criteria for the release of arsenate compounds into the environment are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Calcium arsenate	0.005 mg/M^3, as As	0.01 TLV
Copper arsenate	0.005 mg/M^3, as As	0.01 TLV
Lead arsenate	0.005 mg/M^3, as As	0.01 TLV
Sodium arsenate.	0.005 mg/M^3, as As	0.01 TLV
Zinc arsenate	0.005 mg/M^3, as As	0.01 TLV
Manganese arsenate	0.005 mg/M^3, as As	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Calcium arsenate	0.05 ppm (mg/l) as As	Drinking Water Standard
Copper arsenate	0.05 ppm (mg/l) as As	Drinking Water Standard
Lead arsenate	0.05 ppm (mg/l) as As	Drinking Water Standard
Sodium arsenate	0.05 ppm (mg/l) as As	Drinking Water Standard
Zinc arsenate	0.05 ppm (mg/l) as As	Drinking Water Standard
Manganese arsenate	0.05 ppm (mg/l) as As	Drinking Water Standard

There are channels by which unused and unopened containers of the arsenate pesticides can be returned to the manufacturer for resale. Representatives of the manufacturers also indicate that they would accept contaminated or otherwise unwanted arsenate pesticides for reprocessing provided that the process was technically and economically feasible. However, the great amounts of waste arsenate compounds are of course in the soil and a scheme by which these compounds could be recovered from the soil, reprocessed and recycled into other products while being environmentally desirable would in all likelihood be economically infeasible.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

There are five waste management methods which have applicability to the arsenate compounds and which are currently being used or which might be applied at a National Disposal Site. It should be stressed that regardless of the type of waste treatment process employed, it still would be necessary to deal with toxic arsenic in some form. The following is a discussion of the options for the management of arsenate pesticides.

Option No. 1 - Recycle/Reuse

Representatives of the three remaining manufacturers of arsenic pesticides have described the conditions under which these materials were returned to them for reprocessing or resale in the past. Each firm accepted these arsenate materials for resale without any reprocessing if the batch had originally been made by the firm and if the materials were in their original, unopened containers. Each firm expressed its reluctance to accept the product of other firms. Given the hypothetical situation of a batch of materials which had been contaminated with a material that can be easily removable by means of processing, each firm indicated its willingness to accept it for reprocessing provided that there was an available market for the material.[1555,1711,1712] In light of the recent EPA order lifting the registration of standard lead and basic lead arsenate pesticides, it is expected that these three firms will have a problem in disposing of current stocks and would not accept any return of the lead arsenate products. It was stated that in some situations, unwanted pesticides are being returned to the supplier in spite of the supplier's refusal to accept them. The users have been known to leave sacks of unwanted products at the supplier's loading dock after closing hours. Such an approach can be viewed positively insofar as it places the disposal problem on someone who at least has some facilities for safe handling of the material.[1716]

Option No. 2 - Long Term Storage

The use of large, weatherproof and siftproof storage bins or silos is currently being used for the storage of other arsenic compounds, especially arsenic trioxide.[1547] Waste pesticides already packed in multiwall paper bags could also be safely stored in these large weatherproof bins. This approach is relatively expensive. Land and storage equipment are required for long, unknown period of time before these materials can be moved by sale or disposal to other outlets. Considering the fact that these arsenic compounds are poisonous in all forms, the technique of long term storage has to be considered as adequate and currently practical.

Option No. 3 - Land Spreading

Some users, when faced with unwanted stocks of some of these pesticides, use land spreading as a means of disposal. This approach involves spreading the waste materials over large amounts of land in very light applications so as not to significantly affect any of the crops or plant life growing in the vicinity. The technique might be used for rare or infrequent disposal of small amounts of the material but in light of the fact that these compounds will build up in the soil by repeated application, this method cannot be considered as completely adequate and other methods should be considered first.

Option No.4 - Export

Some foreign countries are still using arsenate pesticides where possible contamination has not become a critical issue as in the United States. The prospect of selling unwanted stocks of the arsenate pesticides to neighboring countries, especially Mexico, is being actively considered.[1712] It is conceivable that many foreign countries might have a specific need for a number of these arsenate pesticides where their use would not create a critical problem. However, although the export of unwanted arsenate pesticides from the United States can be considered as desirable from the viewpoint of solving the domestic disposal problem, the long term effects are the probable global arsenic pollution of the environment.

Option No. 5 - Process for Recovery of Metals in Arsenates

American Smelting and Refining (ASARCO) has a process operating at
its Tacoma, Washington plant whereby they are recovering lead, copper, zinc,
and possible other metals from smelter flue dust which contains large
amounts of arsenic trioxide. The details of the process are proprietary
to ASARCO but it is conceivable that this basic process might be employed
to recover lead, zinc and copper from the arsenate pesticides as well.
However, it should be remembered that this process would still result in
the production of arsenic trioxide which is a disposal problem in its own
right.[1547]

Option No. 6 - Landfill

The disposal of arsenate compounds in sanitary landfills is generally
not acceptable because of the potential danger of ground and surface water
pollution as well as possible occupational hazards resulting from on-site
handling. There are, however, certain approved sites located over nonwater
bearing sediments or with only unusable ground water underlying them and
are completely protected from flooding and surface run-off or drainage such
as those designated as Class 1 sites in California. The disposal of small
stocks of arsenate pesticides or empty containers used to ship arsenate
particles in "Class 1" sites is considered as adequate, provided special
handling techniques as discussed in the previous section are employed to
protect site personnel.

To summarize, the adequate management methods for arsenate wastes
are: (1) recycle/reuse; (2) long term storage; (3) ship to ASARCO for
recovery of the metal values and long term storage of arsenic trioxide;
and (4) landfill in "Class 1" sites.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Arsenates are considered as candidate waste stream constituents for National Disposal Sites for the following reasons: (1) the high degree of toxicity of the compounds; (2) the nondegradable nature of the toxic arsenic component of the compounds; (3) arsenate wastes are present in sizable quantities as contaminated bags and empty containers, surplus pesticides, and contaminated soils; (4) arsenate wastes are widely distributed and are often handled by personnel without adequate training such as farmers; and (5) facilities for treating other arsenic-containing materials such as arsenic trioxide, arsenite and organic arsenical wastes will be required at National Disposal Sites.

The processes recommended for the treatment of arsenate wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Long term storage	First Choice	Best current method as there is no market demand for As_2O_3
Landfill	Second Choice	Disposal site must meet the criteria for a California "Class 1" site; recommended for the disposal of contaminated bags and containers.

Decontamination of soils containing high levels of arsenates as the result of repeated applications has been identified as a problem area. At the present time there does not appear to be a simple and economically feasible method available to render large acreages of arsenic poisoned farm land reusable for the growth of crops.

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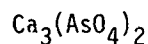
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name calcium arsenate (87)

IUC Name _____ _

Common Names Tricalcium o-arsenate, calcium o-arsenate

Structural Formula

$Ca_3(AsO_4)_2$

Molecular Wt. _____ 398.06 _____   Melting Pt. _1.455 $C^{(2)}$_   Boiling Pt._____

Density (Condensed) 3.62 g/cc$^{(2)}$ @ ___ ___   Density (gas)_____ @ ___ ___ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____   _____ @ _____   _____ @ _____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

   Cold Water   0.0139/100cc @ 25 $C^{(2)}$ Hot Water_____   Ethanol_____

   Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification Poison B   Coast Guard Classification Poison B

Comments___white, amorphous powder_____

_____
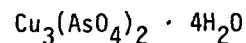
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References (1) 0766
          (2) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name copper arsenate (119)

IUC Name copper II orthoarsenate[1]

Common Names _____

Structural Formula

$$Cu_3(AsO_4)_2 \cdot 4H_2O$$

Molecular Wt. 540.52[1]   Melting Pt. _____   Boiling Pt. _____

Density (Condensed)_____ @____ ____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility
    Cold Water insoluble[1]   Hot Water insoluble[1]   Ethanol_____
    Others: acids, NH_4OH _____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification_____   Coast Guard Classification_____
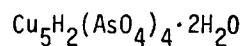
Comments_____

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name <u>copper arsenate</u> (119)

IUC Name <u>copper II dihydrogen ortho arsenate</u>[1]

Common Names_____

Structural Formula

$Cu_5H_2(AsO_4)_4 \cdot 2H_2O$

Molecular Wt. <u>911.42</u>[1]   Melting Pt. _____   Boiling Pt._____

Density (Condensed)_____ @_____ _____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

<u>Solubility</u>

　　Cold Water___<u>insoluble</u>[1]_____   Hot Water_____   Ethanol_____

　　Others:_<u>sol. in acids, NH_4OH</u>____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments_____

_____

_____

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

d. M. Name __Lead arsenate__ (235)

IUC Name _____

Common Names _acid lead arsenate[3] dibasic lead_
_____ arsenate, lead hydrogen arsenate___

Structural Formula

$PbHAsO_4$

Molecular Wt. __347.2[1]___   Melting Pt. _d. 720 C[1]__   Boiling Pt._____

Density (Condensed) _5.79 g/cc[1]_ @____ ____ Density (gas)_____ @ ____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____
Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility
   Cold Water __insoluble_____   Hot Water _slightly soluble[1]_ Ethanol_____
   Others: _sol. HNO_3, caustic[1]___

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification_____   Coast Guard Classification_____

Comments_____

References (1) 1570
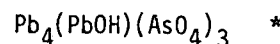
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name <u>lead arsenate (235)</u>

IUC Name _____

Common Names <u>basic lead arsenate</u>

<div style="border:1px solid">

Structural Formula

$Pb_4(PbOH)(AsO_4)_3$ *

</div>

Molecular Wt. _____ Melting Pt. _____ Boiling Pt._____

Density (Condensed)_____ @____'____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____°

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water_____   Hot Water_____   Ethanol_____

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____ <u>Multiwall paper bags</u>

ICC Classification <u>Poison Class B</u>   Coast Guard Classification_____

Comments <u>*Identified as the probable commercial basic lead arsenate[1]</u>

<u>No physical properties available for this complex compound since it occurs as a</u>

<u>mixture of various PbO/As_2O_3 ratios.</u>
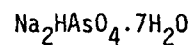
References (1) 1742

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Sodium Arsenate (376)__

IUC Name _____

Common Names _____

Structural Formula

$Na_2HAsO_4 \cdot 7H_2O$

Molecular Wt.[1] __312.01__ [1]   Melting Pt.[2] __125 C__ [1]   Boiling Pt. __-7 H_2O at 100C__ [1]

Density (Condensed) __1.871g/cc__ [1] @_____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55°C and 20°C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

   Cold Water __61 g/100 cc at 15C__ [1]   Hot Water __100g/100 cc at 100C__ [1]   Ethanol __Slightly Soluble__ [1]

   Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification____ Poison B ____   Coast Guard Classification_____

Comments_____

_____

_____

References (1) 1570

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc arsenate (453)

IUC Name _____

Common Names zinc o-arsenate Koettigite _____

Structural Formula

$$Zn_3(AsO_4) \cdot 8 H_2O$$
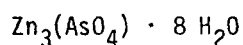
Molecular Wt. ___618.09___   Melting Pt. _H_2O at 100°C_   Boiling Pt._____

Density (Condensed)___3.309___ @ _15_ C[2] Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____   _____ @ _____   _____ @ _____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

    Cold Water___insoluble[2]___   Hot Water_insoluble[2]___   Ethanol_____

    Others:___H_3AsO_4, H_3PO_4, alk[2]___

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments_____

_____

_____

References (1)   0766

       (2)   1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Manganese Arsenate (500)__

IUC Name _____

Common Names_____

Structural Formula

$MnHAsO_4$

Molecular Wt. __194.9[1]__   Melting Pt. _____   Boiling Pt._____

Density (Condensed)_____ @_____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @_____   ·   _____ @_____   _____ @_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

   Cold Water__ Slightly soluble __ Hot Water_____ Ethanol_____

   Others:_____ Soluble in acids ___

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments__ Mfg. no manufacturing data available _____

_____

_____

References (1) 1492

PROFILE REPORT ON ARSENITES

Calcium Arsenite (88), Lead Arsenite (236), Potassium Arsenite (341)
Sodium Arsenite (377), Zinc Arsenite (454), and Copper Acetoarsenite (490)

1. GENERAL

The arsenite compounds are characterized as having the AsO_2 or AsO_3 radical in contrast to the AsO_4 radical of the arsenates. Only two of them are believed to have significant commercial consumption in the United States. Sodium arsenite is used as a poison in baits, a corrosion inhibitor, and a weed killer, while copper acetoarsenite, commonly known as Paris Green, finds general use as an insecticide. The other four arsenite compounds are not being used in significant amounts by any commercial or industrial interests.[1711,1763] Furthermore, it is difficult to even determine where to purchase these chemicals, a fact that is detailed later. For these reasons, the emphasis of this Profile Report will be directed towards the two compounds that have commercial significance in industry or agriculture and which could possibly occur as wastes from their use, or as surplus material. The Profile Report will also present the available pertinent information on the remaining compounds.

Copper Acetoarsenite

Paris Green is the common name for copper acetoarsenite $[(CH_3CO_2)_2Cu \cdot 3Cu(AsO_2)_3]$. In the late 19th century, it was a very common insecticide. It is useful against the potato beetle, the codling moth, and canker worms. It has some inherent disadvantages however, which include the tendency to burn foliage, rapid settling from suspensions and poor adhesive qualities. It has been virtually replaced by lead arsenate and organic pesticides, and is seldom used as an insecticide on crop plants. It is, however, finding considerable use as a larvicide to control mosquitoes.[1742] Paris Green is

also employed for the control of dry wood termites by injection, in solid form, into holes drilled in infested timbers. Production is at least 100,000 lb per year.[1785]

It is widely believed that Paris Green and its homologs are complex compounds of copper metaarsenite and the copper salt of acetic acid. The ratio of the two constituents is normally very close to 3:1. Paris Green is manufactured commercially by reacting sodium arsenite (prepared from white arsenic and caustic soda) with copper carbonate and acetic acid. Production is by means of a batch process. The reaction continues until the insoluble, green product precipitates from the solution. A complete reaction is indicated by a water white supernatant which contains only soda.[1785] This supernatant solution, said to be arsenic free, is dumped.

After application on crops, Paris Green breaks down rather rapidly. Decomposition through hydrolysis results in the formation of soluble arsenic compounds. This undesirable tendency to hydrolyze into soluble arsenic compounds, in addition to the commercial product containing additional soluble arsenic compounds, prevents the use of Paris Green on plants which are not highly resistant to the elements.[1742]

Sodium Arsenite

The common name sodium arsenite is given to a group of several compounds that are used as insecticides in baits and as herbicides for highway and railroad right-of-way weed control. These compounds probably consist mainly of either sodium orthoarsenite (Na_3AsO_3), sodium metaarsenite ($NaAsO_2$),or a combination of the two. This compound is always sold commercially in liquid form. It is manufactured by dissolving arsenic trioxide in liquid caustic soda. The sodium arsenite solution is filtered before drumming and the filter cake resulting from the filtration is buried in public dumps.[1740] The composition of the waste filter cake was not available and the public dump accepting these materials was not identified. A typical, commercial sodium arsenite solution contains 4 to 6 lb of sodium arsenite per gal. of solution. Other uses for sodium arsenite

solutions include treatment of certain plant diseases especially on grapes, subterranean termites, and a cattle, goat and sheep dip.[1728]

As well as can be determined, only two companies remain as major manufacturers of sodium arsenite. They are Chevron Chemical Corporation, and Los Angeles Chemical Company. Chevron Chemical Corporation markets a 42 percent sodium arsenite product under the name of W-41 Corrosion Inhibitor and Sodite Grape Spray, as well as a 55 percent arsenite product called Arsenical Weed Killer. Production of the sodium arsenite solutions from Chevron Chemical Company and Los Angeles Chemical Company are believed to be 200,000 to 400,000 gal. per year on a 4 to 6 lb per gal. basis. Sodium arsenite is shipped in steel drums, the maximum size being 55 gal. It is classified by Department of Transportation (DOT) as a Class B poison.

Other Arsenite Compounds

Very little information is available to define the properties, production methods, uses and the consumption of the other arsenite compounds that require discussion in this Profile Report. Lead arsenite and zinc arsenite are not listed in the three major important reference works on commercially available chemicals.[1571,1670,1790] Calcium and potassium arsenite were mentioned only in one of the three sources. This would indicate that these four arsenite compounds have a very small consumption within the United States. A brief discussion on these four compounds is presented in the following paragraphs.

Calcium arsenite ($CaHAsO_3$) is also known as monocalcium arsenite and is a white powder of varying composition which has high toxicity.[1742] It is classified as a Class B poison by the DOT, and can be used as an insecticide and germicide. No other uses were found outside agriculture.[1492]

There are two lead arsenite compounds which are included in the scope of this Profile Report. The first is lead mataarsenite which has the formula $Pb(AsO_2)_2$. It is insoluble in water and its only listed use is

an insecticide.[1742] It is classified as a Class B poison by DOT and it emits toxic fumes on heating.[0766] The other lead arsenite compound is that of lead orthoarsenite, $Pb_3(AsO_3)_2 \cdot XH_2O$. Generally, it has similar physical and toxic properties as the metaarsenite compound and its only known use is also as an insecticide.

There are two potassium arsenite compounds having properties suitable for commercial use. The first is potassium metaarsenite $(KAsO_2)$. It is soluble in water and is considered very poisonous, the LD_{50} for rats, orally, being 14 mg/kg.[1492] It is considered as a Class B poison by DOT. No reference describing potassium arsenite being useful as a pesticide was found. It was used in the manufacture of mirrors by reducing silver salts to metallic silver, and was, at one time, used in solution for medicinal purposes.[1492] The other potassium arsenite compound is potassium orthoarsenite, K_3AsO_3. It also is very soluble in water and is classified as a Class B poison by DOT. It is doubtful if any arsenicals are being used in medicine today.[1433] It was also determined that experts in mirror plating technology had no knowledge of potassium arsenite currently being used in the plating of mirrors. They indicated that the process would probably be legally banned if not already obsolete.[1769] Thus, there is no evidence of potassium arsenite being used in commercial enterprise.

Zinc arsenite, $[Zn(AsO_2)_2]$ is also known as zinc metaarsenite (ZMA). It is characterized by its low solubility in water and a toxicity that is similar to calcium arsenate.[1742] It is classified as a Class B poison by the DOT and has been used as an insecticide and a wood preservative.[0766]

<u>Market Trends for Arsenites</u>

The arsenical pesticide market has been in broad decline in recent years as a result of the strict government controls placed on them. These materials are highly poisonous in all forms and prolonged application of these and other arsenicals has caused a serious problem of arsenic buildup in the soil. There also is the threat of arsenic being leached out of the soil into streams and rivers where serious damage can occur to the aquatic life.

It is believed that the use of arsenicals will remain at approximately the same levels or may further decrease. Production of the materials will, of course, decrease as demand falls. Thus a large excess of unusable arsenite compounds is not expected to occur.

Sources and Types of Waste

The three major sources of arsenite wastes are: (1) pesticide manufacturers; (2) pesticide residue left in empty containers, and (3) surplus pesticides stored in Department of Defense (DOD) facilities, and possibly state/municipal facilities.

As indicated previously, the sodium arsenite solution is usually filtered before drumming in its production process, and the resulting filter cake is buried in public dumps. The composition of the waste filter cake is not known, but probably contains both sodium arsenite and arsenic trioxide, along with filter aid and water. No arsenic-containing waste is found in the manufacture of copper acetoarsenite.

Both sodium arsenite and copper acetoarsenite are normally formulated as water soluble concentrates or as aqueous solutions. As such, there are usually 0.5 oz to 1 lb of liquid residue left in the empty containers, depending on the shapes and sizes of the containers. The safe and economical disposal of pesticide contaminated containers remains a serious problem that is still unresolved.

Surplus arsenite pesticides currently in storage awaiting disposal in DOD facilities include: 110 gal. of sodium arsenite in Florida, 30 gal. of sodium arsenite in New York, 65 gal. of sodium arsenite in Illinois, 1,620 gal. of sodium arsenite in Alaska, 30,000 lb of 5 percent copper acetoarsenite solution in Florida. No arsenite pesticides stored in state/municipal facilities have been identified.

2. TOXICOLOGY

Human Toxicity

The arsenite compounds are highly toxic materials and are very dangerous even in low concentrations.[0766] The American Conference of Governmental Hygienists has recommended a Threshold Limit Value (TLV) of 0.5 milligrams/meter^3 for all arsenic compounds.[0225] This value represents the conditions to which nearly all workers may be repeatedly exposed without adverse effect.

Acute arsenic poisoning from ingestion results in irritation of the stomach and intestines with accompanying nausea, vomiting and diarrhea. In severe cases, collapse and shock can occur with a weak, rapid pulse, cold sweats, coma or death. The diagnosis of latent chronic arsenic poisoning is difficult since the condition may manifest itself with many different and unpredictable symptoms. Included are disturbances of the digestive tract, liver damage resulting in jaundice, blood and kidney disturbances and a variety of skin abnormalties.[0766]

Toxicity Towards Plant and Animal Life

Sodium arsenite is a strong herbicide while Paris Green harms all but a very few types of plants. Thus they are generally considered toxic towards plant life. No plant toxicity information was available on the other four arsenite compounds but they should be considered as equally toxic towards plants. The extreme toxicity of these compounds towards human life can be considered the same for animal life as well. Extreme precautions must be taken to prevent leaching from areas of application into streams and rivers where the arsenic compounds can adversely affect aquatic plant and animal life.

Emphasis has so far been placed on the arsenic constituent of the arsenite compounds being discussed, but it should not be forgotten that some of the cations involved in these compounds also have toxic properties.

The cations of copper and lead are, under general conditions, also very hazardous toward animal life. Therefore, the toxicity of these cations should at least be considered in the scope of this Profile Report inasmuch as they can render the appropriate arsenites even more toxic. The TLV's of these cations exclusive of arsenic are 1 mg/m^3 and less.[0225]

3. OTHER HAZARDS

The arsenites do not exhibite any explosive, flammable, or volatile properties nor do they present any other hazards.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The arsenite pesticides require special consideration on their storage, handling, transportation and disposal. Storage areas for these compounds should be isolated from locations where food and animal feed are stored. The solid arsenite compounds should be stored in the containers originally packed by the manufacturer. The use of protective clothing, goggles, gloves and dust filtering respirators are recommended for unloading or otherwise handling these pesticides. Similar precautions are recommended for handling any liquid solutions. Spills of the solid materials should be cleaned up using a vacuum cleaner after a fine spray of water has been laid down to prevent dust. The liquid compounds or formulations should be handled in an area such that in case of spills they can be contained for easy cleanup or transfer to a sump where they will not create a hazard if they are absorbed by the ground.

The arsenite compounds are labeled as Class B poisons and all DOT regulations should be followed when shipping, storing or otherwise handling them.

Disposal/Reuse

The wholesale disposal of arsenite compounds into the air, water, or soil must be considered completely unacceptable considering their high toxicities. The U. S. Public Health Service has established a maximum of 0.05 mg/l arsenic content (50 ppb) for drinking water if no other drinking water is available. The ideal maximum is 0.01 mg/l (10 ppb). The acceptable criteria for the release of arsenite compounds into the environment are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Calcium arsenite	0.005 mg/M^3 as As	0.01 TLV
Sodium arsenite	0.005 mg/M^3 as As	0.01 TLV
Copper acetoarsenite	0.005 mg/M^3 as As	0.01 TLV
Lead arsenite	0.005 mg/M^3 as As	0.01 TLV
Potassium arsenite	0.005 mg/M^3 as As	0.01 TLV
Zinc arsenite	0.005 mg/M^3 as As	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Calcium arsenite	0.05 ppm (mg/l) as As	Drinking Water Standard
Sodium arsenite	0.05 ppm (mg/l) as As	Drinking Water Standard
Copper acetoarsenite	0.05 ppm (mg/l) as As	Drinking Water Standard
Lead arsenite	0.05 ppm (mg/l) as As	Drinking Water Standard
Potassium arsenite	0.05 ppm (mg/l) as As	Drinking Water Standard
Zinc arsenite	0.05 ppm (mg/l) as As	Drinking Water Standard

There are channels by which unused and unopened containers of the arsenites can be returned to the manufacturer for resale. Representatives of the manufacturers also indicated that they would accept contaminated or otherwise unwanted material for reprocessing provided that the reprocessing was possible and that a market existed. Foreign markets for arsenite insecticides exist where the benefits of use outweighs the possible detrimental effects. The export of arsenicals should be licensed only when it can be shown that the materials can be used to create an overall environmentally desirable result. Arsenical pesticides are currently being exported in relatively small amounts (at least 300,000 lb in 1970).[1738]

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

There are six waste management methods which have applicability to the arsenite compounds and which are currently being used or which might be applied at a National Disposal Site. These methods apply mainly to the arsenite compounds used as insecticides. The herbicides and soil sterilizers are not expected to create a disposal problem in that if they ever require disposal they can be applied under new highway pavement and similar construction which requires sterile soil. It should also be stressed that regardless of the type of waste process employed, it still would be necessary to deal with toxic arsenic in some form. The following is a discussion of the options for the management of arsenite insecticides. insecticides.

Option No. 1 - Recycle/Reuse

Representatives of the three remaining manufacturers of arsenic pesticides have stipulated the conditions under which these materials were returned to them for reprocessing or resale in the past. Each firm accepted these arsenite materials for resale without any reprocessing if the batch had originally been made by the firm and if the materials were in their original unopened containers. Each firm above expressed its

reluctance to accept the product of other firms. Given the hypotehtical situation of a batch of materials which was unusable but was refinable, each firm indicated its willingness to accept it for reprocessing provided that there was an available market for the material.[1555, 1711, 1712]

Option No. 2 - Long Term Storage

The use of large, weatherproof and siftproof storage bins or silos is currently being used for the storage of other arsenic compounds, especially arsenic trioxide.[1547] Unwanted arsenites, already packed in the manufacturer's containers, could also be stored in these large weatherproof bins. This approach is a relatively expensive one which requires land and storage equipment in need for long, unknown periods of time before these materials can be moved by sale or disposal to other outlets. Insofar as

the arsenic compounds are poisonous in any form, long term storage is a safe method for managing the arsenite wastes.

Option No. 3 - Land Spreading

Some users, when faced with unwanted stocks of some arsenite materials, use land spreading as a means of disposal. This approach involves spreading the waste materials over large amounts of land in very light applications so as not to significantly affect any of the crops or plant life growing in the vicinity. This technique might be used for rare or infrequent disposal of small amounts of waste but in light of the fact that these compounds will build up in the soil by repeated application, this method cannot be considered as completely adequate and other methods should be considered first.

Option No. 4 - Export

Export of arsenite compounds, discussed previously, is not a disposal process but is a means of arsenical management preventing large unwanted overstocks provided that the advantages of their foreign use outweigh any detrimental effects. It should not be considered for the sole purpose of solving a U.S. problem at the expense of a foreign country.

Option No. 5 - Process for Recovery of Metals in Arsenites

American Smelting and Refining (ASARCO) has a process operating at its Tacoma, Washington plant whereby they are recovering lead, copper, zinc and possibly other metals from smelter dust which contain large amounts of arsenic trioxide. The details of the process are proprietary to ASARCO but it is conceivable that this basic process might be employed to recover lead, zinc and copper from the arsenical insecticides and herbicides as well. But it should be remembered that this process would still result in the production of arsenic trioxide which is a disposal problem in its own right.[1547]

Option No. 6 - Landfill

The disposal of arsenite compounds in sanitary landfills is generally not acceptable because of the potential danger of ground and surface water pollution, as well as possible occupational hazards resulting from on-site handling. There are, however, certain approved sites located over nonwater-bearing sediments or with only unusable ground water underlying them and are completely protected from flooding and surface runoff or drainage such as those designated as Class 1 sites in California. The disposal of small stocks of arsenite pesticides or empty containers used to ship arsenite pesticides in "Class 1" sites is considered as adequate, provided special handling techniques as discussed in the previous section are employed to protect site personnel.

To summarize, the adequate management methods for arsenite wastes are: (1) recycle/reuse; (2) long-term storage; (3) ship to ASARCO for recovery of the metal values and long-term storage of arsenic trioxide; and (4) landfill in Class 1 sites.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Arsenites are considered as candidate waste stream constituents for National Disposal Sites for the following reasons: (1) the high degree of toxicity of the compounds; (2) the nondegradable nature of the toxic arsenic component of the compounds; (3) arsenite wastes are present in sizable quantities as contaminated empty containers, surplus pesticides, and from pesticide manufacture; (4) arsenite wastes are widely distributed and are often handled by personnel without adequate training such as farmers; and (5) facilities for treating other arsenic-containing materials such as arsenic trioxide, arsenate, and organic arsenical wastes will be required at National Disposal Sites.

The processes recommended for the treatment of arsenite wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Long-Term Storage	First Choice	Best current method as there is no market demand for As_2O_3
Landfill	Second Choice	Disposal sites must meet the criteria for a California Class 1 site; recommended for the disposal of contaminated empty containers.

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        J. F. Clausen, TRW Systems, May 25, 1972.

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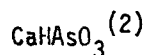   Co., 1969.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name _Calcium arsenite_ (88)

IUC Name _____

Common Names _Mono calcium arsenite_ [3] _____

Structural Formula

$CaHAsO_3$ [2]

Molecular Wt. _164.00_ [1]   Melting Pt. _____   Boiling Pt. _____

Density (Condensed)_____ @ ____ _____ Density (gas)_____ @ ____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____   _____ @ _____   _____ @ _____

Flash Point _____   Autoignition Temp. _____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water_____   Hot Water_____ ,   Ethanol_____

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification _Poison class B_   Coast Guard Classification _Poison class B_

Comments _used as insecticide and germicide; no other listed uses_ [2]. _White powder of varying_
composition. High mammalian toxicity [3]

References (1) 1570
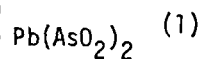   (2) 0766
         (3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Lead arsenite__ (236)

IUC Name __Lead meta arsenite__

Common Names_____

Structural Formula

$Pb(AsO_2)_2$ [1]

Molecular Wt. __421.03[1]__   Melting Pt. _____   Boiling Pt._____

Density (Condensed)__5.85 g/cc__ @____ ____ Density (gas)_____ @ ____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

　　Cold Water__insol._____ Hot Water_____ Ethanol_____

　　Others:___sol. acids_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification__Poison Class B__   Coast Guard Classification_Poison Class B_

Comments __Emits toxic fumes on heating[2]__ ~~Insecticide only listed use~~[2]

References (1)   1570
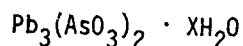　　　　　(2)   0766
　　　　　(3)   1492

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Lead arsenite__ (236)

IUC Name ___Lead ortho arsenite__[1]

Common Names_____

Structural Formula

$$Pb_3(AsO_3)_2 \cdot XH_2O$$

Molecular Wt. __954.45 +XH$_2$0__   Melting Pt. _____   Boiling Pt._____

Density (Condensed) _5.85[1]_ @_____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

    Cold Water___insol.[1]_____ Hot Water_____ Ethanol_____

    Others:__S Alk and NHO$_3$_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification__Poison class B_____   Coast Guard Classification_Poison class B_

Comments_Emits toxic fumes on heating[2] insecticide is only listed use[3]_____

References (1) 1570
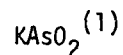
        (2) 0766

        (3) J492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium arsenite (341)

IUC Name Potassium meta arsenite [1]

Common Names _____

Structural Formula

$KAsO_2$ [1]

Molecular Wt. ___146.02 [1]___ Melting Pt. _____ Boiling Pt. _____

Density (Condensed)_____ @____ ____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55°C and 20°C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility
  Cold Water sol. [1] _____ Hot Water sol. [1] _____ Ethanol slightly sol.

  Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification Poison Class B _____ Coast Guard Classification_____

Comments _Very poisonous, LD$_{50}$ for rates orally is 14 mg/Kg. Mieron manufacture - reduce_
silver salt to metallic silver [2]. _1) Merck says item of commerce is approx. $KAsO_2$-$HAsO_2$_ [2].
2) Made into Karsenite solution, Fowlers solution for medicine for chronic dermatides, ____
charea [2]

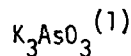References (1). 1570
          (2) 1492

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name _Potassium arsenite_ (341)

IUC Name ___Potassium ortho arsenite___

Common Names_____

Structural Formula

K_3AsO_3 [1]

Molecular Wt. __240.23[1]__   Melting Pt. _____   Boiling Pt._____

Density (Condensed)_____ @____ _____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

     Cold Water_very sol.[1]_____   Hot Water_____   Ethanol_sol.[1]_____

     Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_ Poison class B _____ Coast Guard Classification_____

Comments _Very poisonous. LD$_{50}$ for rates orally is 14 mg/Kg. Mirror manufacture - reduce_
silver salt to metallic silver[2]. 1) Merck says item of commerce is approx. KAsO$_2$-HAsO$_2$[2]
_2) Made into K arsenite solution (Fowlers solution) for medicine for chronic dermatitus,_____
_chorea[2]_____

References (1)   1570

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Sodium arsenite__ [377]

IUC Name __Sodium meta arsenite__

Common Names _____

Structural Formula

$$NaAsO_2 \text{ [1]}$$
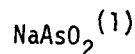
Molecular Wt. __129.91 [1]__ Melting Pt. _____ Boiling Pt. _____

Density (Condensed) __1.87 g/cc__ @_____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____ _____@_____ _____@_____

Flash Point _____ Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water__very sol. [1]__   Hot Water__very sol. [1]__   Ethanol__slightly sol__

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in __steel drums, 55 gallon max [2]__

ICC Classification __poison class B [2]__   Coast Guard Classification __poison class B [2]__

Comments: used in manf. of arsenical soaps, termites, and herbicides for RR and highway
weed control [3]

References (1) 1570
(2) 0766
(3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Zinc arsenite___ (454)

IUC Name ___Zinc in-Arsenite___

Common Names_____

Structural Formula

$$Zn(AsO_2)_2 \text{ (1)}$$
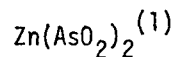
Molecular Wt. ___279.2[1]___   Melting Pt. _____   Boiling Pt._____

Density (Condensed)_____ @_____ Density (gas)_____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @_____   _____ @_____   _____ @_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water___Low solubility[2]___   Hot Water_____   Ethanol_____

Others:_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification___Poison B___   Coast Guard Classification___Poison B___

Comments___Highly toxic, a wood preservative, insecticide. Toxicity similar to calcium___
arsenate[2]

References (1) 0766
           (2) 1742

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Copper Acetoarsenite (490)___

IUC Name _____

Common Names _____

Structural Formula

$(CH_3COO)_2$ Cu $\cdot$ 3 $Cu(AsO_2)_3$ *
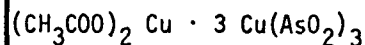
Molecular Wt. ___$669^{(3)}$ *___ Melting Pt. _____ Boiling Pt. _____

Density (Condensed)_____ @____ ____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____ Autoignition Temp.____

Flammability Limits in Air (wt %) Lower_____ Upper_____

Explosive Limits in Air (wt. %) Lower_____ Upper_____

Solubility

Cold Water ___slightly soluble[3]___ Hot Water_____ Ethanol_____

Others: ___soluble in dil. acids___

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in ___fiber drums, metal pails and cans___

ICC Classification ___poison class B___   Coast Guard Classification ___poison class B___

Comments _____

_____ Oral LD_{50} in rats = 22 mg/kg[2] insecticide, wood preservative, pigment
for ships[2] *Not officially accepted,

References (1)   0766
         (2)   1492
         (3)   1742

PROFILE REPORT

Magnesium Arsenite (245)

1. GENERAL

The Profile Reports on Calcium Arsenite (88), Sodium Arsenite (377),
Copper Acetoarsenite (490), Lead Arsenite (236), Potassium Arsenite (341),
Zinc Arsenite (454), and Arsenic Trioxide (51) indicate that for waste
arsenite compounds and arsenic trioxide, long term storage is the best
option for waste management. Disposal of arsenite compounds or arsenic
trioxide in typical landfills is not recommended because of their high
toxicity and appreciable (though slight) solubility. Though the quantity
of arsenite projected for manufacture over the next five years is small,
considerable arsenic trioxide will be collected as a byproduct of copper,
lead, and gold smelting industries and as a residue from destruction by
combustion of organic compounds containing arsenic.[0634]

Even though the arsenite compounds and As_2O_3 are stored in sealed
containers, their solubility creates a potential problem. Ferric and
magnesium arsenites are very slightly soluble. Therefore, the arsenites
and As_2O_3 can be rendered nearly insoluble by addition to a suspension of
magnesium hydroxide, and thus their long term storage made safer.

The physical/chemical properties of magnesium arsenite are not given
because magnesium arsenite is not a compound but a name applied to a group
of compounds.

2. TOXICOLOGY

All arsenic compounds are highly toxic materials and are very dangerous
even in low concentrations.[0766] However, the solubilities of mixtures of
arsenites and magnesium hydroxide are so low that these mixtures are
relatively non-toxic, magnesium hydroxide being given to treat arsenite or

As_2O_3 poisoning. The American Conference of Governmental Hygienists
recommended a Threshold Limit Value (TLV) of 0.5 mg per cubic meter for
all arsenic compounds.[0225] A detailed discussion on arsenite toxicology
is given in the Profile Report on the Arsenite Compounds (88, etc.).

3. OTHER HAZARDS

Magnesium arsenite does not exhibit any explosive, flammable, or
volatile properties nor does it present any other hazards in an alkaline
environment. When reacted with strong acids, the arsenic content of the
material is solubilized.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

As previously indicated, magnesium arsenite is formed in the treatment
of other arsenic wastes. It has no known use. Magnesium arsenite
with magnesium hydroxide should be handled in the same manner as described
in the Profile Report on the Arsenites (88, etc.).

The arsenite compounds are classified by the Department of Transportation
(DOT) as Class B Poisons.

Because the wholesale disposal of arsenite compounds into the air,
water or soil is considered completely unacceptable, aqueous discharge of
arsenic compounds has been limited to concentrations below 1 ppm. Storage
of arsenic compounds including As_2O_3 and the arsenites is usually in large,
waterproof and siftproof storage bins or silos. This approach is expensive,
but usually satisfactory. If the storage period is anticipated to be very
long or the stored material is subject to exposure through natural causes,
As_2O_3 or arsenite compounds should be added to a suspension of magnesium
hydroxide. This mixture should be stored under the controlled conditions
noted above.

The safe disposal of magnesium arsenite is defined in terms of the recommended provisional limits in the atmosphere, in potable water and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Magnesium Arsenite	0.005 (as As) mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Magnesium Arsenite	0.05 (as As) mg/1	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

As previously indicated, magnesium arsenite is made as a product of a waste treatment process. It should be stored in weatherproof and sift-proof storage bins or silos without additional treatment except the water present may be permitted to evaporate. This is a recommended mode of disposal.

The disposal of arsenite compounds in sanitary landfills is generally not acceptable because of the potential danger of ground and surface water pollution, as well as possible occupational hazards resulting from on-site handling. There are, however, certain approved sites located over nonwater-bearing sediments or with only unusable ground water underlying them and are completely protected from flooding and surface runoff or drainage such as those designated as Class 1 sites in California. The disposal of small stocks of magnesium arsenite wastes in "Class 1" sites is considered as adequate, provided special handling techniques as discussed in the previous section are employed to protect site personnel.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Magnesium arsenite is considered as a candidate waste stream constituent for National Disposal Sites for the following reasons: (1) the high degree of toxicity of the compound; (2) the nondegradable nature of the toxic

arsenic component of the compound; and (3) facilities for treating arsenites and other arsenic-containing materials such as arsenic trioxide, arsenate, and organic arsenical wastes will be required at National Disposal Sites.

The processes recommended for the treatment of magnesium arsenite wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Long-Term Storage	First Choice	Best current method as there is no market demand for As_2O_3
Landfill	Second Choice	Disposal sites must meet the criteria for a California Class 1 site; recommended for the disposal of magnesium arsenite contaminated solid wastes.

7. REFERENCES

0225. American Conference of Governmental Hygienists. Threshold Limits
      for 1971. Occupational Hazards, Aug. 1971. p. 35-40.

0634. Sullivan, R. J. Air pollution aspects of arsenic and its compounds.
      Bethesda, Litton Systems Inc., Sept. 1969. 72 p.

0766. Sax, N. I. Dangerous properties of industrial materials. 2d ed.
      New York, Reinhold Publishing Corporation, 1957. 1,467 p.

PROFILE REPORT

Ammonium Chromate (21), Ammonium Dichromate (22),
Potassium Chromate (343), Potassium Dichromate (345),
Sodium Bichromate (379,388), Sodium Chromate (386)

1. GENERAL

The hexavalent chromium (Cr^{+6}) salts of the alkali metals and ammonia
find widespread use in industry and are found as wastes in virtually every
industrial area in the United States.[0317] However, since the trivalent form
of chromium (Cr^{+3}) is also poisonous and hazardous to the environment, it
will also be discussed as part of this Profile Report insofar as it plays an
important role when it occurs in the handling and disposal of waste hexa-
valent chromium compounds. For the purposes of this report, the term "chro-
mates" will be used to describe all the hexavalent chrome oxides in either
the chromate or dichromate form.

Manufacture

Sodium chromate and dichromate are produced by roasting the chrome
ore in the presence of soda ash, lime or a mixture of the two. The
resultant sodium chromate from the roasting process is further processed
to yield the dichromate.

$$2 \ Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$
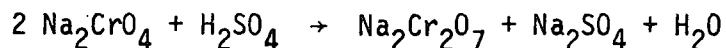
The byproduct sodium sulfate is recovered and sold as chrome salt cake for
use in the paper industry with about 0.2 percent $Na_2Cr_2O_7$. A simplified
flow diagram of this process can be found in the Encyclopedia of Chemical
Technology[1433] and additional details on the manufacture are found in NDC
Pollution Control Review No. 6.[0653]

Potassium chromates and dichromates can be produced by ore roasting using potassium carbonate much in the same manner as with sodium chromates, but a process using potassium chloride and sodium chromate is economically preferable.

$$Na_2CrO_4 + 2KCl \rightarrow K_2CrO_4 + 2NaCl \quad \text{and}$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$
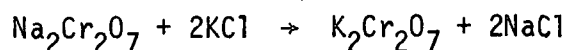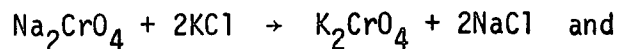
Ammonium chromate and dichromate are also produced by combining the appropriate sodium salt with ammonium sulfate in a process similar to that for the potassium compounds.

$$Na_2CrO_4(NH_4)_2SO_4 \rightarrow (NH_4)_2CrO_4 + Na_2SO_4 \quad \text{and}$$

$$Na_2Cr_2O_7(NH_4)_2SO_4 \rightarrow (NH_4)_2Cr_2O_7 + Na_2SO_4$$
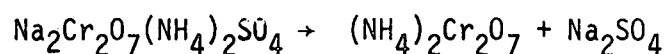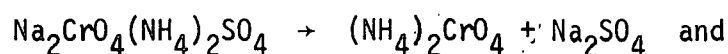
The distribution of $Na_2Cr_2O_7$ consumed by various industries in 1968 is as follows from Chemical Profiles.[1506]

Pigments	40 percent
Leather tanning	18 percent
Chromic acid(plating)	17 percent
Metal treatment	10 percent
Textiles and dyes	6 percent
Export and other	9 percent

The estimated 1972 demand for $Na_2Cr_2O_7$ made in 1968 was 145,000 tons.[1506] The physical, chemical and hazardous properties of these materials are discussed later in this report and are included on the attached worksheets.

Sources and Types of Chromate Wastes

All of the industries mentioned above, with the possible exception of the pigment industry, can be considered significant sources of these

hexavalent chrome (Cr^{+6}) wastes. A situation which serves to illustrate the wide spread use of these materials is that virtually all cooling towers in use as heat sinks in industry and large air conditioned buildings contain chromates which serve as algaecides and corrosion inhibitors. The amount of blowdown, i.e., cooling water removed to prevent mineral buildup in the cooling water from evaporation losses, is in the multiple billions of gallons containing 10 to 300 ppm Cr^{+6}. The more specific details on Cr^{+6} wastes from industry sources are outlined below.

In addition, surplus chromates and dichromates are sometimes stored in Department of Defense (DOD) facilities awaiting proper disposal. These include: (1) anhydrous sodium chromate--33,837 lb in California, 100 lb in Washington; (2) sodium dichromate dihydrate--7qt in Virginia, 500 lb in Georgia; (3) potassium dichromate--3,000 lb in Tennessee.

Metal Finishing Industry

The electro plating and metal finishing industry stands out as a major source of chromium and chromate waste products. A representative of Industrial Filter and Pump Inc. of Chicago, Illinois estimates that in the decorative chrome plating operation only 10 percent to 20 percent of the chrome consumed in the industry winds up on the plated product.[1471,1472]

The wasted chrome compounds occur as a result of rinsing operations, spillage, mists from hot tanks and large amounts of chromates used in cleaning, pickling and post plating solutions which become easily spent and are frequently discarded. The actual chromium plating tanks are in themselves not major sources of chromate wastes. The lifetime of a chromium plating tank can be considered indefinite because of the many available procedures for removing unwanted impurities.

The OPD Chemical Profiles on sodium bichromate and chromic acid indicates that about 40,000 tons of chromium compounds, calculated as chromic acid, will be consumed by the metal finishing industry in 1972.[1506] Assuming that the higher estimates of 20 percent of the chromium purchases will

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be ultimately found on a product, then about 32,000 tons of chromium, calculated as chromic acid, will ultimately end up as various chromate wastes. Lancy has recently estimated that no more than 25 of the largest decorative chrome plating shops in the United States have any type of chrome solution recycling systems.[1474] James Zebers, of Industrial Pump and Filter Corp. estimates that recycling accounts for approximately 30 percent of the total chromium waste.[1471] This would indicate that at least 22,000 tons are subject to single pass, once only use before ending up as wastes.

These chromate compounds are finding their way to waste status for three main reasons. The cleaning-treating baths have too many impurities of the type that makes recovery infeasible for any plant. Small plants that account for about half the total plating work are too small to economically justify recycling equipment. Many plants are permitted to discharge into municipal sewers after reduction of Cr^{+6} to Cr^{+3} due to political and technological reasons which are varied and result from local conditions.

Chromate wastes are at least reduced to the trivalent state Cr^{+3} in the great majority of the shops in the United States. Those few that discharge Cr^{+6} will be restrained from doing so by municipal authorities in the near future. Once in the trivalent form, the Cr^{+3} is either (1) precipitated as the hydroxide by pH adjustment in the plant and picked up by a disposal firm, or (2) the neutralized Cr^{+3} solution is directly discharged to the sewer.

The composition of the chromium wastes from the metal finishing industry varies widely with the type of metals being processed, the metals being plated, the design of the equipment, and other important factors. The levels of chromium normally vary from a few ppm to a few percent of the total waste stream. Wastes from metal finishing may include many other metals such as copper, zinc, cadmium, and nickel. Likely to be included in the stream are grease, oils, acids, organic additives and cleaning agents. The forms and composition of some typical chromium containing metal finishing waste streams have been obtained from various industry sources and are summarized here (Table 1).

TABLE 1

TYPICAL METAL FINISHING WASTE STREAMS CONTAINING CHROMIUM

Waste Description	Form	Source: Industry/Process
3000 ppm of a mixture of chromium, 20% aluminum sulfate and 35% sulfuric acid (trace of copper, nickel, lead)	Liquid	Aluminum anodizing bath with drag out
12.5% chromic acid - dichromate in 10% to 30% sulfuric acid with 5000 to 120,000 ppm chromium (85% as Cr^{+3}) with 100-1000 ppm lead, copper and iron	Liquid	Metal finishing
Dilute chromic acid solution containing chromium +3 at 100-200 ppm and chromium +6 at 2000 to 4000 ppm with traces of organics (combined wash waters).	Liquid	Metal plating
Partially neutralized aqueous plating waste containing 5-10% zinc chromate, and 5-10% zinc phosphate contaminated with various organic oils.	Liquid	Zinc plating
Solutions of chromates and dichromates in sulfuric acid (6-12%) containing 5000-170,000 ppm chromium with copper, lead and traces of organics.	Liquid	Formation of protective and decorative coatings (metals)
0.1-0.5% chromium, 100-400 ppm copper, 100-600 ppm nickel in 5-10% aqueous hydrofluoric-hydrochloric acid.	Liquid	Plating preparation (metal)
1 to 20% chromium in solids concentrations of 10-80% from settling and/or dewatering processes. Includes copper in varying amounts with varying amounts of inert filter aids.	Sludge	Chemical process (plating operations, manufacturing, metallurgical)
100-1000 ppm chromium as alkaline cyanide solutions (6-20%) with copper in varying amounts with possible traces of organics, nickel, lead and zinc.	Liquid	Metal plating (formation of protective and decorative coatings)
5-6% chromic acid in water solution with 1% iron	Liquid	(1) Metal Plating (2) Shipbuilding
9% chromic acid in 13% aqueous sulfuric acid	Liquid	Metal finishing and plating
0.1-1% sodium or potassium dichromate in water, usually sulfuric acid present in a 1-15% concentration	Liquid	(1) Metal Finishing (2) Shipbuilding (3) Plating

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Textile Mill Products

The sources of chromate materials in the textile industries arise from two rather distinct sources. One is the wide spread use of cooling towers in the textile industry which have the normal operating wastes from blow-down of 40 to 400 ppm chromate solutions. The chromate containing blowdown waters are normally fed into the common waste flow for·subsequent treatment within the plant.

The second source of chromate compounds are those used to oxidize and make, wash fast, the sulfur dyes for relatively inexpensive cotton goods. The oxidizing agents are normally the chromate compounds in water/acetic acid. Excess amounts of the chromate oxidizing solution are carried over into rinses from the dying vats along with spent trivalent chromium materials. The waste water from the dye oxidization and rinsing operations are fed into the common waste effluent stream within the mill for subsequent treatment. It is not possible to determine the amount of chromate compounds which are normally consumed in these dye oxidizing steps. However, since Chemical Profiles indicates that 6 percent of the dichromate prodution was utilized by the textile industry one might estimate that about 8,700 tons were consumed in all textile operations including dye oxidization and maintenance of the cooling towers. The larger portion of these chromium compounds occur as wastes. The current trends for using chrome in sulfur dying reflect decreasing use. Sulfur dyes are becoming obsolete and chromate oxidizing agents are being replaced by perborates and peroxides as a result of environmental considerations.

Most of the southern mills have some sort of on-site water treatment facilities whereby the Cr^{+6} and the Cr^{+3} wastes are treated by normal reduction/precipitation techniques. An official of the American Association of Textile Chemists and Colorists indicates that virtually all of the southern mills have responded to the needs for water treatment. They have either entered into joint operation with a neighboring city or they have constructed their own on-site water treatment facilities. The northern

textile mills benefiting from the greater availability of water can be characterized as normally sewering their chromium wastes after reducing the chromates to Cr^{+3}.[1480]

A. D. Little has presented tabulated data for chromium waste effluent as a result of sulfur dying in their rough draft report of textile mill products under the industrial waste studies program for the water quality office of EPA.[0522] This data can be used to calculate chromate wastes if the amounts of sulfur dyed textiles are known.

Pigments

Pigment colors are made from the chromate compounds by various precipitations with barium, lead, molybdenum and zinc. They are employed widely in the paint, printing ink and plastics industries. They account for about 40 percent of the dichromates consumed in the United States.[1506] The process can be batch, wherein the precipitation, washing, and filtering steps are carried out within one or two vats. The operation may also be continuous, employing separate operations in a series of cascades. Most of these pigment compounds are highly insoluble and therefore are not a source of soluble hexavalent chrome. However, zinc chromate is slightly soluble in water and for that reason requires greater attention to reduce the losses during purification. All of the five largest plants have their operations east of the Mississippi river in Cleveland, New York, Delaware, Chicago and New Jersey. The companies contacted in the study all indicated that they are under strict regulations regarding the discharge of chromium wastes and all have their own on-site treatment facilities for Cr^{+6} reduction and hydroxide precipitation. They indicated that the pigment manufacturing processes were operated so as to minimize both chrome compound wastes and the wastes of the heavy metals for economic reasons. It was stated that, whenever possible, rinse waters are recycled to the precipitation tanks in order to reduce the wasting of the heavy metal ions or the hexavalent chrome compounds which often are added in excess to promote precipitation. Some production figures from 1970 were supplied by E. I. DuPont as being estimated of production in the entire industry: chrome yellow, $(PbCrO_4)$ 31,752 tons; molybdate orange, 10,858 tons; zinc yellow, 7,291 tons.

Chromate wastes are generated, however, from the manufacture of solvent-based paints as a result of kettle washings and equipment clean-up. The typical solvent-based paint sludge is characterized by the following composition: 4.5 percent inorganic pigment (excluding titanium dioxide), 8.5 percent titanium dioxide, 14.5 percent pigment extenders, 25.0 percent binders, and 47.5 percent organic solvents. It is estimated that 137,000 lb of chromium, mostly as lead and zinc chromates, are lost through 36,800,000 lb of solvent-based paint sludges each year. The paint sludges are currently being disposed of in sanitary landfills, although incinerator systems to handle these wastes are now under development.

A lesser hazard associated with the chromate-based paints is the paint residue left in containers discarded in municipal dumps. An estimated 963,000 lb of chromium (mostly in the form of chromates) are lost through the 221,000,000 lb of paint residue each year.

The Tanning Industry

The leather tanning and finishing industry is a significant consumer of chromate and dichromate chemicals for use in chrome tanning operations. Sodium dichromate is the only chemical which is normally purchased for chrome tanning. It is reduced to chromium sulfate before hide impregnation and fixing. Some tanning plants purchase the sodium dichromate and convert it within the plant to chromic sulfate. Others purchase the chromic sulfate in powder form from tanning supply houses. Chromic sulfate is the principal chromium waste from the tanning operations and this is discussed in greater detail in the Profile Report on Chromic Sulfate (486).

Photography

Chromate compounds occur in the photographic industry as a result of the gravure and leather press plate making operations. The industry purchases only the ammonium chromates and appear to be the only consumer of these low volume chromate salts. Chromate solutions at about 4 to 5 percent are used to sensitize and polymerize gelatin coatings over copper plates

when exposed to light coming through a photo negative. Unexposed chromate coated gelatins are then washed away in water streams thereby exposing portions of the plate for etching. Chromates occur as wastes from washing the plates as well as from the chromate tanks which require dumping at 4 to 6 month intervals. An average size tank or tray contains 5 to 10 gal. of the solution. These tanks are normally emptied down a sink without any processing. An estimated 500 such plants are performing this type of operation across the nation. The resultant 4,000 lb of dichromates being dumped from this industry do not represent a significant hazard or pollution problem. As part of the manufacture of the lithographic plates discussed above, they are frequently chrome-plated to increase their resistance to wear on the presses. But this is normally done in a commercial plating shop with no different processes than normal chrome plating.

2. TOXICOLOGY

The chromates are very corrosive when in contact with skin and mucuous membranes. They produce ulcerous lesions which heal slowly. Salts of chromic acid have been associated with lung cancer. The Threshold Limit Value (TLV) for the hexavalent chromates Cr^{+6} is 0.1 mg/m^3 air while that for the reduced chromous and chromic ions is 0.5 mg/m3 air.[225]

The chromium containing sludges when occuring as a result of the standard reduction/hydroxide precipitation treatment methods can present a twofold toxicological hazard if landfilled. The sludges can contain soluble chromium salts and complexes which if leached out of the fill can be detrimental. It is also possible for acid species to be landfilled with the hydroxide sludges, dissolve them, forming water soluble chromium compounds. These water soluble materials can find their way to a potable water table from an inadequately placed landfill site.

3. OTHER HAZARDS

The chromates, save those of ammonium ion do not present a critical flammability or explosive hazard. Since they are powerful oxidizers, they should not be mixed with reducing agents or organic materials. Chromates are not corrosive to metals in the solid state. Concentrated aqueous solutions of the chromates at high temperatures will attack metals of which the least resistant are copper and its alloys (brass). Additional information is presented on the attached worksheets.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

This material must be stored so that it will not be subject to high temperatures, nor contact reducing agents. The type of container must be resistant to the particular chromate compound being stored. The creation of dust must be avoided during storage, transfer and handling of the materials. Workers among these materials should be adequately protected from contact of the materials with skin, eyes, or internal organs. Since large ingested doses can cause permanent injuries or death, adequate supervisory control of all operations and education of employees is highly important.

Guidelines considered adequate for the safe handling and storage of chromate wastes can be found in the data sheets of the Manufacturing Chemists Association,[0215,0217] but since chromium is toxic in all forms except in metallic form, the disposal of these materials in a safe manner must be carefully controlled. The Department of Transportation (DOT) classifies ammonium chromate and dichromate as flammable solids and requires a yellow warning label but Sax mentions no such requirements for the sodium and potassium salts.[0766] All additional federal regulations governing the handling, storing, loading and shipping of these materials must be observed.

Disposal/Reuse

Due to the fact that hexavalent chromium is extremely toxic towards marine plant and animal life, its discharge into open waterways is severly restricted. The Federal Water Quality Act of 1965 limits the discharge of this material. Each state is allowed to set its own upper limit for hexavalent chromium, but it is felt that the state levels are all set near the 0.05 ppm level recommended by the U. S. Public Health Service (USPHS) for potable water. The upper limit for discharge of hexavalent chromium to municipal sewage systems is normally set near 5 ppm, because this material can cause severe problems with biological treatment processes in sewage treatment plants unless discharged in low concentrations and dilutes on it's way to the treatment plant. For the safe disposal of chromates, the acceptable criteria for their release into the environment are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Ammonium Chromate	0.001 mg/M^3 as CrO_3	0.01 TLV
Ammonium Dichromate	0.001 mg/M^3 as CrO_3	0.01 TLV
Potassium Chromate	0.001 mg/M^3 as CrO_3	0.01 TLV
Potassium Dichromate	0.001 mg/M^3 as CrO_3	0.01 TLV
Sodium Chromate	0.001 mg/M^3 as CrO_3	0.01 TLV
Sodium Dichromate	0.001 mg/M^3 as CrO_3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Ammonium Chromate	0.05 ppm (mg/l) as Cr	Drinking Water Standard
Ammonium Dichromate	0.05 ppm (mg/l) as Cr	Drinking Water Standard
Potassium Chromate	0.05 ppm (mg/l) as Cr	Drinking Water Standard
Potassium Dichromate	0.05 ppm (mg/l) as Cr	Drinking Water Standard
Sodium Chromate	0.05 ppm (mg/l) as Cr	Drinking Water Standard
Sodium Dichromate	0.05 ppm (mg/l) as Cr	Drinking Water Standard

Reclamation of chromium values from sludges resulting from the treatment of chromate wastes is often technically feasible, but seldom practiced because of economical considerations.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

There are a number of available methods for use in handling hexavalent chromium (Cr^{+6}) wastes in aqueous solutions. Only two on-site treatment methods are used to any large extent in industry. These are reduction-precipitation and ion exchange. The remaining methods are not widely used, in development stages or are otherwise unproven. Finally there remains the practice of sewering large amounts of chrome wastes in both Cr^{+3} and Cr^{+6}.

Option No. 1 - Reduction/Precipitation

By far the most widespread method used for removing Cr^{+6} from industrial waters is chemical reduction followed by precipitation. The pH of the aqueous wastes is adjusted to between 2 and 3 and the hexavalent chromium is reduced to the trivalent state by the addition of suitable reducing agents. These reducing agents may vary depending on the availability of low cost by-product reducing agents from neighboring industries or reducing agents which may occur as wastes from nearby processes. Such reducing agents may include bottled SO_2 or that from flue gas, sodium sulfite and bisulfite from flue gas scrubbing liquids, iron filings, brass and aluminum chips or machining wastes. Plants without a reducing agent occuring as a waste or by-product normally employ sulfur dioxide gas, sodium metabisulfite, or ferrous sulfate. After reduction of the chromium to the trivalent state, the solution is made alkaline to pH 9.5 and the metal hydroxide is precipitated along with the hydroxides of other heavy metals. Aluminum sulfate (alum) or other suitable flocculating agents are often added to aid in precipitation, settling and clarification of the effluent. This procedure can be carried out either in batch type processes or continuous processes and complete equipment systems are available for performing this process on an automated or semi-automated operation. The biggest drawback of this procedure is the removal and disposal of the highly hydrated metal hydroxide

sludges. It is not unusual for these sludges to contain upwards of 75 to 80 percent water by volume. Precipitation and settling is normally a slow procedure and with high effluent flow it is normally necessary to have settling ponds or lagoons in which to allow the slow coagulation process to occur, the clear effluent removed and the sludge dried. No feasible economic process has yet been developed for the reclamation of any valuable metals or other credits from this type of sludge since it often contains various other organic and inorganic material which hinders purification and recovery. In the tanning industry where the chromium wastes are already trivalent it is possible to wash the chromium hydroxide/sludges, add sulfur acid to regenerate the chromic sulfate, and return it to the tan liquor tanks. However, at present this procedure is not considered economically feasible and is practiced very little if at all.

Chromic Hydroxide Sludge Disposal. There are three methods for handling the hydroxide sludges resulting from reduction/precipitation of hexavalent chrome which normally have other matter present. Listed in what is believed to be order of decreasing usage, they are landfill, ocean disposal and incineration. Landfilling involves burying the sludge which normally has been "aged" by storage in ponds where it yields up most of the water entrained in the sludge. Landfills have the advantage of isolating materials in areas where they will remain buried and are not likely to cause problems by contaminating underground water supplies or otherwise damaging neighboring plant and animal life. The disadvantages of landfill arise as a result of improper site selection, inadequate waste preparation, or mixing with acid wastes which could result in dissolution of Cr^{+3} into the leachate. This dissolution could lead to absorption of Cr^{+3} into the desert floor. The subsequent use of the landfill area for recreational or other purposes may be restricted by the materials which have been landfilled.

Ocean disposal of the sludge is accomplished by barging it to a recognized dumping area. Sea disposal has the advantage of not requiring site management other than testing the surrounding sea for waterborne pollutants. Disadvantages include possible conversion of sludges to soluble products harmful to sea life and the possible migration of hazardous concentrations to outside of the dumping area.

Incineration removes the water and organic material from the sludge but the ash normally is not economically recovered and is currently landfilled. The CrO_3 produced from incineration is water soluble while other oxide forms, CrO, Cr_2O_3 and CrO_2 are insoluble and present no problem. It is not known what form of the oxide is likely to occur from normal sludge incineration.

The costs for the chemicals used in the reduction of the hexavalent chromium to the trivalent chromium range from about 6 cents to 22 cents per lb of Cr^{+6} reduced depending on the reducing agents used.[0783] They can also be much less if waste product reducing agents are used. The amount of material necessary to readjust the pH of the solution to about 9.5 varies with the ratio of the acidity to the chromium content. Therefore, no actual figure for pH adjustment can be calculated. Lancy has attempted to predict the cost of metal finishing waste treatment and his work can be used as a guideline to predict costs once a particular waste stream is characterized.[1500]

Option No. 2 - Ion Exchange

Ion exchange processes for chromate removal from aqueous solutions have been used since the advent of chromate resistant resins 10 to 15 years ago. The obvious advantages here are that, due to the concentrative effects, it is possible to apply this process in recycling chromate materials or in concentrating wastes for transport to centralized disposal or conversion. Recent technology has enabled ion exchange to be extended into the fields of large volumes of water containing small concentrations of Cr^{+6} thus making it applicable to chromates from cooling tower blowdown.

Exhausted anion resins are normally regenerated by diluting them with a sodium hydroxide/sodium chloride solution to displace the chromates and then following with a pure sodium chloride solution to completely regenerate the resin. The cost of chemicals for regenerating the resin beds are estimated to be between 4 and 5 cents per pound of chromate as compared

with 17 to 19 cents for purchasing a pound of chromate. The capital costs for an ion exchange system to handle a 100 gpm flow rate with 40 ppm Cr^{+6} is estimated to be about $40,000 to $50,000. This figure of course will vary widely with type of plant, location and type of accompanying materials in the chromate solution.

The manner in which an ion exchange bed operates provides the basis for potential difficulties and disadvantages should the system be put to use. The chromate solution must be free of foreign materials such as organics, greases or solids for efficient operation. These would tend to physically clog the system or deactivate the catalyst bed. This problem can normally be overcome by a filtering process before such wastes enter the exchange beds. The other more serious disadvantage to ion exchange operation is that of the critical dependence on flow. These beds are designed to operate with a particular efficiency at a certain set flow. Should this flow be exceeded for even short periods of time, the efficiency for absorbing the chromate anion decreases drastically resulting in an effluent from the exchange bed which has chromate residues exceeding the designed effluent limits.

Option No. 3 - Discharge to Municipal Sewers

The practice of sewering Cr^{+3} and often Cr^{+6} is still considered to be widespread.[1480,1473] There are several reasons for this type of practice. From discharge permit information, the local sanitary officials normally have a good idea of the discharge levels and locations of discharge points for particular materials in their sewer systems. They can coordinate with industry at the various discharge points and establish levels of cooperation for the discharge of excessive pollutants. Often the case is such that all sources along a sewer line for a particular type of toxic material, chromium in this case, can discharge at apparent excessive but controlled levels by cooperation with sanitary officials and the result will be non-injurious to any waste water treatment facility. There are a number of reasons for this type of practice. Initially, the sanitation

officials do not have, or do not enforce, regulatory guidelines as to the amount of chromium that a particular source may discharge. Secondly, the presence of chromium and other heavy metal ions in sewage water has a significant beneficial effect on the sewage system. The heavy metal ions are instrumental in precipitating sulfides thereby helping to abate the odor problem as well as reduce the corrosive reactions between the sulfides and the underground concrete lines.

The chrome wastes are normally all reduced to Cr^{+3} and precipitated in transit to the sewage treatment plant. It is thus removed in the primary treatment steps and subjected to sludge digestion which does not change its form. The chrome precipitates, combined with the sludges, are then disposed of by the standard techniques such as incineration, landfill or ocean disposal. The long term accumulative effects of these sludges is unknown at the present time. In spite of the benefits that may arise from chromium in the sewer lines, it is felt that the sanitary officials would just as soon have no chrome in their systems due to the inherent problems that arise with chromium's toxicity related to its ultimate disposal.[1510]

Option No. 4 - Direct Precipitation

The direct precipitation of dichromate or chromate ions by the use of barium or lead salts is a workable method but is not normally economically feasible unless a market as pigments for the precipitates is available. The lead and barium compounds used in this precipitation are also highly poisonous, water soluble and relatively expensive. Furthermore, large excesses of the heavy metal cation would be necessary to effect a removal below a safe limit of 1 ppm since barium chromate, for example, has a solubility of about 4 ppm at 25 C.

Option No. 5 - Ion Flotation

Ion flotation is a process by which a surfactant is added to the effluent which reacts with the chromate ion to be removed and forms an insoluble surface active compound. Being surface active, this new material

will tend to concentrate at the interface between the solution and air as in a foam where there are high liquid/air interfaces. It is then possible to skim the foam from the solution thereby removing the chromate and dichromate anions in a higher concentration in the foam than in the solution. Sheppard and Jones refer to such a system which employed a three stage series operation. A feed stream containing 100 ppm dichromate was separated into effluent and foam stream containing 8 ppm and 468 ppm dichromate respectively. The concentration of surfactant in the solution was 400 ppm.[0617] Experiments conducted by Battelle Memorial Institute indicate that favorable removal efficiencies for Cr^{+6} and Cr^{+3} are being accomplished on a bench scale.[0773] The use of this type of system in waste treatment plants at present is not evident.

Option No. 6 - Electrochemical Conversion

Electrochemical reduction can be used in which hexavalent chromium can be electrolytically reduced to the trivalent state on a bed of semiconductive materials through which low voltage current flows. The development of such a process has advanced to the state where it is possible to treat dilute solutions of chromate ion rather effectively and the manufacturers of such equipment have stressed the applicability of such a device for cooling tower blowdown waters. Since the product is trivalent chromium, this procedure might possibly replace the chemical reduction previously discussed. This process does not concentrate chromates in effluents but may have process merit in dealing with concentrates received for ultimate conversion and recovery of chromium at a National Disposal Site.[0617]

Option No. 7 - Electrodialysis

Electrodialysis, also in its developmental stages, offers some advantages over ion exchange for the removal of chromates. The membranes used in this process do not require regeneration and the products from such a treatment process are chromate free water for recycling plus a concentrated solution of the original chromate salt which can also be recycled with or without further purification. The capabilities of the membranes are the

limiting factor at this time and the development of new membranes as well as a more sophisticated electrodialysis cell design may yield an equipment that is effective at chromate concentrations below 100 ppm, present effective limitation.[0617]

Option No. 8 - Adsorption on Activated Carbon

Activated carbon has been shown to remove hexavalent chromium from a synthetic waste solution in lab studies. Carbons produced from coal seem to have the best removal efficiencies. Battelle[0773] has conducted a pilot plant study and demonstrated that the technical feasibility of the process more or less parallels that of ion exchange in that the activated carbon must be disposed of or regenerated.

Option No. 9 - Liquid-Liquid Extraction

The removal of Cr^{+6} in aqueous media can be accomplished by a series of liquid-liquid extractions using an organic phase containing an extractant. Preliminary studies indicate that this process is functional over a wide range of chromate concentrations. The extractants are easily regenerated and the process appears to be adaptable to various volumes of waste flow.[0773]

Option No. 10 - Reduction of Cr^{+6} With Activated Carbon

Only sketchy details are available from an observation made during other activated carbon experiments by Battelle. Incomplete reduction occurs below pH3 with no reduction above pH3.[0773]

Option No. 11 - Reverse Osmosis

Plating shop installation of "R.O." units exist but not necessarily for Cr^{+6} compounds. Battelle studies indicate only fair removal efficiencies for Cr^{+6} but new technology is developing rapidly.[0773] The membranes are susceptable to extremes in pH and hence their use for acidic forms of the chromates are questionable.

To summarize, the adequate management methods for chromate wastes are: (1) reduction/precipitation followed by disposal of the waste chromic hydroxide sludges in either approved landfills or by incineration; (2) ion-exchange; and (3) electrochemical reduction. Direct precipitation of the chromates by the use of barium or lead salts involves potential handling difficulties because of the poisonous heavy metals involved. The other processes discussed--ion flotation, electrodialysis, activated-carbon adsorption, liquid-liquid extraction, activated-carbon reduction, and reverse-osmosis--are all in various stages of development and show promise as near future methods for treating dilute chromate wastes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The chromates and dichromates discussed in this Profile Report are considered as candidate waste stream constituents for National Disposal Sites for the following reasons: (1) the high degree of toxicity of the compounds; (2) hexavalent chromium oxides cannot normally be reduced to the nontoxic elemental chromium form; (3) the chromate and dichromate wastes appear in sizable quantities; (4) a substantial portion of the chromate and dichromate wastes are contributed by small plating shops that cannot afford waste treatment equipment; and (5) the disposal of waste chromium hydroxide sludges can be more adequately handled at a centralized facility and the chromium and heavy metal values present can be more readily recovered if such a need arises.

For the disposal of concentrated hexavalent chromate wastes at National Disposal Sites, it is recommended that a reductive-precipitative facility be constructed. This scheme is by far the most applicable approach for treating chromate concentrates in a National Disposal Site. The sub-process of electro-reduction might have merit to replace the chemical reduction step of the operation and save on necessary reducing chemicals. The technique is efficient and adequate for large scale removal of chromates. The effluent can have 1 to 2 ppm levels of Cr^{+3} or lower.

The permanent containerized storage or proper landfilling of chromium waste sludges or their incinerated residues are recommended for ultimate disposition. The landfill sites used must be located over nonwater-bearing sediments or have only unusable ground water underlying them and must also be completely protected from flooding, surface runoff or drainage, so that all waste materials and internal drainage are restricted to the site. The economics of transportation to the landfill or storage site must be considered in the decision to transport the hydrated sludge or to incinerate it prior to shipment. Such studies will be necessary in site selection and process recommendation for sites in various parts of the nation. The very same facility is usable for many of the toxic metal compounds which would also be likely to need disposal from time to time including cadmium, mercury, lead, copper, and arsenic.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Ammonium Chromate__ (21)

IUC Name _____

Common Names _____

Structural Formula

$(NH_4)_2CrO_4$
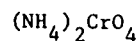
Molecular Wt. __152.09__[1]   Melting Pt. __d__[1]   Boiling Pt._____

Density (Condensed)__1.91__[1] @ __12__ __C__ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____   _____ @ _____   _____ @ _____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water__40.5 g/100 cc__ 30 C[1] Hot Water__d__[1]   Ethanol __insol.__[1]

Others: __slightly soluble in NH_3__

Acid, Base Properties __Aqueous solution is alkaline__[3] _____

Highly Reactive with __Reducing agents[2]. Shock or heat will explode it.__

Compatible with_____

Shipped in __Metal and fiber drums, tank trucks and tank cars__
                                      100 lbs
ICC Classification __Flammable solid, yellow lab__ Coast Guard Classification __same__[2]

Comments __Loses some NH_3 in air, keep well closed__[3]

References (1) 1570
           (2) 0766
           (3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Ammonium dichromate (22)___

IUC Name _____

Common Names_____

Structural Formula

$(NH_4)_2 Cr_2O_7$
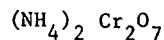
Molecular Wt. ___252.10[1]___   Melting Pt. ___d[1]___   Boiling Pt._____

Density (Condensed)_2.15 g/cc_ @_25 C_ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

<u>Solubility</u>   at 15 C(1)   30 C[1]
   Cold Water___30.8 g/100 cc___   Hot Water_89 g/100 cc at___   Ethanol___sol.___

   Others:_____

Acid, Base Properties_____1% aqueous soln. has pH 3.95_____

_____

Highly Reactive with____reducing agents,_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_flam. solid. yellow label,_ 100 lbs _Coast Guard Classification_____

Comments____very toxic_[2]_, strong oxidizer, decomposition becomes self-sustaining at 225 C

with heat and N_2 evolution[3]_____

_____

References (1) 1570
           (2) 0766
           (3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Potassium Chromate___ (343)

IUC Name _____

Common Names___tarapacaite_____

Structural Formula

K_2CrO_4

Molecular Wt. ___194.20[1]_____ Melting Pt. ___968.3[1]___ Boiling Pt._____

Density (Condensed)___2.732___ @ _20_ $c^{[1]}$ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____ _____@_____ _____@_____

Flash Point _____ Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility
    Cold Water___62.9 g/100 cc 20 $c^{[1]}$ Hot Water___79.2 g/100 cc___ 100 $c^{[1]}$ Ethanol___insol_____

    Others:_____

Acid, Base Properties___Alkaline to phenolphthalein_____

Highly Reactive with___reducing agents, organics_____

Compatible with_____

Shipped in___metal and fiber drums, multiwall paper bags, tank cars and tank trucks__

ICC Classification_____ Coast Guard Classification_____

Comments___irritants, ulcers, lung cancer___(2)___Being replaced by sodium salt_____

References (1) 1570
            (2) 0766
            (3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium dichromate (345)

IUC Name _____

Common Names Potassium bichromate [2]
_____ Red potassium chromate [2] _____

Structural Formula

$K_2Cr_2O_7$
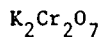
Molecular Wt. ___294.19 [1]___   Melting Pt. ___398 C [1]___   Boiling Pt. __d 500__

Density (Condensed) __2.68__ @ __25__ C [1] Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____   _____ @ _____   _____ @ _____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility   at 0 C[1]   100 C[1]
    Cold Water __4.9 g/100 cc__   Hot Water _102 g/100 cc at_ Ethanol__ insol __
    Others:_____

Acid, Base Properties __10% aq. soln. has 3.57 pH_____

Highly Reactive with____ reducing agents _____

Compatible with_____

Shipped in_ Metal and fiber drums, multiwall paperbags, tank cars and tank trucks

ICC Classification_____ Coast Guard Classification_____

Comments _____

References (1)   1570
           (2)   0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Sodium dichromate___ (379,388)

IUC Name _____

Common Names___sodium acid chromate[2]_____

Structural Formula

$Na_2Cr_2O_7 \cdot 2H_2O$
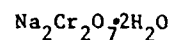
Molecular Wt. __298.1[1]_____   Melting Pt. ___-2H_2O 100 C[1] anh. 356.7[1]___   Boiling Pt.__d 400__[2]

Density (Condensed)__2.52__ @ _13_ c[1] Density (gas)_____ @ _____ °_____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility
Cold Water__238 g/100 cc at 0 c[1]__ Hot Water__508 g/100 cc at 80 C__ Ethanol__insoluble___

Others:_____

Acic, Base Properties_____

Highly Reactive with___reducing agents_____

Compatible with___Metals, wood fiber products_____

Shipped in__Metal drums, fiber drums, multiwall papersacks, tank cars and tank trucks

ICC Classification_____   IATA   Class A, no label
~~Coast Guard Classification~~   no limit(pass and

Comments____MCA requires warning label_____   air)

References (1) 1570

        (2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Sodium chromate (386)__

IUC Name _____

Common Names_____

Structural Formula

Na_2CrO_4
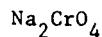
Molecular Wt. __162__[(1)] Melting Pt. _____ Boiling Pt._____

Density (Condensed)__2.710__[(1)] @_____ _____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water__87.3 g/100 cc at 30 C__[(1)] Hot Water_____ Ethanol _slightly soluble_

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with___reducing agents__[(2)]_____

_____

Compatible with___Metals and wood fiber products_____

_____

Shipped in_ Metal drums, paper bags (multiwall), tank cars and tank trucks ___

ICC Classification_____   Coast Guard Classification_____

Comments ___highly toxic, strong oxidizer__[(2)]_____

_____

_____

References (1) 1570

(2) 0766

PROFILE REPORT
Chromic Acid (114)

1. GENERAL

Introduction

Chromic acid is the common name given to chromium VI trioxide, CrO_3. It is also known as chromic anhydride. It is a poisonous, powerfully oxidizing, red, solid material. It is used almost exclusively in the metal finishing industry where approximately half is used in direct decorative chrome plating and the remainder is used in an assortment of metal treating baths including etching, passivation, and conversion coating.[1981] The annual consumption for chromic acid is estimated to be approximately 30,000 tons with 90 percent being used in the metal treating industry and the remaining 10 percent used for catalyst manufacture, refractory, or exported.[1506]

Manufacture of Chromic Acid

Chromic acid is produced by the reaction of sodium dichromate and sulfuric acid. Oleum, i.e. sulfuric acid charged with sulfur dioxide, is also commonly used.[1982, 1983] The mixture is heated to about 400 F whereupon the mixture separates into a chromic acid layer and an upper, less dense, sodium bisulfate layer. The layer containing the product is drawn off and solidified on water cooled flaking rolls while the bisulfate layer, which contains small amounts of chromium compounds, is returned to the supplier for reuse in making sodium dichromate.[1433, 1983] Normally there is no refining of any large amounts of this product which is characteristically 99.5 percent pure. The product is either sold as flake or is ground before packing in steel drums. There is no significant liquid effluent from the process except for occasional water washes from cleaning the process equipment. These washings are directed to sumps or evaporation ponds on the factory premises.

Sources and Types of Waste Chromic Acid

The metal finishing and chrome plating industry is responsible for very large amounts of chromic acid wastes. It is estimated that between 25,000 and 30,000 tons of chromic acid will be consumed in the metal finishing industry in 1972.[1506] Losses occur from metal treating tanks which are customarily dumped as they load up with grease, dirt, etc. The other major source of wasted chromic acid arises from dragout, i.e. the losses that occur from rinsing the parts after plating and metal treating. Equipment is available to minimize losses from dragout and recover reusable water, but the expense in purchasing this equipment cannot normally be justified in terms of the value of recoverable chromic acid. The waste management problems of chromic acid, as well as other hexavalent chrome compounds, are detailed in the Profile Report which discusses the ammonium, potassium, and sodium salts of the chromates and dichromates (21,345, etc.).

The composition of the chromium wastes from the metal finishing industry varies widely with the type of metals being processed, the metals being plated, the design of the equipment, and other important factors. The levels of chromium nominally vary from a few ppm to a few percent of the total waste stream. Wastes from metal finishing may include many other metals such as copper, zinc, cadmium, and nickel. Likely to be included in the stream are grease, oils, acids, organic additives and cleaning agents. The forms and composition of some typical chromium containing waste streams from metal finishing are:

(1) 3000 ppm of a mixture of chromium, 20 percent aluminum sulfate and 35 percent sulfuric acid (trace of copper, nickel, lead).

(2) 12.5 percent chromic acid - dichromate in 10 percent to 30 percent sulfuric acid with 5000 to 120,000 ppm chromium (85 percent as Cr^{+3}) with 100 - 1000 ppm lead, copper and iron.

(3) Dilute chromic acid solution containing chromium +3 at 100 - 200 ppm and chromium +6 at 2000 to 4000 ppm with traces of organics (combined wash waters).

(4) Solutions of chromates and dichromates in sulfuric acid (6-12 percent) containing 5000 - 170,000 ppm chromium with copper, lead and traces of organics.

(5) 0.1 - 0.5 percent chromium, 100 - 400 ppm copper, 100 - 600 ppm nickel in 5 - 10 percent aqueous hydrofluoric-hydrochloric acid.

(6) 5 - 6 percent chromic acid in water solution with 1 percent iron.

(7) 9 percent chromic acid in 13 percent aqueous sulfuric acid.

In addition, surplus quantities of chromic acid are sometimes stored in Department of Defense (DOD) facilities awaiting proper disposal. At present, this includes 800 lb in New Mexico and 200 lb in California.

2. TOXICOLOGY

Chromium trioxide CrO_3, when dry or in solution as chromic acid, is a very corrosive material and a strong oxidizing agent. If it contacts skin or mucous membranes, it can produce ulcerous lesions which heal slowly. The salts of chromic acid have also been associated with lung cancer. The Threshold Limit Value (TLV) for hexavalent chromates (Cr VI) is 0.1 mg/m^3 in air.[0225] Drinking water should contain no more than 0.05 ppm.[1752] The corrosive nature of chromic acid dictates that the material should also be kept away from contacting terresterial plant surfaces. No exact information was available regarding the harmful effects of chromic acid on aquatic plant and animal life but it is reasonable to assume that chromic acid is potentially very harmful.

3. OTHER HAZARDS

Chromic acid does not present a critical flammability or explosive hazard by itself, but since it is a powerful oxidizing agent, it should not be mixed with organic materials or other reducing agents. Even dilute organic solutions containing chromic acid should not be heated for fear of a violent reaction.[0215] Chromic acid is not corrosive to metals in the anhydrous state but concentrated aqueous solutions will attack some metals, the least resistant of which are copper and its alloys (brass).

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4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

When occurring as a concentrated waste product either in solid or
solution form, chromic acid must be stored away from high temperatures or
reducing agents. The correct container must be used for the solid or
solutions. The creation of CrO_3 dust must be avoided during storage,
transfer and handling of the material. Workers should be adequately
protected from contact of chromium trioxide with skin, eyes, or internal
organs. Since small ingested amounts can cause permanent injuries or
death, adequate supervisory control of all operations and education of
employees on the hazards of chromium trioxide is recommended.

General information on the properties and safe handling guidelines
of chromium trioxide are found in the data sheet of the Manufacturing
Chemists Association.[0215] Any and all additional federal regulations
governing the handling, storing, loading, and shipping of these materials
are to be observed.

Disposal/Reuse

The Federal Water Quality Act of 1965 limits the discharge, to open
waterways, of chromium trioxide and all other hexavalent chrome compounds.
Each state is allowed to set its own upper limit for hexavalent chromium
discharge but it is felt that the limits will all be set near 0.05 ppm,
the drinking water Standard recommended by the U. S. Public Health Service.[1752]
The upper limits of hexavalent chromium discharge to municipal sewage systems is
normally set by local authorities at about 0.05 ppm, a relatively low
concentration, since this material, when more concentrated, can cause
severe problems with biological water treatment processes in sewage treatment
plants. Practically speaking, this maximum discharge limit is very often
ignored when the discharge point is far enough from the water treatment plant
so that adequate dilution is usually achieved. Additionally it is felt that

hexavalent chrome is almost always reduced to Cr III and precipitated as the sulfide while in transit within the sewer by various other chemicals contained in the sewage.

For the safe disposal of chromic acid, the acceptable criteria for its release into the environment are defined in terms of the following recommended provisional limits:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Chromic acid in air	0.001 mg/M^3 as CrO_3	0.01 TLV
Chromic acid in water and soil	0.05 ppm (mg/l) as Cr	Drinking Water Standard

The metal finishing industry has been placed under pressure to control the amount of chromium trioxide that is being wasted to sewers and landfills but in many areas the water quality officials have not set levels of compliance or they are still allowing large discharges.[1473] Technology is rapidly developing which will enable the industry to economically recover a significant part of chromic acid for reuse, but the current general concensus is that while the technology may exist, the costs are still too high for economical operation in the average size metal finishing facility. The economics of chrome products may force the installation of chrome recovery. The types of processes which already have applicability towards chromic acid recovery include ion exchange and possibly reverse osmosis. Systems under consideration for potential applicability include electrodyalysis and liquid extraction.

5.   EVALUATION OF WASTE MANAGEMENT PRACTICES

Equipment and processes to handle waste chromic acid in solution can be divided into two main groups. The first group covers the equipment and methods to conserve chromium compounds by reconcentrating, purifying, and reusing them, or returning the concentrates to the manufacturer for reprocessing. The other group covers the method of treating hexavalent

chrome for ultimate disposal such as sewering or landfill without any
attempt at recovery or reuse. The waste treatment processes and equipment
are identified (Table 1), and discussed in considerable detail in the
Profile Report on the ammonium, potassium, and sodium salts of chromate
and dichromate anions (21,345, etc.).

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Chromic acid is considered as a candidate waste stream constituent for
National Disposal Sites for the following reasons: (1) the high degree of
toxicity of the material, (2) chromic acid cannot normally be reduced to the
nontoxic elemental chromium form; (3) chromic acid wastes appear in sizable
quantities; (4) a substantial portion of the chromic acid wastes are con-
tributed by small plating shops that cannot afford waste treatment equipments;
and (5) the disposal of waste chromium hydroxide sludges can be more adequately
handled at a centralized facility and the chromium and heavy metal values
present can be more readily recovered if such a need arises.

For the disposal of concentrated chromic acid wastes at National Disposal
Sites, it is recommended that a reductive-precipitative facility be constructed.
The reduction to Cr III is preferred over direct precipitation of Cr VI because
the required lead and barium reagents are highly poisonous, expensive and
require large excesses to precipitate below safe levels. Precipitation of
these materials, while not recovering chromium resources, is currently the
most reasonable approach for handling these substances based upon current
chrome prices (Table 1). The sub-process of electro-reduction could have
merit in replacing the usual chemical reduction step. This very same batch
process facility would be usable for many of the other heavy metal compounds
which also occasionally require disposal. These include cadmium, mercury,
lead, copper, and arsenic.

The permanent containment and storage or proper landfilling of the
resultant chromium waste sludges or their incinerator residues are recommended.
The economics for transportation to the landfill or storage site will have to
be considered in the decision to transport the hydrated sludge or to incinerate

TABLE 1

METHODS OF CHROMIUM TRIOXIDE CONCENTRATION FOR WATER PURIFICATION AND MATERIAL REUSE

Method	Remarks
Ion Exchange	Used in last 10 to 15 years for industrial chromate removal.
Ion flotation	Not developed enough for industrial use.
Electrodialysis	Not yet efficient enough for industrial use.
Adsorption on activated carbon	Efficient for final water polishing but creates problem of used carbon disposal.
Liquid-liquid extraction	Shows high merit but is only in early development stages
Reverse osmosis	Installations exist but not for chromates. Technology developing rapidly.

METHODS FOR UNRECOVERABLE FINAL DISPOSAL

Method	Remarks
Reduction to Cr III and precipitation by pH adjustment	Use is widespread in industry. Precipitates are normally landfilled.
Direct precipitation with barium or lead	Efficient method if market available for the precipitates as pigments. Not frequently used.
Electrochemical conversion to Cr III	Can be used to reduce to Cr III prior to precipitation, thereby eliminating need for reducing chemicals. Shows promise.

it prior to shipment. In addition, incinerating or dewatering the sludges should also be considered in an effort to make the entire disposal process more efficient from the standpoint of metals recovery.

The other processes mentioned (ion exchange, ion flotation, dialysis, reverse osmosis, liquid/liquid extraction, etc.) will result in reduced amounts of chromic acid wastes when they are employed in the metal finishing industry, but they are not applicable to National Disposal Sites since they are designed to process dilute aqueous wastes which could not economically be transported to a National Site. However one of these processes might be incorporated to purify the water used within the Disposal Site itself.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Chromic Acid___ (114)

IUC Name ___Chromium Trioxide___

Common Names___Chromic Anhydride_____

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┌─────────────────────────────────────┐
│         Structural Formula           │
│  ┌─────────────────────────────────┐ │
│  │                                 │ │
│  │             CrO₃                │ │
│  │                                 │ │
│  └─────────────────────────────────┘ │
└─────────────────────────────────────┘
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Structural Formula

CrO_3

Molecular Wt. ___100.01___   Melting Pt. ___197C decomposes___ Boiling Pt._____

Density (Condensed)_2.70___ @ _20_ C___ Density (gas)_____ @ ___._ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point noncombustible   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower___N/A_____   Upper___N/A_____

Explosive Limits in Air (wt. %)   Lower___N/A_____   Upper___N/A_____

Solubility

   Cold Water_164.9g/100g at 0 C___   Hot Water_206.7g/100g at 100C_ Ethanol_____

   Others:___H_2SO_4_____

Acid, Base Properties___concentrated solutions at elevated temperatures attack most common

metals and some plastics_____

Highly Reactive with_readily oxidisable organics(may ignite); intimate contact with powerful_

reducing agents can cause violent explosions[2]

Compatible with___certain oxidant-resistant plastics and mild steel_____

_____

Shipped in_steel barrels or drums, ICC spec. 6A, B or C or 17H, 37D, 37E_____

ICC Classification_oxidizing material[*]_____ Coast Guard Classification_oxidizing material_

Comments___TLV(ACGIH) 0.1 mg/m³ air_____

_____

[*] in solution DOT classification is corrosive liquid, white label, 1 gallon max._____

References (1) 0215

        (2) 0766

PROFILE REPORT ON

CADMIUM AND CADMIUM COMPOUNDS

Cadmium (81), Cadmium Powdered (82),

Cadmium Chloride (83), Cadmium Oxide (85),

Cadmium Phosphate (86), Cadmium Nitrate (479),

Cadmium Potassium Cyanide (480), Cadmium Sulfate (481)

1. GENERAL

Introduction

Cadmium is a metal which is not found as a free mineral in nature. Since pure cadmium is never found in a natural state and cadmium minerals are not found in concentrated form, metallic cadmium is always prepared commercially as a by-product of primary metal industries, principally the zinc industry. Cadmium is found not only in zinc ore but in lead ore, copper ore and other ores that contain zinc minerals. It is intimately associated with the zinc and when ores containing several minerals are separated, the cadmium remains with the zinc. Since the separation process is not exact, lead concentrate will contain a small quantity of zinc and a proportionally small amount of cadmium.

Cadmium compounds contain the element mainly in the divalent state. Cadmium ions in solution react with carbonates, phosphates, arsenates, oxalates, and ferrocyanides to form white precipitates, usually highly hydrated, whose physical characteristics vary with the conditions of precipitation.

In 1968 about 96 percent of the cadmium produced in the United States was primary cadmium and 4 percent was from secondary production - 45 percent recovered from foreign ores; 36 percent from domestic ores; 15.percent from imported flue dust; 4 percent secondary metal derived from reprocessing scrapped alloys.[1086]

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Cadmium in zinc concentrates from domestic mines is estimated at 5,304,000 lb/year. This is based on mine production of recoverable zinc, a zinc recovery efficiency of 83 percent and an average of 0.227 percent cadmium contained in 60 percent zinc concentrates. Cadmium in imported zinc ores is estimated at 6,208,000 lb/year.[1086]

In 1969, 12,646,000 lb of cadmium were produced in the United States.[1751] This figure includes cadmium metal and equivalent metal content of cadmium sponge used directly in production of compounds. Cadmium potassium cyanide was produced in very small quantity by City Chemical Company of Jersey City, New Jersey--they are not producing it anymore. They were the only company producing the compound and they only made about 5 or 10 lb of the chemical per year.[2219] Individual production figures for the other cadmium compounds discussed in this Profile Report are not available.

Manufacture

Cadmium Metal. Cadmium containing ore is mixed with sodium chloride and coal or coke and heated in a sintering furnace. By subjecting the ore to this chloridizing sinter, nearly complete elimination of cadmium as the chloride can be attained and most of it can be recovered. The dust from the roasters and the chloride fume are digested with sulfuric acid. Any lead present is filtered off as the sulfate and metallic cadmium is precipitated by the use of zinc dust. The remaining zinc chloride and sulfate solution is returned to the sintering operation. The cadmium is purified by distillation or electrolysis.[2039]

The purification of zinc sulfate solutions for lithopone or pigment zinc sulfide manufacture produces some cadmium by zinc dust treatment. Manufacturers of electrolytic zinc also produce considerable cadmium during their purification of zinc solutions in a similar way.

Some cadmium is volatilized in lead smelting and is caught in the flue system, particularly in the bag houses. If present in sufficient quantity, the dust is treated for cadmium recovery, usually by solution in sulfuric acid, followed by zinc dust precipitation.[2039]

Large-scale commercial facilities for the manufacture of cadmium metal include the following:[0624]

Amax; Blackwell, Oklahoma
Asarco; Denver, Colorado
Asarco; Corpus Christi, Texas
American Zinc Company; East St. Louis, Illinois
Anaconda; Great Falls, Montana
New Jersey Zinc; Depue, Illinois

Cadmium Chloride. The chloride may be made by dissolving the metal in an aqueous solution of hydrogen chloride and evaporating in a stream of hydrogen chloride gas. It may also be made by dissolving the oxide or carbonate in hydrochloric acid.[1433]

Cadmium chloride is produced by the following companies:[0624]

Allied Chemical Corporation; Harcus Hook, Pennsylvania
J. T. Baker Chemical Company ; Phillipsburg, New Jersey
Chemetron Corporation ; New Brunswick, New Jersey
The Harshaw Chemical Company ; Cleveland, Ohio
Mallinckrodt Chemical Works ; St. Louis, Missouri

Cadmium Nitrate. The nitrate is made by dissolving cadmium metal, cadmium oxide, or cadmium carbonate in nitric acid and evaporating to incipient crystallation. The anhydrous compound is made by dehydrating the tetrahydrate.[1433]

Cadmium nitrate is produced by the following companies:[0624]

Allied Chemical Corporation; Buffalo, New York
J. T. Baker Chemical Company; Phillipsburg, New Jersey
Chemetron Corporation; Cleveland, Ohio
The Harshaw Chemical Company; Glouscester City, New Jersey
Mallinckrodt Chemical Works; St. Louis, Missouri
The Shepherd Chemical Company; Cincinnati, Ohio

Cadmium Oxide. Cadmium oxide may be made in one of several ways; the pure metal may be distilled in a graphite retort and the vapor permitted to react with air (since the nitride does not form under these conditions, a pure oxide is obtained). This oxide varies in color and should be calcined at low red heat to give an oxide of uniform color. Cadmium carbonate and cadmium nitrate may be heated to their temperatures of decomposition to form the oxide.[1433]

Commercial facilities for the manufacture of cadmium oxide include the following:[0624]

Allied Chemical Corporation; Marcus Hook, Pennsylvania
American Smelting and Refining Company; Denver, Colorado
J. T. Baker Chemical Company; Phillipsburg, New Jersey

Cadmium Potassium Cyanide. Cadmium potassium cyanide is made by dissolving potassium cyanide in an aqueous solution of cadmium carbonate. The precipitate is collected and washed as crystals.[2219]

Cadmium Phosphate. Cadmium phosphate is prepared by interaction of cadmium nitrate with potassium dihydrogen phosphate in the present of the proper amount of sodium hydroxide.[2039]

Cadmium Sulfate. When cadmium metal, oxide, carbonate, or sulfide is dissolved in solutions of sulfuric acid and cooled or evaporated, cadmium sulfate (hydrate) crystallizes out. The anhydrous compound may be obtained by the reaction of dimethyl sulfate on finely divided cadmium carbonate, nitrate, halides, or oxide.[1433]

Commercial facilities for the manufacture of cadmium sulfate include the following:[0624]

Allied Chemical Corporation; Marcus Hook, Pennsylvania
American Smelting and Refining Company; Denver, Colorado
The Glidden Company; Baltimore Maryland

Uses

The chief use of cadmium metal in the United States is in electroplating iron and steel. The industrial and commercial applications for cadmium plating are numerous, including; components for aircraft, automobiles, electrical and electronic apparatus, household applicances, radio and television sets, hardware, and fasteners.[1086]

Cadmium metal is also used in pigments, plastics, alloys, and in making nickel-cadmium batteries. These uses represent more than 90 percent of the cadmium metal consumed in the United States in 1968. Smaller quantities, totaling about 1.1 million lb, were used in fungicides, nuclear energy applications, phosphors for television tubes, photography, lithography, process engraving, glass, X-ray screens, compounds for curing rubber, and various other applications.[1086]

The principal application areas of the other five cadmium compounds have been summarized by Athanassiadis (Table 1).[0624]

TABLE 1 0624

APPLICATION AREAS OF CADMIUM COMPOUNDS

Compound	Uses
Cadmium Chloride	In photography; in dyeing and calico printing; in the vacuum tube industry; in manufacture of cadmium yellow; special mirrors; as ice nucleating agent; lubricant; in analysis of sulfides to absorb the hydrogen sulfide.
Cadmium Nitrate	In making other cadmium salts; in photographic emulsions.
Cadmium Oxide	In phosphors , semiconductors, manufacture of silver alloys, glass; in storage battery electrodes; as nematocide; as catalyst for organic reactions; in cadmium electroplating; in ceramic glazes.
Cadmium Phosphate	Similar uses to those of normal phosphate.
Cadmium Sulfate	In electrodeposition of Cd, Cu, and Ni; in phosphors; in manufacture of standard cadmium elements.

Sources and Types of Cadmium Wastes

The metals industry is the major source of emissions of cadmium into the atmosphere. Cadmium dusts and fumes are produced in the extraction, refining, and processing of metallic cadmium. Since cadmium is generally produced as a by-product in the refining of other metals, such as zinc, lead, and copper, plants refining these materials are sources of cadmium emissions as well as of the basic metal. Also, because cadmium is present in small quantities in the ores of these metals, cadmium emissions may occur inadvertently in the refining of the basic metal.

The major sources of liquid and solid cadmium wastes have been found to include the following: (1) the electroplating industry; (2) nickel-cadmium battery manufacturers; (3) paint manufacturers; and (4) paint residue left in old containers.

The total amount of cadmium wastes from the electroplating industry is estimated to be 1.44 million lb per year. Some of the typical cadmium waste streams from the electroplating industry are:

(1) a liquid slurry containing 5 percent cadmium cyanide and 5 percent sodium cyanide in 10 percent aqueous sodium hydroxide;

(2) a liquid containing 1.5 percent cadmium cyanide and 8.5 percent sodium cyanide in 3 percent canister solution;

(3) a solid containing 3 percent cadmium oxide and 16 percent cadmium metals with alkali carbonates;

(4) 300 to 500 ppm cadmium chromate with aluminum alkaline salts, organic cleaners, and 95 percent water.

Cadmium waste from battery manufacturing is generated mainly in the production of sintered plate nickel-cadmium batteries. One form of the waste is the sludge which settles in the bottom of the baths that are used to impregnate the sintered plates with the active battery ingredients. There is also a liquid waste that comes from the intentional or accidental

discharge of the materials in the impregnation baths and from the rinsing operation (where the sintered plates are rinsed of excess material). It is estimated that there are 3,700 lb of cadmium wastes generated in the manufacture of nickel-cadmium batteries each year. A typical sludge from the production of nickel-cadmium batteries may contain 4 percent cadmium carbonate-hydroxide, 3 percent nickel carbonate, silica, other carbonates, and trace metals (40 percent total solids). A typical impregnation bath may be composed of 8 percent cadmium oxide, 0.6 percent nicklic oxide, 14 percent potassium hydroxide, and trace metals.

In the manufacture of solvent-based paints, sludges are generated from both the washing system and the solvent recovery stills. The combined solvent-based paint sludge is characterized by the following composition: 4.5 percent inorganic pigment (excluding titanium dioxide), 8.5 percent titanium dioxide, 14.5 percent pigment extenders, 25.0 percent binders, and 47.5 percent organic solvents. It is estimated that a total of 5,100 lb of cadmium are lost through 37 million lb of solvent-based paint sludges every year. The cadmium used in paints is usually chemically combined with either sulfur or selenium in the form of cadmium sulfide, cadmium selenide, or cadmium sulfoselenide.

The cadmium containing paint residues left in containers normally discarded in municipal dumps constitute another source of selenium waste. It is estimated that a total of 35,300 lb of cadmium are lost as paint residues every year.

Other sources of cadmium wastes as a contaminant in air or water may include the following: (1) cadmium compound manufacturers; (2) manufacture of cadmium-faced bearings; (3) casting of copper-cadmium alloys; (4) smelting of scrap metal (containing cadmium); and (5) welding of cadmium-plated metal parts.[0624]

<u>Physical and Chemical Properties</u>

The physical and chemical properties of cadmium metal and the six cadmium compounds are included in the attached worksheets.

2. TOXICOLOGY

The inhalation of fumes or dusts of cadmium primarily affects the respiratory tract; the kidneys may also be affected. Even brief exposure to high concentrations may result in pulmonary edema and death. Usually the edema is not massive, with little pleural effusion. In fatal cases, fatty degeneration of the liver and acute inflammatory changes in the kidneys have been noted. Ingestion of cadmium results in a gastrointestinal type of poisoning in its symptoms.

Inhalation of the dust or fumes may cause dryness of the throat, coughing, headache, a sense of constriction in the chest, shortness of breath (dyspnea) and vomiting. More severe exposure results in marked lung changes, with persistent cough, pain in the chest, severe dyspnea and prostration which may terminate fatally. X-ray changes are usually similar to those seen in broncho-pneumonia. The urine is frequently dark. These symptoms are usually delayed for some hours after exposure, and fatal concentrations may be breathed without sufficient discomfort to warn the workman to leave the exposure area.[0624,0766]

Ingestion of cadmium results in sudden nausea, salivation, vomiting, diarrhea and abdominal pain. Symptoms begin almost immediately after ingestion.

A yellow discoloration of the teeth has been reported in workers exposed to cadmium. Cadmium oxide fumes can cause metal fume fever resembling that caused by zinc oxide fumes.[0766]

Two studies made by Princi in the early 1950's indicate that cadmium may not be as great an industrial hazard as is generally considered.[2211,2212] Most of the deleterious effects of cadmium which have been reported are the result of relatively brief exposures to high concentrations of the substance. It is probable, therefore, that in chronic exposures there is a rapid elimination of cadmium from the body and that there is no cumulative effect. Princi observed and ran tests on twenty men who, at times, were exposed to cadmium concentrations as high as 31.30 milligrams per cubic meter of air in their work surroundings.[2212] The tests revealed no serious chronic effects in the workmen from continuous exposure to varying concentrations of cadmium (ranging from .04 to 31.3 mg per cubic meter).

The toxicity of cadmium toward fish was examined by Hiltibran.[2210] His data indicated that cadmium can disrupt energy production by the inhibition of oxygen uptake within the cells, and this disruption can occur at relatively low levels (0.0033 micromoles/ml) and be of such severity as to cause the deaths of fishes, particularly the bluegill.

Most quantitative data on the toxicity of cadmium toward fish are based on specific salts of the metal. Expressed as cadmium, these data indicated that the acute lethal level for fish varies from about 0.01 to about 10 mg/liter depending on the test animal, the types of water, temperature, and time of exposure. Cadmium acts synergistically with other substances to increase toxicity. Concentrations of 0.03 mg/liter in combination with 0.15 mg/liter of zinc causes mortality of very young salmon. In a study of adult American Eastern oysters, the eight week TL_m value for cadmium was 0.2 mg/liter and the fifteen week TL_m value was 0.1 mg/liter.[536]

The relative oral LD_{50} values to the rat are 88 mg/kg for cadmium chloride and 72 mg/kg for cadmium oxide. The estimated LC_{50} value for man is 50 mg/cubic meter of air for cadmium oxide. The American Conference of Governmental Industrial Hygienists (1971) recommended a Threshold Limit Value (TLV) in air of 0.2 mg/cubic meter of air for all the cadmium compounds discussed in this report, except for cadmium oxide. The TLV for

cadmium oxide is 0.1 mg/cubic meter of air.[0225] The U.S. Public Health Service established the permissible criteria for soluble cadmium in public water supplies as .01 mg/liter.[1752]

3. OTHER HAZARDS

The fire and explosive hazard of cadmium metal is moderate in the form of dust when exposed to heat or flame or by chemical reaction with oxidizing agents.[0766]

Cadmium nitrate is an oxidizing material. In contact with easily oxidizable substances it may react rapidly enough to cause ignition, violent combustion or explosion.[0766]

Other than the toxic effects, the other cadmium compounds discussed in this report present no further problems.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Care should be exercised in handling cadmium and its compounds because of their high toxicity. Any material which comes in contact with the skin should be removed with plenty of soap and water.

Cadmium nitrate should be stored in an area where it will be separated from combustible, organic or other readily oxidizable materials. Any spilled nitrate should be immediately removed and disposed of. All of the cadmium compounds discussed in this report should be stored away from foodstuffs, feeds, or any other material intended for consumption by humans or animals.

Adequate procedures for the transportation of cadmium compounds have been established by the Department of Transportation.[0278] Label requirements as well as the maximum quantities permitted to be shipped in one outside container, are also specified.

Disposal/Reuse

The greater portion of cadmium and cadmium compounds present in air and water waste streams can be removed and the cadmium recovered for its value. With the current technology available, and considering the economic factors involved, it is not possible to remove all of the cadmium that is discharged into waste streams. For these reasons, the safe disposal of cadmium and cadmium compounds must still be defined in terms of the recommended provisional limits:

Contaminant In Air	Provisional Limit	Basis for Recommendation
Cadmium metal (powder)	.002 mg/M^3	.01 TLV
Cadmium chloride	.002 mg/M^3	.01 TLV
Cadmium nitrate	.002 mg/M^3	.01 TLV
Cadmium oxide	.001 mg/M^3	.01 TLV
Cadmium potassium cyanide	.002 mg/M^3	.01 TLV
Cadmium phosphate	.002 mg/M^3	.01 TLV
cadmium sulfate	.002 mg/M^3	.01 TLV

Contaminant In Water and Soil	Provisional Limit	Basis for Recommendation
Cadmium metal (powder)	.01 ppm (mg/1)	Drinking water standard
Cadmium chloride	.01 ppm (mg/1)	Drinking water standard
Cadmium nitrate	.01 ppm (mg/1)	Drinking water standard
Cadmium oxide	.01 ppm (mg/1)	Drinking water standard
Cadmium potassium cyanide	.01 ppm (mg/1)	Drinking water standard
Cadmium phosphate	.01 ppm (mg/1)	Drinking water standard
Cadmium Sulfate	.01 ppm (mg/1)	Drinking water standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Removal from Air

The metals industry is the major source of cadmium emissions to the atmosphere. Cadmium dusts and fumes are produced in the extraction, refining, and processing of metallic cadmium. More than 2 million lb of cadmium were released to the atmosphere by the metals industry in 1968.[1086] Air pollution control procedures are employed at some metal refinery plants in order to recover the valuable cadmium that would otherwise escape into the atmosphere. Electrostatic precipitators, bag houses, and cyclones are effectively used for abatement.[0624] However, little information has been found on the specific application of these procedures for the purpose of controlling cadmium air pollution. Procedures for recovering cadmium from exhaust in a copper extraction plant collected significant quantities of valuable cadmium, at the same time reducing local air pollution levels.[0624]

Removal from Water

Option No. 1 - Adsorption with Granular Activated-Carbon Bed. The effectiveness of granular activated-carbon beds to remove cadmium from water has been investigated by Linstedt et al[2218] and Kuzin et al.[1813] Linstedt found in his study that following passage through a column, filled to a depth of 60 in. with 14 to 40 mesh granular activated-carbon, the initial concentration of 50.5 ppb of cadmium was reduced to .6 ppb. This represents a 98.8 percent removal of cadmium from the water. Kuzin's laboratory investigation was principally directed towards the separation of uranium from other metallic compounds in acetate solutions. It was found in the same study, however, that activated carbon possessed a sorption capacity for soluble compounds of 1.9 mg/g carbon. Adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute cadmium wastes.

Option No. 2 - Coagulation and Filtration. A pilot plant study by
Lindstedt et al [2218] showed that coagulation, sedimentation, and filtration
could be used to remove about 95 percent of the cadmium in a water supply
from a secondary water treatment plant. The concentration of the cadmium
in the water before the coagulation process was 5.5 ppb. Coagulation
was achieved by slaking commercial-grade lime and pumping it into the
influent wastewater flow line. The pH was approximately 11 in the
coagulation unit. After lime addition, the wastewater entered a rapid-mix
line. The lime feed point was at the head of the line, and mixing was
achieved through turbulence of the flow. Slow mixing and settling
of the cadmium hydroxide preciptate were achieved in a fiber glass tank
equipped with four vertical baffles and a mixing blade. It can be concluded
that chemical coagulation followed by sand filtration is an adequate method
for removing cadmium from water.

Option No. 3 - Ion Exchange. Ion exchange can be used to remove
cadmium from dilute aqueous waste streams. Cadmium will behave much like
calcium and magnesium and can be removed from an aqueous waste stream by
either a sulfonic acid type cation exchange resin or a carboxylic weak
acid type resin, depending upon the pH of the stream.[1795] The effectiveness
of ion exchange to remove cadmium from water has been investigated by
Linstedt et al.[2218] Linstedt found that the initial concentration of 50.5
ppb of cadmium in the water was reduced to .76 ppb. This represents a
98.5 percent removal of cadmium from the water. The major difficulty in
ion exchange operation is the critical dependence on flowrate. The ion
exchange system is designed to operate with a particular efficiency
at a certain set flow. Should this flow be exceeded, the efficiency for
adsorbing the cadmium ion decreases drastically causing the effluent to
exceed the permissible limit.

Option No. 4 - Reverse Osmosis. The effectiveness of reverse osmosis
to remove cadmium from water has been investigated by Sourirajan.[1812]
Following passage of a cadmium waste stream through a porous cellulose
acetate membrane, it was found that the cadmium concentration was
reduced from 59.1 ppm to 11.2 ppm. This represents an 81 percent removal of

cadmium from the water. With an effluent concentration of 11.2 ppm, the reverse osmosis unit would have to be used in conjunction with some other process (for example, adsorption with activated-carbon) to produce an effluent with a permissible concentration of cadmium.

The other treatment processes for the removal of cadmium from water that have been investigated include adsorption with zirconium phosphate, silica gel and charcoal. Akatsu et al [2220] demonstrated that the cadmium ion was only slightly adsorbed by zirconium phosphate and charcoal and not adsorbed at all by silica gel. These processes are therefore considered as inadequate methods for treating dilute cadmium wastes.

Concentrated Cadmium Wastes

The only adequate method for the disposal of concentrated cadmium wastes is coagulation with lime, then sedimentation followed by sand filtration. The effluent from this process would probably have to be treated further (for example, adsorption with activated-carbon or ion exchange) to reduce the cadmium concentration to a level in compliance with the U.S. Public Health Service recommendation for public drinking water (.01 mg/liter). The cadmium hydroxide sludge produced in this process can be dried and placed in an approved chemical landfill area of the California Class 1 type. Cadmium hydroxide is not very soluble (.00026g/100cc), so contamination of water supplies from the landfill operation should not be a problem. If the cadmium hydroxide sludge is relatively pure, it can be dissolved in sulfuric acid and the cadmium metal recovered by zinc dust precipitation (refer to section on Manufacture).

To summarize, the adequate treatment methods for dilute aqueous cadmium wastes are: (1) activated-carbon bed absorption; (2) coagulation and filtration; and (3) ion-exchange. For the concentrated cadmium wastes, coagulation with lime followed by sedimentation and sand filtration is the only proven and adequate treatment method at present.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Cadmium and cadmium compounds are considered as candidate waste stream constituents requiring National Disposal Site treatment for the following reasons: (1) the extremely high degree of toxicity of all cadmium compounds; (2) the nondegradable nature of the toxic cadmium component of all cadmium compounds; (3) cadmium compounds are present in sizable quantities as wastes from electroplating, paint manufacture, battery manufacture, and the metals industry; (4) a significant portion of cadmium wastes is contributed by small plating shops where treatment is either technically or economically infeasible; and (5) the cadmium hydroxide waste sludges resulting from the treatment of cadmium wastes should be disposed of in California Class 1 type landfills only and are not being adequately handled at present.

It is anticipated that disposal systems to handle both dilute and concentrated cadmium wastes will be required at National Disposal Sites. The processes recommended for the treatment of dilute cadmium wastes at National Disposal sites are:

Process	Order of Preference	Remarks
Coagulation and Filtration	First Choice	Demonstrated technology; can be effectively used to remove both dilute and concentrated cadmium wastes.
Activated-Carbon Beds	Second Choice	Demonstrated technology; recommended unit operation at National Disposal Sites.
Ion Exchange	Third Choice	Demonstrated technology; critical dependence on flowrate and economic factors limit the feasibility of this system.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ___Cadmium (81), (82)___

IUC Name _____

Common Names ___Cadmium_____

Structural Formula

Cd

Molecular Wt. ___112.41_____   Melting Pt. ___320.9 C_____   Boiling Pt. ___767_____

Density (Condensed)_____ @____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

___1 MM___ @ ___394 C___   ___.___ @_____   _____ @_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

   Cold Water__insolulbe_____   Hot Water__insoluble_____   Ethanol_____._____

   Others:____hot sufluric acid, ammonium nitrate_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments_____

_____

References (1) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Cadmium Chloride (83)__

IUC Name _____

Common Names_____

Structural Formula

$CdCl_2$

Molecular Wt. __183.32__   Melting Pt. ___568 C___   Boiling Pt.__960 C____

Density (Condensed)__4.047___ @ _25 C_____ Density (gas)_____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

___10 MM___ @ ___656 C__   __100 MM__ @ __797 C___   _____ @ _____

Flash Point _N/A_____   Autoignition Temp._N/A__

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

    Cold Water _90 g/100 g @ 0 C_____   Hot Water _147 g/mg @ 100 C_   Ethanol _slightly soluble_

    Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments__Hexagonal, colorless crystals_____

_____

_____

References (1)   0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Cadmium Oxide__ (85)

IUC Name _____

Common Names__Cadmium Oxide_____
      (1) amorphous, brown crystals
      (2) cubic, brown crystals

Structural Formula
CdO

Molecular Wt. __128.41__   Melting Pt.(1)1,496C;(2)900C Boiling Pt. 1559C

Density (Condensed) 6.95 @____ ____ Density (gas)_____ @ ____ ____
            8.15

Vapor Pressure (recommended 55 C and 20 C)

__1MM__ @ __1000C__   _____@_____   _____@_____

Flash Point _____   Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

    Cold Water__Insoluble_____ Hot Water__Insoluble_____ Ethanol_____

    Others:____Ammonia salts_____

Acid, Base Properties_____

Highly Reactive with_____

Compatible with_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____
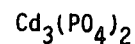
Comments_____

References (1) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name   Cadmium phosphate (86)

IUC Name   Cadmium ortho-phosphate

Common Names _____

Structural Formula

$Cd_3(PO_4)_2$

Molecular Wt. ___527.19_____   Melting Pt. ___1500 C_____   Boiling Pt. _____

Density (Condensed)_____ @____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____   _____ @ _____   _____ @ _____

Flash Point _____   Autoignition Temp. _____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water   insoluble_____   Hot Water_____   Ethanol_____

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

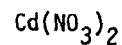ICC Classification_____ Coast Guard Classification_____

Comments_____

_____

References (1) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Cadmium Nitrate (479)

IUC Name _____

Common Names _____

Structural Formula

$$Cd(NO_3)_2$$

Molecular Wt. 236.43_____   Melting Pt. ___350 C_____   Boiling Pt._____

Density (Condensed)_____ @_____ _____ Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @_____   _____ @_____   _____ @_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

    Cold Water 109g/100cc _____   Hot Water 326g/100 CC_____   Ethanol Soluble_____

    Others: ____ Acids; ethyl acetate

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____
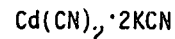
Comments_____

References (1) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __Cadmium Potassium Cyanide (480)__

IUC Name _____

Common Names__Cadmium Potassium Cyanide_____

Structural Formula

$Cd(CN)_2 \cdot 2KCN$

Molecular Wt. __294.68_____ Melting Pt. _____ Boiling Pt._____

Density (Condensed)_1.847_____ @____ _____ Density (gas)_____@ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp.____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water__33.3 g/100CC__   Hot Water__100g/100 CC__   Ethanol__Insoluble____

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments __When heated, melts to a colorless liquid solidifying to a grey, crystaline mass__
__on cooling._____

References (1) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Cadmium Sulfate (481)

IUC Name _____

Common Names Cadmium Sulfate

Structural Formula

$CdSO_4$

Molecular Wt. 208.46 _____ Melting Pt. 1000C _____ Boiling Pt._____

Density (Condensed) 4.691 _____ @ 20C 4C Density (gas)_____ @ _____ _____

Vapor Pressure (recommended 55 C and 20 C)

_____@_____   _____@_____   _____@_____

Flash Point _____   Autoignition Temp._____

Flammability Limits in Air (wt %)   Lower_____   Upper_____

Explosive Limits in Air (wt. %)   Lower_____   Upper_____

Solubility

Cold Water 75.5g/100CC _____ Hot Water 60.8g/100CC _____ Ethanol insoluble _____

Others:_____

Acid, Base Properties_____

_____

Highly Reactive with_____

_____

Compatible with_____

_____

Shipped in_____

ICC Classification_____ Coast Guard Classification_____

Comments_____

_____

_____

References (1) 1492

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-670/2-73-053-f	2.	3. Recipient's Accession No.
4. Title and Subtitle Recommended Methods of Reduction, Neutralization, Recovery, or Disposal of Hazardous Waste. Volume VI, National Disposal Site Candidate Waste Stream Constituent Profile Reports - Mercury, Arsenic, Chromium, and Cadmium Compounds			5. Report Date Issuing date - Aug. 1973
			6.
7. Author(s) R. S. Ottinger, J. L. Blumenthal, D. F. Dal Porto, G. I. Gruber, M. J. Santy, and C. C. Shih			8. Performing Organization Rept. No. 21485-6013-RU-00
9. Performing Organization Name and Address TRW Systems Group, One Space Park Redondo Beach, California 90278			10. Project/Task/Work Unit No.
			11. Contract/Grant No. 68-03-0089
12. Sponsoring Organization Name and Address National Environmental Research Center Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268			13. Type of Report & Period Covered Final
			14.

15. Supplementary Notes

Volume VI of 16 volumes.

16. Abstracts

This volume contains summary information and evaluation of waste management methods in the form of Profile Reports for mercury, arsenic, chromium, and cadmium compounds. These Profile Reports were prepared for either a particular hazardous waste stream constituent or a group of related constituents. Each Profile Report contains a discussion of the general characteristics of the waste stream constituents, their toxicology and other associated hazards, the definition of adequate management for the waste material, an evaluation of the current waste management practices with regard to their adequacy, and recommendation as to the most appropriate processing methods available and whether the waste material should be considered as a candidate for National Disposal, Industrial Disposal, or Municipal Disposal.

17. Key Words and Document Analysis. 17a. Descriptors

Mercury Compounds
Arsenic Compounds
Chromium Compounds
Cadmium Compounds
National Disposal Site Candidate
Hazardous Wastes

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 06F; 06T; 07B; 07C; 07E; 13B; 13H; 19A; 19B

18. Availability Statement Release to public.	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 212
	20. Security Class (This Page) UNCLASSIFIED	22. Price