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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY OR DISPOSAL OF HAZARDOUS WASTE Volume XII Inorganic Compounds



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RECOMMENDED METHODS OF

REDUCTION, NEUTRALIZATION, RECOVERY

OR DISPOSAL OF HAZARDOUS WASTE

Volume XII. Industrial and Municipal Disposal Candidate Waste Stream Constituent Profile Reports Inorganic Compounds

Ву

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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.

> A. W. Breidenbach, Ph.D., Director National Environmental Research Center Cincinnati, Ohio

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1. GENERAL

Introduction

The alkali and ammonium fluorides are similar in their chemistry, toxicology, and other hazards. Because of this, ammonium fluoride, ammonium bifluoride, potassium fluoride, potassium bifluoride, sodium fluoride, and sodium bifluoride are included in a combined Profile Report.

Ammonium Fluroide

Ammonium fluoride is a colorless, crystalline deliquescent solid, supplied commercially as a granular powder. 1492 The salt decomposes on heating, 1433 and corrodes glass. 1492 The physical and chemical properties of $\mathrm{NH}_{4}\mathrm{F}$ are summarized in the attached worksheet.

The salt is prepared by the reaction of anhydrous ammonia and ice-cold 40 percent hydrofluoric acid: 1492

$$NH_3 + HF \rightarrow NH_4F$$

The major uses of ammonium fluoride are:

- (1) etching and frosting glass,
- (2) as antiseptic in brewing beer,
- (3) as mothproofing agent,
- (4) in preserving wood
- (5) in printing and dyeing textiles.

Ammonium fluoride has been suggested as an intermediate in the manufacture of acid-grade CaF₂ (fluorspar) from by-product fluosilicic acid produced in very large quantities by the wet phosphoric acid process. Ol48 The proposed reactions, which have been investigated on a laboratory and pilot scale are:

$$H_2SiF_6 + 6 NH_3 + 2 H_2O \rightarrow SiO_2 + 6 NH_4F$$
 $Ca(OH)_2 + 2 NH_4F \stackrel{\triangle}{\rightarrow} CaF_2 + 2 NH_3 + 2 H_2O$

Ammonium Bifluoride

Ammonium bifluoride is a white, crystalline, transparent solid. Solutions of the salt are acid, and the dry crystals have an acid odor. The commercial product is marketed in flake form, and is hygroscopic at humidities above 50 percent. Ammonium bifluoride corrodes glass readily; it should be stored in a tightly closed plastic, rubber, wood or parafinned container. The attached worksheet contains a summary of physical and chemical properties.

Ammonium bifluoride is prepared on a large scale by reacting anhydrous ammonia and anhydrous ${\sf HF}$:

$$NH_3 + 2 HF \rightarrow NH_4 HF_2$$

The gases are injected into a cooled, packed tower, and the resultant liquid $\mathrm{NH_4}$ HF $_2$ is flaked on a cooled rotary drum. An alternative process, used for the production of crystalline $\mathrm{NH_4}$ HF $_2$, is the batch reaction of ammonium hydroxide solution with aqueous hydrofluoric acid, followed by evaporation, cooling, crystallization, and centrifugation. The mother liquor from the crystallization is recycled to the evaporation step of the process with the next batch of dilute $\mathrm{NH_4}$ HF $_2$ solution.

The major uses of ammonium bifluoride are:

- in combination with hydrofluoric acid, as a commercial glass frosting and etching agent,
- (2) as a laundry sour, because of its capability to decolorize iron stains.
- (3) in the removal of silica scale from steam boilers and automotive radiators.
- (4) in the manufacture of magnesium and magnesium alloys,
- (5) in brightening aluminum,
- (6) in oil well treatment,
- (7) in washing glass television tube blanks and faceplates, greenhouses, and factory windows,
- (8) as a fungicide, in treating wood,
- (9) in breweries and distilleries.

Potassium Fluoride

Potassium fluoride is a white, transparent, hygroscopic crystalline powder, available commercially as either the anhydrous salt, or the dihydrate. Two hydrates are known - $\mathrm{KF.2H_2O}$, and $\mathrm{KF.4H_2O}$. The salt is very freely soluble in boiling water. The anhydrous salt may be stored in aluminum containers. Aqueous solutions of KF corrode glass and porcelain. The physical and chemical properties are summarized in the attached worksheet.

Potassium fluoride is prepared commercially by reacting potassium carbonate with aqueous hydrofluoric acid. Extreme care is necessary in judging the neutralization point, since in concentrated solutions both potassium bifluoride and potassium bicarbonate are stable in the presence of the other. The resultant neutral solution is concentrated and cooled. The anhydrous salt is obtained by arresting the cooling at 50 to 55 C and removing the crystals by centrifuging at this temperature.

If the dihydrate is desired, the solution is cooled to room temperature and the resulting crystals are centrifuged and packaged as moist crystal. The anhydrous salt is also prepared in flake form by passing the hot concentrated solution over a heated rotary drum dryer. Extreme care is necessary in handling the anhydrous salt to prevent rehydration.

The major uses of KF are:

- (1) in the fluorination of organic compounds,
- (2) in flux for hard solder (silver solder),
- (3) to prevent fermentation
- (4) in insecticide formulations,
- (5) for frosting glass,
- (6) as a solvent, in preparing barium titanate crystals,
- (7) as a fire extinguisher in alkali metal fires.

Potassium Bifluoride

Potassium bifluoride is a white, crystalline salt, which assumes one of two solid forms, dependent upon temperature. Between 194 and 239 C, the β -form—a soft white solid—is the stable phase. At 195 C, the β -form changes to the α -form, a hard white solid, stable below 195 C.

Potassium bifluoride is manufactured commercially from potassium carbonate and hydrofluoric acid. A slight excess of HF over the stoichiometric amount is used. The solution is concentrated to a specific gravity of 45 Baume and cooled to form the crystals. The crystals are separated by centrifugation, dried, ground and packaged in polyethylene-lined fiber drums containing 100 or 400 lbs. 1433 The commercial salt contains about 0.5 percent KF.

The major uses of KHF, are:

- (1) as an electrolyte, in conjunction with HF, in the preparation of F_2 ,
- (2) as the basis for most silver soldering fluxes,

- (3) in frosting glass,
- (4) in the preparation of pure anhydrous HF in the laboratory,
- (5) as a co-catalyst, with BF_3 , in the alkylation of benzene with olefins. 1433

Sodium Fluoride

Sodium fluoride is a white crystalline powder, available commercially in three grades--90, 95 and 98 per cent purity-- and two densities-- light (37 cubic in./lb), and dense (23 cubic in./lb). Aqueous solutions are alkaline, and etch glass.

Sodium fluoride is manufactured commercially by reacting soda ash with 40 percent hydrofluoric acid.

$$Na_2CO_3 + 2 HF \rightarrow 2NaF + H_2O + CO_2+$$

The crystals precipitate immediately, 1492 are separated and dewatered, dried, sized and packaged. 1433 The reactors are usually rubber or carbon brick-lined steel. Process piping is rubber hose, stainless steel, or plastic-lined steel. Valves are rubber or plastic-lined diaphragm valves, or plastic-lined plug cocks 1433.

The commercial material is packaged in 100 lb multiwall bags and 125 and 400 lb fiber drums. Sodium fluoride for insecticidal purposes must be colored blue. Some states require that the word "Poison", together with information on appropriate antidotes, appear on the labels of the packages. Sodium fluoride shipped in interstate commerce must carry a Manufacturing Chemists Association (MCA) warning label.

The major uses of sodium fluoride are:

- (1) as insecticide,
- (2) in other pesticide formulations,

- (3) in the fluoridation of water,
- (4) in soldering and metallurgical fluxes,
- (5) in the manufacture of rimmed steel.
- (6) in electroplating,
- (7) as a constituent of vitreous enamel and opal glass mixes,
- (8) in heat treating salts,
- (9) for pickling stainless steel,
- (10) as a disinfectant in breweries and distilleries,
- (11) as a glue and paste adhesive preservative,
- (12) in the manufacture of coated papers.

Sodium fluoride solution is applied topically to the teeth as a 2 percent solution, for prevention of dental cavities. 1492 Sodium fluoride has been responsible for more lethal and acute cases of fluoride poisoning than all other fluorides combined. 1988

Sodium Bifluoride

Sodium bifluoride is a white, free-flowing granular material supplied at a commercial purity of about 99 percent. The material has limited solubility in water, and decomposes into NaF and HF above 150 C. The attached worksheet summarizes the chemical and physical properties of sodium bifluoride.

NaH F₂ is made by reacting soda ash or caustic soda with hydrofluoric acid. An adequate concentration of excess HF is maintained, in order to crystallize the bifluoride. The slurry is dewatered, dried, screened and packaged. Spray drying has been used to some extent. Cooling of the reaction is necessary to avoid self-heating to an undesirably high temperature. The reactors are usually rubber- or carbon brick-lined steel. Process piping is rubber hose, stainless, or plastic-lined steel, with rubber or plastic-lined diaphragm valves or plastic-lined plug cocks.

Sodium bifluoride is available in 100 lb multiwall bags and 125, 375 and 400 lb fiber drums. The salt hydrolyzes readily, and can cause hydrofluoric acid burns to the skin.

Major uses of sodium bifluoride are:

- (1) as a laundry sour and stain remover.
- (2) in bleaching leather and treating hides.
- (3) in plating tin,
- (4) etching and frosting glass,
- (5) cleaning stone and brick building faces.

TOXICOLOGY

Human Toxicity

The use of the fluorides as insecticides and rodenticides is so widespread that sodium fluoride is almost a common household preparation. Because of the innocuous appearance of sodium fluoride prior to the law requiring that it be colored blue, the white powder was easily mistaken for powdered milk, baking powder, powdered sugar, corn starch, or pancake flour. This, coupled with the custom of keeping insecticides in the cupboard along with soaps and washing powders, produced many tragic cases of fluoride poisoning. 1988

The alkali and ammonium fluorides, like the other soluble fluorides can cause both acute and chronic poisoning. Fatal human poisonings generally have taken place after the ingestion, accidentally or by suicidal intent, of a large quantity (5 to 10 grams) of sodium fluoride. The course is violent and brief, with death occurring within two to four hours. The symptoms of acute fluoride poisoning include extreme nausea and vomiting, perspiration, salivation, burning, cramp-like abdominal pains, diarrhea, dehydration and thirst, muscle weakness; hemorrhagic gastroenteritis, muscle weakness, central nervous depression, cyanosis, shock, weak and

thready pulse, shallow unlabored respiration, weak heart tones, paralysis of the muscles of deglutation, carpopedal spasm, spasm of the extremities, and, in extreme cases, death. Lethal dosages of 1-1/2 to 2 grams (25 to 30 grains) expressed as F, of soluble fluorides have been reported. Prompt treatment has averted death in one case where 50 to 80 grams of NaF was ingested. Severe illness can follow ingestion of as little as 66 mg (about 1 grain) of F.

Fluoride kills by a blockage of the normal metabolism of the cells, inhibiting the enzymes involved in essential processes. Vital functions—e.g., the origin and transmission of nerve impulses—cease. Necessary bodily functions controlled by calcium, such as blood clotting and membrane permeability, are interfered with. Cell damage and necrosis produce massive impairment in the function of vital organs. There is a characteristic shock—like syndrome terminally. 1988

Treatment of acute fluoride poisoning emphasizes intravenous and intramuscular injections of 10 percent calcium gluconate solution, intravenous injection of glucose in isotonic saline, gastric lavage with lime-water or l percent CaCl₂ solution, treatment for shock and dehydration, and the absolute necessity for quick response.

The bifluorides hydrolyze, and cause hydrofluoric acid burns in contact with the skin, the mucosa, or the eyes. These burns are extremely painful and unless treated promptly may result in permanent damage, including loss of sight.

Chronic industrial fluorosis, called crippling fluorosis, has been reported in England, Scotland, the mainland of Europe, and Africa; crippling fluorosis, however, has never been seen in the United States. ¹⁹⁸⁸ The disease is not rapidly reversible, and develops after exposures to relatively large amounts of fluoride over protracted periods. Exposures such that 20 to 80 mg or more of fluoride are ingested daily for periods of 10 to 20 years produce the full-blown disease. Crippling effects are limited to the skeleton, ¹⁹⁸⁸ and include "poker back," painful and disabled joints, generalized osteoscleroses, calcification in the tendons and

ligaments, and synostosis. 1492 Mottled teeth are a frequent sympton. 1492

Threshold Limit Value (TLV) for fluoride dusts is 2.5 milligrams per cubic meter as reported by the American Conference of Governmental Industrial Hygienists (ACGIH). The Federal Water Pollution Control Administration (FWPCA) Water Quality Criteria 0536 recommends permissible limit criteria for fluoride in drinking water ranging from 1.7 mg/liter to 0.8 mg/liter, for average daily maximum temperatures ranging from 50 to 90.5 F, and recommends that water for livestock use contain less than 2.4 mg/liter of fluoride ion. The same source 0536 indicates a quality requirement of a maximum of 1 mg/liter of fluoride ion in water intended for use by the canned, dried, and frozen fruits and vegetable industry.

Animal Toxicity

Because of the well-documented history and economic effects of fluorosis of farm animals, ingestion of fluoride has been investigated extensively in many species of animals. In general, symptoms of acute and lethal fluorine poisoning in animals follow those exhibited in man. Sub-acute dosages produce the symptoms of loss of appetite and starvation. Chronic effects, listed in order of appearance on exposed animals are:

- (1) dental lesions (primarily damage to incisor teeth),
- (2) hyperostosis,
- (3) lameness,
- (4) loss of appetite,
- (5) decreased milk production,
- (6) diminution in reproduction.

Herbivorous animals will exhibit the symptoms of acute fluorine poisoning on eating vegetation containing in excess of 5000 parts per million (ppm) of fluoride. Sub-acute effects were observed in cattle experimentally fed with vegetation containing 500 to 1200 ppm of fluoride, for time periods ranging from four months to six months.

Chronic effects, leading to economic losses occur on the continuous ingestion of food by dairy cattle containing 40 to 50 ppm of fluoride. Exposure terms of 5 years or more may be required for the maximum economic loss to occur. Susceptibility varies amongst animal species, ranging from maximum in dairy cattle, to the lower range in turkeys. The farm animals affected include dairy cattle, beef cattle, sheep, chickens, and turkeys.

Plant Toxicity

There are, in general, four types of fluoride effects on vegetation: Visible effects such as necrosis (injured portions of leaves die and become discolored); diminution in the growth or in the yield of fruit or seeds; changes in physiological activities, metabolic activities, and cellular structure with or without visible injury; and deposit or accumulation of fluoride in the plant with increasingly higher fluoride concentrations in its tissues. Plant species vary very widely in sensitivity to soluble fluorides. Sorghum, citrus, fruit trees, conifers and corn are relatively sensitive crops. Alfalfa is quite insensitive.

Comparatively little information is available for relating particulate fluoride levels to vegetation damage in contrast to the large collection of data on the effects of gaseous fluorides. Generally, the fluoride dusts are less toxic than the gaseous fluorides. Dissolved fluorides (NaF) have produced injury resembling that caused by HF in air. Fluoride damage to vegetation through fluoride contamination of the soil, while possible, has not been observed in the field, possibly because of the presence of sufficient calcium and aluminum in the soils to inactivate the fluoride 1668.

3. OTHER HAZARDS

The alkali and ammonium bifluorides, when moist or in solution, are extremely corrosive to glass, porcelain, and most common metals of construction. The bifluorides are non-flammable, but are easily decomposed on heating, yielding highly toxic HF fumes.

The alkali and ammonium fluorides and bifluorides are toxic to all life--yeast, other microorganisms, plant life, both harmful and beneficial--insects, fish and all higher vertebrates. Their use as economic poisons is based on this toxicity.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Care must be exercised in handling the alkali and ammonium fluorides to prevent contact of the materials with the skin or eyes, and to avoid ingestion by inhalation of dust or other means. Food should not be handled in proximity to the soluble fluorides. In case of contact with the bifluorides, the skin and eyes should be flushed with cold water for at least 15 minutes, and prompt medical attention should be secured. In the case of contact with the normal fluorides, the skin should be washed thoroughly; contact with the eyes requires medical attention in addition to thorough flushing with cold water. Contaminated clothing should be removed and washed before re-use.

The alkali and ammonium fluorides are shipped in screw cap bottles, for quantities up to 5 lb; for quantities from 5 lb to 400 lb, polyethylene bag-lined drums or fiber drums are used. In accordance with current manufacturers liability laws, the containers carry a "Poison" warning label, and information on treatment and antidotes for accidental contact and poisoning. The containers should be stored in a cool, dry area, and should be kept tightly closed. 2093, 2094, 2095, 2096

Sodium fluoride shipped in interstate commerce must, as noted earlier, be colored blue, and must carry a Manufacturing Chemists Association (MCA) warning label. There are no current Department of Transportation or Coast Guard regulations which cover shipment or labeling of the other fluorides.

Recommended criteria for acceptable disposal of the alkali and ammonium fluorides, defined in terms of the recommended provisional limits in the atmosphere, water, and soil are as follows:

Contaminant in Air	Provisional Limit	Recommendation
Alkali and Ammonium Fluorides	0.025 mg/M ³ as F	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Alkali and Ammonium Fluorides	0.6-1.7 ppm (mg/l) as F	Drinking Water Standard

The stringency of the recommended criteria are due to both the acute and chronic toxicity of the soluble fluorides. Any excess of soluble fluorides released to a watercourse will not be decreased by natural action to acceptable levels for potable water supply, or for farm animal use unless the stream percolates through or runs over a limestone bed.

Particulate fluorides, released as aerosol fume, can cause both acute and chronic fluorosis in plant employees, and can cause economic damage to crops and farm animals in surrounding areas.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The keystone of any economically feasible process for the minimum environmental impact disposal of any of the alkali or ammonium fluorides must involve either recovery of the fluoride portion of the compound for re-use, or precipitation of the fluoride as calcium fluoride, followed by separation and impact-free disposal of the calcium fluoride via use as a fluorspar substitute, or land burial. With the exception noted under Option No. 1, below, current practice in disposal of the alkali and ammonium fluorides is to vent the material without capture from high temperature operations such as glass manufacture, vitreous enamel processes, and brick manufacutre, ¹⁶⁸⁸ or to flush the fluoride wastes down the sewer after recovery of the economically valuable metal present. These practices are unacceptable. Two current disposal practices, and some possible future options are discussed in the following paragraphs.

Option No. 1 - Tin and Fluoride Pollution Control Process.

A patented process exists for the removal of both the tin and fluoride contents of plating, wash and tin recovery wastes from halogen tin lines used in tin plating. 0653 Basis for the process is the two-stage addition of lime slurry to the wastes in two sequential, compartmented reaction and settling tanks. The underflow from each tank is in part recycled to the feed, or reaction, compartment of the first tank. Most of the tin is precipitated in the first tank, and the part of the underflow from the first tank which is not recycled is sent to tin recovery operations. The majority of the fluoride is precipitated as calcium fluoride in the second tank. That portion of the underflow from the second tank which is not recycled is diverted to disposal operations. The overflow from the second tank is discharged to sewer.

The disposal system employed for the calcium fluoride waste product is not stated. To allow economic recovery, the discharged, alkaline ${\sf CaF}_2$ slurry should be lagooned, and the clarified, fluoride-stripped overflow discharged to sewer. The separated ${\sf CaF}_2$ should then be dried, and re-used as metallurgical grade ${\sf CaF}_2$ in steel mill operations. Where economic recovery is not feasible, the sludge should be added to a landfill.

Option No. 2 - Reaction with Slaked Lime.

The disposal procedure given 0095 for package lots of the soluble inorganic fluorides in the laboratory is to add the fluorides slowly to a large container of water. Stir in a slight excess of soda ash and slaked lime. Allow the slurry to stand, settling, for 24 hrs. The supernatant liquor is then dicanted or siphoned into another container, and neutralized with dilute hydrochloric acid before being washed into the sewer, with large quantities of water. The sludge is added to landfill.

Option No. 3 - Discharge to the Environment

The majority of the sodium fluoride emitted by the glass industry ¹⁶⁶⁸ is vented to the atmosphere. In those few cases where wet cyclones are employed, the sludge is frequently discharged to sewer. Both of these practices are undesirable. Glass industry discharged to sewer in 1968 from wet and dry cyclones contained an estimated 1,700 lb of NaF. About 80 percent of the NaF thus disposed of was discharged in some 300 tons of dilute aqueous waste, with the approximate composition 0.2 percent NaF, 4.7 percent HF, and 95 percent water. The balance of the glass industry NaF wastes were in the form of slightly over 3,000 lb of a mixture of NaF and Na₂CO₃, containing slightly over 10 percent NaF.

In the enamel frit industry, about 80 percent of the plants discharge their NaF fume directly to the atmosphere. 1668 The remaining plants frequently discharge material recovered from stack gas to the sewer, without treatment. These practices are undesirable, and are not recommended. In 1968, the enamel frit industry disposed of an estimated 200 tons of NaF in waste streams sent to sewer. Over half of the fluoride wastes were in the form of dilute solutions in water. The remainder were mixtures of solids—45 percent NaF and 55 percent Na $_2$ CO $_3$.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The alkali and ammonium fluorides are not candidate waste stream constituents for National Disposal Sites. Their treatment by either of the techniques listed below as recommended procedures is not hazardous, does not require costly or sophisticated apparatus, and is economically feasible and technologically practical for waste generation site use.

The procedure recommended for treatment of large quantity, continuous discharges of the alkali and ammonium fluorides is that of Option No. 1-i.e., continuous reaction with an excess of lime, followed by lagooning, and either recovery or landfill disposal of the separated CaF_2 . The procedure recommended for the treatment of package lots and spills of the

alkali and ammonium fluorides is that of Option No. 2-- i.e., reaction in solution with an excess of slaked lime, followed by separation of ${\rm CaF}_2$, and reuse or landfill disposal of the separated ${\rm CaF}_2$.

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HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Ammonium Fluoride (23) Structural Formula		
IUC Name Ammonium Fluoride		
Common Names Neutral Ammonium Fluoride NH ₄ F		
27.04 Subtimes (1) Subtimes (1)		
Molecular Wt. 37.04 Melting Pt. Sublimes (1) (2) Boiling Pt. Sublimes (1)		
Density (Condensed) 1.315 @ 25 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 41.8 g/100g soln@0 C Hot Water 54.1g/100g soln@0 Ethanol Slightly Sol. Others:		
Acid, Base Properties Aqueous solution acid		
Highly Reactive with Quinine salts; soluble calcium salts		
Compatible with iron (dry)		
Shipped in Plastic (polyethylene) bag lined drum; fiber drum (3)		
ICC Classification None Coast Guard Classification None		
Comments <u>Salt is deliquescent</u> , <u>Commercial salt is granular powder</u> . Used in etching and <u>frosting glass</u> ; as antiseptic in brewing beer; preserving wood; moth proofing agent. (2)		
References (1) 0766		
(2) 1433		
(3) 2093		

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Ammonium Bifluoride (544) IUC Name Ammonium Hydrogen Fluoride	Structural Formula		
Common Names Ammonium Acid Fluoride	NH ₄ HF ₂		
67.05			
	6.1 C Boiling Pt. Subl. (gas) @		
Vapor Pressure (recommended 55 C and 20 C)			
Flash Point - Autoignition Temp.			
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	UpperUpper		
Solubility Cold Water 28.45g/100gsoln@0 C Hot Water 85.55g/100gsoln@100 C Ethanol Slightly sol. Others: Acid, Base Properties Strongly acid in solution			
Highly Reactive with glass; silica			
Compatible with polyethylene; plastics; rubber; woo	d; parafinned paper and fiberboard		
Shipped in polyethylene lined drums			
ICC Classification None Coast Guard Classification None Comments Used to etch/frost glass; as antiseptic in brewing beer; moth proofing (1); removal of silica scale (boilers, etc.); oil well treatment; fungicide; laundry soap; in the manufacture of Mg and Mg alloys.			
References (1) 1433 (2) 1492			

HAZARDOUS WASTES PROPE WORKSHEET	RTIES
H. il. Name Potassium Fluoride (544) IUC Name Potassium Fluoride Common Names Potassium Fluoride	Structural Formula KF
Molecular Wt. 58.10 Melting Pt. 860 Density (Condensed)2.481 ⁽¹⁾ @ Density (ga Vapor Pressure (recommended 55 C and 20 C)	as) <u>-</u> -@
Flash Point Autoignition Temp Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	Upper
Solubility Cold Water 92.3 g/100 m1@18 C Hot Water Very Others: Sol liquid NH3 Acid, Base Properties	,
Highly Reactive with glass, porcelain (corrodes) Compatible with Aluminum (anhydrous)	
Shipped in Polyethylene bag lined drums; screw cap ICC Classification None Coast G Comments Used as silver soldering flux, preparation Hydrates very readily to KF.2H ₂ 0	uard Classification None
References (1) 1492 (2) 1433 (3) 2094	

HAZARDOUS WASTES PROPER WORKSHEET	TIES	
H. M. Name Potassium Bifluoride (545)		
Potassium Hydrogen Fluoride IUC Name	Structural Formula	
Common Names Potassium Acid Fluoride	KHF ₂	
Fremy's salt	·	
Molecular Wt. 78.10 Melting Pt. 239 Density (Condensed) 2.37 (2) 0 - Density (gas	C (B) Boiling Pt. Decomposes	
Vapor Pressure (recommended 55 C and 20 C)		
Flash Point Autoignition Temp	_	
Flammability Limits in Air (wt %) Lower		
Explosive Limits in Air (wt. %) Lower	Upper	
Solubility Cold Water 24.5g/100m/@0 C Hot Water 114g/100 Others: - Acid, Base Properties Strongly acid Highly Reactive with Glass; silica		
Compatible with <u>Plastics; rubber</u>		
Shipped in Polyethylene-lined drums; screw cap bottles	3)	
ICC Classification Coast Gu		
Comments Used in silver soldering fluxes; frosting glass; anti-fungal agent for wood;		
e! trolyte for fluorine manufacture. Decomposes on he	ating, into KF and HF(2)	
References (1) 1433 (2) 1492 (3) 2096		

HAZARDOUS WASTES PROPE WORKSHEET	ERTIES
H. M. Name <u>Sodium Flu</u> oride (389)	Structural Formula
IUC Name Sodium Fluoride	oci decarati formula
Common Names Villiaumite	NaF
Molecular Wt. 42.00 Melting Pt. 993	c(1) 2704 c(1)
Density (Condensed) 2.78 @ Density (ga	Boiling Pt. 1704 C
Vapor Pressure (recommended 55 C and 20 C)	
Flack Coint	
Flash Point Autoignition Temp	
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	
Explosive Elimits in All (wt. 8) Lower	Upper
Solubility 4g/100ml 0 C 5g/100ml	le 100 C V slight sol
Cold Water 4g/100ml@0 C Hot Water 5g/100ml	Ethanol
Others:	
Acid, Base Properties Solution in water is basic	
Highly Reactive with -	
·	
Compatible with plastics; rubber; paper	
Shipped in 100 lb multiwall bags and 125 and 400 lb f	fiber drums
ICC Classification MCA warning label Coast G	uard Classification None
Comments <u>Used as insecticide; pesticide; in vitreous</u>	
degassing agent; in flux in fluoridating water; in ele	ectroplating. Sodium fluoride sold
for insecticide uses must be colored blue. Poison label	I required by some states. 127
References (1) 1492	
(2) 1433	

HAZARDOUS WASTES PROPERTIES WORKSHEET
H. M. Name Sodium Bifluoride (546) Structural Formula
IUC Name Sodium Hydrogen Fluoride
Common Names Sodium Acid Fluoride NaHF ₂
Molecular Wt. 62.01 Melting Pt. <u>Decomposes</u> Boiling Pt. <u>Decomposes</u>
Density (Condensed) @Density (gas) @
Vapor Pressure (recommended 55 C and 20 C)
<u> </u>
Flash Point Autoignition Temp
Flammability Limits in Air (wt %) Lower - Upper -
Explosive Limits in Air (wt. %) Lower - Upper -
Solubility (1)
Cold Water 3.25g/100m1@20 C Hot Water 7.5g/100m1@90 C Ethanol -
Others:
Acid, Base Properties Solution is acid
Highly Reactive with glass; steel
Compatible with
Shipped in 100 1b multiwall bags; 125,375 and 400 1b fiber drums
ICC Classification Coast Guard Classification
Used as laundry "sour", in bleaching leather; disinfecting hides; plating tin;
etching/frosting glass; cleaning stone and brick ⁽¹⁾ Decomposes on heating, to
NaF and HF.
References (1) 1433

PROFILE REPORT

Aluminum Fluoride (16), Barium Fluoride (470), Cadmium Fluoride (478)

GENERAL

Aluminum Fluoride

Aluminum fluoride is a white crystalline solid, used principally as an electrolyte component in the electrolytic reduction and refining of aluminum and as a modifier of glass and enamels in the ceramic industry. Pure anhydrous aluminum fluoride is extremely difficult to prepare; the commercial product contains oxyfluoride. The only simple aluminum fluoride compound occurring in nature is the rare mineral fluellite AlF $_3$ · H_2O . Aluminum fluoride used commercially is manufactured by one of the following processes. In one process used currently aluminum fluoride is prepared batchwise by solution of alumina hydrate in 15 percent hydrofluoric acid, followed by continuous crystallization, filtration, and calcination. In another process, alumina trihydrate is heated to between 400 and 700 C and allowed to react with gaseous hydrogen fluoride or the HF evolved in the electrolytic production of aluminum. The recovered aluminum fluoride is recycled to the molten electrolyte used in the cell. In still another process an ammonium fluoaluminate intermediate is decomposed to aluminum fluoride by heating to 700 C. 1433 The physical/chemical properties for aluminum fluoride are summarized on the attached worksheet.

Barium Fluoride

Barium fluoride forms colorless cubic crystals. It is prepared by treating barium carbonate with hydrofluoric acid. Its principal uses are as a flux and opacifier in enamel frits and as a white pigment in record compositions. It is also used to some extent in metal heat-treating baths and in the manufacture of carbon brushes for electrical generators for aircraft. The physical/chemical properties for barium fluoride are

shown on the attached worksheet.

Cadmium Fluoride

Cadmium fluoride forms white cubic crystals. It is prepared by dissolving cadmium, Cadmium carbonate, or cadmium oxide in a solution of hydrogen fluoride and evaporating to dryness. It may also be made by the addition of ammonium fluoride to a solution of cadmium chloride. Cadmium fluoride is used as a fluoride phosphor in cathode-ray-beam tubes and as an impregnating agent in carbon brushes of dynamoes to prevent excessive wear of the brushes. The physical/chemical properties for cadmium fluoride are summarized in the attached worksheet.

2. TOXICOLOGY

For detailed discussion of fluoride toxicology please refer to the Profile Reports on the alkali and ammonium fluorides (23, etc.). The Threshhold Limit Value (TLV) for fluoride dusts is 2.5 milligrams per cubic meter. The recommended permissible limit criteria for fluoride in drinking water is from 1.7 mg/liter to 0.8 mg/liter, and the recommended maximum concentration for fluoride in water for livestock use is less than 2.4 mg/l. 0.0536

The aluminum ion does not contribute to the toxicity of aluminum fluoride. The toxicity of barium fluoride combines the effects of the fluoride and barium ions. The toxicity of barium compounds is discussed in the Profile Report on barium compounds (53, etc.). The permissible maximum for barium in public water supplies is 1.0 mg/liter. Cadmium fluoride toxic effects are due to both fluoride and cadmium ions. Cadmium is moderately toxic to all organisms and is a cumulative poison in mammals. The recommended permissible limits for cadmium in drinking water and for farmstead usé is 0.01 mg/l. 0536

OTHER HAZARDS

The fluorides of aluminum, barium and cadmium, when moist or in

solution, are corrosive to glass, porcelain, and most common metals of construction except nickel.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Care must be exercised in handling aluminum, barium or cadmium fluorides to prevent contact of the materials with the skin or eyes, and to avoid ingestion or inhalation of dust. Food should not be handled in proximity to these soluble fluorides. There are no current Department of Transportation or Coast Guard regulations which cover shipment or labeling of these fluorides.

Recommended criteria for acceptable disposal of these fluorides, in terms of recommended provisional limits in the atmosphere and in water and soil are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Alf ₃	0.025 mg/M ³ as F	0.01 TLV
BaF ₂	0.005 mg/M ³ as Ba	0.01 TLV
CdF ₂	$0.002 \text{ mg/M}^3 \text{ as Cd}$	0.01 TLV
		·
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
	Provisional Limit 0.6-1.7 mg/l as F	
Water and Soil		Recommendation Drinking Water

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

As previously indicated in the Profile Report on alkali and ammonium fluorides (23, etc.) current practice in disposal of many fluorides, except aluminum fluoride in aluminum manufacturing processes, is to vent the material without capture from high temperature operations such as glass manufacture, vitreous enamel processes, and brick manufacture, or to flush the fluoride wastes down the sewer without treatment, where wet collection devices are used for fume abatement. In the primary aluminum industry, aluminum fluoride recovered from process vent streams is disposed of as a mixed cryolite-aluminum fluoride slurry, when the material is not suitable for recycle and reuse in the electrolytic process. These practices are unacceptable. In contrast to these current disposal practices, some environmentally acceptable options are discussed in the following paragraphs.

Option No. 1 - Collection and Return to Process

Aluminum fluoride dusts generated in the handling of the material in the aluminum reduction industry are recovered by mechanical collection devices (cyclones and centrifugal collectors) and returned for reuse to the process system. Aluminum fluoride fumes volatilized from molten electrolyte baths, or mechanically entrained and carried in the vent gases from the electrolytic cells are frequently collected in dry dust abatement devices such as centrifugal collectors, multitube cyclones, and electrostatic precipitators, and recycled to the process for use in the electrolyte. The dusts generated in the preparation of feed for enamel frit furnaces are also frequently recovered by mechanical collectors, and returned for further process use. These abatement and recycle disposal techniques are recommended for use with all mechanically generated aluminum fluoride, barium fluoride and cadmium fluoride dusts. They are also recommended for use, where economically feasible, on thermally generated metal fluoride fumes.

Option No. 2 - Reaction with Slaked Lime

The Manufacturing Chemists Association recommends packaged lots of soluble or slightly soluble fluorides be slowly added to a large container of

water. Then a slight excess of soda ash or slaked lime is stirred into the solution. The slurry formed is allowed to settle for 24 hours. 0955 aluminum fluoride is being treated, the supernatant liquid is decanted or siphoned into another container, and neutralized with dilute hydrochloric acid before being washed into a sewer or stream with large quantities of water. The sludge is placed in a landfill. If cadmium fluoride is the fluoride being treated, cadmium hydroxide (solubility is 0.0026 g/100 g of water) will be precipitated with the slurry formed upon addition of lime. The mixed calcium fluoride-cadmium hydroxide sludge from treatment of cadmium fluoride should be sent to a landfill of the California Class 1 category. The supernatant liquid will require treatment via another process such as ion exchange, reverse osmosis, or activated carbon adsorption to reduce the cadmium content of discharge solutions to less than 0.01 mg per liter of cadmium (see Profile Report on cadmium and cadmium compounds [81, etc.]). If barium fluoride is being treated, the supernatant liquid may be neutralized with sulfuric acid, instead of hydrochloric acid, to form the insoluble barium sulfate. After removal of the barium sulfate by settling, the effluent will contain about 2 ppm of barium. This effluent may be diluted with additional water to meet the permissible criteria of 1.0 ppm for barium in public water supplies (see Profile Report on barium compounds [53, etc.]).

Variations on the above technique should be employed where it is necessary to use wet collection techniques to abate metal fluoride fumes generated thermally.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Aluminum and barium fluorides are not candidate waste stream constituents for National Disposal Sites. Their treatment by either Option No. 1 or Option No.2, is not hazardous, does not require costly or sophisticated apparatus not available to the users, and is economically feasible and technologically practical for waste generation site use. The two disposal options are equally acceptable and selection of the option to be used should be based on economics. Although cadmium fluoride wastes are generated in relatively small quantities and are not considered National

Disposal Site candidates on this basis, the presence of cadmium in those wastes dictates the use of an acceptable treatment. The only treatment deemed adequate is Option No. 2, reaction with slaked lime and subsequent disposal in designated California Class 1 type landfills.

7. REFERENCES

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- 0225. American Conference of Government Industrial Hygienists. Threshold limit values for 1971. Occupational Hazards, p. 35-40, Aug. 1971.
- 0536. Water quality criteria. Report of the National Technical Advisory Committee to the Secretary of the Interior. Washington, Federal Water Pollution Administration, Apr. 1, 1968. 234 p.
- 1668. Robinson, J. M., G. I. Gruber, W. D. Lusk, and M. J. Santy. Engineering and cost effectiveness study of fluoride emissions control. v. l. McLean, Virginia, Office of Air Programs, Environmental Protection Agency, Jan. 1972. 356 p.
- 1988. Simons, J. H., <u>ed.</u> Fluorine chemistry. v. 1. and v. 4. New York, Academic Press, Inc., 1940, 1965. 615 p. 786 p.

	HAZARDOUS WASTES PROPERTIES WORKSHEET	
H. M. Name <u>Aluminum Fluor</u> ide (16 IUC Name <u>Aluminum Fluor</u> ide	Structural Formula	
Common Names	Alf ₃	
	Melting Pt. <u>1040 c⁽¹⁾</u> Boiling Pt. <u>1291 c⁽¹⁾</u> Density (gas)@	
Vapor Pressure (recommended 55 C an <u>16.4 torr @ 1098 c⁽¹⁾</u> Flash Point	60.3 torr 0 1144 c ⁽¹⁾ 254.7 torr 0 1218 c ⁽¹⁾	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		
Solubility Cold Water 0.559 g/100g at 25 C ⁽¹⁾ Hot Water Ethanol Insoluble ⁽¹⁾ Others: aqueous hydrofluoric acid - soluble Acid, Base Properties		
Highly Reactive with		
Compatible with		
Shipped in	Coast Guard Classification none	
References (1) 1433	-	

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Barium Fluoride (470) IUC Name Barium Fluoride Common Names		Structural Formula BaF ₂	
Molecular Wt. 175.36 ⁽¹⁾ Density (Condensed) 4.89g/cc @ 2 Vapor Pressure (recommended 55 C and	5 C Density (gas)	Boiling Pt@	
Flash Point Au	@		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		Upper	
Solubility Cold Water 1.586g/l at 10 C ⁽¹⁾ Others: Acid, Base Properties	_		
Highly Reactive with			
Compatible with			
Shipped in	Coast Guard	Classification <u>none</u>	
References (1) 1433	· · · · · · · · · · · · · · · · · · ·		

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name <u>Cadmium Fluor</u> ide (478 IUC Name <u>Cadmium Fluoride</u> Common Names		Structural Formula CdF ₂	
Molecular Wt. <u>150.41⁽¹⁾</u> Density (Condensed)6.64g/cc <u>@</u>			
Vapor Pressure (recommended 55 C ar	d 20 C)		
@		 Upper	
Solubility Cold Water soluble Others: Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in	Coast Gu		
References (1) 1433			

PROFILE REPORT

Calcium Phosphate (95), Magnesium Oxide (247), Sulfur (413), Zinc Oxide (460), Aluminum Oxide (465), Asbestos (468), Coal (488), Vanadium Pentoxide (513)

GENERAL

Introduction

The inorganic materials treated in this report are part of the materials previously identified as probable candidate waste stream constituents for municipal-type disposal. These materials are generally produced in large tonnage. They are basically nontoxic. Physically, they are all virtually insoluble in water and hence trace concentrations in water supplies would not constitute a hazard. These properties provide a common ground for the disposal of these materials. Therefore, they are discussed here as a group even though chemically, they are not a homogeneous group.

Calcium Phosphate

Calcium phosphate, ${\rm Ca_3(PO_4)_2}$, occurs in nature as the minerals oxydapatite, voelicherite, and whitlockite. In pure state, it is a white, amorphous, odorless powder. The technical grade product is also known as "bone ash". Commercially, it is produced from phosphate rock which is essentially a complex salt of calcium phosphate and other calcium salts. \$1492\$ For example, the principal mineral in the domestic phosphate rock is fluorapatite which can be expressed as ${\rm CaF_2 \cdot 3Ca_3(PO_4)_2}$. By heating the phosphate rock with silica, calcium phosphate is produced as shown in the following reaction: 1662

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + H_2O + SiO_2 \xrightarrow{\triangle} 3Ca_3(PO_4)_2 + 2HF + CaSiO_3$$

The uses of calcium phosphate are: 1492

- in the manufacture of fertilizers, phosphoric acid, and other phosphorus compounds;
- (2) in the manufacture of milk-glass, polishing and dental powders, porcelains, pottery;
- (3) in enameling and in clarifying sugar syrups;
- (4) in animal feeds;
- (5) as a noncaking agent;
- (6) in textile industry;
- (7) as antacid for humans and animals.

Magnesium Oxide

Magnesium oxide, MgO, occurs in nature as the mineral periclase. In pure state, it is a colorless crystal of cubic form. It takes up $\rm SO_2$ and moisture from air. It reacts with water to yield magnesium hydroxide. It is manufactured by calcination of magnesium carbonate or magnesium hydroxide. ¹⁴³³ The oxide produced below 900 C is known as caustic-burned magnesia which can be easily hydrated with water and is chemically reactive. It is used for preparation of $\rm MgCl_2$, oxychloride cements, decolorizing agents, etc. The magnesium oxide produced above 900 C is called deadburned or sintered magnesia which is a dense, highly refractory product used almost exclusively in the manufacture of basic refractory bricks. Magnesium oxide can also be produced economically by decomposition of magnesium chloride or magnesium sulfate. Magnesium chloride can be completely decomposed in the temperature range of 1,300 to 1,700 C. In 1963, the total U.S. production of magnesia was 2.8 million tons. ¹⁴³³ Its uses are: 1433 , 1492

- (1) in the manufacture of refractories, magnesium metal and oxychloride cements;
- (2) as an ingredient in mixed fertilizers (impure grade magnesia);

- (3) in the manufacture of magnesium salts;
- (4) as a neutralizing agent and vulcanization accelerator in the compounding of neoprene and other rubbers (reactive grade Magnesia);
- (5) as a decolorizing agent for solvents in drycleaning industry;
- (6) as an absorbant and a catalyst;
- (7) as an ingredient of various pharmaceutical and cosmetic formulations such as dentifrices and powders;
- (8) as an antacid and laxative for man and as a laxative for young foals, calves, pigs and dogs.

<u>Sulfur</u>

Abundant literature has been published regarding the physical and chemical properties of sulfur, its manufacturing processes and uses. It is suffice to say that sulfur exists in several forms and occurs widely in nature, both as sulfur deposit and in various minerals. Commercially, it is produced from the well-known Frasch process and as a recovered by-product from sour natural gas, refinery gas and coal as a result of pollution control requirements. In 1967, the U.S. production of sulfur by Frasch process amounted to 7 million tons. 1433 Its uses are: 1570, 1492

- (1) in the manufacture of sulfuric acid, carbon disulfide and sulfites;
- (2) in vulcanization of natural rubber;
- (3) in the manufacture of black gunpowder and matches;
- (4) in the manufacture of fungicide, insecticides, plastics, enamels, and metal-glass cements;
- (5) in the manufacture of sulfite paper and other papers;
- (6) in organic sulfur drugs and various medicinal and veterinary uses:

- (7) in bleaching of dried fruits, wood pulp, straw, wool, silk, felt, and linen;
- (8) in the syntheses of dyes.

Zinc Oxide

Zinc oxide, ZnO, is a white, hexagonal crystal. It occurs naturally as the mineral zincite. It is also known as flower of zinc or zinc white. Industrially, it is produced by vaporization of metallic zinc by indirect heating in the presence of CO gas and oxidation of the zinc vapor with preheated air. It may be also prepared from the zinc ore, franklinite $(\text{ZnFe}_2\text{O}_4)$, or from zinc blende (ZnS). Lead blast furnace slag usually contains 10 to 18 percent zinc which can also be recovered as zinc oxide by carbon reduction process. In 1968, the U.S. production of zinc oxide was 213,826 tons. 1433 Its uses are: 1492

- (1) as a pigment in white paints;
- (2) in cosmetics, driers, quick-setting cements;
- (3) in dental cements (with syrupy phosphoric acid or ZnCl₂);
- (4) in the manufacture of opaque glass and certain types of transparent glass;
- (5) in the manufacture of enamels, automobile tires, white glue, matches, white printing inks, porcelains, zinc green;
- (6) as an analytical chemical reagent;
- (7) as an astringent, antiseptic, protective in skin diseases;
- (8) in veterinary applications as dressing in moist eczema and on wounds, otorrhea in dogs.

Aluminum Oxide

Aluminum oxide, Al₂0₃, also known as alumina, occurs abundantly in nature. However, there are so many structural varieties of alumina, their properties, preparations and uses are correspondingly diversified.

Physically, it varies from the amorphous alumina gels to various crystalline forms of alumina and its hydrates. Industrially, aluminum oxide is produced from aluminum hydroxide such as bauxite. For example, α -alumina trihydrate, Al $_2$ O $_3$ ·3H $_2$ O, is produced by the Bayer process in which the bauxite is treated with alkali, under pressure, to yield a sodium aluminate solution. The latter is decomposed by dilution and seeding with already formed alumina trihydrate. Similarly, the amorphous alumina gels can also be produced from a solution of aluminum salts or alkaline aluminates. The world consumption of alumina which is produced from about 18 million tons of bauxite, amounted to approximately 8 million tons in 1960. 1433 The uses of alumina are: 1433 , 1492

- (1) as an adsorbent and desiccant for drying gases and liquids;
- (2) as a catalyst for various chemical reactions such as dehydrogenation, oxidation, polymerization, petroleum cracking and reforming, etc.;
- (3) as abrasives;
- (4) in the manufacture of refractories;
- (5) in adsorption chromatography;
- (6) as filler for paints and varnishes;
- (7) in the manufacture of alloys, ceramic materials, electrical insulators and resistors, dental cements, glass, artifical gems;
- (8) in coating for metals.

Asbestos

Asbestos is a broad term applied to a number of $^{\circ}$ fibrous mineral silicates which differ in their chemical compositions. They may be classified into two large groups:

- (a) serpentine
- (b) amphibole

Belonging to group (a) is the mineral chrysolite, ${\rm Mg_3Si_2O_5(OH)_4}$. Group (b) contains such minerals as anthophyllite ([Mg, Fe] $_7{\rm Si_8O_{22}[OH, F]_2}$), amosite (ferroanthophyllite), crocidolite, tremolite (Ca $_2{\rm Mg_5Si_{22}[OH, F]_2}$), and actinolite (Ca $_2{\rm [Mg, Fe]_5Si_8O_{22}[OH, F]_2}$).

In general, they are fine, slender and flexy fibers; resist fire and most solvents. Canada produces about 42 percent of the world's supply of asbestos and the United States imports about 22 percent of the world's output. In 1961, the total world production of asbestos was estimated to be 2.8 to 3.0 million tons, of which 53,000 tons were produced in the United States and 1.2 million tons in Canada. Its uses are: 1433

- in the manufacture of asbestos cement products such as pipes, sheets, shingles, electrical panels, etc.;
- (2) in asphalt and vinyl floor tiles;
- (3) in the manufacture of asbestos papers, millboards, roofing felts, fire-proof gloves and clothing;
- (4) as brake linings, clutch facings, packings, etc., in automobile industry;
- (5) as an inert filter medium for filtering wine, fruit juice, beer, whisky and pharmaceuticals;
- (6) in missile work, satellites, special packings for atomic energy equipment and reinforced plastics.

Coal

Voluminous publications have been lavished on coal covering every topic of interest from deposit reserves to mining and cleaning processes. It is sufficient to say that coal and steel are the two most important and basic industries in the United States. Its most important use is, of course, as a fuel. It is also used to produce coke, carbon or graphite, fuel gas, coal tar and light oils. In recent years, attempts and processes have been designed to liquefy and to gasify coal in order to circumvent the air pollution problem caused by SO₂, a product of sulfur bearing coal combustion.

Vanadium Pentoxide

Vanadium pentoxide, V_2O_5 , is a yellow to red crystal of rhombic form. It is prepared by heating vanadium compounds in air. Industrially, ammonium vanadate, NH_4VO_3 , is carefully ignited in air to yield vanadium pentoxide. The operation is carried out in stages to lessen the chance of lower vanadium oxides being formed. It can also be prepared by slightly acidifying an alkaline, aqueous solution of ammonium vanadate. Its uses are: 1492

- (1) as a catalyst for various chemical reactions, particularly those involving oxidation such as oxidation of $\rm SO_2$ and $\rm SO_3$ in making sulfuric acid;
- (2) in the manufacture of yellow glass, and for inhibiting ultraviolet light transmission in glass;
- (3) as a developer in photography;
- (4) in the manufacture of aniline black.

Sources and Types of Waste

The main sources of wastes for the materials treated in this report may include the following:

- (1) manufacturers of these materials;
- (2) commercial and industrial operation and processes using them as starting materials or as catalysts;
- (3) users of these materials or other products containing these materials(such as paints, cosmetics, asbestos papers and boards, fertilizers, etc.);
- (4) chemical laboratories and plants using these materials as chemical reagents.

The wastes are mainly of the concentrated type, because they are all insoluble in water. Most of the wastes are unused or contaminated materials or products containing these materials.

Physical and Chemical Properties

The physical and chemical properties of the materials in this report are given in the attached worksheets.

2. TOXICOLOGY⁰⁷⁶⁶, 0643, 0225, 1312

The materials discussed in this report are nontoxic in nature. However, inhalation of the solid particles could cause some physical damage.

Inhalation of fumes of freshly formed magnesium oxide may cause metal fume fever. There is no evidence however that it can produce any true systemic poisoning.

Similarly, inhalation of fresh fume of zinc oxide can cause a disease known as "brass founders' aque" or "brass chills". However, there is no cumulative effect to the inhalation of zinc fume. The zinc oxide dust which is not freshly formed is virtually innocuous. But it can block the ducts of sebaceous glands and give use to a papular, pustular eczema in men engaged in packing this compound into barrels.

Aluminum oxide is nontoxic in nature. It has been reported however that inhalation of finely divided aluminum oxide particles can cause physical damage to the lung.

Vanadium compounds act chiefly as irritants to the conjunctivae and respiratory tracts. Prolonged exposures may lead to pulmonary involvement. Responses are acute, but never chronic. Symptoms and signs of poisoning are pallor, greenish black discoloration of tongue, paroxysmal cough, conjunctivitis, dyspnea and pain in the chest, bronchitis, rales and ronchi, broncho-spasm, tremor of fingers and arms, radiographic reticulation.

Sulfur, coal, and calcium phosphate are basically nontoxic.

Inhalation of asbestos may cause a diffuse fibrosis known as asbestosis and/or cancer. The asbestosis probably begins as a "collar" about the terminal bronchiols. Usually, at least 4 to 7 years of exposure to high concentrations of asbestos dust are required before a serious degree of asbestosis results. Once established, it would continue to progress even after the exposure to asbestos dust ceases. Clinically, the most striking sign of asbestosis is the shortness of breath of gradually increasing intensity, often associated with a dry cough. In the early stages physical signs are absent or slight; in the later stages rales may be heard, and in long-standing cases there is frequently clubbing of the fingers. In the early stages of the disease a chest X-ray reveals a ground glass or granular change, chiefly in the lower lung fields. As the condition worsens, the heart outline becomes "shaggy" and regular patches of mottled shadowing may be seen. Asbestos bodies may also be found in sputum.

Although asbestos has been found to be carcinogenic, the exact causes are not yet clearly understood. The most common form of cancer caused by asbestos is the lung cancer which may appear unaccompanied by asbestosis. 0643 The latent period between exposure and evidence of carcinoma may be even longer than that for asbestosis. Another form of cancer caused by asbestos is the mesothelioma of the pleura and peritoneum. This is a very rare form of cancer which is now considered a frequent cause of death among asbestos workers. 0643 The interval between first exposure and the development of the terminal illness from mesothelioma ranged between 16 and 55 years. Finally, extrapulmonary cancer has also been reported as a cause of death among asbestos workers.

The Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) and the lethal doses or concentration reported are tabulated as follows:

Contaminant in Air	TLV	Lethal Dose or Concentration
Calcium Phosphate		
Magnesium Oxide	15 mg/M ³ (fume)	
Sulfur		
Zinc Oxide	5 mg/M ³ (fume)	ih LC _{CA} : 2500 mg/M ³ , rat
Aluminum Oxide		~ ~
Asbestos	5 fibers/ml* > 5 μ in length	
Coal	2 mg/M ³	
Vanadium Pentoxide	0.5 mg/M ³ (dust) 0.1 mg/M ³ (fume)	

Sulfur and aluminum oxide are generally considered as inert or nuisance particulates when they are present as dusts in air. The proposed ACGIH TLV for these particulates is 10 mg/M 3 or 30 million particles per cubic foot, whichever is smaller. 0225

3. OTHER HAZARDS

With the exception of sulfur and coal, all materials in this report are very stable with respect to fire and explosion hazards. Sulfur and coal are fire hazards when exposed to flame or heat. In the form of dust, sulfur and coal could cause explosion hazard when exposed to flame.

^{*}As determined by the membrane filter method at 430X magnification phase contrast illumination. Concentrations between 5 and 10 fibers/ml may be permitted for 15 minute periods each hour up to five times daily.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The chief concern in handling and storage for the materials in this report is to maintain adequate ventilation and dust control to avoid inhalation of the fume and dust by the workers and fire and explosion hazards. For example, in the asbestos industries, the dusty air should be passed from the ventilators through fabric sleeve filters before discharged to the atmosphere. The filtration is very effective because the asbestos fibers form a mat which becomes an absolute filter. To control the asbestos in the exhaust gases, bag filters are used. Some operations are carried out in wet processes to keep the dust from becoming airborne. Dust-tight casings should be used for conveyor buckets, elevators, etc., which may be equipped with explosion relief vents, if necessary. Since sulfur and coal are combustible, they should be stored in cool and wellventilated areas and kept away from heat, or flame, or oxidizing materials. In shipping, only sulfur is classified by the Coast Guard as a hazardous article. Dusty material like asbestos may be shipped in plastic-coated bags to prevent pollution during transportation.

Disposal/Reuse

Contaminated materials are generally disposed of rather than reprocessed for reuse. The safe disposal of these materials is here defined in terms of provisional limits given below:

Contaminant in Air	Provisional Limit	Basis for <u>Recommendation</u>
Calcium Phosphate	0.01 mg/M 3 as H_3PO_4	0.01 TLV for H_3P0_4
Magnesium Oxide (fume)	0.10 mg/M ³	0.01 TLV

^{*} Whichever is the smaller.

(Continued)

Contaminant in Air	<u>Provisional Limit</u>	Basis for Recommendation
Sulfur	0.1 mg/M ³ or 0.3 m.p.p.c.f.*	0.01 TLV
Zinc Oxide (fume)	0.05 mg/M ³	0.01 TLV
Aluminum Oxide	0.1 mg/M ³ or 0.3 m.p.p.c.f.*	0.01 TLV
Asbestos	0.05 fibers/ml > 5μ in length	0.01 TLV
Coal	0.02 mg/M^3	0.01 TLV
Vanadium Pentoxide (fume) (dust)	0.005 mg/M_3^3 0.001 mg/M^3	0.01 TLV 0.01 TLV
·		
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Calcium Phosphate	0.05 ppm (mg/1)	Stokinger and Woodward Method
Magnesium Oxide	125 ppm (mg/1) a s Mg	Drinking Water Standard
Sulfur	500 ppm (mg/1)	Drinking Water Standard for total dissolved solids
Zinc Oxide	5 ppm (mg/l) as Zn	Drinking Water Standard
Aluminum Oxide	0.5 ppm (mg/1)	Stokinger and Woodward Method
Asbestos	500 ppm (mg/1)	Drinking Water Standard for total dissolved solids

^{*} Whichever is the smaller.
m.p.p.c.f. is million particles per cubic foot

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(Con	tι	nue	a)

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Coal	500 ppm (mg/l)	Drinking Water Standard for total dissolved solids
Vanadium Pentoxide	0.05 ppm (mg/1) as V	Chronic toxicity drinking water studies

5. EVALUATION OF WASTE DISPOSAL PRACTICES

Option No. 1 - Landfill

For the waste disposal of the materials in this report, the landfill method is recommended because the waste materials are all insoluble in water and nontoxic in nature. In fact, most of them originally come from the land as naturally-occurred minerals. Should they be washed into any water source, by rainfall, for instance, they can be easily removed from water by filtration. If a trace concentration of the material remains in the water supply, it would not constitute a hazard. Also, they are in general, chemically stable and will not degrade to yield air or water pollutants. The landfill method therefore offers a convenient and economic way to dispose of the waste materials.

Option No. 2 - Incineration

Combustible materials such as coal and sulfur can also be disposed of by incineration. For coal, the combustion must be complete to insure that no carbon monoxide is produced. For sulfur and coals with high sulfur contents, the exhaust gas must be scrubbed off the sulfur dioxide formed. One convenient way to scrub off the SO_2 is the wet limestone method, where the exhaust gas is scrubbed with an aqueous suspension of finely ground limestone. The limestone suspension usually contains an organic acid stronger than carbonic acid but weaker than sulfuric acid to accelerate

the dissolution of the limestone and thereby increase the scrubbing efficiency. This method is naturally more costly than Option No. 1, particularly in view of the fact that pollution controls for SO_2 are becoming more stringent.

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6. APPLICABILITY TO NATIONAL DISPOSAL SITES

As landfill provides a convenient and adequate means for the disposal of the materials included in this Profile Report, it is concluded that consideration for waste treatment at the National Disposal Site is not warranted.

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H.A.	ZARDOUS WASTES PROPERTIES WORKSHEET	
H. M. Name <u>Calcium phosphate</u> (95)	Structu	ral Formula
IUC Name		
Common Names	Ca ₃ ((P0 ₄) ₂
Molecular Wt. 310.18(1)	Melting Pt. <u>1670 C⁽¹⁾</u> Bo	iling Pt
Density (Condensed) 3.14 ^(T) @		
Vapor Pressure (recommended 55 C and	20 C)	
Flash Point A	utoignition Temp	-
Flammability Limits in Air (wt %)		·
Explosive Limits in Air (wt. %)	LowerUpper	
Others: soluble in acids ⁽¹⁾	Hot Water decomposes (1)	
Acid, Base Properties		
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification		ation
Comments		
References (1) 1570		
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	AZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name <u>Magnesium Oxide</u> (247)		Structural Formula
IUC Name	1	on deciding from the first of t
Common Names	· 	MgO
Molecular Wt. $40.31(1)$ Density (Condensed) $3.58(1)$ @	Melting Pt2800 ((1) Boiling Pt. 3600 C ⁽¹⁾
Vapor Pressure (recommended 55 C an	d 20 C)	
0		
	Autoignition Temp	_
Flammability Limits in Air (wt %)	Lower	Upper
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility Cold Water 0.00062 grams/100 ml Others: soluble in acids and an Acid, Base Properties	monium salts(1)	eams/100 ml Ethanol <u>insoluble(1)</u>
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification	Coast Gua	ard Classification
Comments		
References (1) 1570		
		•

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Sulfur (413) Structural Fo			
IUC Name	7,11010		
Common Names			
Common NamesS8			
Density (Condensed) $\frac{a^2.07}{8.1.96}$ @ Density (gas) @	Pt. 444.6 C ⁽¹⁾		
Vapor Pressure (recommended 55 C and 20 C) $^{(2)}$			
1 mm Hg @ 183.8 €	e <u>`</u>		
1 mm Hg			
Flammability Limits in Air (wt %) LowerUpper			
Explosive Limits in Air (wt. %) LowerUpper			
Solubility (1) Cold Water insoluble Hot Water insoluble Ethano	Islightly soluble		
Others: soluble in CS ₂ , CCl ₄			
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification Coast Guard Classification_	hazardous article		
Comments			
References (1) 1570 (2) 0766			

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Zinc Oxide (460)		Structural Formu	la
IUC Name	•		
Common Names		Zn0	
Molecular Wt. $81.37^{(1)}$ Density (Condensed) $5.606^{(1)}$ @	Melting Pt. 1975 C	1) Boiling Pt.	
Density (Condensed) 5.606 ⁽¹⁾ @	Density (gas	s)@ _·	
Vapor Pressure (recommended 55 C and	d 20 C)	•	
0)
Flash Point	Autoignition Temp		
Flammability Limits in Air (wt %)	Lower	Upper	_
Explosive Limits in Air (wt. %)	Lower	Upper	-
Solubility Cold Water 0.00016 grams/100 ml Others: scluble in acids, alkal Acid, Base Properties	lis, NH ₄ C1 (1)		insoluble ⁽¹⁾
Highly Reactive with		· ·	· · · · · · · · · · · · · · · · · · ·
Compatible with			
Shipped in			
ICC Classification			
Comments			
	<u>,</u>		
References (1) 1570		٥	
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HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name <u>Aluminum Oxide</u> (465)		Structural Formula	
IUC Name			
Common Names		A1203	
Molecular Wt. 101.96 (1)	Melting Pt. 2045 C	(1) Boiling Pt. 2980 C ⁽¹⁾	
Density (Condensed) 3.965 @	$\frac{25}{2} \frac{\text{C}^{\prime\prime\prime}}{\text{Density (gas)}}$)	
Vapor Pressure (recommended 55 C a			
<u> </u>			
Flash Point	Autoignition Temp.	_	
Flammability Limits in Air (wt %)	Lower	Upper	
Explosive Limits in Air (wt. %)	Lower	Upper	
· · · · · · · · · · · · · · · · · · ·		Ethanolinsoluble ⁽¹⁾	
Others:		·	
Acid, Base Properties -			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification	Coast Gua	ard Classification	
Comments		o	
References (1) 1570 °			
		· "	
ICC ClassificationComments	Coast Gua	ard Classification	

HAZARDOUS WASTES PROPERTIES WORKSHEET						
H. M. Name Vanadium Pentoxide (51	.3)					
IUC Name		Structural Formula				
Common Names		v ₂ o ₅				
Molecular Wt. $181.88^{(1)}$ Density (Condensed) $3.357^{(1)}$ @	Melting Pt. 690 C (1) Density (gas)	decomposes(1) Boiling Pt. @ 1750 C				
Vapor Pressure (recommended 55 C and	-					
	Autoignition Temp					
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower	Upper				
Solubility Cold Water 0.8 grams/100 ml @ 2		Ethanol <u>insoluble</u> (1)				
Others:Acid, Base Properties						
Highly Reactive with						
Compatible with						
Shipped in						
ICC Classification		Classification				
Comments						
	,					
References (1) 1570						

PROFILE REPORT

Aluminum Sulfate (17), Calcium Chloride (90), Calcium Hydroxide (94), Potassium Sulfate (352), Potassium Sulfide (353), Calcium Oxide (483)

1. GENERAL

Introduction

The inorganic chemicals in this Profile Report are basically nontoxic. However, they may react violently with water and/or dissolve in water in sufficiently large concentrations to constitute a hazard or nuisance. They are grouped together here in one report because they can be handled by similar disposal processes.

Aluminum Sulfate

Aluminum sulfate, ${\rm Al}_2({\rm SO}_4)_3$, is a white lustrous crystal or powder. The commercial grade is usually produced in the United States directly from bauxite or clay. ¹⁴³³ Finely ground bauxite is digested with sulfuric acid near the boiling point of the solution. The solids are removed by sedimentation. Unless the bauxite or clay is sufficiently low in iron, the solution may also be treated for iron removal by precipitation of iron compounds, using sulfides of potassium or calcium, hydroxides of calcium or ammonium, etc. In 1960, 1.5 million tons were produced in the United States. Its uses are listed as follows: 1433 , 1492

(1) close to two-thirds of total ${\rm Al}_2({\rm SO}_4)_3$ production is used in the paper industry for clarification of process waters, pH control of pulp slurries, setting of certain dyes and setting of size in paper;

- (2) water treatment applications account for another one-fourth of the total production;
- (3) the remainder ${\rm Al}_2({\rm SO}_4)_3$ goes into manufacture of chemicals, pharmaceutical preparations, dyeing operations, soaps and grease, fire-extinguishing solutions, tanning leather, waterproofing concrete, fireproofing and waterproofing cloth, deodorizing and decolorizing petroleum.

Calcium Chloride

Calcium chloride, CaCl_2 , is a colorless cubic crystal, very hygroscopic. When dissolved in water, much heat is liberated. Commercially, about 50 to 60 percent of the calcium chloride sold in the United States is manufactured from natural brines. In 1961, total U.S. production of CaCl_2 was 558,352 tons flake (77-80%) and 226,636 tons liquor (40-45%). Its uses are:

- as a drying and dehydrating agent for organic liquids and in desiccators;
- (2) drying gases in chemical analyses;
- (3) in brine making in refrigeration plants;
- (4) in control of snow and ice on highways, streets;
- (5) in dust control on secondary roads, unpaved streets and highway shoulders;
- (6) in freezproofing of coal and ores, both in shipping and stockpiling;
- (7) in concrete mixes to give quicker initial set, high early strength and greater ultimate strength.

Calcium Hydroxide

Calcium hydroxide, ${\rm Ca(OH)}_2$, also known as slaked lime, is a colorless, orthorhombic or trigonal crystal, or soft, odorless powder and granules. It readily absorbs ${\rm CO}_2$ from air. When ignited, it loses water to form CaO. Commercially, it is prepared from brine, CaO. 1433

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Its uses are: 1492

- (1) manufacture of mortars, plasters, and cements;
- (2) manufacture of soda ash by the Solvay process;
- (3) in dehairing hides;
- (4) in water paints;
- (5) as antiemetic and in infant feeding formulas to decrease sizes of curds formed from cows' milk.

Potassium Sulfate 1433

Potassium sulfate, K_2SO_4 , is a colorless crystal of rhombic or hexagonal form. It occurs in nature as the mineral arcanite. Commercially, it is obtained from the langbeinite ore, $K_2SO_4 \cdot 2MgSO_4$. It is also one of the many products recovered from the Searles Lake brine. In an unusual situation where HCl is valuable, it can be prepared as shown in the following reaction:

$$2KC1 + H_2SO_4 - K_2SO_4 + 2HC1$$

Finally, it can also be produced by burning sulfur with excess of air mixed with steam and then passing the gaseous mixture through a bed of porous KCl briquets.

$$4KC1 + 2SO_2 + O_2 + 2H_2O \longrightarrow 2K_2SO_4 + 4HC1$$

The U.S. production of potassium sulfate is about 500,000 tons/year. Its uses are:

- (1) as fertilizers (technical grade product);
- (2) in the manufacture of potassium alum (KA1(SO_4)₄·12H₂0), potassium carbonate, and glass;
- (3) in the manufacture of SBR latex rubber;
- (4) in smokeless powder;
- (5) as analytical reagent.

Potassium Sulfide 1492

Potassium sulfide, K₂S, is a yellow to brown crystal of cubic form. It is very hygroscopic and unstable. It discolors in air. It may be prepared from reaction of potassium with sulfur in liquid ammonia. Commercially, it is manufactured by (1) heating potassium sulfate with coal:

$$K_2SO_4 + 4C \longrightarrow K_2S + 4CO$$

or (2) reacting potassium hydroxide with hydrogen sulfide:

$$KOH + H_2S - KSH + H_2O$$
 $KOH + KSH - K_2S + H_2O$

Potassium sulfide has little use except as a laboratory reagent and as a depilatory.

Calcium Oxide

Calcium oxide, CaO, also known as lime or quicklime, is white or grayish-white lumps or granular powder. On exposure to air it absorbs ${\rm CO}_2$ and water becomes air-slaked. With a little water it generates much heat and is converted to ${\rm Ca(OH)}_2$, the slaked lime. Industrially, it is manufactured from calcination of limestone (${\rm CaCO}_3$) in a kiln. 1433

$$CaCO_3 \xrightarrow{\triangle} CaO + CO_2$$

In 1964, 13.5 million tons of CaO were produced in the United States. Its uses are: 1433,1492

- (1) in the manufacture of mortar and plaster;
- (2) in various metallurgical processes, for example, as a flux and in forming a molten slag which purifies the metal in the production of pig iron and steel
- (3) in the manufacture of slaked lime, $Ca(OH)_2$;
- (4) as a desiccant;
- (5) in the manufacture of bleaching agents, pesticides, inorganic and organic salts of calcium, and chlorinated lime;
- (6) in water purification and treatment for potable and industrial purposes;
- (7) in paper pulp processing;
- (8) in the manufacture of glass and ceramics;
- (9) in deodorizing vegetable oils and dehairing hides.

Sources and Types of Wastes

The main sources of wastes for the materials in this report are:

- (1) manufacturers of these materials;
- (2) the paper and water treatment industries;
- (3) various metallurgical operations and processes;
- (4) highway and streets maintainence operations;
- (5) construction industry;
- (6) farming operation;
- (7) chemical laboratories and plants using these materials as chemical reagents;
- (8) textile, rubber, glass and ceramics industries.

The wastes may include contaminated materials and process wastes in the form of solid or aqueous solution.

Physical and Chemical Properties

The physical and chemical properties of the inorganic chemicals treated in this report are given in the attached worksheets.

2. TOXICOLOGY 0225,0766,1312,1492

The materials treated in this report are in general nontoxic. However, they are all soluble in or reactive with water to yield solutions or products which may be corrosive or toxic.

When dry, aluminum sulfate is harmless. When dissolved in water, it hydrolyzes readily to form sulfuric acid which is corrosive and would cause rapid destruction of body tissue on contact.

Generally speaking, calcium compounds are nontoxic. In fact, many calcium compounds are used medicinally. Calcium chloride is completely innocuous. Calcium hydroxide and oxide, on the other hand, may be considered as moderately toxic. They have caustic reaction and therefore are irritating to the skin and respiratory system. In the form of dust, calcium hydroxide can cause dermatitus and irritation of the eyes and mucous membranes.

Potassium sulfate is nontoxic. Potassium sulfide is similar to alkali in action: It causes softening and irritation of the skin. If taken by mouth, it is corrosive and irritant through the liberation of hydrogen sulfide and free alkali. Hydrogen sulfide is toxic.

The Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists and the lethal doses reported are given in the following table:

Contaminant	TLV, mg/M^3	<u>Lethal Dose</u>
Aluminum Sulfate		or LD ₅₀ 770 mg/kg mouse
Calcium Chloride		or LD ₅₀ 4000 mg/kg rat
Calcium Hydroxide		or LD ₅₀ 7340 mg/kg rat
Potassium Sulfate		sc LD _{Ca} 3000 mg/kg guinea pig
Potassium Sulfide		· ·
Calcium Oxide	5	•

3. OTHER HAZARDS

Potassium sulfide may explode on percussion or rapid heating. When exposed to flame or by spontaneous chemical reaction, it may cause moderate fire hazard.

Calcium chloride and calcium oxide generate much heat when dissolved in water due to the heat of solution and the reaction to calcium hydroxide in the latter case.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

In storage, the materials in this report should be kept tightly closed and dry, because most of them would absorb moisture and/or carbon dioxide from the air. Adequate ventilation and dust control should be maintained particularly for storing and handling calcium hydroxide. In shipping, potassium sulfide is classified by the U.S. Coast Guard and the U.S. Department of Transportation (DOT) as flammable solid.

Disposal/Reuse

Industrially, contaminated materials probably will not be considered for reprocessing for reuse based on economic considerations. For the safe disposal of these waste materials, the acceptable criteria for their release into the environment are defined in terms of the following provisional limits:

, , , , , , , , , , , , , , , , , , , ,		Basis for
Contaminant in Air	Provisional Limit	Recommendation
Aluminum sulfate	$0.01 \text{ mg/M}^3 \text{ as } \text{H}_2\text{SO}_4$	0.01 TLV for H ₂ SO ₄
Calcium chloride	0.07 mg/M ³ as HCl	0.01 TLV for HC1
Calcium hydroxide	0.05 mg/M ³	0.01 TLV for CaO
Potassium sulfate	0.01 mg/ M_{2}^{3} as $H_{2}SO_{4}$	0.01 TLV for ${\rm H_2SO_4}$
Potassium sulfide	$0.15 \text{ mg/M}^3 \text{ as H}_2^2 \text{S}^3$	$0.01 \text{ TLV for H}_2\text{S}$
Calcium oxide	0.05 mg/M ³	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for . Recommendation
Aluminum Sulfate	250 ppm (mg/1) as SO_4	Drinking water standard
Calcium Chloride	250 ppm (mg/l) as Cl	Drinking water standard
Calcium hydroxide	0.25 ppm (mg/l)	Stokinger and Woodward method
Potassium sulfate	250 $ppm(mg/1)$ as SO_4	Drinking water standard
Potassium sulfide	0.75 ppm (mg/1) as H_2S	Stokinger and Woodward method
Calcium oxide	0.25 ppm (mg/1)	Stokinger and Woodward method

5. EVALUATION OF WASTE DISPOSAL PROCESSES

Since the materials in this report do not all belong to the same chemical family, slightly different processes are required for their disposal.

Option No. 1 - Hydrolysis and Neutralization for Aluminum Sulfate

Aluminum sulfate can be readily hydrolyzed to yield aluminum hydroxide and sulfuric acid.

$$A1_2(S0_4)_3 + 6H_20 - 2A1(OH)_3 + 3H_2S0_4$$

The sulfuric acid formed is neutralized by NaOH and the insoluble aluminum hydroxide is removed by filtration. The latter may be heated to decomposition to yield alumina which has valuable industrial applications.

$$2A1(0H)_3 \xrightarrow{\Delta} A1_20_3 + 3H_20$$

The neutral solution of sodium sulfate may then be safely discharged into sewers or waterways as long as its concentration is below the recommended provisional limit of 250 mg/liter.

Option No. 2 - Carbonate Precipitation for the Chlorides

Calcium chloride can be treated with soda ash to yield the insoluble calcium carbonate.

$$CaCl_2 + Na_2CO_3 - CaCO_3 + 2 NaCl$$

After removing the carbonate precipitate by filtration, the remaining brine solution, when its sodium chloride concentration is below 250 mg/liter, may be discharged into sewers or any other waterways. Calcium carbonate may be calcined to yield the quicklime, CaO.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Lime has many industrial uses and therefore is a valuable by-product.

Option No. 3'- Neutralization and Carbonate Precipitation for CaO and Ca(OH)₂

Contaminated calcium oxide and hydroxide can be neutralized by hydrochloric acid to yield calcium chloride.

$$Ca(OH)_2 + 2HC1 \longrightarrow CaCl_2 + 2H_2O$$

The calcium chloride formed can now be treated as described in Option No.

2. Since calcium chloride is nontoxic, the neutral aqueous calcium chloride solution could also be diluted to a concentration below 250 mg/liter and discharged directly to sewers, rivers, lakes, oceans, or any other waterways.

Option No. 4 - Sulfide Precipitation for K₂S

Potassium sulfide can be converted into insoluble FeS by ferric chloride solution. After removing the FeS precipitate by filtration, the remaining potassium chloride solution can be diluted to a concentration level below 250 mg/liter and discharged to sewers, rivers, lakes, oceans, or any other waterways. If excess ferric chloride solution has been used to precipitate out FeS, the remaining solution should be neutralized with soda ash followed by filtration and discharge of the waste liquid.

Option No. 5 - Dilution and Discharge

Potassium sulfate and calcium chloride are relatively harmless. Dilute solutions of these two chemicals can be released into streams and bays under careful monitoring and control to ensure that their concentration levels are below the recommended maximum of 250 mg/liter.

In summary, the materials in this report are generally innocuous and soluble in water. The contaminated waste can be dissolved in water to form a dilute solution and discharged into streams or bays under careful control. If the waste solution is acidic (as that of aluminum sulfate) or caustic (as that of calcium hydroxide), they should be neutralized with soda ash or hydrochloric acid, filtered to remove the solid, diluted, and then discharged.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

As mentioned at the beginning of this report, the chemical compounds discussed here have been preliminarily classified as probable candidate waste stream constituents for municipal disposal. Based on the discussion of disposal processes, it may be concluded that the waste treatment for these compounds can be adequately handled locally and no consideration for National Disposal Site is warranted.

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HAZARDOUS WASTES PROPERTIES WORKSHEET						
	WU!	KKSHEET				
H. M. Name <u>Aluminum Sulfa</u> te (17)						
IUC Name			Structural Formula			
Common Names		i	A1 ₂ (SO ₄) ₂			
			2. 4.7			
Malania 14 242 15(1)		n: documen	a 770 c(l) p.			
Molecular Wt. 342.15 ⁽¹⁾ Density (Condensed) 2.71 ⁽¹⁾ @	Melting	Density (gas	es @ 770 C Boiling Pt.			
Vapor Pressure (recommended 55 C and		panores (322	/			
<u> </u>	•	•	0			
		ion Temp				
Flammability Limits in Air (wt %)	Lower_		Voper			
Explosive Limits in Air (wt. %)						
Solubility (1)						
Cold Water 31.3 grams/100 ml @ C	C Hot Wa	ater 98.1 gra	ms/100 ml @ 100 C Ethanol_slightly_so	luble		
Others: soluble in dilute acids						
Acid, Base Properties	 					
Highly Reactive with			<u> </u>			
many Readerite Hiteli						
Compatible with						
Shipped in						
ICC Classification		Coast Gu	ard Classification			
Comments						
References (1) 1570						
References (1) 1570				ļ		

	HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name <u>Calcium Chlori</u> de (90)	,	Structural Formula
Common Names		CaC1 ₂
Molecular Wt. 110.99 ⁽¹⁾ Density (Condensed) 2.15 @	Melting Pt. 772 C	Boiling Pt.> 1160 C ⁽¹⁾
Vapor Pressure (recommended 55 C an		
Flash Point	Autoignition Temp	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		
Solubility ⁽¹⁾ Cold Water 74.5 grams/100 ml @ Others: soluble in acetic acid Acid, Base Properties	, acetone	
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification		ard Classification
References (1) 1570		

н	MAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name <u>Calcium Hydrox</u> ide (94)	,	Structural Formula
Common Names		Ca(OH) ₂
Molecular Wt. 74.09 ⁽¹⁾ Density (Condensed) 2.24 @	Melting Pt. <u>- H₂O @ 5</u> Density (gas	580 C ⁽¹⁾ Boiling Pt. decomposes (1)
Vapor Pressure (recommended 55 C and		٥
	@ Autoignition Temp	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		
Solubility (1) Cold Water 0.185 grams/100 ml @	O CHot Water 0.077 gra	ams/100 ml @ Ethanol insoluble
Others: soluble in acids and am Acid, Base Properties	_	
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification		i
Comments		
References (1) 1570		

H.P.	AZARDOUS W WOR	ASTES PR KSHEET	OPERTIE	S
H. M. Name Potassium Sulfate (352) IUC Name				Structural Formula
Common Names	· · · <u>-</u> · · · · · · ·			K ₂ SO ₄
Molecular Wt. <u>174.27⁽¹⁾</u> Density (Condensed) <u>2.662</u> @				
Vapor Pressure (recommended 55 C and	•			
·	lutoi gni ti			
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) Solubility (1)	Lower			Upper
Cold Water 12 grams/100 ml @ 25 of Others: Acid, Base Properties				
Highly Reactive with				
Compatible with				
Shipped in				
ICC Classification		Coas	t Guard	Classification
References (1) 1570	·			

Н	HAZARDOUS WASTES PROPERTI WORKSHEET	IES
H. M. Name Potassium Sulfide (353)	Structural Formula
IUC Name		
Common Names		K ₂ S
Molecular Wt. 110.27 ⁽¹⁾		
Density (Condensed) 1.805 @		
Vapor Pressure (recommended 55 C an	d 20 C)	
	Autoignition Temp	
Flammability Limits in Air (wt %)		U ppe r
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility (1) Cold Water soluble Others: soluble in glycerin	Hot Water_very solu	ble Eth a nol <u>soluble</u>
Acid, Base Properties	· 	
Highly Reactive with		
Compatible with		
Shipped in	(0)	100
ICC Classification flammable solid	Coast Guar	inflammable (C)
Comments		
References (1) 1570		
(2) 0766		
·		
,		

	AZARDOUS WASTES PROPER WORKSHEET	RTIES
H. M. Name <u>Calcium Oxide</u> (483)		Structural Formula
Common Names		CaO
Molecular Wt. <u>56.08⁽¹⁾</u> Density (Condensed) 3.25 - 3.38 @ Vapor Pressure (recommended 55 C an	Density (gas	(1) Boiling Pt. 2850 C ⁽¹⁾
	6	i i
Flash Point Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) Solubility Cold Water 0.131 grams/100 mg (Others: soluble in acids	Lower	UpperUpper
Acid, Base Properties		
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification		uard Classification
References (1)		

PROFILE REPORT

Ammonium Chloride (20), Ammonium Nitrate (24), Potassium Phosphate (351),

Dehydrated Borax (381), Sodium Carbonate (383), Sodium Nitrate (396),

Sodium Orthophosphates (401)

GENERAL

Introduction

The inorganic chemicals in this Profile Report are basically nontoxic. However, when dissolved in water, they may be present in sufficiently large concentrations to constitute a hazard or nuisance. They are grouped together here because they can be handled by similar disposal processes.

Manufacture and Uses

Ammonium Chloride. Ammonium chloride, NH₄Cl, is a white crystalline substance that has a saline taste and is somewhat hygroscopic. The commercial grade is usually produced as a by-product of the Solvay Ammonia-Soda Process (discussed in the paragraph on sodium carbonate). The ammonium chloride is collected from the other products of the ammonia-soda process by crystallization steps carried out under controlled temperature gradients. Another method used for ammonium chloride manufacture is to react ammonium sulfate with sodium chloride in aqueous solution and crystallize ammonium chloride from the resultant mixture. It is used in soldering flux, washing powders, pickling agents for zinc coating and tinning, electroplating and medicine, and in the manufacture of dyes, various ammonia compounds, fertilizer and cement for pipe joints. O955,1492

Ammonium Nitrate. Ammonium nitrate, NH_4NO_3 , a colorless crystalline material, is an important nitrogen fertilizer because of the high nitrogen content (35%) and the simplicity and cheapness of manufacture. It is a vital ingredient in many explosives. A minor, but important, application

is in the manufacture of nitrous oxide, an anesthetic. There are four basic processes for the manufacture of ammonium nitrate: prilling or spraying, the Stengel process, crystallization, and graining. All ammonium nitrate is made by neutralizing nitric acid with ammonia and collecting a solid product from the reaction product. To decrease deliquescence and caking and to obtain the best physical characteristics, ammonium nitrate is produced by graining, or prilling. Graining involves batch cooling of a concentrated solution under proper agitation to produce small rounded pellets or grains which can be used for fertilizer or as an explosive. For fertilizer use the ammonium nitrate is prilled by spraying hot concentrated ammonium nitrate solution from the top of a tower and allowing the droplets to cool and harden during the fall, forming solid particles (prills) about 1/16 to 3/32 in. in diameter. After drying and screening, the prills or grains are conditioned against moisture pickup by coating them with a material such as diatomaceous earth.

Potassium Phosphate. Potassium phosphate, K_3PO_4 , is a white powder that is soluble in water. It is prepared by the action of phosphoric acid on potassium carbonate. It finds use in water treatment as a sequestering agent. When dissolved in water, a strongly basic solution results. 1492

Dehydrated Borax. Dehydrated borax, $Na_2B_4O_7$, or sodium tetraborate, is a hygroscopic white crystalline material. It is prepared either from the mineral kernite found in the Mojave Desert or from the saline brines of Searles Lake, California. Borax, $Na_2B_4O_7 \cdot 10H_2O$ is recovered from kernite by dissolving the mineral in water, filtering the solution and crystallizing the borax. Borax and potassium chloride are recovered from Searles Lake. The borax is then collected by crystallization. By heating, borax is dehydrated to the anhydrous form. It is used as a water softener and in the manufacture of glass, enamels and other ceramic products. O955

Sodium Carbonate. Sodium carbonate, Na₂CO₃, or soda ash--the crude sodium carbonate of commerce, is in the form of a grayish-white powder or lumps that contain 99 percent sodium carbonate. Over 90 percent of the world's production of soda ash is made by the Solvay ammonia-soda process with the remaining quantities being recovered from natural deposits or brines in California and Wyoming. The raw materials for the Solvay process are coke, salt, lime and ammonia. The reactions of the process are as follows:

Soda ash is used in large quantities by the glass, soap, water treatment, chemical, pulp and paper, petroleum, nonferrous metals and textile industries. 1662

Sodium Nitrate. Sodium nitrate, $NaNO_3$, is a colorless, transparent, odorless crystalline material. It is prepared by reacting sodium carbonate with nitric acid or by recrystallization of Chile saltpeter which is impure natural sodium nitrate. It is widely used in the chemical industry, in fertilizers and in making explosives such as dynamite. 1492

Sodium Orthophosphates. The orthophosphates, such as NaH_2PO_4 . $7H_2O$, and $Na_3PO_4\cdot 12H_2O$, with the general formula $Na_{3-x}H_xPO_4(x=0,1,2)$ are used chiefly in packaged detergents and soaps and in water softening. Sodium dihydrogen phosphate has been used as an ingredient in baking powder. The orthophosphates are prepared by treating soda ash with the proper quantities of phosphoric acid. 1492

Physical and Chemical Properties

The physical/chemical properties for the compounds covered by this Profile Report are summarized on the attached worksheets.

2. TOXICOLOGY

The materials treated in this report are not considered particularly toxic. However, soda ash and the basic orthophosphates because of their alkalinity are irritating to the skin, and their dust is irritating to the respiratory tract. Boron compounds such as borax may result in accidental poisoning by oral ingestion and toxic reactions in small children may result through skin absorption. The American Conference of Governmental Industrial Hygienists has not established Threshold Limit Values (TLV) for any of the compounds listed in this report. The lethal doses reported for the compounds are given below:

Contaminant	<u>Le</u>	thal Dose
Ammonium Chloride	im LD ₅₀ :	30 mg/kg, rat
Ammonium Nitrate		
Potassium Phosphate	or LD ₅₀ :	1600 mg/kg, mouse
Borax		
Sodium Carbonate	or LD ₅₀ :	4200 mg/kg, rat
Sodium Nitrate	or LD _{Ca} :	200 mg/kg, rat
Sodium Orthophosphate	ip LD ₅₀ :	326 mg/kg, rat

OTHER HAZARDS

Ammonium and sodium nitrate are fire hazards when in contact with organic materials or other readily oxidizable substances. Ammonium nitrate may explode under confinement at high temperature. A mixture of ammonium nitrate and diesel oil is used industrially as an explosive. Explosions have occurred with ammonium nitrate in ship's holds. However, there have been warehouse fires where ammonium nitrate burned and did not explode. Upon heating, ammonium and sodium nitrate give off toxic fumes of nitrogen oxides. 0955

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

In storage, the materials in this report require special care only with respect to protection from moisture, their alkaline or acid nature when dissolved in water, and the fire or explosion hazards discussed in Section 3. Na_3PO_4 and sodium carbonate are alkaline when dissolved in water and will attack aluminum. NaH_2PO_4 is acid when dissolved and will attack many metals. Both ammonium nitrate and sodium nitrate are classified by the Coast Guard and Department of Transportation (DOT) as oxidizing materials that require a Yellow Label.

Disposal/Reuse

Industrially contaminated materials may on occasion be reprocessed for reuse. If disposal is to be carried out, safe disposal of these materials is here defined in terms of the following recommended provisional limits in air, potable water and in marine habitats:

		Basis for
Contaminant in Air	Provisional Limit	Recommendation
Ammonium Chloride	0.10 mg/M^3	.01 TLV
Ammonium Nitrate	0.05 mg/M ³	Data for Similar Compounds
Potassium Phosphate	0.01 mg/M ³	Data for Similar Compounds
Borax	0.02 mg/M^3	Data for Similar Compounds
Sodium Carbonate	0.02 mg/M^3	Data for Similar Compounds
Sodium Nitrate	0.05 mg/M^3	Data for Similar Compounds
Sodium Orthophosphate	0.01 mg/M ³	Data for Similar Compounds
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Ammonium Chloride	250 mg/l as Cl	Drinking Water Standard
Ammonium Nitrate	45 mg/l as NO ₃	Drinking Water Standard
Potassium Phosphate	0.05 mg/1 as H_3PO_4	Stokinger and Woodward . Method
Borax	0.10 mg/1	Drinking Water Standard
Sodium Carbonate	.10 mg/1	Stokinger and Woodward Method
Sodium Nitrate	$45 \text{ mg/1 as } \text{NO}_3$	Drinking Water Standard
Sodium Orthophosphates	0.05 mg/l as H ₃ PO ₄ *	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Dilution and Discharge

The Manufacturing Chemists Association has recommended disposal of all the materials in this report by discharge into sewers after neutralization and dilution. If each of the materials are diluted to the levels indicated in Section 4 as recommended provisional limits in water and the pH is adjusted to between 6.5 and 9.1, the materials can be discharged into sewers or natural streams. 0095

This acid limit is not applicable directly to the phosphate salts, however, eutrophication is encouraged by phosphate levels above 0.1 mg/l in water. Reference to Section 2 indicates that the salts are not very toxic to mammalian life.

Option No. 2 - Treatment with Sodium Hydroxide

Both ammonium nitrate and ammonium chloride upon treatment with sodium hydroxide liberate ammonia and form soluble sodium salts, either the chloride or nitrate. The liberated ammonia can be recovered and sold. After dilution to the limits noted in Section 4, sodium nitrate or sodium chloride can be discharged into a stream or sewer.

Option No. 3 - Incineration

Ammonium nitrate and ammonium chloride after dilution with water can be charged into a gas fed incinerator. The NO $_{\rm X}$ and/or HCl formed must be removed by appropriate gas cleaning devices (scrubber for HCl and NO $_{\rm 2}$, oxidation or reduction for NO). Though this method is possible, it is not in wide use.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The materials discussed in this report have been classified as probable candidate waste stream constituents for muncipial disposal. Based on the discussion of disposal in Section 5, it may be concluded that the waste treatment of these compounds can be adequately handled locally and no consideration for National Disposal Site treatment is warranted.

7. REFERENCES

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 - 1570. Chemical Rubber Company. Handbook of chemistry and physics. 47th ed. Cleveland, Chemical Rubber Company, 1966. 1,500 p.
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HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Ammonium Chloride (20)	Structural Formula	
IUC Name <u>Ammonium Chlor</u> ide		
Common Names Sal Ammoniac	NH ₄ C1	
Molecular Wt. 53.50 ⁽²⁾ Melting Pt	(1) Boiling Pt. <u>350 C sublim</u> es	
Density (Condensed) 1.54 ⁽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		
Solubility Cold Water 29.7g/100g at 0 C ⁽²⁾ Others: soluble - NH ₄ OH Acid, Base Properties Acid in aqueous solution due to hydroxymathers		
Highly Reactive with Liberates ammonia when treated with	h sodium hydroxide	
Composition		
Compatible with		
Shipped in barrels, multiwall paper sacks		
	ard Classification none (1)	
	ard Classification none	
Comments		
Pofovores (1) 1400		
References (1) 1492 (2) 1570		
ο		
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HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Ammonium Nitrate (24) IUC Name Ammonium Nitrate Common Names Norway Saltpeter NH ₄ NO ₃		
Molecular Wt. 80.05 Melting Pt. 169.6 C ⁽¹⁾ Boiling Pt. 210 decomposes Density (Condensed) 1.725g/cc @ 23 C Density (gas) @ Vapor Pressure (recommended 55 C and 20 C)		
ee		
Flash Point Autoignition Temp Flammability Limits in Air (wt %) Lower Upper Explosive Limits in Air (wt. %) Lower Upper		
Solubility (2) (2) Cold Water 118g/100g at 0 C ⁽²⁾ Hot Water 871g/100g at 100 C Ethanol 2.8g/100g at 20 C Others: alkalies - soluble Acid, Base Properties		
Highly Reactive with <u>Reacts with strong alkalies to liberate ammonia</u> . The mixture of ammonium nitrate with diesel oil is used as an industrial explosive.		
Compatible with		
Shipped in Bags, carloads, truckloads		
ICC Classification Oxidizing material Coast Guard Classification Oxidizing material Comments		
References (1) 1492 (2) 1570		

HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name <u>Potassium Phos</u> phate (351) IUC Name <u>Potassium Phos</u> phate, Tribasic	Structural Formula	
Molecular Ht. 212.31 ⁽²⁾ Melting Pt. 1340 C	K ₃ PO ₄ Boiling Pt	
Density (Condensed)	6	
Flash Point Autoignition Temp.		
Flammability Limits in Air (wt %) Lower		
Solubility Cold Hater Soluble(1) Hot Water Soluble Others:	(1) Ethanol Insoluble(1)	
Acid, Base Properties Strong base in water (1)		
Highly Reactive with		
Compatible with		
Shipped in 275, 300, 400-1b drums ⁽¹⁾ ICC Classification None ⁽¹⁾ Coast Gu Comments Hygroscopic ⁽¹⁾	uard Classification None (1)	
References (1) ₁₄₉₂ (2) 1570		

HAZARDOUS WASTES PROPER WORKSHEET	RTIES
H. M. Name Borax Dehydrated (381)	Structural Formula
IUC Name Sodium Tetraborate	
Common Names	Na ₂ B ₄ O ₇
Molecular Wt. $201.27^{(2)}$ Melting Pt. $741 C^{(1)}$ Density (Condensed) $2.367g/cc$ @ $23 C^{(1)}$ Density (gas	Boiling Pt. <u>1575 Cd⁽²⁾</u>
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	
Solubility Cold Water 1.49g/100g at 0 C ⁽²⁾ Others:	
Acid, Base Properties	
Highly Reactive with	· 1
Compatible with	
Shipped in 100 1b paper bags, boxcars ⁽¹⁾	
ICC Classification None (1) Coast Gu Comments Hygroscopic (1)	uard Classification None (1)
References (1) 1492 (2) 1570	

HAZAR	DOUS WASTES PROPERTIES WORKSHEET
H. M. Name <u>Sodium Carbo</u> nate (383) IUC Name <u>Sodium Carbo</u> nate	Structural Formula
Common Names <u>Soda Ash</u>	. Na ₂ CO ₃
	Density (gas) Boiling Pt. decomposes (2) Boiling Pt. decomposes (2)
	 0
Flash Point Auto Flammability Limits in Air (wt %) Lo Explosive Limits in Air (wt. %) Lo	
Solubility Cold Water_7.lg/100 ml at 0 C ⁽²⁾ Others:	(2) lot Water 45.5g/100 ml at 100 CEthanol Insoluble
Acid, Base Properties <u>Alkaline⁽¹⁾</u>	
Highly Reactive with <u>Acids⁽¹⁾</u>	
Compatible with	
Shipped in Bags, barrels, drums, bulk)
	Coast Guard Classification None (1)
References (1) 1492 (2) 1570	

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name <u>Sodium Nitrate (396)</u> IUC Name Sodium Nitrate		Structural Formula		
Common Names Chile Saltpeter		NaNO ₃		
Molecular Wt. 85.01 ⁽²⁾ Density (Condensed) 2.267 @ 20	Melting Pt. $\frac{308 \text{ C}^{(2)}}{\text{C}^{(1)}}$ Density (gas	Boiling Pt. Decomposes (2)		
Vapor Pressure (recommended 55 C and	20 C)			
Flash Point A	@ utoignition Temp			
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower			
Solubility (2) (1) Cold Water 73g/100 ml at 0 C ⁽²⁾ Hot Water 180g/100 ml at 100 C Ethanol Slightly Soluble Others: Glycerol - soluble Acid, Base Properties				
Highly Reactive with <u>Organic matter</u> /				
Compatible with				
Shipped in Tins, glass bottles, bag	s up to 100 lb, bulk (1)		
ICC Classification ozidizing materia Comments	1 ⁽¹⁾ Coast Gu	ward Classification oxidizing material		
References (1) 1492 (2) 1570				

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Sodium Phosphate (401)	Structural Formula			
IUC Name Sodium Phosphate, Monobasic	Scruccural rormara			
Common Names	NaH ₂ PO ₄ · H ₂ O			
Molecular Wt. $138.05^{(1)}$ Melting Pt. $200C-H_20^{(1)}$ Density (Condensed)2.040g/cc @ 20 C ⁽¹⁾ Density (gas	Boiling Pt.200 C-2H ₂ O ⁽¹⁾			
)			
Vapor Pressure (recommended 55 C´and 20 C)				
Flash Point Autoignition Temp				
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower				
Expressive Limits in Air (wt. 3) Lower	Upper			
Solubility	(1).			
Cold Water 59.9g/100 ml at 0 C(1) Hot Water 427g/100	ml at 100 CEthanol insoluble''			
Others:Acid ⁽²⁾ .				
Highly Reactive with	·			
Compatible with				
Shipped in Bags, drums, barrels				
ICC Classification None ⁽²⁾ Coast Gua	ard Classification None ⁽²⁾			
Comments				
References (1) 1570				
(2) 1492				
	•			

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Sodium Phosphate (401)	Structural Formula			
IUC Name Sodium Phosphate, Dibasic				
Common Names	Na ₂ HPO ₄ · 2H ₂ O			
Molecular Wt. $178.05^{(1)}$ Melting Pt. 92.5 C-H. Density (Condensed) 2.066 @ 15 C ⁽¹⁾ Density (gas	2 ⁰ Boiling Pt			
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				
Solubility Cold Water 82.5g/100 ml at 50 C ⁽¹⁾ Hot Water 96.6g/100 Others: Acid, Base Properties				
Highly Reactive with				
Compatible with				
Shipped in Bags, fiber drums, barrels ⁽²⁾				
ICC Classification none (2) Coast Gu	ard Classification none ⁽²⁾			
Comments				
5				
References (1) 1570				
(2) 1492				
1436				
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HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Sodium Phosphate (401) IUC Name Sodium Phosphate, Tribasic Common Names	Structural Formula Na ₃ PO ₄ 10H ₂ O			
Density (Condensed) $2.536g/cc$ @ 175 $C^{(1)}$ Density (g Vapor Pressure (recommended 55 C and 20 C)	,			
Flash Point Autoignition Temp Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower Solubility Cold Water1.5g/100 ml at 10 C(1) Hot Water_157g/10	UpperUpper			
Others: Acid, Base Properties Basic (2) Highly Reactive with				
Compatible with				
ICC Classification None (2) Coast (Guard Classification None ⁽²⁾			
References (1) 1570 (2) 1492				

PROFILE REPORT

Ammonium Hydroxide (19), Boron Chloride (62), Carbon Monoxide (99) Hydrochloric Acid (aq) (214), Hydrofluoric Acid (aq) (216), Hydrogen Chloride (g) (217), Hydrogen Peroxide (aq., >52%) (219), Iodine (tincture) (223), Mixed Acids (277), Nitric Acid (299), Nitrous Oxide (313), Silicon Tetrachloride (369), Sulfur Dioxide (414), Sulfuric Acid (415), Sulfurous Acid (416), Sulfuryl Fluoride (417), Sulfur Trioxide (509)

1. GENERAL

Introduction

The inorganic chemicals discussed in this Profile Report have been preliminarily identified as probable candidate waste stream constituents for industrial disposal. The grouping is based on broad chemical and/or physical similarities and covers both gases and liquids.

Manufacture and Uses

The industrial processes of manufacturing and uses of the materials in this report are summarized briefly as follows.

Ammonium Hydroxide. Ammonium hydroxide, NH₄OH, also called ammonia water, is essentially ammonia dissolved in water. Ammonia is a very important and basic raw material for modern chemical industry. It is produced in large tonnage by the well-known Haber process in which hydrogen and nitrogen gases react catalytically under elevated temperature and pressure to yield ammonia. In 1965, 8.4 million tons of ammonia were produced in the United States. ¹⁶⁶² The weaker ammonia water (10%) has been used as a reflex stimulant. The stronger ammonia water (28-29%) may be used for the following purposes:

(1) as a detergent and in removing stains, bleaching, calico printing, and extracting plant colors (cochineal, archil, etc.) and alkaloids;

- (2) in the manufacture of ammonium salts, aniline dyes;
- (3) as a chemical reagent and in a wide variety of other uses.

Boron Chloride. 1433 Boron chloride, BCl₃, is a colorless gas produced commerically by chlorination of a mixture of boron trioxide and carbon at a temperature range of 1,600 to 1,800 F. It can also be prepared according to the reactions shown below:

(1)
$$7B_2O_3 + 6NaC1 \xrightarrow{800 \text{ to } 1000 \text{ C}} 2BC1_3 + 3Na_2B_4O_7$$

(1)
$$7B_2O_3 + 6NaC1 \xrightarrow{800 \text{ to } 1000 \text{ C}} 2BC1_3 + 3Na_2B_4O_7$$

(2) $2NaBF_4 + 3MgC1_2 \xrightarrow{500 \text{ to } 1000 \text{ C}} 2BC1_3 + 2NaF + 3MgF_2$

(3)
$$2B_2O_3 + 3SiCl_3 \xrightarrow{600 \text{ to } 1000 \text{ C}} 4BCl_3 + 3SiO_2$$

Its uses are:

- (1) in the manufacture of other boron compounds;
- (2) as an acidic catalyst for organic reactions;
- (3) in the purification of aluminum, magnesium, zinc and copper alloys to remove nitrides, carbides, and oxides.

Carbon Monoxide. 1492 Carbon Monoxide, CO, is a colorless and odorless gas, highly poisonous and flammable. It is produced by partial oxidation of hydrocarbon gases from the natural gas or by the gasification of coal or coke. Its uses are:

- (1) as a reducing agent in various metallurgical processes;
- (2) in organic synthesis, especially in the Fischer-Tropsh process;
- in the manufacture of acids, esters, hydroxy acids, and metal carbonyls;
- (4) in the preparation of some catalysts.

Hydrochloric Acid. Hydrogen chloride, HCl (g), is a colorless gas. Its aqueous solution is the hydrochloric acid. It is produced from four major processes: 1662

- as a by-product in the chlorination of both the aromatic and aliphatic hydrocarbons;
- (2) from the reaction between sulfuric acid and salts of hydrochloric acid such as the common salt, NaCl;
- (3) from the combustion of hydrogen and chlorine;
- (4) from the Hargreaves type reactions such as $4NaC1 + 2SO_2 + O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4HC1$

In 1969, 1.8 million tons were produced in the United States. Its major uses are: 1492

- (1) in the manufacture of pharmaceutical hydrochlorides, various inorganic and organic chlorides, and chlorine;
- (2) in chlorination, isomerization, polymerization and alkylation processes;
- (3) as a chemical reagent.

<u>Hydrofluoric Acid.</u> 1433 Hydrofluoric acid, HF, is a colorless, fuming, corrosive liquid or gas. It is produced in heated kilns by reacting fluorspar, CaF_2 , with sulfuric acid.

The U.S. production of hydrofluoric acid amounted to about 310,000 tons in 1969. Its uses are:

- (1) in the manufacture of fluorinated organics;
- (2) in the manufacture of synthetic cryolite, fluorides, fluoborates, fluorosilicon products;
- (3) in producing nuclear energy feed materials;
- (4) in petroleum industry as an alkylation catalyst;
- (5) in stainless steel industry;
- (6) in etching and polishing glasses.

<u>Hydrogen Peroxide.</u> 1433 , 1492 Hydrogen peroxide, 1420 , is a colorless, heavy liquid or at low temperatures a crystalline solid. It is manufactured by:

- (1) autoxidation of anthraquinone;
- (2) oxidation of a lower secondary alcohol, preferably isopropyl alcohol, to yield H_2O_2 and ketone;
- (3) electrolysis through ammonium persulfate.

In 1969, 70,000 tons of H_2O_2 were produced in the United States. Its uses are:

- (1) as a bleaching agent of cotton textiles (largest uses);
- (2) as an oxidizing agent for organic compounds (second largest application);
- (3) as an oxidizing agent for inorganic compounds;
- (4) in the manufacture of organic and inorganic peroxides;
- (5) in the plastics industry;
- (6) in pharmaceutical preparations, mouth washes, dentifrices, sanitary lotions;
- (7) as a topical antiseptic;
- (8) in rocket propulsion (using 90 percent solution).

<u>Iodine (tincture)</u>. 1433, 1662 Iodine is a violet-black rhombic crystal with metallic luster. It is soluble in water and organic solvents such as alcohol, ether, etc. It is produced by extraction from (1) the nitrate-bearing earth known as caliche in Chile, (2) brine, and (3) seaweed. The U.S. consumption of iodine amounts to about 3,500 tons a year. Its main uses are:

 in the production of potassium iodide for photography (about 38 percent of total iodine is for this purpose);

- (2) in the manufacture of other iodine compounds, germicides, antiseptics;
- (3) as a catalyst in alkylation and condensation of aromatic amines, sulfations, and sulfonations;
- (4) as an additive to salt to meet the requirements of the thyroid gland;
- (5) as an analytical reagent;
- (6) in various nutritional, medicinal and sanitary applications;
- (7) in making artifical isotopes for biochemical, biological and chemical structure research.

Mixed Acids. 1433 Mixed acids are mixtures of sulfuric acid and nitric acid in various proportions. The standard mixed acid contains 36 percent of concentrated nitric acid and 61 percent of concentrated sulfuric acid. It is mainly used for nitrating purposes such as in producing the nitrated cotton. The presence of concentrated sulfuric acid increases the efficiency of the nitration by absorbing the water which is the product of nitration reaction.

Nitric Acid. 1433 Nitric acid, HNO_3 , is a colorless or yellowish, fuming suffocating, corrosive liquid. Virtually all nitric acid produced commercially is obtained by the ammonia oxidation process. Despite the many variations in the manufacturing details, the basic steps are as follows:

(1) Oxidation of ammonia to nitric oxide;

$$4NH_3 + 50_2 - 4N0 + 6H_20$$

(2) Oxidation of nitric oxide to dioxide;

$$2N0 + 0_2 \longrightarrow 2N0_2$$

(3) Absorption of nitrogen dioxide in water to yield nitric acid and release additional nitric oxide;

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

In 1969, the total U.S. production of nitric acid was about 6.14 million tons. Its main uses are summarized as follows:

- (1) About 70 to 85 percent of nitric acid produced is used to produce ammonium nitrate which is used as fertilizer;
- (2) About another 5 to 10 percent is used to produce cyclohexanone which is the raw material for making the monomers for nylon;
- (3) The remaining nitric acid is used for manufacturing various inorganic and organic nitrates and nitro compounds.

Nitrous Oxide. 1433 , 1492 Nitrous oxide, N 20, more commonly known as laughing gas, is a colorless gas with a slight sweet odor and taste. It is prepared by thermal decomposition of ammonium nitrate at a temperature range of 170 to 260 C. It can also be prepared by reaction between hydroxylamine (NH₂OH) and nitrous acid (HNO₂). Its uses are:

- (1) as inhalation anesthetic and analgesic;
- (2) as an oxidizing agent for organic compounds;
- (3) in the manufacture of nitriles;
 - (4) in rocket fuel formulation;
 - (5) in the preparation of whipped cream.

 $\frac{\text{Silicon Tetrachloride.}}{\text{1433}} \quad \text{Silicon tetrachloride, SiCl}_4, \text{ is a colorless, fuming liquid with a suffocating odor. It is decomposed by water into silicic and hydrochloric acids with much heat liberated. Commercially, it is produced by reacting silicon carbide with chlorine gas. The production in the United States is about 35 to 40 million 1b a year. Its main uses are:$

- (1) in producing smoke screen (fumed silica) in warfare;
- (2) in the manufacture of high purity silicon;
- (3) in the synthesis of silicon esters;
- (4) in making special glass for the electronic industry.

Sulfur Dioxide. 1433 Sulfur dioxide, SO_2 , is a colorless gas with a strong pungent, suffocating odor. It is mainly produced by the oxidation of sulfur, and also an undesirable by-product in the exhaust streams of petroleum refining, natural gas processing and coal-burning power plants. About 85 percent of SO_2 produced goes into manufacturing sulfuric acid. The other uses are:

- (1) in the manufacture of pulp and paper;
- (2) as a bleaching agent, refrigerant, and liquid solvent;
- (3) in the manufacture of other chemicals;
- (4) in preserving fruits, vegetables, etc., and as a disinfectant in breweries and food factories. 1492

Sulfuric Acid. 1662 Sulfuric acid, $\mathrm{H_2SO_4}$, is a colorless, oily, corrosive liquid. It is so widely used that it may be considered as the foundation of the modern chemical and petrochemical industries. In 1969, 28 million tons were produced in the United States. Its main uses are given as follows:

- (1) 44 percent of the sulfuric acid produced in the United States is used to manufacture superphosphate (36%) and phosphate-type (8%) fertilizers;
- (2) 21 percent is used in the chemical industry for making phosphoric acid, aluminum sulfate, paper, etc.;
- (3) 10 percent is used in the petroleum industry, mainly in the alkylation process (55%);
- (4) Other major uses are in the manufacture of titanium pigments, steel pickling, rayon, dyes and intermediates, detergents, etc.

Sulfurous Acid. 1433, 1492 Sulfurous acid, H₂SO₃, is a colorless liquid with the suffocating odor of sulfur. It is made by dissolving sulfur dioxide in water. It is used mainly as sulfur dioxide in aqueous solution. It is an excellent low cost reducing agent. In acid solution, sulfurous acid will also act as an oxidizing agent in the presence of reducing agents such as hydrogen sulfide, hydrogen iodide, reduced metal salts, and zinc. Medicinally, sulfurous acid has been used externally in parasitic skin diseases, as a swab in tonsillitis, and as a gastric antiseptic in pyrosis.

Sulfuryl Fluoride. 1492 Sulfuryl fluoride, SO_2F_2 , is a colorless and odorless gas. It is prepared according to the following reactions:

(1)
$$BaC1_2 + 2HS0_3F \longrightarrow Ba(S0_3F)_2 + 2HC1$$

(2)
$$Ba(SO_3F)_2 \xrightarrow{450C} SO_2F_2 + BaSO_4$$

(3)
$$2AgF_2 + SO_2 \longrightarrow SO_2F_2 + 2AgF$$

Sulfur Trioxide. 1492, 1570 Sulfur trioxide, SO_3 , exists in more than one form. α - SO_3 is a silky, fibrous, needle-like crystal. β - SO_3 is metastable asbestos-like fiber. γ - SO_3 is a metastable, vitreous, orthorhombic crystal or colorless liquid (melting point, 16.8 C). It is prepared by catalytic oxidation of sulfur dioxide. Its major use is as an intermediate in the manufacture of sulfuric acid. Other uses are:

- (1) in sulfonation;
- (2) in the manufacture of explosives;
- (3) in the formation of addition compounds with the amines.

Sources and Types of Wastes

A large number of chemicals are covered in this report. Some of the chemicals are the basic raw materials in the chemical industry. Hence, the sources of the wastes are very widespread. Generally, they include

coal-burning power plants, manufacturers and users of these chemicals in various industrial plants, laboratories, and their distributors. For the same reason, the types of wastes to be expected will include both concentrated and dilute wastes in the exhaust gas and liquid streams.

Physical and Chemical Properties

Physical and chemical properties of the chemicals in this report are given in the attached worksheets.

2. TOXICOLOGY 0766,1492

Ammonium hydroxide or ammonia water is an irritant to the eyes and mucous membranes. Corneal ulcers have been reported following splashing of ammonia water in the eye. When heated, it emits toxic fumes. Inhalation of concentrated fumes would cause edema of the respiratory tract, spasm of the glottis, and asphyxia.

The toxic effect of boron chloride is not too well known. However, when heated to decomposition, it would emit toxic fumes of chlorides.

Carbon monoxide is highly poisonous due to its strong affinity for hemoglobin (210 times that of oxygen). It combines with hemoglobin to form the carboxyhemoglobin which is useless as an oxygen carrier. The effect on the body is therefore predominantly that of asphyxia. The symptoms are headache, dizziness, nausea, vomiting, loss of muscular control, unconsciousness, and death.

Hydrochloric acid is strongly corrosive. It is irritant to the mucous membranes of the eyes and the respiratory tract. On contact, concentrated solution would cause severe burns; permanent visual damage may occur. Inhalation of the fume results in cough, choking, and inflammation and ulceration of the respiratory tract. However, in general, hydrochloric acid causes little trouble in industry, other than from accidental splashes and burns.

Hydrofluoric acid is corrosive and poisonous. External contact with liquid or vapor causes severe irritation of the eyes and eyelids which may result in prolonged or permanent visual defects or total destruction of the eyes. Skin contact results in severe burns. Inhalation of vapor may cause extreme irritation of respiratory tract, pulmonary inflammation, congestion, and fluorosis. The symptoms are weight loss, malaise, anemia, leukopenia, and osteosclerosis.

Hydrogen peroxide is not a toxic material. It is, however, a strong oxidizer. Strong solutions can cause burns of skin and mucous membranes.

Iodine is one of few elements required by the human body. A normal person needs about 75 mg of iodine a year to satisfy the requirement of the thyroid gland. Lack of iodine in the body is the cause of goiter. Lack of iodine in the body is the cause of goiter. It is also an antidote to alkaloid poisoning. Iodine vapor is irritating to the lung. But serious exposures are seldom due to the low volatility of the solid. Ingestion of large quantities of iodine would cause abdominal pain, nausea, vomiting and diarrhea.

Mixed acid is a mixture of nitric and sulfuric acids, and its corrosive and toxic effects are those of the constituent acids.

Nitric acid is very corrosive. Its vapor is highly irritating to the skin and the mucous membranes of the eyes and respiratory tract. Continued exposure to the vapor may cause chronic bronchitis and chemical pneumonia. Ingestion of nitric acid causes burning and corrosion of mouth, esophagus, stomach, abdominal tenderness, shock, and death.

Nitrous oxide is not a toxic gas. In fact, it is used as inhalation anesthetic and analgesic. However, in high concentrations, it is narcotic. It is also an asphyxiant.

Silicon tetrachloride may be an irritant to the eyes and respiratory tract but is basically nontoxic. However, when heated to decomposition, it will emit highly toxic fumes of hydrochloric acid. It will also react with water or steam to produce toxic and corrosive fumes.

Sulfur dioxide is corrosive and poisonous. It is dangerous to the eyes because it causes irritation and inflammation of the conjunctiva. It affects the upper respiratory tract and the bronchi. It may cause edema of the lungs or glottis, and can produce respiratory paralysis. Excessive exposure to high enough concentrations of sulfur dioxide can be fatal.

Sulfuric acid is very corrosive to all body tissues. Contact with eyes may result in total loss of vision and skin contact may produce severe necrosis. Inhalation of concentrated vapor may cause serious lung damage. Ingestion may cause severe injury and death.

Sulfurous acid is also corrosive. When heated to decomposition, it emits the toxic fume of sulfur dioxide.

Sulfuryl fluoride is highly irritant and toxic. Inhalation may cause nausea, vomiting, abdominal distress, diarrhea, muscular weakness, convulsions, collapse, respiratory and cardiac failure and death.

Sulfur trioxide is irritant and corrosive to mucous membranes. It may cause coughing, choking, and severe discomfort. When heated to decomposition, it emits highly toxic fumes of oxides of sulfur. It will also react with water or steam to produce toxic and corrosive fumes of sulfuric acid.

The Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists and the reported lethal doses or concentrations for the chemicals are given below. 0255 , 1312

Contaminant	TLV	Lethal Dose or Concentration
Ammonium Hydroxide	$35 \text{ mg/M}^3 \text{ (NH}_3\text{)}$	or LD: 250 mg(NH ₃)/kg, rat
Boron Chloride		ih LC _{Ca} : 20 ppm, rat
Carbon Monoxide	55 mg/M ³	ih LC _{Ca} : 2000 ppm, mouse
Hydrochloric Acid (g)	7 mg/M ³	ih LC _{Ca} : 1000 mg/M ³ , rabbit
Hydrofluoric Acid (aq)	2	ih LC ₅₀ : 1310 ppm, rat ih LC _{Ca} : 1000 mg/M ³ , guinea pig
(g)	2 mg/M ³	ih LC _{Ca} : 1000 mg/M ³ , guinea pig
Hydrogen Peroxide	1.4 mg/M ³	
Iodine	1.0 mg/M ³	or LD _{Ca} : 30 mg/kg, man
Mixed Acids		
Nitric Acid	5 mg/M ³	
Nitrous Oxide	asphyxiant	
Silicon Tetrachloride		ih LC _{Ca} : 8000 ppm, rat
Sulfur Dioxide	13 mg/M^3	ih LC _{Ca} : 1000 ppm, rat
Sulfuric Acid	1.0 mg/M ³	ih LC ₅₀ : 500 mg/M ³ , rat
		or LD ₅₀ : 2140 mg/kg, rat
Sulfurous Acid		
Sulfuryl Fluoride	20 mg/M ³	or LD _{Ca} : 100 mg/kg, rat
Sulfur Trioxide		

3. OTHER HAZARDS

Boron chloride hydrolyzes readily in moist air or water to yield corrosive hydrochloric acid. Carbon monoxide is very flammable. Hydrogen peroxide is a powerful oxidizer, particularly the concentrated solution. Heat is generated during hydrogen peroxide decomposition, and hence it is a fire hazard when heated or contacted with flammable materials. Nitrous oxide supports combustion and can form an explosive mixture with air. A shock can shatter the nitrous oxide container with explosive force. Nitric acid is a powerful oxidizing agent, and can cause a moderate fire hazard by chemical reaction with reducing agents. It can also explode on contact with powerful reducing agents. Similarly, sulfuric acid is also a powerful oxidizing agent and can ignite upon contact with combustibles. Also, sulfuric acid has a strong affinity for water, generating much heat in mixing.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transporation

Corrosive materials such as sulfuric and hydrochloric acid must be handled carefully. Contact with skin and inhalation of the fume should be avoided. They should also be kept away from feed and food products. Flammable chemicals, such as carbon monoxide, should be kept away from heat and stored in cool and well-ventilated areas. Powerful oxidizers such as hydrogen peroxide, nitric acid, etc., should be kept away from reducing agents or combustible materials. Practically every chemical treated in this report should be kept tightly closed in its original container. Utmost care must be excercised to prevent the leaking of carbon monoxide from its containers, because it is highly poisonous and odorless. It should be stored in a very well-ventilated area.

Disposal/Reuse

In general, the chemicals discussed in this report could not be economically reprocessed for reuse when they are contaminated or present in the process waste stream. The notable exceptions are iodine, nitric acid, and under certain conditions, sulfuric acid. Iodine is a valuable commodity. Nitric and sulfuric acid wastes are often in concentrated forms and are susceptible to regeneration. For the safe disposal of these chemicals, the acceptable criteria for their release into the environment are defined in terms of the following provisional limits:

	• •	Basis for
Contaminant in Air	Maximum Exposure Limit	Recommendation
Ammonium Hydroxide	$0.02 \text{ mg/M}^3 \text{ as NH}_3$	0.01 TLV for NaOH
Boron Chloride	0.03 mg/M ³	0.01 TLV for BF_3
Carbon Monoxide	0.55 mg/M^3	0.01 TLV
Hydrochloric Acid	0.07 mg (vapor)/M ³	0.01 TLV
Hydrofluoric Acid	0.02 mg (vapor)/M ³	0.01 TLV
Hydrogen Peroxide	0.014 mg/M^3	0.01 TLV
Iodine	0.01 mg/M ³	0.01 TLV
Mixed Acids .	0.01 to 0.05 mg/M ³	0.01 TLV for ${\rm H_2SO_4}$ and ${\rm HNO_3}$
Nitric Acid	0.05 mg/M ³	0.01 TLV
Nitrous Oxide	0.09 mg/M ³	0.01 TLV for NO ₂
Silicon Tetrachloride	0.1 mg/M ³ as Si	0.01 TLV for Si
Sulfur Dioxide	0.13 mg/M^3	0.01 TLV
Sulfuric Acid	0.01 mg/M ³	0.01 TLV
Sulfurous Acid	0.01 mg/M ³	0.01 TLV for ${ m H_2SO_4}$
Sulfuryl Fluoride	0.20 mg/M^3	0.01 TLV
Sulfur Trioxide	0.01 mg/M ³	0.01 TLV for H ₂ SO ₄

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
'Ammonium Hydroxide	0.01 ppm (mg/1)	Stokinger and Woodward Method
Boron Chloride	0.15 ppm (mg/1)	Stokinger and Woodward Method
Carbon Monoxide	2.75 ppm (mg/1)	Stokinger and Woodward Method
Hydrochloric Acid	0.35 ppm (mg/1)	Stokinger and Woodward Method
Hydrofluoric Acid	0.1 ppm (mg/1)	Stokinger and Woodward Method
Hydrogen Peroxide	0.07 ppm (mg/l)	Stokinger and Woodward Method
Iodine	0.05 ppm (mg/l)	Stckinger and Woodward Method
Mixed Acid	0.05 to 0.25 ppm (mg/1)	Stokinger and Woodward Method
Nitric Acid	0.25 ppm (mg/1)	Stokinger and Woodward Method
Nitrous Oxide	0.45 ppm (mg/1)	Stokinger and Woodward Method
Silicon Tetrachloride	0.50 ppm (mg/1)	Stokinger and Woodward Method
Sulfur Dioxide	0.65 ppm (mg/1)	Stokinger and Woodward Method
Sulfuric Acid	0.05 ppm (mg/l)	Stokinger and Woodward Method
Sulfurous Acid	0.05 ppm (mg/l)	Stokinger and Woodward Method
Sulfuryl Fluoride	1.00 ppm (mg/l)	Stokinger and Woodward Method
Sulfur Trioxide	0.05 ppm (mg/1)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Neutralization

Waste streams containing acids, acidic oxides, or bases can be treated by neutralization (1) to form a neutral solution which can then be discharged safely, or (2) to yield an insoluble precipitate which can be removed by filtration. Belonging to this group are:

- acids: hydrochloric, hydrofluoric, nitric, sulfuric, sulfurous, and mixed acid;
- (2) acidic oxides: sulfur dioxide and trioxide;
- (3) bases: ammonium hydroxide.

In addition, certain halides, such as boron chloride, silicon tetrachloride, and sulfuryl fluoride, can be treated in the same manner.

For the acids, acidic oxides and halides, soda ash-slaked lime solution is most commonly used. In the case of sulfuric and hydrofluoric acids, the insoluble calcium sulfate or fluoride is precipitated out and removed by filtration. In the case of nitric and hydrochloric acids, the neutral solution of nitrate or chloride of sodium and calcium is formed and can be discharged after dilution with water. In the case of halides, the corresponding sodium and calcium salt solution is formed. For example, in the case of boron chloride, a solution of chloride and borate of sodium and calcium is formed.

For the removal of sulfur dioxide from a gas stream, there exists a number of processes involving either regenerative or nonregenerative alkaline absorption. These include, among others, various wet limestone scrubbing processes, scrubbing with an aqueous solution of sodium carbonate,

sodium sulfite, potassium formate or ammonia, suspension of magnesium oxide, molten carbonate salt solutions, alkaline water, and furnace injection of lime, limestone, and dolomite.*

Ammonium hydroxide may be neutralized by nitric acid to form a solution of ammonium nitrate which can be used as fertilizer.

Option No. 2 - Fractionation

Iodine is a volatile material and can be easily recovered by fractionation. Fractionation is a convenient and economic way to reclaim the waste materials, and is particularly recommended for recovering expensive items such as iodine.

Option No. 3 - Incineration

Combustible materials can also be disposed of by controlled incinerations. In this group are carbon monoxide and nitrous oxide. However, burning of nitrous oxides can produce the undesirable oxides of nitrogen, NO and NO_2 , and therefore uncontrolled incineration is not recommended for the disposal of nitrous oxide. Nitrous oxide can be incinerated in a unit designed and operated to produce nitrogen and oxygen products.

Option No. 4 - Dilution and Decomposition by Water

Concentrated hydrogen peroxide is a powerful oxidizing agent. Rapid decomposition is hazardous. Wasted concentrated hydrogen peroxide can be disposed of by dilution with water to release the oxygen. Agitation would

^{*}The relative merits and the stages of development of the various sulfur dioxide removal processes have been discussed extensively in various technical journals. An excellent paper published recently is "Sulfur Recovery" by G. M. Meisel, in Journal of Metals, May 1972.

accelerate the decomposition. After decomposition, the waste stream may be discharged safely.

Option No. 5 - Acid Regeneration

The recovery of sulfuric acid from inorganic and organic wastes for reuse are generally not economical, 1662 unless the following specific conditions can be satisfied: 2478

- (1) An existing sulfuric acid producing plant is available at the site where the waste stream is being generated.
- (2) Concentration of sulfuric acid in the waste must exceed 70 percent.
- (3) The waste stream to be processed must exceed 50 tons/day.
- (4) The organic impurities in the waste must not cause excessive consumption of oxygen.
- (5) The inorganic impurities must be very minor.

In the regeneration process, the spent sulfuric acid stream is thermally decomposed to sulfur dioxide which is then converted back to sulfuric acid in the acid plant by the contact process. If the spent sulfuric acid stream is sufficiently clean but dilute (as in the case of the mixed acid where sulfuric acid is used mainly to absorb the water formed during the nitration process), it can be sent to the acid plant to be fortified for reuse, even though this does not remove the impurities.

Nitric acid forms a constant-boiling azeotrope with water (68% $\rm HNO_3$ + 32% $\rm H_2O$). The normal boiling point of the azeotrope is 120.5 C. Hence, under certain conditions, spent nitric acid can be recovered by steam distillation to yield concentrated acid. On the other hand, the hydrochloric acid-water constant-boiling azeotrope contains only 20.24 percent of HCl. Therefore, regeneration of spent hydrochloric acid by steam distillation is much less desirable.

Option No. 6 - Gas Adsorption

Recovery of gases may be made by adsorption. The most commonly used gas adsorbents are activated carbon, alumina, silica gel, and various molecular sieves. The adsorption may be carried out in fixed or fluidized beds in single- or multi-stage units. After adsorption, the gases can be regenerated from the adsorbents either under reduced pressures or upon heating by a carrier gas or vapor. For gases which do not react or decompose on contact with water, steam is commonly used as the heating medium. By simple condensation, the steam can be easily separated and removed from the gas-steam mixture. Several activated carbon adsorption processes have been developed to adsorb the sulfur dioxide and convert it into sulfuric acid. None of these processes, however, has reached the commercial production stage.

In addition, regenerative organic absorption processes have also been considered for the removal of sulfur dioxide from the waste gas streams. These include the use of dimethyl aniline, xylidine, hydrazine, sodium citrate and other proprietary organic absorbents. All these processes are still under development and have not been commercialized.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The waste stream constituents discussed in this report can be adequately disposed of or recovered in the industrial sites by conventional means. Therefore, it does not appear that consideration for their disposal at the National Disposal Sites is warranted. However, some capacity for sulfur dioxide disposal is required at the National Disposal Sites to handle, for example, a secondary waste gas stream containing SO_2 generated as the result of processing sulfur-containing wastes or burning of sulfur-containing fuels. Currently, the only proven and applicable commercial SO_2 removal process is the Wellman-Lord process of scrubbing the waste gas stream with an aqueous solution of sodium sulfite. Therefore, this process is recommended for the removal of sulfur dioxide at National Disposal Sites.

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HAZARDOUS WASTES PROPERTIES WORKSHEET					
H. M. Name <u>Ammonium Hydrox</u> ide (13))	Structural Formula			
Common Names		NH ₄ OH			
Molecular Wt. 35.05 ⁽¹⁾ Density (Condensed) @@	Melting Pt. <u>-77 C⁽</u> Density (gas	1) Boiling Pt			
Vapor Pressure (recommended 55 C an	d 20 C)	@			
Flash Point Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Autoignition Temp	Upper			
Others:Acid, Base Properties					
Highly Reactive with					
Compatible with		•			
Shipped in		ward Classification			
Comments <u>MCA warning label</u>					
References (1) 1570					

H/	AZARDOUS WASTES PROPER WORKSHEET	RTIES
H. M. Name Boron Chloride (62)		
IUC Name		Structural Formula
Common Names		BC1 ₃
Molecular Wt. 117.17 ⁽¹⁾	Melting Pt107.3	C ⁽¹⁾ Boiling Pt. 12.5 C ⁽¹⁾
Density (Condensed) 1.349 @	11 C Density (gas	.)
Vapor Pressure (recommended 55 C and	i 20 C)	
	@	
Flash Point	Autoignition Temp	
Flammability Limits in Air (wt %)		_
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility		
Cold Water	Hot Water decomp	oses Ethanol decomposes
Others:	_	
Acid, Base Properties		
Highly Reactive with		
Compatible with		
Shipped in		
8		uard Classification
Comments		
References (1) 1570		
· · · · · · · · · · · · · · · · · · ·		

. НА		NASTES PROPER'	TIES		
		• .			
H. M. Name <u>Carbon Monoxide</u> (99)			Struc	tural Formula	
IUC Name	-	ſ		To the total and	
Common Names		· · ·		со	
Molecular Wt. 28.01 ⁽¹⁾	Melting	Pt207 C	1)	Boiling Pt. <u>-191.3 C⁽</u>	1)
Density (Condensed) 0.793 @		D ensity (gas) <u>1.25 grams</u>	/10 O C	
Vapor Pressure (recommended 55 C and	20 C)			,	
@		<u> </u>		<u>@</u>	_
Flash Point A	utoigniti	on Temp. 1204	 _ C		
Flammability Limits in Air(vol %) ⁽²⁾				75	
Explosive Limits in Air (wt. %)					
	-				
Solubility				•	
Cold Water	Hot Wa	iter	·	Ethanol	
Others:	- ·				
Acid, Base Properties				· · · · · · · · · · · · · · · · · · ·	
Highly Reactive with					
Highly Reactive with	 			•	
Compatible with					
					
Shipped in					
ICC Classification $\binom{1}{flammable}$ gas.	red gas	labe)Coa st Gua	ard Classif	ication(1) flammable	gas, bel
Comments					
References (1) 0766		·			1
(2) 1492					
1492					

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name <u>Hydrochloric Acid</u> (214))		· y —	Structural Formula
IUC Name			1	
Common Names			1	HC1 (aq.)
Molecular Wt	Melting	P.t		Boiling Pt
Density (Condensed)@_		Density (gas)_	
Vapor Pressure (recommended 55 C and	d 20 C)			
<u> </u>		9		<u> </u>
	Autoignit	ion Temp		•
Flammability Limits in Air (wt %)	Lower			Upper
Explosive Limits in Air (wt. %)	Lower			Upper
Solubility				
Cold Water	Hot W	ater		Ethanol
Others:				
Acid, Base Properties strongly ac	i di c			
Highly Reactive with				
Compatible with				T.
Shipped in				· · · · · · · · · · · · · · · · · · ·
(1)corrosive liqui ICC Classification white label	d,	Coast	Guar	d Classification(1) white label
Comments				HITTE TAMES
	•			
References (1) 0766				
- (

НА		WASTES PROP RKSHEET	PERTI	ies .
H. M. Name <u>Hydrofluoric A</u> cid (216)	,			Structural Formula
IUC Name			Г	Structural formula
Common Names	·			HF (aq.)
			L	
Molecular Wt	Melting	Pt.		Boiling Pt
Density (Condensed) @				
Vapor Pressure (recommended 55 C and			•	
<u> </u>				
Flash Point A	utoignit	ion Temp		
Flammability Limits in Air (wt %)	Lower			Upper
Explosive Limits in Air (wt. %)	Lower			Upper
<u>Solubility</u>				
Cold Water		ater		Ethanol
Others:	_			
Acid, Base Properties acidic	 			
Highly Reactive with				
Compatible with				
Shipped in (1) corrosive liquid (1) ICC Classification (1) white label	ла ,		2::24	(1)corrosive liquid
		coast	Guar	d Classification white label
Comments				
		·		
References (1) 0766				
References (1) 0/00			•	· .
,				ļ

н		WASTES PROPER' RKSHEET	TIES	
Н. M. Name <u>Hydrogen Chlor</u> ide (217))		Structural For	rmula
IUC Name		1		
Common Names			НС ⁻ (g)	
Molecular Wt36.46 ⁽¹⁾				
Density (Condensed)@		Density (gas)	
Vapor Pressure (recommended 55 C and	d 20 C)			
@				0
Flash Point	Autoignit	ion Temp	-	
Flammability Limits in Air (wt %)				-
Explosive Limits in Air (wt. %)	Lower		Upper	
Solubility (1)				
Cold Water 82.3 grams/100 ml @	O CHot W	ater 56.1 gram	s/100 ml @ ⁶⁰ Ethanol	soluble
Others:			•	
Acid, Base Properties				
Highly Reactive with				
Compatible with				
	 			
Shipped in ICC Classification			(2)	noninflammable .
			ard Classification <u>'</u>	'gas, green gas label
Comments				
Pafarana (2) 1570				
References (1) 1570 (2) 0766				
(2) 0/00				

HAZARDOUS WASTES PROPERTIES WORKSHEET				
	, NO	KKONEET		
H. M. Name Hydrogen Peroxide (219))			C+muntuus] Faumula
IUC Name			Г	Structural Formula
Common Names				H ₂ O ₂ (aq. >52%)
•				
Molecular Wt	Melting	Pt.		Boiling Pt
Molecular Wt		Density (gas)	
Vapor Pressure (recommended 55 C ar				
<u> </u>				
	Autoignit			
Flammability Limits in Air (wt %)	Lower			Upper
Explosive Limits in Air (wt. %)				Upper
Solubility				
Cold Water	Hot Wa	iter		Ethanol
Others:				
Acid, Base Properties				
Highly Reactive with reducing age	ent			
Compatible with				
Shipped in	· · · · · · · · · · · · · · · · · · ·			
ICC Classification		Coast	Guard	(1) corrosive liquid
Comments		coast	duaru	· classification white label
COMMETICS				
References (1) 0766				
3703		,		
		,		
•				

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name <u>Iodine (tinct</u> ure) (22	3)	Structural Formula		
IUC Name	Γ			
Common Names		I ₂		
	Ĺ			
Molecular Wt. 253.809 ⁽¹⁾	Melting Pt. <u>113.5</u> C ⁽¹	Boiling Pt. 184.35 C ⁽¹⁾		
Density (Condensed) 4.93 @	Density (gas)			
Vapor Pressure (recommended 55 C an	d 20 C)			
Flash Point	Autoignition Temp			
Flammability Limits in Air (wt %)	Lower	Upper		
Explosive Limits in Air (wt. %)	Lower			
Solubility ⁽¹⁾				
Cold Water 0.029 grams/100 mg @	20 ^C Hot Water 0.078 gram	20.5 grams/100m1 ns/100 m1 e ⁵⁰ thanol e 15 C		
Others:				
Acid, Base Properties				
Highly Reactive with				
Compatible with				
Shipped in				
ICC Classification		rd Classification		
Comments				
References (1) 1570				
₹ .				

HAZARDOUS WASTES PROPERTIES WORKSHEET						
H. M. Name <u>Mixed Acids</u> (277)		Structural Formula				
Common Names		H ₂ SO ₄ + HNO ₃				
Molecular Wt Density (Condensed)@_	Density (gas	Boiling Pt				
Vapor Pressure (recommended 55 C a		a ·				
Plash Point	Q Autoignition Temp					
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)						
Solubility Cold Water		Ethanol				
Others:Acid, Base Properties						
Highly Reactive with		·				
Compatible with						
Shipped in		,				
ICC Classification	Coast Gu	ard Classification (1) white label				
Comments <u>Mixed acid is a mixture</u>	of nitric acid and sul	furic acid in various proportions.				
References (1) 0766						
	*					
	e.					

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Nitric Acid (299)			Structural Formula	
IUC Name		Γ		
Common Names	•	_	HNO ₃	
	•			
Molecular Wt. 63.01 ⁽¹⁾				
Density (Condensed) 1.50 @	Density	/ (gas)_		
Vapor Pressure (recommended 55 C an	d 20 C)			
	0		<u></u> @	
Flash Point	Autoignition Tem	D		
Flammability Limits in Air (wt %)	Lower		Upper	
Explosive Limits in Air (wt. %)	Lower		Upper	
Solubility ⁽¹⁾				
Cold Water			Ethanol	
Others:				
Acid, Base Propertiesstrongly	acidic			
Highly Reactive with				
Compatible with				
Shipped in				
ICC Classification (2) white label	quid,	ast Guar	d Classification <mark>(2)</mark> white label	
Comments Nitric acid is a powerf			WILL TOP I	
References (1) 1570				
(2) 0766				
			•	
		•	•	

. Н		WASTES PRO RKSHEET	PERTIES	5
H. M. Name Nitrous Oxide (313) IUC Name		•		Structural Formula
				N O
Common Names				N ₂ 0
			<u> </u>	
Molecular Wt. 44.01 ⁽¹⁾	Melting	Pt90.	.8 c ⁽¹⁾	Boiling Pt. <u>-88.5</u> C ⁽¹⁾
Density (Condensed)@_		Density (g a s)	
Vapor Pressure (recommended 55 C an	d 20 C)			
@		@		
Flash Point	Autoigniti	ion Temp		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)				UpperUpper
Solubility (1)				
Cold Water	Hot Wa	ater	 -	Ethanol_soluble
Others: soluble in ether, H ₂ SC	14			
Acid, Base Properties		-		
Highly Reactive with				
Compatible with				
Shipped in				
ICC Classification (2) nonflammable green label	gas,	Coast	Cuard	Classification (2) noninflammable
Comments			Guara	label
connients				
References (1) 1570	· · · · · · · · · · · · · · · · · · ·			
(2) 0766				
		•		

	HAZARDOUS WASTE WORKSHE		IES
H. M. Name <u>Silicon Tetrachloride</u> IUC Name	(369)		Structural Formula
Common Names			SiC1 ₄
Molecular Wt. <u>169.90⁽¹⁾</u> Density (Condensed) <u>1.483</u> @	Melting Pt. 20 C Dens	-70 C ⁽¹⁾ ity (gas)_	Boiling Pt. 57.57 C ⁽¹⁾
Vapor Pressure (recommended 55 C a	ind 20 C)		,
· · · · · · · · · · · · · · · · · · ·	Autoignition To		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower		Upper Upper
Solubility (1) Cold Water decomposes	Hot Water_	decompos	ses Ethanol decomposes
Others:Acid, Base Properties			
Highly Reactive with			
Compatible with			
i	quid, (rd Classification (2) white label
Comments			•
References (1) 1570 (2) 0766			

Н	AZARDOUS WASTES PROPERTIE	S
WORKSHEET		
H. M. Name Sulfur Dioxide (414)		
		Structural Formula
IUC Name		
Common Names	·	so ₂
	<u> </u>	
Molecular Wt. 64.06 ⁽¹⁾	Melting Pt75.5 C ⁽¹⁾	Boiling Pt10.0 C ⁽¹⁾
Density (Condensed) 1.434 @	O _c C Density (gas)	
Vapor Pressure (recommended 55 C and	1 20 C) ⁽¹⁾	
2538 mm Hg @ 21.1 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		
Compatible with		
Shipped in	·	
ICC Classification (1) nonflammable green label	gas, Coast Guard	Classification (1) noninflammable gas
Comments		label
		,
References (1) 0766		
•		

HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Sulfuric Acid (415)	,	Structural Formula
IUC Name		
Common Names	<u> </u>	H ₂ S0 ₄
		(100%) ⁽¹⁾ Boiling Pt.338 C (98.3%) ⁽¹⁾
Density (Condensed) 1.841 @ @	Density (gas	6
Vapor Pressure (recommended 55 C a	nd 20 C)	•
@		
	Autoignition Temp.	
Flammability Limits in Air (wt %)	Lower	Upper
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility		
	Hot Water ∞	Ethanol decomposes
Others:		
Acid, Base Properties strongly a	•	
, , , , , , , , , , , , , , , , , , , ,		
Highly Reactive with		
Compatible with		
Shipped in(1) corrosive li	quid,	
ICC Classification ('/ white label	Coast Gu	uard Classification
Comments		
References (1) 0766		
i		

	HAZARDOUS WASTES PROPERT WORKSHEET	TES
H. M. Name <u>Sulfurous Acid</u> (416)	r	Structural Formula
Common Names		. н ₂ so ₃
Molecular Wt. 83.08 ⁽¹⁾	Melting Pt.	Boiling Pt.
Density (Condensed) <u>Ca 1.03</u> @	nd 20 C)	
Flash Point	Autoignition Temp.	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower	Upper
Solubility Cold Water Soluble Others:		Ethanol <u>Soluble</u>
Acid, Base Properties Acidic		
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification		
Comments Sulfurous acid exists isolated.	in solution only. No fi	ree sulfurous acid has been
7307400		
References (1) 0766		<u>·</u>

HAZARDOUS MASTES PROPERTIES WORKSHEET		
H. M. Name Sulfuryl Fluoride (417) IUC Name	Structural Formula	
Common Names	so ₂ F ₂	
Molecular Wt. 102.06 ⁽¹⁾ Melting Pt136.7 Density (Condensed) 1.7 @ Density (gas		
Vapor Pressure (recommended 55 C and 20 C)		
Flash Point Autoignition Temp		
Flammability Limits in Air (wt %) LowerExplosive Limits in Air (wt. %) Lower		
Solubility (1) Cold Water 10 grams/100 ml @ 0 C Hot Water Others: soluble in CCl ₄ Acid, Base Properties		
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification Coast Gu	ard Classification	
References (1) 1570		

HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Sulfur Trioxide (509)	Structural Formula	
IUC Name Common Names	so ₃	
Molecular Wt. $80.06^{(1)}$ Me Density (Condensed) $\alpha = 1.97^{(1)}$ @ 20 $\gamma = 1.92$ $= 20$ Vapor Pressure (recommended 55 C and 20	α 62.3 C (1) β 32.5 C (1) Iting Pt. γ 16.8 C Boiling Pt. 44.8 C (1) C Density (gas) @ C C	
	e @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @	
Flammability Limits in Air (wt %) Lo Explosive Limits in Air (wt. %) Lo	werUpper werUpper	
Solubility ⁽¹⁾ Cold Water <u>decomposes</u> Others:	Hot Water <u>decomposes</u> Ethanol	
Acid, Base Properties		
Highly Reactive with SO ₃ combines with	water with explosive violence to form sulfuric acid.	
Compatible with		
Shipped in		
ICC Classification	Coast Guard Classification	
References (1) 1570		

PROFILE REPORT

Ammonium Perchlorate (25), Ammonium Persulfate (26),
Sodium Hypochlorite (222), Magnesium Chlorate (246),
Sodium Carbonate Peroxide (384), Sodium Perchlorate (399),
Zinc Chlorate (455), Calcium Hypochlorite (482)

GENERAL

Introduction

The inorganic chemicals in this Profile Report are basically nontoxic. However, they are oxidizing agents that constitute fire or explosion hazards. They are grouped together because they can be handled by similar disposal processes.

Manufacture and Uses

Ammonium Perchlorate. Ammonium perchlorate, $NH_{\Lambda}C10_{\Lambda}$, is a white crystalline material, which is made by a six-operation process which involves reacting sodium perchlorate, ammonia, and hydrochloric acid in an aqueous medium. After cooling and concentrating the reaction mixture by flash evaporation, ammonium perchlorate comes out of solution in a crystallizer. under closely controlled conditions. The $NH_{\Delta}C10_{\Delta}$ crystals are separated from the slurry by centrifugation, washed, and reslurried in saturated $\mathrm{NH_4C10_4}$ solution. The second $\mathrm{NH_4C10_4}$ slurry is centrifuged, and the $NH_{\Lambda}C10_{\Lambda}$ cake produced is washed, dried and sized. The filtrate from the first centrifugation is concentrated to permit crystallization of the excess NaCl present. The slurry produced is centrifuged, and the filtrate returned to the first operation as a raw material. The crystalline NaCl is washed and dried for sale as a by-product. 2489 Ammonium perchlorate is used as an ingredient of explosives, in solid propellant compositions, in pyrotechnic compositions, and as a raw material for the production of perchloric acid and numerous metallic perchlorates.

Ammonium Persulfate. Ammonium persulfate, $(NH_4)_2S_2O_8$, is a strong oxidizing material that occurs as white crystals. It is prepared by electrolysis of acid solutions of ammonium sulfate using electrolytic cells having a stationary catholyte. Usually platinum anodes and graphite cathodes are employed. The ammonium persulfate is recovered by crystallization. Its uses include the manufacture of hydrogen peroxide, the oxidation of inorganic and organic compounds, and electroplating. 0955

Sodium Hypochlorite. Sodium hypochlorite, NaOCl, exists only in aqueous solution. The aqueous solutions generally contain sodium hydroxide. It is employed as a disinfectant and deodorant in dairies, creameries, water supplies, sewage disposal and as a bleaching agent for cotton, linen, jute, paper pulp and oranges. The most common method of manufacture is the reaction between sodium hydroxide solution and gaseous chlorine.

Another method formerly in wide use was the electrolysis of a concentrated salt solution. The electrolytic cells used to manufacture NaOCl did not have any diaphragm and were operated at high current density in nearly neutral solution. The cells were designed with the chlorine given off at the anode. 1662

<u>Magnesium Chlorate.</u> Magnesium chlorate, ${\rm Mg(ClO_3)_2}$, is a white hygroscopic powder that has a bitter taste. It is prepared by reacting magnesium chloride and sodium chlorate followed by crystallization of magnesium chlorate. It is used in medicine, as a defoliant and as a desiccant. ${\rm ^{1416}}$

Sodium Carbonate Peroxide. Sodium carbonate peroxide, $2\mathrm{Na_2CO_3}\cdot 3\mathrm{H_2O_2}$, is a white crystalline powder that is stable at room temperature when dry but decomposes rapidly at 100 C. It is prepared by crystallization from a solution of soda ash and hydrogen peroxide. It is used in household detergents, dental cleansers, bleaching and dyeing compounds, and in formulations for the modification of starch. 1416,1662

Sodium Perchlorate. Sodium perchlorate, NaClO₄, forms white deliquescent crystals. It is prepared by the electrolysis of sodium in steel electrolytic cells which have smooth platinum anodes or lead dioxide anodes and operate at 6.5 to 7.0 volts, 2,500 amps., and at a temperature of 35 to 50 C. The solution is concentrated and crystallized. NaClO₄ is used as analytical reagent and to a limited extent in explosives. The major use is in the preparation of ammonium perchlorate. 2489

Zinc Chlorate. Zinc chlorate, $Zn(ClO_3)_2 \cdot 4H_2O$, is a colorless to yellow deliquescent crystalline material. It decomposes at 60 C. It is prepared by reacting zinc chloride with a solution of sodium chlorate followed by crystallization. 1416

<u>Calcium Hypochlorite.</u> Calcium hypochlorite, $Ca(OCI)_2$ is a white, crystalline solid. It is prepared by chlorination of a slurry of lime and caustic soda with subsequent precipitation of calcium hypochlorite dihydrate which is dried under vacuum. It is used as an algicide, fungicide and bleaching agent.

Physical/Chemical Properties

The physical/chemical properties of the compounds covered by this Profile Report are summarized on the attached worksheets.

2. TOXICOLOGY

The materials treated by this report are not considered particularly toxic. The Amercian Conference of Government Industrial Hygienists has not established Threshold Limit Values (TLV) for any of the compounds listed in this report nor have any maximum allowable concentrations (MAC) in water for man been established. Perchlorates are irritating to the skin and mucous membranes. Chlorates and persulfates can irritate the gastrointestinal tract. If absorbed, chlorates can cause hemolysis

of red blood cells, methemoglobinemia, liver and kidney damage. Five grams of chlorate salt is considered a toxic dose for adults. 1142 Hypochlorites and peroxides are irritating to the skin and mucous membranes.

OTHER HAZARDS

All of the materials included in this report are oxidizing materials and contact with combustible material should be avoided. The perchlorates are powerful oxidizers that explode violently when heated with sulfur, organic matter, or finely divided metal, particularly magnesium and aluminum. Large exotherms occur upon heating. The chlorates explode when exposed to heat or shock and when rubbed in the presence of organic or reducing materials. 1142

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

All the materials in this report must be handled in such a manner that they do not come into contact with reducing substances. They should not be exposed to heat. Contact with the skin should be avoided. Ammonium perchlorate, magnesium chlorate, sodium perchlorate, zinc chlorate, and calcium hypochlorite are classified by Department of Transportation (DOT) and the U. S. Coast Guard as oxidizing materials that require a Yellow Label. 0776

Disposal/Reuse

Industrially, contaminated materials discussed in this report are not usually reprocessed for reuse since these materials are oxidizing agents that may ignite or explode easily when contaminated with organic or reducing materials. When disposal of wastes containing these materials is required, the acceptable criteria for their release into the environment are defined in terms of the following provisional limits:

		Basis for
Contaminant in Air		Recommendation
Ammonium perchlorate	0.01 mg/M ³	Provisional limit for(NH ₄) ₂ SO ₄
Ammonium persulfate	0.01 mg/M^3	
Sodium hyprochlorite	0.02 mg/M ³	0.01 TLV for NaOH
Magnesium chlorate	0.01 mg/M ³	Provisional limit for MgSO $_{m A}$
Sodium carbonate peroxide	0.02 mg/M ³	0.01 TLV for NaOH
Sodium perchlorate	0.02 mg/M^3	0.01 TLV for NaOH
Zinc chlorate	0.01 mg/M^3	0.01 TLV for ZnCl ₂
Calcium hypochlorite	0.025 mg/M ³	Provisional limit for CaF ₂
Contaminant in Water and Soil	Provisional Limit	Basis Recommendation
Ammonium perchlorate	0.05 ppm (mg/1)	Stokinger and Woodward Method
Ammonium persulfate	0.05 ppm (mg/l)	n .
Sodium hypochlorite	0.10 ppm (mg/1)	п
Magnesium chlorate	125 ppm (mg/l) as Mg	Drinking Water Standard
Sodium carbonate peroxide	0.10 ppm (mg/l)	Stokinger and Woodward Method
Sodium perchlorate	0.10 ppm (mg/1)	Stokinger and Woodward Method
Zinc chlorate	5 ppm (mg/1) as Zn	Drinking Water Standard
Calcium hypochlorite	0.125 ppm (mg/1)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Reduction

Disposal of oxidizing agents covered by this report may be accomplished by dissolving the material, adding the resultant solution to a large volume of a concentrated solution of reducing agent (sodium thiosulfate, sodium bisulfite, or a ferrous salt), and then acidifying the mixture with $3M-H_2SO_4$. When reduction is complete, soda ash is added to make the solution alkaline. (If an ammonium salt is present, ammonia will be liberated and will require recovery.) The alkaline liquid is decanted from any sludge produced, neutralized, and diluted before discharge to a sewer or stream. Oppose The sludge (if magnesium or zinc are present) is added to a landfill. This process is considered satisfactory for treatment of the materials covered by this report.

Option No. 2 - Open Burning

Uncontaminated oxidizers, particularly the perchlorate reject materials, process fines, or overruns from grinding or blending operations, are collected and transported to "burn sites" in open-top 30-gal. drums with lids attached. At the burn sites the oxidizers are spread thinly over a layer of excelsior or other flammable dry materials. The flammable materials are ignited by a squib, fired electrically, with the controls at a safe distance. Contaminated materials are left in the containers in which they are collected and the material burned in the container in a similar manner. Though this process is widely used at solid propellant manufacturing sites, it is not considered satisfactory because large quantities of NO_x and HCl are liberated.

Option No. 3 - Incineration

Though not in wide use, dilute aqueous solutions of all the materials covered by this report can be destroyed by injection into an incinerator supported by a gas flame. Scrubbers are required to remove HCl, NO_{X} , and metal oxide particles from the incinerator vent gases. Properly designed and operated incineration is considered a promising near-future method for the disposal of aqueous wastes containing oxidizing materials but additional research is required before the process could be employed on a large scale.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Wastes streams containing hychlorites, chlorates, perchlorates, and persulfates are found in only small quantities, are basically nontoxic, and can be adequately disposed of by the simple reduction technique discussed under Option No. 1. For these reasons, the oxidizing materials included in this Profile Report are not considered as candidate waste stream constituents for national disposal.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Ammonium Perchlorate (25) IUC Name Ammonium Perchlorate	Structural Formula	
Common Names	NH ₄ C10 ₄	
Molecular Wt. $117.5^{(1)}$ Melting Pt. 150 C d Density (Condensed) 1.95g/cc @ $20 \text{ C}^{(1)}$ Density (gas	ecomposes Boiling Pt. decomposes)@	
Vapor Pressure (recommended 55 C and 20 C)		
<u> </u>		
Flash Point Autoignition Temp		
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	UpperUpper	
Solubility Cold Water 20g/100 ml at 25 C(1) Hot Water 88 g/100	(1) ml at 100 C Ethanol 9.908 g/100 g ⁽¹⁾	
Others: Acetone 2.2 6 g/100 g Acid, Base Properties		
Highly Reactive with reducing material	· · · · · · · · · · · · · · · · · · ·	
Compatible with		
Shipped in metal drums with polyethylene liners.		
ICC Classification oxidizing material (1) Coast Guard	ard Classification oxidizing (1)	
Comments		
References (1) 1142		
1010101003 (1) 1142		

HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Magnesium Chlorate (248 IUC Name Magnesium Chlorate Common Names		Structural Formula Mg(C10 ₃) ₂ ·6H ₂ 0
Density (Condensed) 180 g/cc @ 25 Vapor Pressure (recommended 55 C and	<u>C (1)</u> Density (
Flash Point		Upper
Others:Acid, Base Properties		
Shipped in glass bottles ⁽²⁾ ICC Classification oxidizing materi. Comments	al (2) Coast	Guard Classification Oxidizing Materia (2)
References (1) 1570 (2) 1416		

HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name <u>Sodium Carbonat</u> e Peroxid	de (384)	Structural Formula
Common Names		2Na ₂ CO ₃ ·3H ₂ O ₂
Molecular Wt. <u>not a true compound</u> Density (Condensed)@		
Vapor Pressure (recommended 55 C an	d 20 C)	
	@ Autoignition Temp	_
Explosive Limits in Air (wt. %) Solubility	Lower	Upper
Cold Water_soluble Others:Acid, Base Properties	_	
Highly Reactive with reducing subs	tances	
Compatible with		
Shipped in 100 lb fiber drums		
ICC Classification None Comments		ard ClassificationNone
		·
References (1) 1416	,	
		·

НА	ZARDOUS WASTES PROPER WORKSHEET	RTIES
H. M. Name Sodium Perchlorate (399) IUC Name Sodium Perchlorate Common Names		Structural Formula NaClO ₄
Molecular Wt. <u>122.45⁽¹⁾</u> Density (Condensed) <u>2.0 2g/cc</u> @ <u>20</u>		ecomp. Boiling Pt
Vapor Pressure (recommended 55 C and	e	@
Flash Point A Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		Upper
Solubility Cold Water 209g/100 ml at 15 C Others: Acid, Base Properties	_	
Highly Reactive with		ŀ
Compatible with		
Shipped in bottles, drums, kegs ICC Classification oxidizing material Comments		Oxidizing Ward Classification Material
References (1) 1570 (2) 1416		

HAZARDOUS WASTES PROPERTIES WORKSHEET		
H. M. Name Zinc Chlorate (455) IUC Name Zinc Chlorate Common Names	Structural Formula 2n(C10 ₃) ₂ 4H ₂ 0	
(1)	ecomp. Boiling Pt	
@ @ @ @	Upper	
Solubility Cold Water 262 g/100 ml at 20 C Hot Water very sol Others: ether-soluble Acid, Base Properties		
Highly Reactive with		
Compatible with	(2)	
Shipped in Coast Guard Comments Coast Guard Coast	Oxidizing ard Classification Material	
References (1) 1570 (2) 1416		

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Calcium Hypochlorite (48		[ctural Formula
Molecular Mt 235 06		Į		1) ₂ 4H ₂ 0
Molecular Wt. 215.06 Density (Condensed) @@				
		bensity (gas)	·	
Vapor Pressure (recommended 55 C and		_		_
		e ion Temp		
			_	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)				
			орре:	
Solubility	11. 4. 14		_	F., 3 dans
Cold Water very soluble Others:		ter decompose	<u> </u>	Ethanol decomposes
Acid, Base Properties			 	
Highly Reactive with				<u> </u>
Compatible with				
Shipped in				
B.			rd Classif	fication none
Comments				
		···		
References (1) 1570				
				•
				,
			•	•

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Ammonium Persulfate (26) IUC Name Ammonium Persulfate	Structural Formula			
-	(394.) 0.0			
Common Names	(NH ₄) ₂ S ₂ 0 ₈			
·				
Molecular Wt. 228.20 ⁽¹⁾ Melting Pt. 120 C c	(1) decomposes Boiling Pt.			
Molecular Wt. $\frac{228.20^{(1)}}{1.982 \text{ g/cc}}$ Melting Pt. $\frac{120 \text{ C}}{0.0000000000000000000000000000000000$)@			
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	į.			
Solubility	100 C			
Cold Water 70.6 g/100 ml at OC (1) Hot Water 103.8 g/1				
Others: Acetone - insoluble (1)				
Acid, Base Properties				
Compatible with				
Shipped in bottles, drums				
ICC Classification None (2) Coast Gue	and Classification None(2)			
Comments	ara classification none			
Consider CS				
References (1) 1570				
(2) 1416				

Н	IAZARDOUS WASTES PROPER WORKSHEET	RTIES
H. M. Name Sodium Hypochlorite (22	22)	Structural Formula
IUC Name Sodium Hypochlorite		Scruccural rormula
Common Names		NaOC1
Molecular Wt. 74.45 ⁽¹⁾ Density (Condensed) @	Melting Pt	Boiling Pt
Density (Condensed)@	Density (gas	5)
Vapor Pressure (recommended 55 C an	d 20 C)	
	Autoignition Temp	_
Flammability Limits in Air (wt %)		
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility	·	• •
Cold Water <u>Soluble</u>		Ethanol
Others:		
Acid, Base Properties Solution is s	trongly basic	
Highly Reactive with reducing agen	ts	
Compatible with		
Shipped in glass carboys, drums	(1)	
ICC Classification None (1)		uard Classification <u>None⁽¹⁾</u>
Comments <u>present only in solution</u>		
References (1) 1416		

PROFILE REPORT

Ammonium Sulfide (29), Antimony Pentachloride (35), Antimony Trichloride (41), Calcium Carbide (89), Calcium Hydride (93), Lithium Aluminum Hydride (244), Potassium Binoxalate (342), Potassium Hydroxide (347), Potassium Oxalate (348), Sodium Amide (375), Sodium Hydride (391), Sodium Hydrosulfite (392), Sodium Sulfide (404), Sodium Thiocyanate (406) Stannic Chloride (408), Thiocyanates (432)

GENERAL

Introduction

The inorganic materials included in this Profile Report have been preliminarily identified as probable candidate waste stream constituents for industrial disposal. These materials either dissolve readily in water or react with water violently. Their toxicities vary from irritating and corrosive to skin to highly toxic. Many of them emit corrosive and/or toxic fumes when heated to decomposition or by chemical reactions on contact with water or moisture in air. Most of them are not produced in large tonnage.

Manufacture and Uses 1433, 1492

Ammonium Sulfide. Ammonium sulfide, $(NH_4)_2S$, is a colorless crystal at temperatures below -18 C. At higher temperatures, it decomposes into ammonia and ammonium hydrosulfide (NH_4HS) . Ammonium sulfide is prepared by reacting excess of ammonia with hydrogen sulfide. It has limited uses in (1) the application of patina to bronze; (2) photographic developers; and (3) textile manufacture.

Antimony Pentachloride. Antimony Pentachloride, SbCl₅, is a yellow, oily liquid. It loses chlorine readily. The decomposition is appreciable even at 12 C. It is prepared by passing chlorine gas into molten antimony trichloride. It is used as a catalyst when replacing a fluorine substituent with chlorine in organic compounds.

Antimony Trichloride. Antimony trichloride, SbCl₃, is a colorless, rhombic, and deliquescent crystal. It fumes in air. It is prepared by direct chlorination of antimony trioxide, antimony trisulfide or antimony. Its uses are:

- (1) as a catalyst;
- (2) as a mordant in calico printing;
- (3) in the manufacture of other antimony salts and organic syntheses;
- (4) as a chemical reagent.

<u>Calcium Carbide.</u> Calcium carbide, CaC_2 , is a colorless, orthorhombic crystal or in grayish-black, irregular lumps. It decomposes readily on contact with water, producing acetylene gas. It is produced by heating lime and carbon (usually coke or anthracite) in an electric furnace at 2000 to 2200 C. In 1969, 920,000 tons of calcium carbide were produced in the United States. 1929 Its uses are:

- (1) in generating acetylene for lighting (largest use), and welding and cutting metals;
- (2) in the manufacture of calcium cyanamide and lampblack;
- (3) as a reducing, dyhydrating or desulfurizing agent in various chemical and metallurgical processes;
- (4) in signal fires for marine services.

<u>Calcium Hydride.</u> Calcium hydride, CaH₂, is a white rhombic crystal. It decomposes on contact with water. Commercially, it is produced by reacting calcium with hydrogen at atmospheric pressure and a temperature of 300 C. Its uses are:

- in the production of rare metals such as titanium, zirconium, vanadium, niobium, uranium, and thorium from their oxides;
- (2) as a drying agent for drying esters, ketones, halides, air, hydrogen, other gases, etc.;
- (3) as a source of hydrogen.

Lithium Aluminum Hydride. Lithium aluminum hydride, LiAl H_4 , is a white crystalline powder. It is stable in dry air at room temperatures, but it will decompose at a temperature above 125 C or in moist air. It is prepared by the addition of an ether solution of aluminum chloride to a slurry of lithium hydride in ether. It can also be prepared from its elements at 2000 psi and 100 C. It is used as a reducing agent and in the preparation of other hydrides and organic compounds.

Potassium Binoxalate. Potassium binoxalate, KHC_2O_4 , also called potassium acid oxalate, is a colorless, odorless, monoclinic crystal. It is used in removing ink stains, scouring metals, cleaning wood, photography, bleaching stearin, and as a mordant in dyeing.

<u>Potassium Hydroxide.</u> Potassium hydroxide, KOH, is in the form of white or slightly yellow lumps, rods or pellets. It rapidly absorbs moisture and carbon dioxide from the air and deliquesces. Commercially, it is produced by electrolysis of potassium chloride. About 180,000 tons of KOH (90% basis) were produced in the United States in 1969. Its uses are:

- (1) in the manufacture of "soft" soap;
- (2) in producing other potassium compounds and organic syntheses;
- (3) in electroplating, photoengraving and lithography;
- (4) as a chemical reagent;
- (5) as a mordant for wood;
- (6) as a paint and varnish remover;
- (7) in mercerizing cotton.

Potassium Oxalate. Potassium oxalate, $K_2C_2O_4 \cdot H_2O$, is a colorless, odorless, monoclinic crystal, efflorescent in warm, dry air. Its uses are:

- (1) in cleaning and bleaching straw
- (2) in removing stains in photography;

- (3) in examination of blood to prevent its coagulation;
- (4) as a reagent in analytical chemistry.

Sodium Amide. Sodium amide, NaNH₂, also known as sodamide, is a white to olive-green solid with seashell structure. It reacts violently with water to form sodium hydroxide and ammonia. It is produced by reacting ammonia gas with molten sodium or liquid ammonia with sodium in presence of ferric nitrate as a catalyst. Its uses are:

- as a dehydrating agent;
- (2) in the production of indigo, sodium azide, and hydrazine;
- (3) as an intermediate in the preparation of sodium cyanide;
- (4) in ammonolysis, Claisen condensation, alkylation of nitriles and ketones;
- (5) in the synthesis of ethynyl compounds, acetylenic carbinols.

<u>Sodium Hydride.</u> Sodium hydride, NaH, is a silvery needle. The commercial product is a gray-white powder. It reacts explosively with water. It is prepared by passing hydrogen gas into molten sodium dispersed in oil or mixed with a catalyst such as anthracene at a temperature above 250 C. Its uses are:

- in the reduction of oxide scale of metals (sodium hydride used is in solution with molten sodium hydroxide);
- (2) as a reducing agent and reduction catalyst in high temperatures.

Sodium Hydrosulfite. Sodium hydrosulfite, $Na_2S_2O_4$, is a white or grayish-white crystalline powder, with a slight characteristic odor. It oxidizes in air (more readily so in the presence of moisture or when in solution) to bisulfite and bisulfate. It is prepared by the reduction of sodium sulfite, sodium bisulfite, or sulfur dioxide with a reducing agent such as iron or zinc powder, sodium or zinc amalgam or sodium suspension.

The U.S. production of sodium hydrosulfite amounted to about 74 million lb in 1967. Its applications are based mainly on its powerful reducing action. The main uses are:

- as a reducing agent, particularly in dyeing of textiles with indigo and vat dyes;
- (2) in bleaching soaps, straw, ground wood pulp, sugar, molasses and glues.

Sodium Sulfide. Sodium sulfide, Na₂S·9H₂O, is a colorless, tetragonal, deliquescent crystal, with the odor of hydrogen sulfide. Exposure of the crystals to air produces the toxic hydrogen sulfide. Industrially, it may be prepared by (1) heating sodium sulfate with coal, or (2) reacting hydrogen sulfide with sodium hydroxide according to the following equations:

$$H_2S + NaOH \longrightarrow NaHS + H_2O$$
 $NaHS + NaOH \longrightarrow Na_2S + H_2O$

Estimated U.S. production of sodium sulfide in 1965 was 46,000 tons (as 60 to 62 percent solution). Its uses are:

- (1) in dehairing hides (in leather industry), and wool pulling;
- (2) as a reducing agent in the production of amino compounds;
- (3) in desulfurizing viscose rayon;
- (4) in the manufacture of sulfur dyes and rubber;
- (5) as a raw material or intermediate for the preparation of other compounds such as sodium hydrosulfide and polysulfides;
- (6) in ore flotation, metal refining, engraving and lithography, cotton printing;
- (7) as a chemical reagent.

Sodium Thiocyanate. Sodium thiocyanate, NaSCN, is a colorless, rhombic deliquescent crystal. It is prepared by fusing sodium cyanide solid or boiling a solution of sodium cyanide with sulfur or a polysulfide.

NaCn + S
$$\longrightarrow$$
 NaCNS
 4 NaCN + Na₂S₅ \longrightarrow 4 NaCNS + Na₂S

Its uses are:

- (1) in the manufacture of other thiocyanates, especially organic;
- (2) as a drying agent for wool;
- (3) as a stabilizing agent in photography.

Stannic Chloride. Stannic chloride, SnCl₄, is a colorless, fuming, caustic liquid. It is prepared by the direct chlorination of tin which can be in molten state or finely divided suspension in stannic chloride. Its uses are:

- (1) as a mordant;
- (2) in dyeing of fabrics, weighing silk, tinning vessels;
- (3) as a dehydrating agent in organic syntheses;
- (4) reviving colors.

<u>Thiocyanates</u>. Inorganic thiocyanates are, in general, deliquescent crystals which are freely soluble in water and alcohol. Some would decompose on heating. They find some applications in photography, textile industry, and pyrotechnic. Some also find medical uses because they possess antithyroid properties.

Sources and Types of Wastes

The wastes from the materials discussed in this report come from a variety of sources. They include the manufacturers of these chemicals and various industrial plants which use these chemicals in their processes

or operations. The wastes are generally of the concentrated type in the form of unused or contaminated materials. For the majority of materials in this group, there is normally no dilute aqueous waste because they decompose very readily on contact with water.

Physical and Chemical Properties

The physical and chemical properties of these inorganic materials are given in the attached worksheets.

2. TOXICOLOGY 0766,1492

The toxicity of these materials varies from irritating and corrosive to the skin and mucous membranes to highly toxic.

Ammonium sulfide is stable only at temperatures below -18C. At higher temperatures it decomposes into ammonia and ammonium hydrosulfide (NH₄HS). The latter also decomposes easily at room temperatures to yield ammonia and hydrogen sulfide which is highly toxic. Consequently, under normal conditions, ammonium sulfide is irritating to the skin and emits highly toxic fumes.

Antimony pentachloride decomposes easily at room temperatures to produce chlorine gas which is highly toxic. When heated to decomposition, it emits the toxic fumes of antimony and hydrochloric acid. It will also react with water or steam to produce toxic or corrosive fumes. Antimony trichloride is poisonous and irritating to the skin. In general, antimony and its compounds can cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact with fumes or dust.

Calcium carbide itself is nontoxic. However, it generates acetylene on contact with water. When inhaled, acetylene is toxic.

Similarly, calcium hydride is basically nontoxic. Again, it reacts readily with water to yield hydrogen gas and calcium hydroxide.

3. OTHER HAZARDS

The hydrides (sodium, calcium, and lithium aluminum) react violently with water to generate hydrogen gas. Similarly, calcium carbide reacts very rapidly with water to yield acetylene. Both hydrogen and acetylene are highly flammable. They can cause fire and explosion hazards.

Ammonium sulfide is unstable at room temperatures. It decomposes readily to yield hydrogen sulfide. On contact with water or moisture in the air, sodium sulfide also decomposes easily to generate hydrogen sulfide. The hydrogen sulfide evolved can cause a fire hazard or form an explosive mixture with air.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Most of the materials in this group react rapidly with water or moisture in air, producing either flammable or toxic vapors. Therefore, they must be kept tightly closed in dry and cool areas with adequate ventilation. In general, they should not be handled with bare hands. Some also decompose readily upon heating and should be kept away from heat or flame. Toxic substances such as the oxalates should be stored away from food and feed products. In shipping, sodium amide, sodium hydride and sodium hydrosulfite are shipped under the Yellow Label, indicating flammable solids.

Disposal/Reuse

The chemicals discussed in this report are either so reactive with water or unstable with respect to heat that it is normally impractical to attempt to recover them for reuse with the possible exceptions of antimony and stannic chlorides. For the safe disposal of these materials, the acceptable criteria for their release into the environment are defined in terms of the recommended provisional limits.

Lithium aluminum hydride is generally not considered a toxic material. A large dose of lithium compounds has caused dizziness and prostration.

Potassium oxalate and binoxalate are both toxic substances. In general, they are corrosive and produce local irritation. When ingested, they are readily absorbed from the gastro-intestinal tract and can cause severe damage to the kidneys.

Potassium hydroxide is a strong alkali. It is very caustic and corrosive to the body tissue. Ingestion may produce violent pain in the throat and epigastrium, hematemesis, and collapse. If not immediately fatal, stricture of esophagus may develop. Dilute acetic acid may be used as an antidote.

On contact with water or moist air, sodium amide and sodium hydride hydrolyze readily to yield sodium hydroxide and ammonia (from sodamide) or hydrogen (from the hydride). Sodium hydroxide is a strong alkali having the same corrosive and toxic effects as that of potassium hydroxide described in the previous paragraph. Inhalation of ammonia gas would cause edema of the respiratory tract, spasm of glottis, and asphyxia.

The toxic effects of sodium hydrosulfite are similar to those of sulfites. Fairly large doses of sulfites can be tolerated by the human body because they are readily oxidized to sulfates. However, if swallowed, the sulfites may cause irritation of the stomach by liberating free sulfurous acid.

Sodium sulfide is similar to alkali in action. It causes softening and irritation of the skin. If taken by mouth, it is corrosive and irritant through the liberation of free alkali and hydrogen sulfide. Also, exposure of the sodium sulfide crystals to moist air produces hydrogen sulfide which is highly toxic.

Thiocyanates, including sodium thiocyanate, are not normally dissociated into cyanide. They have a low acute toxicity. Prolonged

absorption of thiocyanates may cause various skin eruptions, coryza, occasional dizziness, cramps and convulsions, nausea, vomiting, and mild to severe disturbances of the nervous system.

Stannic chloride may be highly irritating to the mucous membranes of the eyes and the respiratory tract. More severe exposures may result in pulmonary edema and often laryngeal spasm.

The Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists and lethal doses reported for the materials in this report are tabulated as follows: 0225, 1312

Chemicals	TLV	<u>Lethal Dose</u>			
Ammonium Sulfide		or LD _{Ca} : 2 mg/kg, mouse			
Antimony Pentachloride	0.5 mg as Sb/M^3				
Antimony Trichloride	0.5 mg as Sb/M^3	or LD ₅₀ : 675 mg/kg, rat			
Calcium Carbide					
Calcium Hydride					
Lithium Aluminum Hydride					
Potassium Binoxalate					
Potassium Hydroxide		or LD ₅₀ : 1230 mg/kg, rat			
Potassium Oxalate					
Sodium Amide		 :{			
Sodium Hydride		· · · · · · · · · · · · · · · · · · ·			
Sodium Hydrosulfite					
Sodium Sulfide		ip LD ₅₀ : 53 mg/kg, mouse			
Sodium Thiocyanate		or LD ₅₀ : 764 mg/kg, rat			
Stannic Chloride		ip LD ₅₀ : 21/mg/kg, mouse			
Thiocyanate					

Contaminant in Air	Provisional Limit	Basis for Recommendation		
Ammonium sulfide	0.15 mg/M ³ as H ₂ S	0.01 TLV for Hos		
Antimony pentachloride	$0.005 \text{ mg/M}^3 \text{ as Sb}$	0.01 TLV for Sb		
Antimony trichloride	$0.005 \text{ mg/M}^3 \text{ as Sb}$	0.01 TLV for Sb		
Calcium carbide	0.025 mg/M ³	Data on similar compounds		
Calcium hydride	0.025 mg/M ³	Data on similar compounds		
Lithium aluminum hydride	0.00025 mg/M ³	0.01 TLV for lithium hydride		
Potassium binoxalate	0.02 mg/M ³	Data on similar compounds		
Potassium hydroxide	0.02 mg/M ³	Data on similar compounds		
Potassium oxalate	0.01 mg/M ³ as oxalic a	cid 0.01 TLV for oxalic acid		
Sodium amide	0.02 mg/M ³	0.01 TLV for NaOH		
Sodium hydride	0.02 mg/M^3	0.01 TLV for NaOH		
Sodium hydrosulfite	0.02 mg/M ³	0.01 TLV for NaOH		
Sodium sulfide	0.15 mg/M 3 as H $_{2}$ S	0.01 TLV for H2S		
Sodium thiocyanate	0.02 mg/M^3	0.01 TLV for NaOH		
Stannic chloride	$0.02 \text{ mg/M}^3 \text{ as Sn}$	0.01 TLV for Sn		
Thiocyanate	Variable	Depending on the thio- cyanate compound		
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation		
Ammonium sulfide	0.75 ppm (mg/1) as H_2S	Stokinger & Woodward Method		
Antimony pentachloride	0.05 ppm (mg/1) as Sb	Chronic toxicity drinking water studies		
Antimony trichloride	0.05 ppm (mg/1) as Sb	Chronic toxicity drinking water studies		
Calcium carbide	0.125 ppm (mg/1)	Stokinger & Woodward Method		
Calcium hydride	0.125 ppm (mg/l)	Stokinger & Woodward Method		
Lithium aluminum hydride	0.00125 ppm (mg/l)	Stokinger & Woodward Method		
Potassium Binoxalate	0.10 ppm (mg/1)	Stokinger & Woodward Method		
Potassium hydroxide	0.10 ppm (mg/1)	Stokinger & Woodward Method		
Potassium oxalate	0.05 ppm (mg/l)	Stokinger & Woodward Method		
Sodium amide	0.10 ppm (mg/l)	Stokinger & Woodward Method		
Sodium hydride	0.10 ppm (mg/1)	Stokinger & Woodward Method		

Contaminant in Water & Soil	Provisional Limit	Basis for Recommendation
Sodium hydrosulfite	0.10 ppm (mg/1)	Stokinger & Woodward Method
Sodium sulfide	0.75 ppm (mg/1) as H ₂ S	Stokinger & Woodward Method
Sodium thiocyanate	0.10 ppm (mg/1)	Stokinger & Woodward Method
Stannic chloride	0.05 ppm (mg/1) as Sn	Chronic toxicity drinking water studies
Thiocyanate	Variable	Depending on the thio- cyanate compounds

EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Hydrolysis and Combustion

Calcium carbide and the hydrides of calcium, sodium, and lithium aluminum all hydrolyze very readily producing combustible gases. For the disposal of the calcium carbide waste, the material is slowly added to a large container of water. The acetylene gas liberated is burned off with a pilot flame. The remaining residue is lime and can be sent to landfill. For the hydrides, the waste materials may be first mixed with dry sand to minimize the fire hazard before they are added to water. Again, the hydrogen gas liberated is burned off with a pilot flame. The remaining residues are hydroxides and they should be neutralized by an acid before being disposed of.

Option No. 2 - Hydrolysis and Neutralization

Sodium amide hydrolyzes rapidly to form sodium hydroxide and ammonia, both of which can be neutralized by hydrochloric or sulfuric acid. The neutral solution can be safely discharged if the salt content is below the limits set to maintain water quality. Salt mixtures containing antimony chlorides or stannous chlorides will form the very slightly soluble oxides of these metals when dissolved in water and neutralized. Removal of the

oxides is followed by sulfide precipitation described below to ensure removal of the metal ions from solution. The antimony oxides can be sent to a refiner if justified by market conditions or placed in drums and stored at a National Disposal Site. The tin oxides can be refined or landfilled.

Option No. 3 - Sulfide Precipitation

The soluble sodium and ammonium sulfides can be converted into the insoluble ferrous sulfide by reaction with ferrous chloride solution. The ferrous sulfide precipitate may be removed by filtration and reclaimed. Similarly, antimony pentachloride and trichloride can be converted to the corresponding insoluble sulfides by saturating the chloride solutions with hydrogen sulfide. After filtering out the sulfide precipitate, the filtrate solution is neutralized with soda ash and then discharged. The recovered sulfide may be sent to refiners for reprocessing if economically feasible or placed in containers and shipped to a National Disposal Site for storage.

Option No. 4 - Oxidation

When ignited, potassium binoxalate and oxalate are converted into carbonates. The carbonates, particularly sodium carbonate, have many applications Since they are nontoxic, they may also be sent to landfill or simply sewered.

Sodium hydrosulfite is a reducing agent. It can be easily oxidized to yield sodium sulfate with the liberation of sulfur dioxide. The exhaust gas is therefore scrubbed with an aqueous suspension of finely-ground limestone to absorb the sulfur dioxide gas. The soluble sodium sulfate is also converted to the insoluble calcium sulfate which is removed by filtration and sent to landfill. The filtrate is diluted and discharged.

Option No. 5 - Neutralization

Disposal of contaminated potassium hydroxide (solid) can be carried out by first dissolving it in water followed by neutralization with an acid and finally sewered. Similarly, sodium thiocyanate which has a low acute toxicity can be disposed of by dissolving it in a large quantity of water, buffered with slight excess of soda ash and finally neutralized by an acid and sewered. 0095

In summary, the majority of materials in this group can be easily disposed of by reacting with water or by ignition or by neutralization. These procedures are all simple and quite adequate.

6. APPLICABILITY TO NATIONAL DISPOSAL SITE

The disposal processing described herein is of a level that can be quite easily performed adequately in an industrial environment. Most of the treated materials which cannot be economically recovered can be discharged to sewer systems or landfilled. An exception is the stable antimony product, either the oxide or sulfide, which must be carefully controlled and returned to the antimony producers or reclaimers for the recovery of its antimony value. Secondary antimony recovered from various manufacturers and foundries while reprocessing scrap material amounted to 23,664 tons in 1967, about twice as much as the primary antimony produced in the United States for the same year. The depletions of high grade antimony oxide ores indicate that even greater attention should be focused on the secondary recovery of antimony from waste streams containing antimony compounds.

7. REFERENCES

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	HAZARDOUS WASTES PROPERTIES WORKSHEET
H. M. Name Ammonium Sulfide (29)	Structural Formula
IUC Name Common Names	(NH ₄) ₂ S
Molecular Wt. 68.14 ⁽¹⁾ Density (Condensed) @	Melting Pt. decomposes (1) Density (gas) @
Vapor Pressure (recommended 55 C a	nd 20 C)
Flash Point	Autoignition Temp.
!	LowerUpper
Others: very soluble in NH ₃	Hot Water decomposes Ethanol soluble
u	
1	
Shipped in	
1	Coast Guard Classification
References (1) ¹⁵⁷⁰	

HAZARDOUS WASTES PROPER WORKSHEET	RTIES
H. M. Name <u>Antimony Trichl</u> oride (41)	Structural Formula
Common Names	SbC13
Molecular Wt. 228.11 ⁽¹⁾ Melting Pt. 73.4 C Density (Condensed) 3.14 @ 25 C Density (gas	(1) Boiling Pt. 283 C (1)
Vapor Pressure (recommended 55 C and 20 C) (2)	
l mm Hg @ 49.2 C @ Flash Point Autoignition Temp	
Flammability Limits in Air (wt %) Lower	Upper Upper C Ethanol_soluble
Shipped in Coast Gu Comments	
References (1) 1570 (2) 0766	

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name <u>Calcium Carbide</u> (89)		Structural Formula		
IUC Name		·		
Common Names		CaC ₂		
Molecular Wt. 64.10 ⁽¹⁾	Stable Melting Pt. 25-477	C ⁽¹⁾ Boiling Pt. 2300 C ⁽¹⁾		
Density (Condensed) 2.22 @@	Density (gas	e		
Vapor Pressure (recommended 55 C and	1 20 C)			
Flash Point	Autoignition Temp	_		
Flammability Limits in Air (wt %)				
Explosive Limits in Air (wt. %)	Lower	Upper		
Solubility (1)		· .		
Cold Water decomposes	Hot Water decompos	ses Ethanol		
Others:	 .			
Acid, Base Properties		· · · · · · · · · · · · · · · · · · ·		
Highly Reactive with water				
Compatible with				
Shipped in				
ICC Classification	Coast Gu	ard Classification (2) hazardous articl		
Comments				
References (1) 1570				
(2) 0766				

Н	AZARDOUS WASTES PROPERT WORKSHEET	TIES
H. M. Name <u>Calcium Hydrid</u> e (93)		Structural Formula
Molecular Wt. 42.10 ⁽¹⁾	decompose Melting Pt. Ca 600 C	Boiling Pt
Density (Condensed) 1.9 @ @	d 20 C)	
Flash Point Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) Solubility (1)		Upper
1		-
Shipped in ICC Classification Comments	Coast Gua	ard Classification
References (1) 1570 (2) 1492		

Н/		WASTES PROP RKSHEET	ERTIES .		A 17 of ART AN AN ANTIGORE
H. M. Name <u>Lithium Aluminum</u> Hydride			Stru	ctural For	mula
Common Names .	, , , , , , , , , , , , , , , , , , , 		LiAIH	4	
Molecular Wt. 37.95 ⁽¹⁾ Density (Condensed) @	Melting	Pt. @ 125 Density (g	ooses()) C	Boiling Pt	
Vapor Pressure (recommended 55 C and	i 20 C)				
		e ion Temp		,	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) (1) Solubility	Lower		Upper		
Cold Water decomposes Others: slightly soluble in liqu Acid, Base Properties	NH3		•	Ethanol_	slightly soluble
Highly Reactive with (2) water and	alcohols				
Compatible with					
Shipped in					
ICC Classification Comments			Guard Classif	ication	
	<u> </u>				
References (1) 1570 (2) 1492				·	

	ASTES PROPERTIES KSHEET
H. M. Name Potassium Binoxalate (342)	Structural Formula
IUC Name Common Names	KHC ₂ O ₄
Molecular Wt. 128.11 ⁽¹⁾ Melting Density (Condensed) 2.044 @	Pt. decomposes (1) Boiling Pt Density (gas)@
Vapor Pressure (recommended 55 C and 20 C)	
Flash Point Autoigniti	<u>e</u> e
	on Temp
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	UpperUpper
	opper
Solubility (1) Cold Water 2.5 grams/100 ml Hot Wa	ter_16.7 grams/100 m1 [®] 100C Ethanol insoluble
Others:Acid, Base Properties	
Highly Reactive with	
Compatible with_	
Shipped in	
d	Coast Guard Classification
Comments	
References (1) 1570	

H. M. Name Potassium Hydroxide (347) IUC Name Common Names KOH (S) Molecular Wt. 56.11 (1) Melting Pt. 360.4 - 0.7 C Boiling Pt. 1320-1324 C	на
Molecular Wt. <u>56.11⁽¹⁾</u> Melting Pt. <u>360.4⁺ 0.7 C</u> Boiling Pt. <u>1320-1324 C</u>	IUC Name
Molecular Wt. <u>56.11⁽¹⁾</u> Melting Pt. <u>360.4⁺ 0.7 C</u> Boiling Pt. <u>1320-1324 C</u>	
Density (Condensed) 2.044 @ Density (gas) @	Density (Condensed) 2.044 @
Vapor Pressure (recommended 55 C and 20 C)	
Flash Point Autoignition Temp Upper Upper	
Explosive Limits in Air (wt. %) Lower Upper	Explosive Limits in Air (wt. %)
Solubility (1) Cold Water 107 g/100 ml @ 15 C Hot Water 178 g/100 ml @ 100 C Ethanol very soluble Others: Acid, Base Properties caustic	Cold Water 197 g/100 ml @ 15 C Others:
Highly Reactive with	Highly Reactive with
Compatible with	
Shipped in(2) Hazardous	
ICC Classification Coast Guard Classification article Comments	
References (1) ₁₅₇₀ (2) ₀₇₆₆	

Н	AZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name <u>Potassium Oxa</u> late (34)	8)	Structural Formula
Common Names		к ₂ с ₂ 0 ₄ -н ₂ 0
Molecular Wt. <u>184.24⁽¹⁾</u> Density (Condensed) <u>2.127</u> @		(1) 00 C Boiling Pt)@
	@	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) (1) Solubility	Lower	Upper
Cold WaterOthers:Acid, Base Properties		
Highly Reactive with Compatible with		
Shipped inICC Classification		
Comments		ura crassificación_
References (1) ₁₅₇₀		

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Sodium Amide (375)				ructural Formula
Common Names			NaNH ₂	
Molecular Wt. 39.01 ⁽¹⁾ Density (Condensed) @@	Melting	Pt. 210 C	(1) as)	Boiling Pt. 400 C (1)
Vapor Pressure (recommended 55 C and				
	Autoianit	_@ ion Temp		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) (1) Solubility	Lower		Upper	
Cold Water decomposes Others: Acid, Base Properties				
Highly Reactive with water				
Compatible with		<u>.</u>		
Shipped in (2) flammable soli ICC Classification yellow label Comments	d,	Coast G	uard Class	(2) inflammable ification solid, yellow label
References (1) 1570 (2) 0766	•			

	HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name Sodium Hydride (391)		Structural Formula
IUC Name Common Names		NaH
Molecular Wt. 24.0 ⁽¹⁾ Density (Condensed) 0.92 @	Melting Pt. decompos Density (gas	(1) ses @ 800 C Boiling Pt) @
Vapor Pressure (recommended 55 C an	ad 20 C)	@
	Autoignition Temp	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower	Upper
1	•	es Ethanol
Others: <u>soluble in molten sodi</u> Acid, Base Properties		
Highly Reactive with (3) water and		
Compatible with		
Shipped in (2) flammable so	lid.	(2) inflammable
ICC Classification <u>yellow label</u> Comments	Coast Gu	ard Classification <u>solid</u> , <u>yellow</u> label
References (1) 1570 (2) 0766 (3) 1492		

HAZARDOUS WASTES PROPERTIES WORKSHEET			
		· ·	
H. M. Name Sodium Hydrosulfite (39	2)		
IUC Name		Structural Formula	
Common Names	·	Na ₂ S ₂ O ₄	
Molecular Wt. <u>174.13⁽¹⁾</u>	Meltina Pt decompos	es (2) Roiling Pt	
Density (Condensed) @	Density (gas)	
Vapor Pressure (recommended 55 C and			
	•		
Flash Point A	utoignition Temp		
Flammability Limits in Air (wt %)	Lower	Upper	
Explosive Limits in Air (wt. %)			
Solubility (1)	•		
Cold Water very soluble	Hot Water decompos	es ⁽²⁾ Ethanol <u>slightly</u>	
Others:			
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Compatible with			
Shipped in		,	
(3) flammable soli ICC Classification yellow label	d, yellow Coast Gu	(3)inflammable solid ard Classification yellow label	
Comments		,	
·			
References (1) 1492			
(2) 1433			
. (3) 0766		:	

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name <u>Sodium Sulfide</u> (404)			Structural Formula
IUC Name			Na ₂ S·9H ₂ O
Molecular Wt. 240.18 ⁽¹⁾	Melting	decompose Pt. at 920 C	Boiling Pt.
Density (Condensed) 1.427 @		vensity (gas	,
@@		0	
3		ion Temp	
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)			
Solubility (1)			00 ml @ 100 CEthanol slightly soluble
Others:Acid, Base Properties	_		
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification			ard Classification
Comments	·		
References (1) 1570			

ŀ		WASTES PROPERTI RKSHEET	ES
H. M. Name Sodium Thiocyanate (40	06)		Structural Formula
IUC Name			or account formata
Common Names			NaSCN
·		` L	
Molecular Wt. 81.07 ⁽¹⁾	Melting	Pt287 C (1)	Boiling Pt
Density (Condensed)@		Density (gas)_	
Vapor Pressure (recommended 55 C an	d 20 C)		
<u> </u>			
Flash Point	Autoigniti	ion Temp	
Flammability Limits in Air (wt %)			Upper
Explosive Limits in Air (wt. %)	Lower		Upper
Others: very soluble in acetone Acid, Base Properties	_		nl @ 100 C Ethanol very soluble
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification			
Comments			
References (1) 1570			
	_		
	•		

. HA	ZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name Staunic Chloride (408)		Structural Formula
IUC Name		
Common Names		SnC1 _A
·		4
Molecular Wt. 260.50 (1)	Melting Pt33 C	(1) Boiling Pt. 114.1 C
Density (Condensed)@	Density (gas	.)
Vapor Pressure (recommended 55 C and	20 C) (2)	
10 mm Hg @ 10 C		
Flash Point A	utoignition Temp	
Flammability Limits in Air (wt %)		
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility (1) Cold Water_soluble	Hot Water decompos	ses Ethanol
Others: soluble in ether	_	
Acid, Base Properties		
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification		ard Classification
Comments		
References (1) 1570		
(2 _.) 0766		
		•

PROFILE REPORT

Antimony (33), and Antimony Trioxide (45)

GENERAL

The two major antimony producers in the United States are the Sunshine Mining Company, Kellogg, Idaho and NL Industries (formerly National Lead), who operate a smelter in Laredo, Texas to process ore originating in Mexico. In 1971, Sunshine produced 1,708,000 lb of antimony by electrowinning from the NaOH leach of their Ag-Cu ore. The spent leach solution containing 400 lb Sb/day is deposited in a tailings pond, from whence an effluent containing 5 to 40 ppm Sb is emptied into the South Fork of the Coeur d'Alene River. Within one year, continuous recycling based on evaporation of the liquid and recovery of the solids will be instituted, thereby eliminating the current antimony waste.

NL employs conventional smelting in its Laredo, Texas facility. 0663
No production figures are available, but a representative reports that their slag contains 1 percent Sb of which 60 percent is present as antimony metal. This slag is held in outdoor storage on their property.

Over 95 percent of all the antimony used in the United States is alloyed at a 4 or 5 percent concentration with lead in bearings, type metal, etc. $^{0.591,1433}$ Kirk-Othmer 1433 reports that a large amount of the 13,500 tons of antimony used every year is recycled.

Antimony trioxide is an intermediate in the production of antimony metal by smelting. The oxide is won from the ore by volatilization and then reduced to metal. The principal use of antimony trioxide is as a fire-proofing additive in plastics and cloth. O591,1433,0063 Also, it finds commercial application as an opacifier for glasses and ceramics. Production was 6,518 tons and consumption was 9,363 tons in 1968.

2. TOXICOLOGY 0766,1312

The accepted Threshold Limit Value (TLV) of the American Council of Governmental Industrial Hygienists (ACGIH) for antimony or antimony oxides is $0.5~\text{mg/m}^3$ air by inhalation. This represents approximately 10 percent of a dose of $4.7~\text{mg/m}^3$ of antimony metal by inhalation, which had produced clinical symptoms involving the skin, the pulmonary system, and the gastrointestinal tract. LD 50 for antimony metal is 100~mg/kg body weight for the rat for administration by means other than the respiratory tract.

Since antimony pentoxide is chemically similar to antimony trioxide, their toxicities should be approximately the same. Intraperitoneal administration of antimony pentoxide in rats indicates an LD 50 of 4000 mg/kg body weight.

3. OTHER HAZARDS

Finely divided antimony powder may explode; as may amorphous antimony obtained by electrodeposition in an air or enriched oxygen environment. Antimony has a fairly low boiling range of 1300 to 1640 C (depending on the presence of metastable phases), and fumes released on heating are considerably more toxic than the solid form. Antimony metal reacts with most acids (except HCl) to form the highly toxic gas, SbH₃. It also reacts with HCl if zinc is present.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Hazardous exposures to the dusts and fumes of antimony and its oxides have been reported and the use of goggles and respirators is recommended for the handling of these compounds in powdered form. Antimony and antimony trioxide are moderately toxic compounds and should be stored in cool well-ventilated places; away from areas of high fire hazard, and should be

periodically inspected and monitored. Antimony metal reacts with most acids to form the extremely toxic gas stibine, ${\rm SbH_3}$ and caution should be taken in isolating these materials from each other. Both antimony and antimony trioxide are not classified by the Department of Transportation as hazardous materials and there are no specific rules governing their transportation.

Disposal/Reuse

Waste sludges containing antimony are not currently reclaimed for their antimony value because of the soft antimony market for the past several years. For the safe disposal of antimony and antimony trioxide, the acceptable criteria for their release into the environment are defined in terms of the following provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Antimony	0.005 mg/M^3 0.005 mg/M^3 as Sb	0.01 TLV
Antimony Trioxide	$0.005 \text{ mg/M}^3 \text{ as Sb}$	0.01 TLV for Sb
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Antimony	0.05 ppm (mg/1)	Chronic toxicity drinking water studies
Antimony Trioxide	0.05 ppm (mg/1) as Sb	Chronic toxicity drinking water studies

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The present liquid effluent of the Sunshine Mining Company 0591 contains 5 to 40 ppm Sb and present plans call for this to cease when their new recycling system comes onstream sometime in 1972 (Figure 1). 1535 The plant effluent of 9-12 tons/day containing 40 lb Sb/ton and 150 g/l alkalinity equivalent Na₂S (the amount of Na₂S which requires the same amount of acid to titrate to Ph 7 as 150 g/l CaCO₃ requires) is evaporated on a

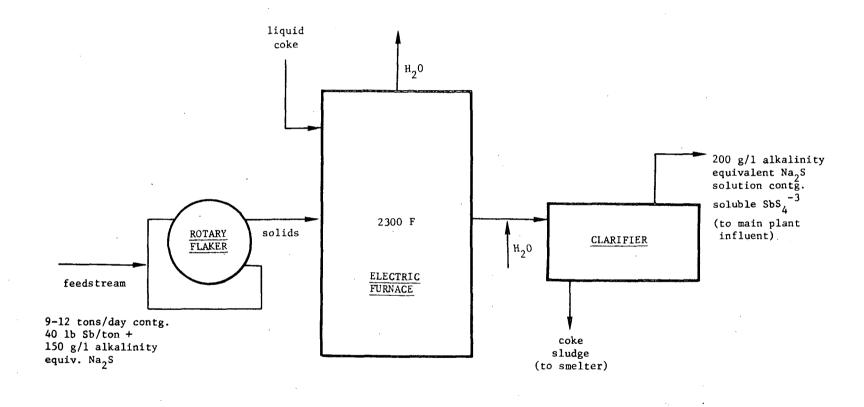


Figure 1. Recycle of Effluent from the Electrolytic Production of Antimony

rotary flaker. The resulting crystals are mixed with liquid coke and reduced at 2,300 F in an electric furnace to Na₂S and other salts. The only air emissions from the furnace are water vapor. Sufficient water is then added to the reduced salts to make a 200 g/l alkalinity equivalent Na₂S solution. This solution is then clarified to remove whatever coke sludge may be present. It contains all the antimony present in the original effluent as soluble thioantimonate ion. In this form it is recycled to the main plant to mix with the antimony plant influent, the NaOH leach of their Ag-Cu ore. It is anticipated that the amount of coke sludge will be approximately zero. Any which does result will be recycled back to the smelter.

The advantages of this recyling system include the recovery of the 40 lb Sb/ton which had hitherto been lost in a settling pond and the recovery of 95 percent of their caustic. From an environmental standpoint, the elimination of settling ponds will stop the flow of 5 to 40 ppm Sb pond effluent into the South Fork of the Coeur d'Alene River and eliminate the SO₂ gas presently venting from these ponds.

The capital cost for this system is \$350,000.00 which is mostly for the electric furnace. Operating costs are estimated to be 6¢/lb Sb recovered, which includes 0.3¢/kwh for furnace power and \$16/ton liquid coke used at the rate of 1 ton/day. No bookkeeping charges will be assessed for plant steam to operate the rotary flaker, since this steam is merely vented now. Likewise, no charges will be assessed for manpower, since present plant labor will be used.

If it is assumed that the Laredo, Texas smelter of NL Industries produces almost all the antimony not produced by the Sunshine Mining Company, the Laredo antimony production amounted to about 5,500 tons in 1968. This figure would not be verified by NL, 0663,1663 but information was made available with regard to the waste produced on a per ton Sb basis and this information has been used for the extrapolation to an assumed 5,500 ton/yr production (Table 1). There is no liquid effluent of any consequence.

TABLE 1
ANTIMONY SMELTER WASTE AT LAREDO, TEXAS (1971)

Waste Material	Amount Produced/Ton Sb	Amount Produ	ced (Total
Ai rborne	3.75 lb/ton		Q.
NO	3.75 lb/ton	10.30	tons/yr
so ₂	22.00 lb/ton	60.50	tons/yr
Hydrocarbons	0.64 lb/ton	1.76	tons/yr
CO	940.00 lb/ton	2,590.00	tons/yr
Particulates [†]	62.00 lb/ton	171.00	tons/yr
Solid			
Slag	8.015 ton/ton	44,000	tons/yr

^{*}Based on assumed annual production of 5,500 tons Sb.

^{*}Includes transient dust from ore unloading and other extraneous sources.

The slag, an insoluble mixture of metals and oxides, contains one percent Sb, of which 60 percent is in the metal form. The slag is held in outdoor storage on the property pending possible reworking or disposal. For the past several years the antimony market has been very soft and it is doubtful that anything will be done with this slag in the foreseeable future.

No information is available with regard to the antimony content of the particulate emissions, but, if it is assumed to be one percent, there would be an airborne emission of approximately 28.1 g Sb/ton Sb produced. Data is available for the volume of stack gases produced as a function of the metal production in a lead smelter. \$\frac{1668}{1668}\$ If it is assumed that this data is directly correlatable with antimony smelter production, the Sb particulate emissions are 7.5 mg/m³, or 15 times the accepted Threshold Limit Value. While this represents a high level of airborne emissions, it is nevertheless a substantial improvement. Only within the past year, have four additional baghouses been installed to achieve this level.

Since virtually all the antimony metal used in the United States is alloyed at a four or five percent concentration with lead in bearings, type metal, etc., its disposal and recycling from secondary sources is a part of the lead recycle-disposal system.

With respect to antimony trioxide, it is ubiquitous in very small concentrations as a fire-proofing additive in plastics and cloth. It is discarded in municipal systems and is not considered to be a pollution problem at present. 0615,0768 Its range of measurement as an air pollutant in 58 urban areas was 0.042-0.85 $\mu \text{g/m}^3$ which is roughly 1/1000 of the Threshold Limit Value of 0.5 mg/m^3 . No human retention has been demonstrated.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Of the two major antimony producers in the United States 0591,0663,1535 1663), one is currently putting a recycling system into operation which will eliminate all waste emissions and the other may have an airborne emissions problem in the form of particulate emissions containing about one percent antimony. It is recommended that a study be performed to determine precisely what total amount of antimony is emitted in this way. The economics of the mining and smelting industry today make it unlikely that this particulate dross could be transformed into something of significant commercial value.

Extensive clinical studies ⁰⁶¹⁵,0⁷⁶⁸ indicate that antimony and antimony trioxide are not generally environmental hazards at present and are not likely to become so in the future.

This lack of hazard together with the very low concentrations present in the smelting dross (airborne particulate and solid) make these unlikely candidate waste stream constituents for national disposal. If emissions are found to be above the acceptable level, they should be treated at the industrial site with standard technology equipment such as scrubbers, cyclones, etc.

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	HAZARDOUS WAST WORKSH		IES		
A. M. Name			Structur	al Formula	
IUC Name ANTIMONY (33)		[Structur	ar rerinare	
Common Names ANTIMONY			Sb		
·		Į			·
Molecular Wt. 121.75	Melting Pt.	630.5	C Boi	ling Pt. <u>l</u>	380 C-1640 C
Density (Condensed)6_618_g/c@_	20 Den	sity (gas)		9	
Vapor Pressure (recommended 55 C a	and 20 C)				
<u> </u>			-		
Flash Point	Autoignition	Temp	- Does not and	toignite	
Flammability Limits in Air (wt %)					
Explosive Limits in Air (wt. %)	Lower		Upper		
Solubility					,
Cold Water 0	Hot Water	0	E	thanol	0.
Others: h. conc. H. SO. aq. r				•	
Acid, Base Properties Very sli	ghtly basic		 		
Highly Reactive with <u>Electrodepos</u>	ited amorphous	Sh may ox	nlodo:		Chil 4-
presence of Zn + HCl. reacts vi	gorously with		μπυε -	-produce:	- 30113 111
Compatible with Air, moisture		-			
					
Shipped in <u>Barrels, trucks</u>					
ICC Classification None			rd Classifica	tion	
Comments No shipping resctri	ctions found				
			_ 		
-					
4					
·					

HAZARDOUS WASTES PROPERTIES WORKSHEET
IUC Name
Molecular Wt. 121.75 Melting Pt. 630.5 C Boiling Pt. 1380 -1640 C Density (Condensed) 6.6189/c@ 20 C Density (gas) @ Vapor Pressure (recommended 55 C and 20 C)
I mm @ 886 C @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @ @
Solubility Cold Water 0 Hot Water 0 Ethanol 0 Others: h. conc. H ₂ SO ₄ , aq. reg. Acid, Base Properties very slightly basic
Highly Reactive with Electrodeposited amorphous Sb may explode produces SbH3 in presence of Zn + HCl, reacts vigorously with Cl2 Compatible with Air, moisture, HCl
Shipped inbarrels, trucks, railroad cars ICC Classification Coast Guard Classification Comments No shipping restrictions found

HAZARDOUS WASTES PROPERTIES WORKSHEET				
II. M. Name IUC Name ANTIMONY TRIOXIDE (45) Conumon Names ANTIMONY TRIOXIDE	Structural Formula			
Molecular Wt. 291.52 Melting Pt. 656 C Density (Condensed) 5.2 g/cc @ 20 C Density (gas)				
Vapor Pressure (recommended 55 C and 20 C) 1 mm @ 574 C @ Flash Point Autoignition Temp. Flammability Limits in Air (wt %) Lower Not flam. Explosive Limits in Air (wt. %) Lower	Upper			
Solubility Cold Water v. sl. Hot Water sl Others: HCl, KOH, HAc Acid, Base Properties Slightly basic	Ethanol 0			
Highly Reactive with Nothing Compatible with				
Shipped in Barrels, trucks, railroad cars ICC Classification None Coast Guar Comments No shipping rescrictions found	d Classification			

PROFILE REPORT

Antimony Pentasulfide (37), Antimony Sulfate (39), Antimony Trisulfide (40), Calcium Fluoride (92), Metallic Mixture of Powdered Magnesium and Aluminum (260), Silica (368), Arsenic Pentaselenide (467), Tantalum (510)

GENERAL

Introduction

The inorganic materials to be discussed in this report have been preliminarily identified as probable candidate waste stream constituents for industrial disposal. These materials are generally insoluble in water. Their toxicity varies from nontoxic to poisonous. Most of them are not produced in large tonnage and their industrial applications are, in general, rather limited.

Manufacture and Uses

Antimony Pentasulfide. Antimony pentasulfide, $\mathrm{Sb}_2\mathrm{S}_5$, is an orange-yellow, odorless powder. It is insoluble in water. The commercial product is made by boiling antimony trisulfide with sulfur in alkaline solution and decomposing the resulting mass with hydrochloric acid to liberate the antimony pentasulfide. It may also be prepared by reacting hydrogen sulfide with hydrated antimony pentoxide suspended in water or a hydrochloric acid solution of antimony pentoxide. It is used: 1492

- (1) as a pigment in paints;
- (2) in vulcanizing and coloring rubber;
- (3) in the manufacture of matches and fireworks.

Antimony Sulfate. Antimony sulfate, $Sb_2(SO_4)_3$, is a colorless crystal. It deliquesces in moist air. With an excess of water, it is converted into an insoluble basic salt. It can be prepared by dissolving antimony trioxide in hot, concentrated sulfuric acid. On cooling, long, silky needles of

antimony sulfate are precipitated from the solution. The precipitates are then removed by filtration, washed free of sulfuric acid with xylene, and finally dried to finished products. Antimony sulfate appears to have little commercial application.

Antimony Trisulfide. 1433 Antimony trisulfide, Sb_2S_3 , is a yellow-orange, amorphous solid which turns black upon standing. It is insoluble in water. It may be prepared by:

- (1) reacting hydrogen sulfide with antimony trichloride;
- (2) heating sulfur with antimony or antimony trioxide under vacuum conditions;
- (3) reacting antimony trichloride with a sodium thiosulfate solution saturated with sulfur dioxide.

Its uses are:

- (1) in the manufacture of pyrotechnics, matches and explosives;
- (2) as a pigment in paints;
- (3) in the manufacture of ruby glass.

Calcium Fluoride. 1433,1492 Calcium fluoride, CaF₂, occurs naturally in the minerals fluorite and fluorspar. The latter is a common mineral found in widely differing deposits. It is mined and purified to yield pure calcium fluoride. The U.S. consumption of fluorspar amounted to about 900,000 tons in 1964. When pure, calcium fluoride is a colorless, cubic crystal or powder. It is practically insoluble in water and becomes luminous when heated. Its uses are:

- (1) as a flux in the steel industry;
- (2) as a primary source of fluorine in the chemical industry;
- (3) in the manufacture of glass, ceramics, enamel, portland cement, abrasives;
- (4) as the light-emitting agent in most fluorescent lighting tubes;
- (5) as a catalyst in dehydration and dehydrogenation processes.

Metallic Mixture of Powdered Magnesium and Aluminum. 0766,1492,1570

Magnesium is a light, silvery white and fairly tough metal. It is produced by electrolysis of fused magnesium chloride derived from brines, wells, or sea water. In fine powder, magnesium can be ignited by a spark or the flame of a match and burns with a dazzling white flame. It is unsurpassed for high intensity light effect. Therefore, it is used in flashlight photography, flares, and pyrotechnics, including incendiary bombs.

Aluminum is also a light and silvery white metal. It is produced by electrolysis of alumina dissolved in a fused bath of cryolite. The finely divided aluminum powder can also be ignited easily and may cause explosions. It also is used as a flashlight in photography, and in fireworks and explosives. The mixture of magnesium and aluminum metallic powder is therefore used primarily in pyrotechnics.

Silica. 1433,1492 Silica, SiO₂, occurs plentifully in nature as sand, quartz, flint, chalcedony, opal, agate, and infusorial earth. It exists in a variety of polymorphic crystalline and amorphous forms as well as a liquid. Among the crystalline forms of silica are quartz, tridymite, and cristobalite in atmospheric pressure and keatite, coesite and stishorite in high pressures. Each of these in turn has its polymorphic forms existing in different temperature ranges. Among the amorphous forms of silica are silica gel, colloidal silica, precipitated silica and fused silica. Its uses are:

- in the manufacture of glass, ceramics, enamels, refractories, abrasives, concrete, bricks, and building stones;
- (2) as a desiccant, an adsorbent, or a catalyst;
- (3) in the manufacture of water glass and soluble silicates, silicon and its alloys, silicon carbide, silicon-based chemicals, and the silicones.

Arsenic Pentaselenide. 1492 Arsenic pentaselenide, $\mathrm{As}_2\mathrm{Se}_5$, is a black, brittle solid with a metallic luster. It is insoluble in water and decomposes when heated in air. It may be prepared by melting a mixture of

arsenic and selenium in correct proportions at about 400 C in a sealed tube filled with nitrogen gas and distilling the resulting mass under reduced pressures to obtain pure arsenic pentaselenide. It may also be prepared by the reaction of an arsenic salt with hydrogen selenide in solution. Arsenic pentaselenide is of limited commercial importance.

Tantalum. 1433,1570 Tantalum, Ta, is a gray, heavy, and very hard metal. It occurs principally in the mineral columbite-tantalite. The metal has a high melting point exceeded only by tungsten and rhenium. At temperatures below 150 C, it is almost completely inert to chemical attack. Commercial production of tantalum is carried out in two major steps: (1) extraction and purification of a pure tantalum compound from the ore; and (2) reduction of such a compound to pure metal. The extraction and purification step may be accomplished by either (1) an alkali fusion of the ore followed by acid treatment to remove most of the impurities and fractional crystallization to obtain a pure potassium fluotantalate, K_2 TaF $_7$; or (2) extraction of the ore by hydrofluoric acid followed by liquid-liquid extraction using methyl isobutyl ketone (MIBK) and precipitation with ammonia to yield hydrated tantalum oxide. The reduction step may be carried out by:

- (1) electrolysis of molten potassium fluotantalate;
- (2) reduction of potassium fluotantalate by sodium pellets;
- (3) reduction of tantalum oxide by carbon or tantalum carbide.

Its uses are:

- in making electrolytic capacitors, lightning arrestors, surge suppressors;
- (2) in fabricating chemical process equipments, nuclear reactors; aircraft and missile parts, surgical instruments;
- (3) as an implant metal for the human body in surgery;
- (4) in special-purpose vacuum tubes.

Sources and Types of Wastes

The wastes of materials discussed in this report may come from the following sources:

- (1) mining and metal refining facilities;
- (2) industrial plants which either produce these materials or use them in their manufacturing processes;
- (3) users of products containing these materials.

Practically, all the wastes are in the form of unused or contaminated materials.

Specifically, arsenic has been used to provide for more heat stability in xerox drums, which normally contain selenium coatings 0.002 in. thick, and this has been identified as a source of arsenic pentaselenide wastes.

The selenium and arsenic coated xerox drums are manufactured and reconditioned at Xerox's Rochester, New York facility. About 1 million 1b of solid wastes containing 95 percent cotton linter, 5 percent aluminum, and 300 ppm selenium and arsenic are generated each year during these operations. Of the selenium and arsenic found in these wastes, there is usually more selenium present than arsenic, and approximately 25 percent of the selenium is combined with arsenic chemically (e.g., arsenic pentaselenide), with the remaining selenium containing less than 1 percent arsenic in them. In addition, there are 5 to 10 barrels acid wastes containing 1 to 3 percent selenium and arsenic generated each year from the same operations.

Physical and Chemical Properties

Physical and chemical properties of the materials in this report are given in the attached worksheets.

2. TOXICITY⁰⁷⁶⁶

The antimony compounds, including the sulfides and sulfate, generally cause irritation and eczematous eruption of the skin, inflammation of the mucous membranes of the nose and throat, metallic taste and stomatitis, gastrointestinal upset with vomiting and diarrhea, and various nervous complaints such as irritability, sleeplessness, fatigue, dizziness, and muscular and neuralgic pains.

The toxic effect of calcium fluoride comes from its fluorine component. In general, inorganic fluorides are toxic and irritant to the eyes and respiratory tract. Acute effects resulting from exposure to fluorine compounds are due to hydrogen fluoride. Among the chronic fluorine poisoning commonly encountered are loss of weight, anorexia, anemia, wasting and cachexia, and dental defects. The very low solubility of the calcium fluoride, however, requires exposure to large quantities of the material to produce these symptoms.

Magnesium, aluminum and tantalum are all nontoxic metals. However, inhalation of magnesium powder may cause irritation of the respiratory tract. Particles of magnesium which perforate the skin or gain entry through cuts and scratches may produce a severe local lesion characterized by the evolution of gas and acute inflammatory reaction, frequently with necrosis. This condition has been known as "chemical gas gangrene". The lesion is very slow to heal. Similarly, aluminum powder can be irritating to the eyes. There are also reports in the European literature of chronic pulmonary disease due to the inhalation of aluminum dust. Tantalum appears to have no ill effect upon the human body. Tantalum metal embedded in the abdominal wall and in the bones of dogs cause no physiological disturbances. So far, the use of tantalum in human surgery has received favorable comments.

Silica occurs abundantly in nature. Prolonged inhalation of silica dusts may result in a diffuse fibrosis known as silicosis. The duration of exposure required for the development of silicosis varies widely from 2 to 30 years. This fibrosis is, to a certain extent, progressive, and may continue to develop for several years after exposure is terminated. The first and most common symptom of silicosis is the shortness of breath on exertion. The most common physical sign is a limitation of chest expansion. There may be a dry cough with increased susceptibility to tuberculosis. Further progress of the disease results in more severe shortness of breath and cough, marked fatigue, extreme dyspnea and cyanosis, loss of appetite, pleuritic pain and total incapacity to work. If tuberculosis does not supervene, the conditions may eventually cause death from either cardiac failure or destruction of lung tissue with resultant anoxemia.

Arsenic pentaselenide is a toxic chemical. Selenium resembles arsenic both chemically and toxicologically. Poisoning due to selenium compounds generally results in qastrointestinal disturbances, respiratory irritation, cough, edema of the lungs, vomiting, diarrhea, abdominal pain or cramps, loss of reflexes, convulsions and ultimately death. Selenium salts also often cause contact dermatitis. Poisoning due to arsenic compounds may be acute or chronic. Acute poisoning, usually from ingestion, results in marked irritation of the stomach and intestines with nausea, vomiting and diarrhea. In severe cases the vomitus and stools are bloody and the patient goes into collapse and shock with weak, rapid pulse, cold sweats, coma and death. Chronic arsenic poisoning, through ingestion or inhalation, causes disturbances of the digestive system such as loss of appetite, nausea, constipation or diarrhea, damage to the liver resulting in jaundice, disturbances to the blood, kidneys and nervous systems. Arsenic can also cause a variety of skin abnormalities including itching, pigmentation and even cancerous changes.

The Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists and lethal doses reported for the materials in this report are given as follows:

Chemicals	TLV ⁰²²⁵	Lethal Dose 1312
Antimony Pentasulfide	$0.5 \text{ mg as } \text{Sb/M}^3$	ip LD ₅₀ : 1000 mg/kg, rat
Antimony Sulfate	0.5 mg as Sb/M^3	ip LD: 1000 mg/kg, rat 1492
Antimony Trisulfide	0.5 mg as Sb/M^3	ip LD _{Ca} : 1000 mg/kg, rat
Calcium Fluoride	2.5 mg as F/M^3	or LD: 5000 mg/kg, guinea
Mixture Powdered Magnesium and		pig ¹⁴⁹²
Aluminum		or LD _{Ca} : 230 mg Mg/kg, dog
Silica		or LD ₅₀ : 3160 mg/kg, rat
Arsenic Pentaselenide	0.5 mg as As/M ³	
Tantalum		

3. OTHER HAZARDS

The antimony sulfides would undergo spontaneous chemical reactions with powerful oxidizers to cause moderate fire and explosion hazards. In addition, both antimony pentasulfide and sulfate would decompose when heated, resulting in a mild fire hazard.

Metallic powder of magnesium and aluminum can be ignited easily.

Arsenic pentaselenide should not be heated to decomposition or have contact with acid or acid fumes since it emits the highly toxic fumes of arsenic and selenium.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

In handling the materials discussed in this report, care must be exercised to avoid inhaling silica dust particles and metallic powder of aluminum and magnesium. In storage, the antimony sulfides and sulfate and arsenic pentaselenide must be stored in cool areas and away from powerful oxidizers and acids. All toxic materials should be kept away from food and feed products. Metallic powder of aluminum and magnesium can be ignited easily. Therefore, they should be kept away from flame, and spark-proof tools should be used where they are being shoveled or otherwise moved by hand. In addition, magnesium should be kept dry, because it will react with water or steam to generate the combustible hydrogen gas. Similarly, antimony sulfate deliquesces in moist air and hence should be kept tightly closed in dry areas.

Disposal/Reuse

For the majority of the materials in this report, recovery of the wastes for reuse appears to be desirable, because they are, in general, not produced in large quantities and are relatively costly. For the safe disposal of these materials, the acceptable criteria for their release into the environment is defined in terms of the following provisional limits:

Contaminant in _Air_	Provisional Limit	Basis for Recommendation
Antimony pentasulfide	$0.005 \text{ mg/M}^3 \text{ as Sb}$	0.01 TLV for Sb
Antimony sulfate	0.005 mg/M ³ as Sb	0.01 TLV for Sb
Antimony trisulide	0.005 mg/M ³ as Sb	0.01 TLV for Sb
Calcium fluoride	0.025 mg/M ³ as F	0.01 TLV for F
Powdered magnesium, aluminum mixture	0.1 mg/M ³	0.01 TLV for inert or nuisance particulates
Silica	0.1 mg/M ³	0.01 TLV for Si
Arsenic pentaselenide	0.005 mg/M ³ as As 0.05 mg/M ³	0.01 TLV for As
Tantalum	0.05 mg/M ³	0.01 TLV

(Cont'd)		
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Antimony pentasulfide	0.05 ppm (mg/1) as Sb	Chronic toxicity drinking water studies
Antimony sulfate	0.05 ppm (mg/1) as Sb	Chronic toxicity drinking water studies
Antimony trisulfide	0.05 ppm (mg/l) as Sb	Chronic toxicity drinking water studies
Calcium fluoride	0.6 - 1.7 ppm (mg/1) as F	Drinking Water Standard for F
Powdered magnesium, aluminum mixture	.25 ppm (mg/l) as Mg	Drinking Water Standard for Mg
Silica		
Arsenic pentaselenide	0.05 ppm (mg/1) as As	Drinking Water Standard for As
Tantalum	0.25 ppm (mg/l)	Stokinger & Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PROCESS

Option No. 1 - Landfill

The materials in this report are insoluble in water and therefore may be conveniently disposed of by landfill. However, arsenic pentaselenide and the antimony compounds are highly toxic and the disposal of dilute wastes containing these constituents by landfill should only be in Class 1 sites located over nonwater-bearing sediments or with only unusable ground water underlying them. For particularly expensive metal such as tantalum and for antimony sulfide and sulfate wastes, recovery should be considered and preferred over disposal by landfill.

Option No. 2 - Long Term Storage for Arsenic Pentaselenide

Large, weatherproof, and siftproof storage bins or silos are currently being used for the storage of arsenic compounds, especially arsenic trioxide. This approach is relatively costly. However, since arsenic pentaselenide is highly toxic and its wastes only appear in small quantities,

long term storage of concentrated arsenic pentaselenide waste may be the only practical and adequate means of disposal. The small quantity of the waste contraindicates its designation as a candidate for National Disposal Site, however, this waste could be stored at such a site.

Option No. 3 - Sulfide Precipitation

The antimony sulfides and sulfate can be recovered from the wastes by first dissolving the wastes in concentrated hydrochloric acid, filtering the resulting solution if necessary, and finally saturating the solution with hydrogen sulfide to precipitate out the antimony sulfide which is then removed by filtration. The sulfides may be marketed or roasted and reduced to recover metallic antimony.

Option No. 4 - Mechanical Salvaging

Expensive metal such as tantalum is worth salvaging, even in small pieces, and should be sorted out mechanically. Since tantalum is chemically inert at ordinary temperatures, scraps of tantalum can be cleaned by removing the contaminants with strong acid.

Option No. 5 - Recovery of Metallic Antimony

Antimony sulfides may be roasted to yield the oxide which can be reduced to metallic antimony by carbon or by salt and scrap iron. The sulfur dioxide produced by the roasting must be scrubbed from the exhaust gas stream. A great number of scrubbing processes are available for this purpose. Among the commonly used processes are scrubbing the exhaust gas containing sulfur dioxide with an acidified, aqueous suspension of finely ground limestone or an aqueous solution of soda ash.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Adequate waste treatment for the waste stream constituents discussed in this Profile Report is commonly found in an industrial environment and therefore, treatment facilities need not be present at a National Disposal Site. The disposal of arsenic pentaselenide and antimony sulfide and sulfate wastes

by landfill must be carefully regulated at approved Class 1 type sites. It is recommended that wastes containing antimony sulfides and sulfate as constituents be returned to the antimony producers or reclaimers for the recovery of their antimony value. Secondary antimony recovered from various manufacturers and foundries while reprocessing scrap material amounted to 23,664 tons in 1967, almost twice as much as the primary antimony produced in the United States for the same year. The depletions of high grade antimony oxide ores indicate that even greater attention should be focused on the secondary recovery of antimony from waste streams containing antimony compounds.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name <u>Antimony Penta</u> sulfide	(37)	Structural Formula	
Common Names		Sb ₂ S ₅	
Molecular Wt. (1) 403.82 Density (Condensed) 4.12(1) @	Melting Pt. 1) decomp Melting Pt. 0 75 C	oses Boiling Pt)@	
Vapor Pressure (recommended 55 C a		a	
Plash Point	Autoignition Temp		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower	Upper	
Solubility (1) Cold Water_insoluble Others:_soluble in HCl, alkal Acid, Base Properties Highly Reactive with	i, NH ₄ HS		
			
Shipped in			
ICC ClassificationComments	Coast Gu	ard Classification	
References (1) 1570			

	HAZARDOUS WASTES PROPER WORKSHEET	TIES	
	MON MORE I		
H. M. Name Antimony Sulfate (39))	Structural Formula	
IUC Name		Scruccular formula	
Common Names		sb ₂ (s0 ₄) ₃	
Molecular Wt. 531.68	Melting Pt ⁽¹⁾ decom	poses Boiling Pt	
Density (Condensed) $3.625^{(1)}$ @	Density (gas)	
Vapor Pressure (recommended 55 C as	nd 20 C)		
<u> </u>			
	Autoignition Temp.		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		=-	
		. — оррег	
Solubility ⁽¹⁾ Cold Water insoluble	Hot Water decom	poses Fthanol	
Others: soluble in acid		· Conditor	
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification	Coast Gua	ard Classification	· · · · · · · · · · · · · · · · · · ·
Comments			
References (1) 1570			
15/0			
			j

	HAZARDOUS WASTES PROPERT WORKSHEET	TES
H. M. Name Antimony Trisulfide (40)	Structural Formula
IUC Name		
Common Names		Sb ₂ S ₃
Molecular Wt. $\frac{(1)}{339.69}$ Density (Condensed) $4.12^{(1)}$ @	Melting Pt. (1) 550 C Density (gas)	Boiling Pt. (1) Ca 1150 C
Vapor Pressure (recommended 55 C ar	nd 20 C)	
@		@
Flash Point	Autoignition Temp	<u>.</u>
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)		
Solubility (1) Cold Water 0.000175 g/100 ml @ Others: soluble in HC1, K ₂ S, N Acid, Base Properties	NH ₄ HS	
Highly Reactive with		
Compatible with		
Shipped in		
ICC Classification	Coast Gua	rd Classification
Comments		
References (1) 1570		

HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name Calcium Fluoride (92)	Structural Formula			
IUC Name Common Names	CaF ₂			
Molecular Wt. (1) 78.08 Melting Pt. (1) 1360 Density (Condensed) 3.18(1) @ Density (gas Vapor Pressure (recommended 55 C and 20 C)	C Boiling Pt. (1) ca 2500 C			
Flash Point Autoignition Temp				
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	Upper			
Solubility (1) Cold Water 0.0016 g/100 ml @ 18 C Hot Water 0.0017 Others: soluble in ammonium salts	g/100 ml @ ²⁶ Ethanol			
Acid, Base Properties				
Highly Reactive with				
Compatible with				
Shipped in				
ICC Classification Coast Gu Comments	ard Classification			
References (1) 1570	9			

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Silica (368)		Structural Formula	
IUC Name			
Common Names		SiO ₂	
Molecular Wt. ⁽¹⁾ 60.08 Density (Condensed) 2.64-2.66 ⁽¹⁾ @	Melting Pt. (1) 1610 C	Boiling Pt. (1) 2230 C	
Vapor Pressure (recommended 55 C an			
<u> </u>		@	
	Autoignition Temp		
Flammability Limits in Air (wt %)	Lower	Upper	
Explosive Limits in Air (wt. %)		Upper	
Solubility (1) Cold Waterinsoluble	Hot Water <u>insoluble</u>	e Ethanol insoluble	
Others: soluble in HF Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification	Coast Guar	d Classification	
Comments Silica exists in a variet			
are those of quartz.			
		,	
References (1) 1570			
	·		
		1	
·			

HAZARDOUS WASTES PROPERTIES WORKSHEET					
H. M. Name Arsenic Pentaselenide	(467)		.		
IUC Name			Structural Formul	a	
Common Names		_	As ₂ Se ₅		
Molecular Wt. (1) 544.62	Melting Pt. (1)	decomposes	_ Boiling Pt		
Density (Condensed)@					
Vapor Pressure (recommended 55 C an	d 20 C)				
<u> </u>					
Flash Point	Autoignition Tem	p			
Flammability Limits in Air (wt %)	Lower	Upp	per	ĺ	
Explosive Limits in Air (wt. %)	Lower	Up	per		
Solubility (1)					
Cold Water insoluble	Hot Water		Ethanol <u>i</u> n	soluble	
Others: soluble in alkali hydro	xides and sulfi	des			
Acid, Base Properties	 -				
Highly Reactive with					
Compatible with					
Shipped in					
ICC Classification					
Comments					
					
References (1) 1492					
	•				

HAZARDOUS WASTES PROPERTIES WORKSHEET					
H. M. NameTantalum (510) IUC Name	Structural Formula				
Common Names	Ta ·				
Molecular Wt. (1) 180.948 Melting Pt. (1) 2996 Density (Condensed) 16.6 @ Density (ga	5 C Boiling Pt. 1 5425 C				
Vapor Pressure (recommended 55 C and 20 C)					
Flash Point Autoignition Temp					
Flash Point Autoignition Temp Flammability Limits in Air (wt %) Lower					
Explosive Limits in Air (wt. %) Lower	Upper				
Solubility (1) Cold Water insoluble Hot Water inso	oluble Ethanol				
Others: Soluble in HF, fused alkali, insolub					
Acid, Base Properties					
Highly Reactive with					
Compatible with					
Shipped in					
ICC Classification Coast Guard Classification Comments					
Consider CS					
References (1) 1570					

PROFILE REPORT Antimony Potassium Tartrate (38)

GENERAL

Introduction

Potassium antimony tartrate, $K(Sb0)C_4H_4O_6 \cdot 1/4H_2O$, occurs as transparent, odorless crystals or as a white powder. It is manufactured by heating antimony trioxide with a solution of potassium bitartrate followed by crystallization. It is used as a textile and leather mordant, medicine (emetic), insecticide and in perfumery. 1442

Physical/Chemical Properties

The physical/chemical properties for potassium antimony tartrate are summarized on the attached worksheet.

TOXICOLOGY

Although potassium antimony tartrate is used medicinally as an emetic, the therapeutic dose is close to the toxic dose. It can cause cough, metallic-taste, salivation, nausea, and diarrhea. Large doses can cause severe liver damage. The dose for an emetic is 30 mg by mouth. The lethal dose for the mouse is reported as LD $_{50}$ 600 mg/kg (as Sb). For man the LD $_{\rm ca}$ is reported to be 2 mg/Kg as potassium antimony tartrate. 1536

OTHER HAZARDS

None.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

There are no special handling or storage requirements. There are no Department of Transportation (DOT) or U.S. Coast Guard shipping requirements but a Manufacturing Chemists Association warning label which states "may be fatal if swallowed" is applied to all containers. It is shipped in 25-, 50-, and 250-lb drums and in 425- and 625-lb barrels. 1416

Disposal/Reuse

Contaminated potassium antimony tartrate is not normally reprocessed for reuse, but instead is treated for disposal.

The safe disposal of potassium antiomony tartrate is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for <u>Recommendation</u>
Potassium Antimony Tartrate	$0.005 \text{ mg/M}^3 \text{ as Sb}$	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Potassium Antimony Tartrate	0.05 mg/1 as Sb	0.01 Drinking Water Studies

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Potassium antimony tartrate is dissolved in water, 6M-HCl is added to the solution to make it acid and the solution is then saturated with hydrogen sulfide. The precipitated ${\rm Sb_2S_3}$ is filtered, washed, dried and packaged for shipment to a company which markets antimony sulfide. Opposite there is no market, the antimony sulfide is placed in storage in containers protected from rain and snow.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Potassium antimony tartrate wastes are easily treated by the process described above in Section 5 at the site of origin. The toxicity of antimony compounds requires that their disposal be controlled to protect man and his environment. If a market for the antimony sulfide recovered from the waste treatment process cannot be identified and permanent storage is required, it is recommended that the antimony sulfide be stored at a National Disposal Site.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES WORKSHEET				
H. M. Name <u>Antimony Potassium Tar</u>	trate (38)	Structural Formula		
IUC Name				
Common Names <u>Tartar emetic</u>		K(SbO)C ₄ H ₄ O ₆ ·1/4H ₂ O		
Molecular Wt. <u>333,94⁽¹⁾</u> Density (Condensed) <u>@</u>	Melting Pt. <u>-1/2H_o0</u>	at 100 C ⁽¹⁾ Boiling Pt		
Density (Condensed)@_	Density (gas)		
Vapor Pressure (recommended 55 C an	d 20 C)			
@				
Flash Point	Autoignition Temp			
Flammability Limits in Air (wt %)				
Explosive Limits in Air (wt. %)	Lower	Upper		
Solubility				
		(2) Ethanol insoluble (2)		
Others:				
Acid, Base Properties <u>Aqueous solut</u>	tion slightly acid ⁽²⁾			
Highly Reactive with				
Compatible with				
Shipped in drums and barrels				
	Coast Gu	ard Classification <u>none⁽²⁾</u>		
Comments				
		· ·		
References (1) 0766				
(2) 1416				

PROFILE REPORT Arsenic (46)

1. GENERAL

Elemental or metallic arsenic, in contrast to most other arsenic compounds, cannot be generally considered as a hazardous waste material. Arsenic does not appear in nature in elemental form and its occurrence as a waste, is insignificant. American Smelting and Refining identifies itself as the only U.S. producer of metallic, elemental arsenic. It is produced in ultra high purity and sold in gram lots. It is used for the doping of semiconductor materials and in alloys of copper, lead and other metals. The alloys are made by adding arsenic trioxide to the molten metal thereby accomplishing the reduction in situ and producing no waste. 1560 American Smelting and Refining is apparently the only U.S. commercial source of these materials and their process details and production figures are proprietary. It is believed that nearly all metallic arsenic is imported and amounts to an estimated 400 tons yearly. O458 Arsenic alloys are valuable commodities and their use patterns indicate that under the most minimal controls, wastes containing elemental arsenic or arsenic alloys will not be generated in significant quantities.

2. TOXICOLOGY

Metallic arsenic is highly toxic when ingested or inhaled. It emits toxic fumes when heated. The Threshold Limit Value (TLV) recommended by the ACGIH is 0.5 mg/M³ air. The vapor pressure data indicates that metallic arsenic at room temperature is safe to leave in the open. Most arsenic compounds are poisonous to both plants and animals. Acute arsenic poisoning in man from ingestion is marked by irritation of the stomach and intestines accompanied by nausea, diarrhea and vomiting. In severe cases the vomitus and stool contain blood and the patient can go into collapse and shock with a weak, rapid pulse, cold sweats, coma and death.

Chronic arsenic poisoning, whether by ingestion or inhalation of airborne arsenic compounds, is very difficult to diagnose because it can cause a varied patten of symptoms. Included are loss of appetite, cramps, nausea, disruptions of the digestive tract, liver damage and a variety of skin abnormalities. 0766

3. OTHER HAZARDS

Arsenic in the form of dust or vapor has a moderate fire hazard when exposed to heat or flame or if allowed to react with powerful airborne oxidizers. The explosion hazard for airborne arsenic when exposed to a flame is considered slight.

Four artificial isotopes of arsenic have been prepared. The type of radiation and their energy levels as well as other radiological information are presented briefly in Sax^{0766} under the compound heading Arsenic.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Metallic arsenic when being shipped, handled or stored should not be subjected to heating which would cause it to vaporize. It should be shipped in sealed glass ampules to prevent oxidation and maintain its purity. It is necessary that the outside container be adequately labeled as to the dangerous properties of the contents. Adequate supervision and education of all personnel are considered a must for people handling this material.

Both the Department of Transportation and the U. S. Coast Guard classify elemental arsenic as a Class B poison and require the poison label on all shipping containers. $^{0.766}$ As such, all regulations governing the handling, storing, loading, and shipping of these materials must be complied with.

Disposal/Reuse

Elemental arsenic usually does not occur as a waste product and any surplus or contaminated material can always be returned to the manufacturer for reprocessing. For the safe disposal of wastes containing small amounts of arsenic, the acceptable criteria for the release of arsenic into the environment are defined in terms of the following provisional limits:

Contaminant and Envirnoment	Provisional Limit	Basis for Recommendation
Arsenic in air	0.005 mg/M ³	0.01 TLV
Arsenic in water and soil	0.05 ppm (mg/l)	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Elemental or metallic arsenic does not occur in any significant amount as a waste material. There are no treatment means by which this material can be made nontoxic. Should it be necessary to dispose of the small quantities of this material, it should be packaged according to federal regulations and shipped back to the supplier or manufacturer. 1560

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Elemental arsenic is not considered as a candidate waste stream constituent for National Disposal Sites because: (1) the material does not normally occur as a waste product; and (2) the material will be accepted for return shipment by supplier or manufacturer for reprocessing. There are, however, significant quantities of wastes containing arsenic compounds, such as arsenic trioxide, arsenates, arsenites, and organic arsenicals and long term storage has been recommended as the preferred management method for the concentrated arsenic wastes at National Disposal Sites. The disposal of wastes containing elemental arsenic can therefore be adequately handled at a National Disposal Site, if indeed such a need arises. Some

commercial disposal organizations also accept this material for permanent encapsulation in DOT 17-H (heavy wall steel drums) and disposal in land-fills. However, in light of the availability of reprocessing, burial of arsenic is neither economically nor environmentally adequate.

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H	IAZARDOUS WASTES PROPER WORKSHEET	TIES	4212
H. M. Name <u>Arsenic (46)</u>		Structural Formula	
IUC Name			
Common Names		As 4	
		4	
Molecular Wt. 299.64(1)	Melting Pt. 814 C @	36 Atm. Boiling Pt. sub. 615	
Density (Condensed) 5.727 @	$\frac{14}{C'}$ Density (gas	.)	-
Vapor Pressure (recommended 55 C ar	nd 20 C)		
<u>1 mm @ 372</u> C	10 mm @ 437	C 1 <u>00 mm</u> @ 518	С
Flash Point			_
Flammability Limits in Air (wt %)	Lower	Upper	
Explosive Limits in Air (wt. %)			
Solubility			
Cold Water Insol.		Ethanol	
Others: Sol. HNO ₃			
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification Poison, Class	B Coast Gu	ard Classification	
Comments Emits toxic fumes when he			
		<u> </u>	
			-
References (1)			
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PROFILE REPORT

Arsenic Trichloride (50)

GENERAL

Arsenic trichloride, AsCl₃, commonly known as butter of arsenic, is a corrosive, highly poisonous, oily liquid at room temperature. Arsenic trichloride can be prepared by a combination of the elements or by one of the following reactions:

$$2As_2O_3 + 6S_2Cl_2 + 4AsCl_3 + 3SO_2 + 9S$$

$$As_2O_3 + 6NaC1 + 3H_2SO_4 + 2AsC1_3 + 3Na_2SO_4 + 3H_2O_4$$

The only current producer of ${\rm AsCl}_3$, Rocky Mountain Research, burns arsenic in a chlorine stream using a proprietary process. Its uses, listed in Merck, are found in ceramics, surface doping of semiconductors, and chlorine containing arsenicals such as the chloro derivatives of arsine ${\rm l}^{492}$

Investigation revealed that the Bodman Chemical Company of Narberth, Pennsylvania is currently the only supplier of AsCl₃ as agent for Rocky Mountain Research. They reported that nearly all the produced AsCl₃ is going into the production of fungicides by Aerojet General Solid Propellant Co. in Sacramento, California. The remainder is being sold as lab reagents and an extremely small amount is used for coating semiconductors. Rocky Mountain Research is manufacturing approximately 6,000 lb per month for Aerojet General while shipping an additional small amount to Bodman Chemicals for laboratory reagents. 1644

Aerojet is consuming AsCl₃ in the custom production of the fungicide oxy bis phenoxarsine(OBPA). The reactions are carried out at the barricaded Sacramento facilities on the same isolated site where solid propellants are manufactured. The synthesis is performed in a batch operation with approximately 500 lb of AsCl₃ per charge. It was reported that the only AsCl₃ waste is contained in a pot residue from the distillation of the first step product of the two-step reaction. This waste is

currently being sealed in 55-gal. steel drums and is being stored on site at Aerojet General. The amount of material that is being stored there is, by Aerojet's opinion, very small and Aerojet feels no need to dispose of the material immediately. Aerojet is waiting until the first phase of this custom synthesis contract is completed so that all wastes can be removed at the same time. Aerojet contemplates controlled incineration and/or landfill for these waste materials by a commercial disposal firm. 1643

2. TOXICOLOGY

The Merck Index indicates that arsenic trichloride is an extremely toxic material. It can cause death through inhalation or by direct application to the skin. It is highly corrosive through release of HCl when exposed to water and can be a serious respiratory tract irritant. 1492 Arsenic trichloride has vapor pressure of 10 mm at about room temperature making air exposure prohibative in areas without ventilation control. The Threshold Limit Value (TLV) is listed at 0.5 mg/m 3 . 0225

Merck has indicated that the lethal short term concentration of AsCl_3 in air for cats is 27 ppm. 1492 No specific data on the harmful effects of AsCl_3 on plant life was found but in light of its corrosive nature and the harmful effects of arsenic compounds in general, it is believed that AsCl_3 is highly poisonous to plant life.

3. OTHER HAZARDS

The Laboratory Waste Disposal Manual indicates that AsCl₃ does not have any significant ignition temperature or flammability limits and can be considered to be generally non-flammable and non-explosive. O095

Its vapor pressure is appreciable and therefore a potential disaster hazard exists should large quantities of this material be spilled or released into the air near habitation. The present producers of this material are shipping in 5-gal. cans to further minimize any disaster hazard.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Because of the highly toxic nature of AsCl₃, special considerations must be taken to prevent direct contact with personnel, animal or plant life. It should be stored in isolated areas away from such items as food products, heat sources, or combustible materials which could create a hazard in case of fire. Arsenic trichloride hydrolyzes in water releasing hydrochloric acid which is the basis for the corrosive nature of AsCl₃. Therefore, AsCl₃ should not be exposed to the atmosphere. In case of spills of arsenic trichloride the area should be evacuated by all personnel immediately. Soda ash or bicarbonate of soda should be applied to neutralize the evolved HCl. The spill should be washed down with collection of the washings which contain As₂O₃.

The Department of Transportation (DOT) classifies AsCl₃ as a Class B poison, requiring a label, and limiting the size of shipping containers to 55 gallons. The use of rubber gloves, safety glasses, a respirator, laboratory coat or equivalent protection must be used when handling this material. All other DOT regulations regarding the storage, shipment, or handling of this material must be followed.

Disposal/Reuse

Arsenic trichloride is a liquid at room temperature and can be distilled for purification. Rocky Mountain Research has a policy of accepting excess amounts of arsenic trichloride or contaminated arsenic trichloride for reprocessing. The returned AsCl₃ is fed into their reactor for subsequent purification. They will also accept certain waste materials containing arsenic trichloride which is reacted with water to liberate HCl and precipitate the arsenic trioxide.

The acceptable criteria for the release of very small quantities of arsenic trichloride into the environment are defined in terms of the following recommended provisional limits:

Contaminant inAir	Provisional Limit	Basis for Recommendation
Arsenic trichloride	$0.005 \text{ mg/M}^3 \text{ as As}$	0.01 TLV for As
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Arsenic trichloride	0.05 ppm (mg/1) as As	Drinking Water Standard for As

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Arsenic trichloride when handled by methods that prevent exposure does not present a serious disposal problem. The two waste management options are discussed below.

Option No. 1 - Recycling/Reprocessing

Rocky Mountain Research, the only current producer of arsenic trichloride, has indicated its willingness to accept excessive or waste arsenic trichloride for reprocessing, purification or disposal. It is fed into their reactor and purified in the same manner as a normal batch. Rocky Mountain Research was not willing to discuss the details of their process and hence an evaluation of the process and the purification technique for AsCl₃ were not available. Rocky Mountain Research's alternate procedure would be to add water to the waste under ventilation control to hydrolyze the arsenic trichloride to arsenic trioxide which is much easier to handle. It is conceivable that any industry that handles AsCl₃ in significant amounts would probably have special facilities available to them for hydrolyzing the AsCl₃ and scrubbing the evolved HCl.

Option No.2 - Landfill

Landfilling of arsenic trichloride is not considered as an acceptable disposal option because of: (1) the high degree of toxicity of the compound; (2) the nondegradable nature of the toxic arsenic component of arsenic trichloride, whereby the compound would not be converted to a less

toxic or non-toxic form in the soil environment; and (3) the reactivity of arsenic trichloride with water to yield arsenic trioxide and corrosive hydrochloric acid. The corrosive potential of arsenic trichloride also indicates that the land burial of arsenic trichloride wastes containerized in metal drums is not an adequate method of disposal.

6. APPLICABILETY TO A NATIONAL DISPOSAL SITE

Considering the very small production and consumption of AsCl_3 as well as provisions for return of waste AsCl_3 by the producer, it is felt that AsCl_3 cannot in itself be considered as a candidate waste stream constituent for national disposal. There are simple methods for hydrolyzing it to $\operatorname{As}_2\operatorname{O}_3$ which is easier to handle and this can be performed by many firms who have simple wash down equipment. However, the charter of a National Disposal Site should include accepting any kind of arsenic containing material and it is probable that such a site would in any case have a simple wash down area for a number of materials. Thus AsCl_3 might be sent to a National Site for a routine hydrolysis. But it is emphasized that processes for the exclusive treatment of arsenic trichloride wastes are not recommended for inclusion in the National Disposal Site scheme.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET
H. M. Name Arsenic Trichloride (50) Structural Formula
Common Names Butter of Arsenic AsCl ₃
Molecular Wt. $181.28^{(1)}$ Melting Pt. -8.5 C ⁽¹⁾ Boiling Pt. 130 C ⁽²⁾ Density (Condensed) 2.163 $\frac{g}{c}$ @ 20 C ¹ Density (gas) $6.25^{(2)}$ @
Vapor Pressure (recommended 55 C and 20 C)
10 mm @ 23.5 c ⁽²⁾
Flash Point N/A Autoignition Temp.N/A
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 Decomposes Hot Water Decomposes Ethanol Soluble Others: HBr, HCl, ether Acid, Base Properties
Highly Reactive with H ₂ O to produce HCl and As ₂ O ₃
Compatible with
Shipped in Steel 5-gallon cans and 55-gallon drums
ICC Classification Poison B, Label, 55 gallons (2) coast Guard Classification Poison B, Label (2)
Comments Corrosive (2)
References (1) 1570
(2) 0766

PROFILE REPORTS ON

Barium Compounds

Barium Carbonate (52), Barium Chloride (53), Barium Cyanide (469)

Barium Nitrate (471), Barium Sulfide (472)

1. GENERAL

Introduction

Barium compounds exhibit a close relationship to the compounds of the other alkaline earth metals, calcium and strontium. Barium behaves generally as a bivalent element, as do the other alkaline earth metals. The solubilities of barium salts are typical of the alkaline earth group. The halides and nitrate are quite soluble, whereas the carbonate and sulfate are insoluble. With the exception of barium sulfate, the salts dissolve partially in carbonic acid and completely in hydrochloric or nitric acid. The sulfate is extremely insoluble and is useful for the determination of the barium ion. 0646

Precipitated parium carbonate is the most important of the manufactured pure barium chemicals. In production tonnage it is second to the principal mineral, barite. The production of barium carbonate has decreased considerably in the last few years. In 1969, there were 114,000 tons of barium carbonate produced in the United States. ¹⁵⁰⁶ In 1970 the production of barium carbonate declined to 61,083 tons. In that same year the production of all other barium compounds totaled 57,000 tons. Of that total it is estimated that there were less than 10,000 lbs of barium cyanide produced. ¹⁸¹⁴ Individual production figures for the other barium compounds discussed in this Profile Report are not available.

Manufacture

All major barium salts in the United States are produced from the chemical grade of barite (BaSO₄). Since barite is highly insoluble, the starting point of the barium-plant process is the reduction of barite to

soluble barium sulfide or black ash. This is then converted to the various barium compounds.

<u>Barium Carbonate</u>. Black ash is dissolved in water and its clear solution is the usual raw material for barium carbonate manufacture. There are two basic methods of manufacture which differ mainly in the way the carbonate ion is introduced.

$$BaS + Na2CO3 - BaCO3 + Na2S$$
 (1)

$$BaS + CO_2 + H_2O \longrightarrow BaCO_3 + H_2S$$
 (2)

The product from the straight-gassing process (equation 2) is more impure than the soda ash product (equation 1). Large scale commercial facilities for the manufacture of barium carbonate include the following 1506:

Barium and Chemicals Incorporated, Painesville, Ohio Chemical Products Corporation, Cartersville, Georgia FMC Corporation, Modesto, California Sherwin-Williams Company, Coffeyville, Kansas.

<u>Barium Chloride</u>. Barium chloride is produced by treating a barium sulfide solution with hydrochloric acid:

$$BaS + 2HC1 \longrightarrow BaC1_2 + H_2S$$

<u>Barium Cyanide</u>. Barium cyanide (Ba(CN)₂) is prepared by reaction of hydrogen cyanide on barium hydroxide suspended in petroleum ether. The dihydrate is formed and then dried carefully under vacuum to yield a product of 95 percent purity. Barium cyanide is produced by Phillips Brothers Chemicals, Incorporated, New York.

Barium Nitrate. Barium nitrate is made by the interaction of a suspension of barium carbonate in a mother liquor with nitric acid, followed by crystallization after filtration. Another method is to dissolve sodium nitrate in a saturated solution of barium chloride, with subsequent percipitation of barium nitrate. The precipitate is centrifuged, washed and

dried. Barium nitrate is produced by Barium and Chemicals, Incorporated, Painsville, Ohio.

<u>Barium Sulfide</u>. Black ash is produced by reducing ground barite with coal at high temperatures. The reaction is:

$$BaSO_4 + 2C \longrightarrow BaS + 2CO_2$$

Barium sulfide is also produced by Barium and Chemicals, Incorporated, Painsville, Ohio.

Uses

The principal application areas of the five barium compounds have been summarized by Miner (Table 1). 0646

Sources and Types of Barium Wastes

The sources of barium wastes may include the following: (1) barium compound manufacturers, and (2) commercial and industrial processes including those from paper manufacturing plants, ceramic and enamel manufacturing plants, etc.

In general, barium wastes can be classified as either diluted or concentrated wastes. Diluted barium wastes include those generated in the waste waters of manufacturers and uses of barium chemicals. Concentrated barium wastes include any unused or contaminated barium compounds that require disposal or recovery.

Physical and Chemical Properties

The physical and chemical properties of the five barium compounds are included in the attached worksheets.

TABLE 1⁰⁶⁴⁶
APPLICATION AREAS OF BARIUM COMPOUNDS

Compound	Uses
Barium Carbonate, BaCO ₃	As rat poison; in ceramics, enamels; in manufacture of paper, barium salts, optical glasses; in case-hardening steels.
Barium Chloride, BaCl ₂	In manufacturing of blanc fixe (precipitated BaSO ₄); as mordant for acid dyes; in weighting and dyeing textile fabrics; as boiler compounds for softening water; as purifying agent in brines; in manufacture of barium colors and of chlorine and sodium hydroxide; as flux for magnesium alloys, in case hardened steels.
Barium Cyanide, Ba(CN) ₂	In electroplating processes.
Barium Nitrate, Ba(NO ₃) ₂	In manufacture of BaO ₂ ; as pyrotechnic for green fire; as green signal lights; in the vacuum tube industry.
Barium Sulfide, BaS	As raw material for other barium compounds.

TOXICOLOGY

Soluble barium compounds are highly toxic when ingested, while insoluble compounds, such as barium sulfate, are generally nontoxic. Inhaled barium compounds cause a benign pneumoconiosis, called baritosis. Ingestion of soluble barium compounds results in strong stimulation of the muscles, including the heart; irritation of the intestinal tract; and irritation of the central nervous system. 0646

The symptoms of barium poisoning are severe abdominal pain with vomiting, dyspnoea, rapid pulse, paralysis of the right arm and leg, and eventually cyanosis and death. The usual result of exposure to the sulfide and carbonate is irritation of the eyes, nose and throat, and of the skin, producing dermatitis. 0766

The five barium compounds included in this Profile Report are all highly toxic and exhibit similar toxicity symptoms. With barium cyanide, however, the toxic effects of both elements of the compound must be considered (refer to Profile Report on Cyanides).

The relative oral LD $_{50}$ values to the rat are 50-200 mg/kg for barium carbonate and 355-533 mg/kg for barium chloride. The estimated oral LD $_{50}$ values for man are 55 mg/kg for barium carbonate and 80 mg/kg for barium chloride. The American Conference of Governmental Industrial Hygienists (1971) recommended a Threshold Limit Value (TLV) in air of 0.5 mg/M 3 for all soluble barium compounds. For cyanides (Ba(CN) $_2$) the TLV in air is 5.0 mg/M 3 . O225 The U.S. Public Health Service established the permissible criteria for barium in public water supplies as 1.0 ppm. This agency also recommends that the concentration of cyanides be kept below .01 ppm for both fish and people.

OTHER HAZARDS

Barium nitrate is an oxidizing material. In contact with easily oxidizable substances it may react rapidly enough to cause ignition,

violent combustion, or explosion. It increases the flammability of any combustible substance. 0096

The fire hazard of barium sulfide by spontaneous chemical reaction is moderate; air, moisture or acid fumes may cause it to ignite. Barium sulfide may react violently and explosively on contact with powerful oxidizers. 0766

Other than the toxic effects, barium carbonate, barium chloride and barium cyanide present no further hazardous problems.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Care should be exercised in handling barium compounds because of their high toxicity. The use of rubber gloves is advisable. Any material which comes in contact with the skin should be immediately removed with plenty of soap and water.

Barium nitrate should be stored in an area where it will be separated from combustible, organic or other readily oxidizable materials. Avoid storage on wood floors. Any spilled nitrate should be immediately removed and disposed of. All of the barium 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 barium cyanide and barium nitrate 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

Disposal or reuse of waste barium compound streams must take into account the toxic nature of these materials. The discharged barium compounds must be treated by the methods described in Section 5 or diluted to a concentration of 1 ppm $(.01 \text{ ppm for } Ba(CN)_2)$.

The safe disposal of barium compounds is defined in terms of the recommended provisional limits:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Barium Carbonate	.005 mg/M ³	.01 TLV
Barium Chloride	$.005 \text{ mg/M}^3$.01 TLV
Barium Cyanide	$.005 \text{ mg/M}^3$.01 TLV
Barium Nitrate	$.005 \text{ mg/M}^3$.01 TLV
Barium Sulfide	.005 mg/M 3	.01 TLV
Contaminant in Water and Soil Barium Carbonate	Provisional Limits l mg/l	Basis for Recommendation U. S. Public Health Service recommendation
•		for public drinking water.
Barium Chloride	1 mg/1	II
Barium Nitrate	1 mg/l	н
Barium Sulfide	1 mg/1	$\mathbf{u} = \mathbf{u}$
Barium Cyanide	.01 mg/1	II .

It should be noted that the recommended provisional limit for the barium compounds (except barium cyanide) in water are less than that of .01 of the ${\rm TL_m}$ for fish. The provisional limit of barium cyanide in public drinking water (.01 mg/l) is also a safe level for fish. It was found that trout could survive a cyanide concentration of .02 mg/l for more than 27 days. 1752

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Waste

Option No. 1 - Precipitation. By far the most widespread method used for removing barium from industrial waters is precipitation with sulfate ion (usually sulfuric acid) in settling ponds. 1794 The precipitate formed, ${\tt BaSO_4}$, is only slightly soluble in water and the resulting effluent from the pond contains about 2 ppm of barium. This effluent would then be diluted with an equal amount of water to meet the permissible criteria for barium in public water supplies (1.0 ppm). 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 precipitate dried. Since barium sulfate is important in the barium industry (see section on Manufacturing) it can be economically recycled. This method can be used for both concentrated and dilute barium wastes. In the case of barium cyanide wastes, the cyanide must be removed first before precipitating the barium with sulfuric acid. The primary method of removing cyanide is to oxidize it to CO_2 and N_2 with an alkaline chlorine solution. Other methods for removing cyanide include ion exchange, electro-oxidation, and reaction with aldehydes (refer to Profile Report on cyanides for additional information). Barium could also be precipitated by chromate ion to form barium chromate. This is a workable method but is not normally economically feasible unless a market as pigments for the precipitate is available.

Option No. 2 - Ion Exchange. Ion exchange can be used to remove barium from dilute aqueous waste streams. Barium 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. The ion exchange unit cannot usually handle an influent concentration load above 1500 ppm. An advantage of ion exchange is that due to the concentrative effects it is possible to apply this process in recycling barium materials or in concentrating wastes for transport to centralized disposal. The major difficulty in ion exchange operation is the critical dependence on flow rate. The ion

exchange system is 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 barium ion decreases drastically causing the effluent to exceed the permissible limit.

Option No. 3 - Reverse Osmosis. The effectiveness of reverse osmosis to remove barium from water has been investigated by Sourirajan. 1812 Following passage of a barium waste stream through a porous cellulose acetate membrane, it was found that the barium concentration was reduced from 34.35 g/liter to 7.35 g/liter. It is conceivable that "R.O." is applicable to dilute barium salt solutions as well, but no data is available to support this assertion. With an effluent concentration of 7.35 g/liter, the "R.O." unit would have to be used in conjunction with some other process (ion exchange for example) to produce an effluent with a permissible concentration of barium.

Option No. 4 - Adsorption on Activated Carbon. Activated carbon has been shown to remove barium from acetate solutions by Kuzin et al. 1813 Although the laboratory investigation was principally directed towards the separation of uranium from other metallic compounds; it was found in the same study that activated carbon possessed a sorption capacity for soluble barium compounds of 0.7 mg/g carbon, thus demonstrating the feasibility of activated carbon adsorption as a near future process for removing soluble barium compounds from water.

The processes mentioned above deal exclusively with barium wastes in the conventional aqueous form. If, however, the barium wastes are present in the particulate form in a gas stream, the usual methods for removal of particulates, such as bag filters, electrostatic precipitation, and wet scrubbers should prevent their escape to the atmosphere. 0646

The best method for disposing of both dilute and concentrated aqueous barium wastes is precipitation with sulfate ion. The technique is efficient and adequate for large scale removal of barium.

The other processes discussed (ion exchange, reverse osmosis, and adsorption on activated carbon) will result in reduced amounts of waste barium but are not applicable as primary treatment methods. These processes should function mainly as a secondary treatment of the effluent from a barium precipitative facility.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the provisions for the recycle and recovery of waste barium by the producers, it is felt that waste streams containing barium compounds do not warrant National Disposal Site treatment. The precipitation method for the removal of barium from waste streams is inexpensive enough for even the small barium manufacturers and users to operate.

In summary, the recovery and/or disposal of barium wastes can be currently handled adequately at the industrial site level and this mode should be continued.

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HAZAR	WASTES PROPERTIES ORKSHEET
H. M. Name Barium Carbonate (52)	Structural Formula
IUC Name	Scruceara Formura
Common Names	BaCO ₃
Molecular Wt. 197.37 Me	g Pt. 1740 @ 90 atm Boiling Pt. <u>Decomposes</u>
Density (Condensed) 4.43 @	Density (gas)@
Vapor Pressure (recommended 55 C and 20	
<u> </u>	<u> </u>
Flash Point Auto	tion Temp
Flammability Limits in Air (wt %) Lo	Upper
Explosive Limits in Air (wt. %) Lo	Upper
Others:Acid, Base Properties	Water 0.0065 g/100g @ 100C@thanol insoluble
Highly Reactive with	
Shipped in Bags, barrels and keg	
ICC Classification	Coast Guard Classification
Comments White powder	
:	
References (1) 0766.	

HAZARDOUS WASTES PROPE WORKSHEET	RTIES
H. M. Name Barium Chloride (53)	Structural Formula
IUC Name	
Common Names	BaC1 ₂
Molecular Wt. 208.27 Melting Pt. 92	5 C Boiling Pt. 1560 C
Density (Condensed) 3.856 @ 24 C Density (ga	s)
Vapor Pressure (recommended 55 C and 20 C)	·
<u> </u>	
Flash Point Autoignition Temp	
Flammability Limits in Air (wt %) Lower	
Explosive Limits in Air (wt. %) Lower	Upper
Solubility Cold Water_ 37.5g/100g @ 26 C Hot Water_ 59 g/1	tong 0 log C Ethanol insoluble
Others:	
Acid, Base Properties	•
Highly Reactive with	
Compatible with	
Shipped in Bags, barrels and kegs	
ICC Classification Coast G	uard Classification
Comments	
References (1) 0766.	
References (1) 0766.	
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	·

ŀ	HAZARDOUS WASTES PROPERT WORKSHEET	TIES
H. M. Name <u>Barium Cyanid</u> e (469)	_	Structural Formula
TUC Name	· .	Ba(CN) ₂
Molecular Wt. 189.40 Density (Condensed) @		
Vapor Pressure (recommended 55 C ar		
Clash Point		@
riash Polite	Autoignition Temp.	
Flammability Limits in Air (wt %)		
Explosive Limits in Air (wt. %)	Lower	Upper
Solubility Cold Water 1 gm/l.5ml Others:		Ethanol 1 gm/20ml
Acid, Base Properties		
Highly Reactive with	· · · · · · · · · · · · · · · · · · ·	
Compatible with		
Shipped in Bags, barrels and ke	egs	
ICC Classification	Coast Gua	ard Classification
Comments		

HAZARDOUS WASTES F WORKSHEET	
H. M. Name Barium Nitrate (471)	Structural Formula
IUC Name Common Names	Ba(NO ₃) ₂
Molecular Wt. 261.38 Melting Pt	592 C Boiling Pt. Decomposes ity (gas)@
Vapor Pressure (recommended 55 C and 20 C)	•
Flash Point Autoignition Temp	emp
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	UpperUpper
Solubility Cold Water 8.7g/100cc Hot Water 34 Others: Acid, Base Properties	
Highly Reactive with	
Compatible with	
Shipped in Bags, barrels, kegs, casks, drums	
ICC ClassificationCommentsIn contact with easily oxidizable subst	Coast Guard Classificationstances it may react rapidly enough to cause
ignition, violent combustion or explosi	
References (1) 0766. (2) ⁰⁰⁹⁶ .	

	HAZARDOUS WO	WASTES PI RKSHEET	ROPER	RTIES
H. M. Name <u>Barium Sulfid</u> e (472)			1	Structural Formula
Common Names		 		BaS
Molecular Wt. 169.43 Density (Condensed) 4.25 @	Melting	Pt	1200 (gas	00 C Boiling Pt
Vapor Pressure (recommended 55 C ar	nd 20 C)			
	Autoignit			
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)				
Solubility Cold Water Soluble Others: Acid, Base Properties				uble Ethanol Insoluble
Highly Reactive with				•
Compatible with				
Shipped in Bags, barrels, kegs				
ICC Classification		Coas	st Gu	uard Classification
CommentsMay react violently ar	nd explosi	veiy on (conta	act with powerful oxidizers.
- -		, .		

PROFILE REPORTS

Beryllium Powder (59), Beryllium Carbonate (473),
Beryllium Chloride (474), Beryllium Hydroxide (475),
Beryllium Oxide (476), and Beryllium Selenate (477)

1. GENERAL

Production

There are two beryllium producers in the United States: the Brush Beryllium Company, Elmore, Ohio 0394 and KBI Industries (formerly Kawecki-Berylco or the Beryllium Corporation of America), Reading, Pennsylvania. 0599 Production amounts to 50 to 75 tons/year (as beryllium metal) divided approximately equally between the two companies. 0458

Each of the two producers has his own methods of winning the metal from its principal ore, beryl, $3\text{Be}0.\text{Al}_2\text{O}_3.6\text{Si}\text{O}_2$. The processes are discussed extensively in the literature. 1433,1417 They both involve the production of $\text{Be}(\text{OH})_2$ as an intermediate step with a 90 percent extraction efficiency (as beryllium metal), followed by calcining to BeO, conversion to BeF_2 , and reduction by Mg to beryllium metal. The metal is then pulverized, sintered, and sawed or ground into desired shapes and parts. If the popular Be-Cu alloys are desired (2-4 percent beryllium, remainder Cu), the BeO is reduced with carbon in the presence of copper. 1677

The French produce Beryllium directly by the electrolysis of BeCl2, but this process is regarded as uneconomical in the United States. 1433-1720

Overall efficiency in going from beryl ore to sintered beryllium parts is about 63 percent. Because the metal is so valuable (about \$60/lb) every effort is made to recycle dross continuously at every step. Both Brush and KBI actively seek their customers' scrap material, which they purchase for \$10 to 20/lb contained beryllium and recycle. This recycled

scrap accounts for approximately 6 percent of the total annual production. 0458 The final waste and slag contains less than 1 percent beryllium as insoluble oxide and is stored currently on the refinery property. 0394

Uses

It is anticipated that prices will remain strong at \$60/1b contained beryllium, so uses will remain limited to fairly exotic applications. Be-Cu alloys have gained some popularity for applications where high electrical conductivity is required together with high strength. These alloys account for approximately half of all the beryllium used today. Another third is used as metal in various applications involving the nuclear and aerospace industries, almost exclusively in projects funded by the Federal Government. While most beryllium metal is used for structural and machine parts, it is also being considered as an additive in powder form to increase the thrust of rocket engines. O458,1433 The amount used in this way is not known.

The high cost of beryllium is due to a number of factors which are not likely to change in the foreseeable future: (1) the lack of mineral resources, (2) the complexity of its extractive metallurgy, (3) the complexity of its fabrication technology, and (4) its toxicity.

Neither the beryllium producers 0599,1720 nor a sampling of principal users 1722,1723,1724 report any significant sale or use of beryllium carbonate, beryllium chloride, beryllium hydroxide, or beryllium selenate, although the hydroxide is an intermediate in the production of metal and oxide. No special problems are associated with this use as an intermediate.

Sources and Types of Beryllium Wastes

Since the beryllium users can practically resell all beryllium scrap to the producer at \$10 to \$20/lb contained beryllium, there is very little scrap material which is actually disposed of as waste. Most of the beryllium wastes are in the form of solid particulates or in a dilute aqueous solution (scrubber liquor), and are generated as a result of the attempts to control the emission of beryllium dusts, fumes, and mists. The sources of these beryllium wastes include beryllium extraction plants and beryllium

users such as machine shops, foundries, ceramic plants, and propellant plants.

2. TOXICOLOGY

Health and Safety Standards

Health and safety standards for beryllium workers and the general public have evolved over a period of 30 years, ever since the first positive diagnoses of berylliosis were made. Currently, the Environmental Protection Agency is formalizing national emission standards, which are based on conditions already observed by all AEC contractors. Almost all beryllium producers, fabricators, and users already comply with these standards, and "little economic impact on the industry" will result from their implementation. An excerpt from the proposed standards is quoted here: 1678

"The proposed beryllium standards are designed to protect the public from 30-day average atmospheric concentrations of beryllium greater than 0.01 microgram per cubic meter ($\mu g/m^3$). Experience over more than 20 years has shown this to be a safe level of exposure. For short-term, periodic exposures, the safe level has been determined to be 25 $\mu g/m^3$ for a maximum of 30 minutes. This periodic exposure limit is the basis for the standard pertaining to rocket-motor firings.

"The proposed beryllium emission standards for extraction plants, machine shops, foundries, ceramic plants, propellant plants, and incinerators designed or modified for disposal of these substances allow the operator to demonstrate compliance with either 1 or 2 below:

- 1. No more than 10 grams of beryllium emitted per 24-hour day.
- 2. No emission that will cause atmospheric concentrations of beryllium to exceed an average of 0.01 microgram per cubic meter of air for 30 days.

"The beryllium emission standards given below are being proposed for rocket-motor test facilities:

- No emissions that will cause atmospheric concentrations of beryllium to exceed 75 microgram-minutes per cubic meter of air within the limit of 10 to 60 minutes.
- 2. No more than 10 grams of beryllium will be emitted per 24-hour day when rockets are fired into a tank and the exhausts are gradually released."

Epidemiology

Although annual beryllium consumption in the 20-year period 1948-1968 increased 500 percent, there have been no new cases except those currently in incubation. O394,1677,1719 Principal means of exposure include the burning of coal. Coal contains 1 to 3 ppm beryllium with peak values of 31 ppm having been reported. Approximately 500 million tons are burned annually.

To date, there is no evidence that anyone has ever contracted berylliosis from handling beryl ore. 1677 There are 812 registered victims in the United States, of which 60 are classified as "neighborhood victims", i.e., they had the misfortune to live near a beryllium plant, but never worked with the material directly. However, they may have come in contact with workers wearing contaminated clothing, etc.

The clinical manifestations of berylliosis are well documented. 1675, 0276,1676,0641,1433,etc. In addition to the manifestations attributable to all beryllium compounds, beryllium chloride, beryllium selenate, and other soluble salts produce dermatitis on contact with the skin. 0641 Although many berylliosis victims have contracted cancer, positive statistical correlation is lacking. There is increasing circumstantial evidence for

possible carcinogenic properties for beryllium in humans, since lung tumors have been successfully induced in monkeys and rats and sarcomas have been induced in rabbits. The 1971 Toxic Substances Annual List 1312 reports that 0.1 mg/M 3 have produced toxic effects in man by inhalation. Reported 50th percentile lethal doses (LD50) for beryllium compounds are:

Beryllium Carbonate:

150 mg/kg in the guinea pig injected

intraperitoneally

Beryllium Chloride:

86 mg/kg in the rat administered orally

Beryllium Hydroxide:

0.35-2.5 mg/kg in the rat injected intravenously, depending on the

crystalline form of the hydroxide

Recent laboratory studies 1720,1721,1725,1744 in which rats and rabbits were injected intratracheally with BeO of respirable particle size (1 to 5μ) indicate that there is a definite inverse correlation beween the toxicity of the BeO and the temperature at which it is calcined. Beryllium oxide calcined at 500 C produced severe pneumonitis and the eventual development of adenocarcinomas. The pathological changes associated with the intratracheal injection of BeO calcined at 1100 C were qualitatively similar, but quantitatively less severe. In contrast, BeO calcined at 1600 C was "almost inert" and produced "minimal" pathologies. Beryllium oxide obtained from rocket firings produced symptoms characteristic of the 1600 C-calcined material.

There is no preferential uptake or concentration of beryllium or beryllium compounds from the environment by any animals or plants, including humans. 0615,0641,0276,1127

3. OTHER HAZARDS

Finely divided beryllium metal may explode to form beryllium oxide, an exceptionally stable compound. All other beryllium compounds react non-violently with varieties of gases, liquids, and solids to eventually form the ultimately stable beryllium oxide.

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage, and Transportation

Procedures for the handling, storage, and transportation of beryllium waste are well-documented. O039,1678,0278 Sintered beryllium inquts or fabricated parts and hot-pressed beryllium oxide shapes require no special shipping or packaging precautions. A label is usually attached to indicate that fumes or dust of this material may be toxic if inhaled.

Beryllium metal powder has a weight limitation of 25 lb net per metal container, when shipped under Department of Transportation regulations. It is classified as a Class B poison, and must be so labeled. No regulations exist for beryllium compounds as such, but the 25 lb rule is generally followed on the theory that controlled ventilation (such as a common laboratory hood) will be available for 25 lb quantities, but may not be available for larger quantities.

Disposal and Reuse

Since the beryllium producers eagerly purchase all available scrap at \$10 to \$20/lb containing beryllium, all users capture as much waste as possible for resale to the producers. O394,0460 There is therefore very little scrap material which is actually disposed of as waste.

The means of collection and control of dust, fume, and mist have been summarized in new regulations being promulgated by the Environmental Protection Agency. 0275,1678 Standard collection techniques such as scrubbers, packed towers, cyclones, and fabric-filter units are currently in use on an industry-wide basis to bring essentially everyone within the new target emission concentration of 0.01 $\mu g/m^3$. Scrubber liquors, etc. are disposed of adequately with other liquid wastes. 0275,0460,0461,1678

Recommended provisional limits for beryllium and beryllium compounds in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis of Recommendation
Beryllium and beryllium compounds in air	0.0001 mg/M ³	EPA proposed standard
Beryllium and beryllium compounds in water and soil	1 ppm (mg/1)	Drinking water standards

For the disposal of beryllium and beryllium compounds, an alternate emission standard of no more than 10 gm of beryllium per 24-hour day for each beryllium producing or beryllium using plant has also been proposed by EPA, and operators have the option of complying with this standard instead of the recommended provisional limits. For rocket-motor test facilities, special beryllium emission standards have been proposed by EPA and these are: (1) no more than 75 μ g-min/M³ within the limit of 10 to 60 min; or (2) no more than 10 gm per 24-hour day, provided the exhausts are trapped and gradually released.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Recycling to Primary Producers

This is most desirable from the standpoints of users, producers, and environmentalists. Beryllium and beryllium compounds are difficult to produce and the primary producers repurchase all available material at \$10 to \$20/lb contained beryllium. 0394,0460 This situation is expected to continue indefinitely. 0458

Option No. 2 - Burial

Liquid, solid, or particulate waste which is too dilute to recycle is buried on private property or in public landfills. Often waste is first burned to produce the insoluble, chemically inert oxide. This is easily and safely done, providing the exhaust gases are scrubbed to remove any

particulates. These procedures were verified with KBI Industries, 0394 two other large beryllium users, 0398,0460 and the County of Los Angeles, California, 0461 which operates several landfills which receive liquid coolant wastes containing beryllium. All independently agreed with this analysis.

Since there have been no new reported cases of berylliosis in 20 years and demand is expected to remain static for the indefinite future, it may be concluded that practices are adequate at present and for the foreseeable future.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Since there have been no new reported cases of berylliosis contracted within the past 20 years and essentially all producers and users already comply with the proposed Environmental Protection Agency standards, it may be concluded that beryllium and beryllium compounds are under adequate control as hazardous wastes.

The continued high demand for scrap at \$10 to \$20/lb contained beryllium makes its recovery extremely attractive for all users. Recovery systems currently in operation keep ambient concentrations below the required 0.01 $\mu g/m^3$. The small amount that does not get recovered is disposed of by burial, or dumping 0461,0039,1678,0398,0460 at no great expense or danger. Recent clinical and laboratory studies 1720,1725,1721,1744 indicate that any beryllium waste can be rendered virtually innocuous by heating to form the oxide and then firing at 1600 C for 16 hr. The resulting material produces the mild symptoms generally associated with dusts of clays, iron oxides, etc.

While it is not known how much beryllium is released to the environment by the burning of coal, investigations in urban and rural areas show a negligible uptake by humans, animals, or plants. 0641,0615,1127

In summary, the recovery and/or disposal of beryllium wastes is currently handled very adequately at the industrial site level and this mode should be continued.

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HAZARDOUS WASTES PROPE ₩ORKSHEET	RTIES
H. M. Name	Structural Formula
IUC Name <u>Beryllium Powde</u> r (59)	
Common Names Beryllium Powder	Be
Molecular Wt. 9.013 Melting Pt. 1282	C Boiling Pt. 2970 C
Density (Condensed) 1.85 g/cc @ 4 C Density (ga	
Vapor Pressure (recommended 55 C and 20 C)	·
Flash Point 1000 F Autoignition Temp. N. J	<u>A.</u>
Flammability Limits in Air (wt %) Lower Moderate	
Explosive Limits in Air (wt. %) Lower <u>Slight</u>	Upper
Solubility	
Cold Water 0 Hot Water Sligh	ntly Ethanol <u>O?</u>
Others: <u>Dilute acid</u> , <u>base</u>	
Acid, Base Properties Slightly basic	
Highly Reactive with H ₂ SO ₄ , HCl, boiling water to evol	ive H ₂
Compatible with other metals, oxides, air	·
Chinadia	
Shipped in	matal roudon
Comments Code of Federal Regulations (Transportation)	
Comments Control Regulations (Transportation)	1, 350, /3-303-/3-303
c	
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HAZARDOUS WASTES PROPERTIES WORKSHEET Structural Formula IUC Name Beryllium Carbonate (474) Common Names Basic Beryllium Carbonate BeCO₃ + Be(OH)₂ Molecular Wt. 112.05 Melting Pt. Boiling Pt. Boiling Pt. Density (Condensed) @ Density (gas) @ Vapor Pressure (recommended 55 C and 20 C) Plash Point N.A. Autoignition Temp. N.A. Flammability Limits in Air (wt %) Lower N.A. Upper Explosive Limits in Air (wt. %) Lower N.A. Upper Solubility Cold Water____ Hot Water Dissociates Ethanol 0? Others: Acids, bases Acid, Base Properties Basic Highly Reactive with Dissociates easily in acids Compatible with Oxides Shipped in ICC Classification Poison B, Poison label, 200 lbsCoast Guard Classification Highly unstable, easily converted to BeO(OH), by heating Code of Federal Regulations (Transportation), Sec. 73,363-73,365

HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name	Structural Formula
IUC Name Beryllium Chloride (475)	Structural Formula
Common Names Beryllium Chloride	BeCl ₂
Molecular Wt. 79.93 Melting Pt. 399 C	Boiling Pt. 483 C
Density (Condensed) 1.899 @ 25 C Density (gas)
Vapor Pressure (recommended 55 C and 20 C)	
1 mm @ 291 C(sublimes) @	
Flash Point N.A. Autoignition Temp.N.A.	
Flammability Limits in Air (wt %) Lower N.A.	
Explosive Limits in Air (wt. %) Lower N.A.	Upper
Solubility	
Cold Water <u>very soluble</u> Hot Water <u>dissocia</u>	<u>ates</u> Ethanol <u>yery soluble</u>
Others: <u>Ether, Benzene, Pyridine</u>	,
Acid, Base Properties <u>Basic</u>	
Highly Reactive with <u>Dissociates readily in aqueous solut</u>	tion
Compatible with <u>insoluble in acetone, NH</u> 3	
	· · · · · · · · · · · · · · · · · · ·
Shipped inlbs	
ICC Classification <u>Poison B, Poison Label 200 to ast Guardian Comments</u> Code of Federal Regulations (Transportation	
Comments code of rederal Regulations (Transportation	1/, 3ec. /3.303-/3.303
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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name		Structural Form	ıla
IUC Name <u>Beryllium Hydro</u> xide (4)	76)		
Common Names <u>Beryllium Hydr</u>	roxide	Be(OH) ₂	
	L	2	
43.04	138 C /do	ocomposoc)	
Molecular Wt. 43.04 Density (Condensed) 1.909 @			
Vapor Pressure (recommended 55 C a			
<u>@</u>			@
· 	Autoignition Temp.N.A.		
Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %)	Lower N.A.	Upper	_
Explosive Limits in Air (wt. %)	Lower	upper	_
Solubility			•
Cold Water <u>slightly</u>	. • • • • •	Ethanol	0?
Others: <u>Acids, Bases, (NH₄) 2</u>	203		
Acid, Base Properties <u>Basic</u>			
Highly Reactive with <u>Acid</u>			
Compatible with			
Compatible with Bases, r		metals	
Shipped in			
ICC Classification Poison B, Poison		rd Classification	
			
Comments <u>Decomposes at 138 C</u>			
Code of Federal Regul	lations (Transportation).	Sec. 73.363-73.365	
			

HAZARDOUS WASTES PROPERTIES WORKSHEET H. M. Name _____ Structural Formula IUC Name Beryllium Oxide (477) Bromellite, Beryllium Oxide Be0 Common Names Molecular Wt. 25.0 Melting Pt. 2530 + 30 C Boiling Pt. 3900 C Density (Condensed) 3.025 @ Density (gas) @ Vapor Pressure (recommended 55 C and 20 C) Flash Point N.A. Autoignition Temp.N.A. N.A. Flammability Limits in Air (wt %) Lower Upper Explosive Limits in Air (wt. %) Lower N.A. Upper___ Solubility Cold Water Insoluble Hot Water Insolube Ethanol Insoluble Others: Conc. H₂SO₄, Fused KOH Acid, Base Properties Slightly Basic Highly Reactive with Very unreactive, extremely stable Compatible with Metals, Oxides, Air, Water Shipped in ICC Classification Poison R. Poison Label 200 16s Coast Guard Classification Comments <u>Extremely stable</u>, good materials properties, very toxic Code of Federal Regulations (Transportation), Sec. 73.363-73.365

HAZARDOUS WASTES PROPERTIES WORKSHEET H. M. Name _____ Structural Formula IUC Name Beryllium Selenate (478) Common Names Beryllium Selenate BeSeO₄·4H₂O Molecular Wt. 224.04 Melting Pt. -2H₂O @ 100 C: -4H₂O @ 300 C Density (Condensed) 2.03 @ 20 C Density (gas) Vapor Pressure (recommended 55 C and 20 C) Autoignition Temp.____ Flash Point ____ Flammability Limits in Air (wt %) Lower____ Upper____ Explosive Limits in Air (wt. %) Lower _____ Upper Solubility Cold Water <u>Very soluble</u> Hot Water <u>Very soluble</u> Ethanol Acid, Base Properties_____ Highly Reactive with Compatible with Shipped in ICC Classification Poison B, Poison Label, 200 1b Coast Guard Classification Comments ____Code of Federal Regulations (Transportation), Sec. 73.363-73.365

PROFILE REPORT Boric Acid (60)

1. GENERAL

Introduction

Boric acid is a white crystalline solid belonging to the triclinic system. Its solubility in water is low at room temperature but is greatly increased by heating.

Boric acid reacts with various pyridine bases to form soft, white, crystalline solids, reported to be nonhygroscopic and, with the exception of the piperidine-boric acid compound, completely hydrolyzed by dissolution in water. 1433

In 1969, there were 138,969 tons of boric acid produced in the United States. 1751

Manufacture

Boric acid is usually manufactured from borax or from colemanite. Granulated borax or a hot saturated solution of borax from the borax refining plant is charged into a reaction vessel. Sulfuric or hydrochloric acid, concentrated or dilute, is added until the solution is acidic. The solution is then cooled to the proper temperature, and boric acid crystals are removed by filtration. If sulfuric acid is used, the mother liquor is cooled further to recover sodium sulfate decahydrate. The crude boric acid may be refined by one or more crystallizations from water to yield purified boric acid.

When boric acid is made from colemanite, the colemanite is ground to a very fine powder and added in proportions to dilute the mother liquor and sulfuric acid at about 90 C. To prevent coating the unreacted colemanite particles with the precipitated gypsum, the slurry is stirred vigorously.

The excess acid is neutralized with lime, the iron is oxidized with permanganate, and the solution is decolorized with activated carbon and filtered. The solution is cooled to crystallize the boric acid. 1433

Large scale commercial facilities for the manufacture of boric acid include the following: 1670

U. S. Borax and Chemical Corporation; Des Plaines, Illinois Ashland Chemical Company; Kansas City, Missouri Baker Chemical Company; Charlotte, North Carolina

Uses

Boric acid has a wide variety of industrial uses. It is used in salt glazing in ceramics and in making glazes and ceramic colors. It is a raw material in making chemicals such as boron trifluoride, fluoborates, includes, and boron carbide. It is used in making boron alloys and ferroboron, which may be used for hardening steel. It is used in washing fruit to inhibit mold. It is used in cosmetics, dye stabilizers, solutions for electroplating nickel, electrolytes for electrolytic condensers, enamels, flameproofing, welding and brazing fluxes, hardening steel by heat treatment, fiber glass, optical glass, borosilicate glass, leather finishing, deliming hides and skins, latex base paints, photography, sand casting magnesium alloys, laundry starch and textile finishing, sizing, and scouring compositions.

Boric acid is used in many pharmaceutical preparations as a nonirritant, mildly antiseptic solution or in protective ointments for inflammations of the skin and mucous membranes and minor cuts and injuries.

Physical and Chemical Properties

The physical and chemical properties of boric acid are included in the attached worksheet.

2. TOXICOLOGY

Boron compounds, with the exception of hydrides are not highly toxic and therefore are not considered to be an industrial poison. Fatal poisoning of children has been caused in some instances by the accidental substitution of boric acid for powdered milk. The medical literature reveals many instances of accidental poisoning due to boric acid, oral ingestion of borates or boric acid, and presumably absorption of boric acid from wounds and burns. The fatal dose of orally ingested boric acid for an adult is somewhat more than 15 or 20 grams and for an infact 5 to 6 grams.

Boron is one of a group of elements, such as lead, manganese and arsenic, which effects the central nervous system. It is cumulative poison and since its antiseptic value is weak, other more active and less harmful therapeutic agents should be employed for medicinal use. Boron poisoning causes depression of the circulation, persistent vomiting and diarrhea, followed by profound shock and coma. The temperature is subnormal and a scaletina from rash may cover the entire body. Boric acid intoxication can come about from absorbing toxic quantities from ointments applied to burned areas or wounds involving loss or damage to such areas of skin, but it is not absorbed from intact skin. When a 5 percent acid solution is used to irrigate body cavities most of the boric acid is absorbed by the tissues. Repeated doses can produce pathological changes in the central nervous system and kidneys. O766

The oral ${\rm LD}_{50}$ value to the rat is 3.5 g/kg for boric acid. The boron equivalent of this is .60 g/kg.

Rainbow trout were unaffected in a 30-minute test in 0.2 percent boric acid (350 ppm boron); in 2 percent boric acid the trout appeared distressed,

but were alive after 30 minutes; after one-half hour exposure to a slurry of solid boric acid (8%), they recovered if placed in running water. The LD $_{50}$ to 15-month old rainbow trout is 339 ppm boron for 48 hours. Safe limits are listed as 30 ppm for bass and 33 ppm for bluegill. 2358

Boron is an essential element to plant growth but is toxic to many plants at levels as low as 1 mg/liter. The Public Health Service has established a limit of 1 mg/liter which provides a good factor of safety physiologically and also considers the domestic use of water for home gardening. 0536

3. OTHER HAZARDS

Other than the toxic effects, boric acid presents no further problems.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT Handling, Storage and Transportation

Workers handling boric acid should wear rubber gloves and a laboratory coat. $^{0095}\,$

Boric acid should be stored in containers away from any material intended for consumption by humans or animals.

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

Disposal/Reuse

United States Borax and Chemical Corporation will accept contaminated and degraded boric acid for reprocessing as long as there is a significant amount of the material to be reprocessed and it is in concentrated form. 2346

U. S. Borax has a plant that manufacturers boric acid in Wilmington, California. The effluent from the plant contains about 3,000 ppm of boron and has been discharged directly into the ocean for many years. Although U. S. Borax plans to discontinue this practice shortly, it is claimed that the marine life around the discharge point has not been affected.

The acceptable criteria for the release of boric acid into the environment are defined in terms of the following provisional limits:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Boric acid in air	0.1 mg/M ³	0.01 TLV for B_2O_3
Boric acid in water and soil	1 ppm (mg/l) as B	Drinking water standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Coagulation and Filtration.

U.S. Borax and Chemical Corporation indicates that boric acid may be removed from aqueous waste streams by reacting the material with appropriate quantities of lime. Lime will react with boric acid to deposit calcium borates which can be filtered from solution. This will not remove all of the borate, however, as calcium borates are soluble in water to the extent of about 0.2 percent B_2O_3 (620 ppm boron). The removal of this residual amount will require more elaborate treatment methods such as ion exchange or adsorption with selected clays. The borates contained in the calcium borate sludge formed in this process are not easily

recoverable, and are usually sent to Class 1 sanitary landfill areas for disposal. 2346

Option No. 2 - Ion Exchange

Rohm and Haas offers a boron specific ion exchange resin (Amberlite XE 243) which will remove boron from solution to extremely low levels (below 1 mg/liter). Since ion exchange systems operate best with dilute solutions, this process could be used in conjunction with coagulation and filtration (discussed above) to produce an effluent with an acceptable concentration of boron. The major drawback affiliated with the use of the Rohm and Haas resin is the high operating costs involved.

Option No. 3 - Adsorption with Clays.

Selected clays might be used for the removal of borate in low concentrations. This process could be used in conjunction with coagulation and filtration to further reduce the boron concentration. Clays, however, are not specific and a large volume would be required per unit of liquor passing the clay body. 2346

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the relatively low toxicity of boric acid, and the provisions for the disposal of the major portion of waste boric acid by the producers, it is felt that boric acid does not warrant National Disposal Site treatment. The problem of small amounts of residual waste boric acid being discharged in the plant effluent is currently being solved by the manufacturers because of the stringent environmental regulations recently imposed. U.S. Borax, for example, will soon connect with a new industrial sewer line that will take the combined effluents of the industries in the area to a secondary treatment plant before discharge to the ocean.

In summary, the disposal of waste boric acid can be handled adequately at the industrial site level and this mode should be continued.

7. REFERENCES

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	HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name Boric Acid (60)		Structural Formula
IUC Name		
Common Names Boric Acid		н ₃ во ₃
Molecular Wt. <u>61.84 ⁽¹⁾</u> Density (Condensed) <u>1.435 ⁽¹⁾ @</u> Vapor Pressure (recommended 55 C a		(1) ecomposes) Boiling Pt. <u>11/2 H₂0 @</u>)@
e		
Flash Point	Autoignition Temp.	_
Flammability Limits in Air (wt %)		·
Explosive Limits in Air (wt. %)		
Solubility Cold Water 6.35 g/100 CC (1) Others: glycerine 28 g/100 CC; Acid, Base Properties Highly Reactive with	methyl alcohol 20.20 g	9/100 CC (1)
Compatible with		
Shipped in		
ICC Classification		ard Classification
Comments		
References (1) 0766		

PROFILE REPORT

Boron Trifluoride (63)

GENERAL

Boron trifluoride is a colorless gas which fumes in moist air and has a pungent suffocating odor. It is nonflammable and does not support combustion. It is normally packaged in cylinders as a nonliquified gas at pressures of 2,000 psig at 70 F. It is very soluble in water with decomposition (forming fluoboric and boric acids) and is heavier than air. ¹³⁰¹ Physical/chemical properties are summarized in the attached worksheet.

Boron trifluoride is used extensively, industrially, as a catalyst in isomerization, alkylation, polymerization, esterification and condensation reactions. Boron trifluoride is also used in gas brazing. Its other uses are as a filling gas for neutron counters and in the preparation of diborane. 1301

Boron trifluoride is manufactured commercially by adding borax to hydrofluoric acid to yield water and $\mathrm{Na_20\cdot(BF_3)_4}$, or by treating boric acid with ammonium fluoride to yield water, ammonia and the compound $(\mathrm{NH_4)_20\cdot(BF_3)_4}$. The boron trifluoride complex is transferred to a generator and is treated with cold fuming sulfuric acid. The reaction mass is slowly heated and the generation of boron trifluoride is controlled by regulating the temperature. 1301

2. TOXICOLOGY

Human Toxicity

Boron trifluoride is very irritating to the respiratory tract. Exposure of the skin and eyes, and breathing of boron trifluoride should be avoided. The American Conference of Governmental Industrial Hygienists in 1971 recommended a Threshold Limit Value (TLV) in air of 2 mg/M³. O225 No medical evidence of chronic effects has been found among workmen who have frequently been exposed to small amounts for periods up to 7 years. In tests on mice, a concentration of 15 ppm for 30 days produced dental fluorosis. The inhalation lethal concentration (LC) for rats is 750 ppm. At high concentrations boron trifluoride causes burns on the skin similar to, but not as penetrating as those from hydrogen fluoride. 1301

Toxicity Toward Plant Life

If allowed to escape, boron trifluoride will kill plant life in the nearby area. Trace amounts of boron trifluoride escaping from a reactor can be detected by the white fumes produced. In Los Angeles, the Los Angeles Air Pollution Control District makes frequent inspections of any users plant. 1304

3. OTHER HAZARDS

Boron trifluoride is nonflammable and does not support combustion. BF_3 hydrolyzes in contact with water, forming fluoboric and boric acids. The boric acid is extremely corrosive to iron, steel, and aluminum.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Boron trifluoride is packaged and shipped in steel cylinders under Department of Transportation and Coast Guard regulations as a nonflammable, compressed gas, taking a Green Label. The filled cylinders have an internal pressure of 2,000 psig at 70 F. Boron

trifluoride cylinders should be handled with all of the precautions used with cylinders of high pressure compressed gases. The cylinders should be protected against impact, assigned a definite dry cool well-ventilated fire-resistant area for storage, and shielded from direct sunlight, the extremes of weather, and temperatures above 125 F. In addition, due to the reactivity of BF $_3$ with water, amines, alcohol, ether and other compounds, traps or check valves should be used in the piping system to prevent suckback of liquid into the cylinder. 1301

Personnel handling the BF₃ should wear chemical safety goggles and rubber gloves, and should be provided with a gas mask for acid gases, or have an independent air/oxygen supply mask available. Dry boron trifluoride can be handled in steel, stainless steel, copper,nickel, monel, brass and aluminum and the more noble metals up to 200 C. At low pressures and for temperatures up to 200 C Pyrex glass can be used. Copper is recommended as the metal for handling the moist gas. Saran tubing, hard rubber, Teflon, polyethylene, Pyrex glass and pure polyvinyl chloride are not attacked at temperatures up to 80 C. 1301

Disposal/Reuse

A definition of acceptable criteria for the disposal of boron trifluoride must also take into account acceptable criteria for the release or treatment of compounds formed during treatment of boron trifluoride. Compounds formed and their disposition are as follows:

Compounds Formed	<u>Disposition</u> Insoluble, place in landfill	
Calcium Fluoride		
Boric Acid	See Profile Report on boric acid (60)	

Safe disposal of BF_3 is defined in terms of the recommended provisional limits in the atmosphere, water and soil. These are:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Boron trifluoride	0.03 mg/M^3	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Boron trifluoride hydrolysis products	0.15 mg/1	Stokinger and Woodward Method

5. EVALUATION OF PRESENT MANAGEMENT PRACTICES

The manufacturers of boron trifluoride do not normally discharge waste streams because the preparation is carried out in a closed system. Boron trifluoride is usually recovered after its use as a Lewis acid catalyst in organic reactions 1415 by distillation, by chemical reaction, or by combinations of the two methods. When amines or ammonia are used to strip BF $_3$ from spent catalyst, NH $_3$ ·BF $_3$ or RNH $_2$ ·BF $_3$ are formed; the boron trifluoride is liberated from the complexes by treatment with sulfuric acid. The amine or ammonia complexes can also be reacted with compounds that form more stable complexes than the boron trifluoride complex, thus liberating boron trifluoride. Selective solvents are sometimes used to extract the spent boron trifluoride catalyst from the reaction media. If a fluoride salt is added to the spent catalyst, a precipitate, BF $_3$ ·MF is formed which upon heating liberates boron trifluoride. The regenerated BF $_3$ from these processes is recycled for reuse.

The method currently employed to dispose of excess or contaminated boron trifluoride, is to discharge the gaseous BF_3 into a water spray. The reaction first gives a precipitate of boric acid and then a solution of fluoboric acid:

$$BF_3 + 3H_20 + B(OH)_3 + 3HF$$

$$BF_3 + HF + HBF_4$$

The fluoboric acid is treated with lime or limestone, and decomposes to calcium fluoride and boric acid. The calcium fluoride produced is either sent to a land fill, or lagooned. The boric acid produced is discharged to sewer; it can be handled as discussed in the Profile Report on boric acid (60).

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is expected that boron trifluoride will either be recovered for reuse or destroyed by the satisfactory procedure discussed above. It is our conclusion that boron trifluoride is not a candidate waste stream constituent for National Disposal Sites.

7. REFERENCES

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- 1301. Matheson gas data book. 4th ed. East Rutherford, New Jersey, Matheson Co. Inc., 1966. 500 p.
- 1304. Personal communication. Mr. Stanfield, Allied Chemical Corporation, to J. R. Denson, TRW Systems, Mar. 16, 1972.
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HAZARDOUS WASTES PROPERTIES
WORKSHEET
H. M. Name Boron Trifluoride (63)
IUC Name Boron Trifluoride
Common NamesBF3
Molecular Wt. 67.82 Melting Pt127.1C Boiling Pt100.4 C
Density (Condensed) 1.57 @-100.4 C Density (gas) 3.077 @ 0 C
Vapor Pressure (recommended 55 C and 20 C)
139.7 Torr @ -120.5 C 760 Torr @ -100.4 C 10 atmos. @ -54.4
Flash Point Autoignition Temp
Flammability Limits in Air (wt %) LowerUpper
Explosive Limits in Air (wt. ") Lower Upper
Solubility
Cold Water 369.4g/100g 6 6 C Hot Water Ethanol Forms Complex
Others: 1.94g/100g H ₂ SO ₄ ; soluble in most organic liquids such as saturated hydrocarbons
<u>-</u> .
Acid, Base Properties <u>Lewis acid</u>
Highly Reactive with HNO ₂ @ 20 C; decomposes in aqueous bases
Compatible with Copper, iron, stainless steel, chromium, mercury
eappoint in any section of the first inches
Shipped in Steel cylinders under pressure, 1500-1800 psi
cylinders are either 6 or 62 lb. BF ₃ - in tube trailers 12,000-13,000 lb. ICC Classification Nonflammable comp. gas
Green label gas Green Label
Critical temp - 12.25
Critical Pressume - 12.25 C
References (1) 1301
Therefores (1) 1301
n'

PROFILE REPORT

Bromic Acid (64)

GENERAL

Bromic acid is a colorless or slightly yellow liquid that turns yellow on exposure to air. It is unstable except in dilute solutions and is almost never sold as bromic acid. 1305 Bromic acid is used as an oxidizing agent in the preparation of dyes, organic compounds, and pharmaceuticals and in the oxidation of mercaptan groups to disulfide groups in wool and hair treatment. When required, it is usually prepared for immediate use by adding sulfuric acid to barium or sodium bromate and the bromic acid recovered as an aqueous solution by subsequent distillation and absorption in water.

Potassium and sodium bromate, because of their use as "neutralizers" in home permanent cold wave kits, are the major bromate wastes. They are generally discharged as dilute solutions, directly to municipal or other local sewer systems.

The limited physical/chemical properties reported for bromic acid are summarized on the attached worksheet.

2. TOXICOLOGY

Bromic acid is not highly toxic, but because it is a strong oxidizing agent it causes severe irritation of the skin, eyes and upper respiratory tract.

Potassium and sodium bromate are the most common sources for bromate ingestion. The mean lethal dosage for bromate has not been established; rabbits succumbed to an oral dosage of 0.5 gm/Kg of NaBrO $_3$, while about 14.2 gm has been the cause of death in a 19 month old child.

Upon heating or standing bromic acid decomposes with liberation of bromine and oxygen. The toxicity of bromine then becomes the controlling factor (See Profile Report on Bromine [65]). Bromine has a Threshold Limit Value (TLV) of 0.7 mg/M³.

OTHER HAZARDS

Bromic acid produces a fire hazard on contact with organic matter. It will corrode most metals other than silver, platinum, and tantalum. 1138

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Bromic acid is handled in the same manner as any aqueous solution of a strong acid which is also a strong oxidizing agent. Contact with reducing substances is permitted only under controlled conditions. Solutions of HBrO₃ should be stored in glass or Teflon, protected from sunlight and extremes of temperatures.

Though bromic acid is almost never shipped it may be shipped under Department of Transportation regulations for a corrosive liquid with a White Label, in properly protected glass containers.

Bromic acid, because of its instability, will probably decompose to bromine and bromides on release to the environment. Safe disposal of bromic acid is defined, therefore, in terms of the recommended and provisional limits for bromine in the atmosphere and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Recommendation
Bromine	0.007 mg/M ³	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Bromine	0.035 mg/L	Drinking Water Studies

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Reduction and Discharge

Small packaged lots of bromic acid may be decomposed by the addition of reducing materials such as sodium thiosulfate, bisulfites or ferrous salts. This method is recommended by the Manufacturing Chemists Association, but procedures for recovery of the bromides produced are not provided. Instead, when reduction is complete, the treatment solution is neutralized with soda ash, and the solution is washed down the drain with a large excess of water. This process is satisfactory for small quantities of bromic acid, but the process is not recommended for larger quantities because valuable bromides will be lost.

Option No. 2 - Reduction and Recovery as Bromide

Bromic acid, like bromine, is recovered from a dilute solution or waste stream by passing an aqueous solution over iron turnings to produce the so-called ferrosoferric bromide. This is decomposed by sodium carbonate, the excess carbon dioxide boiled off and the sodium bromide crystallized and sold. 1138

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Bromic acid is not a candidate waste stream constituent for National Disposal Sites because it is not stable, and therefore, requires treatment at the site where the waste originates. Option No. 2 is the process recommended for treatment of wastes containing bromic acid. This process is simple and can be performed by any plant using bromic acid.

7. REFERENCES

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- 1138. Jolles, Z. E. Bromine and its compounds. New York, Academic Press, 1966. 640 p.
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- 1416. Ross, A. and E. Ross. Condensed chemical dictionary. 6th ed. New York, Reinhold Publishing Corporation, 1961. 1,256 p.
- 2376. Gleason, M. W., R. E. Gosselin, H. C. Hodge, and R. P. Smith.
 Clinical Toxicology of Commercial Products 3rd ed. Baltimore,
 Williams and Wilkins Company, 1969. 1,428 p.

HAZARDOUS WASTES PRO WORKSHEET	PERTIES
H. M. Name Bromic acid (64) IUC Name Bromic acid	Structural Formula
Common Names	нв г о _з
Molecular Wt. 128.92 ⁽¹⁾ Density (Condensed) 3.188 g/cc @ 20 C Density (Vapor Pressure (recommended 55 C and 20 C)	Boiling Pt. <u>decomposes</u> 1000 gas)@
Flash Point Autoignition Temp	
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	
Solubility Cold Water completely miscible Hot Water Others:	: Ethanol
Acid, Base Properties <u>strong acid; strong oxidiz</u>	ing agent
Highly Reactive with <u>Reducing substances; bases; most</u>	
Compatible with <u>Glass</u>	
Shipped in Not usually shipped ICC Classification Corrosive liquid Coast	Guard Classification corrosive liquid
Comments White Label	White Label
References (1) 1416	

PROFILE REPORT

Bromine (65)

1. GENERAL

Bromine is a member of the halogen family and is a brown-red, fuming, heavy and highly corrosive liquid. It is the only non-metallic element liquid at room temperature. Bromine is manufactured in the United States principally at the Ethyl Dow plant at Freeport, Texas, built during the second World War. Other production is from the Michigan brines. About 90 percent of the domestic output is used in the manufacture of ethylene dibromide, an anti-knock fluid, used in conjunction with tetra-ethyl lead in gasoline. This demand is subject to change as lead is phased out of gasoline.

In the United States the chief raw material for bromine manufacture is sea water in which bromine occurs in concentrations of 60 to 70 ppm. It is also manufactured from natural brines. Sea water or brine is acidulated with dilute sulfuric acid to a pH of 3, and chlorinated.

The chlorinated sea water (or brine) is stripped of bromine by air blowing, and returned to the ocean (or re-injected via a deep well). The moist bromine-containing air from the stripping tower, contaminated with a small amount of vaporized chlorine, is reacted with less than stoichiometric quantities of sulfur dioxide and water in an absorption tower to form a solution of bromine in mixed hydrobromic, hydrochloric and sulfuric acids. The mixed solution is reacted with an excess of chlorine and the liberated bromine is steam-stripped from the solution, condensed as liquid, and purified by distillation. Any excess chlorine is recycled, as is the residual sulfuric and hydrochloric acid solution. This manufacturing process creates as waste streams only the sea water or brine from which the bromine was removed. 1138

The physical/chemical properties for bromine are summarized in the attached worksheet.

TOXICOLOGY

Human Toxicity

Liquid bromine rapidly attacks the skin and other tissues, producing irritation and burns which heal slowly. Even very low concentrations of the vapor are highly irritating to the respiratory tract. The chronic effects of inhalation of bromine vapors include reduced red cell and hemoglobin content of the blood. The leucocyte count may increase, sometimes up to fourfold. 1138

The good warning properties of bromine (its pungent, irritating nature and dark brown color) help in preventing dangerous exposure of humans to the vapor. Concentrations as low as 0.3 ppm cause irritation of the eyes. A concentration of 7 ppm of bromine in the air is thought to cause fatal illness in man after exposure of half an hour to one hour. The TLV for bromine, the highest concentration considered safe for 8 hours continuous exposure, is 1 ppm. 1138

Other Toxicity

Bromine reacts rapidly, at ambient temperatures in an aqueous media, with many substances known to be constituents of living matter. With unsaturated aliphatic acids, dibromides and bromohydrins are formed; aromatic aminoacids such as tyrosine undergo ring substitution; amino groups form bromamine derivatives; and thiols are oxidized to sulphinic and sulfonic acids and disulfides. Specific toxic action is illustrated by the rapid germicidal effect of trace concentrations, 0.1 ppm of bromine or less, on the activity of various enzymes. Bromine is more effective than chlorine in killing bacterial spores, yeasts, molds and algae. Bromines toxicity to microorganisms has been put to good use, but like

chlorine the concentration level must be controlled to avoid damage to plants and fish. In swimming pools concentrations of 9 ppm bromine can be reached without irritation to the eyes to swimmers. 1138

OTHER HAZARDS

Bromine may produce a fire on contact with organic matter such as sawdust. Moist bromine reacts with most metals with lead being attacked only slowly. Dry bromine can be contained by monel.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Storage, Handling, and Transportation

Drums for bromine storage are made of monel or of lead-lined steel. Only very dry bromine can be stored in monel. Glass or glass lined containers are also used.

The chemical reactivity of elemental bromine with living matter presents a serious hazard in handling. Prolonged exposure to even very low concentrations of the vapor must be avoided. Effective safety devices which should be at hand when bromine is handled are: water safety showers and eye-wash fountains, safety face shields and rubber gloves. Annydrous ammonia in cylinders can be used to knock down bromine fumes. Liquid spills can be decontaminated with saturated alkaline thiosulfate solution or a lime slurry.

Bromine is classified by the Department of Transportation (DOT) as a corrosive liquid requiring a White Label. Due to the high cost of packing and insurance, bromine is seldom transported overseas. Only small quantities compared to the total production are shipped. Most of bromine produced is consumed in the integrated chemical plants where it is manufactured. Drums (monel or lead lined) with a capacity up to 225 lb are in use for shipping bromine; tank cars with a capacity up to 50 tons 1138 are used for bulk shipment.

Disposal/Reuse

Because the value of bromine is great, little is disposed of. The recommended provisional limits for bromine in the atmosphere and in water and soil are as follows:

Contaminant in Air	Provisional Limit	Basis for <u>Recommendation</u>
Bromine	0.007 mg/M ³	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Bromine	0.035 mg/l	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Bromine is a valuable commodity and is seldom disposed of as a waste. If disposal of contaminated bromine or bromine solution is required, the bromine or bromine solution is returned to the manufacturer for recovery. The manufacturer will in most cases buy the bromine. \$1305\$ If bromine vapor is in a process waste stream, it can be condensed easily. If the bromine is in an aqueous waste stream that is too dilute for shipment, concentration is required. Concentration is accomplished in the same manner used to recover bromine from sea water, i.e., chlorine is used to oxidize any bromide to bromine and the solution is air stripped of the bromine, which is subsequently trapped in an ice cooled condenser. The impure bromine can be used or returned to the manufacturer.

An alternate recovery process is to pass an aqueous waste stream containing bromine over iron turnings to produce so called ferroso-ferric bromide. This is decomposed by sodium carbonate, the excess carbon dioxide boiled off and the sodium bromide crystallized and sold. 1138

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

With the exception of the return of contaminated bromine or bromine compounds to the manufacturer for purification, bromine waste streams can

be best handled at the site where they originate. Designated sites (at the primary bromine producers) should be identified for the economic recovery of bromine from waste streams from the few sources not equipped with recovery systems.

7. REFERENCES...

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HAZARDOUS WASTES PROPERTIES WORKSHEET
H. M. Name Bromine Structural Formula
IUC Name Bromine
Common NamesBr ₂
Molecular Wt. 79.909 Melting Pt7.3 C Boiling Pt. 52.2 C
Molecular \forall t. 79.909 Melting Pt7.3 C Boiling Pt. 52.2 C Density (Condensed) 3.119 @ 25 C(1) Density (gas) 3.5 @ 20 C
Vapor Pressure (recommended 55 C and 20 C)
2 atm @ 78.8 C 3 atm @ 110.3 C 10 atm @ 139.8 C
Flash Point Autoignition Temp
Flammability Limits in Air (wt %) Lower Upper
Explosive Limits in Air (wt. %) Lower Upper
Solubility
Cold Water 3.41 g/100g at 20 C Hot Water 3.33 g/100g at 40 C Ethanol freely soluble
Others: freely in chloroform, CS ₂ , CCl ₄ (1)
Acid, Base Properties
Highly Reactive with Alkali hydroxides, arsenites and other oxidizable materials (1)
rightly Reactive with many indicates, and all a solid. Salatastic master to the
Compatible with
Compactore with
Shipped in 1 and 6.5 lb bottle, 10 gal drums, tank cars, trucks
ICC Classification corrosive liquid <1 qt ⁽²⁾ Coast Guard Classification white label (2)
Comments
References (1) 1492
(2) 0766
!

PROFILE REPORT

Chlorosulfonic Acid (112)

GENERAL

Chlorosulfonic acid is an important item of commerce, tank-car quantities being used as an intermediate in the production of synthetic detergents, drugs, ion exchange resins, and dyestuffs. It has also been used as a smoke-forming agent in warfare. Chlorosulfonic acid may be considered as a mono acid chloride of sulfonic acid, since one chlorine atom has replaced one hydroxyl group. It is a clear, colorless, mobile liquid which decomposes slightly when distilled. It reacts with water with explosive violence and fumes strongly in moist air to form a persistent, irritating aerosol of sulfuric and hydrochloric acids. It also reacts with almost all organic materials; in some cases with charring.

Chlorosulfonic acid is a strong acid containing a relatively weak sulfurchlorine bond. It is a powerful sulfating and sulfonating agent, a fairly strong dehydrating agent, and a specialized chlorinating agent. In most of its applications it is used to form sulfates, sulfonates and sulfonyl chlorides with such organic compounds as hydrocarbons, alcohols, phenols and amines. Many salts and esters of chlorosulfonic acid are known, but most of them are relatively unstable or hydrolyze readily in moist air.

Manufacture of chlorosulfonic acid is accomplished by the direct union of sulfur trioxide with dry hydrogen chloride gas. The sulfur trioxide may be in the form of 100 percent liquid or gas, as obtained from boiling oleum, or may be present as a dilute gaseous mixture obtained directly from a contact sulfuric acid plant. The reaction of sulfur trioxide and hydrogen chloride takes place spontaneously with evolution of a large quantity of heat. 1433 The chemical/physical properties for chlorosulfonic acid are given in the attached worksheet.

2. TOXICOLOGY

Chlorosulfonic acid will cause severe acid burns on contact of the liquid with the skin or mucose, and the vapor is very irritating to the eyes, lungs, and mucous membranes. It can cause acute toxic effects in either the liquid or vapor state. Inhalation of concentrated vapor may cause loss of consciousness with serious damage to lung tissue. Upon ingestion, it will burn and destroy the mucose of the mouth, esophagus and stomach to a serious degree. Contact of the liquid with the eyes can cause permanent destruction of the tissues involved. Even in the vapor state it causes conjunctivitis. O766 Chlorosulfonic acid does not have a Threshold Limit Valve (TLV) established by the American Conference of Governmental Industrial Hygienist (ACGIH) but the TLV of 5 ppm for hydrochloric acid should be considered the maximum level of exposure for an 8-hr work day of a 40-hr work week.

3. OTHER HAZARDS

Chlorosulfonic acid is corrosive, functioning both as a strong acid and as a dehydrating and charring agent. It has an appreciable vapor pressure and through the action of moisture in air (or water) is decomposed to hydrochloric acid and sulfuric acid. Good ventilation should be provided, and goggles, gloves, protective clothing, and face shields should always be worn when handling this material.

The acid itself is not flammable, but may cause ignition by contact with combustible materials. The flammable and explosive gas, hydrogen, is slowly generated by action of the acid on moist metals. 1433

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

When working with chlorosulfonic acid waste or spills, in addition to the protective devices indicated above, a self-contained breathing apparatus should be employed. For small quantities work can be performed in a fume hood, and a laboratory coat, goggles and gloves should be worn. Spills of small quantities should be covered with excess sodium

bicarbonate and the mixture diluted with a large quantity of water. Spills of larger quantities should very carefully be diluted with a large quantity of water and neutralized with lime. 0095

Chlorosulfonic acid is shipped in bottles, 170-1b carboys, 1,600-1b stainless steel drums and 8,000-gal tank cars. It is shipped under Department of Transportation regulations as a corrosive liquid requiring a White Label.

The safe disposal of chlorosulfonic acid is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Chlorosulfonic Acid	.01 mg/M ³	Limit for H ₂ SO ₄
Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
H ₂ SO ₄ (hydrolysis product of chlorosulfonic acid in water)	.05 ppm	Limit for H ₂ SO ₄

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The method of disposal of packaged lots of chlorosulfonic acid recommended by the Manufacturing Chemists Association is satisfactory if the effluent from the disposal process is within the limits for pH, chloride ion, and sulfate ion.

In this procedure chlorosulfonic acid is decomposed by pouring small quantities from behind a shield onto a dry layer of sodium bicarbonate. After mixing thoroughly, the sodium bicarbonate, while being stirred, is sprayed with 6M ammonium hydroxide. Then the sodium bicarbonate is covered with a layer of crushed ice; and while continuing stirring, the sodium bicarbonate mixture is again sprayed with 6M ammonium hydroxide. When evolution of ammonium chloride (which must be trapped and disposed of) has

partially subsided, the sodium bicarbonate solution is neutralized with hydrochloric acid. Following dilution to the concentration permitted for effluents (see Section 4), the treated solution is discharged into a stream or storm sewer. 0095

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that the great majority of chlorosulfonic waste will continue to be best handled at the source of the waste generated. Because the process requires little special equipment and, when performed properly, no new very toxic materials are created, chlorosulfonic acid does not appear to be a candidate waste stream constituent for a National Disposal Site.

7. REFERENCES

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HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name Chlorosulfonic Acid	Structural Formula
IUC Name <u>Chlorosulfonic</u> Acid	
Common Names Sulfuric Chlorohydrin	c1s0 ₃ H
Molecular Wt. 11.653 Melting Pt800	C Boiling Pt151.0C
Density (Condensed) 1.766 @ 18 C Density (gas)
Vapor Pressure (recommended 55 C and 20 C)	
1 torr at 32 C @	
Flash Point Autoignition Temp	
Flammability Limits in Air (wt %) Lower	
Explosive Limits in Air (wt. %) Lower	Upper
<u>Solubility</u>	
Cold Water reacts Hot Water reac	ts violently Ethanol <u>reacts</u>
Others.	
Acid, Base Properties Upon contact with water forms hyd	rochloric or sulfuric acid.
Highly Reactive with Most organic materials; water	
Compatible with	
1600	
Shipped in <u>Carboys, 1600 pound drums, 8,000 gallon tan</u>	
ICC Classification corrosive liquid Coast Gu	
Comments Extremely caustic, corrosive and toxic liqui	a.
References (1) 1416	
References (1) 1416	

PROFILE REPORT

Chrome (113)

1. GENERAL

Introduction

Chromium is a metallic element with properties resembling iron occurring mainly in chrome/iron ore (Fe0 \cdot Cr₂0₃). It is a very infusible, hard, gray metal which is incorporated in the manufacture of stainless steel and other corrosion resistant alloys. Chrome is extensively used as a plating on other metal surfaces to give a hard, corrosion resistant, beautiful surface and also finds wide use as a catalyst. 1570

The ferro chromium alloys are made by silicon reduction of chromite ores in a two-stage process. Initially a high silicone ferro chromium is produced in a submerged arc furnace. Then this product is treated in an open arc type furnace with a synthetic slag containing $Cr_{2}O_{3}$. 1433 To produce chromium metal either electrolytically or by the reduction of chromium compounds, a chemical treatment is necessary to remove the iron and other impurities from the starting materials. Reduction methods start with chromium oxide Cr_2O_3 which has been obtained from chromite ore via sodium bichromate. Commercial chromium metal is produced by reducing $\mathrm{Cr}_2\mathrm{O}_3$ with aluminum, although silicon and carbon are sometimes also used as reducing materials. The aluminum reaction is performed in a refractory lined vessel which contains the exothermic, self-sustaining reaction. Chromium metal can also be produced by the electrowinning of chromium from either chrome alum or chromic acid electrolytes. 1433 As far as can be determined by a review of the literature, no significant amounts of chromium metal appear as wastes from the production processes.

In 1968 approximately 300,000 short tons of chromium were consumed in chromium ferro allloys and chromium metal in the United States. The greatest proportion was used in various ferro chromium alloys. This represents 60 to 70 percent of the chromium ore processed in the United States.

Occurrence as a Waste Product

Chromium, either as a ferro alloy, stainless steel, metallic catalyst or plate, is relatively valuable and normally is not disposed of without reuse. Stainless steel and other alloys have considerable value as scrap metal and these are normally recycled. Chromium plate on scrap metal, such as that coming from scrapped automobiles, normally is recycled, not necessarily for the chrome plate but for the scrap steel. The chrome is believed to be melted down without any prior removal of the chrome plate. The occurrence of ferro chrome alloys and chrome plated metal as recycled scrap is widespread in the United States. At the present time the amount of chrome metal that is actually lost in junk yards and trash dumps is not known.

TOXICOLOGY

Zero valent chromium, as the pure metal or alloy, is considered to be essentially nontoxic to plants and animals. 1492

3. OTHER HAZARDS

The dust of chromium metal is considered a moderate fire hazard. O766 Chromium metal does not exhibit any other hazards.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Chromium does not require special handling when it occurs as a waste in alloys or as a decorative plate on other metal surfaces. The industries that use large amounts of chrome and chrome alloy materials should have a program by which the various types of chrome containing scrap materials are collected and segregated for recycling. No safety precautions are required for the handling of the scrap materials except those which would normally be used for the handling of other common scrap metals. For chrome dust particles, the recommended provisional limit is:

Contaminant in AirProvisional LimitBasis for RecommendationChrome0.01 mg/M³0.01 TLV

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The only feasible waste management option for chrome metal and chrome metal alloys is that of recycling scrap for use in new products. There is a considerable market for this type of scrap material and it is believed that all major industries who work with these metals have a program by which the scrap is segregated and saved for sale to a scrap dealer.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Waste chromium metal and chrome alloys are not candidate waste stream constituents for national disposal. They are essentially non-toxic to both plant and animal life. Additionally, they are very corrosion resistant and do not weather to produce harmful corrosion products. Waste chrome metals and their alloys have inherent value and scrap recovery and recycle programs are widespread in the industry. 1975

7. REFERENCES

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	HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name <u>Chrome (1</u> 13)		Structural Formula
IUC Name Common Names		Cr ⁽¹⁾
Molecular Wt. $51.996^{(1)}$ Density (Condensed) $7.20^{(1)}$ @	Melting Pt. 1890C 28 C ⁽¹⁾ Density (gas	(1) Boiling Pt. 2482 ⁽¹⁾) N/A @ °
Vapor Pressure (recommended 55 C a	and 20 C)	1 mm @ 1616C ⁽²⁾
Flash Point N/A Flammability Limits in Air (wt %) Explosive Limits in Air (wt. %) Solubility Cold Water insoluble (1) Others: sol in dil H ₂ SO ₄ , F	Autoignition Temp Lower N/A Lower N/A Hot Water insolu	Upper N/A Upper N/A
Acid, Base PropertiesHighly Reactive with		
Compatible with		
Shipped inICC Classification		ard Classification
Comments Moderate fire hazard	7.01	
References (1) 1570 (2) 0766		7.1

PROFILE REPORT

Cobalt Nitrate (116), Ferrous Sulfate (198), Stannous Chloride (409), Cobalt Chloride (489)

1. GENERAL

<u>Introduction</u>

The inorganic chemicals in this Profile Report are grouped together because they can be handled by similar disposal processes. Concentrated aqueous solutions of the salts constitute a hazard or nuisance.

Manufacture and Uses

Cobalt Nitrate. Cobalt nitrate, or cobaltous nitrate, $\mathrm{Co(NO_3)_2}$, is a red crystalline material which is deliquescent in moist air. Cobaltous nitrate is prepared by the action of nitric acid on cobalt hydroxide followed by purification through recrystallization. It is used in: 1492

- < }

- (1) sympathetic inks;
- (2) cobalt pigments;
- (3) preparation of cobalt catalysts;
- (4) additives to soils and animal feeds;
- (5) additives to vitamin preparations;
- (6) hair dyes;
- (7) decorations on porcelain.

Ferrous Sulfate. Ferrous sulfate, FeSO₄·7H₂O, crystals or granules are green, and are often brownish-yellow in color from oxidation and efflorescence. The sources of commercial ferrous sulfate are:

- by-product production (from the pickling of steel and from many other chemical operations);
- (2) direct reaction between dilute sulfuric acid and iron;
- (3) oxidation of pyrites in air, followed by leaching and treatment with scrap iron;
- (4) by-product production from ilmenite.

The uses for ferrous sulfate include: 0955, 1492, 1662

- (1) water purification;
- (2) source for other iron salts and oxides;
- (3) fertilizer;
- (4) feed additive;
- (5) writing inks;
- (6) pigments;
- (7) medicine;
- (8) deodorizer;
- (9) metallurgy;
- (10) aluminum etching;
- (11) wood preservative compositions.

Stannous Chloride. Stannous chloride, SnCl₂, is a white crystalline mass that absorbs oxygen from the air to form the insoluble oxychloride. It is prepared by dissolving tin in hydrochloric acid. SnCl₂ is used: 1492

- (1) as a reducing agent in the manufacture of chemicals and dyes;
- (2) in tin galvanizing;
- (3) as a reagent in analytical chemistry;
- (4) as a stain remover;
- (5) in antisludging agents for lubricating oils;
- (6) as a chemical preservative.

Cobalt Chloride. Cobalt chloride or cobaltous chloride, $CoCl_2 \cdot 6H_20$, is prepared by recrystallization of the crude material obtained by reacting hydrochloric acid with cobalt oxide. It is used: 1492

- (1) as an absorbent for ammonia;
- (2) in gas masks;
- (3) in electroplating;
- (4) in sympathetic inks;
- (5) in hygrometers;
- (6) in catalysts:
- (7) in barometers;
- (8) as a flux for magnesium refining;
- (9) as a trace element in feeds and in vitamin B_{12} preparation.

Physical/Chemical Properties

The physical/chemical properties for the compounds covered by this Profile Report are summarized on the attached worksheets.

TOXICOLOGY

Stannous chloride is considered relatively nontoxic. Ferrous sulfate, although used as a diet supplement, has caused death when excessive quantities were ingested. Lowest lethal dose was 0.5 gm. 2376 The cobalt salts have LD₅₀'s which range from 100 to 400 mg/Kg for mouse and rabbit.

With the exception of $FeSO_4$, which has a Threshold Limit Value (TLV) of 1 mg/M 3 as Fe, 0025 the American Conference of Governmental Industrial Hygienists has not established TLV's for any of the compounds listed in this report.

3. OTHER HAZARDS

Cobaltous nitrate is an oxidizing material which, in contact with organic or other readily oxidizable substances, may cause a violent reaction or combustion. Ferrous sulfate in aqueous solution widdeporrode iron and most steels. The iron, cobalt, and tin salts listedialinhydrolyze to produce acid solutions.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

As discussed in Section 3, cobaltous material is an oxidizing material and must be handled and stored as such. It is classified by the Department of Transportation (DOT) and the U.S. Coast Guard as an oxidizing material that requires a Yellow Label. Ferrous sulfate etches iron and aluminum; 316 stainless steel is relatively unaffected by $FeSO_4$, and is used in contact with aqueous solutions. Other than protection from moisture there are no additional handling, storage or transportation requirements for the compounds included in this Profile Report.

Disposal/Reuse

The inorganic chemicals discussed in this report can be reprocessed for reuse if both quality and quantity of the waste discharged are consistent with economic recovery. If disposal is required, the acceptable criteria for the release of these compounds into the environment is defined in terms of the following provisional limits:

	•	Basis for
Contaminant in Air	Provisional Limit	Recommendation
Cobalt nitrate	$0.001 \text{ mg/M}^3 \text{ as Co}$	0.01 TLV for Co
Ferrous sulfate	0.01 mg/M ³ as Fe	0.01 TLV for Fe
Stannous chloride	0.02 mg/M ³ as Sn	0.01 TLV for Sn
Cobalt chloride	0.001 mg/M ³ as Co	0.01 TLV for Co
Contaminant in Water	Provisional Limit	Basis for Recommendation
Cobalt nitrate	0.05 ppm as Co	Chronic toxicity drinking water standards
Ferrous sulfate	0.03 ppm as Fe	Drinking water standard
Stannous chloride	0.05 ppm as Sn	Chronic toxicity drinking water standards
Cobalt chrloride	0.05 ppm as Co	Chronic toxicity drinking water standards

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The Manufacturing Chemists Association has recommended disposal of packaged lots of the materials in this report as follows. The salts are dissolved in a large excess of water, and treated with a slight excess of soda ash which precipitates the cobalt, ferric and tin ions. When the sulfate ion is present, slaked lime is also added to reduce the sulfate ion concentration. After standing 24 hours, the supernatant liquid is decanted into another container and neutralized with hydrochloric acid, and the liquid is diluted further before discharge into a sewer or stream. The sludge is added to a landfill.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Based on the discussion of disposal in Section 5, it may be concluded that after preliminary treatment with soda ash (and lime when sulfate ions are present) the treated waste streams containing the materials discussed in this report can be discharged into municipal sewers or streams. Because waste treatment can be handled adequately locally, these compounds do not merit consideration as candidate waste stream constituents for national disposal.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Cobalt Nitrate (116)			
IUC Name Cobaltous Nitrate			
Common NamesCo(NO ₃) ₂ · 6H ₂ O			
Molecular Wt. $\underline{291.05^{(1)}}$ Melting Pt. $\underline{<100 C^{(1)}}$ Boiling Pt. $\underline{-3H_20}$, 55 $\underline{C^{(1)}}$ Density (Condensed) 1.87g/cc @ 20 $\underline{C^{(1)}}$ Density (gas) @			
Vapor Pressure (recommended 55 C and 20 C)			
Flash Point Autoignition Temp			
Flammability Limits in Air (wt %) Lower Upper Upper Explosive Limits in Air (wt. %) Lower Upper			
Solubility Cold Water 138.8g/100 ml at 0 C ⁽¹⁾ Hot Water very soluble ⁽¹⁾ Others: Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in Glass bottles, wooden barrels ⁽²⁾			
ICC Classification oxidizing material (2) Coast Guard Classification oxidizing material			
Comments			
References (1) 1570 (2) 1492			

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Ferrous Sulfate (198) IUC Name	Structural Formula		
Common Names Copperas, Iron Sulfate	FeSO ₄ · 7H ₂ O		
Molecular Wt. 278.01 Melting Pt. 64 C, -6	H ₂ 0 Boiling Pt. 300 C, -7H ₂ 0		
Density (Condensed) <u>1.898g/cc</u> @_20_C ⁽¹⁾ Density (gas	s)@		
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			
Solubility Cold Water 15.65g/100 m1 (1) Hot Water 48.6g/10	(1) <u>O ml at 50</u> C Ethanol <u>Insoluble</u>		
Others:			
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in Bottles, bags, barrels, bulk			
ICC Classification None (2) Coast Gu	ward Classification None ⁽²⁾		
Comments			
References (1) 1570			
(2) 1492			
·			

HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. M. Name Stannous Chloride (409)	Structural Formula		
IUC Name Stannous Chloride Common Names Tin Chloride	SnC1 ₂		
Molecular Wt. $189.61^{(1)}$ Melting Pt. $264.0 \text{ C}^{(1)}$ Density (Condensed) $3.393g/cc^{1iquid}$ $245 \text{ C}^{(1)}$ Density (gas Vapor Pressure (recommended 55 C and 20 C)	Boiling Pt. 623 C ⁽¹⁾		
Flash Point Autoignition Temp.			
Flammability Limits in Air (wt %) Lower Explosive Limits in Air (wt. %) Lower	Upper		
Solubility Cold Water 83.9g/100-ml at 10 C ⁽¹⁾ Hot Water 269.8g/10	(1) 00 ml at 15 CEthanol soluble ⁽¹⁾		
Others:Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in bottles, drums (2) ICC Classification none (2) Coast Gue	ard Classification none(2)		
Comments			
References (1) 1570 (2) 1492			
, ·			

НА	ZARDOUS WASTES PROPERTIES WORKSHEET
H. M. Name Cobalt chloride (489) IUC Name Cobaltous chloride Common Names	Structural Formula CoCl ₂
Molecular Wt. 129.85 ⁽¹⁾ Density (Condensed) 3.356g/cc @ : Vapor Pressure (recommended 55 C and	Melting Pt. subl. (1) 30 C (1) Density (gas) 20 C)
Flash Point A	utoignition TempUpper
Solubility Cold Water 459/100 ml at 7 C(1)	Hot Water 105g/100 ml at 96 C ⁽¹⁾ Ethanol 54.4g/100 ml (1)
Others: <u>acetone</u> 8.6g/100 m1 ⁽¹⁾ Acid, Base Properties	
r d	
Shipped in Bottles, tins, drums (2) ICC Classification None (2) Comments	Coast Guard Classification None (2)
References (1) 1570	
(2) 1492	

PROFILE REPORTS ON THE COPPER SALTS Copper Nitrate(121), Copper Sulfate(122)

1. GENERAL

The subject copper compounds, copper II nitrate, copper I sulfate, and copper II sulfate, are moderately poisonous materials. It is believed that only the copper II compounds, (cupric nitrate and cupric sulfate) occur as waste materials to any significant extent.

Industries, besides producers, which utilize these materials in various forms include metal plating, metal pickling, and circuit board etching. Normally waste streams that contain these compounds do not exist as pure solutions, but rather are contaminated with other inorganic and organic material. There are cases, however, in which copper sulfate wastes occur as reasonably pure materials. Copper sulfate wastes from pickling have the greatest volume of all sources by far and are fairly pure. Copper nitrate does find uses in electroless plating, but waste volumes from this source are relatively low.

Commercial grade copper sulfate is produced by the action of sulfuric acid on copper ores and scrap copper. The copper sulfate which is formed in the solution is transferred to settling tanks where foreign material is removed. The product solution is then filtered, evaporated, recrystallized, and finally dried. The mother liquor from evaporation/recrystallization is returned to the evaporator, creating no liquid waste other than spills. The sludge that is obtained from settling and filtration is dumped. The process is 99 percent efficient which indicates that waste output is approximately 1 percent of the total production. Production figures for 1963 are estimated at 40,000 tons. Thus, 400 tons per year of waste copper sulfate from production is the current estimate.

There is a significant portion of copper and copper alloy pickling industry where the acid used for copper pickling is still being dumped. Ill9 Included in this waste is an anhydrous copper sulfate sludge which can and should be easily recovered. The actual pickling tanks are rarely dumped since the copper sulfate concentration increases, with use, until saturation and it precipitates out of solution. Additions of sulfuric acid replace precipitated sulfate to "sharpen up" the baths for renewed efficiency. Il21

The manufacture of printed circuit boards creates large amounts of copper wastes. Commonly used etchants include ferric chloride, chromic acid/sulfuric acid, a family of alkaline solutions, cupric chloride and ammonium persulfate. The use of ammonium persulfate materials is decreasing in large shops due to material costs and waste treatment difficulties. The presence of the ammonium ion in spent solutions complicates the normal waste treatment process of precipitation by pH adjustment. When the waste solution is made alkaline, free ammonia is liberated. The ammonia, a noxious air pollutant, also complexes the copper in solution thereby preventing precipitation. Saturday Industrial Filters Corp. claims that additions of ferric chloride to isolated concentrates of this problem solution will break the complexes. The use of hexavalent chrome is also discouraged because of the additional chemical reduction step required in the treatment process, as discussed in the Profile Report on the chromates (21,22,etc.).

The large shops which are close to suppliers often have their spent solutions picked up by the supplier or have in-plant precipitation and flocculation equipment. The small or remote printed circuit board shop must rely on tank truck pick-up, private scavengers, or diluted sewer dumping. In addition, the small shop is more likely to use the chrome/sulfuric and ammonium persulfate etchants, because they have general, all around capability. However, these are the two wastes which are the most difficult to treat. The industry was characterized as having no big problem with bulk disposal of spent solutions. Their real difficulties lie with dragout and rinse waters, which can contain 20 to 100 ppm copper. This rinse effluent must be reduced to levels compatible

with waste water treatment plants. A large firm was noted as having an effluent output of 12,000 gal. per hour. 2352

There are additional printed circuit board copper wastes from the electroless plating used to apply the first layer of copper on the bare composite board. Ammonium and ethylenediaminetetracetic acid (EDTA) complexed copper again present the difficult waste treatment problem in dragout described above. Small shops tend to make up these solutions, use them until they are nearly depleted, and then dump them. The larger shops can afford the analysis of the solutions and make additions required to maintain them. 2349,2350

Metal plating is another significant contributor of copper sulfate and nitrate wastes. The primary source is dragout as the actual plating baths can be maintained indefinitely. Estimates of generated wastes range from 0.1 to 5 percent of the total copper used depending on equipment, stream segregation, shape of the plated part, etc. 2349,2350 Booz-Allen indicates that "finishing effluents from fabricated metal parts" can contain 6 to 300 ppm Cu. 1623

Copper sulfate has enjoyed wide use as a fungicide (applied directly) but this has more or less been replaced by the Bordeaux Mixture (CuSO_4 and Ca[OH]_2 make a flocculent copper hydroxide-calcium sulfate complex). Copper sulfate is also used in fungicides for treating wood. These uses result in small amounts of waste material in containers and preparation equipment. Consumption in agriculture has been as high as 50 percent of the total production. 1501

Copper nitrate is a difficult compound to profile because most of the production and consumption is on a captive basis where it is made and consumed entirely within a company. Captive production is primarily for catalyst manufacture. Commercial copper nitrate is also sought as a raw material for catalyst manufacture. Most of the remainder appears to be used in metal finishing as discussed earlier. Copper nitrate is used in the preparation of a wide variety of chemicals and catalysts, many of which are made at one plant. The types and uses of these catalysts are highly proprietary and little information is available. The assumption

is made that waste dissolved copper nitrate occurs in highly mixed, diverse waste streams.

2. TOXICOLOGY

The compounds of copper exhibit a general toxicity which is less severe than some of the other heavy metals. Sax 0766 describes them as being moderately toxic and says that they may cause both irreversible and reversible damage not generally severe enough to cause death and injury. However, it is also specifically stated that the ingestion of a large quantity of copper sulfate has caused vomiting, gastric pain, dizziness, exhaustion, convulsions, shock, and coma which can finally lead to death. As little as 27 grams have caused death while others have recovered after ingestions of up to 120 grams. Symptoms of nervous system, kidney, and liver damage have also been reported. Copper nitrate is not mentioned as having toxicological properties different from those exhibited by the whole class of copper compounds. The sulfate and nitrate anions, are not considered to be toxic insofar as the toxic properties of compounds containing these anions are normally attributed to that of the cation with which they are bound. 0766

The U.S. Public Health Service indicates that copper in small amounts is generally regarded as nontoxic and is in fact considered essential for human metabolism. In 1942 the maximum permissible concentration of copper in drinking water was raised from 0.2 mg/l to 3.0 mg/l. However, since it does contribute to an undesirable taste, the U.S. Public Health Service has recommended a maximum concentration of 1.0 mg/l. The critical concentration for fish has been established at 0.15 to 0.18 ppm.

Copper sulfate has also been used extensively as a fungicide and its general toxicity towards plants is significant. It has also been established that high concentrations of copper in waste streams will seriously impair the microorganisms that are employed in secondary water treatment processes. For this reason, large scale dumping of dissolved copper in the municipal sewer lines is discouraged by sewage treatment authorities.

3. OTHER HAZARDS

No flammable explosive, or other hazard has been found to exist for these compounds.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Since it is apparent that waste copper compounds can create serious problems with plant and animal life in sewer systems and open waterways, it is necessary to define waste management techniques which will minimize these hazards. Plants and processes must be designed so that no untreated wastes reach open waterways or contaminate the surroundings. Each firm should have the facilities to treat and recover copper from waste streams and temporarily hold any treatment products for ultimate disposal. If a firm is permitted to discharge to municipal sewer systems, suitable holding or pretreatment tanks are required on the plant premises.

Handling, Storage, and Transportation

Dried waste materials containing copper sulfate or copper nitrate can be packed, stored, and otherwise handled as if one were handling the pure compound. Barrels, drums, bags, boxes, and bottles can all be used to store and ship these materials. Protective clothing such as aprons, gloves, and eyewear should be worn to prevent contact with these wastes. All Department of Transportation (DOT) regulations should be followed when shipping or otherwise handling these compounds.

All personnel and supervisory staff who work with these materials should be carefully educated as to the precautions that must be taken to prevent hazardous exposure.

Disposal/Reuse

The U.S. Public Health Service recommends a maximum copper level of 1.0 mg/l (ppm) in drinking water. ¹⁷⁵² The proper levels of copper waste discharge to municipal sewage systems or cooperative industrial waste treatment would of course vary with such parameters as waste water volume, efficiency of the plant, etc. For the safe disposal of copper nitrate and copper sulfate, 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
Copper nitrate	0.01 mg/M 3 as Cu	0.01 TLV for Cu
Copper sulfate	0.01 mg/M ³ as Cu	0.01 TLV for Cu
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Copper nitrate	1 ppm (mg/1) as Cu	Drinking water standard
Copper sulfate	1 ppm $(mg/1)$ as Cu	Drinking water standard

Copper sulfate and copper nitrate both have inherent value when present as concentrates in wastes. Very large amounts of copper sulfate are produced from the numerous copper and copper alloy pickling processes that are carried out in the nation. Waste copper nitrate normally occurs in dilute solutions and is not as likely a candidate for recovery and reuse as copper sulfate. The same is true with any dilute copper waste solutions. However, with increased utilization of solution concentrating equipment, along with waste stream segregation, some dilute copper solutions are being economically recovered. The various means by which solutions can be concentrated and waste copper compounds recovered are discussed later.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

There are two basic waste management practices which involve copper sulfate and copper nitrate. The first method, product recovery, is used

primarily in industries where the waste can be kept pure through segregation and concentration. The other basic waste management option is that of destructive precipitation. This involves either pH adjustment or discharge to sewers.

Option No. 1 - Recovery of Copper Process Byproducts

Since copper sulfate has inherent value as a chemical commodity (80 to 90 cents per pound for purified grades) it is advantageous for the metal finisher to attempt recovery if it is economically feasible. There are several approaches by which valuable copper or copper compounds can be recovered.

As previously described with copper pickling, copper oxide removal continues until the pickling bath becomes saturated with copper sulfate and it settles out of the pickling solution. This nearly pure copper sulfate can be mechanically removed from the tanks, packaged and sent to a commercial reclaiming firm.

There are also in-plant processes for recovering copper metal from pickling solutions. An example of an integrated recovery and waste treatment system is described by Lancy and Pinner who have installed an electrolytic copper removal unit through which is pumped the sulfuric acid pickling solutions. Copper metal is electrolytically plated out thereby regenerating the sulfuric acid to be returned to the pickling tanks. The system is said to be simple to operate and can be easily automated.

Copper sulfate and copper nitrate waste solutions that are generated by the metal plating processes are nearly always dilute solutions (less than 500 ppm copper). Any type of copper recovery process for these dilute solutions will likely require some type of solution concentrating equipment. The addition of this type of equipment is costly, but if the value of chemicals being lost from large volume shops is larger than the cost of installing and operating recovery equipment, then such an approach is justified. The types of process which might be considered for

concentrating a dilute but pure waste stream include reverse osmosis, ion exchange, dialysis, and multiple effect evaporators. The solutions can be concentrated to a point where electrolytic or other copper recovery can be carried out. Alternatively, the concentrates can be returned to plating baths, etc. or sent to a reclaiming firm.

Option No. 2 - Precipitation by pH Adjustment

Precipitation is most suitable for dilute mixed streams where copper will not be recovered for reuse. Soda ash, caustic or other alkaline chemicals can be added to copper bearing solutions to adjust the pH to about 9.5. This precipitates copper as an insoluble hydroxide gel along with the precipitates of other heavy metals which might be present in a mixed solution. Alum or other suitable floccuating agents can also be used to speed up settling, and clarification of the effluent. The treated effluent has characteristic heavy metal levels of 0 to 5 ppm. The alkaline effluent is neutralized before sewering and the resultant sludge is almost always landfilled. This procedure can be carried out in either batch or continuous processes. Turn key equipment systems are available for performing the precipitation on an automated or semi-automated basis.

There are two major disadvantages for using this procedure. The first is the problem of handling and disposing 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 slow and it is necessary to have settling ponds in which to allow the coagulation process to occur. The second major disadvantage of precipitation methods is that no feasible process has yet been developed for the recovery of chemical or metal credits from this type of precipitated waste. The sludge often contains many other organic and inorganic materials which are present in the waste stream before treatment and these hinder effective purification and recovery. These mixed sludges can serve no useful purpose and can only be ultimately disposed. The method is adequate when the pH is made high enough to leave only low ppm traces of pollutants in the effluent. The ultimate disposal of the sludges is discussed later.

Option No. 3 - Dilute Discharge to Municipal Sewers

Much of the major metal finishing industry is located in highly industrial and large metropolitan areas. Significant amounts of copper waste solutions generated in pickling, plating and other related industries are being discharged to existing municipal sewage treatment. O087,1601 The only pretreatment which is customarily given metal finishing wastes before discharge into municipal sewers is neutralization. If the material being discharged is of a considerable quantity, or if the discharge point is close to the sewage treatment plant, it is necessary to closely monitor the discharge to ensure that there will be no undesirable ill effects on the sewage stream.

When discharged to sewers, most of the copper ion will precipitate when it reacts with the sulfides that are found in normal domestic streams. This precipitation occurs in transit to the waste treatment plant and the solids are removed at the primary screening and settling facilities or after secondary biological treatment processes. This method of disposal is considerably widespread and may be considered environmentally acceptable only if the waste water treatment plants receiving these discharges can efficiently deal with the waste loads. In spite of the increased emphasis on recovery and recycling of wastes with value, the trend for using municipal sewers for industrial discharge is actually increasing.

Ultimate Disposal of Sludges from Options 2 and 3

Three ultimate disposal options for these sludges are: (1) landfill, (2) incineration, and (3) ocean disposal. Landfill is believed to be, by far, the most prevalent final disposal procedure but the problem of potential contamination of surrounding land or water tables, due to the leaching of poisonous materials from the sludge, must be considered. Incineration reduces the sludge to an ash residue which can be more easily handled for ultimate disposal but at the same time could also lead

to the formation of poisonous, soluble metal oxides. Incineration also requires additional equipment and a combustible fuel source as well as equipment for air pollution control. Ocean disposal is currently being practiced to a considerable degree by municipal waste treatment plants located near the coast where the primary and secondary sludges can be either pumped or barged out to submarine disposal areas. This disposal approach has been the subject of much recent debate and it is likely that it will not long remain one of the significant sludge disposal options.

Summary of Available Waste Management Options

Recovery Waste copper is a valuable commodity and can be easily recovered.

Precipitation by Best method for dilute streams, mixed streams, or other cases where recovery is not practical.

Dilute discharge to municipal sewers Adequate for dilute streams or mixtures only if treatment facilities can operate to meet local discharge

standards.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The installation of waste treating equipment specifically for copper sulfate and copper nitrate is not recommended for National Disposal Sites for the following reasons: (1) the inherent value of copper and its compounds has led a large proportion of the firms handling these materials to install the various types of copper recovery equipment; and (2) the transport of huge volumes of non-recyclable dilute solutions is simply too expensive. Industry will continue to treat the dilute wastes by destructive precipitation, or discharge to municipal sewers.

As stated in other Profile Reports, it is very likely that a general facility for pH adjustment and precipitation will be required to handle the waste streams generated within the Site itself. This same facility could also be used to treat various heavy metal wastes which might occasionally be sent to the site. These would include waste mixtures containing chromium, zinc, nickel, lead, mercury, copper and other metals.

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HAZARDOUS WASTES PROPERTIES WORKSHEET			
H. in. Name <u>Copper sulfate</u> (122) IUC Name <u>Copper II sulfate pentahydrate</u> Common Names Blue Vitriol, Chalcanthite (1)	Structural Formula CaSO ₄ - 5H ₂ O		
Molecular Wt. 249.68 ⁽¹⁾ Melting Pt. <u>-4</u> Density (Condensed) 2.284 @ Densit Vapor Pressure (recommended 55 C and 20 C)	(1) H ₂ O at 110C ⁽¹⁾ Boiling Pt. <u>-5H₂O at 150</u> C y (gas)@		
Flash Point Autoignition Tem Flammability Limits in Air (wt %) Lower none Explosive Limits in Air (wt. %) Lower none	Upper <u>none</u>		
Solubility Cold Water 31.6g/100 cc at 0 C(1) Others:	100 c(1)		
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in Barrels, drums, boxes, bags, bottles ICC Classification No label required Co Comments	ast Guard Classification		
References (1) 1570			
(2) 0766			

HAZARDOUS WASTES PROPERTIES			
WORKSHEET			
H. M. Name <u>Copper nitrat</u> e (121) Structural Formula			
IUC Name Copper II Nitrate, trihydrate			
Common Names Cu(NO ₃) ₂ · 3H ₂ O			
Molecular Wt. $\frac{241.60^{(1)}}{2.32 \text{ g/cc}^{(1)}}$ Melting Pt. $\frac{114.5 \text{ C}^{(1)}}{2.32 \text{ g/cc}^{(1)}}$ Boiling Pt. $\frac{-\text{HNO}_3 \text{ at } 170 \text{ C}}{2.32 \text{ g/cc}^{(1)}}$ Density (gas)			
Vapor Pressure (recommended 55 C and 20 C)			
Flash Point Autoignition Temp			
Flammability Limits in Air (wt %) LowerUpper Explosive Limits in Air (wt. %) LowerUpper			
Solubility Cold Water 137.8 g/100 cc at 0 C(1) Hot Water 1270 g/100cc at 100 CEthanol at 125 C(1) Others: very soluble in liquid NH 3 Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification Coast Guard Classification			
Comments			
References (1) 1570			
References (1) 1570 (2) 0766			
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	HAZARDOUS WASTES PROPER WORKSHEET	RTIES	
भ. भ. Name Copper Nitrate (121)		Structural Formula	
100 Name <u>Coppér II Nitrate, hexa</u>	hydrate	Structural Tornigra	<u> </u>
Common Names		Cu(NO ₃) ₂ · 6H ₂ O	
			عث
Molecular Wt. <u>295.64⁽¹⁾</u> Density (Condensed) 2.074 g/cc ⁽¹⁾ @	Melting Pt3H ₂ O at	26.4 C ⁽¹⁾ Boiling Pt. N/A	·
Density (Condensed) $2.074 \text{ g/cc}^{(1)}$ e	N/A Density (gas	6	
Vapor Pressure (recommended 55 C a	nd 20 C)		
(ð.			
	Autoignition Temp		
Flammability Limits in Air (wt %)	Lower	Upper	
Explosive Limits in Air (wt. %)			
Solubility Cold Water 243.7 g/100 cc at	(1) O C Hot Water infini	te ⁽¹⁾ Ethanol solubl	e ·
Others:			
Acid, Base Properties			
Highly Reactive with			
Compatible with			
Shipped in			
ICC Classification	Coast Gu	ard Classification	· · · · · · · · · · · · · · · · · · ·
Comments	<u> </u>		
References (1) 1570	•	•	

PROFILE REPORT

Hydrazine (212)

GENERAL

Hydrazine is a clear, oily, water-white liquid with an odor similar to that of ammonia. It is a strong reducing agent, weakly alkaline and very hygroscopic. It will react with carbon dioxide and oxygen in air. Exposure of hydrazine to air on a large surface (as on rags) may result in spontaneous ignition from the heat evolved by its oxidation with atmospheric oxygen. With water it forms the diamide hydrate, $\rm H_2NNH_2$. $\rm H_20$. $\rm 1300$

Hydrazine is formed by reacting equimolar quantities of sodium hypochlorite and ammonia in an alkaline solution to give chloroamine (NH₂Cl). This reacts at elevated temperature with ammonia to give hydrazine:

$$NH_3$$
 + $NaOC1$ + $NaOH$ + NH_2C1
 NH_3 + NH_2C1 + $NaOH$ + N_2H_4 + $NaC1$ + H_2O

A side reaction occurs which leads to the decomposition of hydrazine:

$$2NH_{2}C1 + N_{2}H_{4} \rightarrow N_{2} + 2NH_{4}C1$$

This side reaction is catalyzed by dissolved chloride. Gelatin, glue, amino acids or simple peptides are added to complex the chlorides. 1157 Hydrazine is recovered from aqueous solution by distilling water until the still bottoms approach the composition of hydrazine hydrate. The hydrate is either treated with sodium hydroxide at a temperature above the boiling point of hydrazine and the hydrazine distilled and collected, or treated with aniline which is used to effect removal of the water by azeotropic distillation. 1433

Hydrazine is used in jet and rocket fuels, intermediates for

agricultural chemicals, antioxidants, textile chemicals, explosives, photographic developers, blowing agents, scavengers for chlorine in hydrogen chloride, corrosion inhibitors and scavengers for oxygen.

The chemical and physical properties for hydrazine are summarized in the attached worksheet.

TOXICOLOGY

Hydrazine is a strong irritant and may damage the eyes and cause respiratory tract irritation. If spilled on the skin or eyes, liquid hydrazine can cause severe local damage or burns and can cause dermatitis. It can penetrate the skin. If inhaled, the vapor causes local (irritation of eye and respiratory tract) and systemic effects. For long exposure, systemic effects involve the central nervous system. On exposure to higher concentrations, convulsions and possibly death follow. Repeated exposures may cause toxic damage to the liver and kidney, as well as anemia. 1300, 1993

The exposure limits recommended are as follows: 1300

Threshold limit (ACGIH) $-1.0 \text{ ppm} (1.3 \text{ mg/m}^3)$

Emergency exposure limits -

 $10 \text{ min} - 30 \text{ ppm} (39 \text{ mg/m}^3)$

30 min - 20 ppm (26 mg/m^3)

60 min - 10 ppm (13 mg/m^3)

OTHER HAZARDS

Hydrazine is flammable over a broad range of concentrations: 4.7 to 100 percent. It is hypergolic with some oxidants, such as hydrogen peroxide, nitrogen tetroxide, fluorine, halogen fluorides, and nitric acid. A film of hydrazine in contact with metal oxides, such as those of iron, copper, lead, manganese and molybdenum, may ignite owing to the heat of chemical reaction. Hydrazine vapors in a closed system may explode when exposed to air. In the presence of finely-divided or other high surface area forms of some metal or metal oxides, hydrazine dissociates into nitrogen, hydrogen and ammonia.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Adequate procedures for the safe handling, transportation and storage of hydrazine are described in two publications, 1300,1993 and in the military specification for hydrazine, MIL-P-2705. 1995 Hydrazine is classified by Department of Transportation (DOT) as a corrosive liquid and is shipped under a White Label. Under DOT specifications hydrazine may be shipped in 1-gal. glass bottles packed in cans, in metal barrels or drums of 304 or 347 stainless steel, or in tank cars of 304L, 347 stainless steel, aluminum 103A AL-W, or aluminum 111A100-W-6.

Hydrazine as a waste will generally be encountered as excess material, as contaminated material from spills, or in aqueous streams from chemical process industries. Because of the hazards involved (unpredictable decomposition), hydrazine is usually not recovered in a concentrated form from contaminated or dilute systems. In ponds or holding tanks dilute hydrazine is decomposed by the air and bacteria into nitrogen, hydrogen, water and ammonia. In a concentrated form, hydrazine is destroyed by burning.

The safe disposal of hydrazine is defined in terms of the recommended provisional limits in the atmosphere, water and soil. These recommended provisional limits are as follows:

Contaminant in Air	<u>Provisional Limit</u>	Basis for Recommendation
Hydrazine	0.01 ppm	0.01 TLV
Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Hydrazine	1.0 ppm	Quantity will rapidly oxidize to near-zero concentration

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Hydrazine is generally destroyed by oxidation to water and nitrogen. In dilute solution, dissolved oxygen, catalysis, or bacterial action convert hydrazine to nitrogen, hydrogen, ammonia and water. Therefore, there are no problems in dealing with the products from waste treatment. Current disposal practices for hydrazine are briefly described in the following paragraphs together with recommendations as to adequacy.

Option No. 1 - Open Pit Burning

Hydrazine poured into an open lined pit is burned to nitrogen and water. The transfer of the hydrazine and the ignition must be accomplished by a remote means. 1300 For drum quantities of hydrazine this method is generally acceptable although since excessive NO $_{\rm X}$ might be generated another option would be preferred.

Option No. 2 - Incineration

The Air Force has a minimum of ten trailer-mounted incinerators capable of incinerating up to 6 GPM of hydrazine in a variety of mixtures with water (from 100 percent hydrazine to 100 percent water). The effluents from the units is limited to 0.03 lbs/min NO_X when incinerating hydrazine. These units are acceptable for disposing of large quantities of hydrazine.

Option No. 3 - Catalytic Decomposition

One of the applications for hydrazine is its use as a monopropellant. When hydrazine is passed over a support (usually aluminum oxide) coated with certain metals or metal oxides, it is decomposed into nitrogen, hydrogen and ammonia. The details of catalyst composition are usually found in the classified literature. In most cases the catalyst is expensive, but TRW Systems has preliminary data on a low cost catalyst that should be further investigated.

Option No. 4 - Diluting with Water and Holding

If hydrazine is diluted with water, e.g., after spills, and placed in open lined ponds or holding tanks, the hydrazine is decomposed to water, nitrogen, and ammonia by air oxidation and bacterial action. For small quantities of hydrazine in aqueous solution this method is acceptable if adequate space is available.

Option No. 5 - Chemical Treatment

Small quantities and dilute solutions are collected in open containers and treated with oxidizing compounds such as 10 percent hydrogen peroxide or calcium hypochlorite. The oxidizing agents should be applied slowly until in excess. This method is not recommended except for small quantities because considerable heat is liberated during decomposition.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Hydrazine does not appear to be a candidate waste stream constituent for National Disposal Sites. It is anticipated that packaged hydrazine and hydrazine in aqueous waste streams will continue to be treated at the source of waste generation. The major products of combustion or decomposition are the elements, water, or ammonia which do not present a secondary disposal problem.

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HAZARDOUS WASTES PROPER WORKSHEET	TIES
H. M. Name <u>Hydrazine</u> (212)	Structural Formula
IUC Name <u>Hy</u> drazine	Structural Formula
Common NamesDiamine	
	N ₂ H ₄
W. J	
Molecular Wt. 32.05 Melting Pt. 1.5 Density (Condensed) 1.008 g cc @ 20 C Density (gas	Boiling Pt. 113.5
Vapor Pressure (recommended 55 C and 20 C)	,
0.07 psia @ 40 F 0.36psia @ 80	F 2 9ncin
Flash Point 52. C Autoignition Temp.270	
Flammability Limits in Air (wt %) Lower 4.7%	
Explosive Limits in Air (wt. %) Lower	
Solubility	
Cold Water Miscible Hot Water Miscible	eEthanol Miscible
Others: acetone - miscible	:
Acid, Base Properties $N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$ K	= 8.5 x 10 ⁻⁷
Highly Reactive with Acids, metal oxides	
Compatible with Stainless steel, aluminum	
Compactione with Section 23 Section 3 Telephone	
Shipped in Bottles, drums, tank cars	
ICC Classification Corrosive Liquid, White Label Coast Guard	White Label ard Classification Corrosive Liquid
Comments	
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trial and Municipal Disposal Candidate Waste Stream Com	
Profile Reports - Inorganic Compounds	
7. Author(s) R. S. Ottinger, J. L. Blumenthal, D. F. Dal Por G. I. Gruber, M. J. Santy, and C. C. Shih	rto, 8. Performing Organization Rept. No. 21485-6013-RU-00
9. Performing Organization Name and Address	10. Project/Task/Work Unit No.
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TRW Systems Group, One Space Park	11. Contract/Grant No.
Redondo Beach, California 90278	50,00,000
	68-03-0089
12. Sponsoring Organization Name and Address National Environmental Research Center	. 13. Type of Report & Period Covered
Office of Research and Development	Final
U.S. Environmental Protection Agency	14.
Cincinnati, Ohio 45268	
15. Supplementary Notes	
Valuma VII of 16 valumas	
Volume XII of 16 volumes.	
This volume contains summary information and evaluation	n of waste management methods in
constituents. Each Profile Report contains a discussion of the waste stream constituents, their toxicology and definition of adequate management for the waste material waste management practices with regard to their adequate	other associated hazards, the al, an evaluation of the current
most appropriate processing methods available and wheth considered as a candidate for National Disposal, Industrian Disposal.	her the waste material should be
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