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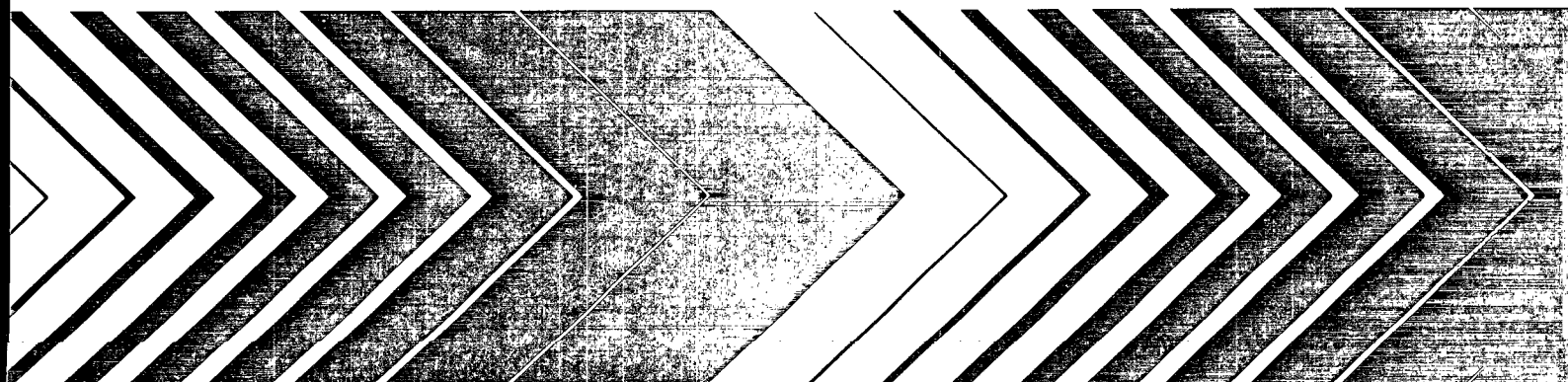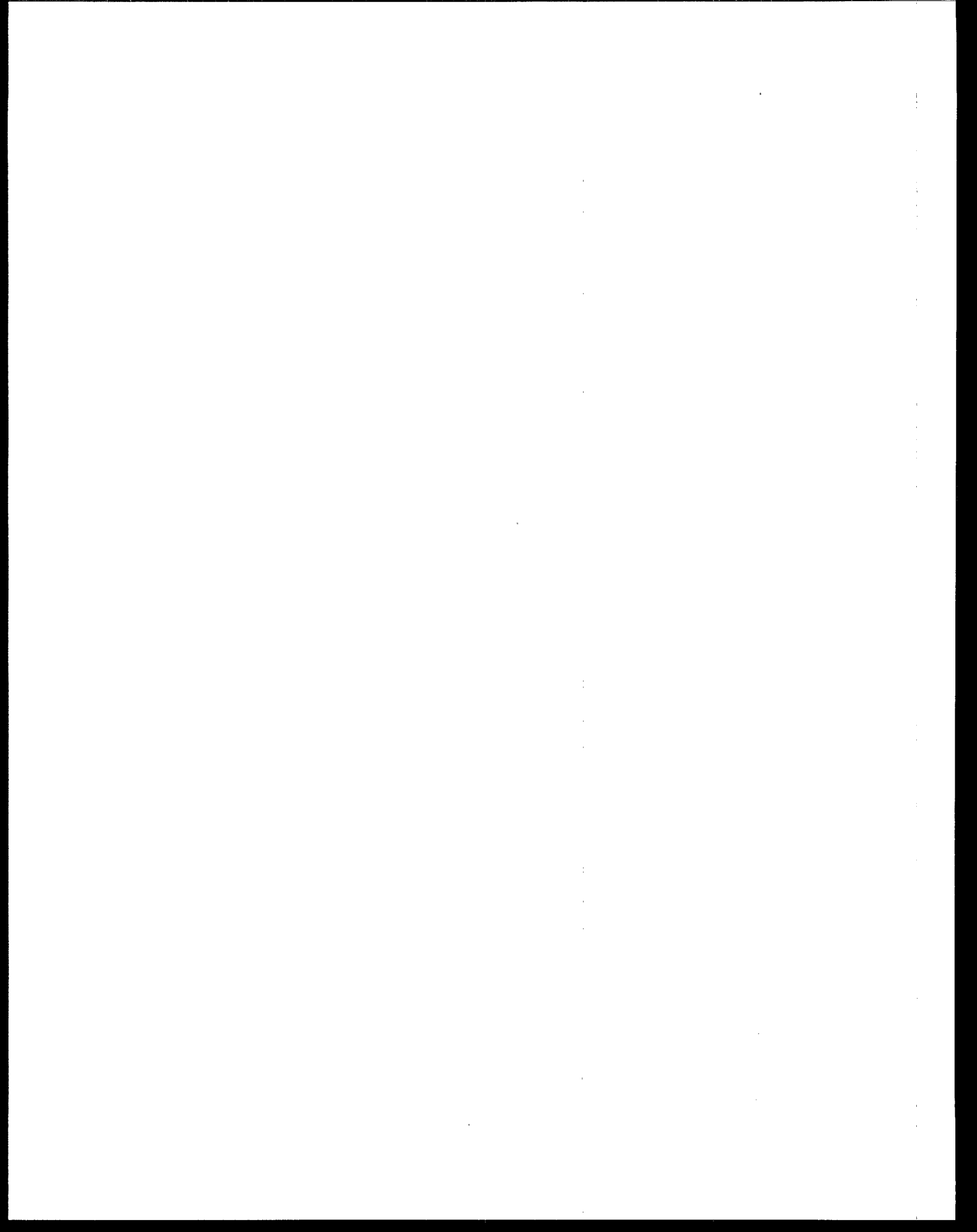
Arsenic & Mercury

Workshop on Removal, Recovery, Treatment, and Disposal

Abstract Proceedings

Alexandria, Virginia
August 17-20, 1992

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ARSENIC AND MERCURY
WORKSHOP ON REMOVAL, RECOVERY, TREATMENT, AND DISPOSAL

Abstract Proceedings

Coordinated by:

Science Applications International Corporation
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Work Assignment Managers:

Ronald J. Turner
Risk Reduction Engineering Laboratory
Office of Research and Development

José Labiosa
Waste Management Division
Office of Solid Waste and Emergency Response

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

WASTE MANAGEMENT DIVISION
OFFICE OF SOLID WASTE AND EMERGENCY RESPONSE
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

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FOREWORD

Today's rapidly developing technologies and industrial practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous waste, and Superfund-related activities. This publication is one of the products of that research and provides a vital communications link between researchers and users.

The workshop on removal, recovery, treatment, and disposal of arsenic and mercury wastes was convened to provide a forum for the exchange of state-of-the-art information among industrial, commercial, and academic experts and the EPA's research and regulatory program offices. This Abstract Proceedings highlights the technical presentations of the workshop.

Additional information may be obtained by contacting the authors or the EPA offices.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

A workshop on removal, recovery, treatment, and disposal of arsenic and mercury wastes was held in Alexandria, Virginia on August 17 through 20, 1992. The goals of the workshop were: 1) to examine the chemical fundamentals and analytical issues related to As and Hg compounds, 2) to disseminate information of the state of practice in source reduction, in technologies that recover or remove As and Hg from industrial wastes, and recycling or reuse processes, and 3) to present a discussion of existing and emerging technologies that treat industrial wastes or contaminated soil and water, and the storage and disposal of treated wastes.

This Abstract Proceedings is organized into two sections: Session A - Arsenic and Session B - Mercury and contains extended abstracts of the paper presentations. The abstracts cover papers on fundamentals; analytical techniques/characterization; removal, recovery, and reuse; and treatment, storage, and disposal.

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INTRODUCTION TO ARSENIC CHEMISTRY AND ANALYSIS

Edwin A. Woolson
EPL Bio-Analytical Services, Inc.
395 N. Memorial Parkway
Harristown, IL 62537
USA
Tel: (217) 963-2143

Arsenic at waste sites may be present from many natural or man-made sources. In all cases, the arsenic present may be subject to metabolism and/or movement (1) through or from the site.

Arsenic occurs naturally in about 245 mineral species (2). These range from the native element or alloys to arsenides, sulfides, sulfosalts, and oxidation products (oxides, arsenites, and arsenates). In addition, a variety of complex organoarsenic compounds may be present at sites containing waste from coal utilization or oil production.

These compounds can oxidize in aerated soil to arsenates and be subsequently reduced to arsenites, various alkylarsines, and trimethylarsine oxide (TMAO). The arsines are volatile and can become dispersed in air to return ultimately as oceanic sediments (3). Organoarsines can be oxidized to methanarsonate or cacodylate. These are a part of the natural cycling of arsenic in the environment. These reactions are a result of oxidation, reduction, and microbial activity.

In sampling for arsenic residues, the nature of the residues expected based on past contamination or environmental concerns must be considered in choosing sample-handling techniques. For instance, if the only concern is how much arsenic is present and not which actual species is present, then no special handling techniques need be employed. However, if differences between arsenate (+5) and arsenite (+3) need to be determined, then considerable care must be taken in handling the samples. Organic arsenicals, in general, are not affected by handling during the sampling or analysis process.

To a large degree, the soil Eh determines the ratio of +3 to +5. Soil Eh is not a function of a single compound or component but of a combination of factors: e.g., iron content, pH, microbial population, and moisture content.

In general, as iron increases, arsenite/arsenate decreases. Arsenate is the predominant arsenic form in aerobic soils. Arsenite, however, is formed at Eh <300 millivolts (mV) over a pH range of 4 to 8, typical soil values. As the Eh decreases due to flooding or a variety of conditions, the arsenite content increases while arsenate decreases. With active microbial populations, some reduction of cacodylic acid or methanearsonic acid to volatile alkylarsines is frequently observed.

What does this imply for waste site arsenic determinations? If the concern is whether the arsenic present is arsenite, the Eh and pH should be measured at the time of sampling. If Eh is >300 mV, arsenate will be predominant and no precautions to prevent oxidation should be necessary (2). If however the Eh is <300 mV, care must be taken to prevent oxidation after sampling. The container may be purged with nitrogen. The sample must be analyzed as quickly as possible since oxidation/reduction can occur even when the sample is frozen. Lowering the temperature slows the reaction.

If the sample is aqueous instead of solid, the addition of ascorbic acid will slow the oxidation of arsenite to arsenate (4, 5). Analysis should be performed as soon after sampling as possible.

After obtaining and preparing the sample, the effect of the extractant on changes in the arsenic species must be considered. Oxidizing reagents such as sulfuric or nitric acids will oxidize arsenite to arsenate. Dilute aqueous salts or non-oxidizing acids (e.g., hydrochloric, phosphoric acids) will not significantly affect the +3 to +5 ratio, although as with sampling, samples should be processed quickly. Arsenite will convert to arsenate with time. The extractant will not change the organic arsenicals to inorganic unless acid digestion is employed, in which case all arsenicals are converted to arsenate.

In aqueous 8 normal (N) hydrochloric acid (HCl) extracts, benzene (and perhaps toluene) will extract arsenite but not arsenate. This extract can then be back-extracted with water to allow separation of arsenate and arsenite.

Following extraction, a cleanup separation is frequently necessary depending on the analysis technique to be used. Metals may be extracted with organic complexation reagents (e.g., dithiazone, quinolinol sulfate) depending on which metals are causing the difficulty. For example, high iron (Fe) levels in extracts will interfere in liquid chromatographic separations of arsenite/arsenate. Iron complexed with quinolinol sulfate can be adsorbed by charcoal and removed as an interferant (6). Aluminum on the other hand is not removed.

The necessity for removal of interfering cations will depend on the metals present at specific sites. Metals which may interfere include but are not limited to: lead, Fe, copper, cobalt, manganese, and calcium. The degree of interference is probably related to the amount of arsenic in solution due to solubility product considerations and will vary at every site.

Detection methods for environmental analysis generally require nanogram to microgram detection ranges (3). One of the detection methods frequently used involves hydride generation (7, 8). The hydrides after generation may then be trapped on glass beads using liquid nitrogen (5, 9). Detection can be by DC discharge (7), microwave emission (10), electron capture, or flame ionization (11) on a gas chromatograph following differential heating.

Arsenite is converted to arsine by sodium borohydride at any pH, whereas arsenate is reduced at pH <4.0. In practice, arsenite is determined at pH >5 and arsenate, methanearsonate, cacodylate, and TMAO are converted to their respective arsines at pH 1.5 (3).

Another means of separating arsenicals involves ion exchange column chromatography. An AG 50W-X8 cation exchange resin (12) can be used to separate arsenicals. At pH >1.5, arsenite and arsenate elute before methanearsonate, followed by cacodylate. Using a mixed resin, AG 1-X8 (100 to 200 mesh), the order of elution is arsenite < methanearsonate < arsenate < cacodylate (13).

Ion chromatography may be interfaced with a quartz furnace detecting a continuous hydride flow by atomic absorption spectroscopy. In this instance, elution order proceeds: cacodylate < arsenite < methanearsonate < arsanillate < arsenate (14).

A refinement of the technique involves High-Performance Liquid Chromatography (HPLC) in combination with graphite furnace atomic absorption (15-17). An intermediate strength anion exchange column is eluted with a water to 0.2 molar ammonium carbonate using a gradient (6). The effluent is passed through a sample cup which holds 50 microliters before going to waste. The flowing sample stream is sampled at about 50-second intervals and the graphite furnace fired. The peaks resulting from furnace firings are summed, the background subtracted, and response factors calculated. The elution order for this system is: TMAO < arsenite < cacodylate < methanearsonate < arsenate. This technique has been used to analyze soil and water samples.

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ARSENIC CHEMISTRY IN RELATION TO THE DISPOSAL AND STABILITY OF METALLURGICAL EXTRACTION WASTES

Robert G. Robins
HydroMet Technologies Limited
31-45 Smith Street
Marrickville NSW 2204
Australia
Tel: 61 2 517 1188
Fax: 61 2 519 9468

The work which is summarised in this presentation was conducted mostly at the University of New South Wales while the author was Head of the Department of Mineral Processing and Extractive Metallurgy. He is now Visiting Professor at the Centre for Minerals Engineering at the same university where the work on arsenic stabilisation is being continued as one of the projects in an Australian Government sponsored Co-operative Research Centre for Waste Management and Pollution Control. The project on Stabilisation of Arsenic Wastes is costed at $1.85M AUD over the 3-year period commencing in 1992.

Most of the material used in this presentation is described in detail in the publications (1-21) cited in the references.

ARSENIC HYDROMETALLURGY (9-14)

The removal of arsenic from process solutions and effluents has been practised by the mineral process industries for many years. Removal by existing hydrometallurgical techniques is adequate for present-day product specifications but the stability of waste materials for long-term disposal will not meet the regulatory requirements of the future. This presentation reviews briefly the aqueous inorganic chemistry of arsenic as it relates to the hydrometallurgical methods that have been applied commercially for arsenic removal, recovery, and disposal, as well as those techniques which have been used in the laboratory or otherwise suggested as a means of eliminating or recovering arsenic from solution.

The various separation methods include: oxidation-reduction, precipitation and thermal precipitation, coprecipitation, adsorption, electrolysis, solvent extraction, ion exchange, membrane separation, precipitate flotation, ion flotation, and biological processes. The removal and disposal of arsenic from metallurgical process streams will become a greater problem as minerals with much higher arsenic content are being processed in the future.

PRECIPITATION OF ARSENIC (1-6, 10, 12, 18)

The insolubility of certain inorganic arsenic(III) and arsenic(V) compounds is the basis of most hydrometallurgical arsenic-removal processes and the insoluble product is often the disposed material. Recently it has been shown that these disposal residues are unstable and will produce a leachate that contains arsenic.

The most common method of removing arsenic from aqueous process streams is to precipitate the sulfide As_2S_3, or calcium arsenate or ferric arsenate. The sulfide has its lowest solubility below pH = 4 but that solubility is significantly higher than has been generally accepted. The sulfide is not usually the form disposed in residues as it is easily oxidised, however there have been attempts to use As_2S_3 in landfill in which anaerobic conditions are maintained and also in cement cast admixes. Recent work on biological formation of arsenic sulfides may have an application in treating process residues.

There are a number of calcium arsenates that can be precipitated from arsenic(V) solutions. At high pH, obtained by lime addition in excess, arsenic concentrations can be reduced to <0.01 mg/L. Those calcium arsenates which are precipitated at pH >8 are not stable with respect to the carbon dioxide in the atmosphere converting them into calcium carbonate with release of arsenic to solution.

Arsenic(V) can be precipitated from process solutions below about pH = 2 with iron(III) to form ferric arsenate, $FeAsO_4.2H_2O$ (scorodite). At low precipitation temperatures the compound is very small in particle size (~ 10nm) and is X-ray amorphous. At temperatures above about 90 degrees C the precipitated compound is crystalline (>100nm) and has a solubility about two orders of magnitude lower than the amorphous material (particle size effect). Ferric arsenate exhibits incongruent solubility at pH > about 2 and will convert very slowly to ferrihydrite, which initially has extremely small particle size (~5nm) and a stoichiometry near $Fe_2O_3.2H_2O$.

The ferrihydrite is in fact "arsenic-bearing ferrihydrite" since it strongly adsorbs the released arsenic, and at least in the short term prevents high arsenic solution levels. Ferric arsenate is therefore not stable in the neutral to high pH region and so is not suited for direct disposal. Ferric arsenate is also not stable in alkaline cement cast admixes.

There are other metal arsenates, such as those of Fe(II), Zn(II), Cu(II), and Pb(II), which are less soluble (and more stable) in the neutral pH region than the calcium arsenates or ferric arsenate, but these have not been seriously considered as disposal forms. Iron(II) arsenate should be investigated further in this respect.

ADSORPTION OF ARSENIC ON FERRIHYDRITE (15, 21-23)

Much attention has been directed to the removal of arsenic from hydrometallurgical process solutions and wastewaters by precipitation and coprecipitation with iron(III). At high concentrations of iron(III) and arsenic(V) and at low pH, precipitation results in the formation of ferric arsenate, $FeAsO_4.2H_2O$. At low concentrations of arsenic(V) and high iron(III) concentrations the coprecipitation of arsenic with ferric hydroxide occurs and is probably the most effective method of removal of arsenic from aqueous solutions and leads to a solid phase that is stable at least for a year or so. The solid coprecipitate has been referred to as "basic ferric arsenate" and in 1985 a controversy began as to whether the coprecipitated material was in fact a compound of iron(III) and arsenic(V) or simply an adsorptive binding of arsenic with ferric oxyhydroxide. There was at that time sufficient evidence to support the latter contention, but the use of the term "basic ferric arsenate" still exists and formulae such as $FeAsO_4.xFe(OH)_3$ are used.

Recently, EXAFS studies have shown that in these materials arsenic(V) is adsorbed to ferrihydrite as a strongly bonded inner-sphere complex with either monodentate or bidentate attachment. Monodentate attachment apparently occurs near the optimal pH 4 to 5 for adsorption.

The adsorption of arsenic(III) on ferrihydrite has also been investigated and although it seems an efficient process there is no evidence that the adsorbed species is arsenic(III). It may be that during the process, air oxidation of arsenic(III) will occur with some ease, as has been shown in preliminary experiments.

TESTING FOR LONG-TERM STABILITY

Testing methods for evaluating the stability of hazardous waste residues have been defined by the US Environmental Protection Agency (EPA) in several "Background Document for Toxicity Characteristic Leaching Procedure" publications. The test methods do not adequately assess the long-term stability of arsenical residues. Improved test methods must be designed which also include a characterisation of physical properties and chemical components (mineralogy) so that predictions of behaviour can be made.

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ARSENIC: SUPPLY, DEMAND, AND THE ENVIRONMENT

J. Roger Loebenstein
US Bureau of Mines
810 7th St. NW
Mail Stop 5208
Washington, DC 20241-0002
USA
Tel: (202) 501-9416

SUPPLY

Arsenic is recovered as a byproduct of processing certain complex ores that are mined mainly for copper, lead, zinc, gold, and silver, and its supply is dependent to a large extent on the demand for these metals. In addition, the supply of arsenic is affected by environmental constraints and the economics of producing a relatively low-value byproduct from low-grade source materials. In general arsenic is regarded as a troublesome impurity in smelting and refining and thus high-arsenic source materials may be penalized at the smelter and refinery or avoided at the mine.

Arsenic trioxide (As_2O_3 or white arsenic), the most important commercial compound, is currently produced principally in Belgium, Chile, China, France, Mexico, the Philippines, and the former USSR, as shown in Table 1. Table 1 shows a country as a producer if that country produced at least 3,000 metric tons in any of the years shown. Currently, the two largest producers are Chile and China. Both countries are expected to increase production capacity progressively over the next few years.

TABLE 1. MAJOR PRODUCERS OF ARSENIC TRIOXIDE (Metric Tons)

Country	1971	1981	1991
Belgium[e]	---	3,000	3,000
Chile	---	---	7,000
China[e]	---	---	10,000
France	8,023	[e]5,200	3,000
Mexico	11,483	6,517	4,960
Philippines	---	---	5,000
Sweden	17,450	6,900	2,500
U.S.S.R.[e]	7,150	7,750	7,000
United States	9,000	7,800	---

[e]Estimated.

Many changes have occurred in producing countries over the last year. Historically Sweden has been an important producer, but production was permanently shut down in 1991, reportedly for environmental reasons. In addition, a Finnish producer ceased operations in 1991 because of low prices for arsenic trioxide. In France one of the two major producers of arsenic trioxide from gold ores, Salsigne, declared bankruptcy. The producers in Mexico and Belgium are under increased pressure to reduce production by governments concerned with environmental problems associated with arsenic and its potential release to the environment.

The result of many developed countries cutting back production has been to spur lesser developed countries to increase production to fill the supply shortfall. For example, US imports of arsenic trioxide from China have grown from nothing in 1989, to about 1,100 metric tons in 1990, and finally to about 7,100 metric tons in 1991, representing over one-fourth of total US arsenic trioxide imports. Consumers report that the Chinese arsenic is generally poor in quality, 97 to 98% pure, and contains a high degree of moisture and

foreign material, such as rocks and pebbles. However, in future years, China will probably improve its quality control rather than risk losing its customers. China is believed to be the only country in the world that produces arsenic trioxide directly from arsenic ores.

Chile was the second largest source of arsenic trioxide imports in 1991, providing slightly less than one-quarter of total US imports. Cia. Minera San José Ltd. produced arsenic trioxide as a byproduct of gold-copper ores roasted at its El Indio smelter. The company is expected to increase production when a new roaster is added to its smelter, sometime in the next year.

For many years, until 1985, arsenic trioxide was produced in the US at ASARCO Incorporated's smelter in Tacoma, WA. The area surrounding the smelter is currently a Superfund site being cleaned up under Environmental Protection Agency (EPA) supervision.

Nearly 80% of ASARCO'S arsenic trioxide production in 1981 was derived from high-arsenic copper concentrates imported from the Philippines. The rest of the arsenic was produced from domestic copper concentrates. When ASARCO shut down in 1985, production was shifted from the US to the Philippines, as shown in Table 1.

DEMAND

All arsenic consumed in the US in 1991 was derived from imported sources. The most important arsenic chemical imported was arsenic trioxide, with minor amounts of arsenic acid and arsenic sulfide imported as well. Demand for arsenic is shown in Table 2. As can be seen, the decline in agricultural chemicals has been made up by the increase in wood preservative use.

TABLE 2. ESTIMATED US DEMAND FOR ARSENIC (Metric Tons, Arsenic Content[1])

	1971	1981	1991
Agricultural chemicals (herbicides, desiccants)	15,600	8,900	5,000
Glass	2,000	1,000	900
Industrial chemicals (wood preservatives)	970	9,100	14,300
Nonferrous alloys and electronics	570	600	1,000
Other	500	400	400
Total	19,640	20,000	21,600

[1]Arsenic trioxide contains 75.7% arsenic by weight.
Source of data: U.S. Bureau of Mines, Arsenic chapter from Mineral Facts and Problems, 1980 and 1985 editions, and author's estimates for 1991.

Arsenic trioxide was imported and then converted to arsenic acid for use in the production of arsenical wood preservatives by three major companies: Hickson Corp., CSI, and Osmose Corp.

Hickson International PLC, Castleford, UK, the parent company of Hickson Corp., has wood preservative plants in Australia, New Zealand, the Republic of South Africa, and the UK, as well as in the US.

LaPorte PLC, UK, is the parent company of CSI, Mineral Research and Development, and Rentokill. CSI manufactures wood preservatives in the US, and Mineral Research and Development formulates arsenical pharmaceuticals for veterinary purposes in the US. Rentokill produces wood preservatives in Liverpool, UK.

Only a few agricultural uses for arsenic remain. ISK Biotech (formerly Fermenta Corp.), Mentor, OH, produced the arsenical herbicide monosodium methanearsonate (MSMA) at a plant in Houston, TX. Atochem Corp., Bryan, TX, was a major producer of arsenic acid for use by cotton growers and wood preservative companies. A company in Israel, Luxembourg Chemicals & Agriculture Ltd., produced sodium cacodylate, an arsenical used as a bait preparation against ants.

Minor amounts of arsenic acid are used by glass companies such as Corning Glass, Corning, NY. Arsenic in the form of arsenic acid is used as a fining agent to disperse bubbles that tend to form when certain types of glass are produced. As a result of EPA regulations that became effective in 1986, arsenic emissions from glass furnaces have been reduced. As shown in Table 2, arsenic usage by the glass industry has declined since 1971.

Chromated copper arsenate (CCA) is the most common arsenic- based wood preservative. Other arsenic-based wood preservatives include ammoniacal copper arsenate (ACA) and fluor chrome arsenate phenol (FCAP). Arsenic trioxide is also used as a reagent in ore flotation.

During the 1930s and 1940s, an estimated 45,000 metric tons of arsenic-based insecticides were used annually in the compound Paris green (copper acetoarsenite) and the arsenates of calcium, chromium, lead, and sodium (1). For many years, until the late 1970s, agricultural chemicals were the most important end use for arsenic, but in the future, because of environmental problems, agricultural chemical use will probably decline to a negligible amount. The only two remaining major agricultural uses for arsenic are as herbicides (MSMA and DSMA) for control of weeds and arsenic acid to aid in the mechanical harvesting of cotton in Oklahoma and Texas. Depending on weather conditions during the cotton harvest, more or less arsenic acid is used. An early frost tends to help dry cotton bolls and reduce arsenic acid consumption.

ENVIRONMENTAL REGULATION

Arsenic has long posed environmental problems because of its well known toxicity, and more recently as a result of the Government's finding that inorganic arsenic is a human carcinogen. Most of the published literature on arsenic emissions dates back to the mid-1970's when the EPA studied the US nonferrous smelting industry and the arsenic industry in depth. In 1978, the Occupational Safety and Health Administration (OSHA) promulgated the final standard on the occupational exposure to inorganic arsenic. OSHA had concluded that inorganic arsenic was a carcinogen and that worker exposure had to be limited. In 1980, EPA listed inorganic arsenic as a hazardous air pollutant, based on its findings that inorganic arsenic was carcinogenic to humans, and that there was significant public exposure to the pollutant. In 1983, EPA estimated that over 85% of the 1,200 tons per year of atmospheric arsenic emissions came from copper smelters and glass manufacturing plants. EPA identified other source categories for which standards were not proposed: primary lead and zinc smelters, zinc oxide plants, arsenic chemical manufacturing plants, cotton gins, and secondary lead smelters (2).

As a result of the necessity to comply with Federal and local regulations on atmospheric emissions of sulfur dioxide and arsenic, ASARCO closed its copper smelter and associated arsenic recovery plant at Tacoma, WA, in 1985. At that time, ASARCO was the only producer of arsenic in the US. Currently, there is no arsenic produced in the US.

EPA regulates the uses of inorganic arsenic under provisions of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (3). A pesticide product may be sold or distributed in the US only if it is registered or exempt from registration under FIFRA. Before a product can be registered as a pesticide, it must be shown that it can be used without "unreasonable adverse effects on the environment", and without causing "any unreasonable risk to man and the environment taking into account the economic, social and environmental costs and benefits of the use of the pesticide". It is then the responsibility of the proponent of initial or continued registration to prove that the pesticide meets the risk and benefit standard of FIFRA above. If at any time EPA determines that a pesticide does not meet this standard for registration, EPA may cancel the registration under Section 6 of FIFRA.

In 1986, EPA issued its final rules on arsenic emissions from copper smelters and glass manufacturing plants. In the following year, EPA issued its preliminary position to cancel most of the nonwood pesticide uses for inorganic arsenicals. Included in the list were lead arsenate, calcium arsenate, sodium arsenite, sodium arsenate, and arsenic trioxide.

Registrations for lead arsenate, calcium arsenate, and sodium arsenite have been voluntarily canceled. The sole registrant of the growth regulator use of lead arsenate requested voluntary cancellation in 1987; the registrant of products containing calcium arsenate requested voluntary cancellation in 1989; and the registrant of products containing sodium arsenite requested voluntary cancellation in 1990 (4).

In 1991, EPA announced its preliminary decision to cancel the registration of products containing arsenic acid used as a desiccant on cotton. EPA provided for a period of hearings before making its final

decision (4). EPA estimated that current usage of arsenic acid is 2 to 3 million pounds per year, representing 5 to 10% of total US acreage (3). Using 2.5 million pounds as an estimate, this quantity represents a usage of about 1,130 metric tons of arsenic acid per year (containing about 600 metric tons of arsenic). Subtracting 600 from the 5,000 metric tons for agricultural chemicals shown in Table 2 indicates that about 4,400 metric tons of arsenic were used in herbicides in 1991.

ENVIRONMENTAL PROBLEMS

In January 1992, a Panamanian ship traveling from New York to Baltimore via the Delaware Bay encountered a storm off the coast of Cape May, NJ, and lost four containers of arsenic trioxide weighing a total of 75 metric tons. Subsequently, the Justice Department filed suit against the owner of the Panamanian freighter to help pay for the cleanup. Some $2.7 million in Superfund cleanup money has been approved by EPA to help cover the costs of the extensive search and recovery of the arsenic- containing drums. Total cost of recovery is estimated at about $5 million. To date, only some of the drums have been recovered. The Commerce Department has prohibited fishing in the vicinity of the spill.

Joseph Brown, a toxicologist with California's Environmental Protection Agency in Berkeley, has recommended that California's Department of Health Services lower its 50 parts per billion (ppb) drinking water standard and establish an even lower regulatory goal of 2 parts per trillion arsenic (5). The 50 ppb is the current Federal standard. A new risk assessment by California's EPA indicates that lifetime consumption of drinking water with levels of arsenic at 50 ppb presents a one-in-100 risk of cancer.

In California, hazardous water has been found primarily in 200 deep wells in Kings, Kern, San Joaquin, and Sonoma counties. The arsenic is believed to enter water supplies from underground deposits in highly porous rock where wells are often drilled, particularly in desert areas and near mountains.

ENVIRONMENTAL STUDIES

The Bureau of Mines is in the process of conducting a series of material balance studies which examine all stages of the flow of materials: from extraction through processing, manufacture of products, use of products, and finally disposal. In these studies, estimates are made of the amounts of material lost at several points along the flow.

Figure 1 is a preliminary drawing of the US materials balance for arsenic in 1989. The figure is separated between processing and materials in use in order to show that no arsenic is consumed from domestic sources—only from imported sources.
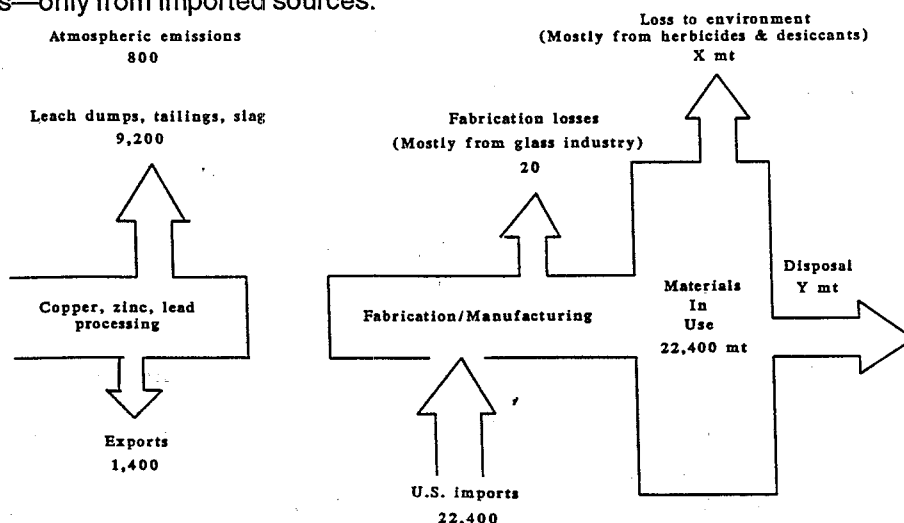
Figure 1. US materials balance for arsenic in 1989 (metric ton units).

On the processing side, arsenic is discarded in leach dumps, tailings, slag, or emitted to the atmosphere. As shown, most arsenic losses, about 10,000 metric tons per year, are emitted during the processing of copper, zinc, and lead. On the use side, estimates are still being developed to determine the quantity of arsenic dissipated to the environment and the quantity being disposed of in landfills and municipal waste dumps, as indicated by the X and Y shown in Figure 1. In 1989, based on demand estimates by the Bureau of Mines, about 4,900 metric tons of arsenic were used in herbicides and desiccants and lost to the environment in the same year in which they were used.

The problem of estimating Y shown in Figure 1 is more difficult because the quantity of arsenic disposed of in landfills depends on the useful life of the arsenical product. The useful life of treated lumber, automobile batteries, and glass products that contain arsenic can vary from 10 to 30 years. Using 20 years as an average, US demand for arsenic in 1969 (1989 less 20 years) was 16,300 metric tons for agricultural uses and 4,300 metric tons for all other uses. Therefore, Y could be about 4,300 metric tons.

SUMMARY COMMENTS

More research is needed to find ways to remove arsenic from the environment or combine it in such a way that it becomes less harmful to the environment. Arsenic is present throughout the Earth's crust and can never be completely eliminated. The cost of reducing arsenic contamination in groundwater must be weighed against its detrimental health effects.

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RECOVERY OF ARSENIC AS A RAW MATERIAL FOR REUSE (CASE STUDIES - MINING WASTES, FLUE DUSTS)

Robert D. Arsenault
Aminex Company
SE 80 Arkada Court
Shelton, WA 98584
USA
Tel: (206)427-8331

INTRODUCTION

Arsenic (As) may be recovered from a variety of byproduct sources and wastes to be used as a raw material to manufacture the arsenical wood preservatives, chromated copper arsenate (CCA) and ammoniacal copper-zinc arsenate (ACZA). The byproduct source may be crude, impure arsenic trioxide (As_2O_3) from smelter flue dust piles or it may be slimes, sludges, and filter cakes from metal refineries, speisses from smelters, arsenate solutions from manufacturing or arsenopyrite wastes and jig or float concentrates from mines. Currently, though, most CCA is made from arsenic acid, which is made from various arsenic trioxides.

In some of these byproducts the value of the copper (Cu) content may be the economic incentive to consider recovery of the Cu and As together for CCA and ACZA. In others the zinc (Zn), cobalt (Co), gold (Au), silver (Ag), or other metal content may be the economic incentive. In each case the recovery method is one designed for the specific raw material source and the contaminants to be recovered.

Crude As_2O_3 can be purified of contaminants and oxidized to arsenic acid, which is used directly to make CCA or ACZA. In this case the contaminants may be antimony (Sb), selenium (Se), bismuth (Bi), Indium (In), lead (Pb), Zn, iron (Fe), Au, Ag, sulfur (S) and copper (Cu). It may be desirable to recover some of these contaminants for their value depending on their concentration in the raw material.

Sodium arsenite or arsenate concentrates and solutions can be used directly to make copper arsenate. The arsenite is oxidized to arsenate with oxygen or hydrogen peroxide and copper sulfate is reacted in the arsenate solution to make copper arsenate [$Cu_2AsO_4 \cdot OH$ and $Cu_3(AsO_4)_2$], which is solubilized with ammonia for ACZA or solubilized with chromic acid for CCA. Care must be taken that undesirable contaminants are not present in the alkaline arsenic solution that will cause CCA or ACZA sludges or corrosion of treating plant equipment.

For example, a sodium arsenate solution byproduct from the manufacture of arsanilic acid and 3-nitro-4-hydroxy phenyl arsonic acid, which was previously wasted by reacting with lime to produce calcium arsenate, was converted to copper arsenate for the solubilization with acqueous ammonia for ACZA. However, the sodium arsenate solution had excessive chloride in it from hydrochloric acid (HCl) used in the precipitation of the 3-nitro feed additive product. The resulting copper arsenate paste for use in ammoniacal solution, even after washing, had 0.48% Cl^-, which would be a corrosion hazard for treating plant equipment and hardware on treated wood. Tests of the chloride-contaminated copper arsenate, when used in formulation to make CCA 2% treating solution, showed that 40 ppm Cl caused 0.2 mil/yr corrosion rate on carbon steel. This is unacceptable corrosion. This is equivalent to 0.2% Cl in the CCA on a 100% basis.

Some of the available crude As_2O_3 has considerable Sb. Other sources have considerable Fe. Both of these elements cause CCA sludges and/or surface residues on CCA-treated wood, and Fe causes sludges and/or surface residue on ACZA treated wood. The maximum amount of Fe that can be tolerated in CCA solution without a rapid increase in precipitation (1) is 75 ppm. The total of Fe and Pb should be limited to 100 ppm (1). Therefore, the extraction and separation processes used for crude sources of arsenic and copper for making CCA and ACZA must be tailored to avoid excessive amounts of contaminants in the arsenic acid or copper arsenate final products.

The case studies which follow are examples of how As was recovered for industrial use and other examples are given which show potential sources and purification routes.

CASE STUDY 1 - EQUITY SILVER MINE, HOUSTON, BC, CANADA

This mine has chalcopyrite ($CuFeS_2$) copper ore and tetrahedrite [$(Cu, Fe)_{12}Sb_4S_{13}$] silver ore. Associated with the tetrahedrite is tennantite [$(Cu, Fe)_{12}As_4S_{13}$] The Cu ore and Ag ore were ground to 300 mesh and leached with a sodium hydrosulfite (NaHS) sodium hydroxide (NaOH) solution (2). The leach solution contained 160 g/L NaOH and 120 g/L NaHS with 200 ppm of Cu catalyst as copper sulfate ($CuSO_4 \cdot 5H_2O$). The pH was adjusted to 8 or 9 with sulfuric acid (H_2SO_4). The pregnant leach solution contained 50 to 60 gLl Sb and 10 to 15 g/L As.

After leaching, separating from the gangue, and recovering the Cu and Ag-laden filtrate, a trace of copper quinone catalyst was added (3). Sulfur was added as sodium sulfide (Na_2S), and pressure oxidation in an autoclave with oxygen produced sodium pyroantimonate [$NaSb(OH)_6$] and sodium pyroarsenate [$NaAs(OH)_6$ (3)]. This autoclave with NaHS, NaOH, O_2, Na_2S, Na_3SbS_3, and Na_3AsS_3 yielded a filtrate containing NaOH, Na_2SO_2, Na_2SO_4, $NaAs(OH)_6$, and $Na_2S_2O_3$. The sodium pyroantimonate was insoluble and was easily filtered off with good separation. This first product was sold.

The filtrate can then be acidified with sulfuric acid to a pH of 8 and copper sulfate added to react with the $NaH_2AsO_4 \cdot 5H_2O$ that resulted from the $NaAs(OH)_6$ in solution. The copper arsenate formed [$Cu_3(AsO_4)_2 \cdot 4H_2O$ and $Cu_2AsO_4 \cdot OH$] can be recovered as filter cake, washed and sold for making CCA and ACZA. Recovery of As is usually greater than 95 to 98% by this method (4).

The filtrate can be recycled for subsequent autoclave charges until the sodium sulfate maximum solubility is reached at approximately 32° C (transition point).

CASE STUDY 2 - TEXASGULF CANADA, TIMMONS, ONT, CANADA

The Zn hydrometallurgical process utilized a zinc sulfate solution for electrolysis called electowinning. Zn electrolyte typically contained impurities of Cu, Co, Ni, and Cd. These are detrimental to the plating of Zn and must be removed prior to electrolysis. These elements were removed by a hot copper sulfate / arsenic trioxide / zinc dust purification procedure. Apparently, zinc dust displaces Cu and As from solution which are thought to precipitate as a metallic couple. Zinc dust ordinarily does not displace Co and Ni from solution, but in the presence of the Cu/As couple such metals are quantitatively precipitated. The byproduct is a cement Cu cake containing various amounts of Zn, Cd, Co, Ni, and As.

This cement Cu cake had greatly reduced market value because of its high As content. However, the As and Cu could be recycled so that neither $CuSO_4 \cdot 5H_2O$ nor As_2O_3 needed to be purchased. Instead, the Cu and As were recovered as copper arsenate and recycled, and the Cu cake was marketable at higher prices. The recovery was accomplished in four basic operations: (1) acid leaching, (2) cobalt removal, (3) caustic leach ,(4) arsenic removal.

The zinc sulfate ore was conventionally roasted to form zinc oxide, and then leached with sulfuric acid to form zinc sulfate solution. This feed solution typically contained 0.5 to 1.0 g/L Cu, 20 to 30 ppm Co, 1 to 2 ppm Ni, and also some Cd. The feed solution was treated with the Zn dust and copper arsenate in order to precipitate the Co, Cu, Ni, and Cd. The final Co levels must be less than 0.1 ppm in order to ensure sufficient purity of the electrolytic Zn.

The precipitated cement Cu filter cake consisting of 20% solids was subjected to a 2% sulfuric acid leach at 95 degrees C which solubilized the Zn, Co, and Cd but left the As in the residue. After about 2 hrs the acid leach slurry was neutralized with NaOH to a pH of 3.5 to 4.0. This precipitated any Cu in solution. The filtrate went to the Co removal circuit where 100% recovery was achieved using potassium permanganate and NaOH for oxidizing the Co and other metals.

The filter cake containing As and Cu was leached with caustic to dissolve the As, using a temperature of 95 degrees and additional NaOH solution and vigorous addition of air to the slurry at a rate of 500 cu. ft. / min / dry ton of acid leach residue. After about 6 to 8 hrs. approximately 95% As recovery was achieved as $NaH_2AsO_4 \cdot 5H_2O$. The filter cake with high Cu content (approx. 65% Cu, 3% Zn, 1% Cd, and less than 0.5% As) was then sold to a smelter as an upgraded cement Cu cake. The filtrate, containing the As, was reduced in pH to about 8 with addition of H_2SO_4. Copper sulfate was added, the amount varying with the As content, and the slurry maintained for about 2 hrs. A copper arsenate filter cake (approx. 25% Cu, 27% As) was recovered for use in replacing the purchased arsenic trioxide which was formerly used in purifying electrolytic zinc solution.

Arsenic recovery (75 tons recycled) was about 98%. The filtrate containing 20 to 30 gpl Na was recycled to the leaching plant as reagent for jarosite precipitation.

Later it was discovered that zinc arsenate was co-precipitating with copper arsenate, so that while the As in the filter cake was a constant 27%, the Cu percentage varied widely. It was also discovered that zinc arsenate could be used as a purification agent, thus lowering the need for zinc dust and for operating at low pH levels.

CASE STUDY 3 - PURIFICATION OF ARSENIC TRIOXIDE - MT. ISA MINES LTD (MIM), AUSTRALIA

Crude arsenic trioxide from various smelter sources may be contaminated with Pb, Sb, Si, Se, Au, Ag, Co, and Fe. Some typical examples are shown in Table 1.

Crude arsenic trioxide (As_2O_3) may be leached by hot water (5) or by ammoniacal solution, and the As dissolves into solution and is recovered by drying while some metals that cause sludge in CCA and ACZA, such as Fe, remain in the residue. Au can be recovered in the residue for further processing.

Hot water extraction has the advantage that Fe, Pb, Ag, and Si would not be dissolved from the crude As_2O_3 and would not cause sludges in CCA and ACZA solutions or surface residues on treated wood. The Ag and Au can be recovered for their value in the residues. Arsenic trioxide of greater than 99% purity can be produced. In the hot water extraction process As_2O_3 is soluble to the extent of about 7.5% at 210 degrees F, but at 90 degrees F its solubility is 3%. Therefore, 4.5 lbs of As_2O_3 would be purified for every 110 lbs of water heated to boiling and cooled.

Energy requirements are much less when aqueous ammonia is used to leach As_2O_3 from crude material. However, certain metals, including Pb, Sb, Zn, Co and oxides or sulfates of Ag are soluble in ammoniacal solution. Silver salts value cannot be recovered unless reduced with hydrogen gas (6) or other reducing agent in ammoniacal solution. Pb will cause precipitates and sludges in CCA and ACZA. However, when these contaminants are not present, ammoniacal solution is the most economical purification method. Fe and Au are left behind in the residue and the Au can be recovered for its value.

The solubility of As_2O_3 in aqueous ammonia at 70 degrees F increases from 3% at 0% NH_3 to about 20% at 6% NH_3 and then decreases to 7% at 8% NH_3 concentration and 2% at 10% NH_3. At 160 degrees F the solubility of As_2O_3 is 55% at 9 to 10% NH_3 and decreases on either side of this maximum. Therefore, hot ammonia solution is a more energy efficient extraction method than hot water if the dissolved impurities can be tolerated.

CASE STUDY 4 - SHERRITT GORDAN MINES, LTD., FORT SASKATCHEWAN, ALBERTA , CANADA

Sherritt Gordan used a hydrometallurgical process for recovery of non-ferrous metals such as Ni, Co and Ag. Sulfuric acid hot solutions were the medium in which the metal ions were reduced to metallic form by a partial pressure of hydrogen gas. Other reducing agents that can be used include sodium borohydride.

The hydrogen reduction process began with leaching the finely ground ore or filter cake with hot concentrated sulfuric acid. The recommended leach temperature for dissolution of silver is 200 degrees C, which is 130 degrees C below the boiling point of H_2SO_4. Ag precipitates as silver sulfate upon dilution with water or by crystallization when leach liquor is cooled below 170 degrees C. During dissolution the evolved gas consists of 98% SO_2 and 2% H_2. Though silver sulfate precipitates on cooling the sulfuric acid, the silver salt contains entrained H_2SO_4 and is difficult to handle. Therefore, it is desirable for Ag recovery to dilute the leach solution with water at a minimum of 66% dilution. This will avoid the necessity of cooling the system. Also, dilution with water precludes the formation of a double ammoniacal -sulfate silver salt precipitate and a slower rate of silver reduction.

Silver sulfate was dissolved in ammonia solution, forming soluble ammines. The maximum solubility occurs at NH3/Ag molar ratio range of 0.5/1.0 to 1.5/1.0. Increasing the temperature to 50 degrees C increases silver salt solubility. This solubility behavior is similar to that of arsenic trioxide in ammoniacal solution. Increasing the solute concentration above the maximum causes a dramatic lowering of the solution concentration of Ag. Hydrogen gas partial pressure of 5 to 10 kg/cm^2 and a temperature of 110 to 125 degrees C are the recommended reduction conditions.

The leaching phase with concentrated H_2SO_4 causes As, Ag, Se, Cd, and Cu to dissolve. Other metals,

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TABLE 1. ELEMENTS IN VARIOUS CRUDE ARSENIC TRIOXIDES

APPROXIMATE PERCENT ELEMENTS

SOURCE	As	Pb	Sb	Si	S	Se	Sn	Au	Ag	Na	Co	Cu	Fe	Bi	Zn
A §	46-56	.45-.5	17-25 Sb +3 and +5						2 oz/ton					<0.1 - 0.3	
B	15	9	47					0.01 oz/ton	10.5 oz/ton					1.0	
C	70	0.5	0.6	0.2								1.2	0.9	0.1	0.5
D	42	0.3	32	0.1									0.01		0.03
E	13.5	14.7	0.5				0.2			0.2		13.6			2.8
F	69				9.8			0.10 oz/ton	0.80 oz/ton			1.2	5.0	1.7	
G	57			3.0											
H ‡	53			6.0		0.64				10.0		0.2		5.0	
I #	56			5.0				0.24 oz/ton		5.0		0.2	7.0		
J	68		0.4		0.3			0.12 oz/ton				0.04	1.6		

§ 32,000 ton stockpile has been recycled
‡ 1,250 tons stored in concrete bunker, processing uneconomical due to Se
# now sealed in stopes of mine

including Sb, Pb, Ni, Sn, and Te become insoluble salts in H_2SO_4. Dilution and cooling with water to optimum acid concentrations causes the dissolved salts to precipitate. Arsenic can be separated from the sulfuric acid leach solution by treating it with hydrogen sulfide, forming arsenic trisulfide, As_2S_3, which is insoluble in water. By filtering, it can be recovered and then leached with nitric acid to form a mixture of arsenic acid, H_3AsO_4, and sulfuric acid, with NO_2 as an off-gas. Alternatively, the dilute acid leach solution containing the soluble As and any Se or Cd can be neutralized with caustic and oxidized with oxygen, forming sodium arsenate. This can then be reacted with copper sulfate to form copper arsenate for use with CCA and ACZA.

Other metals are recovered by hydrogen reduction in ammoniacal solution. These metals include Cu in ammonium carbonate solution (7), Cu in ammonium sulfate solution (8), nickel in ammonium carbonate system and molybdenum in ammonia - ammonium sulfate system. Copper in sulfuric acid is also reduced by hydrogen to the metal (9). Reduction of these metals in ammoniacal solution occurs at 150 to 200 degrees C and 20 to 30 kg/cm² of hydrogen partial pressure.

CASE STUDY 5 - EXTRACTION OF ARSENIC FROM SPEISSES AND OTHER SOLID SOLUTIONS BY OXIDATIVE LEACHING

Various sludges, slimes, filter cakes, arsenopyrites and speisses from refineries, mines and smelters can be leached with either acid or alkaline solutions to recover metals and arsenic. The metals may be extracted more rapidly in an autoclave under oxygen pressure for oxidation of the metals. Examples of these methods are given below.

1. Speiss containing approximately 60% Cu, 21% As, 15% Pb, 1.8% Sb, 1.7% Fe, 1% S, 0.65% Sn, 0.56% Ag, 0.4% Ni, 0.2% Zn, 0.06% Se and 0.38 oz/ton Au was ground to -200 mesh and leached with concentrated sulfuric acid at 100 degrees C under an oxygen partial pressure of 100 psi for 1 hour. Extraction of Cu and As were 99.7% and 91.5% respectively. Both Pb and Ag were only slightly solubilized under these oxidizing conditions, each averaging about 10 ppm in solution. The Cu and As were precipitated from the undiluted leach solutions by neutralizing with sodium carbonate to pH 6. The product contained approximately 45% Cu, 16% As, 0.5% Sb, 1.9% Fe, 0.2 % Zn and smaller amounts of other elements. This material has approximately three times too much Fe for CCA and ACZA raw materials. Additional processing by dissolving the product in ammoniacal or caustic solution would precipitate out the Fe.

2. The speiss in Example 1 was leached with ammonia/ammonium carbonate solution with an exothermic reaction at approximately 55° C under an oxygen partial pressure of 20 psi for 1 hour. Cu and As were extracted at 99.3% and 90% efficiency. However, a considerable amount of Pb was solubilized , ranging from 3.8 to 6 gpl in the leach solution. This resulted in the Pb coprecipitating with As when the solution was boiled to expel NH_3 and CO_2. The product had 44% Cu, 16% As, and 0.45% Pb. The Pb caused a precipitate in CCA solution made with the product.

3. Sherritt Gordan Mines, Ltd., Fort Saskatchewan, Alberta uses ammoniacal solution leaching of Co, Cu and Ni after pressure leaching of arsenopyrite with oxygen to convert sulfur to SO_4. As is released and oxidized. Co and Cu are soluble in ammoniacal solutions. The ammonium sulfate byproduct is sold as a fertilizer. The ammoniacal oxygen leach process was also used by International Nickel Co. of Canada Ltd. in the Port Colborne, Ontario, and Sudbury Districts.

4. Kennecott Minerals Co. used a patented oxidizing sulfuric acid leach in a pressure autoclave to extract Cu from flue dust. The dust contained 13.8% Cu, 11% As, and 17% Pb. After leaching, the dry residue contained 1.3% Cu, 12.5% As, 2.2% Bi, 0.4% Sb, 20% Pb as insoluble sulfate, 12.5% Fe, and 0.8% Mo. The Pb could have been leached with NaCl brine, forming soluble lead chloride. The residue could have been leached with caustic to extract the As from $FeAsO_4 \cdot 2H_2O/Fe_3(AsO_4)_2 \cdot 6H_2O$.

5. Sumitomo Metal Mining, Ltd. uses a process (21 patents) that incorporates pressure oxidation leaching of nickel cobalt sulfide residue from a hydrometallurgical treatment process of laterite ore. The process utilized continuous oxygen pressure with sulfuric acid leaching to produce cobalt sulfate and nickel sulfate in solution. Versatic acid was used to solvent extract the metals by controlling pH with NH_3. The metals are stripped from the versatic acid with hydrochloric acid to give a solution of nickel and cobalt chlorides. Co extraction from a nickel-cobalt chloride solution is performed in a mixer-settler using tri-n-octylamine. Co is completely extracted and separated from the nickel and then stripped with water or dilute HCl to yield cobalt chloride.

The NH_3 used for pH control is recovered as $(NH_4)_2SO_4$, which is subjected to a double decomposition reaction with $Ca(OH)_2$ at high temperature to recover NH_3 and gypsum.

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2NH_3 + CaSO_4 + 2H_2O$$
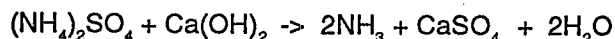
The NH_3 is recovered and recycled to the extraction process.

This process, or variations of it, could be utilized for high As/Co ores in North America where gravity concentrates contain 40 to 50% As, 10 to 15% Co and 1500 oz/ton Ag. Ores from mines near Cobalt, Ontario such as Pan Continental, Agnico Eagle, Silverfields, Teldyne and Canadaka produce high As/Co/Ag concentrates. Combinations of oxygen/ammoniacal solution leaching would leach the As, Co and Ag from the concentrates. Dilution with sulfuric acid and optimized pH control would cause formation of double ammine sulfate salts, allowing selective As and Ag precipitation and Co filtration.

6. The U. S. Bureau of Mines utilized ferrous chloride-oxygen pressure leaching of a Co/As/Ag ore such as the Canadaka Mine, Cobalt, Ontario concentrates. The concentrate contained 9.7% Co, 0.36% Cu, 2.8% Ni, 45.5% As, 10.6% Fe, and 720 oz/ton Ag. The major mineral was cobaltite (CoAsS). During the ferrous chloride-oxygen leach, Co, Cu, and Ni are solubilized as chlorides and As is converted to arsenate ion. Silver was rejected to the leach residue as the insoluble chloride. It was subsequently extracted by cyanidation, though it could have been extracted with acqueous NH_3. Extractions of Co, Ni, and Cu were in the 97 to 98% range. Silver extractions were 99% with a cyanide consumption of 4 lb/ton of concentrate. During ferrous chloride-oxygen treatment 23.5% of the As was solubilized. However, during this extraction the objective was to leave the As insoluble. As was removed from process solutions by raising the pH to 2.1 with Na_2CO_3 and adding ferric chloride, required to precipitate insoluble $FeAsO_4 \cdot 2H_2O$ (10).

The $FeAsO_4 \cdot 2H_2O$ precipitate contains Fe^{+3} and As^{+5}. It will pass the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) test for As leachability. However, this could be further processed to produce copper arsenate for reuse in making CCA and ACZA. Hydrochloric acid will solubilize $FeAsO_4 \cdot 2H_2O$, but removal of Fe and Cl from AsO_4^{+3} would be difficult. $FeAsO_4 \cdot 2 H_2O$ could be reduced to $Fe_3(AsO_4)_2 \cdot 6H_2O$, with Fe^{+2} and As^{+5} with a reducing agent such as SO_2 (11) and then solubilized in ammoniacal copper solution to precipitate out the Fe. The $Cu_3(AsO_4)_2 \cdot 4H_2O$ and $Cu_2AsO_4 \cdot OH$ would remain in the filtrate for subsequent recovery on evaporation and recovery of the ammonia.

A concentrate containing 45.6% As, 12% Bi, 9% Co, 4% Fe, 6.3% Ni, 2.8% S, and 11.9 oz/ton Ag was oxidized with chloride-oxygen at 100 degrees C and 50 psi O_2 for 24 hrs. About 25 to 33% of the As was solubilized; and 99% of the Co and 97 to 98% of the Ni and 99% of the Ag was solubilized. However, the process was designed to precipitate As as $FeAsO_4 \cdot 2H_2O$ by adding $FeCl_2 \cdot 4H_2O$; and PbS was added to extract Bi from the ore when extraction was 60% complete. When $FeCl_2 \cdot 4H_2O$ concentration was doubled Bi extraction was 85% and As extraction was 92%. $CuCl_2$ could replace $FeCl_2$ to produce copper arsenate for use in CCA and ACZA manufacture.

CASE STUDY 6 - CONVERSION OF CALCIUM ARSENATE AND PYRITE WASTES TO COPPER ARSENATE FOR CCA AND ACZA

Calcium arsenate is a residual waste material that is stored at several locations where there were Au and Ag mining sites and Cu and Ag smelters years ago. At one site there is about 1500 to 2000 tons of calcium arsenite/calcium arsenate mixture in a holding pond with a double layer liner. This material is 11% As, 7% Sb, 15% Fe, 3% Pb and 32% Ca. Another BC mine has a calcium arsenate sludge contaminated with Sb from a silver mining operation.

Calcium arsenate wastes can be leached with sulfuric acid to produce sodium arsenate and gypsum. This has not been commercially done for the production of arsenicals for wood treating. However, if a copper arsenate can be produced free from objectionable impurities this is a source of arsenic. Calcium will cause sludges in both CCA and ACZA solutions. Sulfate will interfere in the chemistry of ACZA ammoniacal fixation reactions with Cu, Zn, and As.

Since some of the As is likely in the form of arsenite, the calcium arsenate wastes should be slurried and batch leached with sulfuric acid and overpressure of oxygen or air in order to oxidize the arsenite. A hot brine leach would be necessary to remove the Pb. This would be followed by a recovery of the iron in a hot caustic solution, causing the As to become available as sodium arsenate, from whence it can be reacted with copper sulfate to make copper arsenates.

The Getchell Mining property near Winnemuca, Humboldt County, NV has ponded arsenic sulfides that were stored in the 1960s from an Au mining operation of arsenical ore containing the minerals orpiment and realgar. The ore floatation concentrate contained 30 to 40% As. The sulfide material in the holding ponds contains 3 to 3.5% As. The ponding of the wastes was done in the 1962 to 1963 period. This property at one time had a roaster and arsenic trioxide was produced Another Au mining operation in South Dakota produces huge quantities of arsenopyrite waste. Arsenopyrite (FeAsS) mineral wastes are present at Leadville, CO; Lead, SD; Thompson Falls, MO; Polaris, ID; Eureka, NV; Big Creek, ID; Balmertown, Ontario, Canada; Roxbury, CN and other mining sites. Glaucodot mineral [(Co,Fe)AsS], proustite (Ag_3AsS_3), cobaltite (CoAsS), smaltite ($CoAs_2$), skutterudite ($CoAs_3$), erythrite [$Co_3(AsO_4)_2 \cdot 8H_2O$], annabergite [$Ni_3(AsO_4)_2 \cdot 8H_2O$] all occur at Cobalt, Ontario, Canada. There are 29 known arsenical minerals. All of these wastes and minerals present the potential of recovery of precious metals and As. However, the high sulfur content or the high calcium content of arsenopyrites and calcium arsenates, respectively, make recovery impractical at this time. The possibility exists for sulfur oxidizing bacteria such as *Thiobacillus* or sulfate production by *Chromatia* bacteria from the sulfide ores. If this is feasible it would be an inexpensive recovery method. Otherwise, oxidative leaching would be required.

SUMMARY

Each type of arsenic recovery system must be tailored to recover all of the valuable metals while producing an arsenic oxide or copper arsenate that is free of objectionable levels of Fe, Pb, Sb, Cl, and Mn that might cause corrosion or sludges in treating solutions and surface residues on the CCA and ACZA treated wood. Process flow charts, major equipment characteristics, and operating parameters are available from the author and from the cited references.

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ALTERNATIVE PRESERVATIVE SYSTEMS: PROS & CONS

H. M. Barnes and D. D. Nicholas
Mississippi Forest Products Utilization Laboratory
Department of Forest Products
School of Forest Resources
Mississippi State University
PO Drawer FP
Mississippi State, MS 39762-5724
USA
Tel: (601) 325-2116

INTRODUCTION

This paper provides an overview of the advantages and disadvantages of new generation wood preservative systems and treating processes. Historically, the wood-preserving industry has used three major preservative systems: creosote, pentachlorophenol, and waterborne inorganics. The oldest wood preservative system, creosote, was initially used for the domestic treating industry in the 1870s when crossties were treated for the L & N Railroad in Pascagoula, MS using the full-cell process developed by Bethell in 1838. Commercial treating processes remained unchanged until the early 1900s with patents being issued for the Rueping and Lowry empty-cell processes for use with oilborne systems.

The first patented waterborne system, acid copper chromate, was brought to the marketplace in 1929 and was followed shortly by a new oilborne system, pentachlorophenol ("penta"), in 1931. Before the decade was out, the remaining two major commercial waterborne systems, chromated copper arsenate (CCA) and ammoniacal copper arsenate (ACA) were developed. Historical summaries can be found in the literature (1, 2).

In recent years, changes in treatment technology and preservative systems in the US have arisen from two principal factors: (1) environmental concerns, including promulgated air and water quality standards, and the effect of treated wood on man and non-target organisms; and (2) the energy crisis, especially in regard to oil and oil-based preservative systems. Of these two, environmental concerns predominate. Four criteria should be used to judge candidate wood-preservative chemicals.

> The first of these is safety. Wood preservatives should be safe to handle and use with respect to both processing operations and final product consumption.

> Additionally, these systems must be effective in order to provide the consumer with acceptable product performance. In this regard, both the amount of biocide (retention) and the penetration of the biocide are critical.

> Preservative permanence is an additional requirement for acceptable performance. All preservatives will deplete from treated wood over time, but acceptable systems do so at a slow rate. Both processing and exposure parameters affect the permanence of preservative systems.

> Lastly, preservative systems must be cost-effective. Not only the raw material cost of the components of a given system need to be considered, but also the energy and processing costs along with environmental costs must be taken into account.

Competitive materials should be judged using the same criteria. Often, alternatives to treated wood products appear environmentally benign, but when examined closely yield high environmental and energy costs for their production. The advantages for using a renewable natural resource should not be overlooked. It has been estimated that the failure to control wood-destroying insects and fungi would require the additional cutting of over 300 million acres of forests, a significant consideration in these days of concern about global warming. Currently, over 336 million cubic feet of wood are treated with wood preservatives and fire retardants. As shown in Figure 1, waterborne preservatives represent the largest component of this production.

Figure 1. Volume of wood treated in 1990 by preservative type.
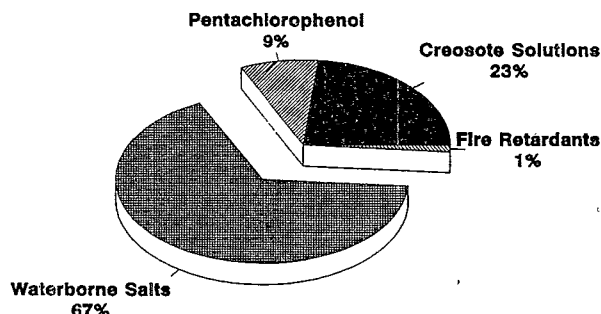
ALTERNATIVE PRESERVATIVE SYSTEMS

In the past 15 years, a considerable amount of research activity has focused on the development of new biocides for wood preservative systems. These new candidates include waterborne, oilborne, and aqueous emulsion systems which generally exhibit lower mammalian toxicity and should pose less danger to the environment than the traditional systems. Two waterborne preservatives that show promise are dual component systems: ammoniacal copper/didecyldimethylammoniumchloride and cupramine/dimethyldithiocarbamate. Borates also show promise, but their use is limited because they are highly susceptible to leaching.

Several new biocides have potential as oilborne preservative systems. These include an isothiazolone, chlorothalonil, iodopropynylbutyl carbamate, and propiconazole. In addition to these biocides, copper naphthenate and oxine copper are reemerging as commercial wood preservatives. The environmental impact of these new biocides varies but in general they pose fewer problems. All of these biocides are effective wood preservatives but have limitations. For example, iodopropynylbutyl carbamate and propiconazole are effective only in above-ground applications. Furthermore, although the isothiazolone and chlorothalonil are excellent broad spectrum wood preservatives, they are less cost-effective than currently used systems. The liability of new copper-based systems to copper-tolerant fungi is also a concern.

Emulsion systems hold promise for the future. The advent of micro-emulsions may allow for the combination of otherwise dissimilar biocides into effective formulations which would require less preservative for effectiveness. At the same time these systems eliminate the need for excessive amounts of petroleum based carriers.

Research to date suggests that it is desirable to incorporate durable water repellents into preservative formulations in order to improve the weathering and leaching performance of treated wood products. These systems are essentially wax emulsion systems, and several commercial products are available for use with CCA treatments. Other approaches, such as the incorporation of oil in CCA systems, also hold promise for better product performance and reduced leaching rates. Experimental polymer systems have been researched as co-treatments for CCA treatment with some success. It is anticipated that further progress in this area will be forthcoming in the future.

ALTERNATIVE TREATING PROCESSES

The Bethell, or full-cell, process was developed in 1838 by John Bethell to treat timbers for the Royal Navy with creosote. The process utilizes an initial vacuum (22 in Hg or greater) to evacuate the air from the wood. After evacuation, the treating cylinder is filled with preservative fluid and the pressure is increased to a maximum dependant upon the species of wood being treated. Pressure is maintained until the wood cell lumens are completely filled with preservative solution. This process is used primarily with waterborne preservatives such as CCA and results in the maximum absorption of solution into the wood.

In order to reduce the uptake of solution and minimize the dripping of preservative solution and subsequent holding time after treatment, commercial treaters have turned to a modified full-cell process. In this process, a short term (10 min), low intensity (nearly equal to 10 in Hg) vacuum is used in conjunction with a final vacuum period after the pressure period. Wood treated using this modification typically exits the treating cylinder with significantly lower moisture content.

A modified Lowry process, designated the alternating pressure method (APM), has been used successfully in Australia for many years to treat partially seasoned pine with CCA preservatives. After introduction of the preservative, pressure is quickly cycled between maximum pressure and atmospheric pressure. This process has the advantage of being less energy intensive since the need for initial kiln-drying is eliminated.

In situ fixation of CCA has been achieved with the patented MSU Process developed by W. C. Kelso, Jr.. The process is a modification of empty-cell processing whereby the CCA components are fixed in the wood prior to removal of the wood from the cylinder. Typically, 95 to 99% of the components are fixed yielding a product with half of the water found with wood treated with a full-cell process. The process eliminates dripping and the wood is safe to handle immediately upon exiting the cylinder.

Considerable research has been undertaken to accelerate the fixation of chromium and arsenic containing preservatives. Rapid fixation schemes generally use one of four methods: hot air heating, hot water fixation, steam fixation, or hot oil heating. Each method has its advantages and disadvantages. The key factors affecting fixation are wood moisture content, temperature, concentration, and time. In general, moist wood is essential to proper rapid fixation since the fixation reactions are essentially ionic. Failure to maintain a moist environment can lead to excessive leaching of components.

Compared to fixation at ambient temperature, accelerated fixation generally proceeds at a rate one to three times faster for each 10 degree C rise in temperature. Leaching rates for CCA components also depend upon the concentration. There is evidence that the leaching of arsenic from CCA-treated wood in laboratory studies is greater for concentrations below commercial production norms. Presumably this is because the reaction sites on the wood are filled by adsorbed copper leaving the arsenic in a less fixed state. At normal commercial retentions, this behavior disappears. Care must be taken in interpreting small-scale laboratory results, implications from which may not be applicable to commodities treated in full production sizes. An excellent discussion of accelerated fixation can be found in the literature (3).

DISPOSAL OF TREATED WOOD

Disposal of wood products treated with CCA, penta, and creosote is becoming a major environmental issue. Restrictions on landfill disposal are increasing and will soon preclude this option. Therefore, other methods of disposal are being studied. In this regard, creosote-treated wood is the easiest to dispose of because it can be incinerated in commercial boilers without creating environmental problems. Penta-treated wood can be incinerated, but scrubbers are needed and licensing is difficult. CCA-treated wood is also more troublesome, and additional research will be required to develop cost-effective systems.

One approach to the disposal of organics has been to remove the metal hardware and shred the wood. The wood is then placed in a reactor to remove organics and the residual wood is composted. With CCA, research has focused on extraction/destruction of the wood followed by recovery and reuse of the preservative components. Reuse of treated products in large sizes (e.g., poles) is being accomplished to a limited extent by peeling and retreatment. This disposal problem will undoubtedly accelerate the acceptance of new preservative systems. Data currently being generated should help develop total life cycle management costs for treated wood products.

FUTURE TRENDS

Environmental concerns are likely to continue to drive the treated-wood industry. Advances in plant design, process control, and sanitation continue to improve in order to meet existing and future regulations. The development of new and/or modification of existing preservative systems will likely provide the industry with new alternatives that will make it easier to comply with the ever changing environmental and safety regulations. However, it will also require that the industry become more sophisticated because the new preservative systems will probably require much more stringent quality control measures in order to attain equivalent performance and thus enable the industry to compete with alternate products.

The move on the part of the industry to a "use category" system for setting standards should allow for more specific preservatives for specific uses. The use of combination biocides has the potential for reducing the total amount of preservative injected into wood, hence lowering potential environmental impact. Advancing treatment technology, such as supercritical fluid treatment, may allow treaters of the future to put biocides into the wood structure in such a way that they are more effective and less leachable and this will permit the use of lower concentrations.

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POTENTIAL FOR RECOVERY OF CCA FROM F035 WOOD PRESERVING OPERATIONS

Tom Lewis III
Lewis Environmental Services, Inc
RJ Casey Industrial Park
Pittsburgh, PA 15233
USA
Tel: (412) 322-8100
Fax: (412) 322-8109

INTRODUCTION

Lewis Environmental Services, Inc., has developed the ENVIRO-CLEAN PROCESS: a patent pending process for the reclamation of metals such as chromium, copper, zinc, and cadmium from process waste streams. This two-step process utilizes granular activated carbon and electrolytic recovery to produce a saleable metallic byproduct. The process generates no sludge or hazardous waste and the effluent meets Environmental Protection Agency (EPA) discharge limits based on metal levels. The process has effectively demonstrated that it can treat a matrix of multiple metals in a single stream with positive results. This process has treated waste sources from the wood preserving, metal finishing, and painting industries.

Under a Small Business Pollution Prevention Grant, Lewis Environmental Services Inc., modified its ENVIRO-CLEAN PROCESS as an overall approach to remediating hazardous soil contaminated with Chromated Copper Arsenate (CCA) salts for a major producer of wood- preserving chemicals. Currently, the producer offers a CCA- contaminated soil disposal service to its licensees. Shortly, the cost of disposing of this material will increase dramatically, impacting the producer's ability to continue offering this service. The new disposal technique will require stabilization of the contaminated soil with cement. This technique is expensive and will rely on the availability of landfill space. Wood-preserving producers are investigating new recovery approaches which will eliminate the disposal of hazardous CCA waste. It was positively demonstrated that CCA-contaminated soil can be acid leached and upgraded to a nonhazardous level. The acid leaching technique is simple and does not require elaborate equipment design or process conditions.

CCA PROCESS DESCRIPTION

The process consists of a counter-current acid leaching technique to contaminated CCA soil where it would pass the EPA Leach Toxicity Test and be reclassified as nonhazardous waste. The volume of leach acid with the recovered chromium and copper metals will be recycled back into the operation. Any rinse waters required to clean the processed soil will be processed by the ENVIRO-CLEAN PROCESS. The ENVIRO-CLEAN PROCESS operates in a very simple manner similar to a filter; the system consist of a tank, pump, and two carbon filters. This system design and sizing makes it applicable to small and medium size waste generators. Also the granular carbon is reusable and capable of recovering heavy metals over numerous treatment cycles. The implementation of this combined process scheme would eliminate the need to dispose of CCA-contaminated soil, which is a hazardous waste, as well as recover valuable metals such as copper and chromium.

SOIL CHARACTERISTICS

A 5-gallon sample of CCA-contaminated soil was received from the producer for testing. The soil was green/gray in color with pieces of wood and stones. The acid leached soil was free flowing and light gray in color. Table 1 presents the analysis of the contaminated and the acid leached soils for chromium and copper.

TABLE 1. SOIL ANALYSIS VIA ACID LEACHING

Item	Plant Soil	Acid Leached Soil	% Removal
Chromium (mg/KG)	6070.0	58.6	99.03
Copper (mg/KG)	4370.0	221.0	94.94

PROCESSED SOIL CHARACTERISTICS AND MANAGEMENT

All the customer soil samples (five samples) passed the Toxicity Characteristic Leaching Procedure (TCLP) test. The two main leach constituents chromium and arsenic averaged 0.8 mg/kg and 0.9 mg/kg respectively over the various TCLP tests. The leach acid analysis from a second stage sample contained 3330, 13300, and 22990 mg/L of chromium, copper, and iron. Table 2 presents the TCLP test results from a typical soil sample.

TABLE 2. TCLP TEST RESULTS OF ACID LEACHED SOIL[1]

Tests	Results (mg/l)
Arsenic	0.71
Chromium	0.22
Copper	0.77

[1] The leachate Information - TCLP: Solid Material, 100% Solids 100 grams charged to the extractor, Initial pH 3.5

ENVIRO-CLEAN PROCESSING RESULTS

The acid leach samples were water washed with one volume of water equal to the acid leach volumes. These solutions contained moderate levels of chromium, copper, and arsenic; the resulting concentrations of the combined wash waters were 41.4, 94.8, and 3.0 mg/L respectively. There was consistent repeatability of leaching based on TCLP test results. All samples passed based on the standardized leach procedure.

Wash water generated from the final cleaning of processed soil was treated through an activated carbon system. The activated carbon system consisted of two filters each containing 180 grams of activated carbon. About 2000 ml of wash water was treated at a flowrate of 15 ml/min. The effluent was crystal clear. The effluent contained on average 0.01, 0.01, and 0.22 mg/L respectively for chromium, copper, and arsenic. Table 3 list the results of the carbon treatment test.

TABLE 3. CARBON TREATMENT DATA

Sample	chromium(mg/1)	copper(mg/1)	arsenic(mg/)
feed	41.40	94.90	3.0
time 30 min	0.01	0.01	0.22
time 60 min	0.02	0	0.3
time 90 min	0.01	0	0.22
time 120 min	0.01	0	0.17
time 150 min	0.01	0	0.14

ENVIRONMENTAL ADVANTAGES

Wood preserving operations gain the following environmental benefits by utilizing the ENVIRO-CLEAN PROCESS:

1. It allows a wood treating site or chemical manufacturer to perform closed-loop recovery of valuable chemicals and water.

2. The production and handling of CCA-treated wood products generates a hazardous waste, in the form of CCA-contaminated soil. This soil is "treated" and reclaimed, eliminating the need to dispose of this material.

3. Chromium, copper, and arsenic are recycled back into the process. The water used to wash the soil is processed through the ENVIRO-CLEAN PROCESS to remove trace metals and the rinse water is reused as a source of clean water.

FACILITY DESCRIPTION

Lewis Environmental Services, Inc, is located in Pittsburgh, PA and is a permitted waste recycler under Pennsylvania's Beneficial Recycling and Reuse classification. We are in operation and able to receive liquid waste or activated carbon utilized in our process for heavy metal recovery.

The wood preserving chemical producer is located in Georgia, and plans to install a soil cleaning system based on our design. We are planning to conduct a pilot scale test in 1992 to verify process parameters and scale-up factors.

REUSE OF WOOD PRESERVATIVE THAT CONTAINS ARSENIC

William Joseph Baldwin
Hickson Corporation
3941 Bonsal Road
Conley, Georgia 30027
USA
Tel: (404) 362-3970

INTRODUCTION

Inorganic pentavalent arsenical compounds of varying formulations have been used as wood preservatives in substantial quantities for over 50 years (1). Currently, there are five arsenical wood preservative formulations listed in The American Wood-Preservers' Association Standards (2). These include three chromated copper arsenate (CCA) formulations, i.e., Types A, B, and C, ammoniacal copper arsenate and ammoniacal copper zinc arsenate. Of these, CCA Type C, which consists of 34.0% arsenic (as As_2O_5), 18.5% copper (as CuO), and 47.5% hexavalent chromium (as CrO_3), is the predominant arsenical wood preservative used in the US today. CCA-treated wood is used in applications such as decks, docks, foundation and marine piling, fences, and utility poles.

The manufacture and use of arsenical wood preservatives is heavily regulated. The formulation of CCA is regulated by the Occupational Safety and Health Administration (OSHA); however, the Environmental Protection Agency (EPA) governs the use of arsenical preservatives and regulates stormwater runoff. Moreover, EPA's effluent guidelines for arsenical plants prohibit the discharge of process wastewaters into navigable waters.

Although hazardous waste generated at arsenical plants has been regulated since the initiation of the program in 1980, EPA amended its regulations under the Resource Conservation and Recovery Act (RCRA) in late 1990 by listing wastewaters, process residuals, preservative dripping, and spent preservatives as hazardous. Furthermore these regulations, referred to as Subpart W, establish standards for treating plant design, operation, inspections, and closure (3).

PROCESS DESCRIPTION AND FEED STREAM CHARACTERISTICS

CCA is shipped to the treating plant by tank truck as a 50% concentrate with the composition noted previously and 50% water. Upon arrival at the plant, the preservative is transferred to a concentrate storage tank. When needed, the arsenical preservative is diluted with water to a 1 to 2% working or treating solution through a closed system metered mixing device and transferred to a work tank.

Arsenical preservatives are applied by pressure processes. Two methods, referred to as full cell and empty cell, are available; however, in practice, full cell and a hybrid of the two referred to as modified full cell are used commercially. The difference is that in a full cell treatment (as the name implies) the wood cells are full of treating solution; in a modified full cell treatment there is less liquid in the wood.

In general, during arsenical treatment, untreated wood is placed on rail or tram cars which are winched or pushed into the treating cylinder. The door is closed, a vacuum is applied to the cylinder to remove air from the wood cells, and the treating solution is transferred through piping from the work tank to the treating cylinder. Pressure is applied to force the treating solution into the wood after which the solution is returned to the work (storage) tank for reuse. A final vacuum is pulled with all excess preservative returned to the work tank, pressure is returned to atmospheric, the door is opened, and the treated wood is pulled from the cylinder and placed on the drip pad.

In accordance with the regulations, existing pads must be assessed by an independent registered professional engineer. This annual assessment must document items such as materials of construction, slope, curb or berm, structural strength, and crack repair.

All solution dripping onto the pad, as well as washdown water and rainwater, flows to a collection sump

from which it is transferred to the dilution water tank. It should be noted that at some plants this transfer involves filtration, e.g., bag or sock filters, to remove wood chips, dirt, labels, etc. from the liquid. The dilution water is in turn blended with additional CCA concentrate to make fresh treating solution.

As noted previously, treatment with the CCA preservative requires the use of water as a diluent. As such, CCA plants collect and use, in process, all dripping, rainwater, run on, and water used to clean the drip pad. Contaminated process water is not discharged.

RESIDUAL CHARACTERISTICS AND MANAGEMENT

The amount of dripping, now classified as hazardous waste, collected from an arsenical plant varies by the treating process previously described. Dripping is also a function of species, e.g., southern pine vs. hem-fir; dimension, e.g., 2 x 4 in. vs. 2 x 10 in. vs. 5/4 x 6 in. etc.; temperature and moisture content. "Typical" dripping can range from less than a quart (from tram dripping only) to 50 to 100 gallons per charge for a rapid cycle plant treating southern pine.

As mentioned previously, EPA's listing also applies to wastewaters that come in contact with process contaminants, e.g., rainwater that mixes with wood dripping on the pad. So, regardless of concentration, rainwater collected on the drip pad is considered hazardous waste until it is reclaimed. Table 1 illustrates the volume of rainwater that will be classified as hazardous at arsenical plants of varying size throughout the US.

TABLE 1. HAZARDOUS WASTE GENERATION AT TREATING PLANTS DUE TO SUBPART W

Plant Location	Average Annual Rainfall	Pad Size 75'x100'	100'x150	100'x250'
		Annual Tons of Hazardous Waste		
Southern Washington	36.80"	718	1435	2392
Houston, TX	47.07"	918	1836	3060
Mobile, AL	64.64"	1260	2521	4202
Atlanta, GA	48.61"	948	1896	3160
Nashville, TN	48.49"	946	1891	3152
Pittsburgh, PA	36.30"	708	1416	2360
Richmond, VA	44.07"	859	1719	2865
Chicago, IL	33.34"	650	1300	2167

It should be noted that prior to the Subpart W listing, the majority of treating plants were small quantity generators, i.e., generated less than 1 ton of waste per month.

ENVIRONMENTAL ADVANTAGES

The arsenical wood preserving industry collected and reused process water, i.e., dripping and rainwater, prior to the listing of such materials as hazardous in 1990. Nevertheless, this material is now classified as hazardous and it is conservatively estimated that 400,000 tons of "rainwater" are collected, i.e., generated, annually by the 429 arsenical plants in the US. Fortunately, this water can be used in process and thus avoids disposal. Moreover, wood properly treated with arsenical preservatives has a service life seven to ten times greater than untreated wood, thus conserving our forest resources.

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OSMOSE WATER PURIFICATION SYSTEM TO REMOVE CCA CONTAMINANTS FROM WATER

A. A. (Gus) Staats
Osmose Wood Preserving, Inc.
PO Drawer O
Griffin, GA 30224
USA
Tel: (404) 228-8434

INTRODUCTION

The Osmose Water Purification System is manufactured by Zenon Environmental Systems exclusively for Osmose Wood Preserving, Inc. and the wood treating industry. Osmose Wood Preserving, Inc. is an American-based company which manufactures chromated copper arsenate (CCA) used in wood preservation. Zenon Environmental Systems is a Canadian-based firm which specializes in water treatment systems. With the advent of Stormwater and other regulations which affect the wood treating industry, Osmose went in search of a water treatment system that could consistently produce clean water from water contaminated with CCA.

Osmose located Zenon Environmental Systems, which developed the present system to remove CCA from contaminated water. CCA is a waterborne wood treating preservative that is used in many markets across the country. Water contaminated by CCA can be cleaned to a state where the arsenic and chromium values are at or below the Drinking Water Standard. In addition, it will produce a concentrate that can be reused in the treating process. This state-of-the-art water treatment system can be used to purify surface water such as ponds, streams, stormwater runoff or groundwater. The Osmose Water Purification System has been successfully employed to clean up both surface water and groundwater.

PROCESS DESCRIPTION

The Osmose Water Purification System can be modified to meet the specific needs of each particular waste stream of CCA contaminated water. A typical system would be composed of three components. The first would be a prefilter; next would be the primary method of membrane separation; and the last phase of the system would be an ion exchange polishing unit. The prefiltration stage will remove suspended solids from the wastewater stream. The size of the filtration unit will depend on the suspended solid particle size. Removal of the suspended solids is necessary to protect the reverse osmosis membrane system. The reverse osmosis membrane system is the main portion of the treatment train which is utilized to remove approximately 95% majority of the dissolved CCA from the wastewater. A high pressure process pump is utilized by the RO unit to force wastewater across the surface of a selective reverse osmosis membrane. The membrane selectively allows the passage of water molecules through and rejects dissolved contaminants.

Two exit streams result from this separation process. The first stream is called the RO concentrate which is composed of membrane-rejected material and has the highest concentration of undesirable contaminants. The second stream is called the RO permeate which is membrane-accepted material which has a very low concentration of the contaminants. The final stage of the system that can be employed, if necessary, is the ion exchange system which will remove most of the remaining metals from the RO permeate. The ion exchange system is composed of anion and cation resins which remove negatively and positively charged ions, respectively.

FEED STREAM CHARACTERISTICS

Table 1 is a summary of chemical analysis which was achieved during the actual use of the Osmose Water Purification System during an accidental spill of CCA wood treating solution in Canada. As can be seen in the data, the RO unit removed between 99.1 and 99.8 percent of the target contaminants. Table 2 gives the comparison of effluent quality between the waste influent, treated effluent, and Vancouver tap water.

TABLE 1. SUMMARY OF CHEMICAL ANALYSIS

Sample Stream	Chromium mg/L	Copper mg/L	Arsenic mg/L	TOC mg/L
RO Feed	40.1	5.15	24.4	33*
RO Concentrate	90.8	22.4	57.7	N/A
RO Permeate	0.3658	0.0085	0.0394	N/A
Ion Exchange	0.0030	0.0043	0.0251	17
Discharge Tank	0.0333	0.0060	0.0229	N/A
RO % Removal	99.1%	99.8%	99.8%	N/A
IX % Removal	100.0%	99.9%	99.9%	48%
*Estimated				

RESIDUAL CHARACTERISTICS AND MANAGEMENT

The waste streams generated through this system are the permeate and the concentrate streams. The concentrate stream can be recycled back into the RO, or if the appropriate percentage removal has been achieved, it can be removed and utilized in a current wood treating plant as makeup water or disposed. The permeate stream, in most cases, can be discharged to a local POTW or used as makeup water in a wood treating facility. The advantage of this system is that it produces very little hazardous waste (filter wash resin, etc.).

ENVIRONMENTAL ADVANTAGES

As stated previously, there is very little hazardous waste produced when utilizing this system because the separated waste water streams can be recycled back into a treating plant for use as makeup water. Alternative systems require regeneration of resins, disposal of filters, or disposal of some type of chemical binding agent. Depending on the feed stream, the RO membrane will usually last 2 to 3 years before a thorough cleaning is necessary. The ion exchange resin beds are periodically flushed and regeneration is not needed on a regular basis because of the reduced concentrations of metals which enter the ion exchange system.

FACILITY DESCRIPTION

The Osmose Water Purification System can be permanently placed onsite or used as a completely mobile emergency unit. The system is produced in 10, 20, 50 and 100 gallon per minute (gpm) units which can be combined or upgraded as the need arises. The system is very versatile and has been proven in field operations throughout the US and Canada.

TABLE 2. EFFLUENT QUALITY COMPARISON

Element Analyzed	Waste Influent mg/L	Treated Effluent mg/L	Vancouver Tap Water mg/L
Phosphorus	0.7	<0.01	<0.01
Arsenic	23.9	<0.04	<0.04
Lead	<0.005	<0.005	<0.005
Cobalt	<0.004	<0.004	<0.004
Barium	0.04	<0.004	<0.004
Chromium	34.7	<0.001	<0.001
Copper	11.5	<0.002	1.2
Aluminum	0.6	<0.01	0.09
Magnesium	3.6	<0.01	0.15
Strontium	0.1	<0.002	0.07
Molybdenum	0.01	<0.001	<0.001
Cadmium	<0.001	<0.001	<0.001
Nickel	<0.02	<0.002	<0.002
Manganese	0.57	<0.001	0.01
Vanadium	<0.001	<0.001	<0.001
Zinc	1.2	<0.002	0.05
Iron	0.79	<0.002	0.07
Calcium	29.3	<0.01	1.4

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THE CASHMAN AND OTHER HYDROMETALLURGICAL PROCESS TREATMENTS OF POLYMETALLIC ARSENICAL DUSTS, SLUDGES, AND WASTES

Richard S. Kunter
Richard S. Kunter & Associates
25958 Genesee Trail Road, No. K324
Golden, Colorado 80401-5742
USA
Tel: (303) 526-1868
Fax: (303) 526-1718

INTRODUCTION

Artech Systems, Inc. has developed a low pressure and temperature chloride leach process called the "Cashman Process" to extract metals from arsenical flue dusts and residues and fix the arsenic in an environmentally stable form as ferric arsenate. The process was pilot tested at Hazen Research in an integrated plant including continuous recycle from August 1989 to October 1989 during which several tons of flue dust were processed. Based on this pilot program, the process was deemed technically feasible and produced commercially salable products. Residues from this pilot program were subjected to a long-term stability test jointly designed by PTI environmental services and the US Environmental Protection Agency (EPA).

Pressure oxidation particularly of sulfide ores containing arsenic such as practiced by Homestake Mining Company at the McLaughlin Mine in California also precipitates arsenic as ferric arsenate from aqueous slurries acidified with sulfuric acid; however the pressure and temperatures requirements of the process are higher than that required by strong chloride brine leaches such as the "Cashman Process". Less base metals are soluble in sulfuric acid compared to hydrochloric and they therefore remain in the residue.

The economic recovery of metals from ores, concentrates and byproducts having a significant arsenic content represents a considerable challenge to the metallurgical industry.

A wholly pyrometallurgical process approach is becoming less acceptable because of ever more stringent regulatory and environmental constraints. In a copper smelter, for example, attempts to keep flue dust in closed circuit result in the buildup of impurities which cannot be tolerated because of the deleterious effects of arsenic, bismuth, antimony, etc. on copper quality. In these smelters such problems can be overcome by utilizing a hydrometallurgical process to treat a portion or all of the resulting flue dust. This would give the pyrometallurgical facility the advantage of lowering or eliminating the flue dust recirculating load, thereby increasing the facility capacity, and at the same time allowing the facility to process feeds with a greater arsenic content. However, in instances of treating arsenic rich feeds, a wholly hydrometallurgical approach may offer the cleanest solution.

In the selection of a hydrometallurgical process, one of the most important concerns should be the long-term stability of the arsenic-containing residue. Ever-changing environmental standards should convince the smelting industry that the superior environmental performance of a process has great advantages, both politically and operationally. The arsenical residue disposal problem will grow since many of the future sources of the common base metals (copper, lead, zinc), as well as gold, have arsenic contents that effectively preclude their processing by conventional pyrometallurgical methods alone.

The fume/flue dust or electrostatic precipitator dust that is recovered from the off-gases of many smelter and roasting operations typically contains arsenic and metals of value, and is often considered hazardous. In some instances, these hazardous flue dusts have been disposed of without regard to their hazardous nature. Because the arsenic component of the flue dust is in a chemically unstable/soluble form, weathering of such flue dust dumps can lead to the contamination of local groundwater systems.

The metallurgical industry is faced with two problems in the treatment of arsenic containing feeds. In addition to the development of economic extraction processes for metals, the industry must also develop processes which address ever-increasing environmental concerns. From a combined economic and engineering point of view, there is a great incentive to solve both problems simultaneously. This means developing flow sheets that allow for the economic recovery of the contained metals as well as the stabilization of the arsenic in a residue that will meet current and future environmental regulations. Hydrometallurgical processes such as the Cashman Process and pressure oxidation provide the necessary solutions in many cases.

THE CASHMAN PROCESS

The Cashman Process was initially developed to treat arsenic-containing base metal sulfide concentrates. Subsequent work showed that by the choice of appropriate operating parameters, the basic principles of the process could be applied to effectively treat arsenical flue dusts.

The Cashman Process is a hydrometallurgical process utilizing a hydrochloric acid leach under somewhat elevated temperature and pressures which solubilizes metals of economic interest such as copper, zinc, lead, silver, gold, nickel, cobalt, and bismuth and simultaneously leaves toxic elements such as arsenic in an environmentally stable leach residue. The Cashman Process uses a patented hydrochloric acid leach process (Patent No. 4,655,829) developed by CSS Management Corporation in Skykomish, Washington. Artech is the licensee of the Cashman Process and is currently conducting efforts to identify and develop commercial applications for the Cashman Process.

To bring about the oxidation of arsenic(III) to arsenic(V) necessary for the precipitation reactions as well as the oxidation of the base metal sulfides and arsenopyrite, oxygen (sometimes as air) is used. The effectiveness of the Cashman Process depends largely on the leach chemistry as well as efficiency of oxygen dispersion throughout the reaction slurry, which is achieved by use of a low temperature, low pressure autoclave with an efficient mixing and gas injection system.

Materials of construction are always a matter of concern when developing design engineering and operating criteria. When calcium chloride is used as one of the reactants in the Cashman Process, the pregnant leach slurry contains solubilized base metal chlorides which are corrosive toward standard materials of construction. For these reactions, acid-resistant brick-lined autoclaves are required. Ancillaries such as piping and pumps must also be corrosion resistant. Although materials of construction are a concern, reliable components are readily available.

Reagent additions are determined by the chemistry and mineralogy of the feed. Operating conditions for each feed type are typically of low temperature and pressure. The reactor is heated indirectly with steam. Reaction time depends on grind size, pulp density, and mineralogy and is typically 30 to 60 minutes for a flue dust that contains only small quantities of sulfides.

STABILITY OF ARSENIC-CONTAINING SOLIDS

The chemistry of arsenic is complex and much of the early work on the composition and stability of arsenic-containing solids precipitated from solution is difficult to interpret. In most hydrometallurgical processes, the arsenic is precipitated as ferric arsenate ($FeAsO_4$). Recent studies have indicated that in order to minimize the solubility of the arsenic in the precipitate, the Fe:As cation ratio in the precipitate should be greater than the inferred stoichiometry of 1:1. This means that excess ferric ions and other cations are co-precipitated with the ferric arsenate. In addition, the studies indicate the temperature and pH (acidity) of precipitation should be controlled to produce a crystalline ferric arsenate product.

These conditions are difficult to maintain in typical commercial hydrometallurgical operations. Many processes designed to recover valuable base metals from arsenic rich sources are also designed to minimize iron dissolution because the recovery of base metals from iron rich solutions is often difficult. This apparent dissolution selectivity is achieved by either actually preventing the iron minerals from dissolving, or causing them to dissolve simultaneously and reprecipitate in a form other than ferric arsenate. This results in an arsenic compound that is unstable and has relatively high solubility.

In summary, most of the proposed hydrometallurgical processes for treating arsenic-containing feeds result in residues that are not chemically stable and not of low solubility because (a) the acidity (pH) regime in which the arsenic compound was formed is unsatisfactory and/or (b) there is insufficient cation concentration in solution to precipitate the arsenate anion "completely".

In order to meet environmental disposal requirements, other processes may require additional processing stages, either to re- treat the leach residue, and/or to precipitate the soluble arsenic from the leach slurry before disposal or treatment for recovery of valuable metals. The Cashman Process obviates the need for these additional stages because it permits the precipitation of all the arsenic in the feed in a stable non-soluble form in a single unit operation. Furthermore, Artech is successful at producing residues that better the toxicity tests using stoichiometric iron to arsenic ratios of 1.2 : 1. Selected samples of the leach residues have been chemically and mineralogically characterized and shown to be mixtures of predominantly crystalline ferric arsenate and gypsum.

CASHMAN PROCESS DESCRIPTION

In base metal smelters, dusts emanating from roasting, smelting and converting operations typically contain arsenic, bismuth, cadmium and antimony as process impurities as well as valuable base and noble metals. The base metals are present in the fume/flue dust as complex mixtures of oxides, ferrites, etc. while the arsenic is typically present as arsenic(III) oxide. In order to dissolve the base metals from the flue dust, during the Cashman Process a reaction slurry of about 20% solids is made acidic. If the flue dust has a relatively low iron content, an additional iron source is required. Calcium chloride is used so that the base metals are dissolved as chloro complexes. The arsenic is co-precipitated primarily as ferric arsenate but also as a mixture of copper/iron and other complex metal arsenates with gypsum (hydrated calcium sulfate) which are very stable.

Implementing the Cashman Process at an existing smelter site is generalized as follows: After solid/ liquid separation of the leached slurry, the pregnant leach liquor can either be processed by a combination of selective precipitation, solvent extraction/ion exchange and electrowinning techniques to recover the dissolved base metals separately, or in bulk form as a mixed oxide / hydroxide / carbonate base metal precipitate which can be recycled to the smelting furnace. This proprietary conversion reaction (called the metathesis reaction) has been developed by Artech to convert chlorides to oxide products, and to recycle the chloride in the Cashman Process, thereby substantially eliminating residual chloride content in the products which might cause corrosion damage in subsequent unit operations.

Generally a plant utilizing the Cashman Process would include the following:

        Feed preparation
        Autoclave leaching, filtration, and disposal of process residue
        Metals recovery
        Barren stream recycle

FEED PREPARATION

Mineralogical and metallurgical test work are used to identify the optimum reagent additions required to provide maximum metals recovery and maximum environmental performance. Most feed constituents of less than 85 mesh generally do not require grinding, although screening and wet grinding can be utilized, where necessary. The material to be treated is slurried with recycled calcium chloride brine, sulfuric acid, and a source of iron (if sufficient iron is not contained in the waste) and is then introduced into the autoclave.

AUTOCLAVE LEACHING, FILTRATION, AND DISPOSAL OF RESIDUE

Materials are leached in an autoclave under somewhat elevated temperature and pressure conditions for 30 to 120 minutes. The hot leached slurry is then pressure filtered to produce a solid residue and a leach liquor. The solid residue generally contains sulfates, iron oxides, silica, sulfides, and ferric arsenate. The leach liquor may contain dissolved metals such as copper, lead, zinc, silver, mercury, bismuth, cadmium,

and gold. The solid residue is washed with water prior to disposal. Metals recovery operations are applied to the filtered leach liquor and the barren liquor containing the chloride is then recycled.

METAL EXTRACTIONS

The metal extractions for the same eight feedstocks are shown in Table 1.

TABLE 1. CASHMAN PROCESS METAL EXTRACTIONS FOR EIGHT FEEDSTOCKS (1)

Material	Gold	Silver	Copper	Lead	Zinc	Bismuth	Cadmium
Feed # 1	93.75%	N/D	80.40%	47.46%	97.84%	N/D	98.78%
Feed # 2	N/D	93.10%	N/D	61.57%	98.11%	N/D	N/D
Feed # 3	95.78%	N/D	89.11%	N/D	74.89%	N/D	95.37%
Feed # 4	69.53%	74.03%	90.71%	80.91%	81.98%	N/D	99.09%
Feed # 5	N/D	N/D	94.45%	42.35%	83.34%	29.95%	98.85%
Feed # 6	90.37%	72.05%	90.56%	45.40%	56.78%	98.30%	91.44%
Feed # 7	49.63%	88.59%	96.44%	86.27%	90.59%	94.71%	98.47%
Feed # 8	64.38%	96.77%	94.41%	61.74%	97.12%	92.63%	99.37%

N/D = Not Determined

FEED STREAM ANALYSES

The analyses of eight feedstocks and residues processed by the Cashman Process are presented in Table 2.

TABLE 2. ANALYTICAL RESULTS FOR CASHMAN PROCESS RESIDUES AND UNPROCESSED FEEDS (1)

Material	Analytical Results (%)							
	As	Ag	Ba	Cd	Cr	Hg	Pb	Se
Feed # 1	11.6200	0.0110	n/a	0.5340	0.0160	0.0040	2.6800	n/a
Residue # 1	5.4200	0.0010	n/a	0.0065	0.0106	0.0001	1.4080	n/a
Feed # 2	11.2500	0.0160	n/a	n/a	<0.001	<0.001	44.5000	n/a
Residue # 2	7.9400	0.0010	n/a	n/a	n/a	<0.001	14.9500	n/a
Feed # 3	5.3400	0.0190	n/a	0.1656	0.0115	<0.001	1.8980	n/a
Residue # 3	4.9200	0.0010	n/a	0.0070	0.0133	0.0002	1.8960	n/a
Feed # 4	2.9650	0.0090	0.0540	1.0050	<0.001	0.0001	23.7000	0.0004
Residue # 4	3.1300	0.0030	n/a	0.0100	n/a	0.0001	4.9500	n/a
Feed # 5	1.4150	0.0061	n/a	0.1860	0.0069	0.0001	0.4920	0.0001
Residue # 5	1.0100	0.0017	n/a	0.0160	n/a	n/a	0.2700	n/a
Feed # 6	7.7700	0.0163	0.1792	0.1660	0.0110	0.0003	9.5600	0.0002
Residue # 6	8.5750	0.0022	n/a	0.0030	n/a	n/a	1.5500	n/a
Feed # 7	2.0600	0.0160	n/a	0.1560	0.0125	0.0012	1.9700	n/a
Residue # 7	2.0800	n/a	n/a	0.0017	0.0118	0.0030	1.0740	n/a
Feed # 8	22.9000	0.0603	n/a	2.9500	n/a	<0.0001	25.9000	n/a
Residue # 8*	15.9000	0.0015	n/a	0.0140	n/a	n/a	7.4900	n/a

n/a = Not Analyzed

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METALS RECOVERY

The best method of recovering metals from the leach liquor will vary, depending upon the quantity and the type of metals present. The following discussion first focuses on the most likely metal recovery methods, but also identifies alternatives developed for Anaconda flue dust which could be employed, if necessary. Not all flue dusts or residues would necessarily have present all of the metals cited in the tables in this abstract or alternatively may have other metals not mentioned present.

The Cashman Process can be utilized at existing smelting facilities to eliminate hazardous flue dust from the smelting process. Treating the flue dust would generate two products: a non-hazardous residue primarily consisting of $CaSO_4$ (calcium sulfate), SiO_2 (silica) and $FeAsO_4 \cdot 2H_2O$ (ferric arsenate or scorodite); and a mixed metal oxide/carbonate precipitate that could be recycled to the smelter feed to combine with and, in part, replace the fluxing components.

Artech has piloted a proprietary elevated temperature and pressure precipitation procedure (metathesis) which allows the precipitation of metal oxides and hydroxides from a chloride solution. Using this procedure to precipitate all the metals solubilized during the leaching stage produces a precipitate consisting of metal oxides, metal hydroxides, metal carbonates, and CaO. This precipitate could then be either recycled to the smelting furnaces or directed to other metal recovery operations at the facility. For instance, the precipitate could be digested with sulfuric acid and directed to existing solvent extraction circuits.

Continuous pilot-scale tests on the treatment of the flue dusts have confirmed flow sheets for producing products such as copper oxide or electrolytic copper, zinc oxide, bismuth oxychloride, lead sulfate, silver cement, cadmium sponge, and mercury. Both batch and continuous production have been piloted for Artech's proprietary metal oxychloride to metal oxide conversion reaction (metathesis).

Bechtel Corporation has completed an engineering design of a Cashman Process plant for a Superfund flue dust project incorporating many of the metal recovery steps discussed in this abstract. The Bechtel report states that the "process plant is designed to be zero discharge and has no water effluent".

RESIDUE CHARACTERISTICS

The toxicity results for the eight feedstocks illustrated in this abstract are shown in Table 3.

TABLE 3. TOXICITY RESULTS FOR CASHMAN PROCESS RESIDUES AND FEEDS (1)

Material	Type of Test	Extract Number	As	Ag	Ba	Cd	Cr	Hg	Pb	Se
Feed # 1	EP TOX	N/A	52.0000	0.0090	<0.001	11.4000	0.0070	0.0010	0.8000	<0.001
Residue # 1	EP TOX	N/A	0.1300	0.0500	<0.001	0.0700	0.0660	0.0030	2.7000	<0.001
Feed # 2	EP TOX	N/A	23.0000	0.0050	0.0100	26.0000	0.0050	0.0004	1.28000	0005
Residue # 2	EP TOX	N/A	0.3500	0.0200	0.0050	0.8000	0.0050	0.0006	2.94000	.0340
Feed # 3	EP TOX	N/A	28.0000	<0.001	<0.001	33.6900	0.0040	<0.001	2.2000	<0.001
Residue # 3	EP TOX	N/A	0.0030	0.0350	<0.001	0.4870	0.0210	0.0001	1.5000	<0.001
Feed # 4	EP TOX	N/A	0.6000	0.0100	0.4000	10.000	<0.001	0.0004	7.00000	.0009
Residue # 4	EP TOX	N/A	0.0400	0.0400	0.0100	0.0400	0.0200	0.0005	2.38000	.0001
Feed # 5	EP TOX	N/A	0.3500	0.0010	<0.0001	33.2200	0.0280	<0.0001	53.40000	.0001
Residue # 5	EP TOX	N/A	3.6000	0.0001	<0.0001	0.0660	0.0230	<0.0001	1.3000	<0.0001
Feed # 6	TCLP	2	0.0099	0.0300	0.0990	65.000	0.0400	0.0001	0.67000	.3500
Residue # 6	TCLP	1	0.0500	0.0100	0.0900	0.160	0.0400	0.0001	0.14000	.0350
Feed # 7	TCLP	1	1,300.00	0.0190	0.0190	36.600	0.2000	0.0020	1.69000	.2000
Residue # 7	TCLP	1	1.200	0.0100	0.0100	0.030	0.0100	0.0006	1.56000	.0560
Feed # 8	TCLP	1	2,100.00	0.0090	0.0600	41.400	0.0090	0.0004	9.28000	.0580
Residue # 8*	TCLP	1	1.100	0.0100	0.0100	0.169	0.0100	0.0009	15.90000	.1000

* This sample is in the process testing stage as of 2/25/91 (only two scoping tests performed to date).

NOTE: The EPA has identified feed # 5 as a K064 waste

N/A = Not Applicable

LONG-TERM STABILITY TESTING

Independent test work conducted in 1989 and 1990 by PTI Environmental Services (2) of Boulder, Colorado to simulate the long term stability of leach residues derived from treating copper smelter flue dusts by the Cashman Process substantiate the long term stability claims of the Cashman Process leach residues. The EPA approved the procedures used by the independent test firm for this test work. In the test work, arsenic and cadmium in aqueous solution were extracted from leach columns and their concentrations were monitored over several months. The report on these tests concluded that it would take 4 to 8 million years to gradually leach all of the arsenic from a 3-meter thick pile of Cashman Process residues openly exposed to the environment. Additionally, the suitability of several substrates to mitigate any solubilized arsenic and cadmium were investigated. Some of these tests demonstrated that the leachate which passed through the substrate passed drinking water quality standards for cadmium and arsenic. The long term stability test information from the above report provides a basis for making a technically appropriate choice of disposal sites.

ADVANTAGES OF THE CASHMAN PROCESS LEACH OVER OTHER PRESSURE LEACH SYSTEMS

- Oxygen partial pressure is not the rate determining factor in the oxidation of iron and arsenic, but oxygen dispersion and pulp agitation are critical.

- Temperatures and pressures are significantly lower than for other autoclave systems.

- During the oxidation leach, the arsenic is precipitated in a highly stable form in a residue that significantly betters the TCLP test requirements. Cashman Process residues, if left exposed will take millions of years to gradually release their potentially hazardous constituents back into the environment.

- The process leaches base and precious metals and precipitates the arsenic in a single stage leach (other processes require two or more stages).

ADVANTAGES OF THE CASHMAN PROCESS LEACH OVER CONVENTIONAL FLUE DUST MANAGEMENT OR TREATMENT PROCESSES

- The Cashman Process could replace the usual procedure of recycling flue dusts within the smelter, thereby allowing for increased smelter throughput, increased metal purities and less dust handling problems.

- Smelters could accept ores and concentrates higher in impurity element content, and still achieve product specifications.

- Readily leachable arsenic trioxide or other arsenic complexes are converted to stable ferric arsenate. Arsenic is estimated to leach from these materials over millions of years, which would virtually eliminate loading of groundwater with arsenic.

- Long-term management and potential liabilities associated with discarding waste products can be minimized.

- Waste volumes can be reduced by the removal of metals.

- Natural resources are conserved because otherwise discarded metals are returned to industrial use.

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ARSENIC EXTRACTION FROM SILT AND CLAYS

Adolfo R. Zambrano and Dennis D. Chilcote
BioTrol, Inc.
11 Peavey Road
Chaska, MN 55318
USA
Tel: (612) 448-2515

INTRODUCTION

The application of BioTrol Soil Treatment System (BSTS) to the remediation of arsenic-contaminated soils results in the separation of a residual fine fraction of the soil which essentially carries the bulk of the arsenic and which is constituted primarily by a matrix of silt and clay(s). In general, this fraction does not warrant a high remediation cost by extraction techniques due to its small volume and as a result, alternative technologies such as solidification and stabilization become very attractive.

The opportunity to study an entire site with the characteristics of the fine fraction previously described was a welcome challenge.

SITE CHARACTERISTICS

The Whitmoyer Laboratories Superfund Site, located in Lebanon County, Myerstown, PA, was dedicated to the production of veterinary pharmaceutical products and for some 30 years produced organo-arsenical compounds, primarily arsanilic acid (C_6H_8-$AsNO_3$) and carbarsone (C_7H_9-AsN_2O_4). On-site treatment of contaminated groundwater made extensive use of arsenic precipitation as calcium and ferric arsenates which were stored in lagoons.

Two soil samples from this site were used in this study: an "average" soil sample having an arsenic content of 1035 ppm, and the "worst" soil sample having an arsenic level of 3650 ppm. Both samples had average values for silt and clay of about 85% and Cation Exchange Capacities of 14 mEq/100 g.

EXPERIMENTAL DESIGN

In order to compensate for the lack of an arsenic species distribution in the soils, the performance of mineral acids and bases alone and in combination with complexing agents and polar organic solvents were evaluated to select the two most effective extractive agents.

DESIGN IMPLEMENTATION

The search for the best two leaching agents was carried out as follows: 1) A series of 12 single-stage leaching extraction tests was performed with a single extractant or a combination of extractants plus a complexing agent or polar solvent using the "average" soil sample; 2) The best four performing extractants or extractant-complexing agent combination from the previous series were retested using the "worst" soil sample; 3) The best two performing extractants from the four-test series were re-evaluated in multistage cross-current leaching extraction tests to simulate a continous operation.

All leaching extraction stages were conducted using a 35% solids slurry and were extracted for 4 hours at room temperature (22 degrees C ± 2).

RESULTS AND DISCUSSION

Single Stage Extractions

"Average" Soil: Acidic Leaching at pH = 1.0. These results are summarized in Table 1. Although the

three acids tested gave poor performances, sulfuric acid appeared to outperform both the nitric and hydrochloric acids. The performance of hydrochloric acid was most improved in the presence of sodium thiosulfate.

TABLE 1. ACIDIC ARSENIC EXTRACTION FROM "AVERAGE" SOIL AT pH = 1

REAGENTS		PROCESSED	STREAMS	Total Arsenic,	TCLP-Arsenic,	Arsenic Extracted,
NAME	LEVEL, lb/STon	Name	kg or l	ppm	ppm	%
H_2SO_4	165	Soil	0.30	974.0		
		Leachate	0.98	17.9		5.7
HNO_3	190	Soil	0.28	1119.0		
		Leachate	1.16	0.5		0.2
HCl	140	Soil	0.27	1051.0		
		Leachate	1.05	0.4		0.2
HCl	120	Soil	0.28	836.0		
DP-3	1.3	Leachate	1.05	2.0		0.9
HCl	135	Soil	0.26	1109.0		
Na_2SO_3	20	Leachate	1.63	2.2		1.3
HCl	175	Soil	0.28	896.0	1.4	
$Na_2S_2O_3$	20	Leachate	1.15	31.6		12.7

"Average" Soil: Basic Leaching at pH = 11.0. These results are given in Table 2. These data show that the performance of the hydroxyl ions is improved by the presence of the carbonate ions and the performance of these two ions is in turn improved by the presence of Cyquest DP-6 antiprecipitant. Also the performance of hydroxyl ions is substantially improved in the presence of ethanol.

TABLE 2. BASIC ARSENIC EXTRACTION FROM "AVERAGE" SOIL AT pH = 11

REAGENTS		PROCESSED	STREAMS	Total Arsenic,	TCLP-Arsenic,	Arsenic Extracted,
NAME	LEVEL, lb/STon	Name	kg or l	ppm	ppm	%
NaOH	10	Soil	0.27	1070.0		
		Leachate	1.35	26.0		10.8
NaOH	20	Soil	0.29	1148.0		
Na_2CO_3	380	Leachate	1.22	69.2		20.2
NaOH	14					
DP-6	1.3	Soil	0.30	691	1.4	
Na_2CO_3	370	Leachate	1.01	124.0		37.7
NaOH	56	Soil	0.30	691.0	0.1	
Ethanol	200	Leachate	0.97	140.0		62.0

"Worst" Soil: Basic Leaching at pH = 11.0. The comparable performance of four lixiviant solutions are summarized in Table 3. Any one of these lixiviants could be used to optimize a conceptual process remediation scheme.

TABLE 3. BASIC ARSENIC EXTRACTION FROM "WORST" SOIL AT pH = 11

REAGENTS		PROCESSED	STREAMS	Total Arsenic,	TCLP-Arsenic,	Arsenic Extracted,
NAME	LEVEL, lb/STon	Name	kg or l	ppm	ppm	%
NaOH	95					
Na2S2O3	20	Soil	0.30	1440.0	0.2	
Na2CO3	375	Leachate	1.15	658.0		63.7
NaOH	55					
NaOCl	20	Soil	0.30	1450.0	0.2	
Na2CO3	335	Leachate	1.17	536.0		59.0
NaOH	115					
DP-6	1.3	Soil	0.30	1206.0	0.2	
Na2CO3	375	Leachate	1.27	568.0		66.6
NaOH	100					
Ethanol	200	Soil	0.30	1538.0	0.3	
Na2CO3	347	Leachate	1.19	489.0		55.8

Multistage Simulations

Typical results for the two types of soil used in this study are depicted in Figure 1 for the evaluation of Na2CO3 and Cyquest DP-6 but without NaOH additions.
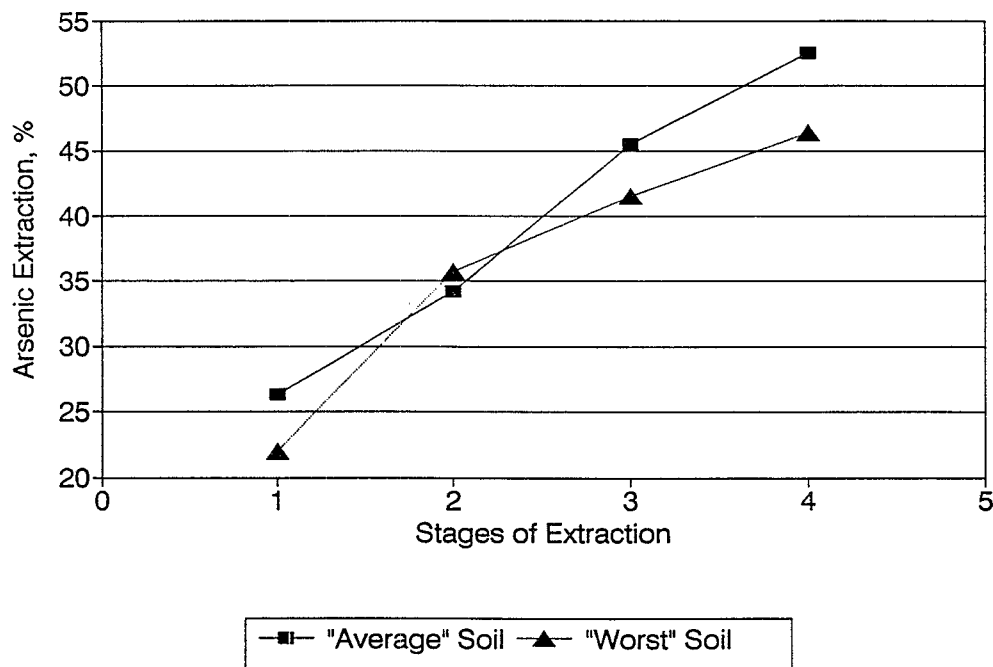
Figure 1. Arsenic extraction using sodium carbonate and Cyquest DP- 6.

CONCLUSIONS

The experimental data and the general observations during the course of the treatability study can be summarized as follows:

Leaching with sulfuric, nitric, or hydrochloric acid at pH = 1 does not accomplish any significant arsenic removal.

Under basic conditions, sodium carbonate in combination with sodium hydroxide and a chelating agent can extract about 65% of the total arsenic. In the absence of sodium hydroxide the extraction efficiency decreases. (Compare results in Table 3 and Figure 1.)

For leaching extraction times beyond 4 hours, solid-liquid separation by filtration becomes very difficult.

Because ethanol can also extract more than 60% of the total arsenic, its utilization as the major solvent will also drastically reduce the filtration difficulties associated with soil matrices made up primarily of silt and clay(s). Solvent recovery and recycling can be accomplished through distillation.

A conceptual process flowsheet for the removal of arsenic- bearing contaminants other than the ferric arsenates is shown in Figure 2 for the case of extraction with sodium carbonate and Cyquest DP-6. An order-of-magnitude installed cost of $5 million was estimated within a -30% +50% accuracy for a 20 tons per hour remediation plant. The operating cost to remediate 100,000 cubic yards of soil was estimated at $160 per cubic yard, exclusive of excavation, debris removal, and equipment capital recovery.
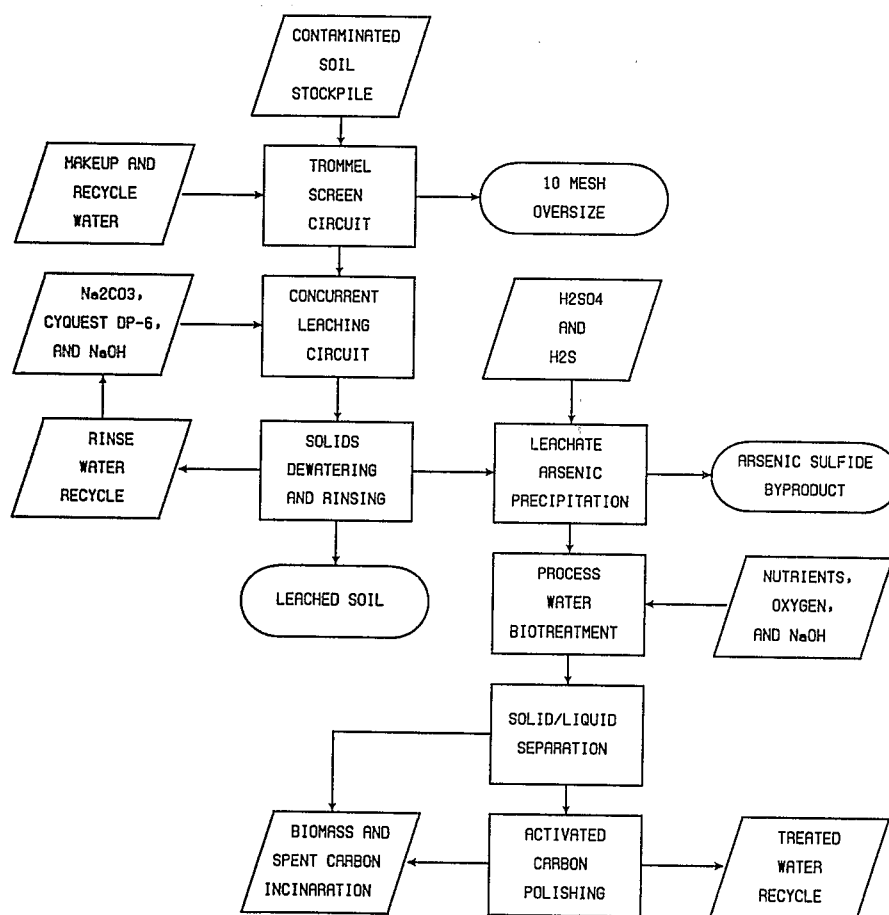

Figure 2. Conceptual site remediation flowsheet.

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THE BEHAVIOR OF ARSENIC IN A ROTARY KILN INCINERATOR

Robert C. Thurnau
US Environmental Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268
USA

INTRODUCTION

Arsenic has always been an element of environmental interest. Its toxicity to the human body has been well documented, and its regulation from an environmental standpoint has appeared in several statutes. With the toxicity problems of hazardous waste and its treatment/disposal being better understood, releases of trace elements (especially arsenic) through incineration were thought to be a potential danger. The data base to understand and predict the impact from incinerating arsenic-laden wastes was very sparse (1-5) and thus the Environmental Protection Agency/Office of Research and Development (EPA/ORD) undertook the task to study arsenic's fate under a variety of combustion conditions. This paper will discuss the partitioning of arsenic as observed during a controlled incineration study on an arsenic-containing synthetic waste and on a Superfund soil containing arsenic as a primary contaminant.

APPROACH

EPA/ORD operates a research facility dedicated to the study of hazardous waste incineration and the conditions that influence the different environmental release pathways. To address the question of arsenic partitioning to the different streams, ORD through its Incineration Research Facility (IRF) systematically evaluated the following variables:

> Kiln and afterburner temperature
> Waste feed chlorine content
> Initial arsenic concentration
> Effects on Toxicity Characteristic Leaching Procedure (TCLP)

For the parametric study, a synthetic mixture containing arsenic trioxide and other metals was mixed into a homogenous solution and metered onto a clay/organic matrix as the material was fed to the incinerator. For the study of the Superfund soil, the soil matrix was fed to the incinerator in the same condition as received, but the total chemical identify of the arsenic was unknown. The test conditions for the Superfund soil were similar to the parametric test conditions except the kiln oxygen was a new variable.

Samples of kiln ash, scrubber liquor, and scrubber exit flue gas were collected with EPA-validated sampling methods and analyzed for arsenic to determine its partitioning.

RESULTS

The expectation at the beginning of the experiments was that arsenic, with its relatively high vapor pressure, would be volatile and be increasingly displaced from the waste as the combustion temperature increased. The data collected however, showed that the arsenic, although influenced by the kiln temperature, was tending to be found in the ash. This relationship was not only clear, but reproducible with a linear regression correlation coefficient of 0.97 for the parametric test data. The same type of trend was also observed for the arsenic in the Superfund soil with a regression coefficient of 0.84.

A series of experiments were carried out to determine the effect of the afterburner temperature on arsenic partitioning. The data collected for afterburner temperatures of 1800, 2000, and 2220 degrees F indicate that the partitioning of arsenic is independent of afterburner temperature. This experiment was not conducted on the Superfund soil.

The interaction of chlorine with trace metals during incineration to form new compounds with different boiling points has been suggested as a possible mechanism for explaining the observed partitioning data for several of the trace metals studied. To determine if changes in waste feed chlorine concentration had an effect on the partitioning of arsenic, tests were conducted in which feed chlorine concentration was varied from 0 to

8 percent, while the other experimental parameters were held constant (kiln temperature = 871 degrees C (1600 degrees F), afterburner temperature = 1093 degrees C (2000 degrees F)).

The results for arsenic partitioning to the kiln ash, flue gas, and scrubber liquor were collected and under the conditions studied during these tests, arsenic partitioning did not vary with changes in feed chlorine concentration. This observation is consistent with equilibrium calculations which do not predict a relationship between arsenic vapor pressure and chlorine content.

The feed rate of arsenic during the parametric tests was designed to be constant throughout the test series, but in reality varied from 1173 to 2112 mg/hr. Data collected illustrate the effect of varying the feed rate of arsenic on partitioning to the incinerator effluents for all parametric tests conducted at constant kiln temperature. For the range of feed rates experienced during this test series, no statistical correlation was found between the arsenic feed rate and arsenic partitioning to the different effluents.

TCLP values for arsenic in the Superfund soil and in the kiln ash were also collected. In all cases, the act of incinerating the soil increased the mobility of the arsenic in the ash as evidenced by the higher arsenic concentrations in the leachate compared to the untreated soil. These data do not show a statistical relationship between variations in kiln temperature and kiln ash arsenic TCLP values. However, the data do suggest a relationship between kiln oxygen levels and the ash TCLP arsenic values. Specifically, at the higher kiln exit oxygen concentrations the kiln ash TCLP values for arsenic were lower. On average, kiln exit oxygen concentrations around 11% resulted in arsenic TCLP values that were about 4.6 times lower than the 7% kiln exit oxygen concentrations.

DISCUSSION AND CONCLUSIONS

Previous data gathered on the partitioning of arsenic during the incineration of hazardous wastes were inconclusive with regard to its distribution, and thus the potential for environmental release was not fully understood. With the implementation of the Land Ban Rules, there was additional concern on the part of EPA that the chemical composition of hazardous waste incinerated in the future would change. Metals such as arsenic might be found at higher concentrations, thus increasing the potential for additional arsenic releases to the environment.

Incineration data generated during tests at the IRF showed that the distribution of arsenic to the different residual streams associated with hazardous waste incineration (in both a synthetic matrix and a "real world" matrix) generally favored the solid phase, or ash, rather than the gas or vapor phase. Both sets of data showed that the temperature of the kiln directly affected how much arsenic was volatilized. Over the temperature range studied, 816 to 927 degrees C (1500 to 1700 degrees F) for the parametric study and 816 to 982 degrees C (1500 to 1800 degrees F) for the Superfund soil, the amount of arsenic volatilized increased with increased temperature. The increase in volatility was much less pronounced in the parametric study with the net change being only 9% over the 200 degrees F temperature range. The change in arsenic partitioning to the ash was more pronounced in the Superfund soil, with an observed difference of 36% over a temperature range of 300 degrees F.

An increase in arsenic volatility with increased kiln temperature is predicted based on the thermodynamic data, but the extent to which arsenic is retained by the ash in these experiments was unexpected. The chemical form that the arsenic assumed during incineration may be responsible for some of the unexpected partitioning to the ash. Also, the arsenic may have become chemically or physically bound with the solid matrix and not easily released to the flue gas.

The TCLP results associated with the Superfund soil residuals were very interesting. Incineration altered the soil matrix to the extent that arsenic was much more mobile in the kiln ash than in the native soil. Even though the concentration of arsenic in the native soil was high, it was retained by the soil, which was not a hazardous waste as defined by TCLP. The leachate concentrations were well below the regulatory TCLP limit of 5 mg/L. As the amount of oxygen in the kiln decreased, the arsenic TCLP values for the kiln ash increased, although the kiln ash leachate concentrations did remain below the regulatory limit. Again, the chemical form of the arsenic and the components of the matrix are unknown, but probably are responsible for this phenomenon. The importance of this observation will be reflected in the operating conditions of an incinerator burning this soil, along with the added costs for subsequent ash treatment, if required.

The incineration of soils contaminated by organics and arsenic may be a feasible remediation option for

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destroying the organic compounds. The results of these studies suggest that by selectively optimizing the incineration conditions, arsenic can be retained in the ash where it can be effectively handled.

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REMOVAL OF ARSENIC FROM WASTEWATERS AND STABILIZATION OF ARSENIC BEARING WASTE SOLIDS

L.G. Twidwell, K.O. Plessas, and T.P. Bowler
Metallurgy-Mineral Processing Engineering Department
Montana College of Mineral Science and Technology
Butte, MT 59701
USA
Tel: (406) 496-4208

INTRODUCTION

An extensive compilation of references concerned with arsenic removal from wastewaters, stabilization of waste materials, and treatment of arsenic bearing wastes has been assembled by the authors. This compilation will be available at the conference. The emphasis of the presentation will be on removing arsenic from wastewaters and stabilizing arsenic-bearing solids. A review of the literature on arsenic removal and stabilization will be presented and experimental results from studies conducted at Montana Tech will be discussed. Studies to be discussed include: arsenic removal from solution; stabilization of arsenic-bearing waste materials; and treatment of arsenic bearing metallurgical waste and byproducts.

STUDIES AT MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY

Arsenic Removal from Solution

Comba (1) investigated the removal of arsenic from solution by the formation of mimetite, a lead chloroarsenate ($Pb_5(AsO_4)_3Cl$). His results demonstrated that arsenic could be effectively removed from solution as a crystalline precipitate to concentrations below the detection limit (by AA analysis), i.e., the arsenic concentration was below 0.2 µg/L (ppb). The free energy of formation for mimetite was determined to be -625 ± 2 kilocalories/mole. The equilibrium stability diagram for the lead-arsenate-chloride system (using the determined free energy value) is presented in Figure 1. Note the low solubility of arsenic at natural water pH levels. The filterability of the mimetite was excellent because the morphology of the precipitate was small crystalline spherites. The lead left in solution could be stripped from solution as lead hydroxide, lead carbonate, or lead phosphate.

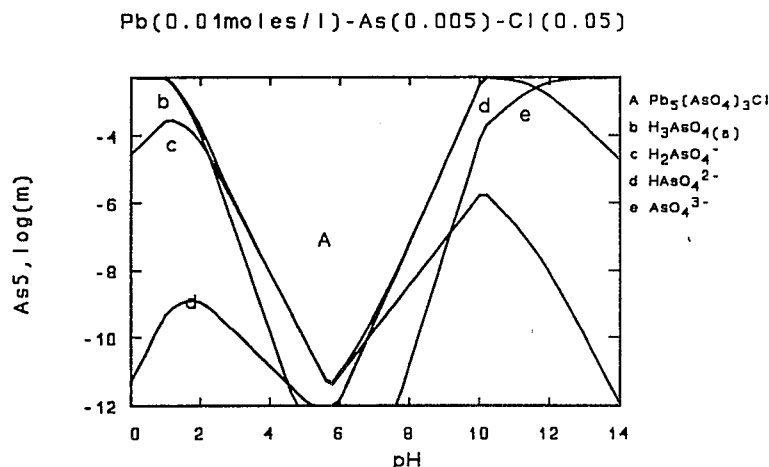$Pb(0.01 moles/l) - As(0.005) - Cl(0.05)$

Figure 1. The Pb-As-Cl-H_2O system.

Because the lead chloroarsenate test work was so successful, attempts to form other chloroarsenates using non-toxic cations were attempted (2). Excellent arsenic removal was achieved and the results are

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presented in Table 1. These solution/solid mixtures have been aged in closed containers for approximately 4 years and are currently being reanalyzed for solution arsenic and for phase identification.

TABLE 1. ARSENIC REMOVAL FROM SOLUTION		
System	Arsenic (V), ug/lit	pH
Starting Conc.	10^6	
Ca-As	91.6	12.7
Ca-As-Cl	0.7	12.6 (8 samples)
Ca-As-P	<0.5	12.6
Ca-As-P-Cl	<0.5	12.6 (5 samples)

Bowler (3) investigated the removal of arsenic from solution by a variety of techniques. He accomplished essentially complete removal by precipitation/adsorption using calcium hydroxide additions. His results are in agreement with the results reported previously by Nishimura and Tozawa (4) and Robins and Huang (5). The solid products pass the Toxicity Characteristic Leaching Procedure (TCLP) test for arsenic but, as has been reported by Robins (6), the solid product is not appropriate for long-term chemical pond storage.

Bowler (3) and Plessas (7) investigated arsenic removal by precipitation at elevated temperatures. They demonstrated that arsenic may be effectively removed from elevated pH and temperature solutions by precipitation of maghemite/magnetite. The test work was conducted in the pH range 7 to 11 (3), 8 to 10 (7) at temperatures of 70 to 80 degrees C (3), 90 degrees C (7). Successful arsenic removal was achieved to below the drinking water standard (7). The precipitated products passed the TCLP test.

Honores (8) noted in a study (concerned with the recovery of metal values from copper smelter slags) that during the removal of copper by iron cementation that greater than 90% of the arsenic was also removed. Plessas (7) followed up on this noted effect and investigated arsenic removal by cementation using iron. She investigated the removal of arsenic from synthetic wastewaters (at various pH levels) by flowing solutions over iron scrap (in a column setup). Arsenic concentrations in the range 1 to 5 mg/L were achieved at pH levels of 5 to 6. It is presently not clear whether the removal was by reduction of arsenate to arsenic metal or was due to adsorption by oxidized iron on the surface of the iron scrap.

Stabilization of Arsenic-Bearing Waste Materials

Four experimental studies have been conducted at Montana Tech on stabilization of solid waste materials. The technologies utilized were vitrification (9, 10) (one study) and cement/lime stabilization (11-13) (three studies). Twidwell and Mehta (10) proposed that a way to dispose of copper smelter flue dust was via conversion of the arsenic to calcium arsenate which could then be dissolved in copper smelter slag. Copper slags were doped with arsenic by dissolution of calcium arsenate in molten slag. Slags were then subjected to the EP toxicity test (refer to Table 2) and also leach tested in a water environment for up to 7 years. Arsenic release was minimal from the glassy slag test materials.

Three studies have been conducted that used cement or cement/lime mixtures for stabilizing various arsenic-bearing materials, e.g., copper smelter flue dust (11), calcium and iron arsenate contaminated soils (12), and ferric hydroxide precipitated solids (13). Tang (11) investigated the stabilization of copper smelter flue dust with cement/lime and the influence of stripping copper from flue dust (by a pyrometallurgical process) on the stability of the final arsenic bearing residue. He demonstrated as a part of his study that flue dust was stabilized by the addition of cement (25%)/lime (10%), i.e., the mixtures passed the TCLP test for arsenic, lead, and cadmium. This result was in agreement with test results generated by ARCO (14) (who have signed a ROD for disposal of 360,000 tons of flue dust by cement/lime stabilization). The findings of

both studies agreed that passing the TCLP test required that sufficient cement/lime must be present to ensure that the TCLP solution pH be in the range 10 to 11.

A treatability study (on NPL site material) conducted by Twidwell and Chatwin (12) demonstrated that cement stabilization of calcium and iron arsenate/arsenite contaminated soils were not stabilized by cement

alone. The presence of cement and a high pH in the TCLP test solution were not sufficient for the mixtures to pass the TCLP test. An additional stabilization roast was required. A brief summary is presented in Table 3. The roast/cement stabilization technology was chosen as the alternative for cleanup at the Whitmoyer NPL site.

TABLE 2. EP TEST RESULTS FOR DOPED COPPER REVERBERATORY SLAG SYSTEMS						
As in Slag, %	Extraction Solution Analysis, mg/L					
	As[b]	Cd[b]	Cr[b]	Pb[b]	Zn	Cu
0.5[a]	0.016	0.093	0.016	0.226	0.30	0.239
0.8[a]	0.047	0.000	0.007	0.149	0.010	0.474
2.1	0.448	0.000	0.006	0.169	0.082	0.526
3.3	0.421	0.000	0.004	0.150	0.084	0.270
5.2	0.901	0.000	0.007	0.150	0.151	0.294
9.1	0.415	0.001	0.007	0.148	0.060	0.050
19.4	0.802	0.002	0.007	0.149	0.036	0.008

[a] As received (undoped) copper reverb slag
[b] EPA designated characteristic concentration for As, Cr, Pb is 5 mg/L; for Cd is 1 mg/L

TABLE 3. STABILIZATION OF WHITMOYER NPL SITE MATERIALS		
Arsenic Content, %	Cement/Waste	TCLP, mg/liter (pH)
1.3	3 3R	5.02 (11.3) 0.11 (11.4)
	1 1R	15.80 (11.0) 0.43 (11.5)
	0.5 0.5R	39.9 (11.6) 0.45 (11.5)
17.8	3 3R	5.0 (11.8) 0.99 (11.7)
	1 1R	72.2 (11.4) 10.8 (10.3)
R designates roasting at 700°C for 1 hour.		

A third study was conducted by Twidwell and McGrath (13) to evaluate whether organic arsenic (monosodium methylarsonate, MSMA) could be stripped from a salt brine solution (containing approximately 2 g/L arsenic) and the product stabilized by cement. Five solution treatment techniques were investigated (four precipitation and one solvent extraction). The final recommended procedure, i.e., the use of ferric precipitation (with an iron/arsenic mole ratio of ten) resulted in excellent results, e.g., 2.3 gpl arsenic was reduced to 8 to 30 µg/L. TCLP results on the solid products ranged from 0.296 to 0.715 mg/L.

The products from the ferric stripping studies were subjected to roast stabilization (chosen because of the success achieved in the Twidwell, Chatwin study and the success achieved by Tozawa, Nishimura and Umetsu (15)). Roast stabilization was unsuccessful. The roasted solids actually leached more arsenic in the TCLP tests than the unroasted precipitated products. Roasting in the presence of cement (1 part cement/1 part ferric product) was successful and resulted in TCLP values that were three to five times less than the results on the untreated ferric product.

Treatment of Arsenic-Bearing Metallurgical Wastes and Byproducts

One of the major arsenic-bearing metallurgical waste byproducts from smelting is flue dust. Vast quantities of flue dust currently exist; some containing up to 20% arsenic (9). Flue dust continues to be experimentally investigated at Montana Tech. Anderson (16) experimentally surveyed the use of a number of elevated temperature roasting techniques for recovering arsenic from copper smelter flue dusts. He specified optimum experimental conditions for removing arsenic as arsenic oxide from the dusts. Mehta (17) developed means for producing calcium arsenate (by roasting) in the flue dust and Mehta and Twidwell (10) investigated disposal of flue dust by dissolution in smelter slag.

Newhouse (18) and Arratia (19) applied the Copper Segregation Process (20) to the dust and to the dust mixed with lime, respectively. They demonstrated that the presence of lime mixed with the dust retained arsenic and allowed for approximately 60% copper recovery. Tang (11) studied the recovery of copper from cement/lime stabilized flue dust (as stated previously). Neira (21) developed reductive roast processes for stripping arsenic from flue dust as relatively high purity metal (99.5%).

Several investigations have been performed to develop a process for producing copper without the formation of arsenic-bearing flue dust. Beuerman and Twidwell (22, 23) investigated the recovery of copper from high arsenic concentrates (and the retention of arsenic in the concentrate residue) by a non-smelting segregation treatment. Excellent copper recovery was achieved but arsenic was volatilized. Gregory (2) continued the research to demonstrate complete retention of arsenic in the concentrate residue (without the emission of arsenic or sulfur dioxide gas) by a lime roasting/segregation process. He demonstrated over 90% copper recovery without any arsenic emission.

Other byproduct treatment processes include studies by Flynn (25) to remove arsenic from lead blast furnace speiss as arsenic metal and by Peterson (26, 27) who developed techniques to recover arsenic from speiss as arsenic metal or as arsenic sulfide.

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TREATMENT OF LANDBAN-VARIANCED ARSENIC WASTES AT TSDFs

Jesse R. Conner and Paul R. Lear
Chemical Waste Management, Inc.
Geneva Engineering and Technology Center
1950 South Batavia Ave.
Geneva, Illinois 60134
USA
Tel: (708) 513-4808

INTRODUCTION

Normally, traditional chemical stabilization processes are able to immobilize arsenic in contaminated soils, incinerator ashes, and other wastes to well below US Environmental Protection Agency (EPA) requirements using the Toxicity Characteristic Leaching Procedure (TCLP) for remedial actions where the waste is to be landfilled on-site after treatment. A sampling of results from treatability studies and commercial stabilization operations at Chemical Waste Management Inc. (CWM) is given in Table 1.

TABLE 1. TYPICAL STABILIZATION RESULTS ON ARSENIC-CONTAINING WASTES

Waste Description	Test Type*	Arsenic Content (mg/l or mg/kg)		
		Total (mg/kg)	Untreated Leach	Treated Leach
Contaminated soil	TCLP	56.9	0.10	0.04
Hazardous waste (H.W.) landfill leachate	TCLP	44.0	4.20	0.016
H.W. Incinerator ash, fluid bed	TCLP	47.6	0.07	0.019
H.W. Incinerator pond sludge	TCLP	24.7	0.30	<0.01
"	EPT	24.7	0.30	<0.01
Pesticide sludge	EPT	1250.0	19.0	0.14
" "	Cal WET	1250.0	52.0	5.20
Pesticide soil	EPT	400.0	0.60	0.27
" "	Cal WET	400.0	28.0	6.50
Phosphoric acid filter cake	TCLP	7950.0	70.0	1.580

* Test Methods: TCLP = Toxicity Characteristic Leaching Procedure; EPT = Extraction Procedure Toxicity Test; Cal WET = California Waste Extraction Test

However, in California a different test, the WET or CAM, is used to establish acceptable immobilization for such on-site disposal. This test is much more severe, especially for arsenic (most especially where the arsenic is present as an organic species) and lead, and often results in WET failures where the material passes the TCLP. CWM has developed a simple, cost-effective, one-step stabilization formulation that allows the treatment of most of these wastes to pass both the TCLP and WET protocols. For more difficult cases, more complex, multi-step processes were required; they are discussed in following paragraphs.

Certain arsenical species, arsenic trisulfide and organic arsenicals primarily, are very difficult to stabilize by conventional chemical means. Because of this, EPA established a Best Demonstrated Available

Technology (BDAT) leaching standard based on vitrification (1) for D004 (arsenic characteristic) and transferred this standard to K031, K084, P011, P012, P036, P038 and U136 non-wastewater codes in the "third-third" Land Disposal Restrictions (LDR). Due to lack of treatment capacity, EPA granted a 2 year national capacity variance for these waste codes, until May 8, 1992 (2). Since 1988 CWM has been conducting extensive research and development on arsenic stabilization at its Geneva Research Center. This work has resulted in an extensive database on immobilization of arsenic in a wide variety of waste streams and to different regulatory standards and test protocols.

This database was shared with the EPA before the third-third LDRs were finalized in 1990. At that time, the chemical stabilization of arsenic trisulfide sludge from phosphoric acid manufacture and organo-arsenicals in a variety of wastes had still not been successfully accomplished on a commercial scale. More recently however, CWM research has resulted in practical formulations and processes for nearly all of these especially difficult-to-treat wastes. This paper discusses these two difficult types of arsenic-bearing waste streams. Waste characteristics, process description, and treated residue characteristics are discussed for each waste type.

ARSENIC TRISULFIDE WASTE FROM PHOSPHORIC ACID PRODUCTION

Arsenous trisulfide (As_2S_3), especially in high concentrations, is very difficult to immobilize chemically because of its solubility under the high pH conditions of conventional stabilization processes. This waste is produced from the "wet process" of food-grade H_3PO_4 manufacture from phosphate rock. Arsenic is an impurity in the rock, and must be removed from the raw acid by precipitation with H_2S gas. The precipitate is removed by settling and filtration

Waste Characteristics

These wastes typically are highly acidic from the residual phosphoric acid, with arsenic concentrations in the 0.5 to 4% range, although some samples may contain even higher concentrations. Other solids in the waste stream consist of other metals precipitated along with the arsenic, as well as large amounts of filter aids such as diatomaceous earth and other solid impurities. In some cases, the waste also contains cement used to eliminate free liquid in the filter cake or sludge. It is bright yellow in color and has a relatively mild sulfide odor. This waste is unusual in that while most metal sulfides decompose in acids to yield soluble metal salts and H_2S, arsenous trisulfide is stable and relatively insoluble under acid conditions, but fairly soluble in alkalies.

Process Description

A large number of conventional stabilization techniques were tested on this waste, with either negative or highly variable results. Research into the literature of arsenic chemistry indicated that the best approach would be to oxidize the As^{+3} to As^{+5} under alkaline conditions, forming the arsenate anion which can then be precipitated by cations such as Ca^{+2} or iron to form low- solubility species. This approach, in fact, worked well using lime, calcium, or sodium hypochlorite, and a stabilization reagent. A similar treatment scheme was developed by a waste generator (3). We have now demonstrated at full production scale a reliable two-step process that is being implemented at several CWM sites. Full-scale testing has been completed and CWM fixed sites were in production as of May 8, 1992 when the existing treatment variance terminates.

Characteristics of the Treated Residue

Both laboratory and full-scale tests yielded arsenic TCLP leaching levels below 0.5 mg/L in all cases, and below 0.05 mg/L (the drinking water standard) in many instances. Table 2 gives a summary of bench-scale testing results and Table 3 the full-scale pilot test results at two different CWM sites. These results show that the system chosen is effective for the stabilization of arsenous trisulfide wastes. Furthermore, full-scale pilot tests yield results comparable to the bench-scale results. The process is not sensitive to the type of oxidizing agent used: all three tested yielded good results. Similarly, a variety of conventional stabilization reagents can be used. This flexibility allows a treatment site to tailor its procedure to cost-effectiveness of reagents available and to other facility restraints.

TABLE 2. SELECTED RESULTS OF BENCH-SCALE STABILIZATION TREATABILITY TESTING FOR ARSENOUS TRISULFIDE WASTES

Sample	Alkaline Reagent	Oxidation Reagent	Stabilization Reagent	Arsenic Content (mg/l or mg/kg)		
				Total (mg/kg)	Untreated Leachate	Treated Leachate
1	Hydrated Lime	$Ca(OCl)_2$	Bed Ash	23000.	>100.0	0.25
2	Hydrated Lime	$Ca(OCl)_2$	CKD*	37200.	>100.0	0.22
2	Hydrated Lime	H_2O_2	CKD	37200.	>100.0	0.04
3	Cement**	$Ca(OCl)_2$	Hydrated Lime	10300.	>30.0	0.03
4	Hydrated Lime	$Ca(OCl)_2$	CKD	6390.	>30.0	0.04
5	50% NaOH	NaOCl	Bed Ash	1750.	>20.0	2.0

* Cement Kiln Dust
** Pretreated at generator's facility

TABLE 3. SELECTED RESULTS OF FULL-SCALE STABILIZATION TREATABILITY TESTING FOR ARSENOUS TRISULFIDE WASTES

Sample *	CWM Site	Alkalinity Reagent	Oxidation Reagent	Stabilization Reagent	Arsenic Content in Treated Waste Leachate (mg/l)
1	Lake Charles	50% NaOH	NaOCl	Bed Ash	0.43
3	Emelle	Cement**	$Ca(OCl)_2$	Lime/Cement	<0.10
1	Lake Charles	Hydrated Lime	NaOCl	Bed Ash	<0.14

* See Table 2 for waste description and bench scale results
** Pretreated at generator's facility

The exact cost of our method for arsenous trisulfide wastes depends heavily on reagent usage, especially that of the oxidizing agent, and therefore on the arsenic content of the waste as well as on other factors. Reagent cost is expected to range in the area of $250 to $550 per ton of waste treated. This is high compared to most stabilization systems, but is still less expensive than other options that are commercially available.

VETERINARY PHARMACEUTICAL PROCESS WASTES AND HIGH-LEVEL ORGANIC PESTICIDE CONTAMINATED SOILS AND SLUDGES

Waste Characteristics

Species such as cacodylic acid (dimethylarsinic acid) present in wastes containing weed killers and other organo-arsenic compounds are difficult to immobilize by conventional methods. Additional organic compounds encountered in veterinary pharmaceuticals include 4-hydroxy-3-nitrobenzene arsonic acid, 2-hydroxy-3-nitrobenzene arsonic acid, 4-nitro-phenylarsonic acid, and their metal salts. These organics may be encountered in highly concentrated form and in organic matrixes, or as contaminants in soils, sludges, and other wastes. In the former case, incineration is usually indicated, and it is very expensive because of the necessity to dilute the organic with other incineration feed stock because of arsenic concentration problems. In the latter case however stabilization is preferable from both cost and operational bases, if the LDR requirement of 5.0 mg/L by the TCLP test can be met.

Five samples of organo-arsenical wastes from a remediation site were tested in this project at laboratory scale. Three were concentrated in arsenic, at 14,300 to 31,700 mg/kg, and two were slightly contaminated soils at about 140 mg/kg. The analyses and leachabilities of the untreated wastes are shown in Table 4.

TABLE 4. SELECTED RESULTS OF BENCH-SCALE STABILIZATION TREATABILITY TESTING FOR ORGANO-ARSENICAL WASTES

Sample	Waste Type	Stabilization Reagent	Arsenic Content (mg/l or mg/kg)		
			Total (mg/kg)	Untreated Leachate	Treated Leachate
1	Concentrated Waste #1	Portland cement	14300.	518.	60.5
1	" "	Quicklime	14300.	518.	16.7
1	" "	Proprietary system #1	14300.	518.	16.4
2	Concentrated Waste #2	Portland cement	19800.	427.	9.61
2	" "	Quicklime	19800.	427.	5.00
2	" "	Proprietary system #2	19800.	427.	0.42
3	Concentrated Waste #3	Portland cement	31700.	1060.	36.4
3	" "	Quicklime	31700.	1060.	21.1
3	" "	Proprietary system #2	31700.	1060.	1.48
4	Contaminated soil #1	Portland cement	139.	1.20	<0.25
4	Contaminated soil #2	Portland cement	134.	1.36	<0.25

Process Description

Again, a large number of conventional stabilization techniques were tested on this waste, with either negative or highly variable results. It was evident from the literature that the destruction of the organic species, at least to the point of releasing the arsenic, would be necessary so that arsenic could be immobilized as a metal arsenate. A major research project was initiated in cooperation with a generator to deal with certain wastes in this category, and preliminary results to date are being presented here for the first time. After considerable testing, a method was found that accomplished this goal in most cases. This process is considered proprietary by CWM and may be the object of patent applications. It is now being tested at pilot scale at one of CWM's Treatment, Storage, and Disposal Facilities (TSDFs).

Characteristics of the Treated Residue

Table 4 gives some of the results of this program. In the case of the soils, it was found the arsenic leachability was not a problem, since the untreated soils leached at levels below the LDR requirement. Nevertheless, some testing was done to determine whether this level could be further reduced by conventional stabilization methods. A simple Portland cement system gave good results, reducing leachability to below limits of quantitation (LOQ) for this matrix, <0.25 mg/L.

The untreated concentrated wastes exhibited high total levels of arsenic and very high leaching levels. In general, the leaching level increased with the total concentration of arsenic in the waste. With wastes #2 and #3, conventional stabilization with cement or lime reduced the leachability substantially, but not to the required LDR levels. The proprietary system #2 was effective in reducing leachability to well below the LDR level of 5.0 mg/L. In the case of waste #1, however, this proprietary system, and another one (#1) achieved only the same leaching level as quicklime - more than 16 mg/L - and well above LDR requirements. However, leachability was substantially reduced by a factor of about 10, taking into account the effect of dilution from the stabilization reagents and process water.

Additional work is underway to improve immobilization of waste #1. In addition, continuous treatability testing is being done on other organo-arsenical wastes to improve and optimize the process. The arsenic work has already had extended application to the immobilization of other organo-metal problem wastes.

FACILITIES

Chemical Waste Management Inc. operates central Resource Conservation and Recovery Act (RCRA) TSDFs at a number of locations throughout the US. Seven of these TSDFs perform stabilization treatment and disposal on a wide variety of hazardous wastes. It is currently expected that two of these facilities will process arsenous trisulfide wastes, and likely organic arsenicals as well. These facilities are at Lake Charles, Louisiana and Emelle, Alabama. All of the CWM facilities can stabilize and dispose of the more conventional arsenic wastes.

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CHARACTERIZATION OF ARSENIC-CONTAINING MINING/SMELTING WASTES IN THE CLARK FORK BASIN, MT AND SOME POTENTIAL REMEDIAL TECHNOLOGIES

Mike Bishop.
U.S. EPA
Federal Building
301 S. Park
Drawer 10096
Helena, MT 59626
USA
Tel: (406) 449-5414

INTRODUCTION

The headwaters of the Clark Fork River are located in southwestern Montana. Within the area known as the upper Clark Fork River Basin, world-class mining and smelting operations existed for a period exceeding 100 years. During the course of these operations a variety of arsenic-containing extraction, beneficiation, and processing waste streams were released. The historic releases of mining and smelting wastes have resulted in situations where threats exist to human health and the environment.

Four Superfund sites are located within the upper Clark Fork River Basin that collectively involve one of the largest Superfund investigations in the nation (1). The National Priorities List (NPL) sites located within the Basin include the Silver Bow Creek/Butte Area, Montana Pole, Anaconda Smelter, and Milltown Reservoir sites (Figure 1). Of these sites, all but the Montana Pole site involve a variety of mining and smelting wastes that contain characteristic arsenic concentrations.

Figure 1. Location of Superfund sites in the Clark Fork Basin.

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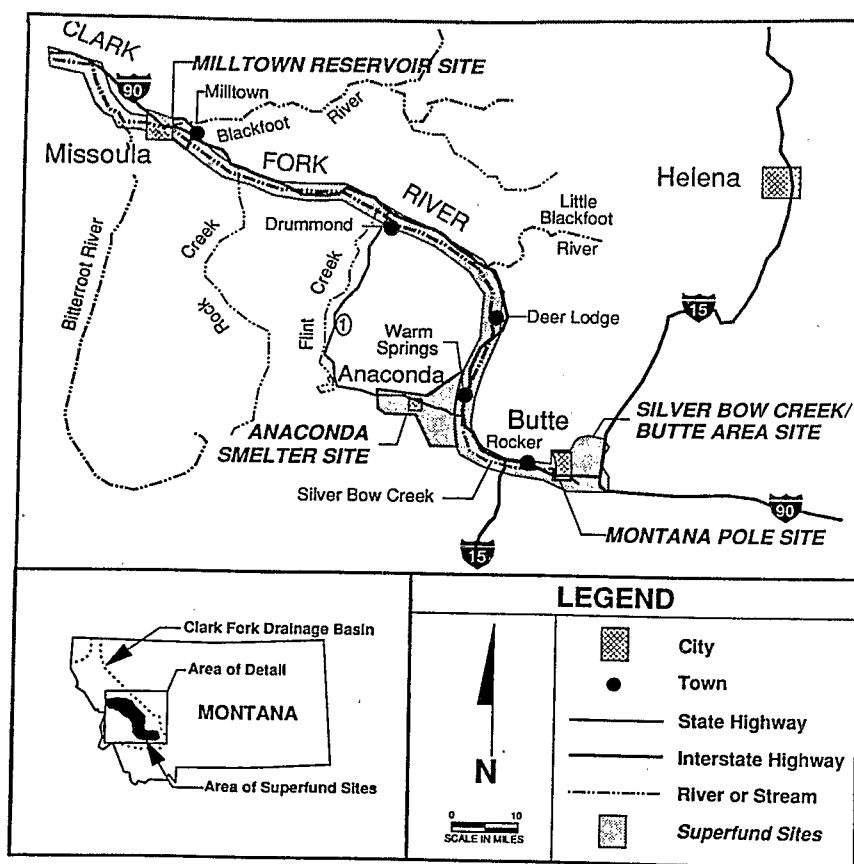
PURPOSE

The purpose of this presentation is to discuss analytical methods used to characterize these NPL sites, review concentrations of arsenic that are typical of the waste types associated with these NPL sites, and to summarize technologies that have been used within the Clark Fork Basin to remediate potential exposure to these wastes. Current efforts to develop innovative technologies for the treatment of mining wastes will also be discussed.

ANALYTICAL METHODS

Three analytical approaches are generally used in association with the Clark Fork Superfund sites to characterize arsenic concentrations in the solid wastes described previously including: the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) method 1311, the EPA contract lab program (CLP) acid extractable metals (CLP SOW 788) and X-ray fluorescence (XRF).

The circumstances for applying each of these procedures are explained in a regional Clark Fork Lab Analytical Protocol (2), and Laboratory Analytical Protocol for X-ray Fluorescence Analysis of Solid Media (3). Differences in analytical values (4) and problems associated with each analytical approach will be discussed.

WASTE TYPES

Waste types identified at the NPL sites previously identified include waste rock, mill tailings, flue dust, arsenical wood treating waste, slag, and contaminated stream sediments.

Waste rock is the rejected material resulting from mining operations which is usually disposed of near the source. Over 125 years of mining in Butte, approximately 100 major waste rock dumps were developed containing millions of yards of waste covering hundreds of acres. Waste rock was also extensively distributed along railroad lines as ballast. The chemical composition of waste rock is highly dependent on the source materials being mined (5).

Tailing deposits resulting from numerous smelting operations in the upper Clark Fork Basin are extensive. In Butte three major accumulations of tailings exist including the Yankee Doodle, Clark, and Colorado tailings. The Clark and Colorado tailings alone include over 1,250,000 cubic yards of material (5). Additional large volumes of tailings occur at the Ramsey Flats directly adjacent to Silver Bow Creek. Tailings from the Anaconda Smelter are contained in the Red Sands area and the Anaconda and Opportunity tailings ponds. These tailings deposits, which have resulted from over 100 years of smelting operations, extend over an area exceeding 4,000 acres and are up to 90 feet in depth (6).

The texture of the tailings deposits decreased as more aggressive methods of ore processing developed, allowing lower concentration ores to be economically processed. The chemical composition of tailings deposits are as variable as the source of ore being mined at the time and the geochemical processes that have secondarily altered the original matrix (7). Generally, higher concentrations of arsenic and other metals are associated with older tailings from higher grade ores which were processed using less efficient extraction technologies.

Flue dust is a smelting waste that results from collection of solid particulates before they are released to the atmosphere via smokestacks. Flue dust represents one the highest concentration waste streams associated with the Clark Fork Basin (8). Arsenic concentrations in flue dust generally exceed the 1 percent level (10,000 ppm) and may range as high as 15 percent. The Anaconda Smelter NPL site has more than 315,000 cubic yards of flue dust in a variety of storage sites.

Treatment of mine timbers with arsenic became popular after it was discovered that timbers treated with creosote posed a potential fire hazard in the underground mines. The Rocker timber framing and treatment plant (Figure 1) used arsenic produced at the Anaconda Smelter for treatment of mine timbers until 1957. During a cleanup action in 1989 approximately 1,000 cubic yards of wood treating waste was removed that contained arsenic concentrations in the range of 1 to 30 percent (9). The site is undergoing additional investigation to determine the arsenic concentrations of waste remaining that must be remediated.

Slag is the vitrified waste remaining following roasting and removal of the precious metals. On the Anaconda Smelter NPL site 1.7 million cubic yards of heap roasting slag deposits remain (6). As with the mining/smelting wastes, the heap roasting represents a low technology process applied to high concentration ores resulting in high concentration wastes. In addition to the heap roasting slag, massive quantities of granulated slag also remain on the Anaconda Smelter site (10).

During the 150 years of mining which occurred in the Clark Fork Basin, Silver Bow Creek, a stream which forms the headwaters of the Clark Fork River, was historically used as an industrial sewer. During this long history, it is estimated that 3 to 10 million cubic yards of mining/smelting wastes were released to the river system where they have mixed with stream sediments. This waste type has characteristic concentrations different than the waste sources themselves.

REMEDIAL TECHNOLOGIES

Remediation efforts within the Clark Fork Basin have included removal/disposal of waste materials, partial removal/addition of amendments/capping, removal, partial removal and capping, lime amendments, calcium oxide and calcium hydroxide/lime amendments, deep plowing, injection and a variety of tilling procedures. An overview of these technologies will be presented.

INNOVATIVE TECHNOLOGIES

Remedial project managers are required to use innovative technologies when there is a potential for comparable or superior treatment performance or implementability, fewer (or lesser) impacts than other approaches, or lower costs for similar levels of performance than demonstrated technologies. The availability of innovative technologies for mining wastes (containing arsenic) are limited. Congress recognized the need for the further development of promising new treatment technologies for mining wastes when they appropriated funds for the establishment of a pilot program for the treatment of mining waste (11).

This mine waste pilot program, operating under the direction of EPA's Risk Reduction Engineering Lab, through the Department of Energy's Component Development and Integration Facility and the Montana College of Mineral Science and Technology, has conducted a literature search of technologies that may have application to mining waste. Mine waste types have also been researched.

Three mine waste types have been selected for demonstrating new technologies. These include: acid mine drainage at a remote alpine site, in-situ treatment of near stream mining waste deposits, and treatment of acidic waters such as those residing in the abandoned Berkeley open pit mine. An update of the status of the mine waste pilot project will be provided.

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SOLIDIFICATION/STABILIZATION OF ARSENIC COMPOUNDS

Frank K. Cartledge
Department of Chemistry
Louisiana State University
Baton Rouge, LA 70803-1804
USA
Tel: (504) 388-3459

INTRODUCTION

Solidification/stabilization (S/S), also known as chemical fixation or encapsulation, is widely applied to waste streams and contaminated soils. The most common form of the technology uses a cement or pozzolanic binder to convert the waste to a solid (if necessary) and depending on the constituents of the waste stream and the binder, may reduce toxicity and/or water solubility of hazardous materials and may create a monolithic waste form that limits contaminant mobility due to its low permeability and small surface area.

The process is most commonly applied in cases where the contaminants of concern are heavy metals in cationic forms, e.g., Cd^{2+}, Cr^{3+}, Pb^{2+}. However, applicability to a wide variety of waste materials including As wastes has been proposed. The author is not aware of a commercial scale treatment where As concentrations in the waste stream were high; however there have been remediations of contaminated soils containing low concentrations of As and many bench-scale studies have been carried out.

PROCESS DESCRIPTION

Several detailed descriptions of S/S have appeared that include extensive discussions of the range of applicability of the technology to a variety of waste streams and also descriptions of the equipment available to carry out the process (1, 2). Cementitious S/S is essentially similar to concrete production and handling. The waste is combined with cement, water, sometimes aggregate material, and sometimes admixtures of a number of types, and mixed under low shearing force. The product may resemble a concrete slurry which is pourable and moldable for a period of several hours, and which can have appreciable strength after curing. Alternatively, a soil-like solid material with little strength may be produced.

In cases for which S/S has been classified as a Best Demonstrated Available Technology (BDAT), some reasonably clear guidelines exist from the US Environmental Protection Agency (EPA) specifying performance criteria for the product. These include: a) the demonstration of no free liquids using the paint filter and liquids release tests; b) development of a minimum strength (usually specified as 50 psi) as evidence that cementing reactions have taken place; and c) meeting waste stream-specific leachability requirements (3).

Depending upon the ultimate disposal of the treated wastes, additional performance criteria or more stringent leachability requirements may be imposed by state or Federal regulatory agencies. For instance, an extensive hydrogeologic characterization of the disposal site may be required and may justify standards of waste treatment that are closer to drinking water standards.

Binding agents that are commonly used are Portland cement, cement and fly ash, lime and fly ash, and dust from cement kilns or lime kilns. The matrix that is formed in these cases is essentially the same and consists of calcium silicate hydrates and smaller amounts of calcium aluminate hydrates. In cases where lime is the main constituent, the curing process is somewhat different and involves absorption of carbon dioxide from the air to form calcium carbonate as the principal matrix constituent. A variety of additives is used in the process, including:

Standard cement additives - set accelerators or plasticizers

Clays - adsorb both metal ions and organics

Silicates - enhance gel formation and precipitate metal ions

Silica fume - reduce permeability and increase strength

Emulsifiers - reduce interferences from organics

Iron salts - reducing agents for Cr(VI) and form insoluble complexes

Sulfide or phosphate salts - form less soluble mixed salts

The cement- or pozzolan-based S/S process generally does not require sophisticated equipment or extensive worker training. In contrast, blending the waste with liquid asphalt or bitumen is more energy intensive, more complex from the point of view of volatilization of components of the waste, and somewhat more expensive. This technology is not widely practiced.

APPLICATIONS TO ARSENIC COMPOUNDS

Arsenic wastes are grouped together for discussion of treatment standards in the land disposal regulations promulgated by the EPA (4). Considerable discussion is allocated to S/S, since it was considered by EPA to be a "potentially applicable technology." However, S/S is not currently considered BDAT for any arsenic waste or wastewater. The following quote indicates the reasons:

> "EPA has relatively inconclusive performance data for stabilization of arsenic in three different wastes using nine different binders. Analysis of these data indicates that the effectiveness of any particular stabilization binder appears to be highly dependent upon the waste types. This result is what might be expected giving (sic) the chemical nature of arsenic and the relative sensitivity of the effectiveness of stabilization processes with respect to the presence of organics and organo-metallics."

Treatment standards include the following: for nonwastewaters, 5.6 mg/L or 5.0 mg/L in EP (or Toxicity Characteristic Leaching Procedure—TCLP) leachates; for wastewaters, 5.0 or 0.79 mg/L in total composition. Clearly, EPA would like to establish the 0.79 mg/L standard for all As wastewaters, but it has received many comments that such a stringent standard is not always attainable.

In specific language, EPA does not preclude the use of S/S for treatment of As (particularly inorganic As) wastes, but recommends that its use be determined on a case-by-case basis. Given the wide range of chemical characteristics of As wastes, such a position is quite reasonable. Nevertheless, as a result of these misgivings, there has not been a large-scale demonstration or remediation in which As concentrations in the wastes have been high or for which As was the major toxic element of concern. On the other hand, there are many results available from treatability or leaching studies on a laboratory scale, and these are summarized in the following paragraphs.

Inorganic arsenic wastes have been most closely studied. Arsenic does not form an insoluble hydroxide and hence the mechanism that operates during S/S of many heavy metal cations does not apply for As. As(III) is commonly observed in solution as AsO_2^-, and As(V) as AsO_4^{3-}, and these oxo-anions are typically water-soluble. Arsenic sulfides are also commonly encountered in wastes, and these may also have significant solubilities under the basic conditions typical of S/S. The leachate results from a variety of As-containing wastes subjected to S/S with a number of binders have been summarized by Conner (1).

When the As concentrations in the waste are high (>635 mg/kg), leachate concentrations often can be brought below 5 mg/L, but usually not below 0.79 mg/L. Treatment sometimes actually increases the leachability, presumably because of different speciation under basic conditions. Similar results have been reported for other TCLP leaching studies, and column and long-term equilibrium batch leaching experiments indicate that As leaches at an elevated rate compared to most heavy metal cations.

In our work (refer to Table 1), both arsenate and arsenite have been solidified with a wide range of binders using a weight percentage of 10% with respect to As, and the results range from entirely satisfactory (arsenate using Portland cement and soluble sodium silicate or silica fume additives) to very unsatisfactory (arsenate or arsenite using 1:1 Portland cement and type F fly ash).

TABLE 1. TCLP LEACHATE CONCENTRATIONS FROM SOLIDIFIED WASTES: 1 YEAR (OR 28 DAYS) OF CURE

Binder[a]	Leachate Concentration, mg/L				
	Pb(II)[b]	As(III)	As(V)	Cr(III)	Cr(VI)
OPC	35 (48)	1.7 (2.1)	1.4 (1.7)	0.4 (0.4)	2500 (1400)
OPC, no gypsum	43 (2.2)	3.1 (2.7)			3200 (2400)
1:1 OPC:Type F FA	0.9 (0.3)	430 (540)	94 (7.9)	0.7 (0.2)	2900 (1600)
20:1 OPC:SiO$_2$	25 (24)	2.3 (2.4)			2500 (1600)
20:1 OPC:Na$_2$SiO$_3$	28 (1.8)	2.0 (3.5)	0.4 (0.1)	0.5 (0.2)	2500 (1800)
10:1 OPC:Bentonite	46 (1.4)	2.4 (30)			2400 (1700)
10:1 OPC:Organoclay	40 (16)	1.1 (3.0)			2800 (2400)
20:1 Type IA:SiO$_2$	41 (5.2)	2.5 (3.1)	0.4 (0.1)	0.2 (0.2)	2800 (1900)
20:1 Type IA:Na$_2$SiO$_3$	35 (44)	1.6 (1.2)			2700 (3300)
White	54 (1.0)	0.9 (1.7)	10 (3.6)	0.4 (0.2)	2900 (2000)
20:1 White:Na$_2$SiO$_3$	38 (6.0)	1.0 (2.5)	15 (8.0)	0.8 (0.2)	2800 (2000)
Lumnite	4 (400)	240 (140)			3700 (2300)
Refcon	190 (680)	190 (150)			3600 (1900)
Pyrament	1.7	47	4.4	1.4	2800

[a] OPC = Type I portland, FA = fly ash, SiO$_2$ = silica fume, Na$_2$SiO$_3$ = Type N soluble sodium silicate, White = portland with low iron content. Lumnite and Refcon are specialty cements that are for refractory applications and high in alumina content. The water to binder weight ratio is 0.5, and the metal to binder ratio is 0.1.
[b] The salts used are Pb(NO$_3$)$_2$, NaAsO$_2$, Na$_2$HAsO$_4$·7H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, and Na$_2$CrO$_4$·4H$_2$O.

Arsenate has been classified as a moderate retarder of cement and tricalcium silicate hydration reactions based on calorimetry (5). We have investigated both arsenite and arsenate effects using solid-state nuclear magnetic resonance spectroscopy and find that % hydration of the cement silicate phase is significantly retarded by arsenate, and more so by arsenite. After 1 year of cure however, both kinds of arsenic salts show only mild overall retardation in terms of % hydration, but both salts are very great retarders of silicate polymerization. Thus, the silicate matrix is quite different in the presence of As(III) and As(V).

We have periodically monitored our samples by powder X-ray diffraction in order to attempt to identify crystalline phases that are forming as a result of waste addition. In most cases any new crystalline salts, if formed, are present in such low concentrations that they are not evident in the already complex diffraction pattern of the cement. This is not true with arsenates. A crystalline material is formed in major amounts, NaCaAsO$_4$·7.5H$_2$O, and this species is present in both cement and cement/fly ash binders. Even when As(III) is solidified with cement, minor amounts of the same crystalline product are formed. The formation of this salt depends upon the availability of significant amounts of Na as well as Ca, and in all cases we are adding the arsenic compounds as Na salts.

While following the hydration reactions of As(III) samples solidified in cement/fly ash, we noted an initial normal, albeit slow, conversion of the aluminate phase from tetrahedral to octahedral. After 28 days of cure, however, that conversion had begun to reverse itself, and after 14 months almost all the octahedral Al had reverted to tetrahedral Al. Furthermore, there is some indication that the silicate phase is undergoing depolymerization. The spectral changes leading to the latter conclusion are still within the range of experimental error ($\pm 4\%$), but they clearly indicate the necessity to monitor these changes over even longer periods of time.

After seeing the effects noted above in the As(III)/OPC/FA mixture, we quickly ran some OPC/FA control samples containing no waste. We see similar effects in both the aluminum and silicon spectra, although the extent of reversion is lower at 1 year in the absence of As. Both As(III) and As(V) appear to catalyze the aluminate phase changes. Such long-term effects that alter the matrix have serious consequences for the application of leach modelling to long-term predictions of release rates for contaminants. The As(V) samples, for instance, show clearly enhanced leachability after 1 year of cure compared

to 28 days (Table 1). We are continuing to monitor these samples, and will have additional data after 2 years of cure to report in August.

S/S of As-containing waste streams clearly shows promise as an effective treatment technology. However, significant questions about the range of applicability remain. Furthermore As salts induce changes in the S/S binding matrix that first become evident after long cure times, suggesting that leachability testing will have to be carried out after much longer cure times than is currently practiced for S/S.

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VITRIFICATION OF WASTE STREAMS CONTAINING RCRA METAL COMPOUNDS

J. G. Hnat, John Patten, and Christopher Jian
Vortec Corporation
3770 Ridge Pike
Collegeville, PA 19426-3158
USA
Tel: (215) 489-2255

INTRODUCTION

Abstract

Vortec Corporation has been developing an Advanced Combustion and Melting System (CMS) which oxidizes the organic constituents of a hazardous waste and chemically combines the heavy metal components into a glass matrix. This paper summarizes Vortec's ongoing research work on the vitrification of Resource Conservation and Recovery Act (RCRA) metal containing wastes. Both laboratory analyses and pilot scale testing are being conducted. The work has been supported by Department of Energy (DOE) and Environmental Protection Agency (EPA) as well as by internal Vortec research funds. A significant portion of Vortec's industrial process research is devoted to the development of innovative approaches to waste recycling and the vitrification of organic and heavy metal contaminated waste materials.

Previous Research

The development of the Vortec Combustion and Melting System (CMS) initially concentrated on the melting of glass batch materials with the objective of improving the efficiency of glass manufacturing operations. However, the application of the technology to vitrifying waste materials was soon suggested. Vortec has recently processed several industrial waste materials containing high concentrations of heavy metals including arsenic. The preliminary data suggest that a portion of the heavy metals are being retained in the glass matrix. Further work is being conducted by Vortec (the SITE program) to identify the partitioning of the metals as they are processed accurately.

Glass manufacturing operations in the past have added approximately 3000 ppm of As_2O_3 (arsenic trioxide), as an agent to assist in the removal of bubbles formed during the manufacture of glass materials. In general, the removal of the bubbles (called fining) produces a superior quality product that is aesthetically pleasing to the customer. The mechanism by which the bubbles are removed involves the evolution of oxygen from the arsenic compound, at elevated temperatures, with the subsequent migration of the oxygen into the already existing bubbles. As the bubble diameter increases, the buoyant force driving the bubble to the surface of the glass melt is increased and the time at temperature required to remove the bubbles is reduced.

The use of arsenic as a fining agent in glass is obsolete. Less expensive combinations of compounds are now being used. However there is a body of research on the behavior of arsenic trioxide in glass melts. These data would suggest that as much as 90% of the arsenic compound could be retained in the glass, and usual practice would expect anywhere from 50 to 90% to be retained depending on the temperature at which the melter is being operated and the type of glass being manufactured.

Brief descriptions of previous research programs that have direct application to the remediation of materials containing RCRA metals are presented in following paragraphs. Characterization of the waste streams for a selected number of the materials are presented along with typical Toxic Characteristic Leaching Procedure (TCLP) results. Each waste stream has significant variations in composition and successful vitrification will require the addition of different amount and composition of glassmaking components.

Vortec is developing a multi-fuel capable advanced high temperature process heater for melting and other high temperature industrial applications, based on patents previously developed. Vortec designed, fabricated, and installed a nominal 15 to 20 ton/day advanced process heater test loop in Harmarville, PA.

The system has been used to test the melting of waste glass, waste fiberglass contaminated with organics, utility flyash, and waste dust. This program is a DOE-supported effort under the Advanced Coal-Fired Glass Melting Process Heater Program, DOE Contract DE-AC22-91PC91161.

Vortec Corporation is the prime contractor on a DOE SBIR program to demonstrate the application of Vortec's CMS, using coal as a fuel, to waste fiberglass recycling. Phase I of the program demonstrated the feasibility of oxidizing the organic contaminants in waste insulation fiberglass material, and produced a cullet suitable for recycling to a manufacturer's furnace.

Vortec has completed Phase I of an EPA SBIR contract to demonstrate the feasibility of using the CMS with natural gas as the primary fuel, to oxidize the organic contaminants in waste insulation fiberglass material, and produce a cullet suitable for recycling to a manufacturer's furnace. The program is currently in Phase II, the objective of which is to characterize effluents from the system to assure environmental compliance. The Hazardous Flyash and Industrial Process Dust Vitrification project, also for EPA, has as its objective the assessment and feasibility demonstration of vitrifying municipal solid waste incinerator flyash in the CMS to produce products that can pass TCLP, thus helping to recycle this material into value added products.

Vortec is currently conducting a SITE program for EPA. The objective of this program is to verify the effectiveness of the CMS for the oxidation and vitrification of contaminated soils in dry or slurry form that are representative of materials found at EPA Superfund sites.

Materials Previously Processed

The CMS has successfully demonstrated the vitrification of several different classes of materials. Postconsumer waste glass has been processed in the form of commercially obtained glass cullet. During the startup phase of the development program, glass cullet was the feed material that was the easiest and most uniform in physical properties, simplifying its melting and control. Subsequently, waste insulation fiberglass, utility flyash, municipal solid waste incinerator flyash, aluminum processing dust, and sewage sludge incinerator ash have all been successfully processed to form a vitrified product capable of passing the TCLP test. Vortec is preparing to conduct further testing to demonstrate the CMS's capability to vitrify additional contaminated soils and sludges, auto shredder fluff, and filter cakes of various compositions from the chemical processing industry.

PROCESS DESCRIPTION

System Description

Vitrification tests are being conducted using Vortec's CMS located at the University of Pittsburgh Applied Research Center in Harmarville, PA. An isometric sketch of the pilot plant test system arrangement is shown in Figure 1. The major components in the test system are a counter-rotating vortex (CRV) combustor/suspension preheater, a cyclone melter, a glass separator/reservoir, material storage facilities, a pneumatic feed assembly, a cullet quench assembly, and a flue gas scrubber assembly. Vortec's test facility also contains supporting subsystems and assemblies for cooling water supply, combustion air supply and preheating, instrument and service air supply, natural gas and coal fuel supply, flue gas cleanup, and system control. Descriptions of the major components in the pilot scale test system are presented in following paragraphs.

MAJOR COMPONENT DESCRIPTIONS

Counter-Rotating Vortex Combustor/Preheater

The CRV combustor is designed to provide rapid suspension preheating of the waste materials to their melting temperature. This is accomplished via convective and radiative heating of the feedstock materials in the combustion zone of the CRV combustor.
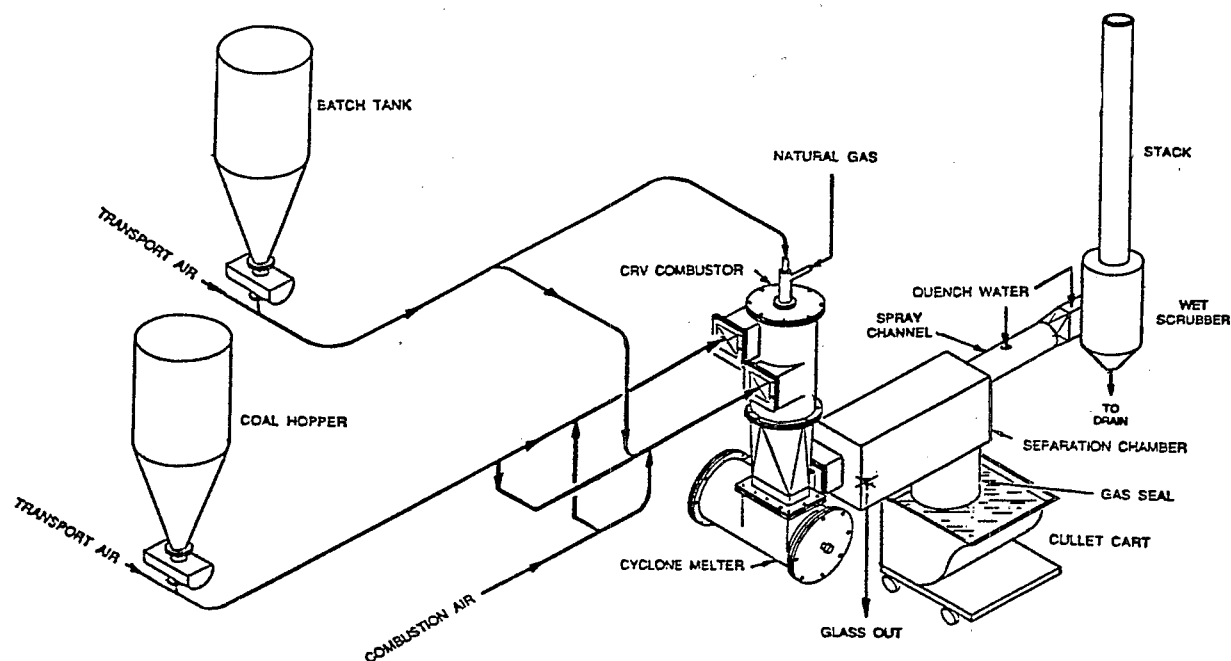
Figure 1. Illustration of pilot scale cyclone melting system.

A variety of fossil fuels can be utilized in the CRV combustor, including pulverized coal, oil, and gas. Inasmuch as the feedstocks are preheated in suspension and turbulently mixed with the combustion air introduced into the combustor, the process also provides an effective means of incinerating any organic or other combustibles in the waste materials. In most applications, fuel and waste along with other appropriate ingredients can be introduced axially along the centerline of the CRV combustor.

Combustion air is introduced tangentially through two inlet arms such that the direction of rotation of the air streams are opposed to each other. The CRV preheater assembly provides a region of intense turbulence in the upper section of the CRV combustor for good flame stability, followed by a region of plug flow at the exit of the CRV combustor.

The CRV combustor/preheater is refractory lined and water cooled with the water temperatures and refractory temperatures continuously monitored. Typical reactor temperatures in the CRV combustor vary between 1200K (1700 degrees F) and 1900K (2960 degrees F) depending on the type of feedstock being utilized. The nominal air preheat temperature for the experiments is 870K (1100 degrees F). In spite of the relatively high air preheat temperature utilized, NOx levels are low, typically less than 200 ppm, due to the rapid temperature quenching by the feedstock materials.

Cyclone Melter and Separation/Reservoir Assembly

Combustion products and preheated batch particulate material exiting the CRV combustor/preheater are introduced tangentially into the cyclone melter where melting occurs and the molten glass is separated centrifugally from the gases. The cyclone melter is refractory lined and water cooled with water temperatures continuously monitored. The molten glass and combustion gases exit tangentially from the cyclone melter and enter a rectangular, refractory lined separator/reservoir where the vitrified product (glass) is removed from the system. The combustion gases are directed to a flue gas quench/scrubber assembly, and the molten vitrified product exits a tap hole on the bottom of the separator/reservoir.

The separator/reservoir assembly also contains an overflow pipe that interfaces with a cullet collection cart in the event that the glass flow entering the separation chamber exceeds the flow capability of the tap

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hole. The molten glass exiting the tap hole in the glass separator/reservoir assembly falls into a chute where water is introduced to quench the glass and transport the quenched glass (cullet) into a cullet collection cart.

Flue Gas Quench/Scrubber Assembly

The gas quench assembly consists of a channel connected to the discharge of the glass separator/reservoir assembly with water spray nozzles for quenching the exhaust gases from nominally 1700 degrees K (2600 degrees F) to 365 degrees K (197 degrees F). The flow passes to a scrubber and is then discharged to the atmosphere by an induced draft fan.

Pulverized Material Storage and Pneumatic Feed Assembly

Pulverized batch materials are stored in a 4.25 cubic meter (150 cubic foot) pneumatic transport vessel which is supported on weigh cells to determine feed rate during operation. A fugitive dust control system creates a negative pressure at the vessel interface and draws dusty air through a fabric filter located outside the test building, exhausting clean air to the environment.

Mixing is accomplished in the vessel via a pneumatic system designed for this particular application. A calibrated rotary feeder meters material from the storage vessel to the process. The material is pneumatically transported to the process at solids-to-air weight ratios up to 60-to-1.

STREAM CHARACTERISTICS

Typical Feed Stream Compositions

Vortec has been conducting demonstration testing using its CMS facility at U-PARC. These tests typically process 1000 to 1500 lbs per hour of batch composed of a combination of waste and glass making additives. Table 1 presents the RCRA metals content of several waste streams that are being investigated using the Vortec CMS. These wastes, in some cases, contain heavy metals at concentrations that make the passing of the TCLP uncertain.

Vortec is conducting a SITE demonstration test in which a clean surrogate soil will be spiked with oxides and salts of the four RCRA heavy metals as indicated in Table 1. This soil will be mixed with additives to produce a batch composition satisfactory for the formation of a vitreous product. Extensive testing will be conducted during the test to establish the partitioning of the metals arsenic, cadmium, chromium, and lead.

As required by the SITE Q/A plan, the batch material entering the system, the effluent water leaving the air pollution control device, and the flue gases will all be sampled and tested for these heavy metals. In addition, the glass stream will be tested for total metals and also to determine if the vitrified product will pass TCLP.

Product Characteristics

As indicated in Table 1, six waste streams are being investigated to determine if the waste can be vitrified and to establish that the vitrified product will pass the TCLP test. As indicated in the table, four of the six vitrified products tested have passed TCLP even though the untreated waste has concentration of heavy metals several orders above the limits.

The other two wastes, spent potliners and EPA surrogate soil, are scheduled for CMS testing later in 1992.

FACILITY DESCRIPTION

Vortec CMS Pilot Plant Facilities

Vortec's advanced combustion/melting test system is installed in the physical plant facilities at the University of Pittsburgh Applied Research Center (U-PARC), Harmarville, PA. Vortec has the exclusive use of the High Bay Area within Building B11, which has plan dimensions of 40 x 100 ft, and a height of 64 ft This area includes a tower for support of test equipment, and a 5-ton bridge crane. The tower is a structural steel frame with four elevations above grade, extending to a height of 43-1/4 ft and plan dimensions of 15 x 40 ft. The crane support is arranged so that crane service is provided to the full plan area of the high bay.

Truck access to the test area is provided by a 15 ft high x 15-1/3 ft wide roll-up door. Except for the slurry preparation and feeding subsystem, the facility has all the equipment and utilities necessary to conduct this research and development program.

TABLE 1. WASTE STREAM CHARACTERIZATION

Elements	Contaminated Soil PPM	Spent Potliners Average PPM	EPA Surrogate Soil Vortec SITE Test PPM	Waste Water Treatment Incinerator Ash PPM	MSW Flyash PPM	Hazardous Baghouse Dust PPM
Arsenic	540	13	200	27	981	NR
Barium	NR	100	NI	390	984	NR
Cadmium	30	2.5	200	10	57	523
Chromium	52	16	1000	610	601	957
Lead	380	22	2500	860	3433	13641
Mercury	6	25	NI	<.01	<200	NR
Selenium	50	0.5	NI	17	2	NR
Silver	606	1	NI	4.46	<30	NR

Typical TCLP Results from Vitrified Product

Arsenic	0.9			0.05	<0.05	<0.02
Barium	0.14			<1.2	<1.0	<0.5
Cadmium	0.001	Test Scheduled	Test To Be	<0.07	0.05	<0.05
Chromium	0.02	For Late 1992	Conducted	<0.10	0.1	0.2
Lead	<0.003		June 17,1992	0.5	3.3	1.5
Mercury	ND			<0.0003	0.0093	ND
Slenium	NR			<0.05	<0.050	<0.025
Silver	NR			<0.01	<0.1	ND

ND=Not Detected
NI=Not Included
NR=Not Reportred

ELEMENTAL MERCURY IN SOIL AND THE SUBSURFACE: TRANSFORMATIONS AND ENVIRONMENTAL TRANSPORT

Ralph R. Turner
Environmental Sciences Division
Oak Ridge National Laboratory[1]
Oak Ridge, Tennessee 37831-6036

Disposals and spills of both small and large quantities of elemental mercury in terrestrial environments have been a common occurrence. The subsequent behavior and environmental fate of such mercury is controlled by a host of factors, not all of which are fully understood at this time. The physical properties and solubilities of elemental mercury and its oxidation products can be used to predict how disposals and spills will behave, but the range of the environmental settings is so large that relying on theoretical predictions alone can be risky. Important physical properties of elemental mercury to consider are its liquid state, high density, high surface tension, and volatility.

When spilled onto porous media the liquid state and high density will tend to drive the mercury ever deeper. This tendency is counteracted somewhat by the high surface tension of the metal which favors "beading" and trapping in pore space. Although much less volatile than water, elemental mercury does evaporate sufficiently to create a significant vapor pressure in surrounding air and may migrate significantly through porous media via this mechanism. While the solubility of elemental mercury is relatively low, the metal is subject to oxidation to far more soluble compounds. However, solubility of pure compounds is not a very good indicator of mobility in the environment.

Soluble species of mercury exhibit a very high affinity for solids which often bind the mercury so tightly that only destruction of the solid will release the mercury. In addition, soluble mercury can react with other compounds to form secondary compounds, e.g., sulfides, under certain conditions which are far more insoluble than the original metal. Under some conditions a small fraction of inorganic mercury in soils may be converted to alkylated species (e.g., monomethyl and dimethyl). The latter process is only poorly understood at this time but is likely to be important in the evaluation of human and ecological risk.

Experience in characterizing and cleaning up several spills of elemental mercury at a nuclear weapons plant in Oak Ridge, Tennessee is useful to review. Early attempts to recover quantitatively large (50 tons) spills of the metal onto soil or unsealed floors usually met with failure due both to the rapid percolation into every available pore and fissure. Attempts at excavation created new fissures which simply drove the mercury deeper. Smaller (few pounds) spills tended to remain in the upper soil profile as finely divided beads which tended to coalesce if the profile was disturbed by sampling or excavation.

Soil borings at former spill sites have not generally detected very much mercury perhaps reflecting operation of the "nugget effect" in these explorations for spilled mercury. With a few exceptions, groundwater monitoring has likewise failed to show any consistent relationship between spill sites and the groundwater concentrations. Inclusion of suspended matter in groundwater analyses has seemed to account for most of the elevated mercury concentrations. Results of US Environmental Protection Agency (EPA) standardized leaching protocols (EP, TCLP) applied to soils from the site have shown no relationship between total mercury concentration in the soil ($\mu g/g$) and performance on the leaching tests (mg/L). Variability in the forms of mercury present in the soils has been shown to account for this observation.

These experiences have suggested that better methods of characterizing spill sites are needed and that availability of physical and chemical speciation information is essential (1) to fully characterize sites, (2) to conduct a realistic risk assessment, and (3) to select the most appropriate corrective action.

RESEARCH PROGRAM FOR DEALING WITH MERCURY IN SOIL AT NATURAL GAS INDUSTRY SITES

David S. Charlton, Craig R. Schmit, Daniel J. Stepan, and Frank W. Beaver
Energy and Environmental Research Center
University of North Dakota
Grand Forks, ND 58202
USA
Tel: (701) 777-5000

James M. Evans
Environmental and Health Research
Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, IL 60631
USA
Tel: (312) 399-8329

INTRODUCTION

The past use of elemental mercury in monitoring and control instrumentation at natural gas industry sites has resulted in soils contaminated by mercury. The most common types of mercury-filled instrumentation in the gas industry are flowmeters (manometers) that are used to measure the volume of gas flowing through metering stations.

The Energy and Environmental Research Center (EERC) has been contracted by the Gas Research Institute (GRI), with support from the US Department of Energy (DOE), to investigate potential issues related to and alternative remediation technologies for elemental mercury spills. The investigation of elemental mercury spills is an outgrowth of a broader research program focused on issues related to a variety of potential contaminants in gas industry wastes and products.

SOURCES OF MERCURY CONTAMINATION

Mercury-filled flowmeters have been the traditional design used in the gas industry for the past half century. Even though mercury flowmeters are being replaced with newer designs that use no mercury, a number of meters with elemental mercury still exist. Flowmeters may contain 8 to 10 pounds of mercury. Soils in the immediate area of some mercury flowmeters have become contaminated with mercury due to leakage, spills, equipment failure, vandalism, and operator error. A better understanding of these sources of mercury contamination has resulted in more effective containment systems and improved management practices, resulting in a drastic reduction in mercury reaching the soil surface.

However, gas metering sites remain that were contaminated in the past with elemental mercury. Because of the small amounts of elemental mercury involved, most of these sites probably have relatively small volumes of mercury-contaminated soil, perhaps one to two cubic yards per site. Nevertheless, the gas industry is interested in the most efficient, cost-effective, and feasible technologies for remediating these sites.

ENVIRONMENTAL REGULATIONS

Mercury became a concern within the gas industry first as a worker safety issue. Some gas companies voluntarily began cleaning up their sites because of this issue. Site cleanups resulted in mercury-contaminated soils that were sent to hazardous waste landfills for disposal. Of particular concern, therefore, to the gas industry has been the May 8, 1992 deadline under the Land Disposal Restrictions (LDR), also called "Land Ban." After that deadline, certain types of mercury-contaminated wastes can no longer be sent to hazardous waste landfills without meeting specific treatment requirements.

For D009 wastes with total mercury concentrations greater than 260 mg/kg, which are typical of many gas metering sites, the required Best Demonstrated Available Technology (BDAT) is roasting or retorting, with condensation and recovery of the volatilized mercury. Within the gas industry, there are concerns that roasting or retorting may not be the most economical and efficient technology for dealing with mercury-contaminated soils and that the national capacity does not exist to deal with the potential volume of contaminated soils that could require treatment.

The regulations do provide mechanisms for addressing these two concerns. One available mechanism is to apply for a treatability variance when the BDAT is inappropriate for the waste. Another available mechanism is to apply for a national capacity variance when it can be demonstrated that there is insufficient capacity nationwide to handle the volume requiring treatment. However, both of these mechanisms can cause substantial delays in initiating a remediation effort.

An additional regulatory consideration is that individual states can impose more restrictive corrective action levels than those required at the Federal level. As an example, a number of states currently require cleanup to background levels, determined on a case-by-case basis.

The regulatory issues discussed above are primarily those affected by the Resource Conservation and Recovery Act (RCRA) and its amendments. However, there are other Federal programs and regulations that also affect the cleanup of mercury-contaminated soils, including those related to the Occupational Safety and Health Administration (OSHA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, "Superfund"); and the Clean Air Act Amendments.

MERCURY RESEARCH PROGRAM

To address the potential environmental impacts of elemental mercury at gas industry sites in the context of a changing regulatory framework, an interdisciplinary research program was designed and implemented. Specifically, within the context of that program:

A mercury workshop was organized and conducted for the gas industry at GRI headquarters in Chicago, Illinois, on February 10-11, 1992. A total of 62 people, representing the gas industry, the research community, and remediation companies, participated in the workshop. A proceedings volume will be available in the near future (1).

A literature review was conducted and a bibliographic database was constructed to identify relevant mercury- related literature. A summary report is being written based upon key references (2).

Computer models are being assessed for their applicability to mercury migration in the subsurface.

A risk assessment model is being developed for mercury- contaminated sites. Risk models can be used as mechanisms for setting site-specific cleanup levels or they can be used in ranking sites for cleanup.

Sampling, preservation, and analytical protocols for mercury-contaminated solids and liquids are being evaluated and developed as necessary.

Laboratory experiments are being conducted evaluating: 1) leaching techniques applied to mercury-contaminated materials and 2) mercury speciation in subsurface environments.

Mercury-contaminated gas industry field sites are being characterized and instrumented in several parts of the country. Sites have been selected to represent a range of site-specific variables.

Existing and developing remedial technologies are being reviewed to deal with mercury in soils. A summary report is being written based upon this review (3). In addition, one remedial technology has actually been tested, and others will be tested in response to a recently circulated Request for Proposal (RFP).

REMEDIATION OPTIONS

A major goal of this research program is to develop an understanding of mercury contamination at gas industry sites so that the impacted materials can be remediated in an efficient and cost-effective manner. To evaluate the range of remediation options available to the gas industry, information was solicited from companies and researchers that have available or are developing remedial technologies for mercury-

contaminated soils. The remediation options were grouped into six categories: 1) chemical treatment, 2) physical treatment, 3) thermal treatment, 4) biological treatment, 5) immobilization, and 6) electrolytic treatment.

A technology based on one of these six remediation options, physical separation, was tested using native soil from the southwestern US spiked with elemental mercury. This particular remedial technology was selected for testing because a unit was already under development as a mobile prototype unit and preliminary information suggested that the unit, based upon established mining technologies, might be effective in separating elemental mercury from soil.

Other technologies will be selected for development and testing based upon an evaluation of proposals solicited through the recent circulation of an RFP. That RFP was sent to companies and researchers known to have experience in dealing with elemental mercury or related contamination.

SUMMARY

This ongoing research program has been designed to address a range of key issues regarding elemental mercury contamination at gas industry sites. An integrated, multidisciplinary research approach is being used to develop a better understanding of the complex interactions that can occur between mercury and a range of variables at the sites. A better understanding of these complex interactions is crucial to the design and evaluation of remedial technologies that are suitable for application by the gas industry where mercury contamination has occurred.

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MERCURY CONTAINING HAZARDOUS WASTES: GENERATION AND POTENTIAL REDUCTION

Wayne Brooke-Devlin
Versar Inc.
6850 Versar Center, PO Box 1549
Springfield, VA 22151
USA
Tel: (703) 750-3000 x312

In 1983 (the last year for which figures were available), US industries consumed the following percentages of that year's mercury supply (1):

    Alkaline batteries.....................48%
    Chlorine and caustic soda...............16%
    Electrical and instruments.............13%
    Paints and other.......................23%

Recognizing that these industries produce mercury-containing waste, the US Environmental Protection Agency (EPA) has characterized the following industrial wastes and promulgated Best Demonstrated Available Technology (BDAT) standards for their treatment prior to land disposal:

D009 - Any waste that is characteristically hazardous based on the concentration of mercury in the leachate as determined by the Toxicity Characteristic Leaching Procedure (TCLP)

P065 - Mercury fulminate

P092 - Phenylmercuric acetate

U151 - Mercury

K071 - Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used

K106 - Wastewater treatment sludge from the mercury cell process in chlorine production

MERCURY CELL BATTERIES

The largest single use of mercury is in the production of batteries. This industry utilizes mercury and several mercury compounds in the manufacture of mercury cell batteries.

During battery manufacturing, mercury-containing wastewaters can result from the cleanup of metallic mercury and mercury compound spills, or from washes of process equipment. Mercury- containing nonwastewaters can result from off-specification product, from spills of mercury metal or mercury compounds, and from wastewater sludges generated in the treatment of mercury containing wastewaters. These wastes will most likely be categorized as D009 and/or U151 code wastes and will be treated to the required mercury levels (0.030 mg/L (total) for U151 wastewaters, 0.20 mg/L (total) for D009 wastewaters, 0.20 mg/L (TCLP) for D009 nonwastewaters and U151 retorting residues, and 0.025 mg/L (TCLP) for U151 nonwastewaters that are not retorting residues) through the suggested BDAT methods (sulfate precipitation for wastewaters; roasting or retorting for nonwastewaters).

In 1975 the EPA estimated that battery production, which accounted for 39% of domestic mercury use that year, contributed less than 0.9% of that year's quantity of mercury lost to the environment through industrial waste (2). Now, with the adoption of BDAT treatment levels, it is probable that the percentage of industrial mercury lost to the environment through battery production waste streams is even smaller. In industries where small on-site spills, periodic equipment washes, non-standard product, and wastewater

sludges are the major sources of waste, it is not surprising that only small amounts of mercury-containing wastes are produced. When treated to BDAT levels the amount of waste due to battery manufacturing is not expected to be significant.

The adoption of nickel-cadmium or lithium battery cells would eliminate mercury cell wastes. However, though both types of cell are in production, they have not yet replaced mercury-containing batteries.

In 1983 something on the order of 3,700,000 pounds of mercury entered the environment via end-user battery disposal (3). EPA figures show that in 1973 about 5% of battery mercury was being recycled. The significance of waste from the mercury using industries pales in comparison to the waste from disposable batteries. Increased battery recycling has the potential to reduce overall mercury wastes greatly.

CHLORINE/CAUSTIC SODA PRODUCTION VIA MERCURY CELLS

The second largest use of mercury is in the production of caustic soda and chlorine. This industry employs a flowing stream of mercury as the cathode terminal in an electrolytic decomposition cell.

In caustic soda/chlorine manufacturing, mercury-contaminated wastewaters can be produced during the washing of cell room floors and end boxes and from direct contact cooling of the hydrogen stream. Mercury-containing nonwastewaters can be produced from wastewater treatment and the precipitation of brine purification solids and from retort ash. The EPA has identified K071 and K106 as two types of wastes which result from caustic soda production.

As wastewaters and nonwastewaters the K106 waste code covers many of the mercury-contaminated wastes from mercury cell caustic soda plants. The K071 code applies to plants which do not use prepurified salt and must therefore include a solids precipitation step before allowing brine solution to enter the mercury cell. Since some of this brine is made up from a recycle stream of spent brine from the mercury cell, some mercury may also precipitate in this step, thus contaminating the precipitation solids.

BDAT calls for the treatment of K071 wastes by acid leaching since their low concentrations (25 to 120 mg/kg) of mercury make retorting difficult. Under BDAT, K106 wastewaters are to be treated by precipitation using sulfate or hydrazine followed by filtration to reduce their total mercury concentrations to 0.030 mg/L. The K106 nonwastewaters are to be retorted until their mercury concentrations are below 0.20 mg/L TCLP for wastes which initially contained concentrations above 260 mg/kg, and below 0.025 mg/L TCLP for wastes which initially contained a lesser concentration of mercury.

In 1975 the EPA estimated that of the 449,608 kg of mercury used in the caustic soda industry that year about 229,760 kg (51.1%) was lost to the environment as wastes. In 1980 the EPA estimated that of the 325,768 kg of mercury used by the caustic soda industry that year approximately 154,000 kg (47.3%) was lost as waste. Though the 3.8% decrease in the ratio of mercury used to mercury waste during this period is not great, the 28% decrease in total mercury use and the resulting 33% decrease in overall mercury loss is very significant.

During this time period the percentage of total caustic soda production capacity provided by mercury cell plants fell from 25% to 19% (4). This trend continued through the 80s. In 1980 there were 27 mercury cell plants in operation. In 1984 there were 24, and in 1990 the EPA estimated that only 20 mercury cell plants remained in operation. It is expected that with the passage of time the remaining facilities will also be phased out. However, even without this gradual attrition, immediate reductions in mercury waste are expected to occur due to the application of BDAT treatment standards.

Two alternatives to mercury cell technology are currently available: diaphragm cell and membrane cell. Neither of these technologies produces a caustic with as high a degree of purity as that from mercury cells. Nevertheless, all new US installations during the last 20 years have been of one of these two types, which indicates the industry's desire to abandon the potentially hazardous mercury technology.

ELECTRICAL AND INSTRUMENTATION USES

Mercury's high density, volatility, low electrical resistivity, and other physical properties make it an

ideal material for a number of electrical and instrumental uses. Mercury has found use as the contact material in some types of electrical switches, as the conductor in a number of electrical devices, and as the vapor in some gaseous discharge lamps. It has also been widely employed in the manufacture of thermometers, barometers, and other pressure/temperature sensing devices (5).

Due to the wide variety of manufacturing processes involved, it is difficult to determine the contribution of the electrical and instrumental uses of mercury to the problem of mercury-contaminated waste. However, it is probable that in these manufacturing industries (as in battery manufacturing) such wastes occur primarily as a result of spills and process equipment washes. Therefore, electrical and instrument production wastes are likely to be of the same types (D009 and U151) and on the same order as battery wastes, and when treated to the previously-described BDAT standards for these wastes will constitute only a small fraction of annual mercury wastes.

Though still used, mercury switches and devices have largely been replaced by electronic equivalents. Electronic devices have also to some degree replaced both mercury thermometers and barometers. Nevertheless, the increasing demand for outdoor security lighting and the greater accuracy of mercury-based pressure and temperature devices ensure that mercury-containing electrical equipment and devices will remain in production for the foreseeable future. Fortunately, end use recycling of mercury from these products is not difficult. In 1975 the EPA estimated that of the 191,000 kg of mercury in electrical and instrumental end products approximately 82,700 kg (43%) was recycled. Again, improved recycling could greatly reduce the total waste from these sources.

PAINTS AND OTHER SOURCES

Phenylmercuric acetate (P092) and phenylmercuric oleate when used as a bactericide in stored latex paint or as a fungicide in applied latex paint accounted for slightly more than 12% of the mercury used in 1983. In 1990 the EPA found that these compounds were still being manufactured and used as preservatives in latex paints. In paint formulation operations wastes are likely to be mainly due to spills and equipment washes. Therefore, these wastes are likely to be on the same order as those from battery production.

BDAT treatment of P092 wastewaters calls for oxidation of the organic mercury compound followed by precipitation and filtering to yield a wastewater with a total concentration of less than 0.030 mg/L. The P092 nonwastewaters are to be treated to mercury concentrations of either 0.20 or 0.025 mg/L TCLP (depending upon whether their initial concentration exceeded 260 mg/kg) through incineration or retorting. The small expected amount of waste and the applicable BDAT standards are likely to make the contribution of paint production to mercury wastes minimal. Recycling of used paint is not considered a viable waste reduction method.

Dental amalgam represents a further 3% of the mercury used in this category. Wastes from this source are difficult to assess but are expected to decline as composite materials gain greater acceptance in the dental profession. In the past, recycling of recovered amalgam has been excellent due to the value of the material. The application of D009 and U151 are expected to improve this recovery in the future. The remaining 8% of annual mercury consumption has in the past been used for the production of explosives, pigments, pharmaceuticals, and chemical catalysts.

In recent years mercury fulminate (P065) has been eliminated from explosives manufacturing due to its instability. (Though BDAT levels have been established for this compound, they find no current application.) Where possible mercury compounds have been replaced by other compounds in pigments, and by less toxic compounds in medicine. Their use in the catalytic manufacturing of plastics has largely been supplanted by alternate processes. The contribution of these sources to mercury wastes is likely to continue to decrease. The wastes from these sources are expected to be minimized through application of D009 and U151 BDATs.

In conclusion, recycling (or replacement) of mercury batteries, and further reductions in the use of mercury cells in the production of caustic soda hold the greatest promise for significantly reducing mercury wastes. Based on current trends the number of mercury cell chlor-alkali plants are expected to decrease

with time. The wastes from these and other mercury-using industries are expected to be diminished by adoption of BDAT treatment limits. The future of battery recycling or replacement efforts has yet to be determined.

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RECENT ADVANCES IN THE ANALYTICAL TECHNIQUES FOR THE QUANTIFICATION OF MERCURY AND MERCURY COMPOUNDS IN DIFFERENT MEDIA

Eric Prestbo and Nicolas S Bloom
Brooks Rand, Ltd
3950 6th Avenue, Northwest
Seattle, Washington 98107
USA
Tel:(206) 632-6206

Research and development at Brooks Rand is focused on improved methods for the collection and analysis of individual mercury species in the entire range of environmental samples (air, water, soil, and tissue). The long-term goal of this work is to understand the sources, sinks, and chemical transformations of mercury in the environment. By doing so, it will be possible to isolate the most efficient methods to remediate existing mercury problems and also monitor the result of a remediation strategy.

The method used is a cold vapor atomic fluorescence technique, based upon the emission of 253.7 nm radiation by excited Hg° atoms in an inert gas stream. The challenge has been to extract quantitatively and separate individual mercury species in complex environmental sample matrices. Recently, new advances have been made in the laboratory which have improved upon the existing techniques. Also, mercury sampling methods have historically been flawed, resulting in concentrations that are systematically high. Furthermore, accurate results depend on proper storage and sample handling in the laboratory.

The most recent findings regarding improved analytical techniques, sample handling, and sample storage of mercury in environmental samples will be presented. A comparison will be made to other current methods, exploring both the advantages and disadvantages inherent in the analytical methods for mercury. Finally, future research questions and needs will be addressed.

MERCURY IN SEDIMENTS - HOW CLEAN IS CLEAN?

Gary N. Bigham and Elizabeth A. Henry
PTI Environmental Services
1601 Trapelo Road, Waltham, MA 02154
USA
Tel: (617) 466-6681

INTRODUCTION

Sediments are often the repository for both organic and inorganic contaminants in aquatic environments. Numerous techniques have been developed to characterize the distribution of contaminants and to estimate or predict effects on water quality and aquatic biota. This paper will describe several approaches to development of sediment quality criteria and their applicability to mercury. The behavior of mercury in aquatic systems will be discussed and the requirements for effective sediment criteria for mercury will be described.

SEDIMENT CRITERIA

In the 1970s, regulatory consideration of sediments was related to permitting dredging and dredged material disposal. Techniques were also developed to estimate the potential water quality impact of aquatic disposal of dredged sediments (1). Since then, research on the behavior of sediment contaminants *in situ* and their effects on benthic macroinvertebrates and other organisms has led to attempts to develop sediment quality criteria to protect aquatic organisms.

Several methods have been developed for deriving sediment criteria (2). In general, the methods evaluate the toxicity of either interstitial water or bulk sediment to aquatic macroinvertebrates. Interstitial water methods include comparing measured contaminant concentrations to water quality criteria, performing bioassays, and predicting the concentration of selected contaminants based on the total sediment concentration and organic carbon concentrations. Sediment criteria methods based on analysis of bulk sediments include bioassays of spiked or unspiked sediment, characterization of benthic macroinvertebrate communities, or both.

Methods such as the Sediment Quality Triad (3) and the Apparent Effects Threshold (4) link site-specific observations of contaminant concentration, macroinvertebrate community structure, and bioassay results. All of these methods evaluate effects on or potential toxicity to aquatic organisms residing in contact with the sediments.

MERCURY IN THE AQUATIC ENVIRONMENT

Although some forms of mercury can be directly toxic to aquatic macroinvertebrates, the primary hazard of mercury in sediments is an indirect one. Mercury undergoes methylation in sediments and it is the methylmercury species which are highly bioaccumulated in the aquatic food chain. Methylmercury has been observed to be concentrated by 10^6 in fish tissue compared to the surrounding water (5). The hazard to humans is related to consumption of methylmercury-contaminated fish. Sediment quality criteria related to toxicity to macroinvertebrates are, therefore, not appropriate for mercury.

Mercury methylation in sediments is a biologically-mediated reaction (6) and is favored in anoxic sediments over oxic sediments (7). Although many bacteria and fungi are capable of methylation, the principal methylators of mercury in both saline and freshwater anoxic sediments are sulfate-reducing bacteria (8). Measuring the activity of anaerobic sulfate-reducing bacteria may be important for predicting the rate of methylmercury production.

Once methylmercury is created, its behavior in an aquatic ecosystem will be influenced by a number of factors. Methylmercury is strongly adsorbed to organic and inorganic particles and can undergo bacterial

demethylation. The pH of the system will influence the chemical form of the methylmercury (i.e., chloride, hydroxide, or ionic). Each of these factors can be significantly different between, for example, acidified seepage lakes, eutrophic lakes, rivers, or estuaries.

The mechanism by which methylmercury enters the food chain and is eventually transferred to fish tissue is not well known. Methylmercury produced in sediment may move into the water column by one or more of the processes of diffusion, advection, resuspension, or bioturbation. Measurement of *in situ* methylmercury flux rates may be possible now with the development of new analytical techniques for very low (< 1 part per trillion) methylmercury concentrations (9). Once in the water column, methylmercury can become incorporated into phytoplankton by diffusion through the cell wall or by adsorption to the cell surface. Methylmercury will then accumulate in zooplankton which graze on phytoplankton and, similarly, in planktivorous and piscivorous fish.

Despite numerous studies, there is little evidence that a direct correlation exists between mercury concentration in sediments and the methylmercury concentration in fish tissue. Other parameters such as lakewater pH, lake volume and maximum depth, and lake water alkalinity appear to influence methylmercury accumulation in fish (10, 11). Sediment quality criteria for mercury based on sediment mercury concentration toxicity are, therefore, not directly related to human health or ecological risk.

REQUIREMENT FOR SEDIMENT MERCURY CRITERIA

Sediment mercury criteria should be based on achieving acceptable concentrations of mercury in fish tissue. Based on new analytical techniques, measurement of *in situ* rates of methylmercury production may be possible. Indirect measurements may also be useful. For example, the sulfate-reduction rate in sediments may be an indicator of methylmercury production rate. The actual mechanism by which methylmercury becomes associated with phytoplankton is critical. Methylmercury-cell association may be influenced by ambient water composition. Much research remains to be done to identify the factors which influence the rates of mercury methylation.

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EFFECT OF CHEMICAL FORM OF MERCURY ON THE PERFORMANCE OF DOSED SOILS IN STANDARD LEACHING TESTS: EP AND TCLP (1)

Ralph R. Turner
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831
USA
Tel: (615) 574-7856

INTRODUCTION

There are few regulatory and/or advisory criteria for mercury in contaminated soils, sediment, and waste. Typically, action or cleanup guidelines are developed on a case-by-case basis. The most widely applied criterion for mercury in solid material is the performance of solid samples analyzed with leaching procedures developed by the U. S. Environmental Protection Agency (EPA). These protocols, along with others, have been used to classify wastes under the Resource Conservation and Recovery Act (RCRA) (1). Leaching results, expressed as the concentration of mercury in the laboratory-generated leachate, are compared to 200 µg/L. Results above this criterion are classified as having failed the RCRA "toxicity characteristic." The 200 µg/L limit represents 100 times the Drinking Water Standard for mercury and requires the sample to contain at least 4 µg/g. The latter value is derived by multiplying the established limit, 200 µg/L, by the solution-to-solid ratio in the test, 0.02 L/g.

Theoretically, any sample containing total mercury less than 4 µg/g could not fail the protocol and be accordingly classified as hazardous under RCRA. Rarely, if ever, will all the mercury in a soil or waste be completely leachable in a protocol. Therefore, soil containing considerably higher concentrations of mercury than 4 µg/g could theoretically pass the protocol. On September 25, 1990, an earlier leaching protocol, called the Extraction Procedure (EP), was replaced with the Toxicity Characteristic Leaching Procedure (TCLP) (40 CFR 261). While there are some minor differences between the TCLP and the EP protocols, most notably the composition of the extraction fluid, the established limit remained 200 µg/L.

Application of the EP to a variety of mercury-contaminated soils and solid wastes from US Department of Energy (DOE) facilities in Oak Ridge, Tennessee has not shown any consistent relationship between test results and total mercury concentrations. Low yields of leachable mercury (less than the RCRA limit of 200 µg/L) have not been uncommon for samples containing several thousand ppm of total mercury and even for samples exhibiting visible beads of mercury. Conversely, some soils with relatively low concentrations of total mercury have exhibited high leachability of mercury (>200 µg/L) and been classified as hazardous under RCRA.

In addition to the previously-described anomaly, highly mercury- contaminated sediments removed from storm sewers initially exhibited low leachability of mercury (17 out of 21 samples yielded leachate with <200 µg/L after initial dewatering). Subsequently, these sediments exhibited high leachability of mercury (31 out of 31 samples yielded leachate with >200 µg/L following re-analysis after dry storage for up to 3 years). The increase in solubility was hypothesized to have been caused by surface oxidation of elemental mercury contained in the dried sediments. While still in the storm sewer any oxidation products on the surface of the elemental mercury would be washed away continuously. Immediately after drying, the solubility of the mercury would be controlled mainly by the solubility of clean elemental mercury (reported to be about 60 µg/L), and thus less than the 200 µg/L RCRA limit. The oxidation product would initially be insoluble mercurous oxide (HgO) which, in turn, may partially decompose to more soluble mercuric oxide. The reported solubility of mercuric oxide (about 53000 µg/L) is sufficient to yield a leachate exceeding 200 µg/L.

As previously discussed, pure mercury compounds have different solubilities in aqueous solutions. Generally, organic and inorganic mercury compounds (except mercuric sulfide) are sparingly soluble while elemental mercury is relatively insoluble in aqueous solutions (2). For this reason, mercuric sulfide and elemental mercury, if submitted in pure form to either of these protocols, would be expected to pass at much

higher concentrations than compounds such as mercuric oxide. The adsorption capacity of soils and solid wastes is also expected to reduce the solubility of any pure compound added to the soil or waste.

The objectives of this study were to determine which forms of mercury in soil exhibit the highest leachability as analyzed by the EP and TCLP protocols and to determine whether headspace mercury vapor readings from soil samples are indicative of leaching performance. The four mercury compounds studied were elemental mercury (Hg^0), mercuric sulfide (HgS), mercuric oxide (HgO), and mercurous oxide (Hg_2O). Whether the two leaching procedures yield equivalent results was also addressed.

MATERIALS AND METHODS

Uncontaminated soil was collected from the Bear Creek Valley on the Oak Ridge Reservation. The soil was a shaley silt loam from the Ap horizon. These soils are acidic (pH_{water} = 4.7) and exhibit cation exchange capacities ranging from 5 to 10 mEq/100 g. Dried soil was crushed using a mortar and pestle and sieved through a 2 mm screen. Additional analyses to characterize the dry sieved soil included total mercury (0.72 µg/g), organic carbon (2.08%), and particle size distribution (18.27% sand, 71.26% silt, and 10.46% clay). Glass bottles (4 oz) were filled with 100 g of dry, sieved soil, and fitted with teflon-lined closures. Four different mercury compounds (Hg^0, HgS, HgO, and Hg_2O) at four different concentrations (0, 100, 1000, 10000 µg/g) were studied. Each treatment was done in triplicate. Elemental mercury was first washed with distilled water to remove oxide, and only shiny beads of Hg^0 were used to dose the soil. After dosing, samples were shaken vigorously to blend the mercury compounds with the soil.

Shaken samples were allowed to equilibrate for at least 1 h before headspace vapor readings were taken. A Jerome Model 411 Gold Film Mercury Vapor Analyzer was used to measure the mercury vapor at room temperature (22 to 24 degrees C). To take a reading, each sample bottle was opened enough to insert the Jerome sampling tube and a 10 s scan was performed. Sample headspace volume (about 50 mL) was considerably less than the volume (125 mL) of air drawn by the Jerome and thus uncontrolled dilution of the headspace sample occurred. Each sample was read three times with the exception of some of the soils dosed with the highest amounts of Hg^0 which saturated the Jerome.

Leaching protocols were carried out using the entire contents of the sample bottle in order to eliminate any lack of homogeneity that could arise from taking sub-samples. While the two protocols are very similar, some minor differences exist (40 CFR 261). Because the soil collected from the Bear Creek Valley site was already acidic (pH ≤5.0), no acetic acid was added in the EP extraction. The extraction fluid for the TCLP contained acetic acid and thus contrasts with the EP fluid in this potentially important aspect.

RESULTS AND DISCUSSION

The results from the trials wherein the Jerome analyzer was used to measure headspace mercury vapor were not always highly reproducible based on the replicate trials. General trends among the compounds were observed. Elemental mercury yielded some of the most variable vapor results, especially within the same concentration. These highly variable measurements may be due to the way each sample was shaken and the corresponding position of the mercury bead(s) at the time of measurement or to the uncontrolled dilution with room air during headspace sampling. Generally, the higher the dosed soil concentration the higher the headspace vapor reading. For the Hg^0 dosed soil very few readings could be obtained from samples dosed to 10,000 µg/g because the gold film on the Jerome monitor saturated (>1.99 mg/m^3).

Because the Jerome analyzer is engineered to detect elemental mercury and the other compounds tested have very low or no vapor pressures, it was not initially expected that the other three test compounds (HgS, HgO, and Hg_2O) would yield detectable vapor. Mercuric sulfide showed the most consistent headspace mercury vapor readings. At all concentrations, HgS yielded 0.000 to 0.001 mg/m^3 of Hg. Mercuric oxide samples at the 100 and 1000 µg/g dosing levels also resulted in very low mercury vapor readings (0.000 to 0.014 mg/m^3). At 10,000 µg/g, the vapor readings in soil dosed with HgO ranged from 0.006 to 0.081 mg/m^3. Mercurous oxide caused increased vapor concentrations with increased soil concentration. Detection of significant elemental mercury vapor over Hg_2O may be explained by the fact that this compound is subject to disproportionation and may, therefore, contain some elemental mercury.

Results from the two leaching protocols are summarized in Table 1. As expected, different test results were obtained for the different mercury compounds, dosed concentrations, and leaching protocols. None of the dosed concentrations for Hg^o and HgS yielded leachate concentrations in EP or TCLP exceeding 200 µg/L, the RCRA limit. In fact, the EP leachate concentrations in the HgS dosed soils are similar to the blank concentration of non-dosed soil (Table 1). Using the EP protocol, only HgO at doses of 1000 and 10,000 µg/g and Hg_2O at 10,000 µg/g resulted in leachate concentrations exceeding 200 µg/L.

Leachate concentrations exceeding the RCRA limit were also found at the 1000 and 10,000 µg/g doses for both HgO and Hg_2O using the TCLP protocol. With one exception (HgO at 100 µg/g) the TCLP yielded similar or higher leachate concentrations than the EP (see subsequent discussion). For HgO and Hg_2O at the 10,000 µg/g dose level, the TCLP leachate concentrations were 10 times higher than the EP results. The TCLP leachate concentrations for soil dosed with Hg_2O at the 10,000 µg/g dose are similar to the pure compound solubility value (53 mg/L) given in Kaiser and Tolg (2). A possible explanation for the much higher than expected solubility of Hg_2O could be a result of disproportionation of mercurous mercury to elemental and mercuric mercury. This could also explain why the Hg_2O dosed soils yielded high vapor readings. The purity of the various mercury compounds was not verified independently and thus, sufficient HgO could have been present in the Hg_2O to increase the apparent solubility of Hg_2O.

The sample headspace vapor results clearly indicated that presence or absence of headspace vapor could not be used to predict performance of a soil or waste on the leaching protocols. Nonetheless, measurement of headspace vapor may provide other useful information about potential human and ecological risks associated with the tested sample. For example, our study has shown that a soil sample containing one percent by weight (10,000 µg/g) elemental mercury could pass the TCLP leaching test but

TABLE 1. AVERAGE MERCURY CONCENTRATIONS OBTAINED FROM TWO LEACHING TESTS*

Dose		EP Results			TCLP Results		
(µg/g)	Compound	(µg/L)	S.E.	C.V.(%)	(µg/L)	S.E.	C.V.(%)
100	Hg^o	1.86[b]	0.21	19.4	8.89[b]	0.29	5.74
	HgS	0.38[c]	0.17	76.3	1.63[c]	0.61	65.0
	HgO	65.7[a]	8.77	24.2	38.5[a]	0.99	4.47
	Hg_2O	42.8[a]	0.56	2.3	53.8[a]	9.68	31.2
1000	Hg^o	17.2[b]	3.72	37.6	25.5[b]	4.39	29.8
	HgS	0.22[c]	0.05	36.4	1.67[c]	0.29	29.9
	HgO	220.[a]	46.0	36.2	258.[a]	10.5	7.07
	Hg_2O	114.[a]	20.16	30.4	491.[a]	195.	68.9
10000	Hg^o	47.6[b]	5.24	19.1	51.6[c]	0.46	1.55
	HgS	2.48[c]	1.19	83.1	2.15[d]	0.39	31.6
	HgO	6270.[a]	861.	23.8	57200.[a]	7030.	21.30
	Hg_2O	3200.[a]	694.	37.5	36600.[b]	1590.	7.52
0	BLANK	0.42	0.31	129.	0.30	0.03	16.7

*For each dosing level and test, averages followed by the same letter ([a,b,c,d]) are not significantly different at the 5% level (Duncan's Multiple Range Test applied to log-transformed data).

have a sample headspace vapor concentration (e.g., >2 mg/m³) that exceeds both the "derived" ambient air (0.001 mg/m³;28 CFR Pt II 38) and the industrial hygiene (0.05 mg/m³;29 CFR 1910.1) standards by orders of magnitude. This fact alone is a compelling reason to treat such a sample as a hazardous waste regardless of its leaching performance.

The leaching results suggest that reliance on the EP or TCLP alone to classify waste or soil could lead to a significant underestimation of the risks posed by a poorly characterized solid and inappropriate disposal. Wastes or soils containing mercury predominantly in the elemental or sulfide forms would be particularly subject to misclassification if only limited process or site knowledge is available. We suggest that a tiered approach, incorporating headspace vapor analysis, analysis for total mercury, and application of TCLP, is necessary to fully evaluate the degree of hazard associated with mercury- contaminated soils and wastes.

Ideally, information on the speciation of mercury in the solid phase would also be desirable, but such measurements are expensive and well beyond the analytical capabilities of most laboratories. Obviously, headspace vapor analysis conveys some information about speciation of the mercury and this analysis can be performed routinely at low cost. No standardized protocol for performing headspace mercury vapor measurements currently exists but developing such protocols is straightforward and can be patterned after headspace analysis for volatile organic compounds. Analytical capability to perform total mercury analyses is almost universal and entails less equipment and produces less chemical laboratory waste than performance of a leaching protocol such as the TCLP. Thus, it seems logical always to screen samples for headspace mercury vapor and to perform total mercury analysis prior to making a decision about the need to perform the more expensive leaching protocol also.

Currently there exists no federally regulated, uniform guideline for total allowable mercury levels in soil. After May 8, 1992 debris and soil failing TCLP and containing mercury at a concentration >260 µg/g was banned from disposal by landfilling (40 CFR 268) and such material now requires pretreatment (thermal) before landfilling. Soil containing less than 260 µg/g but that fails the TCLP will be classified as hazardous. The US DOE's Oak Ridge Y-12 Plant in Tennessee has adopted a 12 µg/g interim maximum concentration for mercury in soil as proposed by Bashor and Turri (3). This value incorporates potential mercury risks from inhalation and direct ingestion, and is similar to the value (20 µg/g) suggested by EPA (40 CFR 55:145, July 27, 1990) as an "action level". More recently, Revis et al. (4) recommended that a 722 µg/g limit of mercury in soil would suffice for the Y-12 Plant site because a large percent of the mercury contamination had been bound in the HgS form, at least in contaminated sediment and floodplain soil.

This study has confirmed Revis' suggestion that the form of mercury contamination must be assessed in order to establish an appropriate limit. Soil can contain much higher concentrations of relatively insoluble, non-volatile HgS and probably constitute negligible human health risk where smaller concentrations of other mercury forms should trigger immediate attention. Transformations among forms of mercury, especially those that increase the mobility and bioavailability of mercury obviously complicate this issue and bear further consideration.

There are currently no regulatory criteria or guidelines which apply to waste or soil samples which do exhibit detectable headspace mercury vapor. We suggest that headspace mercury vapor concentrations that exceed 10% of the industrial hygiene workroom standard of 0.050 mg/m³ could constitute an inhalation hazard under certain circumstances (e.g., confined or poorly- ventilated space). Solid waste or soils which exhibit such headspace vapor concentrations should be classified as hazardous. We also suggest that materials exhibiting detectable headspace mercury vapor (e.g., 0.001 mg/m³ using the Jerome Model 411 analyzer or similar instruments), but less than 0.005 mg/m³, should be classified as hazardous if total mercury exceeds 20 µg/g. These proposed headspace vapor guideline values are preliminary and may need further support based on risk analysis.

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INTER-LABORATORY TESTING FOR MERCURY BY TCLP AND SOURCE REDUCTION IN THE LAMP MANUFACTURING INDUSTRY

Vincent D. Meyer
National Electrical Manufacturers Association
GTE Electrical Products
100 Endicott Street
Danvers, MA 01923
USA
Tel: (508) 750-2322

INTRODUCTION

This paper presents the results of extensive inter-laboratory testing of fluorescent lamps by the Lamp Technical Committee of the National Electrical Manufacturers Association (NEMA) in cooperation with the Environmental Protection Agency (EPA) using the Toxicity Characteristic Leaching Procedure (TCLP). Included in this paper will be a report on the significant progress the lamp industry is making to reduce the amount of mercury used in fluorescent lamps.

Disposal of spent fluorescent lamps containing small amounts (about 0.01%) of mercury is becoming a problem. Disposers of spent fluorescent lamps encountered a serious problem in determining if these lamps exceed the regulatory threshold of 0.2 mg/L when applying the standard EPA test for toxicity characteristics under the Resource Conservation and Recovery Act (RCRA) and reported their concerns to US lamp manufacturers. In dealing with this situation, US lamp manufacturers through NEMA reported to the EPA Office of Solid Waste the wide variation in results obtained by the disposers of fluorescent lamps and initiated a series of inter-laboratory tests.

The inter-laboratory testing had three objectives:

To confirm the variation among various laboratories in performing TCLP on fluorescent lamps

To isolate within the TCLP the step or steps that give rise to the variations

To attempt to determine the testing conditions or causes of the variation in results and to suggest methods of obtaining consistent test results

The first two objectives have been successfully met by this series of inter-laboratory tests; however, it was not possible to find testing conditions which would eliminate the large variation in test results.

METHODOLOGY

The testing was designed to isolate the effect of each step in the TCLP on variability. Beginning with the final step in TCLP of analysis for mercury, the testing progressed through four phases:

(I) Analysis of standard solutions of mercury to quantitatively determine the ability of each laboratory to analyze for soluble mercury

(II) Analysis of aliquots of solutions obtained after the filtering step in TCLP, prepared at one llaboratory, to determine quantitatively the variability when analyzing for soluble mercury in the extraction fluid

(III) Extraction of crushed lamps prepared at one laboratory to determine the agreement among laboratories when extracting, filtering, and analyzing crushed lamps

(IV) TCLP tests for mercury in whole fluorescent lamps to determine quantitatively the agreement among laboratories when the complete TCLP is performed on fluorescent lamps

Each phase included a sample containing no mercury, a blank. In each phase the samples were

identified only as A, B, C, D and laboratories were requested to perform the appropriate procedure for TCLP and/or analysis for mercury.

Standard 4-ft. fluorescent lamps were used. All lamps were selected from lamps made consecutively on a high-speed lamp manufacturing machine with a history of consistently producing duplicate lamps. Blank lamps were made by turning off the mercury dispensing apparatus during the manufacturing process immediately after the test lamps were produced.

IMPLEMENTATION

Initially seven different laboratories were chosen to participate in these inter-laboratory tests. The laboratories included both the laboratories of US lamp manufacturers and independent laboratories experienced in performing TCLP. During the final phase of the testing a laboratory chosen by EPA was included. The laboratories were numbered 1 to 8 and otherwise not identified.

Phase I - Samples of standard solutions of mercury were prepared by dissolving metallic mercury in nitric acid followed by appropriate dilution. The solutions were shipped to the individual laboratories with the following instructions:

"This is the first in a series of tests designed to improve the inter-laboratory correlation of the TCLP for mercury. The enclosed four solutions contain mercury in a five percent nitric acid solution. Analyze for mercury concentration using method 7470. Report results in mg/L."

Phase II - For this phase of the test one laboratory performed TCLP on four samples and stopped the procedure after filtering. To obtain various concentrations of mercury, samples were prepared as:

A) Three standard fluorescent lamps leached in same volume of extraction fluid as sample D; B) A solution of mercury oxide, HgO, at 0.2 mg/L to determine capability to recover soluble mercury; C) Leaching solution (extraction fluid #1) to act as a blank; D) One standard fluorescent lamp leached in prescribed amount of extraction fluid #1. The following instructions were provided each participating laboratory:

"In the near future each participating laboratory will receive four liquid samples which have been obtained by following the TCLP, but the procedure will have been stopped after completion of the filtering step. The four samples will include an aliquot from a large, single container obtained by leaching crushed fluorescent lamps and one sample will have been obtained by leaching a known quantity of mercury oxide. The sample obtained by leaching mercury oxide will act as a 'standard' solution. Samples will be shipped to laboratories in insulated, cooled containers. Upon receipt the laboratories should refrigerate the samples and inform the person designated in the instructions shipped with the samples. When all laboratories have received the samples, a date for mercury analysis will be selected and samples will be analyzed at all laboratories on the designated day. As with the standard solution test all laboratories must use Method 7470 and report the measured mercury concentrations in mg/L."

Phase III - For this phase of the test one laboratory performed the initial step of crushing fluorescent lamps and then shipped the samples to the laboratories. The following instructions were provided each participating laboratory:

"This is the third in a series of tests designed to improve the inter-laboratory correlation of the TCLP for mercury. The enclosed four samples were obtained by crushing fluorescent lamps such that the resulting material is capable of passing through a 9.5 mm sieve. Using the entire sample in each case, perform TCLP extraction and filtration as per 40 CFR Parts 261, 264, 265, 268, 271 and 302 dated June 29, 1990. Analyze for mercury concentration using method 7470. Report results in mg/L."

Phase IV - For this final phase of the test whole lamps from the lot of standard lamps and one lamp containing no mercury were provided to each laboratory with the following instructions:

"This is the fourth in a series of tests designed to improve the inter-laboratory correlation of the TCLP for mercury. The enclosed four samples are fluorescent lamps manufactured to our specifications and aged for specific time periods. Using the entire sample in each case, perform TCLP extraction and filtration as per 40 CFR Parts 261, 264, 265, 268, 271 and 302 dated June 29, 1990. Analyze for mercury concentration using method 7470. Report results in mg/L. Please keep records of how the procedure was interpreted. See attached notes on recording procedure."

Each laboratory was also provided with a questionnaire to record details of the procedure used in performing the TCLP.

RESULTS

TABLE 1. PHASE I, STANDARD SOLUTIONS OF MERCURY

Sample Identification	Concentration of Mercury in mg/L			
	IR-A	**IR-B**	**IR-C**	**IR-D**
As Made	**0.000**	**0.113**	**0.565**	**1.017**
Laboratory 1*	0.000	0.010	0.050	0.100
Laboratory 2	0.000	0.090	0.490	0.990
Laboratory 3	0.001	**	0.410	0.780
Laboratory 4	0.000	0.080	0.585	1.000
Laboratory 5	0.002	0.108	0.529	0.944
Laboratory 6	< 0.01	0.10	0.49	0.94
Laboratory 7	0.0550	0.1310	0.5650	0.8600
Mean (excluding Lab 1)	**0.011**	**0.102**	**0.512**	**0.919**
Std Dev	0.022	0.019	0.063	0.084
Coefficient of Variation- SD/M	1.92	0.191	0.123	0.092
Recovered (Mean/As Made)	n.a.	90%	91%	90%

* After the fact Laboratory 1 reported a calculation error of a factor of 10
**Solution B lost at Lab 3

TABLE 2. PHASE II, SOLUTIONS AFTER THE FILTERING STEP IN TCLP

Sample Identification	Concentration of Mercury in mg/L			
Description	**2R-A**	**2R-B**	**2R-C**	**2R-D**
	3 lamps	0.2mg/L HgO	blank	1 lamp
Laboratory 1	0.518	0.204	<0.001	0.699
Laboratory 2	0.57	0.23	0.008	0.71
Laboratory 3	0.43	0.19	0.004	0.60
Laboratory 4	0.51	0.250	n.d.	0.69
Laboratory 5	0.52	0.242	0.005	0.782
Laboratory 6	0.35	0.20	<0.01	0.55
Laboratory 7	0.601	0.348	n.d.	0.827
Mean	**0.500**	**0.238**	**<0.004**	**0.694**
Std Dev	0.085	0.054	0.004	0.096
Coefficient of Variation- SD/M	0.170	0.225	0.626	0.138

TABLE 3. PHASE III, CRUSHED LAMPS

Concentration of Mercury in mg/L

Sample Identification Type of Lamp	CL-1 Normal	CL-3 Normal	CL-4 Normal	Mean of Three	CL-2 No Hg
Laboratory 1	0.0067	0.0056	0.0176	0.010± .007	<0.0005
Laboratory 2	0.31	0.46	0.44	0.40 ± .08	n.d.
Laboratory 3	0.43	0.48	0.55	0.49 ± .06	n.d.
Laboratory 4	0.56	0.45	0.53	0.51 ± .06	n.d.
Laboratory 5	0.55	1.23	1.04	0.94 ± .35	<0.01
Laboratory 6	0.082	0.14	0.093	0.105± .03	<0.001
Laboratory 7	1.57	2.20	5.50	3.09± 2.11	n.d.
Mean	0.501	0.709	1.167	0.793	
Std Dev	0.518	0.763	1.94	1.21	
Coefficient of Variation- SD/M	1.03	1.08	1.66	1.53	

TABLE 4. PHASE IV, WHOLE LAMPS

Concentration of Mercury in mg/L

Sample Identification Type of Lamp	WL-1 Normal	WL-2 Normal	WL-4 Normal	Mean of Three	WL-3 No Hg
Laboratory 1	0.021	0.013	0.0006	0.012± 0.01	0.021
Laboratory 2	0.56	0.52	0.65	0.58± 0.07	n.d.
Laboratory 3	0.39	0.39	0.53	0.44± 0.08	n.d.
Laboratory 4	0.31	0.52	0.57	0.47± 0.14	n.d.
Laboratory 5	1.3	1.52	2.8	1.87± 0.81	0.02
Laboratory 6	0.01	0.02	0.02	0.02± 0.006	<.01
Laboratory 7	0.08	0.10	0.07	0.08± 0.02	n.d.
Laboratory 8	0.320	0.650	0.760	0.577± 0.229	<0.001
Mean	0.374	0.467	0.675	0.505	
Std Dev	0.421	0.492	0.911	0.630	
Coefficient of Variation- SD/M	1.13	1.053	1.35	1.25	

DATA ANALYSIS

Phase I demonstrated that the individual laboratories are capable of performing quantitative analysis for soluble mercury over the range of concentrations of interest with a coefficient of variation of about 0.14 (mean of the Coefficients of Variation excluding the blank) and recover about 90% of the formulated amount of mercury.

Phase II demonstrated that all of the laboratories are capable of quantitatively recovering soluble mercury from the leaching solution. The soluble mercury solution was prepared by dissolving enough HgO in the extraction solution to produce a mercury concentration of 0.20 mg/L. The mean for all of the laboratories was 0.238 mg/L or 19% higher than the formulated amount. The coefficient of variation was 0.225. It is difficult to explain the results for samples 2R-A (3 lamps) and 2R-D (1 lamp). The filtered extract for the sample 2R-A (3 lamps), which presumably has three times the amount of leachable mercury as sample 2R-D (1 lamp) yielded less detected mercury. The amount of mercury extracted did not correlate in a simple way with the amount of extractable mercury in the samples.

Phase III results clearly show that there is a dramatic increase in the variation in results when the leaching and filtering steps by individual laboratories are included in the testing on very similar lamps. The

coefficient of variation has increased to about 1.5. For the previous phases the coefficient of variation averaged about 0.15 (excluding blanks).

Phase IV results clearly show that there remains a wide variation in results obtained by different laboratories when the laboratories use similar lamps to perform TCLP for mercury. The coefficient of variation was about 1.2.

During Phase IV of the testing each laboratory completed a questionnaire describing details of the procedure they used. This was an attempt to find differences in interpretation and implementation of the TCLP for mercury in fluorescent lamps. While difference among the laboratories were identified, no correlation could be found between the results of TCLP and these procedural differences.

Specifically, no correlation could be found between the number of tumbling containers used for each lamp, the pH of the solution after extraction or the number of pieces that the aluminum end cap was cut into before extraction.

In summary, these inter-laboratory tests clearly show that the laboratories are capable of quantitatively analyzing for mercury and can quantitatively recover soluble mercury in the TCLP solution, but wide variation in test results among different laboratories originates in the extraction and filtration steps of the TCLP when performing TCLP for mercury in fluorescent lamps.

SOURCE REDUCTION

All fluorescent lamps contain elemental mercury. Standard 4- and 8-ft. lamps contain between 35 and 75 mg. Very small fluorescent lamps including the compact fluorescent contain about 10 mg or less.

Lamp manufacturers have for many years been attempting to reduce the amount of mercury in fluorescent lamps. Significant progress has been made in this source reduction effort. A recent survey by NEMA of current manufacturing practices revealed a 14% reduction in the average mercury content of a standard 4-ft. 1-1/2 inch diameter cool-white fluorescent lamp from 1985 to 1990. These manufacturers also predicted a further decrease of about 35% by 1995. (Refer to Table 5.)

TABLE 5. PREDICTED DECREASE IN MERCURY IN FLUORESCENT LAMPS

YEAR	MERCURY FILL
1985	48 mg
1990	42 mg
1995	27 mg

These mercury reductions have been achieved by the use of more efficient dosing techniques during the manufacturing process incorporated into newer high speed production equipment. The projected figure for 1995 of 27 mg of mercury used in a 4-ft fluorescent lamp is close to the present practical limit needed for efficient lighting performance so that reductions below this amount will probably be very small. Nevertheless, 27 mg of mercury represents only about 0.01% of the total weight of a 4-ft. lamp.

It has been shown that the disposal of lamps containing mercury accounts for approximately 0.2% of the total discards of mercury (1). These lamps are efficient sources of white light, typically being three to four times more efficient than an incandescent lamp. Consequently, their use results in significantly less power use along with associated reductions in a variety of power plant stack emissions, including mercury. Studies show that the substitution of incandescent lamps by lamps containing mercury results in a net reduction of environmental mercury releases (1). Typically, for the average mix of fossil fuels, nuclear power, and hydro used in the US, this reduction is approximately three times the mercury contained in the lamp, depending on lamp type.

A recent Dutch government study concerning the environmental aspects of lighting concluded:

> "It is remarkable how the total quantity of mercury that is released when the incandescent lamp is used is larger than when, for example, the fluorescent lamp is used, when the fluorescent lamp has a bad name on account of the mercury it contains."

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MANAGEMENT OF MEDICAL MERCURY BATTERY WASTES THROUGH SOURCE SUBSTITUTION

John L. Price
Broward County Office of Integrated Waste Management
200 Park Central Boulevard South, Suite 3
Pompano Beach, FL 33064
USA
Tel: (305) 968-3861

In the early 1980s, solid waste managers in Broward County, Florida, began to integrate mercury management into Broward's overall waste management system. Led by T. M. Henderson, Director of the Resource Recovery Office, early efforts focused on proper management of mercury after entry into the system. Late in 1990, Henderson shifted gears into diversion of mercury-containing wastes before they reached facilities and landfills. Utilizing a source substitution strategy, the county devised a program which is currently diverting nearly one ton of mercury yearly from just one point source: mercury medical batteries. Both solid waste and medical officials were surprised this substitution proved to provide a cost savings to area hospitals.

BACKGROUND

Predominantly urban Broward County, Florida, contains about 1.2 million people in the Fort Lauderdale area of south Florida. Among the population characteristics impacting municipal solid waste (MSW) management decisions are a large senior segment and a sizable seasonal winter influx.

The cornerstones of Broward's solid waste management system are two mass burn resource recovery facilities with a combined 4500 ton per day capacity. Best available emission control equipment installed after careful selection and at considerable expense ensures that mercury (and other) emissions are well below existing and forecasted Federal, state, and local limits. Ash residues are placed in secure monofills adjacent to plant sites. Residential and commercial recycling activities augment these facilities. Two landfills with multiple liners, leachate collection systems, and monitoring wells round out the system. Four Broward cities utilize a parallel MSW composting facility with unprocessable residues entering resource recovery facilities or landfills.

IDENTIFYING THE SOURCE AND MANAGEMENT OPTIONS

Dry cell batteries were identified as a major source of mercury in the Broward County MSW stream in a 1987 waste composition study by Cal Recovery Systems. "Button" and medical batteries were targeted as major mercury sources to be diverted from Broward's MSW before the Resource Recovery Facilities began operations in mid 1991.

In early February 1991, concurrent with implementation of its button battery recycling program, the county began research and planning on the medical battery phase of its expanded mercury management program. Preliminary investigation of the costs of a county-funded recycling effort showed that it was prohibitive. Further, the fact that these battery wastes were commercially generated as opposed to the household-generated button batteries raised another issue: Should county dollars be used to assist only certain businesses (hospitals) in defraying costs of doing business (waste management)?

These considerations prompted the decision that county staff would function as an information resource presenting the problem and options to area hospitals regarding proper battery and mercury-containing waste management. The hospitals, having legal responsibility for management of waste generated, would be asked to select the option appropriate to their individual operations. The selected option had to comply with applicable waste management regulations. County staff would control and monitor the hospitals' response.

During the research phase of the project, one hospital professional was extremely valuable to county staff. In addition to explaining medical battery uses, E. Kurnia, a biomedical engineer at Memorial Hospital in Hollywood, also suggested what was to become the preferred course of action for area hospitals regarding mercury medical batteries: substitution of an alternate type of battery. Memorial Hospital was the first area hospital to implement changes and to realize a cost savings as a result. Other hospital, battery industry, and governmental professionals at the local, state, and national level also provided helpful information.

Discussions with appropriate hospital personnel in Broward County hospitals over the next three months surveyed the types, uses, and quantities of medical mercury batteries. Mercury-containing wastes from broken medical instruments, spill cleanup, and used thermostats and switches were also discussed. Understanding of applicable Federal, state, and local waste management requirements was confirmed. It was emphasized that mercury batteries and all mercury-containing wastes were not acceptable at either Broward County resource recovery facilities or landfills.

Current waste management procedures were surveyed. Alternative waste management options were presented and discussed with particular attention to costs. The following options were presented in order of desirability from an environmental impact point of view (most through least). This order of desirability in many cases held true from a cost point of view as well (least through most).

1. Substitute a less hazardous alternative

2. Return used batteries to supplier

3. Manage via hazardous waste management vendor

Discussions with hospital personnel confirmed that mercury 8.4 volt medical batteries were widely used to power telemetry cardiac monitors in Intermediate Care or "step down" units and portable Holter cardiac monitors. One hospital had switched to the more benign zinc air battery in its telemetry cardiac monitors about five years ago because it performed better. Battery usage per year per hospital ranged from 100 to nearly 16,000 depending on the number of beds and occupancy rates (Table 1). Almost without exception, area hospitals were disposing mercury medical batteries in regular or biohazardous waste containers.

ONE TON OF MERCURY DIVERTED

When advised of the composition of these batteries and viable options, most hospital administrators were quick to change use and waste management procedures. The most popular option with respect to mercury 8.4 volt medical batteries was to substitute a zinc air battery. The zinc air battery is usually more expensive but in many cases lasts longer than its mercury counterpart. One drawback is that the zinc air battery will continue to discharge even when not in use while the mercury will not. However, this is not a problem when the monitors are in constant use as in most hospitals.

Four hospitals switched to a combination of zinc air and low mercury alkaline batteries due to equipment compatibility and cost considerations. Stocks of mercury batteries (usually less than one month's supply) were depleted or returned to suppliers. In many cases, mercury batteries from stocks were collected when discharged and returned to suppliers for proper management or managed as hazardous wastes through established vendors.

By the summer of 1991 most hospitals had eliminated their use of mercury batteries or initiated proper management policies. The amount of mercury diverted from Broward's waste stream is staggering. Each 8.4 volt mercury battery weighs about 1.8 ounce (1) of which nearly 1/2-ounce is mercury (2). Based on surveys more than 63,000 of these batteries were entering Broward's waste stream from hospitals alone each year. That is in excess of 1,750 pounds or nearly one ton of mercury per year (Table 1).

Area hospitals managed to divert this ton of mercury and save money in the process. Taking into account the extra expense of alternate batteries and the avoided costs of managing mercury battery wastes,

TABLE 1. DIVERSION OF 8.4 VOLT MERCURY MEDICAL BATTERY WASTES FROM BROWARD COUNTY, FLORIDA, MSW STREAM 1991 BY HOSPITAL

	Number of Beds Using Monitors	Mercury Batteries Number (lbs mercury)		Management Option
1.	70+	15,708	(442)	Substitute Zinc
2.	40	12,893	(363)	Substitute Zinc
3.	45	5,844	(164)	Substitute Zinc
4.	52	5,328	(150)	Substitute Zinc
5.	32	4.176	(117)	Substitute Zinc
6.	n/a	4,000	(113)	*Return to Vendor
7.	16	3,600	(101)	*Return to Vendor
8.	16	3,216	(90)	Substitute Zinc
9.	18	3,000	(84)	Substitute Zinc
10.	48	3,000	(84)	Substitute Zinc, Alkaline
11.	n/a	2,300	(65)	**Substitute Zinc
12.	8	96	(3)	Substitute Alkaline
13.	88	0	(0)	Use Ni-Cadmium
14.	35+	0	(0)	Use Alkaline
15.	12	0	(0)	Use Zinc
16.	0		(0)	***Use Low Mercury Alkaline

Total   63,161 (1776)

Note: "Zinc":Zinc Air type batteries; "Ni-Cadmium":Nickel Cadmium rechargeable batteries; "Alkaline":9 Volt Alkaline batteries with standard mercury content; "Low Mercury Alkaline":9 Volt Alkaline batteries with less than .025% mercury content.

  * Corporate investigation of nationwide Zinc Air substitution
 ** Existing use of Low Mercury Alkaline in some applications
    normally powered by Mercury batteries
*** No telemetry monitors: Holter monitors only

there is a net savings in most cases. At least one hospital was able to purchase alternate batteries at the same cost. With a longer alternate battery life, this hospital was able to cut battery costs by more than 25% (based on the first 2 month's experience) before taking into account the additional avoided costs of waste management (3). This was the key in program adoption and continuation.

MONITORING

Although cost savings go far toward ensuring hospital adherence to these new waste management policies, county staff structured three procedures to reinforce and monitor the situation. Both the public and private sectors were involved.

First, private waste haulers who service area hospitals agreed to specifically notify their customers that mercury batteries were not acceptable in their regular trash containers. Customers were further informed that discovery of such disposal would result in substantial cost increases and/or termination of service. Second, stepped-up load inspections of hospital containers were initiated at the Broward resource recovery facilities soon after they began operation. This roughly coincided with the time when most hospitals had adopted new waste management practices. Ongoing inspections targeting hospital loads among others are part of operational plans at both resource recovery facilities and landfills.

Lastly, the Broward County Office of Natural Resource Protection agreed to perform battery use and waste management inspections at all hospitals as part of their annual hazardous materials licensing inspection. The effectiveness of these annual inspections was shown within a few weeks. An imminent scheduled inspection prompted a call from a hospital biomedical engineer to confirm that his battery use and management procedures would be acceptable. To date no deviation from acceptable waste management practices has been detected. However, monitoring will be ongoing.

CONCLUSIONS

When informed of battery waste management implications and options, Broward area hospitals were cooperative (and in some cases enthusiastically so) with county staff in improving the situation. Functioning as an information exchange resource with input from many hospital professionals, one county project coordinator was able to facilitate the diversion of nearly one ton of mercury per year from Broward's waste stream in just a few months. Costs to Broward County and the hospitals were minimal and, indeed, in most cases, cost savings were realized by the hospitals. This cooperative approach based upon information exchange will be helpful as Broward County expands its management efforts to other types of commercially generated wastes.

NOTES

1. Weight of one discharged Duracell TR146X 8.4 volt mercury battery as weighed on postal scale at Broward County Governmental Center Mailroom 2/20/91.

2. Duracell TR146X mercury battery contains 27% HgO according to 3/8/91 Telefax from George Wallis, Director of Environmental Affairs, Duracell, Needham, MA. HgO contains 92.6% mercury by weight according to George Riley, Director, Environmental Monitoring Division, Broward County Office of Natural Resources Protection, 4/9/91 telephone conversation.

3. E. Kurnia, Biomedical Engineer, Memorial Hospital of Hollywood, FL, 5/29/91 telephone conversation.

RECOVERY OF MERCURY D-009 AND U-151 WASTE FROM SOIL USING PROVEN PHYSICAL AND GRAVIMETRIC METHODS

Michael W. Chintis
GZA GeoEnvironmental, Inc.,/Hunter Mining Co.,
141 East Palm Lane
Phoenix, AZ 85004
USA
Tel: (602) 495-1833

INTRODUCTION/BACKGROUND

GZA GeoEnvironmental, Inc., in conjunction with Hunter Mining Co., (GZA/HM), has developed a viable, cost-effective, and practical process to recover elemental mercury from soil. Many techniques were investigated with most proving inefficient or impractical for field use. GZA/HM came to the conclusion that modifications and refinements of mining technology would produce results most compatible to US Environmental Protection Agency (EPA) standards and its philosophy of protecting human health and the environment. The technology developed removes/recovers in excess of 99.8% of the elemental mercury present in the soil.

In focusing on the removal of elemental mercury as the primary objective three important tasks have been accomplished: 1) the primary source of mercury mobility throughout the environment described in the EPA's Toxicological Profile for Mercury published in December 1989 (i.e., transformation from elemental to ionic and volatilization) can be eliminated; 2) any remaining residuals of mercury salts in the effluent process streams can then be cost- effectively treated or immobilized, if required; and 3) a valuable and reusable resource can be recovered for use as was originally intended.

The GZA/HM process uses only physical and gravimetric techniques to separate mercury from the spill matrixes and does not incorporate any thermal or chemical methods that could increase the possibility of creating new waste streams or vapor releases to the atmosphere.

PROCESS DESCRIPTION

Material Sizing

The first step, and arguably the most important, is to size the matrix containing the elemental mercury uniformly. For gravimetric systems to work properly with a high degree of efficiency, material entering the separation equipment must be of a uniform size in order to take full advantage of varying specific gravities. The material sizing process uses pressure washing and screening to produce the uniform matrix required to enter the separation section of the unit.

The proper mesh size screen was selected after tests demonstrated that washed material rejected was free of elemental mercury. Additionally, most of the mercury oxidation products passed through the screen as well and were not present in the discharge.

In summary, when soil containing elemental mercury is adequately washed and scrubbed, mercury in all its forms will pass through a properly-sized screen, thus greatly reducing the amount of material requiring further processing.

Separation of Mercury from Matrix

Numerous pieces of equipment were tested in determining which apparatus would most efficiently recover/remove elemental mercury from a soil matrix. The best device proved to be a dual rotating bowl mechanism followed in series by a cleanup concentrate process for the specific matrix to complete mercury separation from heavy sands. A description of the separation process follows.

The properly sized material containing the elemental mercury enters an apparatus consisting of two vessels operated in series. The vessels consist of dual rotating bowls inside a housing. The inner walls of the bowls are rubber or plastic spirals designed specifically to capture elemental mercury. Slurried mesh material is fed to the center of the bottom of the bowl. The heavier elemental mercury and insoluble mercury salts are caught in the lower riffles of the bowl and the lighter tails overflow the top of the bowl. The heavier material containing the mercury, mercury salts, and black sands is discharged from the bottom of the bowl. The elemental mercury is siphoned off and the remaining material is passed to the second stage for further separation of heavy ends.

This staged process consistently produces reduction in mercury concentrations exceeding 99.8% and can operate at ranges of 1/2 to 6 tons per hour. A typical demonstration test for this staged process cleaned 93.0% of the material volume to levels below 11 ppm total mercury concentration in a single pass (from an initial concentration of approximately 5000 ppm).

In summary, this demonstration succeeded in reducing the mercury concentrations in soil from 5000 ppm to 11 ppm in 93% of the soil volume.

EVALUATION OF EFFLUENT STREAMS

The GZA/HM process, by not incorporating any form of thermal vaporization or chemical reaction to clean soil, produces only four possible effluent streams. These streams are accounted for as follows:

Cleaned soil produced from two areas of operation: 1) the screen reject material which has been washed at the entry to the recovery process; and 2) tailings from the rotating bowls. Tailings from the concentrator stage can be reintroduced back into the rotating bowls. The cleaned soil exiting the process from screening and separation typically represents 93% of the total soil volume and consistently contains less than 15 ppm mercury.

Elemental mercury recovered from the concentration stage is returned to stock for use as was originally intended.

Heavy sands containing minute particles of elemental mercury plus mercuric oxides in a magnetite matrix are stockpiled. When operations at a site are complete the small volume of heavy sands/matrix containing residual mercury will require some further processing. Disposal and/or treatment options for this low-volume residual will depend on client and oversight agency agreement parameters.

Water is recycled during operations and since no chemicals are introduced to the system to solubilize mercury, a buildup of ionic concentration of mercury has not been observed and is not anticipated. This has been substantiated by sampling of water during demonstration testing.

QUALITY ASSURANCE/QUALITY CONTROL

Demonstration tests and treatability studies have been conducted with EPA QA/QC protocols and analytical results and mass balance reports are available upon request. Samples were taken to ensure representativeness of matrix and delivered to a certified environmental laboratory for analysis. Field and internal lab QA/QC protocols plus sample analyses were conducted with procedures consistent with EPA's procedures for verification of Best Demonstrated Available Technology (BDAT).

The tests/demonstrations were conducted at a reputable mining research and development company. Some QA/QC procedures used in gathering this data were modified from the guidelines presented in EPA Guidebook for Submission of Data for the Land Disposal Restriction (LDR) program for the following reasons:

Elemental mercury does not disperse evenly throughout a soil matrix; therefore, GZA/HM increased the quantity of the sample for total digestion analysis from 0.2 grams to as much as 10 grams. The increase in sample size will assure representativeness and negate the possibility of an uneven distribution of mercury residuals generating false positive data.

When tests were conducted using spiked matrix, accurate weighing of mercury inoculant was substituted for total mercury analysis in preparing the pre-test matrix and evaluating test efficiency.

SUMMARY

The GZA/HM process utilizes the high specific gravity of mercury and adapts basic mining techniques into a process capable of recovering 99.8% of elemental mercury from soil matrixes. Once a valuable resource has been recovered, any trace mercury residuals remaining in the soil discharge can be immobilized or be subjected to further reduction techniques (if the trace concentration levels exceed any oversight parameters).

This process is adaptive to many site variables such as concentration levels of mercury, soil types, presence of utilities, remoteness, and quantity of waste. A small mobile unit has been built and mounted on a 25-foot trailer pulled by a 3/4-ton truck. This unit is designed specifically for the Natural Gas Industry and is capable of cleaning 2 tons per hour.

This mercury recovery process was designed to comply with state/local health and environmental regulations. By using gravity separation in a water medium the chance of mercury vaporization has been virtually eliminated. Workers will only be subjected to handling high concentrations when siphoning the elemental mercury discharged from the spiral concentrator to storage flasks.

An added advantage to the gravity separation approach is that most of the equipment the process unit comprises is readily available in the mining community. Additionally, this equipment has been proven reliable through years of operation and can be assembled to handle large or small volumes of contaminated soil.

Using a process that does not employ thermal or chemical methods, GZA/HM has developed a patented process compatible with EPA goals established by the Resource Conservation and Recovery Act (RCRA) which consistently produces recovery rates exceeding 99.8%. This technology is capable of processing the soil volumes necessary to meet estimated LDR national capacities becoming effective in May 1992. Additionally, waste once destined for land disposal can now be processed on-site, eliminating the continuing liability and responsibility a generator faces when hazardous waste is placed in a landfill.

TREATMENT AND MERCURY RECOVERY FROM ELECTRICAL MANUFACTURING WASTES

H. H. Dewing and R. B. Schluter
US Bureau of Mines
Rolla Research Center
1300 N. Bishop Avenue, PO Box 280
Rolla, MO 65401
USA
Tel: (314) 364-3169

The US Bureau of Mines Rolla Research Center characterized mercury-containing waste and used a thermal desorption process to remove and recover the contained mercury. The wastes were generated by an electrical parts plant engaged in the assembly of mercury-containing switching devices and consisted of discarded Bakelite phenolic resins and paper insulating materials mixed with soil and other trash. The average mercury content of the materials was about 400 ppm. Numerous characterizations of the waste showed that the mercury was tightly adsorbed and could not be readily removed or concentrated by leaching or gravity separation techniques.

Both laboratory and rotary kiln thermal desorption tests were conducted and showed that mercury content of the wastes was reduced to less than 15 ppm in 2 h at 400 degrees C. Air flow through the retort improved thermal desorption efficiency while vacuum operation was of little benefit in lowering temperature requirements. Off-gases from decomposition of organic materials were burned in a high temperature afterburner. The off-gases were subsequently cooled in a heat exchanger to condense the water vapor, and finally, the mercury vapor was condensed and adsorbed from the off-gas by activated charcoal. Mercury recovery was over 99.99% of the desorbed mercury.

Thermal desorption processes have had wide application to many mercury-containing wastes, and historical experience in mercury mining has demonstrated the potential cost effectiveness.

DEVELOPMENT OF BDAT FOR THE THERMAL TREATMENT OF K106 AND CERTAIN D009 WASTES

Arthur E. Dungan
The Chlorine Institute, Inc.
2001 L Street, NW, Suite 506
Washington, DC 20036
USA
Tel: (202) 775-2790

INTRODUCTION

The Land Disposal Restrictions (LDR) for the Third Third Scheduled Wastes (55 FR 22520; June 1, 1990) prohibit the land disposal of certain wastes including K106 and D009 nonwastewaters in the high mercury subcategory beginning May 8, 1992. The final rule requires that such wastes be retorted/roasted prior to land disposal.

K106 wastes are listed wastes resulting from treatments of the effluent from the mercury cell chloralkali process. D009 are characteristic wastes exhibiting toxicity due to mercury. These wastes are produced in chloralkali manufacturing facilities using the mercury cell process. Seventeen facilities accounting for about 15% of the chlorine produced in the US use this technology.

Prior to the promulgation of the final rule pertaining to the Third Third Scheduled Wastes, the Chlorine Institute (the "Institute") commented to the Environmental Protection Agency (EPA) that the proposed Best Demonstrated Available Technology (BDAT) for the mercury cell process was, in fact, not demonstrated. The Institute and the various mercury cell chloralkali producers argued that the K106 and D009 wastes generated in the chloralkali process were different from the cinnabar ore processing that was the basis of the BDAT. Nevertheless, EPA finalized the rule based on this technology.

After the regulations were promulgated, the Institute and seven mercury cell chloralkali producers determined that the best course of action to follow was to attempt to develop the technology that could be used to treat the wastes.

In the summer of 1990, Hazen Research, Inc. was contacted to develop and demonstrate technology for thermal treatment of nonwastewaters containing mercury. The project consisted of two phases. Phase 1 included the characterization of representative wastes, establishment of the affected variables and completion of preliminary design and costs. Phase 2 of the project included the construction and operation of a pilot plant to demonstrate the thermal process. This work was begun in late 1990 and was completed in 1991.

The process objectives were as follows:

(1) Develop the technology to treat K106 and D009 process wastes that meet the LDR requirements: ash that is less than 260 ppm total mercury and less than 200 ppb Toxicity Characteristic Leaching Procedure (TCLP) extract mercury.

(2) Recover the metallic mercury.

(3) Obtain operating and design data for the engineering, construction, and operation of commercial plants for each participant.

(4) Meet the requirements of project's research, development and demonstration (RD&D) permit for emissions to the atmosphere and effluents to the local publicly owned treatment works (POTW).

PROCESS DESCRIPTION

The K106 nonwastewaters tested contained the following:

24 - 57%   Water
1 - 12%   Mercury, dry basis
0.4 - 15% Sulfur, dry basis
3 - 15%   Inorganic salts, primarily sodium chloride, dry basis

The bulk of the remainder was filteraid which, depending on the type used, could be carbon or diatomaceous earth.

The D009 nonwastewaters that were the primary focus of the testing were process wastes. These were either graphite or activated carbon used to make and purify the sodium hydroxide or sludges from the cell house sump. Mercury content of these wastes varied from less than 1% to more than 20%.

The wastes were first fed into a furnace (thermal processor) equipped with a two stage afterburner. The gas leaving the furnace was cooled through two stages of scrubbing and cooling using a combination of water and sodium hydroxide. A final stage of scrubbing and cooling in a venturi and separator vessel was employed. Metallic mercury was recovered from each stage of the scrubbing/cooling process. The trail gas exiting the final stage of the cooling was passed through sulfur impregnated carbon to remove residual mercury before being discharged to the atmosphere. The ash produced in the furnace was periodically removed. Analyses of the ash were taken to determine total mercury and TCLP mercury extract. The water collected from the various scrubbers/separators was collected in holding tanks. Prior to discharge to the POTW, it was treated in a system similar to that used in the mercury cell process to generate the K106 wastes. Ambient air checks of the area surrounding the process equipment were conducted to determine fugitive mercury emissions.

PILOT PLANT TEST RESULTS

1. Ash Levels - Levels were consistently below the EPA requirements ranging between 0.03 and 64 ppm total mercury. TCLP levels varied from less than 1 to 23 ppb.

2. Mercury Balance - Table 1 summarizes the overall mercury balance for the entire project. Individual balances on each of the test runs varied widely. The reason for the large variation is believed to be differences in the mercury content of the wastes fed to the furnace and relatively short running times. The mercury collected in the carbon columns and the effluent treatment system can be fed back into the furnace with the bulk of it recovered.

TABLE 1. OVERALL MERCURY DISTRIBUTION AND BREAKDOWN OF OUTPUT STREAMS

Overall Mercury Distribution

	Quantity, Pounds	%
Input Stream, Total	712	100
Output Stream, Total	705	99%

Breakdown of Output Streams

	Quantity, Pounds	%
Recovered Mercury	467	66.2
Mercury in Carbon Columns	210	29.7
Mercury in Effluent Treatment Solids	28	4.0
Mercury in Ash	0.04	0.06
Total	705	100

3. Mercury emissions to atmosphere through the stack were very low. Actual emissions were less than 0.003 lb/hr (less than 0.006% of mercury fed to the furnace.)

Ambient mercury levels were monitored throughout the project. In some instances mercury levels exceeded the OSHA limits mandating the need for respirators. Early in the process testing, the unit was shut down and modified to reduce fugitive mercury emissions, primarily from the furnace. Additional modifications will be made in the commercial units to reduce fugitive emissions.

It is expected that the commercial facilities will be able to achieve existing NESHAP regulations for mercury cell chloralkali facilities.

4. All tests were conducted in accordance with appropriate testing and sampling procedures and applicable quality assurance/quality control protocols.

ALTERNATE TECHNOLOGY

Thermal processing of certain mercury containing wastes has been practiced for many years through batch thermal processors (retorts). This technology has been limited to the processing of relatively high levels of mercury in the waste (typically in excess of 30%) and with small throughputs. Based on the historical data available, the Institute and the participating members believed that this batch technology could not be applied to high volume, low mercury content wastes. The newly developed technology can be scaled up or down depending on the throughput required.

SUMMARY

The project allowed for the successful development of the technology to treat K106 and certain D009 wastes in accord with the LDR requirements. Four of the participating companies have initiated construction of such facilities. These companies have been granted case-by-case extensions to the LDR to allow for continued land disposal of these wastes until May, 1993. While the startup date for the facilities varies for the different companies, all are working diligently to achieve a startup date by May, 1993.

Capital cost for such a facility can vary depending on many factors, such as size, location, required utilities, etc. It is believed that a facility to handle from 2 to 20 tons per day of waste would cost about $5 million. Raw materials consist primarily of fuel for heating the wastes to the required temperature along with sodium hydroxide for scrubbing. Staffing for long-term operations and maintenance have not been determined.

It has been reported in the press that one member company which is building a single facility to handle the wastes form two chloralkali plants expects to invest $6.5 million and employ 10 people in its operations. Based on past discharges of mercury to hazardous wastes landfills, mercury recovery should be about 25 tons per year.

FURTHER INFORMATION

This abstract is developed from documents submitted to EPA on a confidential business information basis in December, 1991 by the Institute in support of case-by-case extension applications of several member companies. Although the mechanism has not been finalized, it is the intention of the participants to share this technology to non-participants on a cost recovery basis.

The cost of the project was approximately $3.5 million. The technology is applicable to wastes generated from mercury cell chloralkali processes and may have application elsewhere. The Institute is prepared to let anyone who signs a secrecy agreement read the detailed report at the Institute's offices. Contact is Art Dungan (Tel: 202 775-2790).

ACKNOWLEDGMENT

The technology described was developed through a task group of the Chlorine Institute, Inc. The technology is owned by the seven participating companies. These include ASHTA Chemicals, Inc., BF Goodrich Chemical Corporation, Georgia Pacific Corporation, Olin Corporation, Pioneer Chlor Alkali Company, Inc., PPG Industries, Inc. and Vulcan Materials Company. These companies are applying for a patent for this technology. The project manager for the members was J. W. Hutchins of PPG. The technology was developed at Hazen Research, Inc., Golden, Colorado. Project manager for Hazen was C.W. Kenney.

MERCURY REMOVAL WITH IONAC ION EXCHANGE RESINS

F. X. McGarvey
Sybron Chemicals, Inc.,
Birmingham, NJ 08011
USA
Tel: (609) 893-1100

Ion exchange resins have proven to be useful in the removal of mercury from aqueous streams, particularly at low concentration levels (1 to10 ppb). The application of ion exchange resins requires an understanding of the chemistry of mercury as it occurs in the natural environment. Mercury has been used in the electrochemical industry as conductive liquor in the preparation of caustic. Mercury is also used in gold mining and may be associated with cyanide complexes. Mercury will also occur in water supplies contaminated with mercury as an industrial waste.

Ion exchange applications usually treat mercuric salts. For example, water supplies which contain chlorides will frequently find the mercuric complex $HgCl_3^-$ or $HgCl_4^=$. These compounds are quite stable and can be picked up on anion exchange resins.

$$M[HgCl_3^-] + Resin\ Cl \rightarrow Resin\ HgCl_3 + MCl$$
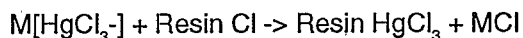
The anion exchange resin can be regenerated with strong acid solutions, but this is done with difficulty since the mercury salts are not highly ionized and have low conductivities in solution. Also mercury forms complexes with many organic compounds including carbon itself. One of the most difficult salts from the standpoint of the food chain is $Hg(CH3)2$, mercury dimethyl. Compounds of this type enter the food chain resulting in mercury accumulation in fish. Since these compounds are not ionized, they are difficult to remove by conventional ion exchange (1).

While conventional ion exchange resin will concentrate mercury complexes, these resins are not particularly selective for mercury ions. Resin containing the iminodiacetic acid group will pick up mercury selectively from calcium and magnesium. This type of resin can be helpful with cationic mercury. In conjunction with anion exchange resins, mercury can be reduced significantly in potable waters.

Another type of resin contains a S-H+ functionality on the aromatic ring of a styrene-divinylbenzene copolymer. This resin functions on the insolubility of sulfide compounds of mercury and forms almost irreversible linkage with mercury so long as oxidation of the sulfur group is prevented. Regeneration is possible with 20% sulfuric acid in cases where resin recycle is desired.

Other resins selective for mercury (2) are also under study. One promising resin is the macroporous glycidylmethacrylate- ethylenedimethacrylate type copolymer which has a selective group formed when the copolymer is contacted with ammonia

$$R\text{-}COOH_2CH\text{-}CH_2NH$$
$$|$$
$$OH$$
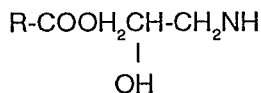
This resin has been shown to remove mercury from waste streams containing copper, cadmium, zinc, and other divalent cations. Regeneration can be achieved with nitric acid. While there several groups working on selective resin for mercury removal, none have shown the absolute selectivity of the -SH group. The sensitivity of this functional group for oxidation indicates that care must be taken if this resin can function in the field.

IONAC ION EXCHANGE RESIN STUDIES

Several studies are underway with Ionac ion exchange resins. These are summarized in following paragraphs.

Anion Exchange Resins

Ionac AFP-329 and Ionac ASB-1P have been used in southern New Jersey to treat a potable supply which contains mercury. Initial tests showed that mercury was present as the chloride complex and a field study has been underway for two years conducted by the State of New Jersey. This is an example of a potable water study using resins which are included in the FDA list of acceptable resins shown in CFR 173.25.

Thio Resin

Several studies have been underway with SR-4 to remove mercury from waste streams. One installation used this resin to remove mercury from battery wastes from an industrial plant. The mercury level was reduced from 30 ppb to less than 0.5 ppb. No regeneration was attempted.

SR-4 was used to remove mercury from a cyanide solution containing gold and silver. This was achieved without removal of gold and silver cyanide complexes which would have been absorbed with the mercury complex if conventional resin had been used (3).

Ionac SR-4 has been used to remove mercury from waste streams associated with mercury cell caustic wastes and this effort continues at various plants.

Iminodiacetate Resins

Where mercury occurs as a divalent cation, SR-5 can be used to selectively remove mercury in some cases. Copper and cobalt tend to compete effectively against mercury, but sufficient selectivity can be achieved to make additional tests of interest.

ECONOMICS OF MERCURY REMOVAL

Most toxic streams contain mercury in low concentration so that a selective resin can be used in an irreversible fashion with final disposal of the loaded resin in a hazardous waste site or in some type of oxidative chemical destruction where the mercury is held or recovered. The cost savings can be substantial as illustrated in the following example.

If mercury is present at 5 parts per billion (5 μg/L) level and must be reduced by 90% to 0.5 part per billion, Ionac SR-4 has a capacity of 0.7 equivalent per liter of resin:

Volume waste (5 μg/liter) = 0.7(201/2) grams per liter

$$\text{Volume} = \frac{0.7(100.5)}{4.5 \times 10^{-9}} = 15.6 \times 10^9 \text{ liters/liter resin}$$

It is extremely unlikely that an ion exchange bed would be able to treat 15 x 10^9 bed volumes without serious packing and general failure of the column. A value of 10,000 bed volumes may be achievable in cases where the waste is quite free of suspended solids. For this case a cubic foot of SR-4 values at $300/ft^3 could treat almost 40,000 gallons of waste and concentrate the waste into a cubic foot volume (7.5 gallons). The degree of concentration is more than 5000. Based on $100 to dispose of a liquor per 100 gallons ($1/gallon), the disposal of resin would be about $750 as compared to $40,000. Under these conditions resins can easily justify a single cycle.

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DEVELOPMENT OF BACTERIAL STRAINS FOR THE REMEDIATION OF MERCURIAL WASTES

Joanne M. Horn
Center for Environmental Diagnostics and Bioremediation
University of West Florida
11000 University Pkwy.
Pensacola, FL 32514
USA

Maren Brunke, W.-D. Deckwer, and K.N. Timmis
National Research Center for Biotechnology
Mascheroder Weg 1
3330 Braunschweig
Germany

INTRODUCTION

The biotoxicity of mercury (Hg) resides in the ability of charged forms of the metal to bind and inactivate enzymes. Organomercurial compounds also accumulate in higher organisms and cause systemic disease. While Hg(II) and Hg-containing compounds are highly toxic, they are still being anthropogenically mobilized into the biosphere at sufficient rates to create environmental hazards.

Since the total amount of extant Hg is finite and unchangeable, remediation of Hg pollution can only be aimed at altering its ionic form to a less toxic species and/or sequestering it, ideally in forms which can be recycled for further use.

An alternative remediation strategy currently being examined involves converting Hg(II) to the more inert, volatile elemental form [Hg(0)] by employing the mechanism of bacterial Hg resistance which relies on the reduction of Hg(II) to Hg(0) through the activity of a cytosolic mercuric reductase. Such bacterial reduction systems might be utilized for either on-site remedial situations, since volatilized Hg(0) is both less toxic and less bioavailable, or within contained bioreactors from which the reduced Hg(0) could potentially be recovered.

Specific bacterial mercury resistance (Hg^r) involves both the mercuric reductase and, since Hg(II) also inactivates membrane proteins, a Hg-specific transport system which protects the membrane and other cellular components by shuttling Hg from the cell surface to the intracellular mercuric reductase.

Narrow spectrum Hg^r confers resistance only to mercuric ions. Broad spectrum mercury resistance includes, in addition to the transport and reductase enzymes, an organomercurial lyase which protonolytically cleaves carbon-Hg bonds. The broad spectrum Hg^r systems, through the successive activities of the lyase and the reductase, additionally provide resistance to organomercurial compounds.

Both narrow and broad spectrum Hg^r mechanisms have been found in a wide range of bacteria. Hg^r structural genes are encoded in a single operon that is primarily regulated by the *merR* gene product, which is itself transcribed contiguous to, but in the opposite direction from, the *merTPABD* operon. The *merT* and *merP* gene products are involved in Hg(II) uptake and transport, *merA* specifies the mercuric reductase, and *merB* encodes the organomercurial lyase. *merD*, the most promoter-distal gene identified, has been associated with a transcriptional coregulatory function.

We report here the generation and selection of *Pseudomonas putida* strains with heightened mercurial detoxification properties by constitutive hyperexpression of the *merTPAB* genes. We have also genetically combined the ability to reduce Hg(II) at increased rates under conditions of high concentration with a benzene degradative pathway. Derivative strains are thus able to dissociate the chemically dissimilar components of an organomercurial compound, phenylmercuric acetate (PMA), into its metal and aromatic elements, and separately detoxify each. While these strains were originally conceived for intended use in contained bioreactors for treatment of industrial waste streams, they have attributes which may contribute to on-site treatment of Hg-containing pollutants in contaminated soils and waters as well.

This project was conducted under the auspices of the Biochemical Engineering and Microbiology Divisions of the National Center for Biotechnology, Braunschweig, Germany, where process development utilizing these strains is currently in progress.

PROCESS DESCRIPTION

Constitutive overproduction of proteins conferring detoxification of and resistance to organomercurials was accomplished by random mutagenesis of two strains of P. putida with a mini-transposon containing the merTPAB genes. The mini-transposon encodes the organomercurial resistance determinants flanked by the inverted repeats of Tn5, which have been abbreviated to 19 basepairs. The transposase gene (tnp') is located externally with respect to the Tn5 transposing element, and merR and merD, specifying mer regulatory proteins were eliminated from the construct (1).

Since mini Tn5-merTPAB insertions into recipient chromosomes were assumed to be generally random with respect to target locii, it was reasoned that insertions downstream of proximal host promoters could result in increased mer expression, with a coincident rise in Hg(II) and PMA resistance (PMA'). Thus, subsequent selection for mini-Tn5 merTPAB-mutagenized P. putida derivatives which demonstrated increased resistance to organomercurials was undertaken. Isolates were selected which showed up to 86% increase in Hg^r over a control P. putida strain harboring a single copy of a wildtype narrow range mercurial resistance operon (encoded by Tn501) under control of its own promoter. Resistance to organomercurials was also increased: some derivatives demonstrated growth in up to 80µg/ml PMA, while 10µg/ml is normally used as the minimal inhibitory concentration of this compound.

Since the enzymatic activity of the merA gene product, mercuric reductase, is assayable in crude cell extracts, it was used as a measure of mer gene expression. Up to a four fold increase in mercuric reductase activity (above the Tn501-containing control strain) was found in given isolates. Furthermore, the expression of merA, in contrast to the activity of wildtype mer operons, was found to be constitutive; the addition of Hg(II) was not required for mini-Tn5-encoded merTPAB expression.

Elevated merTPAB expression corresponded with increases in Hg^r and PMA^r. A statistically significant correlation between mer expression, as indicated by mercuric reductase activities, and resistance to (organo)mercurials was demonstrated. These findings were in sharp contrast to previous studies which have attempted to produce the same results in Escherichia coli. It has been shown that as mer expression increases as a result of heightened gene dosage in E. coli, but these increases are not manifested in a concomitant rise in Hg^r of whole cells; rather, increased expression is cryptic (2-4).

It has been shown that Hg^r in E. coli is limited by Hg(II) transport, and it was postulated that a limitation in the availability of membrane insertion sites for the MerT transport protein may account for this observed lack of correlation between mer expression and resistance (4). The contrasting correlative relationship observed in P. putida not only allowed selection of overproducers, but contributes towards their potential utility in mercurial treatment schemes (see following).

Growth rates of P. putida merTPAB-mutagenized derivatives were determined to assess the effect of merTPAB hyperexpression on culture growth rates. While a P. putida strain containing a wildtype inducible narrow spectrum mer operon was unable to grow when initially exposed to toxic concentrations of HgCl$_2$, the P. putida merTPAB-hyperexpressing isolates showed no effects of Hg(II) on culture growth, even when inoculated into media containing Hg(II) at normally toxic concentrations.

One P. putida host strain mutagenized with mini-Tn5 merTPAB, P. putida F1, contains a chromsomally-encoded pathway for the complete catabolism of benzene and toluene (5). P. putida F1 is capable of using these compounds as a sole source of carbon and energy, resulting in their total mineralization. Since the mini-Tn5 merTPAB-containing F1 derivatives encode the organomercurial lyase they are presumably capable of cleaving the Hg(II) moiety from PMA, and using the produced benzene as an energy source. When tested for this ability we found these derivatives were indeed able to grow on minimal salts media with PMA as a sole carbon source. By coupling Hg(II) cleavage and reduction with benzene degradation, a novel catabolic pathway was generated.

FEED STREAM CHARACTERISTICS

The described *P. putida merTPAB* hyperproducing strains are highly resistant to (organo)mercurials, demonstrate increased rates of Hg(II) reduction, and constitutively express these capabilities. Thus they can survive in and detoxify highly contaminated mercurial-containing wastes. This may be a virtue in dewatered effluents for example, or for potential on-site remediation efforts.

Cell death due to toxic effects of high Hg(II) concentrations before expression can be fully induced, which was observed in *P. putida* strains containing the wildtype Hg^r system, is prevented. Likewise, in mercurial wastes which are too low in concentration to induce the reducing capability of the wildtype operon, these isolates would also prove useful, as their reductive capability is completely independent of Hg concentration.

Combining the overexpression of Hg-C cleavage and reduction with benzene/toluene catabolism allows the resulting strain to detoxify Hg and benzene components, both chemically dissimilar moieties of PMA, separately by different pathways present in the same recombinant organism. Mixtures of organomercuric compounds could potentially be treated, as the lyase has wide substrate specificity and can cleave Hg from a variety of organomercurials; the reductase would then act on the produced Hg(II). Since this process is enzymatically based it specifically targets mercuric salts and organomercurial compounds.

When benzene or toluene are present, either as copollutants or as the organic component of an organomercurial, they would be mineralized completely. Since we have shown that these activities are sufficiently high to support growth on PMA, it may be possible to drive this system without requiring the addition of exogenous nutrients. Furthermore, since benzene is totally catabolized, there is no possibility of producing toxic aromatic endproducts which might hinder further cellular metabolism.

PRODUCT CHARACTERISTICS AND USE

Initial process development of bioreactors utilizing Hg(II)-reducing bacteria has shown that reduced Hg(0) can be retained within a fixed bed bioreactor. This offers the possibility of reclaiming Hg(II) removed from reactor input in a concentrated, significantly less toxic and potentially reutilizable form.

ENVIRONMENTAL ADVANTAGES

Currently available technologies for Hg removal involve either ion exchange or adsorptive matrixes. These methods have the disadvantages of being non-selective, they can generate a secondary solid waste, are costly, and since Hg is non-selectively and/or permanently bound, it cannot be recovered for further recycling. Since the biotransformative system described here however is enzymatically driven, it is selective. Furthermore it does not utilize expensive resins, and the reduced Hg(0) can potentially be recovered from closed bioreactor systems.

Since these bacterial strains are derivatives of naturally-occurring soil organisms, the risks of deliberately releasing them for on-site bioremediation may be significantly reduced. They also have the ability to survive under normal environmental conditions. Their complement of Hg reducing genes are stably inserted into the chromosome and by themselves, have no capability to transfer to other locii within the same organism or to the native biota.

The product of this system, Hg(0)l, is relatively inert in comparison to its substrate, and thus less toxic to biological organisms. Hg(0) is also less bioavailable, since under a wide variety of conditions it is volatile, or at least insoluble. The bioreduction of mercury therefore produces a form of the metal which has significantly less impact on the biosphere.

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THE RECOVERY OF MERCURY FROM MINERAL EXTRACTION RESIDUES USING HYDROMETALLURGICAL TECHNIQUES

Robert G. Robins and Lakshman Jayaweera
HydroMet Corporation Limited
31-45 Smith Street
Marrickville NSW 2240
Australia
Tel: 61 2 517 1188
Fax: 61 2 519 9468

HydroMet Corporation Limited commenced its business in Sydney, Australia in 1987. It has since become a public company listed on the Sydney Stock Exchange. In April 1992 a new share issue to raise capital for plant development was oversubscribed and the company will proceed to the construction of a treatment plant at Newcastle and additional plant at Port Kembla (both in New South Wales, Australia).

The company's principal activities are in the industrial waste management and resource recovery sectors of the mineral processing industry. Its activities include the processing of industrial smelter residues and the manufacture of a range of metal and chemical products from those residues. Presently the company is the largest producer of high grade selenium in the southern hemisphere. HydroMet undertakes general hydrometallurgical research and development specialising in contaminated waste treatment.

PROCESS DEVELOPMENT

The basis of process development for mercury removal and recovery from mineral concentrates and residues is thermodynamic modelling of the system, taking into account the speciation of mercury in aqueous solution and the solubilities of both mercury(I) and mercury(II) compounds. Computer modelling techniques involve the use of a number of well-known codes such as MINTEQA2 but also an in-house program, DIASTAB, for plotting stability diagrams. Some of the diagrams that have been generated with DIASTAB will be used to illustrate the stabilities of mercury species in relation to recovery processes.

The selective leaching of mercury from some concentrates and solid residues can be accomplished by the formation of a range of soluble mercury(II) species that can be obtained by complexation with certain reagent ligands (such as chloride, bromide, chlorobromide, cyanide, bromocyanide, ammonium, acetate, citrate, EDTA, etc.). The potential effectiveness of these reagents is illustrated by their effect on the solubility of mercuric oxide.

The removal of mercury from hydrometallurgical solutions has been accomplished by the unit processes of precipitation, ion exchange, solvent extraction, adsorption, membrane diffusion, cementation, electrolysis, precipitate and ion flotation, and using biological methods. The most common process is the precipitation of an insoluble mercury(I) or mercury(II) compound (such as oxide, carbonate, sulfide, sulfite, sulfate, phosphate, basic sulfate, iodate, and several organic mercury(I) compounds). The relative solubility of some of these compounds will be illustrated with stability diagrams.

HydroMet has been involved in developing a number of commercial (or tentatively commercial) processes for the removal and recovery of mercury from mineral concentrates and solid residues. The mercury end-product in most cases has been a high-grade mercury concentrate that is sold on the international market. Some of the treatment processes that have been developed and some of the processes investigated are described briefly in following paragraphs.

SELECTIVE LEACHING OF SULFIDE CONCENTRATES

The presence of mercury in sulfide concentrates causes problems in most cases and results in commercial penalties. In some concentrates the mercury exists as a separate simple mineral such as

cinnabar and can often be selectively dissolved. HydroMet has found that an acidic (HCl) chlorobromide leach with a hypochlorite-bromine oxidant was extremely effective in the case of one particular Australian complex sulfide concentrate. Initial mercury concentrations as high as 6 g/kg, in one particular sample, could be reduced to less than 5 mg/kg in the first stage. A commercial process has been developed for this concentrate in which the mercury is recovered from the leach solution as a mercury(I) sulfite precipitate.

Many variations of the mercury sulfide/halide leach process have been investigated by HydroMet since most processes have been concentrate-specific. In the case of more complex mercury sulfide impurity minerals, which often contain arsenic, antimony, bismuth, thallium, selenium etc., more complex leach procedures have been adopted in laboratory investigations, but mercury recovery in those cases was more difficult.

A more conventional leach process for cinnabar is hypochlorite leaching (sometimes electrolytically assisted) followed by either carbon adsorption or zinc cementation to yield a Zn-Hg amalgam.

CEMENTATION OF MERCURY

The recovery of elemental mercury from complex leach solutions with iron, zinc, and aluminium has been investigated with a view to several different specific applications. Some of these will be mentioned.

RECOVERY OF MERCURY FROM GOLD-CYANIDE SOLUTIONS

Mercury often occurs in precious metal bearing minerals and forms soluble cyanide complexes during a cyanide leach process. The mercury is then finally deposited on the adsorption carbon, on the electrolysis cell cathodes and in the tailings pond. In all cases there are further problems.

A number of ion exchange resins (including Duolite A-7, Ionac A-305, and Schering TN02327) have been investigated for removing both the mercury and gold as cyanide complexes from the leach solutions. Gold and mercury can be selectively eluted but not with a complete separation. The ion-exchange process appears to have an application in some Australian situations.

SELECTIVE PRECIPITATION OF MERCURY SULFIDE

Mercury has been selectively precipitated with thioacetamide to yield sulfide from a copper-mercury solution obtained by sulfuric acid leaching of a hydrometallurgical process residue. Mercury sulfide is insoluble over a broad range of pH but forms sulfide complexes with sulfide and bisulfide ions which result in a small degree of solubility in neutral-to-alkaline solutions. Thioacetamide will quickly precipitate mercury sulfide from a sulfate solution at a pH of about 2 so that it can be removed by filtration before significant copper is also precipitated.

Thioacetamide and thiourea are useful sulfide precipitating reagents at low pH since the generation of hydrogen sulfide, as would be obtained with sodium sulfide or bisulfide solutions, is minimal.

TREATMENT OF MERCURY-SULFUR RESIDUES

Sulfuric acid is often produced from SO_2 gas generated by roasting sulfide concentrates which contain trace levels of mercury. The roaster gas is contaminated with mercury and this is usually partly removed by weak acid scrubbers and mist Cottrells. The wash liquor from these units can then be treated to remove the dissolved mercury by cementation with aluminium metal pellets to produce a solids residue which is predominantly elemental mercury and sulfur in strong physical association (about 15% Hg and 70% S, with Pb and SiO_2 among other constituents).

This residue is treated in a HydroMet-designed plant to upgrade the mercury by leaching the sulfur with sulfite solution and then recovering a high-grade elemental sulfur. The mercury residue can then be retorted to produce elemental mercury that is converted to a range of chemicals.

RECOVERY OF MERCURY AND SELENIUM FROM ROASTER GAS

Another process for removing mercury from roaster gases is a sulfatization procedure similar to that adopted at the Outokumpu zinc plant at Kokkola in Finland in 1970. After dust removal from the mercury bearing off-gases, they are contacted with a recirculating 85 to 90% sulfuric acid in a sulfatizing tower and then in a weak acid scrubber to remove chloride which is in the form of HCl gas and $HgCl_2$ gas. When selenium-bearing concentrates are treated in this way the product from the sulfatizing unit contains selenium. This product is washed to remove the soluble salts leaving a complex mercury-selenium precipitate which can be represented by the formula:

$HgSO_4.xHg(0,S,Se,Te)$.
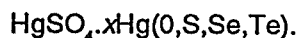
The HydroMet process for recovering both mercury and selenium from this residue involves a controlled potential sulfite-chloride leach procedure in which mercury can be precipitated as Hg_2SO_3 and selenium recovered as the element.

ETHYLENE LEACHING

HydroMet is currently developing a process in which ethylene gas is the reagent used to form a strong complex with mercury(II). The process is operated at a gas pressure of 4 atmospheres and after the leach procedure HgO can be precipitated by releasing pressure.

HIGH VACUUM MERCURY RETORT RECOVERY STILL FOR PROCESSING EPA D-009 HAZARDOUS WASTE

Bruce Lawrence
Bethlehem Apparatus Company, Inc.
890 Front Street
Hellertown, PA 18055
USA
Tel: (215) 838-7034

INTRODUCTION

Bethlehem Apparatus Company developed a continuous-feed vacuum triple distillation process for mercury in 1955. Since then, high purity instrument grade triple distilled mercury has been sold to industrial, institutional, and educational accounts principally in the US and more recently to several foreign accounts. In the early 1970s Bethlehem developed a mercury retort process for the recycling of fever and industrial thermometers. This process has gone through a variety of changes over the past 15 years and now is a relatively high-vacuum system that can handle a wide variety of mercury-bearing waste products.

PROCESS DESCRIPTION

Mercury-bearing materials are placed into the retort either in a 55-gallon steel drum or on trays. Larger materials can be placed directly into the retort without the support of a container. The retort is a bell type unit that is hydraulically raised and lowered. Once the materials are loaded onto the stationary base, the top bell unit is lowered and fastened. The joining members of the retort are sealed with a water cooled gasket. Once sealed, a vacuum is drawn down to approximately 25 inches mercury column. Condensers, water traps, and particle traps are located between the retort and the vacuum pump.

Inside the retort are electrical radiant heaters that raise the inside temperatures to 1250 degrees F. Mercury is vaporized at these temperatures and directed to the condenser where the saturated air stream of mercury vapor is condensed because of the water cooled jackets. Condensed mercury is allowed to spill into a reservoir for transfer to our triple distillation process.

Water vapor or dirt particles that are carried with the mercury vapor pass through the mercury condenser and are subsequently trapped in chambers between the vacuum pump and the condenser. If there are large amounts of water in the material processed, then water will spill into a trap located directly on the vacuum pump.

Exhaust air from the vacuum pumps is drawn through a series of treated activated charcoal absorption units to remove mercury vapor, chlorine and acid fumes, and odors. The final exhaust air is vented directly into the condenser room where it can be readily measured from mercury vapor content. Since the exhaust air is vented into a work area, the mercury vapor levels are kept to below .05 milligrams per cubic meter (current OSHA standard). (See Figure 1.)

Major process streams include mercury batteries, thermometers, mercury switches (glass and metal), quartz lamps, thermocouples, ignitron tubes, fluorescent lamps, and absorption-activated charcoal. Currently aqueous solutions cannot be handled since a large proportion of the mercury salts are carried over in the distillation process. Materials like mercury chloride also cannot be handled since the system is predominantly stainless steel.

Major equipment characteristics include:

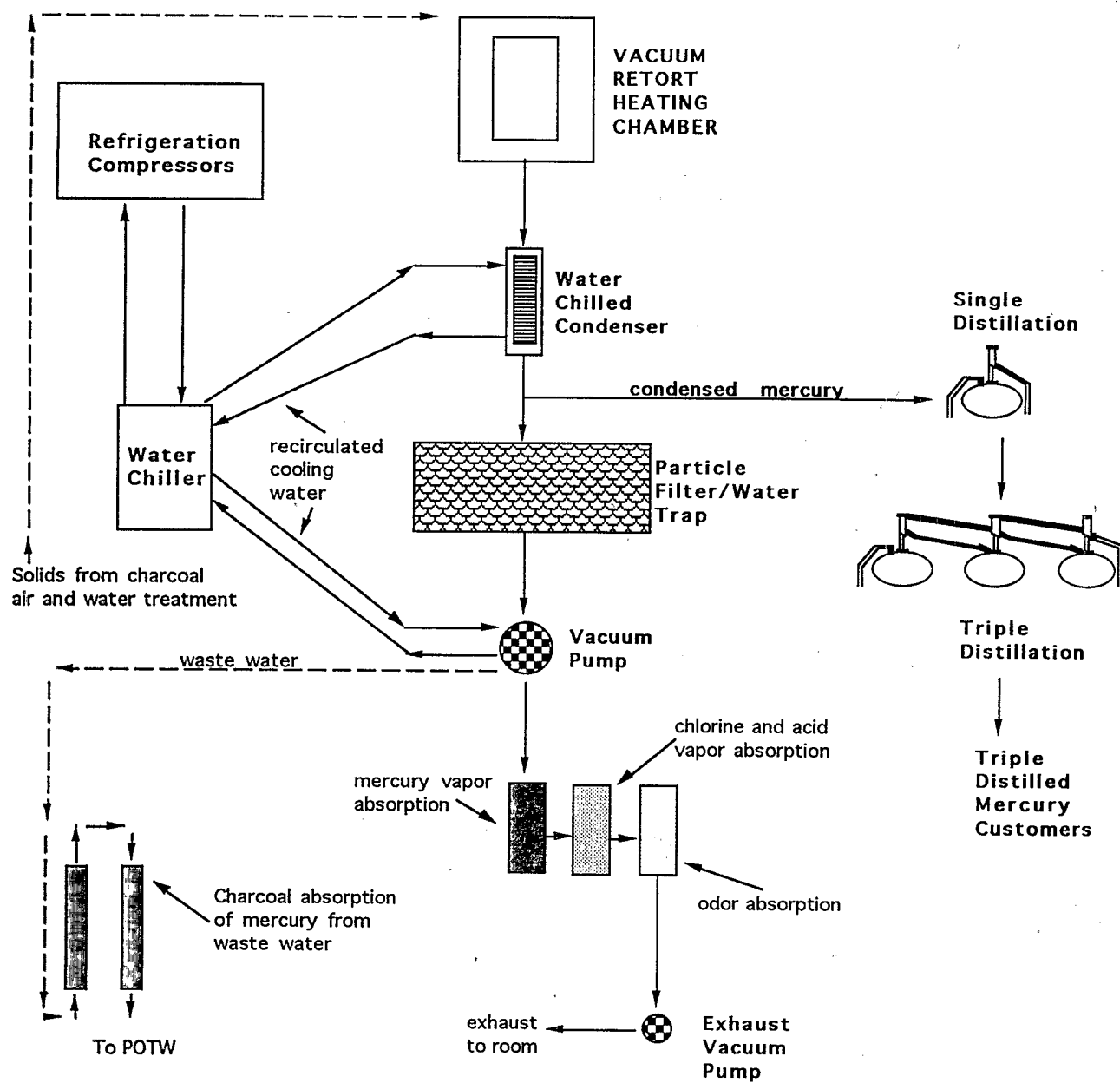A stainless steel chamber capable of holding a 29-inch mercury column vacuum at 1,350 degrees temperature

Figure 1. Mercury vacuum retort system.

A stainless steel connection from the heated vacuum chamber to the water cooled stainless steel condenser

A stainless steel condenser with independent waste connections for water cooling flow

Water pump to transfer water through condenser and return to chilled water source

Chilled water source including independent pumps, compressor, and temperature controllers

Filter media to trap dirt particles and retain condensed water

Vacuum pump capable of pulling 28-inch mercury column

Water cooling attachment to vacuum pump connected to independent chilled water supply

Activated charcoal media to absorb mercury vapor, chlorine or acid fumes, and odors

FEED STREAM CHARACTERISTICS

Typical feed stream characteristics include standard metal and glass materials. Most plastics can be processed; however, polyvinylchloride is kept to a minimum because of the chlorine content. Other halogen materials are also kept to a minimum. The only metals rejected are lithium, arsenic, and thallium. Quartz glass is accepted; however, it must be crushed if the mercury is contained inside a hermetically sealed unit.

Dirt, soils, and sludge-like material can be processed as long as there is not a high degree (over 40%) of water content. If mercury is contained in an aqueous solution then it must be filtered or precipitated into a fairly solid form before the material can be retort processed. If feed streams have a high proportion of water then the water carries a large proportion of the solids during distillation. The solutions could be run at lower temperatures to distill off the water but this takes a long time and causes problems in the distillate collection systems.

Radioactive materials are not accepted, nor are explosives, acids, and alkaline materials. Due to regulatory restraints we can not process any materials from wastewater treatment processes or any listed wastes with K, U, or P codes. We also do not handle any organomercurials.

Our system is a batch-feed process that handles 55-gallon drum volumes of material for each batch. If a feed stream is a large quantity of low mercury concentration (less than 5%) we would prefer the generator concentrate the mercury into something like charcoal filter media where the mercury levels are much higher.

PRODUCT USE

All mercury recovered from the retort process is pumped to our scrap mercury processing system. Here the mercury is pumped into a single distillation unit that subsequently feeds into our continuous-feed vacuum triple distillation units. The distilled mercury is then packaged and sold to industrial accounts for use in items like fluorescent lighting, dental amalgams, and mercury switches.

Scrap metals that are recovered from the mercury retorts are sold to scrap metal recycling organizations. We have recycled steel, aluminum, brass, copper, nickel/cadmium, lead, and zinc in this manner.

Oil is sometimes generated from the condensation of certain types of plastics that are run through the retort. In these cases the oil is mixed with our vacuum pump waste oil, which is filtered and run through mercury absorption activated charcoal. The cleaned oil is sent off-site for fuel blending.

RESIDUAL CHARACTERISTICS

There are seven types of residual materials from the retort process:

Mercury - triple distilled and sold, approximately 25 tons a year.

Glass, dirt, and other residuals (refer to Table 1) - sent to industrial landfill for non-hazardous waste, approximately 20 tons a year.

Metals sent to scrap metal recycling centers, approximately 20 tons per year.

Water, which is pH balanced, filtered, and treated in activated charcoal for mercury removal. Processed water is than sent to local sewage treatment plant. Current amounts average 20 to 50 gallons per day.

Oil from the retort and vacuum pumps. Filtered, treated, and fuel blended. 50 to 100 gallons per year.

Solids from the charcoal absorption and waste water treatment. Returned to retort for mercury removal.

Residues from still bottoms that contain low-level mercury with high levels of lead, cadmium, and silver. This is sent off-site for treatment and disposal in hazardous waste landfills. Annual quantity is approximately 1/4 ton.

TABLE 1. TOTAL MERCURY AND TCLP TEST RESULTS ON RESIDUAL MATERIALS THAT WERE PROCESSED IN THE BETHLEHEM VACUUM RETORT SYSTEM (1)

SAMPLE	TOTAL MERCURY MG/KG	TCLP EXTRACTION MG/L
Mercury Capillary Tubes	4.47	.068
Switches, Metal	30.2	.0058
Charcoal, activated	1.13	<0.01
Condenser Muds	9.2	.001
Plastic Relays	65	.0025
Tyvek &, Rubber Gloves	.57	<0.001
Switches, glass	2	.0002
Zinc air cells	1.72	.0003

ENVIRONMENTAL ADVANTAGES

Bethlehem's high-vacuum retort system offers the greatest environmental advantage over other systems because of the very low air emissions. Since our exhaust air is low in volume (approximately 1 cubic foot per minute per retort) we can readily scrub all the mercury from the air prior to emission. While this can theoretically be done with larger-volume air systems, the amount of scrubbing material required is much greater. In addition there is virtually no fugitive air emission from the outside of the retort. Low-vacuum systems will give off high levels of mercury vapor which causes a work environment hazard as well as emission problems.

FACILITY DESCRIPTION

Bethlehem Apparatus Company is a recycling facility for characteristic D009 mercury. We have seven retort recovery furnaces operational, with four more updated units under construction. Bethlehem will need to use 1 of the 11 retorts to process its own material. The remaining 10 units are available for processing materials from outside generators. Each retort unit can process 35 tons of material per year. Since the process does not require permitting, we can increase our capacity to 22 retort units in our existing facility.

REFERENCE

1. All analytical data performed by Benchmark Analytics, Hellertown, PA 18055

NON-THERMAL PROCESSING OF K106 MERCURY MUD

Michael Rockandel
Innochem Engineering Ltd.
#850 -1441 Creekside Dr.
Vancouver, BC
Canada V6J4V3
Tel: (604) 736-3381
Fax: (604) 736-3110

INTRODUCTION (1, 2)

Electrolytic mercury cell chlorine producers use a sulfidation technique in wastewater treatment to achieve Department of Energy (DOE) standards for water disposal. The sulfide treatment process generates an Environmental Protection Agency (EPA) designated K106 mud which is classified as a hazardous high mercury subcategory waste. The K106 mud was banned from landfilling on May 8, 1991. Industry has continued to dispose of the material to landfill under a 2-year national capacity variance.

In the "Regulations on Land Disposal Restrictions" (40CFR 268.41) the EPA has designated retorting as the Best Demonstrated Available Technology (BDAT) and the standard treatment technology for K106 mud. The EPA recognized the potential deleterious impact upon retorting of chloride salts in the K106 mud and identified the possibility of pretreating prior to retorting. On April 16, 1992 the EPA granted permission to Georgia-Pacific to utilize the Innochem non-thermal treatment process to treat their K106 mud generating a low mercury subcategory disposable waste and a high mercury subcategory concentrate requiring thermal processing.

Innochem Engineering has developed a hydrometallurgical process for the treatment of K106 mercury contaminated wastes. The process can achieve a measure of performance equivalent to that offered by retorting. The process offers advantages over the retorting alternative including: no atmospheric emission potential, operator familiarity, continuous operation, and low capital cost.

The process has been tested in the laboratory and in a continuous mini-plant. The test work was conducted at the Montana College of Metallurgy, Science and Technology in Butte, Montana under the guidance of L. Twidwell. Chemical analysis of the treated muds and extracts was performed at certified state laboratories. Muds from three different chloralkali plants, a decommissioned chloralkali plant, and elemental mercury contaminated soils have been tested.

A commercial plant is being designed for Georgia-Pacific in Bellingham, Washington. The plant will have a capacity of about 200 tons/year of K106 mud and is scheduled for startup in the fall of this year.

TEST PROGRAM

The mercury content of the K106 solids can vary from under 1% to near 20%. The typical mercury content however is 1 to 5%. The mercury is in various forms including: mercurous and mercuric chlorides, sulphide, elemental mercury, and species adsorbed on clay and activated carbon components. Total mercury extraction is favoured by a combination of both acidification and oxidation. The on-site abundance of inexpensive sodium hypochlorite and drying acid (sulfuric acid) made these the logical reagents. A review of the available literature and simulation of the chemistry with Eh-pH predominance diagrams streamlined the hunt for the optimum process parameters.

Several alternatives were considered for recovery of mercury from the leach solution. Low cost, simplicity of application, low toxicity, and ease of removal from solution made iron cementation the preferred route.

An extensive test program was undertaken comprising both laboratory investigation and continuous pilot confirmation. Several leaching variables were examined with the key ones being: pH, Oxidation Reduction Potential (ORP), temperature, type of acid, residue washing, and contact time. Cementation variables explored were: pH, retention time, type of iron, and contactor design.

The program successfully developed a treatment technology for K106 mud. The residue analysis was typically 60 to 100 ppm total mercury with Toxicity Characteristic Leaching Procedure (TCLP) <0.025 mg/L. The key test findings are summarized below:

A two-stage leach is preferred.

Leaching kinetics are very fast.

Sodium hypochlorite must be added well in excess of stoichiometric levels to be effective.

Elevated chloride tenor (10%) is essential.

Moderate temperature elevation (50 degrees C) is beneficial.

There is no performance advantage of hydrochloric versus sulfuric acid.

Residue washing is critical. A brine wash is required at high mercury levels.

To achieve the very low mandated TCLP levels (<.025 mg/L), stabilization of the residue with sulfide is preferred.

Cementation is best performed in a rotating contactor.

Inexpensive ground steel scrap is an effective cementation media.

Optimum cementation pH is in the range of 2 to 4.

PROCESS DESCRIPTION

The Georgia-Pacific plant in Bellingham, Washington will employ the Innochem leach technology. Significant variation has been observed in the composition of the muds tested which could result in modification of some of the leach parameters. The following description which is primarily directed at the Georgia- Pacific mud should be considered a process generalization.

Currently at the Georgia-Pacific facility, wastewater consisting of runoff, spills, and brine purges is sulfidized at ambient temperature at a pH near 5. The low percent solids sulfidization product is clarified in Adams Tube Filters yielding a water effluent which achieves DOE disposal guidelines. The backflushed solids are thickened and filtered on a rotary drum filter. The cake is disposed of in restricted landfill (K106 mud).

The wastewater treatment process will be modified to include a clarifying thickener between the sulfidation reactor and the Adams Filter. The reduced solids loading feeding the Adams filters will substantially increase the operating cycle and life of the filter tubes while reducing the usage of filteraid. The impact upon waste generation could be significant with current K106 mud containing 60 to 80% by weight filteraid. The thickened solids are delivered to the treatment process at 10 to 20% by weight solids.

The first stage leach conducted at a pH of 5 to 6 extracts 98.5% of the mercury from the K106 mud (30,000 ppm Hg dry basis) producing a residue of about 300 ppm mercury. Sodium hypochlorite is proportioned to the incoming mud flow and is typically 70 to 100 #/DT of K106 mud. The leach product is then transferred to the first of two vertical wash towers (thickeners). The overflow solution is transferred to cementation while the washed and thickened residue is pumped to the second leach.

The second leach is aggressive with pH = 2 to 3. Sodium hypochlorite is added at 20 #/DT of initial K106 mud. The second leach reduces the mercury to under 100 ppm, increasing the recovery to 99.8%. The second leach product is washed in the second vertical washing tower using either plant waste brine or

cementation product solution. The tower overflow solution is used as a washing fluid in the first wash tower. The underflow will be dewatered on an existing conventional rotary vacuum filter. At Georgia-Pacific the filter cake will be repulped and refiltered with the K071 brine mud prior to disposal. The residue designated as a K106 and K071 low mercury subcategory waste will be disposed of in a restricted landfill.

The first wash tower overflow containing 1,000 to 2,000 mg/L mercury flows to the cementation step. The pH is reduced to the range of 2 to 4 prior to flowing into the rotary contactor. Mercury cements onto the surface of the iron and reduces to <1 mg/L in under 30 minutes of contact time. Iron dissolves to produce about 2,000 mg/L ferrous ions. The cementation solution can be oxidized with subsequent iron removal and be recycled to the second washing thickener or alternatively can be wasted to the sulphide treatment step. The soft mercury amalgam formed on the surface of the iron is attrited by the mill's tumbling action and overflows the contactor.

The cement at about 40 to 50% mercury is dewatered and washed on a filter press prior to packaging in polyethylene drums. The cementation product containing 99.8% of the starting mercury represents about 7.5% of the starting material weight. The cement impurities are essentially iron and its alloying agents. The cement is an ideal feedstock for thermal refining and will be custom refined.

FEED STREAM CHARACTERISTICS

The composition of K106 wastewater treatment mud can vary substantially depending upon the flexibility built into the chloralkali plant, the quality of the feed sodium chloride, and the plant's operating status. The K106 mud can be contaminated with soil, carbon filter backflush material, brine, mud, and floor spills. Several K106 muds have been examined by SEM-EDAX. The range of analysis is shown in Table 1.

TABLE 1. ANALYSIS OF K106 MUD (DRY BASIS)

ELEMENT	RANGE OF ANALYSIS (%)	TYPICAL ANALYSIS (%)
S	0.7 - 2.8	2.7
Fe	0.5 - 5.7	2
Si	16 - 40	37
Mg	0.0 - 24.4	2
Cl	1.0 - 14.0	1
Ca	0.1 - 11.0	4
Na	1.0 - 7.6	2
Al	1.7 - 4.2	2
K	0.2 - 0.5	0.3

The mercury can be present in various forms but mercuric sulphide is predominant. Other forms of mercury which are believed to be present include: mercuric and mercurous chloride, elemental mercury, and species adsorbed on clay and activated carbon particles. The analysis of mercury can again vary dramatically. Waste high in activated carbon can contain up to 20% mercury. The analysis of the materials examined in this study is shown in Table 2.

The sulfide precipitate is very fine and is typically under 5 microns in size. The K106 will generally have 40% of its mass contained in the minus 5 micron fraction. This largely accounts for the high percentage of filteraid added to the wastewater clarification step.

PROCESS ADVANTAGES

The Innochem mercury treatment process offers many advantages over the alternative retorting (BDAT), the most important being:

Produces a mercury concentrate suitable for thermal refining

Technology familiar to operators of chloralkali plants

Technology which uses common on-site chemicals

Process without atmospheric emission potential

Technology which operates continuously

Technology applicable to D009 wastes

Low energy requirements

Low capital cost

TABLE 2. MERCURY CONTENT OF K106 MUDS (DRY BASIS)

SAMPLE DESCRIPTION	MERCURY ANALYSIS (%)
Georgia-Pacific #1	3.0
Georgia-Pacific #2	3.3
Georgia-Pacific #2	3.5
Company X	3.9
Company Y	0.8

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BIOLOGICAL AND PHYSIO-CHEMICAL REMEDIATION OF MERCURY-CONTAMINATED HAZARDOUS WASTE

Conly L Hansen
Nutrition and Food Science & Biological and Irrigation Engineering
Utah State University
Logan, UT 84322-8700
USA
Tel: (801) 750-2188

David K. Stevens
Civil and Environmental Engineering
Utah State University
Logan, UT 84322-4110
USA
Tel: (801) 750-3229

INTRODUCTION

Mercury pollution is a serious problem for humans and other animals. Mercury can be removed from water by chemical precipitation; for example, a method for removing ionic mercury from water is addition of sodium sulfide. The insoluble mercuric sulfide (HgS) that forms is removed as a sludge that is then landfilled (1).

Chemical methods of mercury detoxification are not adequate. It has become evident that mercury can be solubilized from HgS under conditions that could be present in a landfill; *Thiobacillus ferrooxidans* can facilitate solubilization and volatilization of Hg^0 from HgS (2, 3).

Biological detoxification using mercury-resistant bacteria in a completely mixed, aerobic biological treatment process has been shown to have a capability for long-term removal of mercury from polluted water or soil slurry (4, 5). Detoxification is an enzyme- catalyzed process in which ionic mercury is reduced to volatile metallic mercury by mercuric reductase, a soluble flavoprotein located in the cytoplasm (6-8). Mercuric reductase can convert both Hg^+ and Hg^{++} to Hg^0 (9). The elemental form is easily removed from the growth medium, thus facilitating the removal of mercury from polluted water (10). A schematic of the process for removal of Hg^{2+} from aqueous solutions is shown in Figure 1.
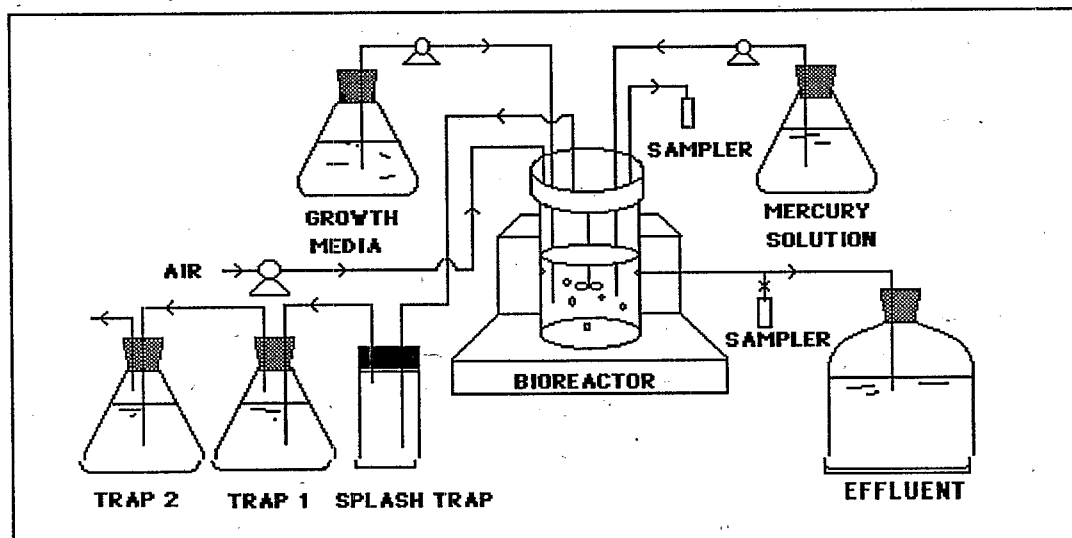

Figure 1. Schematic of biological process for removing Hg^{2+} from aqueous solutions

METHODS

Experiments to better characterize the process were carried out at Utah State University between September 1991 and May 1992. The growth substrate was a defined buffered minimal salts media supplemented with sucrose. It consisted of: 3.0 g potassium phosphate monobasic (KH_2PO_4); 7.0 g potassium phosphate dibasic ($K_2HPO_4 \cdot 3H_2O$); 1.0 g ammonium sulfate ($[NH_4]_2SO_4$); 2.0 g sucrose ($C_{12}H_{22}O_{11}$) and 1.0 L distilled water. Aeration rates were held constant at 1.5 LPM to simplify analysis of the fate of the reduced mercury.

Three influent mercury concentrations (nominal levels of 2, 20, and 40 mg/L), 3 mean cell residence times (12, 20, and 28 hr), and 3 temperatures (15, 22.5, and 30 degrees C) were employed in a 2^3 factorial design with a replicated center point, at a nominal influent chemical oxygen demand (COD) of 2,500 mg/L. The experimental design is given in Table 1.

To start the continuous runs, a batch culture was inoculated with 5% (v/v) stored culture and the defined growth medium and mercury stock solution were added to the reactor on a 1:1 volumetric basis to obtain the desired influent concentration. The reactor was allowed to operate and was monitored periodically for influent and effluent Hg and COD, effluent Volatile Suspended Solids (VSS), bacterial Colony Forming Units (CFU), Dissolved Oxygen (DO), pH, redox potential, and Hg volatilization for a time period equivalent to about four Hydraulic Residence Times (HRT) (mean cell residence times) to achieve steady-state conditions.

After about four residence times, the reactor reached steady state, as indicated by constant concentrations of reactor COD, VSS, [Hg], CFU, DO, pH, and redox potential (data not shown). After the reactor reached steady state, sampling was performed at least once each residence time for these parameters to characterize the reactor under the run conditions. At least two samples were used for each determination. At the end of a run, the culture was stored at 4 degrees C, the fermenter was cleaned, feed flow rate was modified, and the culture was allowed to reach steady state at the new levels. Parameters were averaged over the steady-state period.

Samples were preserved in a .04% sulfuric acid solution and stored at 4°C until analysis. COD was determined using the Closed Reflux, Colorimetric Method (11). VSS was determined using the APHA method, "Fixed and Volatile Solids Ignited at 550°C" (11). The 50 ml samples were collected from the reactor using a grab technique.

Influent, effluent, and off-gas total mercury was determined by the Cold-Vapor Atomic Absorption Spectrometric Method (11). A Buck Scientific Mercury Analyzer System, Model 400A was used for analysis. Five ml samples were placed in 5ml of 50% nitric acid and stored at 4 degrees C until analysis. Off-gases were trapped in a solution consisting of 3% potassium dichromate and 14% sulfuric acid in distilled, deionized water.

Additional measurements included reactor DO, pH, and redox potential to ensure the reactor was aerobic and well buffered. DO was determined using an Orion Research Model 97-08 Oxygen Electrode connected to an Orion Research Model 720 pH/ISE Digital Meter. The pH was determined using a Corning Scientific Instruments Model 10 pH Meter. Redox potential was measured with a Corning Model PS-19 ORP Meter.

RESULTS AND DISCUSSION

Averaged steady-state concentrations for selected measured parameters are shown in Table 1. A number of observations from the data are discussed in following paragraphs. A factorial analysis of these experiments was carried out to determine which of the variables studied had a significant impact on the mercury removal performance of the system. The results of the analysis for influent mercury concentration, temperature, and hydraulic retention time are given in Table 2. Results for the other parameters measured are not presented here but are available in a full report from the authors.

TABLE 1. EXPERIMENTAL DESIGN AND SELECTED RESULTS

Temperature	HRT	Hg In	$[Hg]_e$ mg/L	Removal Efficiency %	CFU #/mL	Redox potential
-1	-1	-1	0.028	98.6%	195,000	189.2
-1	1	-1	0.010	99.5%	10,080,000	175.5
1	-1	-1	0.053	97.4%	710,000	171.4
1	1	-1	0.230	88.5%	4,520,000	179.8
-1	-1	1	18.632	6.8%	440	268.6
-1	1	1	17.876	8.7%	314	249.0
1	-1	1	15.358	15.0%	290,000	256.4
1	1	1	4.213	88.1%	3,600,000	146.0
0	0	-0.31579	1.087	92.8%	22,460,000	140.9
0	0	-0.31579	1.970	86.9%	44,330,000	136.3

-1 : low level of indicated variable
0,-0.316 : medium level of indicated variable
1 : high level of indicated variable

TABLE 2. SIGNIFICANCE OF ESTIMATED MAIN EFFECTS AND INTERACTIONS

Variable	Significance of Effect on	
	$[Hg]_e$	% Removal
Main effects		
Temperature (T)	-[1]	-
Hydraulic Residence Time (HRT)	-	+[2]
Influent Hg ($[Hg]_i$)	+	-

[1] - means effect of variable is not significant at the 95% confidence level
[2] + means effect of variable is significant at the 95% confidence level

The growth behavior of the microorganisms responsible for the reduction of Hg^{2+} to Hg^o and the effect of mercury concentration on that behavior were examined. During all runs of the experiment, the system was operating very close to washout conditions; in all cases, conventional measures of process performance showed that the system had failed. The COD removal was essentially zero and VSS, a commonly used measure of active biomass in wastewater treatment, was near zero. Thus, conventional approaches to evaluation of growth kinetics of the bacteria responsible for mercury removal were not used here.

Instead of using VSS as the measure of biological activity, CFU was much more indicative of mercury removal performance. Figure 2 shows the relationship between mercury removal efficiency and CFUs. From this plot, there is a clear threshold CFU value of about 10^6 /ml, below which there is little or no Hg removal and above which Hg removal is nearly complete. This behavior has been observed previously in our laboratory and suggests that these mercury-resistant organisms are able to detoxify their environment
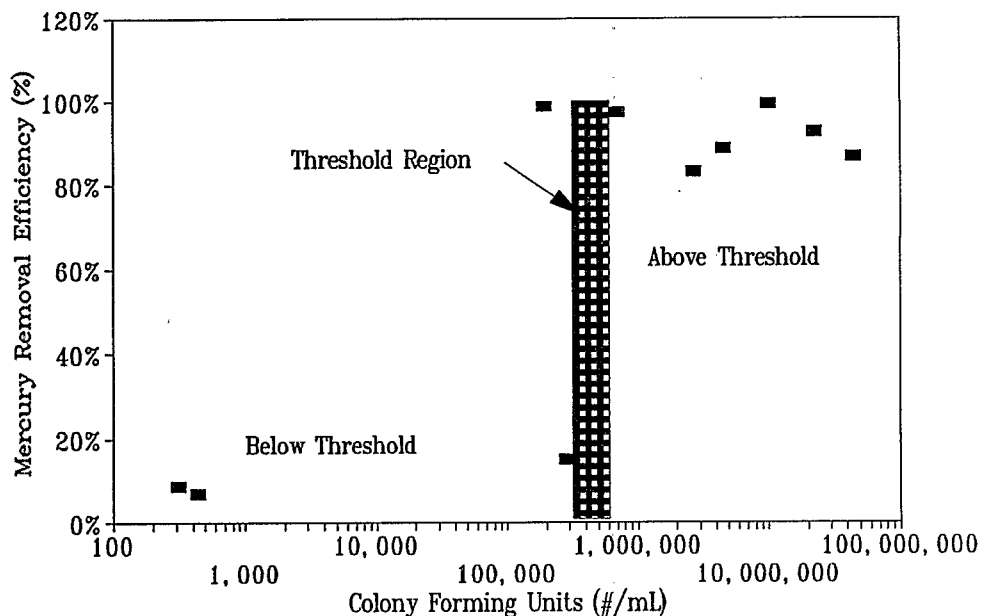
Figure 2. Mercury removal efficiency vs. colony forming units

by removing mercury at very low biomass densities, and thus if their numbers are above the approximate threshold of 10^6 units/mL, good mercury removal efficiency should be possible.

At the higher concentrations, some of the influent mercury precipitated, probably as mercuric hydroxide, mercuric oxide, or mercuric chloride (12) to a level of soluble reactor [Hg] of 15 to 18 mg/L. The solubility of these minerals is very low - in pure water at pH 7, the solubilities of $Hg(Cl)_2$, $Hg(OH)_2$, and HgO are approximately 10^{-10} - 10^{-12} molar Hg^{2+} at 25°C. The high ionic strength (>0.12 M) in the reactor medium increases the solubility, as does the formation of Hg complexes with chloride, hydroxide, sulfate, and ammonium to the levels seen here. In equilibrium with HgO precipitate, the concentration of the complex $Hg(OH)_2$ will be about 10^{-4} M or 20 mg/L Hg and may dominate the mercury in solution in the reactor (12). This value is consistent with the concentrations observed in the reactor during runs 5, 6, and 7 as shown in Table 1. Thus, in wastewaters it is unlikely to expect reactor soluble mercury concentrations in excess of 20 to 30 mg/L.

The runs for which CFU are below the threshold correspond to those runs for which the nominal influent $[Hg^{2+}]$ was 40 mg/L. This suggests the possibility of inhibition or toxicity of mercury to these organisms at elevated concentrations.

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