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EXECUTIVE SUMMARY

Dillon Consulting Limited was retained by the Department of Indian and Northern Affairs Canada (DIAND) to assess and prepare a report on the current market, technology and feasibility for managing arsenic trioxide currently stored underground at the Giant Mine site in Yellowknife. The report is not intended to be a detailed assessment but is to provide indications of current technologies, first order estimates and initial economic requirements for the Departments planning purposes.

Information was obtained from several sources. The Internet was a primary source for initial information pertaining to companies handling arsenic trioxide in some capacity which then directed further inquiries. Information accuracy was confirmed by contacting named companies directly and by cross checking with government databases. The U.S. Geological Survey Web site contained a large quantity of current information regarding the economics, usage and the outlook for arsenic as a marketable commodity. The Economics of Arsenic, 1990 edition, published by Roskill Information Services in the UK was another useful source of data for all aspects of arsenic trioxide usage. Technical information on the processing and handling of arsenic trioxide was extracted from case studies and scientific reports authored by various groups.

The prospect of selling arsenic trioxide on the open market looks hopeful. Arsenic trioxide has been used for many purposes in the past including: agricultural chemicals (pesticides and herbicides), wood preservatives, glass manufacturing and metal alloys. Environmental concerns have reduced the use of arsenic trioxide in all sectors with the exception of wood preservatives. Three wood preservative companies: Hickson Corp., Osmose Corp. and CSI all located in the United States have the capability to accept large, continuous shipments of arsenic trioxide from Giant. All three companies expressed some interest in the product during information inquires. Hickson Corp. received approximately 20,000 tons of crude arsenic trioxide in the 1980's from Giant and were interested in the results of Giant's research into upgrading the crude material. This interest has been renewed in the past year with intermittent correspondence. Osmose Corp. received arsenic trioxide from Miramar Con Mine, Yellowknife, NT., treatment plant until about 1990. CSI has not had dealings with mines in the NWT but expressed interest. All three companies would require the crude product in Giant's storage vaults be upgraded to a minimum of 95% arsenic trioxide and a number of other impurities (particularly antimony and iron) would have to be reduced before it would be considered as an acceptable product. The electronics Industry has an increasing market for pure arsenic metal, but only uses small volumes of product and requires very high purity of the material, 99.9999%, making it an unlikely target market for the material stored by Giant.

The stored arsenic trioxide would have to be upgraded to a minimum of 95% before being widely marketable. Purities of 99% or higher would command a better price. Two purification methods are currently in common use, sublimation and solvent extraction. Sublimation involves a process of heating the arsenic trioxide containing material to a high enough temperature sufficient to convert the trioxide to a gaseous state. The gas is then passed through a series of condensers to produce a purified product. An alternate method uses hot water to dissolve the arsenic trioxide, leaving behind impurities. The trioxide is then recrystallized as a product with at least 99% purity. Con Mine in Yellowknife constructed a processing plant to purify arsenic trioxide from a tailings pond sludge using the hot water leach method. The plant was in operation through the 1980's and successfully treated Con's stockpiled arsenic trioxide to produce 99.7% pure arsenic trioxide. The material was sold to Osmose Corp. in the U.S.. The gold and silver present in the treatment residue were successfully reclaimed, contributing to the economic success of the plant.

Approximately 137,000 ounces of gold are believed to be present in the baghouse dust kept in the arsenic trioxide storage vaults at Giant Mine. Several metallurgical processes have been developed to recover precious metal values from mine wastes containing high levels of arsenic. Con Mine successfully developed a method to extract gold and silver from the residue produced in the arsenic trioxide treatment plant. Rough calculations suggest that removing the arsenic trioxide would leave a gold concentration in the dust greater than that currently being mined by Giant. Economic factors suggest that any attempt to purify the arsenic trioxide for sale should probably include recovery of the gold contained in the dust.

Accessing and conveying the material to the surface for processing would require careful design to minimize health and environmental hazards. The primary concern would be the generation of dust. Inhalation of the arsenic or absorption through the skin can be fatal. The recovery of arsenic will present a number of technological challenges because, while Giant has considerable experience placing the arsenic trioxide underground, it has not moved or recovered significant material. A small quantity of material was successfully accessed in the 1980's and sent to the U.S. for sale and testing.

A number of technologies and methods are available to complete on-site treatment of the material to render it environmentally inert. The most environmentally stable form of arsenic is as a ferric arsenate. Arsenic naturally occurs in this form. The cost of converting arsenic trioxide into ferric arsenates can be high as a molar ratio of 3 or 4:1 iron to arsenic is required. The conversion is carried out in an autoclave as the process requires temperatures of 130-140°C and a pressure of 100 psi. A process under development at McGill University will use ratios of 1.1:1 iron to arsenic. Iron arsenate sulphate hydroxy compounds are another stable arsenic form produced in an autoclave but they also require a large amount of iron and some sulphur. Arsenic sulphates can be produced in a roaster and are considered stable enough for long term disposal. A pilot scale process has been developed to produce arsenic sulphide in a bioreactor with an efficiency rate six times that of chemical means. Conversion of the waste to calcium arsenate is no longer considered a suitable disposal method as the calcium reacts with CO_2 in the atmosphere to form calcium carbonate, thereby releasing the arsenic into the environment. A potentially low cost method for on-site disposal may be to combine the arsenic trioxide with a chemical cement to produce a hardened product. In some instances the cement may be reusable for structural purposes, eg. road beds. The substances produced from any of these processes could be disposed of safely in tailings ponds.

Off-site treatment or disposal options appear to be quite costly, with initial estimates in excess of 750 $/ton. The amount of material to be disposed of and the resultant cost make this option unlikely.

The problem of handling large amounts of arsenic trioxide appeared in most literature regarding precious metal mines. Several case studies were obtained discussing options for disposing of arsenic trioxide and have been included in Appendix H of this report. The most pertinent study was carried out by Nerco Con Mine and outlines the methods used to dispose of a large amount of arsenic trioxide in an economically and environmentally acceptable manner. Giant has also studied the options for marketing the arsenic trioxide and has produced a number of reports detailing the technological requirements to handle and process the waste material. Copies of these reports were not obtained but would provide specific information on the Giant Mine case.

1.0 INTRODUCTION

Giant Mine in Yellowknife, NT processes refractory ores using roaster technology. After 40 years of mine operation a significant amount of material has accumulated as a by-product of the roasting process. An average of 78% of this material is arsenic trioxide. Arsenic trioxide is a highly toxic material which must be carefully managed. Dillon Consulting Limited was retained by the Department of Indian and Northern Affairs (DIAND) to assess and prepare a report on the current market, technology and feasibility for managing the arsenic trioxide currently stored in underground vaults on the mine site.

This report is not intended to be a detailed assessment of arsenic trioxide management options rather, it has been prepared to provide an indication of current technologies, first order estimates, and initial economic requirements for Departmental planning purposes.

1.1 Scope of Work

The specific areas of interest that were researched for this report, as outlined in the terms of reference (TOR), included the following:

1) current market and conditions for the product in its' raw state and as an upgraded/refined material. This includes a list of the known producers, similar sources and industrial users. Any future known trends should be identified if they may affect the market (ie: changes in its use in the wood preservative industry). This should include an economic review including the material value versus the cost of getting it to market.

2) technology, requirements and feasibility to upgrade the product to the market standards.

3) current technology, markets and feasibility of processing the material to recover additional products. (ie: gold)

4) technology, requirements and feasibility of accessing and conveying the material to surface or otherwise gaining access to it for management purposes.

5) current technologies and feasibility available to process the material on-site to render it environmentally inert and unavailable (ie: solidification, encapsulation, autoclave, etc.). This should include utilizing the Con autoclave or other similar technology.

6) current companies, approved facilities and locations that can accept the material for on or off-site management/treatment/ disposal.

7) current technology and feasibility of long term surface storage.

8) any other management options which may be available or emerging

9) provide information on relevant projects, pilot projects, parallel or applicable projects & technologies, case studies, experts, references or standards/legislation the contractor may obtain during their work.

The above assessments should address any residual waste byproducts resulting from on-site processing.

1.2 Background

Arsenic is a naturally occurring substance that is found most often in compounds with sulphur, either alone or in combination with various metals (eg. arsenopyrites). It is recovered as a by-product of processing certain ores where the primary product is copper, lead, zinc, gold and/or silver. Royal Oak's Giant Mine, a gold producing mine located in Yellowknife, NT., produces arsenic mainly as arsenic trioxide through the roasting process of arsenic gold ores.

Since the 1950's, the arsenic trioxide generated at Giant Mine has been stored in underground chambers. During the late 1970's research and development was carried out by at Giant to produce a marketable grade of arsenic trioxide and as a result a pilot plant was built. In 1980, Giant Yellowknife signed a contract with a U.S. consumer to sell their raw 504Darsenic trioxide product, resulting in the construction of a storage silo and truck load out facility. (Roskill, 1990)

In 1987, shipments and sales of arsenic trioxide from Giant stopped and a research programme was initiated to upgrade the arsenic trioxide to produce a more marketable product. A decision was expected by the end of 1989 concerning production from the project and a start-up date was tentatively set for January 1991 (Roskill, 1990). Shifting priorities after the purchase of Giant by Royal Oak put this project on hold (1991 Canadian Minerals Yearbook, Pg. 9.1).

Currently, Giant Mine has accumulated approximately 260,000 tons of baghouse dust.

2.0 METHODOLOGY

A literature search of available sources was carried out to determine options available for the disposal of large amounts of crude arsenic trioxide mine waste as specified in the Scope of Work. An Internet search was conducted for "arsenic trioxide" using all of the available search engines. A number of subsequent searches were carried out using key words to narrow down the returned information fields. Information gained from sites located through these searches served as the basis for further searches of libraries both on and off the "net", and provided the contact numbers for companies and agencies that dealt with arsenic trioxide in some capacity. Companies and government agencies were contacted directly and information relating to arsenic trioxide was gathered over the phone or by fax. Individuals contacted often provided information on additional sources that were then utilized. The information obtained through personal communications has been reported directly. The opinions expressed are those of the people contacted.

An abridged set of Appendices has been included with this report. All appendix references prefixed by a 1(eg. App. 1-B) can be found in this set. Another more comprehensive set of appendices has been produced as a separate document. All appendix references prefixed with a 2 can be found in this document. Appendix references without a prefix can be found in both appendices.

2.1 Sources

A number of different sources were used during the information search including the Internet, government personnel, industry and an assortment of libraries. The major sources of information used were:

- The "Internet". Searches were carried out using available search engines for "arsenic trioxide" and variations such as "arsenic trioxide - remediation".
- Chemical and wood preservative manufacturers
- Roskill Information Services, The Economics of Arsenic, 1990
- U.S. Geological Survey - Minerals Information Sheets, 1995-1996
- U.S. Geological Survey - Mineral Commodity Summary, February 1997
- Canadian Minerals Yearbook, 1991

- Mines and Minerals Activities, 1993
- Natural Resources Canada Minerals and Metals Sector, On-line Information
- Statistics Canada, On-line Trade Query
- Canadian Institute of Treated Wood
- The Legislative Assembly Branch Library, Yellowknife, NT
- The NRC Library, Vancouver, BC
- The Natural Resources Library, Ottawa, ON
- Natural Resources Canada - CANMET
- DIAND Environmental Library
- Canada-NWT Business Centre
- Environment Canada
- Department of Resources, Wildlife and Economic Development
- Canadian Intellectual Property Office
- Environmental disposal companies
- Waste remediation companies
- Workers Compensation Board
- Department of Safety and Public Services
- Industry Canada
- U.S. Department of Commerce, National Technical Information Service

3.0 DATA COMPILATION

The information presented in this section has been taken directly from the literature or from personal communications with various individuals from within the industry or knowledgeable about arsenic trioxide. This information has been placed in point form to present individual pieces of data for consideration by the reader. References following each point reflects the document being quoted as indicated by each header.

3.1 Economics

Arsenic trioxide is used in a number of different products including wood preservatives, glass manufacturing, agricultural chemicals and nonferrous alloys. Of these, the wood preservative industry accounts for 90% of all arsenic based products consumed in the U.S. (U.S.G.S., Mineral Commodities Summaries, Pg. 1). The wood preservative industry has shown steady growth in its' use of arsenic trioxide whereas other end users have shown a steady decline. (Roskill, Pg. ii). The market research therefore focused on the wood preservative industry and the inorganic chemical supply industry as being the most likely markets for the by-product stored by Giant. In order to assess the marketability of the arsenic trioxide in Giant's storage vaults, a number of wood preservative and chemical companies were contacted. These companies are listed in the table below.

COMPANY	COMPANY TYPE	COMMENTS
BDH Chemicals Canada, Ltd.	Chemical	No longer distribute arsenic trioxide.
All Chemie, Ltd.	Chemical	Purchase ultra-high purity material.
Transene Co., Inc.	Chemical	Purchase high purity and small quantities.
Wego Chemical and Mineral Corp.	Chemical	Interested, but depends on purity.
Canaimex, Inc.	Import/Export	Importer/exporter.
Amalgamet Canada	Chemical	Distributor for French supplier.
Spectrum Bulk Chemicals	Chemical	Lab grade, 99% or higher.
Great Western Inorganics, Inc.	Chemical	Manufacturer of arsenic trioxide.
Hickson, Inc.	Chemical/Wood Preservative	Major wood preservative manufacturer.
Chemical Specialties, Inc.	Chemical/Wood Preservative	Major wood preservative manufacturer.
Osmose, Inc.	Chemical/Wood Preservative	Major wood preservative manufacturer.
Diachem Industries, Inc.	Wood Preserving	No longer use arsenic.
Napier International Tech., Inc.	Wood Preserving	No longer use arsenic.
Pierce and Stevens Canada, Inc.	Wood Preserving	No longer use arsenic.
Chem-Craft	Wood Preserving	Do not use arsenic.
Solignum, Inc.	Wood Preserving	No longer use arsenic.
Korzite Coatings	Wood Preserving	Do not use arsenic.

Each of the companies contacted identified their requirements of a useable arsenic trioxide product. These requirements are as follows:

All Chemie, Ltd.
Fort Lee, NJ
Products: As - metal, As_2S_5, As_2O_5, As_2O_3, As_2S_3.

- Distributor of ultra-high purity material, 99.99% or higher. (Pers. Com. 1997)

Transene Co., Ltd.
Rowley, Ma
Products: As_2O_5, As_2O_3.

- Purchaser of high purity material, greater than 99% and in small quantities for use in the electronics industry. (Pers. Com., August 08, 1997)

Wego Chemical and Mineral Corp.
Great Neck, NY
Products: inorganic chemicals.

- Purchase product with a purity of 99% at a minimum. Product is obtained from China. (Pers. Com., August 01, 1997)

Canaimex, Inc.
Montreal, PQ

- Import/export company that does not use the product themselves but would transport it to markets. (Pers. Com., August 07, 1997)

Amalgamate Canada
Toronto, ON

- Distributor for an arsenic trioxide producer in France. Distribute arsenic trioxide in purities of 98.5% or greater. (Pers. Com., August 05, 1997)

Spectrum Bulk Chemicals
New Brunswick, NJ
Products: As - metal, As_2O_5, As_2O_3.

- Distributor of lab grade quality material, and in relatively small quantities. (Pers. Com., August 01, 1997)

Great Western Inorganics, Inc.
Arvada, CO
Products: arsenic acid, arsenic disulphide, As_2S_5, As_2O_5, $AsBr_3$, $AsCl_3$, AsI_3, As_2O_3, As_2S_3, arsenic triselenide.

- Manufacturer of arsenic trioxide but not a user. (Pers. Com., August 14, 1997)

Hickson, Inc.
Conley, GA
Products: wood preservative, including CCA.

- Manufacturer of arsenical wood preservatives.
- Accepted delivery of approximately 20,000 tons of arsenic trioxide from Giant in the 1980's.
- Operate the largest arsenic acid plant in the world.
- Feedstock specifications are: 95% arsenic trioxide, <400 ppm iron, <1,000 ppm lead and <100 ppm chloride. (Pers. Com. 1997)

Chemical Specialties, Inc.
Harrisburg, NC
Products: wood preservatives, including CCA.

- Manufacturer of a line of products for use in the wood preservative industry, primarily CCA.
- Purchase in excess of 10 MM lbs. of arsenic trioxide from several countries around the world in bulk bags of 1.0 or 1.7 metric tons.
- Process arsenic trioxide into arsenic acid at their Harrisburg, NC facility.
- Plant feedstock requirements are: 95-99% arsenic trioxide, 500-5,000 ppm iron, 0.5-1.0% antimony, <300 ppm mercury, <100 ppm chloride, <0.5% water. (Pers. Com. August 12, 1997)

Osmose Inc.
Memphis, TN
Products: wood preservatives, including CCA.

- Purchased arsenic trioxide from Con mine until approximately 1990.
- Manufacture arsenical wood preservatives, specifically CCA.
- Feedstock requirements are: 99% arsenic trioxide, <0.02% iron, <0.02% lead and <0.01% chloride. (Pers. Com. August 14, 1997)

In addition to contacting companies that handle arsenic trioxide, several referenced sources were consulted to determine the current market conditions for the product, producers, similar sources, industrial users and trends in the market. These are as follows:

Roskill Information Services, The Economics of Arsenic, 1990

- Arsenic trioxide accounts for 97% of world arsenic production. World production was estimated at 54,800 tons in 1987, up from 40,000 tons per year in the late 1970's but less than peak levels of 70,000 tons per year in the late 1960's. Over the years the arsenic industry has increasingly been affected by environmental factors, particularly in the USA and Western Europe where the actions of environmental organizations have curtailed some operations. This has likely added to the potential supply of arsenic being much greater than the demand.

- A treatment plant at Giant Mine in the N.W.T. has produced raw arsenic trioxide as a by-product from their gold roaster unit. Between 1979 and 1980, research was carried out on producing a marketable grade of trioxide and a pilot plant was built. In 1980, Giant signed a contract with a U.S. consumer to sell their raw trioxide production, and construction work was started on a storage silo and truck load out facility. The construction work was completed in early 1981, and 1,093 tonnes of raw arsenic trioxide were shipped to the U.S. consumer during the year. In 1987, shipments and sales of arsenic trioxide stopped and a research programme was initiated to upgrade the arsenic trioxide in order to produce a more saleable product. A decision was expected by the end of 1989 concerning production from a gold/arsenite project in Yellowknife, NWT, and a start-up date set for January 1991. The plant was to produce approximately 8,000 tonnes/year of arsenic trioxide and 2,000 ounces/year of gold. The project would only proceed if a market could have been secured for at least half of the planned arsenic production.

- The sales of arsenic trioxide from Giant Mine between 1981 and 1987 were:

Year	**Volume (tons)**
1981	1,093
1982	1,361
1983	726
1984	1,119
1985	2,055
1986	368
1987	---

- Campbell Red Lake Mine in Ontario has a production capacity of 1,360 tons of arsenic trioxide per annum. In both 1985 and 1986, they produced approximately 1,270 tons of arsenic. The principal use of the arsenic is in wood preservatives. All arsenic is exported, mainly to the USA.

- Cominco opened a new US $13 million arsenic recovery plant at the Con Mine in the N.W.T. in late 1983. Feed for the plant came from a 65,000 ton stockpile accumulated over 25 years prior to 1970. Building of the plant had been prompted by a directive from the NWT Water Board to Cominco in which they were requested to find the best way of disposing the stockpile, which was determined to be a potential environmental hazard. Stabilization and permanent impoundment of the sludge had been rejected as unacceptable to future generations, and wasteful of the contained gold, silver and arsenic values. The 5,000 tpd capacity plant was scheduled to process 32 tpd of sludge in order to produce 15 tpd of arsenic trioxide with a purity of 99.5% arsenic trioxide together with gold and silver. Most of the trioxide output was shipped throughout North America for wood preservative and agricultural chemical end uses.

- Cominco Ltd. also operated an integrated smelter and refining complex at Trail, BC. An arsenic pentoxide solution was produced there as a by-product of other metallurgical operations until January 1989 when Cominco's Electronic Materials Division was bought by the Johnson Matthey Corporation. Arsenic trioxide is no longer produced.

- Equity Silver Mines Ltd. of British Columbia produced calcium arsenate which was disposed of in the U.S. Currently they are mining a grade of ore with a very low arsenic content and are not producing arsenic products.

- Environmental pressure groups and organizations have fought for thorough investigations of the toxicities of arsenic compounds and, where applicable, have paved the way for appropriate legislation to minimize the exposure of individuals to toxic arsenic compounds.

- In June 1984 the US Environmental Protection Agency issued a rule restricting the use of three major types of wood preservatives: creosote, inorganic arsenical and pentachlorophenol. This measure:

  a) prohibited consumer sales of wood treatment products containing these chemicals: manufacturers would be required to label their products for trade use only, (although consumer sales are a very small part of the total market).

  b) required new protective measures for staff in wood treatment plants. In 1986, OSHA announced an industry assistance programme to help plants monitor arsenic levels as required by law. If the arsenic level is higher than 10 micrograms per cubic meter of air, operators will be required to wear respirators.

  c) proposed a new consumer awareness programme for consumers of treated timbers (with the long-term sanction that if the industry cannot organize it, the EPA may require the labelling of all such timber). This aspect of the rule was upheld by a Federal judge in mid-1985.

  d) required a reduction in the hexachlorobenzene and hexachlorinated dibenzodioxin contamination found in pentachlorophenol.

  e) prohibited the use indoors, with some exceptions, of wood products treated with pentachlorophenol or creosote, unless the wood is subsequently sealed with varnish or shellac. (Pp. 140-141)

- The EPA decided that all three of these wood preservatives exceeded the agency's risk criteria for cancer-causing potential, but it was decided not to seek a ban because of the great benefits wood preservatives give to society. If an alternative preservative without the same risks could be developed, the risk/benefit balance may change and there may be cause to ban these preservatives.

- Work has been done to find alternatives to arsenic in current preservatives with less toxic elements such as zinc, fluorine, chlorine and boron.

Statistics on the lumber industry and associated arsenic trioxide trade numbers and costs are found in Appendix B of this Report.

- Markets for CCA treated lumber market sector. Table 1
- Comparison of wood treatment costs. Table 2
- Imports of arsenic trioxide and pentoxide and acids by major trading countries, 1984 - 1987. Table 3
- Europe and the USA: Arsenic trioxide prices, 1976 to 1989. Table 4

U.S. Geological Survey - Minerals Information, 1996

- The U.S. was the world's largest consumer of arsenic in 1996, accounting for about two-thirds of world demand.
- On a contained metal basis, arsenic trioxide accounted for 99% of American imports in 1996.
- China is the world's largest producer of both arsenic trioxide and arsenic metal accounting for 44% and 84% respectively of American imports.
- Overall consumption of arsenic remained relatively unchanged in 1997, for the third straight year.
- Arsenic trioxide was consumed in the production of arsenic acid for formulation of CCA by the three principal producers of arsenical wood preservatives in the U.S.: Hickson Corp., Conley, GA; CSI, Harrisburg, NC and Osmose Corp., Memphis, TN. The wood preservative industry accounts for 90% of total arsenic demand.
- With the major market for arsenic being the production of arsenical wood preservatives, the demand for arsenic is closely tied to the home construction market, where wooden decks containing arsenical preservatives have become ubiquitous.
- In 1988 about 450 million cubic feet of wood were treated with waterborne preservatives (98% estimated to be CCA). In 1984, 300 million cubic feet were treated. In 1994, 500 million cubic feet were treated and in 1995 450 million cubic feet were treated. In 1995, waterborne preservatives were used for about 75% of all

treated lumber.

- The apparent demand for arsenic trioxide in wood preservative declined slightly in 1996 despite an increase in housing starts. Restocking by wood preservative manufacturers and carry-over from the 13% housing growth in housing starts in 1994 may have served to boost the apparent demand in 1995.

- Future demand for arsenic is expected to closely follow that for new home construction, although the replacement and renovation markets could increase as a percentage of total market share. The prohibition on use of CCA preservatives in certain applications and the greater acceptance of alternative preservatives could negatively affect this demand.

- Arsenic consumed in agricultural uses continued to decline following the EPA's 1993 cancellation of arsenic acid for use as a cotton desiccant.

- The average customs value for imported arsenic trioxide in 1996 was 22 cents per pound, down approximately 2 cents per pound from that of 1995. Prices for high-grade (minimum 99%) arsenic trioxide generally are quoted at an 8 to 12 cent per pound premium to low-grade (minimum 95%) arsenic trioxide.

- Commercial-grade arsenic trioxide is recovered from the smelting or roasting of nonferrous metal ores or concentrates in at least 18 countries.

- Although environmental pressures may continue to cause curtailment of existing capacity, given the abundance of high-arsenic residues from nonferrous metal processing, world supplies of arsenic trioxide are expected to remain adequate to meet projected need. The following Economic tables have been duplicated and are provided in Appendix II-B of this Report.

Arsenic Supply-Demand Relationships. Table 5

U.S. Imports for Consumption of Arsenical. Table 6

Arsenic Trioxide: World Production. By Country. Table 7

U.S. Geological Survey - Minerals Information, 1994

- In 1994 local and state concern over the toxicity of chromated copper arsenate (CCA) wood preservatives led to State restriction on their use in certain applications. Responding to the concern that CCA could leach from timbers and accumulate in invertebrate marine life, New Jersey became the first State to restrict their use in certain marine applications. Effective July 19 1994, restrictions on the use of CCA pressure-treated wood were imposed along four rivers that are rich in shellfish. Accordingly, CCA treated wood will be prohibited in the construction of new or rebuilt marine structures at marinas containing slips for five or more boats. However, in recognition of a lack of alternative materials, pilings were exempt from the ban. Alternative materials for planking include plastic lumbers and South American hardwood.

- Mexican trioxide has the advantage of bulk shipping via rail cars allowing consumers to avoid having to handle and dispose of contaminated drums.

U.S. Geological Survey, Mineral Commodity Summaries, February 1997

- The total value of arsenic metal and compounds consumed in was estimated at $20 million.

- A recently developed alternative, ammoniacal copper quaternary, which avoids using chrome and arsenic, has yet to gain widespread usage. Non-wood alternatives such as concrete, steel or plastic lumber may be substituted in some applications for treated wood. A South American hardwood, ipe, which requires no chemical treatment, has been used in some localities in ocean front boardwalks.

- Salient Statistics - for the U.S. are provided in Table 8 of Appendix II-B of this Report.

Canadian Minerals Yearbook, 1991

- Approximately 40 tonnes of stockpiled arsenic trioxide material from Giant was shipped to the U.S. for testing.

- Recovery technology includes the electrostatic precipitation of dust, cooling of the arsenic containing gases, and collection of arsenic trioxide in the baghouse which grades 85 to 93%.

- Since the Royal Oak takeover, Giant's White arsenic oxide (WAROX) plant project to treat crude arsenic (currently 85% pure) to produce high-quality industrial product (99% pure) has been placed on hold. This project would involve using sintered metal technology for recovering arsenic pentoxide to be used in the wood preservative industry.

- Arsenical wood preservatives are used wherever rot or insect damage may occur, such as in building foundations, fence posts, submerged footings and utility poles. Substitutes are increasingly being found for most of arsenic's major end uses, although arsenic may be the preferred material due to its lower cost and superior qualities.

- In September 1991, the Commission of the European Communities issued council directives relating to restriction on the marketing and use of arsenic and its' compounds. These include prohibition of arsenic compounds for the following: prevention of fouling by micro-organisms, plants or animals the hulls of boats; cages, floats, nets and any other appliances or equipment used for fish or shellfish farming; any totally or partly submerged appliances or equipment; and preservation of wood. The ban does not apply to solutions of inorganic salts of the CCA (copper chromium arsenic) type employed in industrial installations using vacuum or pressure to impregnate wood.

- The outlook for arsenic at this time seemed somewhat uncertain, although supplies are abundant and demand is expected to remain relatively flat.

- Canadian Arsenic Production and Trade, 1989-1991 is provided in Table 9 of Appendix II-B.

Mines and Minerals Activities, 1993

- The Mineral Production of the Northwest Territories between 1984-1993 is provided in Table 9 of Appendix II-B.

Natural Resources Canada Minerals and Metals Sector, On-line Information

- Canada consumed 125 tons of arsenic trioxide in 1991. Consumption data for 1992 to 1995 was considered confidential and therefore is not reported. Table 11 in Appendix II-B of this Report provides further consumption statistics.

Statistics Canada, On-line Trade Query

- Statistics Canada provides statistics on both Canadian Exports and Imports which are provided in Tables 12 & 13, respectively in Appendix II-B of this Report.

3.2 Arsenic Trioxide Market Processing

Several methods exist for processing crude arsenic trioxide into higher grade material. General information on the sublimation process and the water extraction process was found in Roskill's, The Economics of Arsenic, 1990. Information on other processing technologies was found in patent abstracts and in case studies. It is unknown whether the technologies described in the patents are in use. The Con Mine and El Indio Mine case studies describe processes that are currently operating or have successfully operated recently.

References has been made directly from the Patents and/or Patent holders therefore, these are named and page referenced accordingly.

PATENT NUMBER	PROCESS TYPE	COMMENTS
Cdn. Patent No. 1314149	Evaporation into a gas stream.	See abstract in appendix D.
U.S. Patent No. 3923478	Scrubbing of flue gas with aqueous solvent.	Referenced in Cdn. Patent No. 1314149, deals with flue gas having a high sulphur dioxide component.
U.S. Patent No. 4588564	Removal of arsenic trioxide from scrubbing water.	Referenced in Cdn. Patent No. 1314194.
U.S. Patent No. 4605812	Catalyzed removal of arsenic from gases.	Referenced in Cdn. Patent No. 1314194.
U.S. Patent No. 4489046	Evaporation of arsenic trioxide in a furnace.	Referenced in Cdn. Patent No. 1314194, could also be used to recover gold values.
U.S. Patent No. 4244735	Caustic leach and crystallization.	Referenced in Cdn. Patent No. 1314194, could also be used to recover gold values and render arsenic inert.
Swiss Patent No. 273779	Evaporation and recrystallization of arsenic trioxide.	Referenced in Cdn. Patent No. 1314194.
German Reference No. 131840	Extraction using sulphuric acid.	Referenced in Cdn. Patent No. 1314194.
Con mine process	Multi stage hot water leach.	See Appendix I.
El-indio gold mine process	Precipitation from flue gas.	See Appendix I.
U.S. Bureau of Mines	Sulphuric acid leaching.	See Appendix 2-I.

Roskill Information Services, The Economics of Arsenic, 1990

- The flue dusts from the roaster or smelter are collected by Cottrell Electrostatic precipitator; combined with galena or pyrite to prevent arsenite formation, and then roasted so that the arsenic trioxide is vaporized. The vapour passes through a series of condenser "kitchens", encountering progressively lower temperatures from 220°C to 100°C or less, and recondenses to 90 to 95% pure arsenic trioxide. This material can then be purified further by resublimation in a reverbatory furnace. From here the trioxide passes through another series of kitchens. In those with a temperature of 120°C to 189°C, arsenic trioxide of 99% to 99.9% purity condenses. The poorer grades from the other "kitchens" are either recycled or marketed as crude arsenic trioxide of a minimum 95% purity.

- Arsenic trioxide can be separated from impurities by dissolution in water. Arsenic trioxide is fairly soluble in water at temperatures approaching 100°C whereas its common impurities are not. The arsenic trioxide solutions are separated from the insoluble impurities and vacuum cooled to yield arsenic trioxide of at least 99% purity.

Canadian Patent No. 1314194

Patent Holder: Derka, Jaroslav R.

- The arsenic trioxide is evaporated into a non reactive carrier gas (eg. nitrogen) in a heated chamber, a fluidized bed or an electrical plasma reactor. The arsenic trioxide is precipitated from the gas into a fluidized bed of arsenic trioxide particles cooled by water evaporation. The final size of the arsenic trioxide particle can be controlled. The material from which the arsenic trioxide is removed can then be treated to remove valuable metal components (eg. gold). (Derka, Jaroslav R., Pp. 5-15)

- Arsenic trioxide has a higher solubility in ammonia than in hot water and an ammonia leach process can be used to purify arsenic trioxide. This process is not currently being used. (Derka, Jaroslav R., Pg. 2)

U.S. Patent No. 3923478

- The arsenic trioxide is scrubbed from the 350-400°C roast gas using a (preferably aqueous) solvent. The system is kept closed. The product is concentrated and crystallized out of the solution. Any unwanted deposits formed are removed by dissolution in unsaturated arsenic trioxide solution. By using systems in parallel and switching liquid flows, it is possible to run a continuous process with minimal solid or liquid effluent. (Derka, Jaroslav R., Pp. 2-3)

U.S. Patent No. 4588564

- Arsenic trioxide is recovered from flue gas scrubbing water. The crude arsenic trioxide crystals collected are purified by treatment with 50-150 g/l hydrochloric acid at a temperature of less than 30°C. (Derka, Jaroslav R., Pg. 3)

U.S. Patent No. 4605812

- Arsines are removed from a hydrocarbon or inert gas stream by contacting the stream with a copper (II) chromate catalyst. (Derka, Jaroslav R., Pg. 3)

U.S. Patent No. 4489046

- The arsenic containing waste is melted under oxidizing conditions in a furnace forming an oxide slag melt. Turbulence is caused in the melt while a reducing atmosphere is maintained to support the formation of arsenic trioxide which is then driven off and recovered by condensation. (Derka, Jaroslav R., Pp. 3-4)

U.S. Patent No. 4244735

- The arsenic is precipitated as an insoluble, non-polluting ferric-arsenic compound, carried through a chloride leach step to recover metals in the waste and then disposed of. Alternately, the arsenic can be recovered using a caustic leach and crystallization process. (Derka, Jaroslav R., Pg. 4)

Swiss Patent No. 273779

- A mechanical process operating at 500-600°C and 0.5-1.0 mm of H_2O vacuum is used to evaporate arsenic trioxide from the waste product. The arsenic trioxide vapours are recrystallized. (Derka, Jaroslav R., Pp. 4-5)

German Patent No. 131850

- Flue gases containing sulphur dioxide, arsenic trioxide, halides and dust are cleaned by washing with a circulating sulphuric acid solution. The solution is adjusted to a very low concentration of sulphuric acid to allow dissolution of the halides. The sulphuric acid solution is separated and subjected to a vacuum evaporation to vaporize the halides and crystallize the arsenic trioxide. (Derka, Jaroslav R., Pg. 5)

The Con Mine Separation Process

- A two stage counter current leach at an operating temperature of 95°C is used to extract arsenic trioxide from waste material. Hydrogen peroxide is added to enhance leach kinetics. The crystallization liquor is thickened and filtered using powdered activated carbon to remove crystallization modifiers and to enhance product purity. The hot pregnant liquor is passed through four stages of evaporative cooling and crystallization in growth type units. The crystallized product obtained is 99.8% pure arsenic trioxide. (Anthony, David H.; Pg. 140)

El-indio gold mine process

- Gases from the roaster are passed into an oxidation chamber with enough ambient air to allow complete conversion of all sulphates to oxides. The oxidation temperature is 750°C. The gas from this chamber is passed through a heat exchanger to cool it to 390±10°C. This cooled gas is passed through two electrostatic precipitator to remove all particulate matter. The gas exiting the precipitator at 300°C contains arsenic trioxide vapour and is rapidly cooled to 120°C in a hatch chamber. The arsenic trioxide precipitated out of the gas in this step is collected in a baghouse. The product collected has a purity of 97% to 97.5%. (Smith, E.H. and Parades, Eduardo, Pp. 154-157)

U.S. Bureau of Mines

- Sulphuric acid is used to dissolve arsenic and metals present in the smelter dust. The temperature is controlled between 24 and 90°C to determine the amount of a particular metal extracted. Solids are filtered out and the temperature is lowered to precipitate the metals. Sulphur dioxide is sparged into the solution to precipitate the arsenic trioxide. (Chementator, April 1990, Pg. 23)

3.3 Gold Recovery Technology

The amount of gold present in the stockpiled flue gases at Giant has been estimated at about 137,000 ounces. The literature was reviewed and attempts were made to contact a referenced company that is developing new processes to recover precious metals from waste products in order to determine the feasibility of recovering gold from the waste material. It is unknown whether any of the following processes are currently in use. These process/patents, as well, are referenced to the author or patent holders.

COMPANY	PROCESS	RESULTS/COMMENTS
Artech Recovery Systems, Inc.	Cashman process	International patent holders for Cashman process.
EMR Microwave Technology Corp.	Microwave energy processes.	Uses microwaves to facilitate extraction of precious metals from tailings deposits.
U.S. Patent No. 4615731	Hydromettalurgical recovery process	Referenced in Cdn. Patent No. 1314149, see App. 2-E
U.S. Patent No. 4244735	Hydromettalurgical recovery process	Referenced in Cdn. Patent No. 1314149, see App. 2-E

Artech Recovery Systems Inc.
Golden, CO

- A single step hydrochloric acid-oxygen leach is carried out as 120°C and 60 psi. Base and precious metals are dissolved as chlorides and later recovered by precipitation or solvent extraction and electrowinning. Arsenic is precipitated as ferric arsenate which can be disposed of more readily than arsenic trioxide. (Chementator, April 1990, Pp. 22-23)

- Attempts were made to contact Artech Recovery Systems Inc. but were unsuccessful.

EMR Microwave Technology Corp.
Fredricton, NB

- Microwaves are used to introduce energy into the waste material. The company has contributed directly to the development of new extraction techniques to allow recovery of precious and strategic metals from existing concentrate and tailing deposits.

U.S. Patent No. 4615731

- Precious metals are separated from an aqueous acid solution containing gold, one or more metals from the platinum group and one or more of the nuisance elements: bismuth, lead, tin, arsenic and antimony. The aqueous acid is treated with sulphur dioxide in the presence of selenium and a halide to reduce and selectively precipitate selenium and the precious metals which are then separated from the solution. (Derka, J.R., Pg. 3)

U.S. Patent No. 4244735

- Arsenic is precipitated as an insoluble ferric arsenate compound in the first processing step and carried through a chloride leach step, in which it is insoluble, to recover the metals. The metals in solution are separated from the ferric arsenate precipitate and recovered. The ferric arsenate precipitate is disposed of. (Derka, J.R., Pg. 3)

3.4 Materials Handling

Information on accessing and conveying the arsenic trioxide material to the surface was not readily available. The specifics of this type of operation are dealt with on a case by case basis. Some general information on potential problems were obtained from telephone conversations with the Environmental Protection Division of RWED and the Worker's Compensation Board. Other information regarding personal protection requirements and Transportation of Dangerous Goods was obtained from Environment Canada.

Environmental Protection Division, RWED (Pers. Com., 1997)
Yellowknife, NT

- The material is stored in stopes on the first and second levels of the mine. Removal should not prove prohibitive from a technological stand point as Giant has stored the material for years and has considerable experience handling it.

- As the material was placed into the stopes it seems likely that it should be possible to remove it safely through mechanical means. It is obvious that occupational Health and Safety would have protocols regarding arsenic handling.

- TDG regulations would apply to the arsenic trioxide if it were shipped off-site. Giant would have to be registered as a hazardous waste producer, the carrier would have to be registered as a hazardous materials carrier, the receiver would have to be registered as a hazardous materials user and a TDG manifest would be required.

Worker's Compensation Board (Pers. Com. 1997)
Yellowknife, NT

- Dust generation would be the main concern for workers. Self-contained breathing apparatus and full protective chemical suits may have to be used when workers are in direct contact with the arsenic trioxide material. Health and environmental monitoring programs would have to be initiated.

Copies of the TDG and MSDS information obtained from Environment Canada have been included in Appendix I-F and II-F of this Report.

3.5 Waste Stabilization and Storage

Research literature indicates that arsenic trioxide is soluble in water at a level of 12.1 g/l at a temperature of 0°C (Stefanakis, M. and Kontopoulos, A., Table III, Pg. 294), which is significantly higher than the CCME remediation criteria of 50 mg/l for freshwater aquatic life. The solubility of arsenic trioxide increases with temperature and at extremes of pH. Arsenic trioxide is not suitable as a disposal option for arsenic if there is any possibility of water contacting the waste material. (Kyle, J. H. and Lunt, D., Pg 347).

A number of companies were contacted and several studies were reviewed in order to determine options for the stabilization and storage of arsenic trioxide. Each of these are listed in the following table and appropriately referenced below.

Company/Group/Patent	Process/Technology	Comments
Stark Encapsulation, Inc.	MetlCAP encapsulation process.	Can form reusable cement substance, see App. G.
U.S. Government	Zeolite-hydraulic cement containment medium.	See App. G.
Phytotec, Inc.	Phytotechnology.	Uses plants to take up arsenic from waste material, see App. 2-G.
Center for Bioremediation	Utilize bioreactor technology to remediate arsenic containing waste material.	See App. G.
University of Alberta, environmental research group.	Assorted technologies.	They have not done specific arsenic work, but would be interested.
U.S. Patent No. 4244735	Precipitation as ferric-arsenic compound.	Referenced in Cdn. Patent No. 1314149, See App. D.

Stark Encapsulation Inc.
Cleveland, OH

- A proprietary process is used to bind the arsenic into a hardened chemical cement matrix. This material can then be disposed of or reused as a cement (eg. in roadbeds). Treatment prices ranged from 20-80 U.S.$ per ton depending on the properties of the arsenic containing medium, the concentration of arsenic in the waste and the intended fate of the product. (Pers. Com., 1997)

U.S. Government

- A process was developed to contain arsenic in a zeolite-hydraulic cement medium. Zeolite in amounts from 5-60 weight % is mixed with portland cement in amounts from 95-40 weight %. A chosen amount of small particle size hazardous material is added to this mixture and more portland cement is added. Water is added to produce a free flowing paste which is poured into molds and hardens.(Brown, Patrick M. *et al*, Pp 5-7)

Phytotec, Inc
Monmouth Junction, NJ

- Plants are used to "phytoremediate" contaminated material. Contaminants are absorbed by the plants which are then stabilized and landfilled or processed to remove the metal. A process is being developed to remediate arsenic, but will not be ready for at least another year. (Pers. Com., 1997)

Center for Bioremediation
Weber State University, Ogden, UT

- Biological processes are used to convert waste material into usable or disposable forms. Work has been done at the pilot plant scale to convert arsenic into arsenic sulphide which is considered stable enough to be stored in a landfill. Reported efficiencies were six times those of chemical methods. A process is being developed to purify arsenic trioxide to a level high enough for it to be used by the wood preservatives industry. (Pers. Com., 1997)

University of Alberta, Environmental Research Group
Edmonton, AB

- The possibility of freezing and storing arsenic containing mine waste in permafrost has been studied. Work has not been done with arsenic trioxide specifically, but interest was expressed in developing options for gold mine tailings treatment and disposal. (Pers. Com., 1997)

U.S. Patent No. 4244735

- Arsenic is precipitated as an insoluble ferric-arsenic compound. The arsenic is rendered less hazardous by fixing it with ferric ions and this material can be disposed of. (Derka, Jaroslav R., Pg. 4)

Two studies on disposal options for arsenic trioxide were reviewed to collect background information on the solubility of various arsenic compounds. The Sefanakis study has been included in Appendix I-G and II-G and the Lundt study has been included in Appendix I-I and II-I.

Production of Environmentally Acceptable Arsenite-Arsenates From Solid Arsenic Trioxide
Stefanakis, M. and Kontopoulos, A.

- Arsenic trioxide produced by roasting can be effectively stabilized as ferric arsenate. Increased pH and temperature at precipitation adversely affects arsenic solubility. Mixed Fe(II)-Fe(III) arsenates were less suitable for arsenic removal than ferric-arsenates.

- A molar ration of 7:1 Ca:As was required to achieve a solubility in compliance with environmental standards. Calcination at 800°C rendered calcium arsenates acceptable at a molar ratio of 3:1 Ca:As.

An Investigation of Disposal Options for Arsenic Trioxide Produced from Roasting Operations
Kyle, J.H. and Lunt, D.

- Ferric arsenate precipitates produced a very low solubility product, but required large quantities of oxidant, lime and ferric sulphate to produce. These precipitates showed low solubility but required large amounts of production chemicals.

- Calcium arsenate showed low solubility but long term thermodynamic stability has been proven to be deficient. Chemical solidification of arsenic trioxide or of calcium arsenate showed promise from an economic standpoint.

A representative from CANMET was contacted and options for stabilization and storage were discussed. (Pers. Com. 1997)

- Calcium arsenate was once considered an option but long term testing has shown that calcium carbonate was formed upon exposure to air and the arsenic was released.
- Arsenic can be adsorbed onto ferric hydrate which passes leaching tests and is dischargeable. A molar iron to arsenic ratio of 3:1 is required. The product has a low density and a high volume. Theoretically the iron could react with carbon dioxide in the air to form iron carbonate, and release the bound arsenic. The process has been found to be more suitable for arsenic in solution.
- Arsenic can be converted to $FeAsO_4{\bullet}H_2O$ at 130-140°C and 100 psi in an autoclave. A dense thermodynamically stable product is formed. Product formed is the same as stable arsenic compounds found in nature.
- $FeAsO_4{\bullet}H_2O$ can be formed at atmospheric pressure using chloride media. The oxidation step is rate limiting and can be accelerated with hydrogen peroxide. Corrosion problems have hindered the development of this process.
- Very low solubility iron arsenate sulphite hydroxy compounds (Bukovskyite) can be formed in autoclaves. Iron demand is high.
- Lead iron arsenate hydroxide (pyromorphite) compounds show low solubility but the involvement of lead complicates the environmental aspects of material storage.
- Low solubility arsenic sulphide can be formed in a roaster and stored in tailings ponds. The process is used at a mine in Chile. Maintenance of the equipment can be problematic due to large amounts of arsenic contamination.

3.6 Materials Management

Three waste handling companies were identified in Alberta that could handle the disposal of arsenic trioxide waste. Telephone conversations were carried out with each company to determine the disposal services offered by each company as well as approximate prices for each option. Requested information was obtained from Custom Environmental Services.

COMPANY	SERVICES OFFERED	COMMENTS
Custom Environmental Services/Proeco Corporation	Secure landfill, incineration, treatment	See Appendix H
Environmental Management	N/A	N/A
Phillip Environmental	N/A	N/A

Custom Environmental Services/Proeco Corp.
Edmonton, AB

- Secure landfill would be reliant upon the make-up and concentration of the waste material. The estimated disposal cost was $Cdn. 750 per ton. Incineration was estimated to cost $Cdn. 1,300 per ton.

- Treatment would be an option depending on make-up and concentration of the waste material. Estimated costs were $Cdn. 1,600 per ton. All final prices would be dependant upon the volume and location of the material. Transportation costs could be very high.

The Ontario Waste Exchange and the Canadian Chemical Exchange were both contacted but were unable to provide information on disposal options for the arsenic trioxide waste.

3.7 Other Studies

Several case studies discussing methods of handling arsenic containing mine wastes were obtained and reviewed. Copies of the Con mine, El Indio and Windarra Nickel/Gold Project are provided in Appendix II-I, abridged copies are included in Appendix I-I.

LOCATION	TITLE	FINDINGS
Yellowknife, NT Con Mine	Nerco Con Mine Arsenic Plant - Environmental Management Through Resource Recovery	The sale of arsenic trioxide and the recovery of gold and silver values was economically viable.
La Serena, Chile El Indio gold mine	How St. Joe Gold's El Indio Mine has Become a Major Producer of High Quality Crude Arsenic Trioxide.	Crude arsenic trioxide can be successfully produced and marketed.
Laverton, WA Windarra Nickel/ Gold Project	An Investigation of Disposal Options for Arsenic Trioxide Produced from Roasting Operations	Combining unprocessed mine tailings or calcium arsenate with portland cement appeared to be a feasible disposal option.
Yellowknife, NT Giant Mine	Truck Transfer Facility Enterprise, NT	Outlined the requirements for constructing a truck to rail transfer station.

Con Mine Case Study

- A study was carried out to determine disposal options for 70 000 tons of arsenic containing sludge stockpiled over 30 years of roaster operation. Chemical fixation methods, physical processing methods and resource recovery methods were identified evaluated for arsenic treatment on the basis of process feasibility, environmental stability and economics. Increased arsenic trioxide prices in 1980 made resource recovery feasible.

- Hot water leaching was determined to be more environmentally acceptable than a fuming process. A two stage counter current leach process was developed capable of treating 20 stpd of raw arsenic trioxide sludge. 12 stpd of 99.8% pure arsenic trioxide was recovered from the plant. 8 stpd of residue containing 1.2 ounces gold/ton and 3.5 ounces silver/ton was left over from the processing. The residue was stockpiled until metallurgical processes could be developed to extract the gold and silver values. Final inert residues were stored with mill tailings in tailings ponds.

- In 1985 process problems caused the plant to be shut down. Further lab studies were carried out and the plant reopened in 1987. Industrial hygiene among plant operators was identified as a problem until a formal training program was developed.

- It was estimated that approximately 5 years was the required treatment time to allow for full treatment of the arsenic sludge. Revenues obtained from the sale of recovered arsenic trioxide, gold and silver were projected to cover the plant's operating costs.

- Currently, the treatment plant is not in operation but was successful in treating all the arsenic trioxide material in the 1980's. A method was developed to successfully remove the gold and silver from the process residue.

El Indio Gold Mine Case Study

- Gold ores with a high arsenic content are processed using roaster technology. Arsenic trioxide is produced as a by-product. The roasting process is conducted under reducing conditions to prevent the formation of less volatile pentavalent arsenates and antimoniates, loss of stable sulphide sulphur, excessive formation of oxidized iron compounds and formation of low melting point eutectics. Roaster gases containing sulphates of arsenic and antimony, labile sulphur and other volatiles are passed through two cyclones in parallel to remove particulate matter before being passed into a post-combustion chamber. Sufficient ambient air is admitted to completely convert all sulphates to oxides at a temperature of 750°C. The gases are cooled to 390±10°C and passed through an electrostatic precipitator to remove particles. Arsenic trioxide is gaseous at this temperature and passes through the precipitator. The gas stream is cooled to 120°C in a hatch chamber and arsenic trioxide is precipitated out.

- Solid arsenic trioxide is collected in a bag house. The solids are transferred to bins beneath the baghouse and conducted via screw-feeders and elevators to storage bins. The arsenic trioxide is passed from the storage bins through Vacu-press densifiers and then into 25 and 30 gallon drums. The drums are strapped 12 or 6 to a pallet and trucked to port where they are exported in containers.

- Arsenic trioxide of an average purity of 97.3% is produced and shipped to market.

- An increased capacity in the flotation/cyanide plant, the added value to concentrates by roasting and a strong demand for arsenic trioxide contributed to the addition of a second roaster unit, to enter service in late 1989. Arsenic trioxide production doubled to approximately 30 tons per day.

- Arsenic trioxide production required the implementation of human and environmental controls, including air and water sampling and routine biological monitoring of staff.

- The arsenic trioxide marketing effort required about three years to refine, but sales were brought in line with production and "...El Indio feels reasonably confident that it is established as a long term supplier to the arsenic market.".

Windarra Nickel/Gold Project Case Study

- This study investigated disposal options for arsenic trioxide only. Marketing options were considered impractical.

- Solubility testing was carried out on calcium arsenite, calcium arsenate, ferric arsenite, ferric arsenate precipitates formed from arsenic trioxide waste and on cements formed by mixing the arsenic trioxide waste or the precipitates with portland cement on its own or with additives (silica flume or flyash). Solubility of the precipitates was tested using the standard Multiple Extraction Procedure with a synthetic groundwater solution as the extractant. Calcium arsenite was found to precipitate leach much more readily than calcium arsenate. Ferric arsenite and ferric arsenate were less soluble than their calcium counterparts.

- Arsenic leaching from the cement solidified products was investigated using a standard Dynamic Leach Test. Calcium arsenate and ferric arsenate mixed with cement leached much more slowly than the untreated arsenic trioxide mixed with cement. The addition of silica or flyash negatively affected the fixation of arsenic in the cement matrix and produced much higher leach rates than the straight arsenic-cement mixture. Calcium arsenite interfered with the setting reaction of the cement, and would not harden.

- Ferric-arsenic compounds showed very low solubility but required large amounts of process chemicals. Calcium arsenate formed a low solubility precipitate but the long term stability of calcium arsenate is known to be poor. Solidification with cement appeared to be the most economically feasible disposal option.

Truck Transfer Facility, Enterprise NT

- Giant was involved in a program to investigate the best ways of producing and distributing a high quality White ARsenic OXide (WAROX) product. The study examined the technical aspects of reclaiming and upgrading the product and included a market study. Upon investigating various shipping alternatives, it became clear that bulk rail shipments were easily the least expensive way to go. Giant is thought to have extensive experience in control and handling of WAROX compounds.

- A tentative shipping schedule called for the dispatch of approximately 150 tons per week of high quality product to American markets. Based on an 80 ton payload, 1 hopper car would be loaded every four days. The product was to be in a free-flowing, dust-free granular form with a bulk density of about 90 lbs/cu. ft.

- Arsenic trioxide would be transported to the transfer station using trucks with a volume of approximately 1200 cu. ft. and a payload of 22 tons. The payload could be expanded to 33 tons using a "pup" trailer in the typical rig configuration. The truck would be equipped with four loading hatches and four bottom dump hoppers to be fitted with flexible boots to control dust during off-loading. The arsenic trioxide would be transported from the truck to a 100 ton storage bin via a CamBelt conveyor. The CamBelt would be fully enclosed and equipped with "boots" to prevent dust losses at inlet and outlet points. The arsenic trioxide would be transferred from the storage bin to a rail car.

- Appendix A of the Truck Transfer Report contained emergency action measures to be taken in case of a spill at the surface arsenic load-out facility.

4.0 DATA MANAGEMENT

4.1 Economics

The information gathered from reference sources and from telephone conversations with a number of companies indicates, that the waste material with arsenic trioxide levels of 78 to 95 % is not marketable. At a minimum, 95% purity is considered "low grade" and is the lowest level accepted for most commercial operations. Some companies however, will purchase material below 95% to blend with higher grade material forming a 95% final composite. 99% or greater purity is considered "high grade" and is quoted at an 8 to 12 cent per pound premium over low grade product (U.S. Geological Survey - Minerals Information Sheet, 1996, Pg. 2). The average customs value for imported arsenic trioxide (U.S.) in 1996 was 22 cent/pound, down 2 cent/pound from 1995. The decline was attributed to the lower value of some off-grade material imported from Chile used for blending with high purity material. High purity trioxide from Mexico averaged 33 cents/pound (U.S. Geological Survey - Minerals Information Sheet, 1996, Pg. 2).

The U.S. accounts for approximately 2/3 of total world demand for arsenic trioxide and China is it's largest single supplier. A total of 28,000 tons of arsenic trioxide, with a total value of 13.4 million $U.S., were imported in 1996, 11,000 tons of which came from China (Ibid., Pg. 3, Table 1). The wood preservative industry accounted for 90% of U.S. demand and it's three principle producers: Hickson Corp., Osmose Corp. and CSI were identified as the most likely end user's for Giant's by-product.

The market for arsenic trioxide as a wood preservative is closely tied to the housing construction market (e.g. wooden decks). In 1988, 450 million cubic feet of lumber were treated with waterborne preservatives (98% of which was estimated to be CCA). In 1993, 470 million cubic feet were treated with waterborne preservatives (75% of all treated lumber). Approximately 500 million cubic feet were treated in 1994 (80% of all treated wood) and in 1995, 450 million cubic feet of lumber were treated with waterborne preservatives (75% of all treated wood). The apparent demand for arsenic trioxide declined slightly in 1996 despite an increase in housing starts. In 1995, figures may have been influenced by a carry over from a 13% increase in housing starts in 1994 (U.S.G.S. - Minerals Information Sheet, 1996, Pages 1 to 2).

All three of the major wood preservative companies in the U.S. expressed interest in the Giant mine's product. Hickson was familiar with Giant as they had received shipments of arsenic trioxide from them in the 1980's. Sales were suspended to allow Giant to develop a process to upgrade the trioxide to a higher purity product (Pers. Com., Hickson). Contact between Hickson and Giant has been renewed in the past year with intermittent correspondence. Osmose purchased product from Con Mine while Con's arsenic plant was in operation. CSI expressed cautious interest in the material but raised concerns regarding contamination of the flue dust with other materials (Pers. Com., CSI). The iron, lead, chloride, antimony and mercury levels may have to be reduced to bring them in line with the requirements of the various companies. There is some variation in feedstock requirements dependant on the end user firm.

Environmental pressures have reduced the use of arsenic in several of it's traditional end uses as safer alternatives have been developed. The use of arsenic in the agricultural chemicals market (herbicides and pesticides) dropped from 20% of all arsenic consumed in the U.S. in 1990 to 4% in 1996 as alternative products became accepted. All other end uses have shown a similar decline with the exception of the wood preservative industry which has grown from 70% of all arsenic consumed in the U.S. in 1990 to 90% in 1995 (U.S.G.S. - Mineral Information Sheets, 1994 to 1996). A potential alternative to arsenical wood preservatives is Ammoniacal Copper Quaternary (ACQ), which avoids the use of both arsenic and chrome. Recently developed, this product may result in an impact the arsenic market. It has yet to gain widespread usage.

Several potential sources of arsenic trioxide exist in Canada, at least one of which is currently producing arsenic products for sale. Giant Mines, Yellowknife has been stockpiling arsenic trioxide in underground vaults since the mine opened. Approximately 20 000 tons of this material were shipped to Hickson Corp. in the early to mid 1980's. Plans to construct a WAROX plant to upgrade the bag house dust to a 99% pure industrial product were developed starting in 1987. This project was put on hold when Royal Oak acquired the Giant Mine (Roskill, 1990, Pg. 21). Dickenson Mines' Red Lake Division produced about 1,360 tons of trioxide in 1985 and 1986 from its gold roasting operation. This product was exported to the U.S. (Ibid., Pp. 21- 22). Arsenic is no longer produced as a product as it is converted to ferric arsenate in an autoclave and stored (1991 Canadian Minerals Yearbook, Pg. 9.2). Nerco Con Mine, Yellowknife sold high quality arsenic trioxide to Osmose Corp. until about 1990 (Pers. Com., Osmose Corp.). Arsenic trioxide was produced using an arsenic recovery plant opened in late 1983 while the Con mine was owned by Cominco. The feed source was arsenic sludge stockpiled from the mine's opening until 1970 (Roskill, 1990, Pg. 22). Cominco produced an arsenic pentoxide solution at an integrated smelting and refining facility near Trail, BC until 1989 (Ibid., Page 22). Gallium arsenide was produced at Trail starting in 1981 but production stopped after a market failed to develop (Nerco Con Mine, Annual Reports). Cominco now produces copper-arsenate which is sold to Hickson Corp. Placer Dome's Campbell gold mine converts arsenic into ferric arsenate in an autoclave which is disposed of in ponds (1991 Canadian Mineral Yearbook, Pg. 9.2). Equity Silver Mines Ltd. produced calcium arsenate which was disposed of in the U.S. until 1984. This mine has since closed down.

Reported Canadian consumption of arsenic is confidential from 1992 to 1995, but is given as 125 tons in 1991. Canada exported 37,194 kg of arsenic in 1996 for a value of 54,216 $Cdn. (Statistics Canada, On-line Information). The exports information did not indicate the specific compounds exported but indicates an average price of $1.46 per kg.

Approximately 215,000 tons of baghouse dust had been accumulated and stored underground at Giant mine by 1988 (Giant Report, Warox Transfer Facility). At an average collection rate from the baghouse of 12-15 tons a day (1995 Annual Report, Pg. 5) this amount will have grown to approximately 259,000 tons of material by 1997. In 1988, the material was estimated to contain 77.6% arsenic trioxide and 126,913 ounces of gold (Giant Resources Ltd.; Annual Report; Pg. 26). In 1995, the purity of arsenic trioxide was estimated to be between 85 and 95% (wt/wt). The amount of gold was estimated at 0.10 - 0.15 oz/ton of dust (1995 Annual Report, Pg. 5). Calculations using the 1988 numbers as a base and applying the 1995 values to subsequent production puts the total volume of material at 259,000 tons, containing 206,000 tons of arsenic trioxide and 132,456 ounce of gold by 1997. Based on an average price of 786 $Cdn./ton (determined using the average value per ton of 1996 U.S. imports) the arsenic trioxide has a value of $Cdn. 162 million. Based on a gold price of $Cdn 300 per ounce the gold would be worth approximately $Cdn.39.7 million. These figures give total value of $Cdn.202 million to the product stored at Giant.

Transport costs were estimated at 40 $Cdn. per ton for rail shipment and 120 $Cdn. for truck shipment. This equates to shipment cost of $Cdn. 8 to 24 million for the entire 206,000 tons. These figures may be low, and could range as high as 300 to 400 dollars per ton due to the hazardous nature of the material. These figures increase transport costs to $Cdn. 62 to 82 million.(Pers. Com., Royal Oak)

Con Mine constructed a treatment facility to process approximately 7,300 tons/year of arsenic trioxide waste material, producing 4,000 tons/year of purified arsenic trioxide product. The capital cost for this facility in 1981 was $Cdn.13 million. The operating costs were estimated at less than $Cdn.650 per ton. A plant of this scale would be capable of processing Giant's current production and very little more. Giant would need to process a considerably larger volume per year to impact on the stored waste. Based on a 20 year time frame for eliminating the arsenic stored in the vaults, the processing plant would need to process approximately 12,500 tons of stored material plus 5,000 tons of currently produced material for a yearly total of 17,500 tons. Approximately 15,000 tons of arsenic trioxide product would be produced each year. Scaling Con Mine expenditures up to meet the Giant Mine requirements would mean a capital cost of $Cdn. 22 million with an operating cost of $Cdn. 650 per tonne. This results in a total cost to treat and transport the current and future arsenic of $Cdn.214 to 270 million (dependent on transport costs) with a recovery of $Cdn.202 million. These numbers can not be considered complete without factoring in the cost of accessing the material from the vaults. Estimates on these costs were not obtained due to the specificity of the problem and the number of variables involved.

World production of arsenic trioxide was estimated at 42 100 tons in 1996 (U.S.G.S. - Minerals Information Sheet, 1996, Table 4). Estimated U.S. imports of arsenic trioxide in 1996 were 29,000 tons. Based on a 20 year reduction plan, Giant would account for 60% of U.S. demand and 37% of world production, tying with China as the world's single largest producer (1996 production values).

4.2 Arsenic Trioxide Market Processing

The information gathered indicates that it is possible to successfully separate and market arsenic trioxide from gold mine wastes. There are two primary methods: sublimation, where the arsenic trioxide is evaporated from the waste material and then cooled to form a high purity precipitate and solvent extraction, where the arsenic is dissolved into an aqueous solution and recrystallized into a purer product. Both methods have been used successfully.

Con Mine in the N.W.T. successfully developed a solvent extraction treatment process allowing it to treat 20 stpd of arsenic sludge from its' 70,000 ton stockpile, producing 12 stpd of 99.7% pure arsenic trioxide product. This product was shipped to Osmose Corp. in the U.S. in extra strength 45 gallon drums. The 8 stpd residue contained 1.2 ounces gold/ton and 3.5 ounces silver/ton. The plant cost approximately 13 million dollars to build. Revenues from the sale of arsenic trioxide and the value of the recovered gold and silver were expected to cover the plant's operating costs.

The El Indio gold mine in Chile uses a high temperature oxidation process to convert arsenic sulphates into arsenic trioxide gas. The gas is cooled and filtered through two electrostatic precipitator to remove unwanted particles and then cooled further to release arsenic trioxide crystals. Approximately 5,000 tons per year of arsenic trioxide are produced and sold on the international market.

4.3 Gold Recovery Technology

Over 100,000 ounces of gold are estimated to be present in the arsenic trioxide waste material kept in Giant Mine's storage vaults. Recovery and sale of this gold would help offset the costs incurred during any processing of the arsenic trioxide for purification or storage purposes. The ability of Con Mine to recover the gold and silver from the residue of the arsenic trioxide upgrade process contributed to the economic viability of their processing plant.

Several patents have been taken out on metallurgical processes to recover precious metals from tailings waste and information was obtained outlining biological, chemical and microwave methods for recovering metals from mining wastes, indicating that metal recovery from tailings is possible. It is unknown if any of these methods are currently in use.

4.4 Materials Handling

Specific information on conveying arsenic trioxide from underground storage vaults to the surface for processing could not be found. Processes such as these must be developed on a case by case basis.

The primary concerns are minimization of dust and exposure of dust to water. Arsenic trioxide is a highly toxic, highly soluble material and may be fatal if inhaled, swallowed or absorbed through the skin.(TDG) Workers coming into direct contact would need to wear chemical protective clothing and positive pressure self-contained breathing apparatus. (TDG) Giant Mine has experience in the handling of arsenic trioxide material as 7,400 tons of material were shipped to U.S. buyers from 1981 to 1987 and an on site truck loading station was designed in conjunction with a study carried out by Giant in 1987-1989 on the feasibility of upgrading the arsenic trioxide. They do not have experience in removing the arsenic from it's storage vaults however.

4.5 Stabilization and Storage

A number of technologies are available for the on-site stabilization and storage of the arsenic trioxide waste material. The literature indicates that the most stable form of arsenic for long term storage is as a ferric arsenate compound formed in a process requiring a molar iron to arsenic ration of 3-4:1. Currently Dickenson mine's Red Lake Division in Ontario and Placer Dome's Campbell gold mine in Ontario convert arsenic byproducts to this form in an autoclave and store it in ponds.

Conversion of arsenic into calcium arsenate is no longer considered a viable disposal option as thermodynamic data indicates that the calcium reacts with carbon dioxide in the air to form calcium carbonate. The arsenic is released as a result of this conversion. This problem may be overcome if the calcium arsenate precipitates undergo calcination at temperatures in excess of 700°C to convert the amorphous structure into a crystal structure (Stefanakis *et al*, Pg. 290).

Conversion into arsenic sulphide may be the most economic chemical binding method as the processing can be carried out in a roaster. Giant currently operates a roaster on site to preprocess gold ores prior to cyanization treatment.

Several processes are available to encapsulate the arsenic in a cement medium. From an economic standpoint, studies have indicated this may be the most viable option. U.S. government researchers have developed a process using zeolite and portland cement and Stark Encapsulation markets a process under the tradename MetlCAP that claims to completely bind the arsenic particles using a mixture of chemicals and cement. The cement formed using the MetlCAP process can be reused as a structural material.

Other options such as phytoremediation or bioremediation show promise but are still at a developmental level.

4.6 Materials Management

Data on materials management could only be obtained from one company which provided cost estimates for landfilling, incineration and treatment of the waste material. It is unlikely that the material could be landfilled and incineration is not possible, leaving only the treatment option. Based on this company's prices, off-site disposal costs would be on the order of $Cdn. 300 million.

4.7 Other Studies

Three case studies concerning the management of arsenic trioxide mine waste were obtained and reviewed. Two of the studies, Con Mine and El Indio mine, indicated that arsenic trioxide could be processed to a sufficiently high purity level to be sold on the world market. The studies illustrated two different situations.

In the Con Mine study, arsenic trioxide was produced after the mine's on site arsenic trioxide disposal efforts were deemed environmentally inadequate. A process was developed to produce 99.8% pure arsenic trioxide from tailings pond sludge.

The El Indio case study demonstrated how the production and sale of arsenic trioxide can be used to maximize the profitability of a mine. The arsenic trioxide was viewed as a potential product to be developed, not merely as a waste product produced while refining gold.

The third case study did not address the prospect of purifying and marketing the arsenic trioxide beyond stating that the demand for arsenic trioxide is not high and therefore disposal options must be looked at. The conclusion was that the most insoluble forms or arsenic are also the most expensive to produce. Recommendations were made to study methods of stabilizing arsenic trioxide in a cement matrix.

During the late 1980's, Giant studied the possibility of processing the arsenic trioxide using sintered metal technology to produce a high quality product to be marketed as WAROX (White Arsenic Oxide) (1991 Canadian Minerals Yearbook, Pg. 9.1). All aspects of the process appear to have been considered including the construction of a truck to rail transfer facility near the community of Enterprise, NT. Communications with Hickson Inc. indicated that transport of the arsenic trioxide by rail would be a requisite part of any sales agreement. A copy of the transfer facility report was obtained from DIAND's environmental library and reviewed. Copies of reports detailing other aspects of the process (eg WAROX plant design, Surface Arsenic Load-Out facility) were not obtained, but could be of use in determining options for the management of Giant mine's arsenic trioxide waste material.

5.0 SUMMARY

Dillon was retained to provide a brief assessment of options for managing the arsenic trioxide contained in underground storage vaults at Giant mine in Yellowknife, NT. The study was intended to provide indications of current technologies available for all aspects of handling the waste.

The research suggests that the market for arsenic trioxide lies chiefly with the wood preservative manufacturers. The prevailing trend is to develop safer alternatives to arsenical products, but the wood preservative industry has remained consistent in its demand for arsenic trioxide. The demand for arsenic is not expected to grow much beyond current levels. Three companies contacted expressed interest in purchasing material from Giant, but marketing the large volume of material stored by the mine will require careful planning.

Osmose Corp., Hickson Corp. and CSI in the U.S. would be the most likely purchasers of any product from Giant. Hickson purchased material from Giant in the early 1980's, and Osmose purchased material from the Con mine's treatment plant until 1990 when Con's stockpile of arsenic trioxide material was exhausted. All three companies required the product to be at a minimum purity level of 95% with 99% being most favourably priced. CSI indicated that some lower grade material was purchased to blend with higher quality material but 95% was the purity most often purchased. The purification can be carried out using a hot water leach or a sublimation process. In 1981, Con chose the hot water leach process for use at its' treatment plant as they felt it was the more environmentally responsible option.

Any purification method chosen should incorporate extraction of residual gold from the arsenic containing dust. Approximately 130,000 ounces of residual gold are contained in the waste material. The economic success of the Con mine treatment plant was due in part to the successful reclamation of the residual gold and silver with the arsenic trioxide.

Accessing the material and conveying it to the surface or otherwise gaining access to it for management purposes would require careful monitoring. Arsenic trioxide is a known carcinogen, potentially fatal if inhaled or ingested and can be absorbed through the skin. Precautions would be required to minimize direct worker contact with the material and keep dust generation low. Routine biological monitoring of staff and constant air and water monitoring are required at facilities processing arsenic trioxide. Giant has had considerable experience handling arsenic trioxide and currently processes the material safely.

A number of technologies are available to render the material environmentally inert either for long term surface storage or for storage in containment vaults. Arsenic trioxide is very soluble, and must be converted to a less soluble form if contact with water is a possibility during long term storage. Iron arsenic compounds produced in an autoclave tend to be the most insoluble. Large amounts of iron are required for the process which results in higher costs for this method. Arsenic sulphur compounds also have low solubility and have the advantage of being produced in a roaster or by biological means. Calcium arsenates are no longer considered acceptable for arsenic storage due to reactions with atmospheric carbon dioxide. The arsenic trioxide can be mixed with chemical cements to form a stable product. The cement physically and chemically binds the arsenic, rendering it unavailable to the environment. In some cases the cement can be reused for structural purposes (e.g. roadbeds). Studies have shown cement encapsulation to be the most economically viable long term disposal option.

Initial estimates for off site disposal started at $Cdn. 750.00 per ton, before considering transportation costs which range from $Cdn. 40 to 120 a ton. Considering the large volume of arsenic trioxide to be dealt with, this option is not economically feasible. The total cost for off-site disposal would be in excess of $Cdn. 220 million.

Case studies indicate the material can be dealt with in several ways. One method is to convert the arsenic into a more stable form to reduce the potential environmental impact. Processing costs for this option can be high. The preferred method is to convert the arsenic trioxide into a saleable product, thereby at least partly recovering processing costs. A program is currently underway at the El Indio mine in Chile to market arsenic trioxide produced from a roaster unit. Con mine treated 70,000 tons of stockpiled arsenic trioxide sludge starting in 1981. The project ended in 1990 when the supply of arsenic trioxide was used up. During this period, the sale of arsenic trioxide combined with the value of recovered gold and silver covered the cost of operating the plant.

Table 1
Disposal Cost Summary*

Disposal Method	**Feasibility**	**Capital Cost (a)**	**Operating Cost**	**Transport Cost**	**Cost Recovery**	**Estimated Total Cost**
Secure Landfill (b)	Difficult	0	$750/ton	$40-120/ton	0	$205-225 million
Offsite Treatment (b)	Yes	0	$1600/ton	$40-120/ton	0	$425-445 million
Off-site Incineration (b)	No (Impossible)	0	$1300/ton	$40-120/ton	0	$347-368 million
Bioremediation	Under Development	$20 million	$7390/ton	0	0	$1,542 million
Cement Stabilization (c)	Yes	$20 million	$20-80/ton	0	0	$25-31 million
Phytoremediation (d)	Under Development	N/A	$40-694/ton	0	0	$10-180 million
Ferric Arsenate (e)	Yes	$20 million	$5.09/lb of As removed	0	0	$1,684 million
Arsenic Sulphide (e)	Yes	0	$2.19/lb of As removed	0	0	$725 million
Marketing	Yes	$20 million	$650/ton	$40-120/ton	$202 million	$10-30 million profit

* The cost of accessing the material has not been included as general information on this process could not be obtained.

(a) Capital costs are based on the Con mine's treatment plant capital cost, scaled up to meet Giant's processing requirements.

(b) Off-site disposal method values were based on costs supplied by Proeco.

(c) Cement stabilization values were supplied by Stark Encapsulation.

(d) Phytoremediation capital costs are included in operating costs. Values were supplied by Phytotec Inc.

(e) Stefanakis and Kontopoulas, Pg. 289, Table II. Prices were adjusted to 1983 levels.

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APPENDICES I

APPENDIX A

Abbreviations

Abbreviations

CSI	-	Chemical Specialties Incorporated
CCA	-	Copper Chromate Arsenate
tpd	-	tons per day
tpy	-	tons per year
stpd	-	short tons per day
ACC	-	Acid Copper Chromate
ACA	-	Ammoniacal Copper Arsenate
CZC	-	Chromated Zinc Chloride
U.S.G.S.	-	United States Geological Survey
TDG	-	Transportation of Dangerous Goods
WAROX	-	White ARsenic OXide
lbs/cu. ft.	-	pounds per cubic foot

APPENDIX B

Graphs

TABLE 3

TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS 1/

(Metric tons, arsenic content)

	1992	1993	1994	1995	1996
U.S. supply:					
Imports, metal	740	767	1,330	557	252
Imports, compounds	23,300	20,900	20,300	22,100	21,200
Total	24,000	21,600	21,600	22,700	21,400
Distribution of U.S. supply:					
Exports 2/	94	364	79	430	36
Apparent demand	23,900	21,300	21,500	22,300	21,400
Estimated U.S. demand pattern:					
Agricultural chemicals	3,900	3,000	1,200	1,000	950
Glass	900	900	700	700	700
Wood preservatives	17,900	16,200	18,000	19,600	19,200
Nonferrous alloys and electronics	800	800	1,300	600	250
Other	400	400	300	400	300
Total	23,900	21,300	21,500	22,300	21,400

1/ Data are rounded to three significant digits, may not add to totals shown.

2/ Metal only.

TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS, 1990-94 1/

(Metric tons, arsenic content)

	1990	1991	1992	1993	1994
U.S. supply:					
Imports, metal	796	1,010	740	767	1,330
Imports, compounds	19,900	20,700	23,300	20,900	20,300
Industry stocks, Jan. 1	100	100	--	--	--
Total	20,800	21,800	24,000	21,600	21,600
Distribution of U.S. supply:					
Industry stocks, Dec. 31	100	--	--	--	--
Exports 2/	149	233	94	364	79
Apparent demand	20,500	21,600	23,900	21,300	21,500
Estimated U.S. demand pattern:					
Agricultural chemicals	4,200	5,000	3,900	3,000	1,200
Glass	800	900	900	900	700
Wood preservatives	14,400	14,300	17,900	16,200	18,000
Nonferrous alloys and electronics	800	1,000	800	800	1,300
Other	300	400	400	400	300
Total	20,500	21,600	23,900	21,300	21,500

1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits; may not add to totals shown.

2/ Exports for 1990 include compounds; exports for 1991 through 1994 include metal only.

APPENDIX C

Economic Data

CSI
CHEMICAL SPECIALTIES, INC.

FAX TRANSMISSION

TO: **Paul Greene**

FROM: **Jill Wilson**

COMPANY: **Dillon Consulting**

DATE: 8/13/97 **PAGE 1 OF 1**

FAX #: **403-873-3328**

RE: **Arsenic Trioxide**

If you do not receive all pages please contact sender at 704-455-5181, extension 234.

Our plant manager, Steve Novak, has briefed me on the phone conversations he has had with you and Craig Thomas. Per his request the following is our current specification for arsenic trioxide:

As_2O_3	95-99%
Fe	500 – 5000 ppm
Sb	0.5% - 1.0%
Hg	< 300 ppm
Cl	< 100 ppm
H_2O	< 0.5%

If I can be of any further assistance in this matter please give me a call at the number shown above. This appears to be an interesting project you've undertaken.

Cc: S. Novak

CSI PO BOX 610 5910 PHARR MILL ROAD HARRISBURG, NORTH CAROLINA 28075
PHONE 704-455-5181 FAX 704-455-5987

CSI

FAX TRANSMISSION

TO: Paul Greene

FROM: Jill Wilson

COMPANY: Dillon Consulting

DATE: 8/14/97 **PAGE 1 OF 1**

FAX #: 403-873-3328

RE: General Info CSI

If you do not receive all pages please contact sender at 704-455-5181, extension 234.

In regards to our company and what we do, we are a subsidiary of Laporte plc out of Bedfordshire, UK. We produce a line of products for use by the wood treatment industry – primarily CCA (combination of copper, chrome and arsenic). We purchase in excess of 10 MM lbs. of arsenic trioxide yearly from several countries around the world.

We have three facilities for production of CCA but the processing of arsenic trioxide into arsenic acid is done at our Harrisburg, NC facility only. We buy the arsenic trioxide in bulk bags of either 1 MT or 1.7 MT capacity.

I realize this isn't a lot of information but hopefully it's what you need at the moment. Please keep me informed as to the progress of your project.

Cc: S. Novak

CSI PO BOX 1330 5910 PHARR MILL ROAD HARRISBURG, NORTH CAROLINA 28075
PHONE 704-455-5181 FAX 704-455-5987

ARSENIC

By Daniel L. Edelstein

The United States was the world's largest consumer of arsenic in 1996, accounting for about two-thirds of world demand. Domestic apparent demand for arsenic metal and compounds has remained relatively stable over the past 4 years, averaging about 2,000 metric tons of contained arsenic per year. All domestic arsenic requirements were met by imports; arsenic production in the United States was last reported in 1985. On a contained metal basis, arsenic trioxide accounted for 99% of imports in 1996. China, the world's largest producer of both arsenic trioxide and arsenic metal, was the leading source of U.S. imports of both products. Including material shipped through Hong Kong, China accounted for 44% and 84%, respectively, of trioxide and metal imports.

Legislation and Government Programs

Because of the toxicity of arsenic and its compounds, several environmental and workplace regulations proposed or amended during 1996 specify limitations for arsenic releases or exposure levels. In May, the Environmental Protection Agency (EPA) issued rules that raised the minimum level of substance release that requires public notification for 202 substances under the Community Right-to-Know Act of 1986, for its list of extremely hazardous substances (EHS); the list includes four arsenic compounds. However, the reportable quantities for these compounds remained unchanged at the minimum 1 pound per occurrence (U.S. Environmental Protection Agency, 1996b). In July, EPA proposed adding seven groups to the list of industry groups subject to the reporting requirements of the Community Right-to-Know Act, including coal mining, metal mining, and electric utilities. Arsenic compounds were cited as contaminants in coal and oil combustion products at electric powerplants (U.S. Environmental Protection Agency, 1996a).

In July, the Occupational Safety and Health Administration (OSHA), as part of a Presidential directive to remove or revise standards that are out of date, duplicative, or not needed to maintain employee health and safety, proposed revision of medical surveillance requirements for certain workers exposed to inorganic arsenic, including elimination of the semiannual sputum cytology examinations and reduction from semiannual to annual the frequency of required chest x-rays for workers 45 years of age or older or workers having had 10 or more years of exposure to arsenic at levels above the action level. In reevaluating the sputum-cytology provision, OSHA found no studies that addressed the efficacy of this test as a screening tool for lung cancer for employees specifically exposed to inorganic arsenic. Similarly, the efficacy of providing semiannual chest x-rays as a screening tool had not been established (U.S. Department of Labor, 1996).

Consumption

Overall consumption of arsenic remained relatively unchanged in 1996, for the third consecutive year. Estimated demand for arsenic in wood preservatives, which accounted for about 90% of total arsenic demand, was essentially unchanged from that of 1995, despite growth in the domestic housing industry; housing starts and construction spending rose by about 9% and 4%, respectively. Demand for arsenic by wood preservative formulators in 1995 had been boosted by in-process construction and restocking by distributors of pressure-treated lumber following the 1994 surge in housing. Arsenic trioxide was consumed in the production of arsenic acid for formulation of chromated copper arsenate (CCA) wood preservatives by the three principal producers of arsenical wood preservatives: Hickson Corp., Conley, GA; CSI, Harrisburg, NC; and Osmose Corp., Memphis, TN. Osmose also produces arsenic acid for the glass industry as a fining agent to disperse air bubbles.

The demand for arsenic metal for nonferrous alloys especially battery-lead alloys, plummeted for the second consecutive year. Consumers, fearing disruption from Chinese suppliers, may have over-brought in 1994, reducing their need for metal purchases in the 2 subsequent years. Some of the surplus metal inventories may have been exported in 1995, accounting for a rise in metal exports. Also, continued growth in market share for maintenance-free automotive batteries, which require little or no arsenic, may be further lowering demand for arsenic metal. Commercial grade arsenic metal 99% pure, is used in lead- and copper-based alloys as a minor additive (0.01% to 0.5%) to increase strength in the posts and grids of lead-acid storage batteries and to improve corrosion resistance and tensile strength in copper alloys. About 15 tons of high-purity arsenic metal, of 99.9999% or higher purity, was used in the manufacture of crystalline gallium arsenide, a semiconducting material used in optoelectronic circuitry, high-speed computers, and other electronic devices.

Arsenic consumed in agricultural uses continued to decline following the EPA's 1993 cancellation of arsenic acid for use as a cotton desiccant. The remaining agricultural use for arsenic was as an herbicide for control of weeds. ISK Bioscience, Mentor, OH, produced the arsenical herbicide monosodium methanearsonate (MSMA) at a plant in Houston, TX.

Prices

Prices for arsenic trioxide are not published. The average customs value for imported arsenic trioxide in 1996 was 22 cents per pound, down by about 2 cents per pound from that of 1995. The decline was attributed mostly to the lower value of some off-grade material imported from Chile for blending with high-purity material. High-purity trioxide from Mexico averaged 33 cents per pound. Prices for high-grade (minimum 99%) arsenic trioxide generally are quoted at an 8- to 12-cent-per-pound premium to low-grade (minimum 95%) arsenic trioxide. Owing to lowered demand and surplus supplies, prices for arsenic metal declined sharply, the Chinese import price averaging 40 cents per pound, down almost 40% from that of 1995.

World Review

Commercial-grade arsenic trioxide was recovered from the smelting or roasting of nonferrous metal ores or concentrates in at least 18 countries. High-arsenic smelter or roaster dusts and residues that usually are not processed to commercial-grade trioxide are recovered in several other countries as well as at plants in countries producing commercial-grade material. This material is frequently stockpiled and could be available for future processing. Ghana is one such country that has the estimated capacity to produce about 9,000 tons per year of crude trioxide from gold roasting operations. Most countries do not report their arsenic production, and world production values have a high degree of uncertainty. China was the world's largest producer as well as the major source of U.S. imports. Chinese production was estimated to have declined sharply in 1996 owing to the combined impact of environmental constraints, treatment of lower arsenic content ores, and weather-related problems. In France, Societe d'Exploitation Pyrometalurgie Salsigne, formed in November 1992, began commercial production of arsenic trioxide in 1993. The company which purchased the gold smelter and roaster formerly operated by Mines et Products Chimiques de Salsigne, has the capacity to produce significant quantities of refined arsenic trioxide. However, the company faced financial difficulties in 1995 and had filed for bankruptcy. Production had been halted by yearend 1995, and the plant remained idle throughout 1996. A second producer, Metaleurop SA, with capacity to produce about 6,000 tons per year of high purity trioxide, reportedly processed some imported crude trioxide from Ghana.

In Chile, production from the roasting of gold-copper ores at the El Indio Mine increased in 1996, countering the decline in Chinese production. U.S. imports from Chile rose more than 270%, making it the second largest source for domestic imports of arsenic trioxide. Included in both imports and production from Chile in 1996 were an estimated 2,000 tons of stockpiled off-grade material, not previously counted as production, that was imported for blending with high-grade trioxide.

Arsenic metal, which accounts for only 3% of world demand for arsenic, was produced by the reduction of arsenic trioxide. Commercial-grade arsenic metal, 99% pure, accounted for the majority of world arsenic metal production and was produced only in China. High-purity arsenic, 99.9999% pure or greater, for use in the semiconductor industry was produced by about 10 companies. Furukawa Electric Co. Ltd. in Japan and Preussag AG in Germany were believed to be the world's largest producers, with capacities of 30 and 15 metric tons per year, respectively.

Outlook

With the major market for arsenic being the production of arsenical wood preservatives, the demand for arsenic is closely tied to the home construction market, where wooden decks containing arsenical preservatives have become ubiquitous. According to data published by the American Wood Preservative Institute, demand for treated wood rose precipitously in the 5-year period ending in 1988. In 1988, about 450 million cubic feet of wood were treated with waterborne preservatives (98% estimated to be CCA), compared with 300 million cubic feet in 1984. Demand softened in the 1989-91 period before resuming its upward trend. In 1995, the last year for which data are available, the quantity of wood treated with waterborne preservatives, was about 450 million cubic feet, down from about 500 million in 1994. In 1995, waterborne preservatives were used for about 75% of all treated lumber.

The apparent demand for arsenic trioxide in wood preservatives declined slightly in 1996 despite an increase in housing starts. Restocking by wood preservative manufacturers and carry-over from the 13% growth in housing starts in 1994 may have served to boost apparent demand in 1995. Future demand for arsenic is expected to closely follow that for new home construction, although the replacement and renovation markets could increase as a percentage of total market share. The prohibition on use of CCA preservatives in certain applications and the greater acceptance of alternative preservatives could negatively affect future demand.

Despite environmental regulation that has led to global dislocations of production over the past decade, including cessation of production in two historically large producing countries, Sweden and the United States, new suppliers have emerged to fill the voids. Although environmental pressures may continue to cause curtailment of existing capacity, given the abundance of high-arsenic residues from nonferrous metal processing, world supplies of arsenic trioxide are expected to remain adequate to meet projected need. Environmental regulation may, in fact, encourage commercial production from existing stockpiles of noncommercial material.

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1995 Wood Preserving Industry Production Statistical Report.

TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS 1/

(Metric tons, arsenic content)

	1992	1993	1994	1995	1996
U.S. supply					
Imports, metal	740	767	1,330	557	252
Imports, compounds	23,300	20,900	20,300	22,100	21,200
Total	24,000	21,600	21,600	22,700	21,400
Distribution of U.S. supply					
Exports 2/	94	364	79	430	36
Apparent demand	23,900	21,300	21,500	22,300	21,400
Estimated U.S. demand pattern					
Agricultural chemicals	3,900	3,000	1,200	1,000	950
Glass	900	900	700	700	700
Wood preservatives	17,900	16,200	18,000	19,600	19,200
Nonferrous alloys and electronics	800	800	1,300	600	250
Other	400	400	300	400	300
Total	23,900	21,300	21,500	22,300	21,400

1/ Data are rounded to three significant digits; may not add to totals shown.

2/ Metal only.

TABLE 2
U.S. IMPORTS FOR CONSUMPTION OF ARSENICALS 1/

Class and country	1995 Quantity 2/ (metric tons)	1995 Value (thousands)	1996 Quantity (metric tons)	1996 Value (thousands)
Arsenic trioxide				
Belgium	786	$420	579	$314
Bolivia	--	--	120	55
Chile	3,210	1,260	8,790	2,930
China	15,900	8,230	11,000	5,650
France	2,820	1,550	2,480	1,360
Hong Kong	1,510	619	1,380	681
Mexico	3,560	2,560	2,980	2,140
Philippines	1,080	430	612	231
United Kingdom	1	2	--	--
Other	195	90	18	20
Total	29,000	15,200	28,000	13,400
Arsenic acid				
Canada	--	--	(3/)	2
Israel	(3/)	3	1	13
Total	(3/)	3	1	14
Arsenic metal				
China	491	709	212	185
Germany	37	2,000	10	2,110
Japan	29	1,400	29	1,480
United Kingdom	--	--	(3/)	23
Other	(3/)	3	--	--
Total	557	1,100	252	3,790

1/ Data are rounded to three significant digits; may not add to totals shown.

2/ Data erroneously reported as "thousand metric tons."

3/ Less than 1/2 unit.

Source: Bureau of the Census.

TABLE 3
AVERAGE ARSENIC PRICES

(Cents per pound)

	1995	1996
Trioxide, Mexican	33	33
Metal, Chinese	66	40

Source: Calculated from Bureau of the Census import data.

TABLE 4
ARSENIC TRIOXIDE 1/ WORLD PRODUCTION, BY COUNTRY 2/ 3/

(Metric tons)

Country 4/	1992	1993	1994	1995	1996 e/
Belgium e/	2,000	2,000	2,000	2,000	2,000
Bolivia	633	663	341	362 r/	370
Canada e/	250	250	250	250	250
Chile e/	6,016 5/	6,200	6,300	6,400	9,000
China e/	15,000 r/	14,000 r/	18,000 r/	21,000 r/	15,000
France e/	2,000	3,000	6,000	5,000	3,000
Georgia e/	1,500	1,000	500	400	400
Germany e/	300	300	300	250 r/	250
Ghana e/ 6/	500	500	500	500	500
Iran e/	492 5/	500	500	500	500
Japan e/	50	40	40	40	40
Kazakstan e/	2,000	2,000	1,500	1,500	1,500
Mexico	1,293	4,447	4,400 e/	4,500 e/	4,300
Namibia 7/	2,456	2,290	3,047 r/	1,661 r/	1,100
Peru 8/	644 r/	391 r/	286 r/	285 r/ e/	285
Philippines e/	8,000	2,000	2,000	2,000	2,000
Portugal e/	150	150	150	100	100
Russia e/	2,500	2,000	1,500	1,500	1,500
Total	45,800 r/	41,700 r/	47,600 r/	48,200 r/	42,100

e/ Estimated. r/ Revised.

1/ Including calculated arsenic trioxide equivalent of output of elemental arsenic and arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production.

2/ World totals and estimated data are rounded to three significant digits; may not add to totals shown.

3/ Table includes data available through Apr. 1, 1997.

4/ Austria, Hungary, the Republic of Korea, South Africa, Spain, the United Kingdom, and former Yugoslavia have produced arsenic and/or arsenic compounds in previous years, but information is inadequate to make reliable estimates of output levels, if any.

5/ Reported figure.

6/ Estimated commercial byproduct of gold ore roasting. Does not include additional byproduct production of noncommercial grade material estimated at 4,000 tons in 1992, and up to 9,000 tons per year in 1993-96.

7/ Output of Tsumeb Corp. Ltd. only.

8/ Output of Empresa Minera del Centro del Peru (Centromin Peru) as reported by the Ministerio de Energia y Minas.

ARSENIC

(Data in metric tons, unless otherwise noted)

Domestic Production and Use: All arsenic metal and compounds consumed in the United States were imported, principally from China. More than 95% of the arsenic consumed was in compound form, principally as arsenic trioxide. Three principal manufacturers of wood preservatives consumed most of the arsenic trioxide for the production of arsenic acid for formulation of chromated copper arsenate (CCA) wood preservatives. Arsenic acid was also consumed by one manufacturer of arsenical herbicides. Metallic arsenic was consumed in the manufacture of nonferrous alloys, principally in lead alloys used in lead-acid batteries. About 15 tons of high-purity arsenic was consumed in the manufacture of semiconductor materials. About 90% of all arsenic was consumed in the production of wood preservatives; the balance was consumed in glass manufacturing, agricultural chemicals, nonferrous alloys, and miscellaneous uses. The value of arsenic metal and compounds consumed was estimated at $20 million.

Salient Statistics—United States:	1992	1993	1994	1995	1996^e
Imports for consumption:					
Metal	740	767	1,330	557	250
Trioxide[1]	30,700	27,500	26,800	29,000	29,000
Arsenic acid	40	—	5	([2])	1
Exports, metal	94	364	79	430	20
Consumption, apparent, arsenic content	23,900	21,300	21,500	22,300	22,000
Price, cents per pound, average:[3]					
Trioxide, Mexican	29	33	32	33	33
Metal, Chinese	56	44	40	66	53
Net import reliance[4] as a percent of apparent consumption	100	100	100	100	100

Recycling: Process water and contaminated runoff collected at wood treatment plants are reused in pressure treatment. Gallium arsenide scrap from the manufacture of semiconductor devices is reprocessed for gallium and arsenic recovery. Domestically, no arsenic is recovered from arsenical residues and dusts at nonferrous smelters, although some of these materials are processed for recovery of other metals.

Import Sources (1992-95): China, 50%; Chile, 16%; Mexico, 12%; and other, 22%.

Tariff: Item	Number	Most favored nation (MFN) 12/31/96	Non-MFN[5] 12/31/96
Metal	2804.80.0000	Free	13.2¢/kg.
Trioxide	2811.29.1000	Free	Free.
Sulfide	2813.90.1000	Free	Free.
Acid[6]	2811.19.1000	2.3% ad val.	4.9% ad val.

Depletion Allowance: 14% (Domestic), 14% (Foreign).

Government Stockpile: None.

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ARSENIC

Events, Trends, and Issues: Domestic demand for arsenic in the wood preservative industry was relatively unchanged in 1996, despite projected growth in the domestic housing industry. Demand in 1995 had been boosted by in-process construction and restocking by distributors of pressure-treated lumber following the 1994 surge in housing construction. The apparent demand for arsenic metal for nonferrous alloys, especially battery-lead alloys, remained low for the second consecutive year. Consumers, fearing disruptions from Chinese suppliers, may have overbought in 1994, reducing their need for additional material in the subsequent 2 years. Also, continued growth in market share for maintenance-free automotive batteries, which require little or no arsenic, may be further lowering demand for arsenic metal.

Because of the toxicity of arsenic and its compounds, numerous environmental and workplace regulations proposed or amended during 1996 specify limitations for arsenic releases or exposure levels. In May, the Environmental Protection Agency issued revised rules for reportable quantities, under the Community Right-to-Know Act of 1986, for its list of extremely hazardous substances, which includes numerous arsenic compounds. The reportable quantity for arsenic compounds remained at 1 pound. In July, the Occupational Safety and Health Administration, as part of a review process to modify out-of-date regulations, proposed revision of medical surveillance requirements for certain workers exposed to inorganic arsenic, including elimination of the semiannual sputum cytology examinations and reduction, from semiannual to annual, of the frequency of required chest x-rays.

World Production, Reserves, and Reserve Base:

	Production (Arsenic trioxide)		Reserves and reserve base[7] (Arsenic content)
	1995	1996[e]	
United States	—	—	
Belgium	2,000	2,000	
Chile	6,400	6,500	World reserves and reserve base are thought to be about 20 and 30 times, respectively, annual world production.
China	13,000	13,000	
France	5,000	4,000	
Kazakstan	1,500	1,500	
Mexico	4,500	4,500	
Namibia	2,300	2,300	
Philippines	2,000	2,000	
Russia	1,500	1,500	
Other countries	2,600	3,000	
World total	41,000	41,000	

World Resources: World resources of copper and lead contain about 11 million tons of arsenic. Substantial resources of arsenic occur in copper ores in northern Peru and the Philippines and in copper-gold ores in Chile. In addition, world gold resources, particularly in Canada, contain substantial resources of arsenic.

Substitutes: Substitutes for arsenic compounds exist in most of its major uses, although arsenic compounds may be preferred because of lower cost and superior performance. The wood preservatives pentachlorophenol and creosote may be substituted for CCA when odor and paintability are not problems and where permitted by local regulations. A recently developed alternative, ammoniacal copper quaternary, which avoids using chrome and arsenic, has yet to gain widespread usage. Nonwood alternatives, such as concrete, steel, or plastic lumber, may be substituted in some applications for treated wood. A South American hardwood, ipe, which requires no chemical treatment, has been used in some localities in oceanfront boardwalks.

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[e] Estimated.

[1] Arsenic trioxide (As_2O_3) contains 75.7% arsenic by weight.

[2] Less than ½ unit.

[3] Calculated from Bureau of the Census import data.

[4] Defined as imports - exports + adjustments for Government and industry stock changes.

[5] See Appendix B.

[6] Tariff is free for Canada, Israel, Caribbean Basin countries, and designated Beneficiary Andean and developing countries.

[7] See Appendix C for definitions. The reserve base for the United States was estimated at 80,000 tons.

APPENDIX D

Arsenic Trioxide Market Processing Data

Consommation
et Corporations Canada

Bureau des brevets

Ottawa, Canada
K1A 0C9

Consumer and
Corporate Affairs Canada

Patent Office

(11) (C) **1,314,149**

(21) 554,182

(22) 1987/12/11

(45) 1993/03/09

(52) 53-176

(51) INTL.CL.^{5} C22B-30/04

(19) (CA) **CANADIAN PATENT** (12)

(54) Methods of Recovering Arsenic Values from Waste

(72) Derka, Jaroslav R. , Canada

(73) Same as inventor

(57) 27 Claims

[illegible]

ABSTRACT

A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process comprising the step of evaporating the arsenic values from the arsenic containing material into a gas stream which gas stream does not react with the arsenic values. A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process utilizing electrical energy for evaporation of arsenic trioxide in an evaporator into a gas stream and after separation of arsenic trioxide and any residue, the clean gas may be recycled to the evaporator thus minimizing possible emissions permitting the process to be carried out in a closed circuit thus substantially eliminating emissions.

FIELD OF INVENTION

This invention relates to methods of recovering arsenic values from arsenic bearing materials.

BACKGROUND OF THE INVENTION

Ores containing arsenic have to be subjected to an arsenic removal step prior to the extraction of other values. A typical example is gold ore - arsinopyrite.

The removal of arsenic is most often accomplished by roasting.

When roasted, Arsenic is oxidized to As_2O_3, and at the roasting temperature leaves the Roaster as a vapour together with the oxidation products of Sulphur, - Sulphur Dioxide and Sulphur Trioxide. The presence of Sulphur oxides with Arsenic complicates the subsequent Gas Cleaning step, resulting in an impure (crude) Arsenic Trioxide dust being trapped in a bag-house, following precipitation from the gas stream by the addition of cold air. The off-gas is usually discharged to the atmosphere with consequent environmental problems.

A major consumer of Arsenic Trioxide (As_2O_3) is the wood preservative industry. Since As_2O_3 from the roasting operation is not of a sufficient purity, a further refining step has to be employed.

Refining is usually accomplished by one of two approaches:

(a) Hot Water Leach, by one of two approaches.

(b) Ammonia Leach

(a) Hot Water Leach:

Approach 1

Hot water is used to dissolve the As_2O_3 from the crude feed material. Undissolved solids are separated from the solution by filtration, and the filtered solution is either cooled or evaporated in a crystallizer to form As_2O_3 crystals.

*

B

Approach 2

Due to the positive effect of temperature on solubility of As_2O_3, pressure leaching may be employed with a higher water temperature hence obtaining a higher solubility of As_2O_3. The cost of energy with this approach is improved over Approach 1 but still remains very high.

(b) Ammonia Leach:

The Ammonia Leach process has an advantage over the hot water leach approach in that the solubility of As_2O_3 is higher in ammonia solution. However the only user of this process of which the inventor is presently aware has presently ceased operations due to technical difficulties.

Both approaches additionally have a common problem. Re-contamination of the residue is caused by a reaction between dissolved Arsenic and the Iron content of the residue, resulting in a slimy material which is difficult to filter. Since this residue contains in some cases significant amounts of precious metals, this is a serious problem. Further these approaches are generally complicated and have a high operating and capital cost.

U.S. patent 3923478 teaches pyrites-roast gas at 350-400 degrees C composed mainly of SO_2 with As_2O_3, iron oxide dust, SO_3, and other impurities being scrubbed in a closed system with a solvent (preferably aqueous) for As_2O_3. The product is obtained by concentration and crystallization and unwanted deposits formed are removed by dissolution in unsaturated As_2O_3 solution. Using systems in parallel and switching liquid flows makes possible continuous operation, it is alleged, with minimal solid or liquid effluent.

Thus a process and an apparatus is asserted as having been provided for recovering arsenic trioxide from a gas by washing out the oxide from the gas with a liquid having the ability of dissolving arsenic trioxide. The purported invention is characterized that non-desired deposits in the apparatus formed in connection with a saturated solution are removed by

dissolution with an unsaturated solution of arsenic trioxide. See also corresponding Canadian Letters patent 1033538.

U.S. patent 4588564 relates to a process for recovering arsenic trioxide from scrubbing water used to scrub the flue gas of sulfide ore smelting. The crude arsenic trioxide crystals collected from the scrubbing solution which contains plaster as an impurity are purified by treating with hydrochloric acid of a concentration of 50-150 g/l at a temperature not higher than 30°C.

U.S. patent 4605812 purports to teach a process for the removal of arsenic from gases whereby arsines are removed from streams of hydrocarbons or inert gases by contacting the streams with copper (II) chromite catalyst.

U.S. patent 4615731 purports to teach a hydro metallurgical process for treating a feed comprising an aqueous acidic solution containing dissolved therein one or more precious metals selected from the group, platinum group metals and gold and one or more of the nuisance elements bismuth lead, tin, arsenic and antimony, to separate the precious metals from the nuisance elements comprising:

(i) treating the aqueous acidic solution with sulfur dioxide in the presence of selenium and a halide to reduce and precipitate selectively selenium and precious metals, and

(ii) separating the precipitated components from the remaining solution; thereby separating selenium and precious metals from the nuisance elements.

U.S. patent 4489046 purports to teach a method for converting an arsenic-containing waste product to a depositable, substantially arsenic-free form by fuming-off the arsenic content thereof. The method comprises melting the waste product under oxidizing conditions in a furnace to form an oxidic slag melt; causing turbulence of the melt, while maintaining a reducing atmosphere supporting the formation of arsenic (III) oxide at the furnace

temperature driving-off arsenic content of the waste product substantially in the form of gaseous arsenic (III) oxide; separating the formed oxide by condensation and recovering the same and removing from said furnace a substantially arsenic-free depositable slag.

U.S. patent 4244735 purports to teach a process for the hydrometallurgical recovery of metals, such as, lead, silver, gold, antimony, and bismuth from materials such as flue dust in the presence of arsenic, comprising precipitating arsenic as an insoluble ferric-arsenic compound in the first processing step, carrying the insoluble arsenic compound through a chloride leach step, in which it is insoluble, to recover the metals, and disposing of the residue in which the arsenic has been fixed with ferric ions to render it non-polluting, or alternatively, recovering the arsenic by caustic leach and crystallization.

Swiss patent 273779 purports to teach a continuous refining process which it is purported, can be done more intensively and is carried out in equipment which consists of a lined vessel, screw feeder with a rotating disc mounted on it and bearing fixed knives, screening plates. Silite heaters and a discharging screw, moving inside the vessel. The product to be refined is fed on to the rotating disc of the screw feeder having a sealed hopper. The distance between the cover and the disc is relatively small (i.e. 1/5 to 1/8 of the diameter of the disc), as a result of which uniform heating of the reaction zone is obtained and dust-formation of the incoming material is eliminated. The product to be refined is fed on to the disc, which is red-hot (500-600 degrees C), and the Arsenic trioxide is purported to immediately begin to evaporate, which causes the original thickness of the layer of material to diminish. The solid residue, which comprises about 10% of the original material put on the disc, is removed by the fixed knife and the screw being conveyed to the hopper. In this way the disc is cleaned ready for the fresh deposit of material. The vapours of the trioxide go along into a crystallizer of

the usual type. The device operates under minimum vacuum (0.5-1.0 mm of water column).

German reference 131850 purports to teach that Sulphur dioxide gases containing As_2O_3, halides and dust, are cleaned by washing with circulating H_2SO_4 solution of which the concentration is adjusted to such a low value that the halides are being dissolved, separating the H_2SO_4 solution and subjecting this solution to a vacuum evaporation to evaporate the halides and crystalize As_2O_3. The purified H_2SO_4 is recycled.

Once again these approaches are generally complicated and have high operating costs and capital costs.

It is therefore an object of this invention to provide an improved process for the recovery of Arsenic values.

It is a further object of the invention to provide such process at reduced operating and reduced capital costs.

Further and other objects of the invention will be realized by those skilled in the art from the following Summary of the Invention and Detailed Description of Embodiments thereof.

SUMMARY OF THE INVENTION

According to one aspect of the invention, a process is provided for the recovery of Arsenic values from Arsenic containing material which may also contain Sulphur in one embodiment the Arsenic being in the form of As_2O_3, the process comprising the step of evaporating (in a wet or dry state) the Arsenic values from the Arsenic containing material into a gas stream which gas stream does not react with the Arsenic values. The gas stream is then cooled to precipitate the Arsenic. The residue from which the arsenic was evaporated may then be treated for removal of the metal values. The simplicity of the process is reflected in relatively low operating costs and relatively low capital expenditures. Without the presence of Sulphur, the As_2O_3 vapour can be well cleaned of any carry-over solids (prior to precipitation) giving a high purity As_2O_3 product, acceptable to for example the wood preserving industry. Preferably the evaporation of the Arsenic values is as arsenic trioxide (As_2O_3) near its boiling point.

According to another aspect of the invention the evaporation of the arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil or hydrocarbon gas.

(b) Fluid bed heated by combustion of oil or hydrocarbon gas or by electrical energy.

(c) Electrical plasma reactor.

According to another aspect of the invention the arsenic values (for example the arsenic trioxide) are precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water evaporation. Thus the As_2O_3 is deposited on the surface of a cold particle causing it to grow to a form of little balls. The size of the balls of As_2O_3 may be controlled by the amount of precipitation onto the coarse particles. Thus "dusting" during handling of the "balled" material is reduced.

According to another aspect of the invention the process may be carried out utilizing electrical energy for evaporation of arsenic trioxide in an evaporator into a gas stream and after separation of the residue and precipitation of arsenic trioxide, the clean gas stream may be recycled back to the evaporator thus minimizing possible atmospheric emissions.

Thus, according to another aspect of the invention the process may be carried out in a closed circuit thus substantially eliminating emissions giving rise to substantial and significant environmental benefits.

According to another aspect of the invention the process may be carried out utilizing combustion of oil or hydrocarbon gas for evaporation of arsenic trioxide in the evaporator. Due to production of combustion products with this process the gas after cleaning can be vented.

The invention will now be illustrated with reference to the following drawings of embodiments of the invention and the detailed description of the embodiments thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow sheet illustrating a process carried out according to an embodiment of the invention.

Figure 2 is a flow sheet illustrating another process according to another embodiment of the invention.

Figure 3 is a flow sheet illustrating another process according to another embodiment of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

With reference to Figures 1 and 2, two processes are disclosed schematically according to the flow sheets. The difference between the processes relate to the energy source used to generate the heat in the evaporator to evaporate the Arsenic trioxide (As_2O_3).

With reference to Figures 1 and 2, the crude material containing arsenic trioxide 10 is exposed to heat in the evaporator 50. The arsenic trioxide vapour is transported from the evaporator 50 by a stream of other gas e.g. Nitrogen (See Figure 3) and the mixture leaves at a temperature of 250 - 500 degrees C (preferably 350 - 450 degrees C.) 12.

The evaporator 50 could be a:

(a) heated chamber - (for example for fine material which wouldn't stay in a fluid bed)

(b) fluid bed

heated by oil or hydrocarbon gas combustion, (Figure 1), or by electrical energy (Figure 2). The carry-over solids (residue) 24 are removed from the hot gas stream in a solids separator 52, preferably in a double filtration baghouse.

The separated residue 24, usually containing other metallic values is then available for further treatment as the major portion of arsenic was removed. The clean gas 14 containing As_2O_3 vapour, or As_2O_3 vapour and water vapour and other gases, depending on the source of energy used in the evaporator, is then cooled in cooling and As_2O_3 removal section S_4 by injection of water, preferably condensate 20 from the scrubbing circuit to a temperature:

(a) above boiling point of water (110-200 degrees C.) and the precipitated Arsenic trioxide is then removed in the cold baghouse.

b) just above point of Arsenic trioxide precipitation (depending upon concentration of arsenic trioxide in the vapour), generally between 300 degrees C. to 460 degrees C., and the precipitation is accomplished by further cooling in a fluid bed of Arsenic trioxide by spray of water (preferably condensate from scrubbing circuit) 20, to produce a desirable coarse product 26. (See Figure 3). The remaining gas is then scrubbed of Arsenic trioxide in a scrubber - cooler 56 and excess water vapour is condensed. The condensate 20 is recycled for cooling of the hot clean gas 14. The surplus 22 will be disposed of. The scrubbed cooled gas is then:

(a) recycled to the evaporator as Arsenic trioxide vapour carrier via 18 - if electric energy is utilized for heating of the evaporator.

(b) sent to stack. (See 18 of Figure 2).

With reference to Figures 1 and 2, equipment suitable for use

(1) as the evaporator 50 may comprise:

(a) Fluid bed heated by an electrically preheated circulating gas.

(b) Fluid bed heated by inserted electrical heaters.

(c) Fluid bed heated by combustion of oil or hydrocarbon gas.

(d) Evaporation chamber heated by either electricity or by combustion of oil or hydrocarbon gas fine grained crude.

(2) for Solids separation 52 may comprise:

(a) High temperature bag-house, preferably two in series.

(3) For cooling and As_2O_3 removal referred to at 54, the equipment may comprise:

(a) A fluid bed of coarse As_2O_3 particles cooled by spraying with a scrubber solution or water 20. As_2O_3 deposits on the cold particles thus allowing the production of a coarse particle As_2O_3 product. The remaining As_2O_3 dust is removed in a cold bag-house and can be sent to either product storage or back for evaporation.

(b) Injection of scrubber condensate directly to hot gas-adiabatic cooling. The precipitated As_2O_3 is removed from the gas stream in a cold bag-house and sent to product storage.

(c) combination of both - cooling to temperature of As_2O_3 saturation by injection of condensate or water, then precipitation of As_2O_3 as per (a).

(4) As Scrubber and Water Condenser shown at 56:

(a) Scrubbing traces of As_2O_3 from the gas stream is accomplished in a tower or a venturi using the condensate from the following condenser. The amount of condensate to be used for scrubbing is determined by the consumption of Arsenic bearing scrubber solution used for gas cooling.

(b) As a Water condenser:

The water condenser can be a tray or preferably a packed tower which is cooled, depending on scrubber efficiency, by:

- directly injected cooling water - recycled, indirectly cooled condensate

Depending on the temperature of the cooling water, the Gas Cooling-Water Condenser may employ an additional cooling (for example, heat pump) so that a minimum of water vapour is recycled to evaporate.

The operating conditions may be as follows:

(1) Evaporator 50

Temperature 300-600 degrees C., preferably 350-450 degrees C. Pressure in freeboard - approximately minus 1 inch of H_20.

(2) Hot bag-house

Temperature 300-400 degrees C. Pressure - approximately minus .5 psig.

(3) Precipitator

Temperature 80-150 degrees C. Pressure - approximately minus 1 psig.

(4) Cold bag-house

Temperature 80-150 degrees C., preferably 110-120 degrees C.

(5) As_20_3 Scrubber

Temperature 65-80 degrees C., preferably 71 degrees C. Pressure - approximately minus 2.1 psig.

(6) Water Condenser

Temperature 5-10 degrees C., preferably lowest possible.

As many changes can be made to the embodiments without departing from the scope of the invention, it is intended that all material contained herein be interpreted as illustrative of the invention and not in a limiting sense.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE AS FOLLOWS:

1. A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process comprising the step of evaporating the arsenic values from the arsenic containing material into a gas stream which gas stream does not react with the arsenic values.

2. The process of Claim 1, wherein the arsenic is in the form of As_2O_3.

3. The process of Claim 1, wherein the gas stream is, after solids separation, cooled to precipitate the arsenic.

4. The process of Claim 2, wherein the gas stream is, after solids separation, cooled to precipitate the arsenic.

5. The process of claim 2, 3, or 4, wherein the evaporation of the arsenic values is as arsenic trioxide (As_2O_3) near its boiling point.

6. The process of Claim 1, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

   (a) A chamber heated by a combustion of oil, hydrocarbon gas or by electrical energy; or

   (b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy.

7. The process of Claim 2, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas, or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy; or

(c) Electrical plasma reactor.

8. The process of Claim 3, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas, or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy.

9. The process of Claim 4, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas, or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy.

10. The process of Claim 1 further comprising the step of the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

11. The process of Claim 2, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from

the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

12. The process of Claim 3, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

13. The process of Claim 4, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

14. The process of Claim 6, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

15. The process of Claim 7, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

16. The process of Claim 8, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

17. The process of Claim 9, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from

the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

18. The process of Claim 10, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

19. The process of Claim 11, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

20. The process of Claim 12, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

21. The process of Claim 13, wherein the size of the particles may be controlled by the amount of precipitation of the arsenic onto coarse particles.

22. The process of Claim 14, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

23. The process of Claim 15, wherein the size of the particles may be controlled by the amount of precipitation of arsenic onto coarse particles.

24. The process of Claim 16, wherein the size of the particles may be controlled by the amount of precipitation of arsenic onto coarse particles.

25. The process of Claim 17, wherein the size of the particles may be controlled by the amount of precipitation of arsenic onto coarse particles.

26. A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process utilizing electrical energy for evaporation of arsenic trioxide in an evaporator into a gas stream and after separation of arsenic trioxide and any residue, the clean gas may be recycled to the evaporator thus minimizing possible emissions permitting the process to be carried out in a closed circuit thus substantially eliminating emissions.

27. The process of Claim 1, wherein the process utilizes combustion of oil or hydrocarbon gas for evaporation of arsenic trioxide in an evaporator.

*

FIG.1.

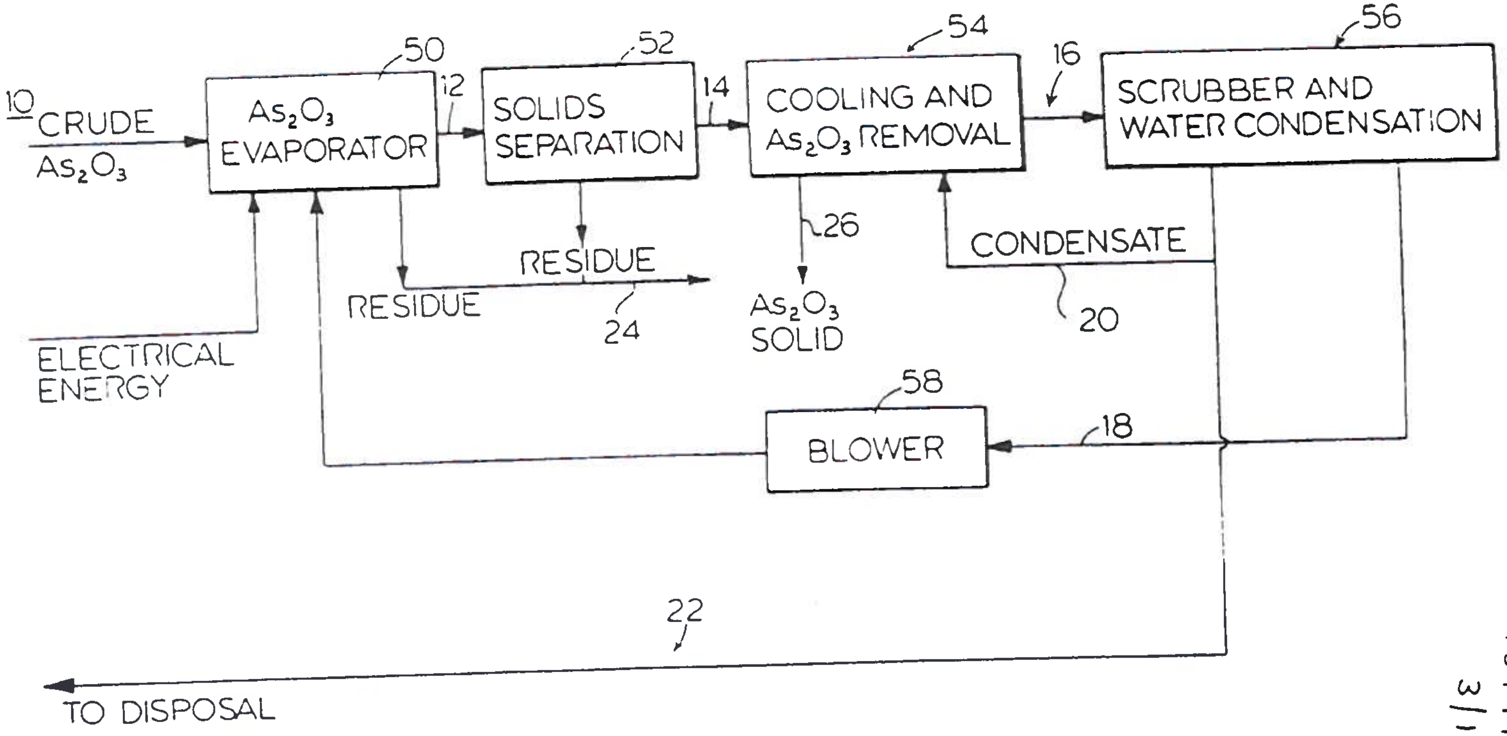

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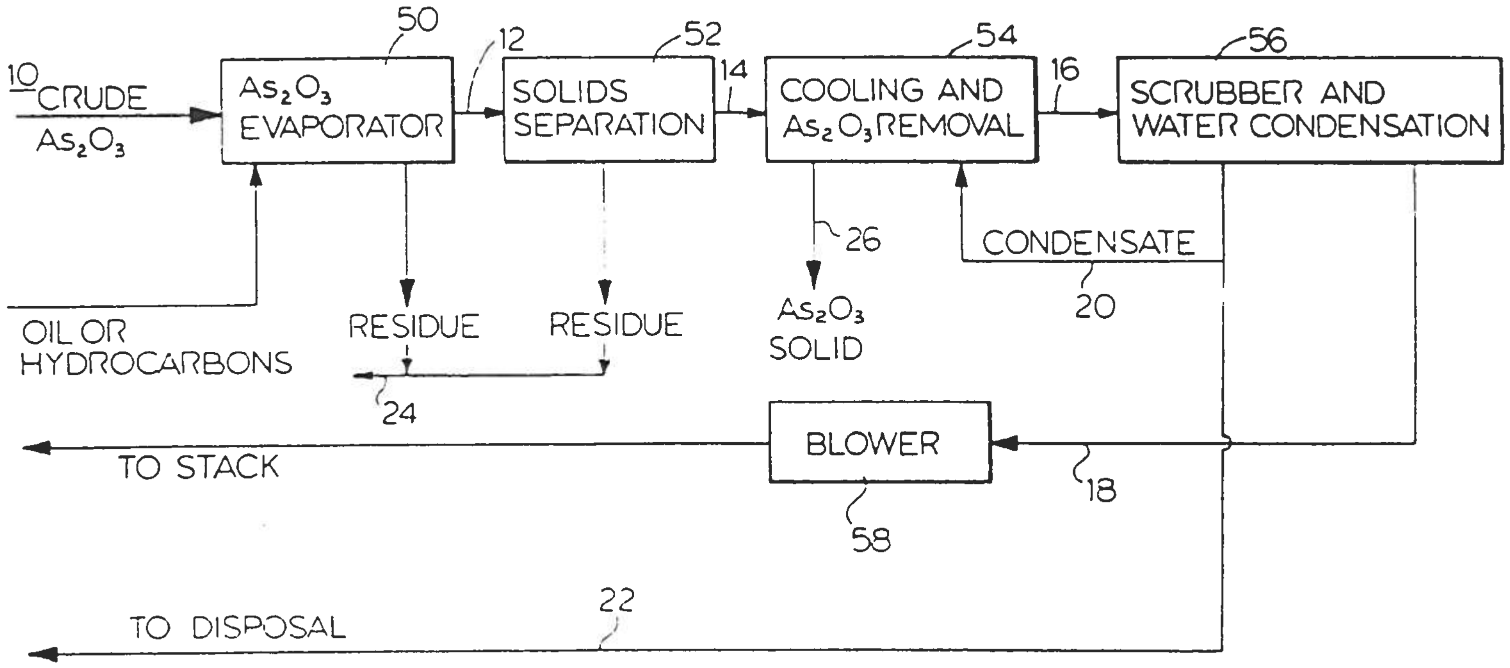
FIG. 2.



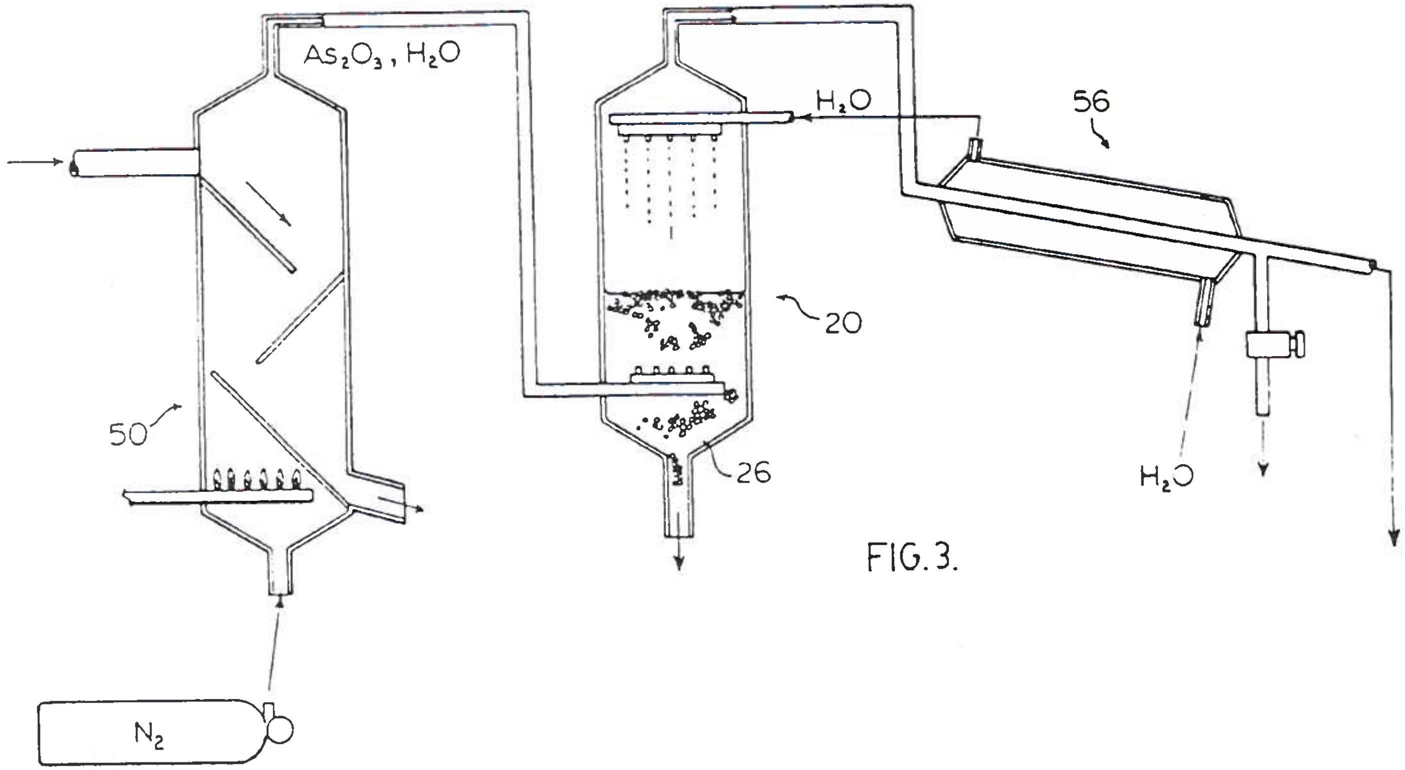


FIG. 3.

APPENDIX E

Gold Recovery Data

APPENDIX F

Materials Handling & Storage Data

* *
*   TRANSPORT OF DANGEROUS GOODS (TDG)   *
*   *
*   Canadian Centre for Occupational Health and Safety   *
* * * * * * * * * * * * * * * * * Issue: 97-1 (February, 1997) *

RECORD NUMBER: 243
SHIPPING NAME: Arsenic trioxide
NOTE:
Classification 9.2 applies if regulated limit is exceeded.
PRODUCT IDENTIFICATION NUMBER: UN1561
CAS REGISTRY NUMBER: 1327-53-3
CLASSIFICATION: 6.1
9.2
PACKING GROUP: II
REGULATED LIMITS: 230 Kg
SPECIAL PROVISIONS:

109. For the purposes of sections 2.17, 2.23, 3.28 and 3.29 of these Regulations, the consignor shall determine the regulated limit related to this product or substance in accordance with Schedule XIII.

*** LIMITS TO MODE OR METHOD OF TRANSPORT ***

PASSENGER ROAD/RAILWAY VEHICLES: Maximum net quantity per package is 25 kg

*** EMERGENCY RESPONSE GUIDELINE ***

GUIDE 151 NAERG96
SUBSTANCES - TOXIC (NON-COMBUSTIBLE)

POTENTIAL HAZARDS

HEALTH
Highly toxic, may be fatal if inhaled, swallowed or absorbed through skin
Avoid any skin contact
Effects of contact or inhalation may be delayed
Fire may produce irritating, corrosive and/or toxic gases
Runoff from fire control or dilution water may be corrosive and/or toxic and cause pollution

FIRE OR EXPLOSION
Non-combustible, substance itself does not burn but may decompose upon heating to produce corrosive and/or toxic fumes

APPENDIX G

Waste Stabilization & Storage Data

What does Metlcap® do?

Metlcap® is a patented chemical cement, for the treatment of hazardous heavy metals, on or in contaminated lands (earth, clay, etc.), waters, and in industrial wastes.

The eight (8) metals designated by the US Environmental Protection Agency (EPA) under the Resource Conservation and Recovery Act (RCRA) are: **arsenic, barium, cadmium,chromium, lead, mercury, selenium and silver.**

Metlcap® combines chemically and physically with the metals to: **stabilize, encapuslate, and solidify** the harmful components in a hardenable chemical cement matrix, that is an insoluble compound.

Other metals, not on the list of hazardous metals, alloys and substances, may also be treated in this manner. (Patent applications are pending in Canada and Mexico.)

This simple method reacts quickly, and renders the hazardous metals **physically immobile, inert and, essentially, harmless**. This economical method is especially useful in remediating hazardous heavy metals:

- On or in contaminated land, soils, sub-soil strata, and waterways;
- In Industrial waste streams, including machining waste, pickle liquor, plating sludge, baghouse dusts, foundry casting sand and media, fly ash, incineration bottom ash, grit-blast waste from removal of coatings, underwater washout and buildup of contaminants in wetlands, navigable waters, bays and harbors; and
- By Small Quantity Generators, performing on-site remediation of generated hazardous waste metals, within 90 days from date of creation of hazardous waste, using **METLCAP®** LAB kits.

Metlcap® remediates toxic, hazardous heavy metals:

(1) On or in contaminated lands and waterways, (2) industrial waste streams from manufacturing, and (3) in laboratory wastes. Metlcap® produces a hardenable cement that can achieve compressive strengths high enough for use as a reusable resource material for roadbed paving base, or other building and construction materials, including low-level radiation shielding.

Metlcap® pretreatment of hazardous wastes containing heavy metals, now required before landfilling, is in compliance with U.S. EPA Land Disposal Restrictions, Subpart D - Treatment Standards, CFR 268.40

METLCAP®

What are some of the remediation methods utilizing METLCAP®

METLCAP® patented chemical cement, is designed for the treatment of hazardous heavy metals, on or in contaminated lands (earth, clay, etc.), waters, and in industrial wastes.

The eight (8) metals designated by the US Environmental Protection Agency (EPA) under the Resource Conservation and Recovery Act (RCRA) are: **arsenic, barium, cadmium,chromium, lead, mercury, selenium and silver.**

METLCAP® combines chemically and physically with the metals to: **stabilize, encapuslate, and solidify** the harmful components in a hardenable chemical cement matrix, that is an insoluble compound.

What are the remediation methods utilizing METLCAP®?

- Deep Soil Mixing (DSM)
- Shallow Soil Mixing (SSM)
- Jet Soil Mixing (JSM)
- Conventional Soil Mixing (CSM)
- Sludge / Soil Stabilization (SSS)
- High Pressure Injection Grouting (HPIG)
- Slurry Wall Containment Construction (SWCC)
- Mining Lands Reclamation (MLR)
- Combinations of Remediation Methods
- Other Combinations (Currently in Development).

What is Metlcap? | What does it do? | How was it tested? | Applications? | Remediation methods?
Tax incentives | Product availability | Table of results | Homepage

Homepage || What does it do? || How was it tested? || Applications
Remediation methods || Tax incentives || Product availability || Table of results

CENTER FOR BIOREMEDIATION

Weber State University

Issue 001
January 1997

Notes from the Center for Bioremediation Team

A special thanks to Governor Michael Leavitt, Dr. Suzanne Winters, Senator Robert Bennett, Darin Bird and Susan Dixon for their efforts in transferring water and soil remediation capabilities and supporting equipment from the former U.S. Bureau of Mines (USBM) to the Center for Bioremediation.

With closure of the USBM nearly one year ago, the Center was conceived to retain valuable remediation technologies, resources, and expertise within Utah. The Center was formed from collaborative relationships between scientists at the USBM, Weber State University, and the University of Utah. In July, 1996, the Center received State of Utah Center of Excellence status. Program focus is on research, development, and commercialization of improved bioprocesses for metal and mixed metal-organic removal and metal recovery from soils, waters, ores, and mixed metal-inorganic-organic wastes.

Recent transfer of additional remediation equipment, a mobile soil treatment plant and supporting remediation analytical equipment, strengthens the Center's development and marketing base. This will assist the Center in moving former USBM technologies into the private sector.

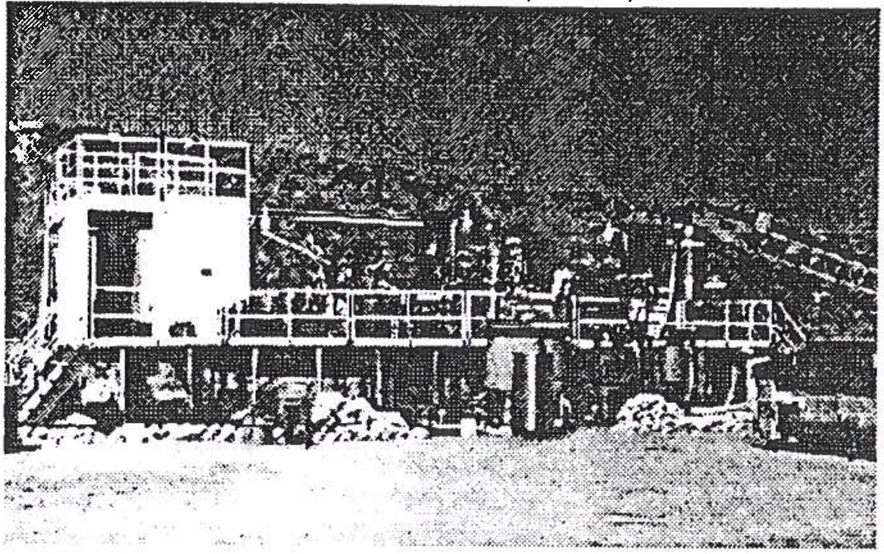
NAS Miramar Lead Removal Demonstration

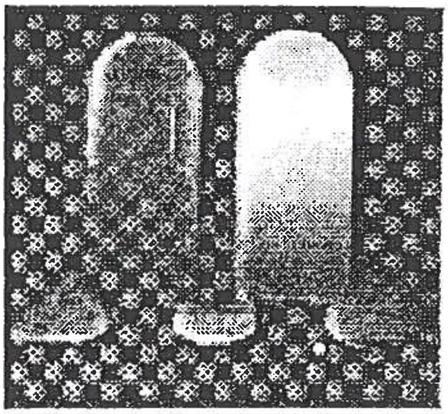
A mobile soil treatment plant successfully demonstrated on-site remediation of lead-containing firing range soils at Miramar Naval Air Station, near San Diego, CA. The mobile plant consists of adapted minerals-processing and soil-washing equipment and uses a combination of physical, chemical, and biological methods to remove bullets and clean lead from firing range soils.

The mobile plant was developed in response to increasingly stringent environmental regulations and observations linking firing range soils to ground and surface water contamination. It was developed and tested in collaboration with Rice University AATDF, U.S. Army Corps of Engineers Waterways Experimental Station (WES), Bureau of Mines, Bureau of Reclamation, and the U.S. Navy. The plant, configured on a 48' trailer to be operational with a 24-48 hour setup, is now co-owned by the Center and WES.

Demonstrated process rates up to 3,000 lb/hr effectively removed bullets and lead from firing range soils. Process and equipment advances will allow remediation of a broader range of soils and contaminants.

Mobile Lead Remediation Plant at NAS Miramar, October, 1996





A selenium-reducing cell-free preparation in calcium alginate beads produced the red amorphous selenium precipitate on the left. The vial on the right contains a beforetreatment bead sample.

Immobilized Microbes and Enzymes

Center research is testing immobilized enzymes (cell-free preparations) derived from field-proven microbes. Two common problems in bioremediation are: (1) microbial sensitivity to contaminants and (2) over-growth/displacement of desired microbes by site bacteria.

Immobilized live microbes and enzyme preparations, have been demonstrated to remove contaminants from environments toxic to unprotected live microbes. Enzyme preparations were produced from cyanide-oxidizing and selenium-reducing microorganisms and immobilized in alginate (seaweed extract) beads.

Cyanide enzyme preparations increased rates of cyanide destruction and functioned at higher cyanide concentrations than do the live cyanide-oxidizing bacteria. Immobilized preparations of live cyanide-oxidizing bacteria tolerated higher cyanide levels than did unprotected bacteria.

Combined enzyme preparations simultaneously removed up to 102 mg/L cyanide and 31.1 mg/L selenium from mining solutions . Simultaneous cyanide and selenium removal, using live microbes, is not possible because cyanide kills or inhibits seleniumreducing bacteria.

Center Custom Microbial Culture Services Assist Industrial Remediation Efforts

The Center for Bioremediation develops custom microbial cultures for remediation of metal and mixed metal/organic contaminated waters and soils. Remediation efficiencies can be greatly improved by development and application of custom site- and contaminant-specific cultures. Our approach uses both indigenous microbes and cultures from the Center microbial repository

Based on the environmental needs of a client, custom cultures are developed and adapted for application to specific environmental settings. Center custom cultures have been used for on-site remediations and to accelerate closure of gold heap leach operations. One gold operation, which is no longer productive, has 1-2 million gallons of cyanide and heavy-metal contaminated water which must be treated before closure. This project uses two sets of custom cultures, one for cyanide degradation and a second for heavy metal removal. Once cyanide is removed, the second set of microorganisms will be introduced to remove heavy metals from the water and to stabilize metals in the heap.

AQUATRACK - A New Non-invasive Subsurface Pollution Mapping and Monitoring Technology

AQUATRACK, a novel technology that can map and monitor subsurface waters and pollution plumes using surface readings, has been developed by Hydro Geophysics. Hydro Geophysics, a geophysical company working with the Center, has used AQUATRACK to map metal- and organic-contaminated waters, acid mine drainage, and drainage field seeps.

Primary advantages of this technology are:

- Ability to map and monitor subsurface waters and pollution plumes from the surface
- Minimal well drilling
- Insures proper implementation of remediation technologies

The Center and Hydro Geophysics have several cooperative surveys planned for next spring. Hydro Geophysics can be contacted through the Center or at (801) 966-1239 (Dr. Jerry Montgomery).

Winter is the Time of Year for Biotreatability Studies

Due to near or below-freezing temperatures, winter is often not the ideal time to initiate bioremediation projects. However, winter is the ideal time to perform laboratory biotreatability studies for your remediation project. This way, a remediation plan can be in place before spring arrives.

Biotreatability testing includes site-specific soil and water toxicity studies, nutrient optimization, and determines the custom culture for your specific remediation problem and environmental conditions. Toxicity studies determine if there are toxic compounds present that would inhibit microbial growth and interfere with remediation efforts. Nutrient optimization studies optimize microbial nutrient requirements for growth and economics. Most biotreatability studies run about 6-8 weeks and require about one gallon of soil and/or water.

Cooperative Opportunities

The Center is looking for additional industry and government cooperators to participate in research, development, and testing of existing and new bioremediation technologies. Participation in any development phase is welcome.

The Center provides a valuable multi-disciplinary professional resource with capabilities to meet diverse environmental remediation challenges. Partnerships offer additional benefits through potential faculty interaction, opportunities for students and site operators to be trained in research, and testing of interest to the cooperator.

Center Publications - 1996

Montgomery, J.R, siackhams F., Phillips, T.A., and D.J. Adams. **Tracking Mine seeps, In situ Leach Solutions, and Pollution Plumes using Electromagnetics.** Randol Gold Forum Proceedings, squaw Valley, CA, May, 1996.

Heyrend, T., Adams, D.J., and D. Hayes. **Arsenate Reduction to Arsenite by Two Pseudomonas Species Isolated from Mine Drainage waters; Microbial Arsenic Removal using Upflow GAC Columns**. Randol Gold Forum Proceedings, Olympic Valley, CA, May, 1996.

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Adams, D.J., Fukushi, K, and s. Ghosh. **Developrnent of Enriched Microbial Cultures for Enhanced Metal Removal.** American Chemical society Emerging Technologies in Hazardous waste Management Vlil Proceedings, Bimmingham, AL, September, 1996.

Pickett, T.M. and D.J. Adams, **Advances in Biosensor Technology.** American Chemical Society Emerging Technologies in Hazardous Waste Management Vlil Proceedings, Birmingham, AL, September, 1996.

Winkler, U., Pickett, T.M., and D. Hudig. **Fractionation of Perforin and Granzymes by Immobilized Metal Amnity Chromatography (IMAC).** Joumal of Immunological Methods, 191, June, 1996.

Montgomery, J.R. Blackham, F., and T.A. Phillips. **Tracking Underground Water Through the Use of Electromagnetics.** American Chemical Society Emerging Technologies in Hazardous Waste Management Vlil Proceedings, Birmingham, AL, September, 1996.

Phillips, T.A. and J.R Montgomery. **Development of a Mobile Treatment Unit for the Removal of Lead from Military Rifle Ranges.** American Chemical Society Emerging i Technologies in Hazardous Waste Management Vlil Proceedings, Birmingham, AL, September, 1996.

Onguri, K.V., Babu, G.R.V., Adams, D.J., Wolfram, J.H., and K.D. Chapatwalla. **Biotreatment of Mine Water-Containing Cyanides by Using Immobilized Cell Technology.** In Press.

Center Technologies

- Microbial Arsenic Removal
- Microbial Biopolymer Uranium-Lead Removal
- Microbial Enzymatic Nitrate Destruction
- Microbial Enzymatic Cyanide Destruction in Heaps and Process Solutions

- Microbial/Enzymatic Selenium Removal
- Microbial Metal Stabilization
- Surface Tracking of Subsurface Pollutants
- Mobile Soil Remediation Plant
- Accelerated Bioleaching Process
- Site Evaluation and Biotreatibility Studies

Approach | Technologies | Capabilities | Cooperative Opportunities | Newsletter | Publications |
Staff | Home

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PRODUCTION OF ENVIRONMENTALLY ACCEPTABLE ARSENITES-ARSENATES FROM SOLID ARSENIC TRIOXIDE

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Abstract

Many arsenical sulfide ores or concentrates are being treated lately by roasting, resulting in the production of arsenic trioxide. In view of the environmental limitations imposed on its disposal, a number of process options have been investigated for its transformation into environmentally acceptable forms. In the present paper, the stability of calcium arsenite and arsenate, and of ferrous and ferric arsenate produced from solid As_2O_3 have been investigated. As_2O_3 was dissolved in water and the resulting As was precipitated as calcium arsenite or arsenate with $Ca(OH)_2$. The effect of the Ca/As ratio in solution, precipitation pH, and thermal treatment of the resulting precipitate on its stability is reported. Further, As was precipitated as ferrous or ferric arsenates with lime and Fe^{2+} or Fe^{3+} additions. The effect of the Fe/As ratio in solution, pH and temperature of precipitation, and Fe^{2+}/ Fe^{3+} ratio on the stability of the resulting precipitate is reported.

results in an increase of the As solubility. Therefore, mixed ferrous - ferric arsenates are less suitable for arsenic removal and fixation than the ferric arsenates.

Table VII
Precipitation and Stability of ferous-ferric arsenates

	Feed composition			Filtrate analysis			Precip. Analysis				Solubility pH=5
Exp No	Fe t g/l	Fe t/As (M)	Fe^{2+}/Fe_t %	Ca g/l	As mg/l	Fe mg/l	Ca %	As %	Fe %	SO_4^{2-} %	As mg/l
1	23.8	1.6	100	0.54	2	0	19.5	13.4	17.3	31.5	1.5
2	32	2.15	100	0.52	1.5	200	20.5	11.95	22.1	32.5	4.0
3	47.6	3.2	100	0.46	0.1	1500	26.3	6.7	17.7	33	6.0
4	23.8	1.6	77.5	0.48	3	0	27.5	11.7	15.0	33	5.0
5	23.8	1.6	50	0.53	3	0	28.5	11.4	15.3	36	4.0
6	23.8	1.6	9.4	0.51	2	0.6	23.2	11.3	12.5	36.8	6.0
7	32	2.15	77.5	0.53	1	0	23.8	8.9	11.4	34.5	0.6
8	32	2.15	50	0.42	1	0	24	9.3	17.5	36	0.4
9	32	2.15	11	0.50	1	3.2	21.5	9.2	15	38	0.5
10	47.6	3.2	80	0.33	0	7.3	16.4	6	17.5	36	6.5
11	47.6	3.2	45	0.45	0.3	0	23.8	5.7	17.5	42.5	2.6
12	47.6	3.2	20	0.58	0.6	0.3	25.3	6.3	14.8	43.3	0.6

trate

Conclusions

The issue of arsenic disposal in an environmentally acceptable manner may be successfully tackled taking into account the following:

1 As_2O_3 produced by roasting can be effectively stabilized in the form of ferric arsenate. The process route envisaged is presented in the elementary block diagram shown in figure 8.

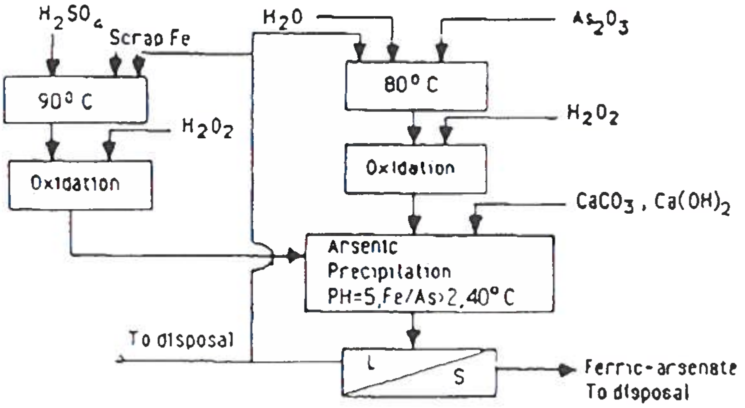

Figure 8 Proposed elementary block-diagram for the fixation of solid As_2O_3 as environmentally acceptable ferr ic arsenate

the

The arsenic solubility of the ferric-arsenate precipitate produced by the route proposed in figure 8, at pH=5 is lower than 0.5 mg/l, and the residual As in the liquid is of the order of 0.6 mg/l.Increase of the precipitation pH and temperature had an adverse effect on the arsenic solubility

2. Mixed Fe(II)-Fe(III) arsenates are less stable than ferric-arsenates

3. Calcium arsenates are more insoluble than calcium arsenites for the same Ca/As ratio. To comply with environmental regulations a Ca/As ratio of 7 is required to achieve arsenic solubility of 0.4 mg/l. Calcination at 800°C rendered calcium arsenates acceptable at Ca/As=3.

4. Calcination of calcium arsenites in the temperature range of 500 to 800° C decreased the arsenic solubility, but not to the degree of being acceptable. A higher calcination temperature is probably required as it was indicated by the residual calcium arsenite indentified in the X-ray diffraction spectrum of calcined precipitate.

Acknowledgements

The financial support of the General Secretariat of Research and Technology of Greece (Research Grant No.901) is gratefully acknowledged. Thanks are also due to Mr. D. Ligros for his assistance in the experimental work.

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ABSTRACT

A zeolite-hydraulic cement containment medium for mining and mineral processing waste material comprising: a hydrated zeolite and a hydraulic cement in a volume ratio of zeolite to cement of from about 1:9 to about 1.1, in which the containment medium is in the form of a monolith and contains less than 50% by volume of the mining or mineral processing waste material.

ZEOLITE-HYDRAULIC CEMENT CONTAINMENT MEDIUM

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention generally relates to a zeolite-hydraulic cement containment medium for hazardous wastes. In particular, the invention relates to a process for preparing a zeolite-portland cement containment medium from a paste prepared by mixing zeolite in amounts from 5-60 weight percent with portland cement in amounts from 95-40 weight percent until a blend is achieved. Thereafter, a chosen amount of small particle size hazardous wastes material is blended with zeolite to form a wastes-zeolite mixture, which is mixed with portland cement. Water is added with mixing to the waste zeolite/portland cement mixture to produce a free flowing paste, and the paste mass is poured into appropriate molds to form a cement monolith after about 7 days.

The zeolite-hydraulic cement containment medium of the invention is not encumbered by the disadvantages attendant to the use of portland cement per se, and is therefore able to contain: (1) high-concentrations and high loading levels of arsenic in the presence of high concentrations of other hazardous elements; (2) high amounts of metal cations which normally make soluble complexes with arsenic in the presence of high arsenic and high metal concentrations; and (3) arsenic in the presence of cations with which it normally makes soluble complexes, and the arsenic is contained in higher concentrations than is usual in portland cement monoliths.

Control of pollution is one of the main concerns in the environment today, and mining, mineral and metallurgical processing wastes in the U.S. accumulate at the rate of thousand of tons per day, and thereby exposes the environment to great risks of pollution. In the field of inorganic hazardous wastes from mining and mineral processing industries, such as the copper mining and processing industry, it has been found that large amounts of oxy-anion wastes (such as arsenic) cannot be disposed of economically. Further, the most common way to solidify and stabilize mining and mineral processing waste solids and waste sludges is cementation using a hydraulic material.

However, cements and other hydraulic material are the most common media for the solidification-stabilization of hazardous waste, and these containment materials after cementation and disposal (by ocean or land) are accompanied by several disadvantageous aspects in that - salts of manganese, tin, zinc, copper, and lead are active in reducing the physical strength of these cements, and anions such as phosphate, iodate, borate, and sulfide retard the setting of these cements, to the extent that, if sufficient quantities of these anions are present, the cement never hardens. In all of these cases, the ions to be contained leach from the cement matrix to some extent.

There are a number of cement-based processes that use various additives in substantial amounts to aid portland cement in the containment of hazardous substances. A general classification of these cement-based processes is a follows: cement/lime, cement/clay, cement/sorbent, and cement/polymer.

pH of the waste containment system to basic values, typically 8-10 in order to form insoluble oxides, insoluble hydroxides, or insoluble calcium salts. Weaknesses of this system are: (1) Some hazardous materials exist as anions which are soluble as calcium salts; and (2) some hazardous cations form hydroxides or complexes at basic pH ranges which are soluble to some extent.

In the cement/clay process, clays are used to adsorb hazardous materials. Weaknesses of this system are: (1) The loading capacities of clays vary with the ion or material being attached (in some cases this loading capacity is quite small); (2) Anions do not adhere well on clays; and (3) The ions or materials are adsorbed or absorbed on clays and not strongly bonded chemically. This means the attached ions or materials may be washed off the clay under the proper conditions. The clay can therefore act as a chromatography bed.

The cement/sorbent system is similar to the cement/clay system, the difference being that the material used to adsorb the hazardous substance is not clay. Sawdust, for example has been used to adsorb oils prior to encapsulation in concrete. The disadvantages of the cement/sorbent systems are essentially the same as the cement/clay system. Additionally, biodegration of the sorbant may occur if the sorbant is organic.

Cement/polymer systems usually consist of the polymer acting as a permeation limiting device by filling cement pores with hydrophobic materials, and by microencapsulation of the waste material. Usually, there is no direct reaction between the waste constituents and the polymer, and the system does not constituents. Biodegration of the polymer may occur. Leaching of exposed hazardous constituents may occur if the cement monolith becomes cracked or broken.

Accordingly, in mining and mineral processing industries, such as the copper mining and processing industry, which produces large amounts of oxy-anion wastes, such as arsenic, there is a need to devise means whereby these oxy-anion wastes can be disposed of economically, as the present way of solidifying and stabilizing mining and mineral processing wastes solids and wastes sludges by cementation is uneconomical.

SUMMARY OF THE INVENTION

One object of the invention is to provide a method for producing a hydraulic containment medium for mining and mineral processing wastes materials that is effective for containment of transition metals, heavy metals, and oxy-anions, such as arsenic.

Another object of the invention is to provide a method for producing a hydraulic containment medium for mineral processing wastes containing arsenic from the refining of copper, lead, cobalt and gold ores.

A yet further object of the invention is to provide a method for producing a hydraulic containment medium for solid wastes or sludges.

In general, the method of the invention utilizes a zeolite-hydraulic cement containment medium for hazardous wastes. The containment medium is prepared by obtaining a zeolite-hydraulic cement paste prepared by mixing from about 5 to 60

APPENDIX H

Materials Management Data

PROECO Corporation
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Edmonton, Alberta, Canada
T6P 1L6
(403) 440-1825 tel
(403) 440-2428 fax

FAX TRANSMISSION

To:	***Paul Green***
Company:	**Dillon Consulting Limited**
Fax:	**403-873-3328**

Total pages: 13
Date: August 18, 1997

Regarding: Disposal Options for Arsenic Trioxide Dust

As per our conversation last week I have put together some information for your review.

There are 3 possible disposal options for this waste material: secure landfill, treatment and incineration. Treatment may be an option depending on the chemical makeup and concentrations of the waste material, but this option would be the most expensive. The secure industrial landfill option would be reliant upon the make-up and concentration of the waste material. This option would be the most cost effective if it meets the criteria. The incineration option would fall in between the other 2 options from a costing standpoint.

Final pricing would be dependent upon the volume of material requiring disposal and the location of the material. Transportation charges may prove to be prohibitive if the site is located in a remote area.

Estimated disposal costs would range from $750/tonne for secure landfill to $1,300/tonne for incineration to $1,600/tonne for treatment.

If you have any questions give me a call at 1-800-661-5792.

Sincerely yours,
PROECO Corporation

Gary Demeriez

Gary Demeriez, B.Sc.
Sales Manager - Western Canada

GD/DILL0001.DOC

APPENDIX I

Case Studies

#2

An Investigation of Disposal Options for Arsenic Trioxide Produced from Roasting Operations

J H KYLE[1] AND D LUNT[2]

INTRODUCTION

Arsenic is classified chemically as a metalloid. That is, it has properties intermediate between those of metals and non-metals. Like non-metals, it combines with many metals to form arsenides (eg arsenopyrite FeAsS, niccolite NiAs, sperrylite $PtAs_2$), but like metals it forms sulphides and oxides (eg realgar AsS, arsenolite As_2O_3). Arsenic is distributed widely in the Earth's crust at an average concentration of 1.5 mg/kg and is present in more than 150 minerals.

The most common commercial source of arsenic is as arsenolite or arsenic trioxide (As_2O_3), a by-product from the extraction of base and precious metals such as copper, lead, zinc and gold. Its major uses are in the production of agricultural pesticides, in wood preservation, and in the glass industry.

Most arsenic compounds are highly toxic, causing dermatitis, acute and chronic poisoning, and possibly cancer. As little as 0.1 grams of arsenic trioxide can be fatal if ingested. It is also highly toxic to plants and animals. Other forms of arsenic, such as arsenic pentoxide (As_2O_5), are also toxic but generally less so.

Production of arsenic trioxide

Arsenic trioxide is a by-product of the roasting of arsenical base metal ores, or auriferous arsenopyritic ores and concentrates.

With the latter, two stage roasting is normally practiced. During the first stage at about 500°C, the arsenopyrite is converted to pyrrhotite and the arsenic is volatilised as arsenic trioxide. It is collected by cooling the off-gases to about 140°C. The second stage, at about 650°C, involves the conversion of the pyrrhotite to hematite and the volatilisation of sulphur as sulphur dioxide.

The arsenic trioxide produced can be of varying purity. It must be either sold on the world market or disposed of in an environmentally acceptable manner. With world production of arsenic trioxide increasing, the sale of this product is becoming increasingly difficult and disposal options for arsenic trioxide need to be investigated.

Disposal options for arsenic trioxide

Arsenic trioxide is reasonably soluble in water. Its solubility increases with temperature, and at both extremes of pH. At low pH, arsenious acid, H_3AsO_3, is formed and at high pH, the anions $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} are progressively formed.

Because of its solubility, arsenic cannot be safely disposed of as arsenic trioxide if it is likely to come in contact with water. As such, it must be either isolated from contact with water and/or converted to a more insoluble form that poses no danger of leaching at unacceptable rates into water catchment areas or groundwater aquifers.

This paper investigates some disposal options available for arsenic trioxide, and their relative efficiencies in minimising the solubility of the arsenic in water.

EXPERIMENTAL PROCEDURES

Arsenic trioxide samples

Arsenic trioxide produced by the roaster at the Western Mining Corporation Windarra Nickel/Gold Project was used in all the testwork. Two separate samples (labelled A and B) were used. They were collected about 12 months apart in 1990 and 1991. The analyses of the samples are reported in Table 1.

TABLE 1

Analyses of arsenic trioxide samples from Windarra nickel/gold project, Laverton WA.

Sample	As_2O_3 (%)	CaO (%)	SO_4 (%)	Fe_2O_3 (%)	SiO_2 (%)
A	47.5	12.6	16.1	1.6	1.5
B	70.0	3.0	11.3	3.0	-

The high calcium content of the waste is due to the addition of limestone to the roast off-gases to neutralise sulphuric acid generated in the process.

Arsenic trioxide dissolution

Water, dilute sulphuric acid, or dilute sodium hydroxide solutions were used as solvents. The solids and solutions were mixed at room temperature, the pH adjusted with dilute H_2SO_4 or dilute NaOH while stirring continuously in a glass reactor. The slurries were allowed to equilibrate for one hour before the solution was sampled for arsenic assays. The process was then repeated at 60° and 90°C. Solution samples taken at elevated temperature were immediately diluted to prevent precipitation of the arsenic trioxide. Comparison of assays for total arsenic by atomic absorption spectroscopy with assays for arsenic(III) by titration with potassium iodate confirmed that virtually all the soluble arsenic was present as arsenic(III).

Arsenic trioxide oxidation

Arsenic trioxide samples were dissolved in water at 90°C. Hydrogen peroxide (50 per cent solution) was then added gradually to the slurry over a period of one hour to a total amount of 1.1 times the stoichiometric requirement according to the equation

$$2\,AsO_3^{2-} + H_2O_2 \longrightarrow 2\,AsO_4^{3-} + 2\,H^+$$

The reaction was highly exothermic and the solution became very acidic due to the hydrogen ions produced in the oxidation process. The As(III) to As(V) reaction was monitored by analysing the reactant solution for As(III) by titration with potassium iodate.

Arsenic precipitation

Arsenic(III) and arsenic(V) solutions were used to prepare precipitates of arsenite or arsenate salts. Lime slurry was added to

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NERCO CON MINE ARSENIC PLANT - ENVIRONMENTAL MANAGEMENT THROUGH RESOURCE RECOVERY

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Abstract

This paper deals with the Nerco Con Mine arsenic trioxide plant. This operation has demonstrated that a major environmental liability can become an asset through commitment to resource recovery.

The mine was originally owned and operated by Cominco Ltd. From 1940 - 1970, the gold ore was refractory in nature, and was roasted, prior to cyanide leaching and gold precipitation. An arsenic trioxide sludge was produced as a byproduct, and over 70,000 tons were stockpiled.

As a condition of the 1981 water licence, the mine was required to establish environmentally acceptable storage areas. Rather than install a potential long-term liability, an Arsenic Plant was constructed in 1983, to recover the arsenic trioxide as a high grade product using a weak acid leach and crystallization process, tested at Cominco's Technical Research Centre.

When the plant was operating consistently, it was found that the chemistry was unreliable. Leach and crystallization modifiers were felt to be the problem, but were not identified, or removed in the existing process. The plant was shut down in late 1985 and used for tailings water treatment, while further research work continued. This identified the need for several process additions.

Nerco Minerals Inc. purchased the mine in late 1986, and directed a successful remodelling and start-up program in early 1987. The plant is now producing a high purity, crystalline product. Residues from the process contain significant gold and silver values.

General

Nerco Con Mine, Ltd. is located near the City of Yellowknife on the north shore of Great Slave Lake. The mine was operated by Cominco Ltd. until late 1986, at which time it was purchased by Nerco Minerals Inc. It was the Northwest Territories' first gold mine, pouring the first two bricks on September 5, 1938.

In 1941 a roasting plant was added to the cyanidation mill to treat the refractory gold ore. A wet scrubber was operated downstream of the roaster to retrieve the arseniferrous wastes from the roaster off gases. The scrubber effluent was pumped to arsenic storage basins where the slurry was allowed to settle by gravity, forming an arsenic trioxide sludge. The supernatant was decanted and returned to the scrubber for re-use.

Initially one rock basin located on the property was used for storage of the arsenic sludge but later a second basin from the adjacent Negus Mine was used. Accumulation of arsenic sludge continued until November 1970, when the amount of gold-bearing arsenopyrite dropped and roasting was discontinued.

Storage of Arsenic - A Long-Term Problem

The two storage basins contained over 70,000 tons of arsenic sludge and posed a potential environmental hazard. In the summer the surface of the sludge would partially dry out resulting in airborne arsenic trioxide. Surrounding surface water and groundwater were considered threatened by leachate containing soluble arsenic which could possibly escape through the deteriorating dams.

The sludge contains 50% arsenic trioxide as well as 0.70 oz/ton gold and 1.20 oz/ton silver. The material is extremely difficult to handle. It is toxic, very fine, with an average particle size of 85% minus 5 microns, and forms a thixotropic mass containing 35% moisture.

During the late 1970's, the storage ponds became an issue with the N.W.T. Water Board. Conditions were included in the Con Water Licence to submit "detailed proposals for the containment and reclamation of all arsenic oxide storage areas located on the property..."

Cominco Ltd. contracted a consulting engineering firm to undertake a review of alternative methods of dealing with the arsenic sludge. The alternatives considered were divided into three main categories:

- Chemical Fixation Methods - involved the addition of chemicals that will react with the arsenic to form insoluble arsenic compounds.
- Physical Processing Methods - involved the containment of the arsenic sludge within an impermeable system.
- Resource Recovery Methods - involved the processing of the arsenic sludge to recover precious metals and the arsenic trioxide for re-use.

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All of the alternatives were evaluated on the basis of their process feasibility potential for eliminating emissions of arsenic to the environment and economics. Chemical fixation methods and physical processing methods were eliminated due to their high capital and/or operating costs. There were also leaching risks associated with the chemical fixation methods.

Resource recovery was considered technically feasible but the high capital and operating costs meant that a detailed marketing study was required. There were also potential environmental problems associated with the proposed pyrometallurgical process, particularly in the areas of fume and dust control.

Attention was turned toward a new physical containment method which, if successful, would provide a politically and environmentally acceptable alternative. Studies to freeze the sludge in-situ, either naturally or artificially, were initiated. It was concluded that although technically feasible, it would be a costly and difficult method to execute. Long-term monitoring would also be required.

Resource Recovery

A resurgence of market prices for arsenic trioxide in 1980 rekindled interest in the resource recovery alternative.

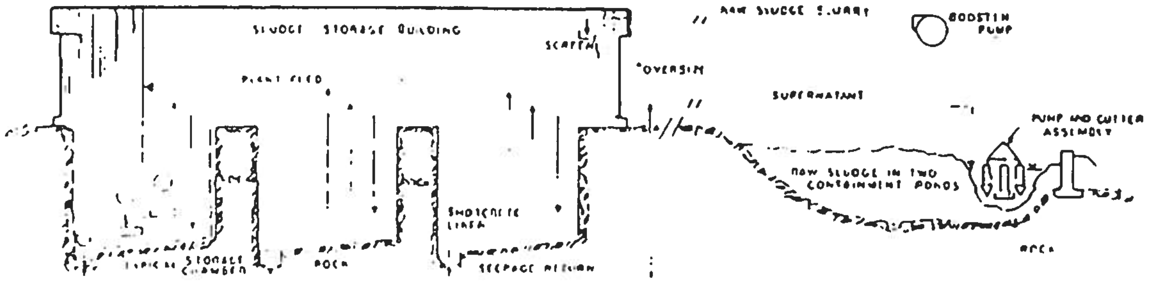
Cominco researchers were aware of the potential of a hot water leach and precipitation process, from work done on other material at their metallurgical complex at Trail, B.C. Although the capital and operating costs of the hot water leach process were higher than a fuming method, the leach process was chosen as being environmentally superior. A laboratory test program was conducted at the Technical Research Centre in Trail during 1980, which established the process design parameters for a full scale plant.

Detailed engineering was then conducted, and Cominco Ltd. received approval from the Water Board in March 1981 to proceed with plans to build the Con Arsenic Trioxide Plant. The plant was built in 1982, and commissioned in early 1983.

Process Design

A system had to be designed that would ensure a constant raw sludge supply, but reclaiming sludge in the winter was out of the question. The system had to be able to reclaim 10,000 tons of raw sludge in the summer and stock it in protected storage for easy winter recovery to feed the plant.

Tanks for stocking the reclaimed sludge were rejected in favour of water-tight chambers excavated below grade in solid rock. Three chambers were blasted out, each 40 feet deep and 60 feet in diameter. These were shotcreted, with drainage sumps cut into the underlying rock so that the chambers could be monitored for seepage. The chambers are covered with a low building, heated to prevent freezing of the material.



SLUDGE STORAGE AND RECOVERY SYSTEM

NERCO CON MINE, LTD.

SLUDGE STORAGE AND RECOVERY SYSTEM
PROCESS FLOW SHEET

DRAWING NO CON 2100

Drawn By L.T | Scale NONE | Date: JUN 15/85 | Rev REV 0

		SLUDGE STORAGE AND RECOVERY SYSTEM PROCESS FLOW SHEET DRAWING NO CON 2189			
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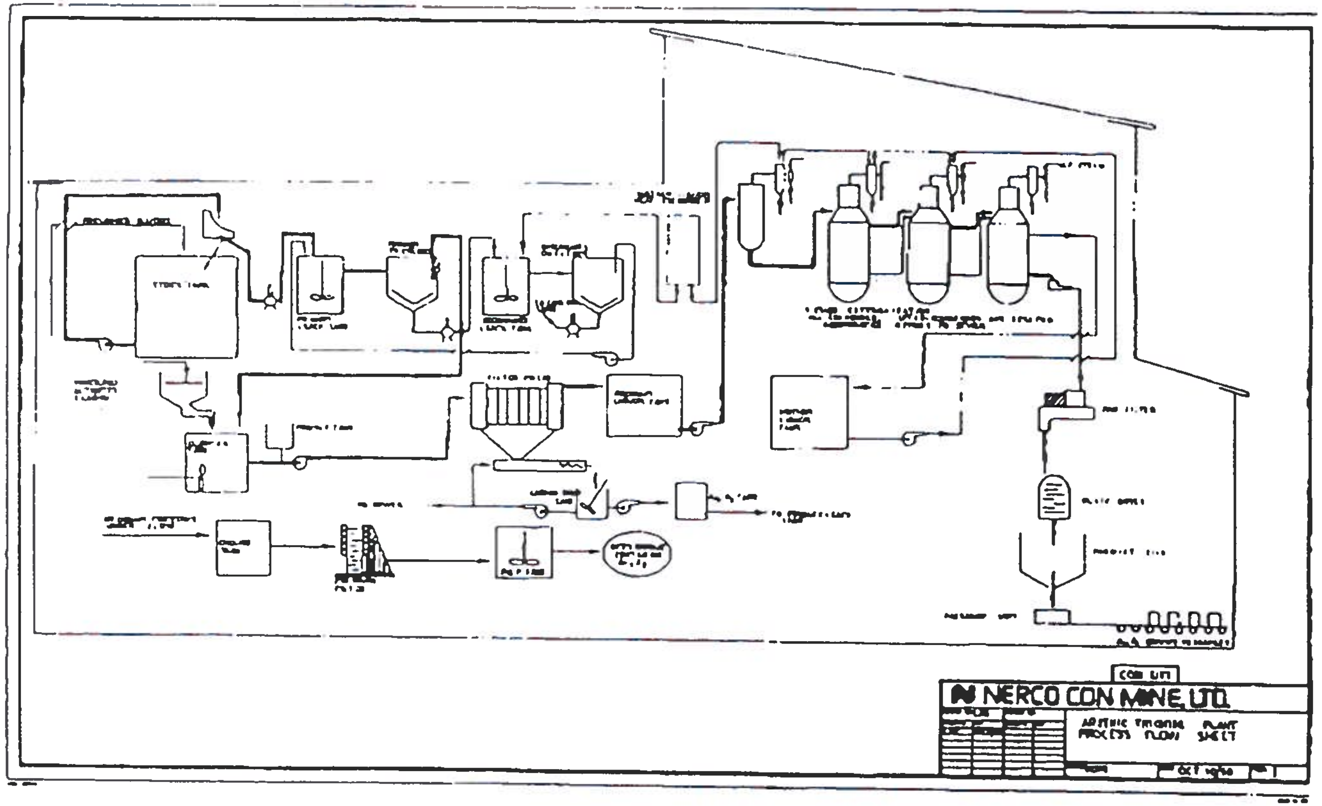

The extraction process is a two stage countercurrent leach operating at 95°C. The primary stage treats raw arsenic sludge at 20 stpd, extracting over 90% of the available arsenic trioxide, and the secondary stage recovers the remainder. Key process developments are the addition of small amounts of hydrogen peroxide to enhance the leach kinetics, and clarification methods which include thickening followed by powdered activated carbon filtration to remove crystallization modifiers and enhance product purity.

The hot pregnant liquor is subjected to four stages of evaporative cooling and crystallization in growth type units. Over 75% of the process heat released in crystallization is recovered using mother liquor recycle as the cooling medium in surface condensers. In winter, the remaining 25% is used to pre-heat incoming ventilating air. This is believed to be the first commercial application of this technology to produce arsenic trioxide, which is an extremely difficult material to crystallize successfully.

The product from the final stage is dewatered to less than 0.1% moisture and stored in a silo capable of holding four days' production. The arsenic trioxide produced is 99.8% pure and is packaged in extra strength 45 gallon steel drums in 1,000 lb. increments.

The 8 stpd of residue left after the arsenic trioxide is recovered contains 1.2 oz. of gold/ton and 3.5 oz. of silver/ton. This material is currently being stockpiled. Metallurgical evaluation is underway to determine the requirements for precious metals recovery. Final inert residues will be disposed of in the tailings pond, along with 750 stpd of mill tailings.

Problems Associated with Start-up and Operation

As might be expected when starting a plant using untested technology to produce a new product, there were many areas in the plant which required modifications of the process and/or the equipment. The majority of the problems could probably have been avoided by completing a more rigorous metallurgical research and process design program, and by ensuring that adequate hygiene management equipment and procedures were in place, prior to attempting construction and start-up.

From a process standpoint, a major problem was the transport of corrosive, high density slurry in small volumes. In several areas, piping had to be replaced to minimize flow restrictions, increase process flexibility and make allowance to flush out lines. Several pumps had to be replaced to reduce damage to the product, increase or decrease flow rates, reduce maintenance requirements and improve ease of operation.

An area of immediate concern was the dewatering plant. A solid bowl centrifuge was chosen for primary dewatering, however it degraded the final product. A cake was produced which had high moisture content, could not be successfully dried and could not meet product size specifications.

The centrifuge was replaced with an horizontal pan filter which achieved an acceptable discharge moisture content without degrading the product. The dryer discharge was thereby free flowing and dust free.

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Unfortunately, the pan filter and dryer have proven to require excessive operator attention and maintenance. By virtue of the equipment design, neither operation or maintenance can proceed in an environmentally acceptable fashion. This area of operation is currently being evaluated in order to identify and install equipment which will perform the same function, while improving worker health and safety.

Crystallization of arsenic trioxide proved to be difficult from a metallurgical and operational standpoint. Several design problems were found with the crystallizers and their condensers. Three of four units were modified and the fourth was completely replaced. Instrumentation for the crystallizers proved unreliable, resulting in difficult operation. Extensive modification of instrumentation was necessary to allow consistent operation.

As constructed, the plant had very poor ergonomics. Extensive modification was required to allow access to operating areas, equipment, manways, control valves, etc. Plant lighting was very poor, and extensive modification was required.

After two years operation, several mechanical modifications allowed plant availability to exceed 90%. Operator hygiene also improved significantly over this period, proving that the plant could operate consistently and safely. It became obvious, however, that more research work was required, if the plant was to produce consistently.

The presence of crystallization modifiers was suspected to be the cause of inconsistent metallurgical performance. These modifiers were felt to be associated with organic material, which formed part of the feed stock, in varying amounts. This was evidenced by a yellow tint in the crystallization liquor, which varied in intensity as production rates rose and fell. Product colour also varied, between a buff colouration during periods of poor productivity, and near-white when productivity was good.

The plant was shut down in late 1985, and converted to a water treatment plant in order to treat tailings pond water on an emergency basis. During an eight month period, research work continued, in an attempt to identify the crystallization modifiers, and determine the process requirements necessary to ensure their removal.

A laboratory scale mini-plant was constructed in mid-1986. A test program was undertaken which was much more rigorous than the laboratory work used to model the initial design. As a result, the research team was successful in duplicating the inconsistent metallurgical performance experienced in the full scale plant. This allowed evaluation of process modifications which would remove crystallization modifiers and allow consistent production to proceed.

A carbon filtration system was developed which includes mixing of powdered activated carbon with the crystallization liquor, then removing the carbon using a filter press. The resulting solution is water clear, and crystallizes quickly and reliably. Product purity and colour are excellent.

Nerco Minerals Incorporated purchased the Con Mine from Cominco in late 1986. The arsenic plant was modified to incorporate the carbon filtration system, and re-started in early 1987. Productivity and product purity have been excellent, and the plant continues to improve its availability.

Hygiene Control: Training of Operating and Maintenance Personnel

The people working at the Con Mine in 1983 were effective in the operation and maintenance of a 40-year old gold mill. Training these people to work in an environment which included high pressure steam, pumps with mechanical seals, extensive instrumentation, high temperature slurries and a complex hygiene control program proved to be difficult. This difficulty was compounded when key equipment items failed to perform their requirements as designed.

At start-up in 1983, a formal training program was non-existent for any aspect of the operation or its maintenance. As might be expected, several problems were encountered with operator hygiene, plant operating consistency and maintenance procedures.

Training programs now in place include a comprehensive indoctrination, written job procedures for routine and non-routine work, a modular operations training program, respirator training, welding safety and tank entry training and equipment maintenance training for some of the equipment items peculiar to the plant.

The training programs are integral to the hygiene control program, which includes extensive environmental and biological monitoring, a comprehensive plant entry/decontamination procedure, respiratory protection and engineering controls throughout the plant.

Conclusions

The plant modifications, re-commissioning and re-start directed by Nerco Minerals has been very successful. A major component of this success has been the commitment to extensive training of operators and tradespeople in both hygiene control and a specialized area of work.

The plant is now operating at close to 90% availability. The product purity is very high, at +99.8% As_2O_3. Product colour is near white, generally +92% reflectance, and +96% lightness using a chromameter.

The commitment by Cominco Ltd. and Nerco Minerals to pursue resource recovery of a toxic waste has involved a high degree of risk. Over the long term, however, it will ensure that the arsenical wastes are permanently stablized.

In about five years, the two containment ponds will no longer exist. Three products, being arsenic trioxide, gold and silver will have been produced in sufficient quantity to pay off the plant's operating costs. In this way, an environmental liability will have become an economic asset.

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#4

HOW ST. JOE GOLD'S EL INDIO MINE HAS BECOME A MAJOR PRODUCER OF HIGH QUALITY CRUDE ARSENIC TRIOXIDE.

E. H. Smith and Eduardo Paredes

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Santiago, Chile

Abstract

The El Indio high grade gold/silver/copper mine is situated in an arsenic anomalous geological zone, which has necessitated the installation of a de-arsenifying roaster, with the dual objectives of producing arsenic-free calcined flotation concentrates and a readily saleable crude arsenic trioxide. How these objectives have been successfully attained by precise metallurgical and mechanical controls both in the roaster and in the effluent-gas train is described in this paper, with some attention being given to the necessary environmental monitoring.

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Marketing

The crude arsenic trioxide marketing policy of St. Joe Minerals Corp./Compañía Minera El Indio was based upon a consultants report issued in 1981. Ref. 5.

This report showed total demand in 1980 as 41,800 tons arsenic trioxide, which included 18,000 tons of crude (normally defined as less than 99.0% of As_2O_3), with the expectation that by 1990 demand would have risen to 55,500 tons and 28,300 tons respectively. See Table V.

Table V. Aggregate Supply-demand Balance
(metric tons)

Year	Estimated Future: Production	Consumption	Balance
1981	46,400	47,000	- 600
1982	57,400	50,500	+ 6,900
1983	64,200	52,500	+ 11,700
1984	65,200	53,500	+ 11,700
1985	65,200 *	55,500	+ 9,700
1990	65,200 *	55,500	+ 9,700

Source: Consultex * The 1985 high/low scenario range runs from 96,700 tons to a low of 55,200.

Based upon installed roaster capacity it was expected that El Indio crude arsenic trioxide production would be about 5,000 t annually, which proved to be the case once initial start-up problems were overcome.

In view of the very limited market for crude arsenic trioxide a great deal of patience and determination to meet customers quality and packaging needs was required plus the preparedness to stockpile unsold product.

Among the market related problems that had to be overcome were, (1) the product bulk density was increased by a densifier, (2) impurities levels, particulary iron and carbon black had to be reduced by good dust collection in the gas train, and (3) packaging had to meet international regulations for a toxic product.

This marketing effort has required about 3 years, but now sales are in good balance with production, and El Indio feels reasonably confident that it is established as a long term supplier to the arsenic market.

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Arsenic Trioxide Management Feasibility Study

APPENDICES II

October 6, 1997

Arsenic Trioxide Management Feasibility Study
Yellowknife, NT

Indian and Northern Affairs Canada

95-2832-04-01

Submitted by

Dillon Consulting Limited

APPENDICES II

TABLE OF CONTENTS

APPENDIX A

Abbreviations

Abbreviations

CSI - Chemical Specialties Incorporated

CCA - Copper Chromate Arsenate

tpd - tons per day

tpy - tons per year

stpd - short tons per day

ACC - Acid Copper Chromate

ACA - Ammoniacal Copper Arsenate

CZC - Chromated Zinc Chloride

U.S.G.S. - United States Geological Survey

TDG - Transportation of Dangerous Goods

WAROX - White ARsenic OXide

lbs/cu. ft. - pounds per cubic foot

APPENDIX B

Graphs

TABLE 1

Table 46: USA: Markets for CCA treated lumber market sector

Market sector	% share
Residential remodelling	49%
Residential construction	24%
Farm use	10%
Non-residential	8%
Other	9%

Source: Arsenic Metallurgy Fundamentals and Applications 1988

TABLE 2

Table 49: USA: Comparison of wood treatment costs

Preservative type	Unit	Kg/ unit	Price/ unit	Retention (kg/cu.m.)	Cost ($/cu.m.)
Tar oils:					
Creosote	USgal	4.45	0.83	128.15	23.45
				144.17	26.38
				192.22	35.17
Coal tar	USgal	4.54	0.80		
Creosote/Coal tar	USgal	4.54	0.815	128.15	23.03
				144.17	25.92
				192.22	34.54
Organic solvent:					
Pentachlorophenol	lb.	0.45	0.53		
5% pentachlorophenol in petroleum P9 type A	USgal	3.58	0.86	4.81a	23.03
				6.41a	30.76
				8.01a	38.42
				9.61a	46.12
22% pentachlorophenol in Co solvent	USgal	3.63	3.30	4.81a	38.85
5% pentachlorophenol in petroleum P9 type A	USgal	36.3	1.46	6.41a	51.56
				8.01a	64.63
Copper naphthenate (8% Cu)	lb.	0.45	0.91	7.21b	232.37
Copper naphthenate in in petroleum P9 type A (2% Cu)	USgal	3.63	2.34	9.61b	310.06
				10.89b	351.38
				12.01b	387.40
Copper naphthenate in petroleum P9 type A (4% Cu)	USgal	3.90	4.29	19.22b	530.07
Copper naphthenate in petroleum P9 type C (4% Cu)	USgal	3.47	2.39	7.21b	248.26
				9.61b	330.90
				10.89b	375.04
				12.01	413.89

Table 49 cont/.............

Table 49 continued

Preservative type	Unit	Kg/ unit	Price/ unit	Retention (kg/cu.m.)	Cost ($/cu.m.)
Cu-8 (solubilised)	lb.	0.45	18.00		
2% Cu-8 in petroleum P9 Type C	USgal	3.29	3.32	1.92	100.65
				2.56	133.84
TBTO	lb.	0.45	6.65	1.92	52.27
2% TBTO in petroleum P9 Type C	USgal	3.29	1.73	2.56	69.92
Waterborne					
ACC	lb.	0.45	1.25	4.00	11.50
				8.01	22.07
				9.93	27.37
CCA/ACA	lb.	0.45	1.00	4.00	8.83
				5.13	11.30
				6.41	14.13
				9.61	21.19
				12.81	28.25
				40.05	88.29
CZC	lb.	0.45	0.50	7.21	7.95

Notes: a - kg. of pentachlorophenol, b - kg. of copper

Source: "Wood preservation in the USA" by Darrel D. Nicholas and Ron Cockcroft, International Research Group of Wood Preservation, Stockholm, 1982

TABLE 3

Table 61 : Imports of arsenic trioxide, pentoxide, and acids by major trading countries, 1984 to 1987 (t)

	1984	1985	1986	1987
France(2) from:				
Australia	-	-	-	414
West Germany	-	-	116	0
Italy	-	191	156	177
Peru	-	-	-	902
UK	105	-	163	248
USA	-	168	-	-
Others	107	50	26	319
Total	212	409	461	2,060
West Germany(1) from:				
Belgium	178	138	205	99
Others	205	190	146	155
Total	383	328	351	254
India(3) from:				
Belgium	...	...	...	128
France	...	...	...	-
Others	...	...	...	235
Total	...	...	...	363
Italy(1) from:				
Belgium	195	124	...	213
France	253	160	...	273
West Germany	148	...	...	-
Others	26	169	-	365
Total	622	453	...	851
New Zealand(4) from:				
China	124	136	...	133
France	239	150	...	-
UK	1,503	1,610	...	0
Others	71	195	...	402
Total	1,937	2,091	...	535
Norway from:				
UK	149	128	...	211
Others	36	51	...	300
Total	185	179	...	511
USA(5) from:				
Australia	-	-	1,256	-
Belgium	844	1,497	-	1,646
Bolivia	-	100	-	-
Canada	4,767	3,670	1,923	2,013
Chile	-	190	1,660	4,809
France	1,261	3,606	6,273	5,442
Japan	-	372	-	-
Mexico	-	3,397	4,409	4,468
Netherlands	-	236	-	-
South Africa	-	113	1,211	1,381
Sweden	3,914	2,998	7,067	4,836
UK	2,422	2,109	1,510	1,072
Others	3,280	178	1,801	2,378
Total	16,488	18,466	27,111	28,045

(1) Mostly arsenic trioxide
(2) Arsenic trioxide only
(3) Mostly arsenic pentoxide and acids
(4) Arsneic pentoxide and acids only
(5) Arsenic acid and arsenic trioxide

TABLE 4

Table 79: Europe and the USA: Arsenic trioxide prices, 1976 to 1989

		UK (£ per t, 99-99.5%)	USA (crude, 95%, bulk, carlots fob Tacoma	
			US$/sh.ton	USc/lb
1976		240 - 260	230	11.5
1977		240 - 260	230	11.5
1978		240 - 260	230	11.5
1979	August	400 - 480	230	11.5
	September	450 - 490	230	11.5
1980	January	480 - 520	230	11.5
	March	550 - 600	230	11.5
	April	575 - 600	230(1)	11.5
	May	600 - 650	230	11.5
	July	650 - 700	535	26.8
	August	700	535	26.8
	October	800	635	31.8
1981	January	700 - 775	635	31.8
	February	750	635	31.8
	March	750	685	34.3
	June	800 - 850	700	35.0
	September	850 - 900	700	35.0
1982	January	850 - 900	800	40.0
	August	750 - 800	800	40.0
	October	700 - 725	800	40.0
1983	June	850	800	40.0(3)
1984	January	700	800	40.0(3)
	February	650	800	40.0(3)
1985	January	700 - 750	800	40.0(3)
	September	650 - 700	800	40.0(3)
1986	August	650 - 700	800 - 900(2)	42.0 - 45.0(3)
1988	April	No change	No change	No change
	June	Withdrawn(4)	"	"
1989	January	"	700 - 740	35.0 - 37.0
	November	"	No change	No change

(1) This price was long published in Chemical Marketing Reporter, but had probably ceased to be the price quoted by Asarco before this date.

(2) Arsenic trioxide crude, 99%, bulk, carlots, fob warehouse

(3) The USBM reported the year-end price in 1983, 1984 and 1985 to be 33 cents per lb. The basis of quotation then changed when Asarco ceased selling arsenic from Tacoma.

(4) Price withdrawn on 13th June 1988.

Source: UK; Metal Bulletin. The above prices are the copyright of Metal Bulletin PLC and reproduced with its permission, US; Chemical Marketing Reporter and others.

TABLE 5

TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS 1/

(Metric tons, arsenic content)

	1992	1993	1994	1995	1996
U.S. supply:					
Imports, metal	740	767	1,330	557	252
Imports, compounds	23,300	20,900	20,300	22,100	21,200
Total	24,000	21,600	21,600	22,700	21,400
Distribution of U.S. supply:					
Exports 2/	94	364	79	430	36
Apparent demand	23,900	21,300	21,500	22,300	21,400
Estimated U.S. demand pattern:					
Agricultural chemicals	3,900	3,000	1,200	1,000	950
Glass	900	900	700	700	700
Wood preservatives	17,900	16,200	18,000	19,600	19,200
Nonferrous alloys and electronics	800	800	1,300	600	250
Other	400	400	300	400	300
Total	23,900	21,300	21,500	22,300	21,400

1/ Data are rounded to three significant digits; may not add to totals shown.

2/ Metal only.

TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS, 1990-94 1/

(Metric tons, arsenic content)

	1990	1991	1992	1993	1994
U.S. supply:					
Imports, metal	796	1,010	740	767	1,330
Imports, compounds	19,900	20,700	23,300	20,900	20,300
Industry stocks, Jan. 1	100	100	--	--	--
Total	20,800	21,800	24,000	21,600	21,600
Distribution of U.S. supply:					
Industry stocks, Dec. 31	100	--	--	--	--
Exports 2/	149	233	94	364	79
Apparent demand	20,500	21,600	23,900	21,300	21,500
Estimated U.S. demand pattern:					
Agricultural chemicals	4,200	5,000	3,900	3,000	1,200
Glass	800	900	900	900	700
Wood preservatives	14,400	14,300	17,900	16,200	18,000
Nonferrous alloys and electronics	800	1,000	800	800	1,300
Other	300	400	400	400	300
Total	20,500	21,600	23,900	21,300	21,500

1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits; may not add to totals shown.

2/ Exports for 1990 include compounds; exports for 1991 through 1994 include metal only.

TABLE 6

TABLE 2
U.S. IMPORTS FOR CONSUMPTION OF ARSENICALS 1/

Class and country	1995 Quantity 2/ (metric tons)	1995 Value (thousands)	1996 Quantity (metric tons)	1996 Value (thousands)
Arsenic trioxide:				
Belgium	786	$420	579	$314
Bolivia	--	--	120	55
Chile	3,210	1,260	8,790	2,930
China	15,900	8,230	11,000	5,650
France	2,820	1,550	2,480	1,360
Hong Kong	1,510	619	1,380	681
Mexico	3,560	2,560	2,980	2,140
Philippines	1,080	430	612	231
United Kingdom	1	2	--	--
Other	195	90	18	20
Total	29,000	15,200	28,000	13,400
Arsenic acid:				
Canada	--	--	(3/)	2
Israel	(3/)	3	1	13
Total	(3/)	3	1	14
Arsenic metal:				
China	491	709	212	185
Germany	37	2,000	10	2,110
Japan	29	1,400	29	1,480
United Kingdom	--	--	(3/)	23
Other	(3/)	3	--	--
Total	557	4,100	252	3,790

1/ Data are rounded to three significant digits; may not add to totals shown.

2/ Data erroneously reported as "thousand metric tons."

3/ Less than 1/2 unit.

Source: Bureau of the Census.

TABLE 7

TABLE 4
ARSENIC TRIOXIDE: 1/ WORLD PRODUCTION, BY COUNTRY 2/ 3/

(Metric tons)

Country 4/	1992	1993	1994	1995	1996 e/
Belgium e/	2,000	2,000	2,000	2,000	2,000
Bolivia	633	663	341	362 r/	370
Canada e/	250	250	250	250	250
Chile e/	6,016 5/	6,200	6,300	6,400	9,000
China e/	15,000 r/	14,000 r/	18,000 r/	21,000 r/	15,000
France e/	2,000	3,000	6,000	5,000	3,000
Georgia e/	1,500	1,000	500	400	400
Germany e/	300	300	300	250 r/	250
Ghana e/ 6/	500	500	500	500	500
Iran e/	492 5/	500	500	500	500
Japan e/	50	40	40	40	40
Kazakstan e/	2,000	2,000	1,500	1,500	1,500
Mexico	4,293	4,447	4,400 e/	4,500 e/	4,300
Namibia 7/	2,456	2,290	3,047 r/	1,661 r/	1,100
Peru 8/	644 r/	391 r/	286 r/	285 r/ e/	285
Philippines e/	5,000	2,000	2,000	2,000	2,000
Portugal e/	150	150	150	100	100
Russia e/	2,500	2,000	1,500	1,500	1,500
Total	45,800 r/	41,700 r/	47,600 r/	48,200 r/	42,100

e/ Estimated. r/ Revised

1/ Including calculated arsenic trioxide equivalent of output of elemental arsenic and arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production.

2/ World totals and estimated data are rounded to three significant digits; may not add to totals shown.

3/ Table includes data available through Apr. 1, 1997.

4/ Austria, Hungary, the Republic of Korea, South Africa, Spain, the United Kingdom, and former Yugoslavia have produced arsenic and/or arsenic compounds in previous years, but information is inadequate to make reliable estimates of output levels, if any.

5/ Reported figure.

6/ Estimated commercial byproduct of gold ore roasting. Does not include additional byproduct production of noncommercial grade material estimated at 4,000 tons in 1992, and up to 9,000 tons per year in 1993-96.

7/ Output of Tsumeb Corp. Ltd. only.

8/ Output of Empresa Minera del Centro del Perú (Centromin Peru) as reported by the Ministerio de Energia y Minas.

TABLE 8

Salient Statistics—United States:	1992	1993	1994	1995	1996[e]
Imports for consumption:					
Metal	740	767	1,330	557	250
Trioxide[1]	30,700	27,500	26,800	29,000	29,000
Arsenic acid	40	—	5	(2)	1
Exports, metal	94	364	79	430	20
Consumption, apparent, arsenic content	23,900	21,300	21,500	22,300	22,000
Price, cents per pound, average:[3]					
Trioxide, Mexican	29	33	32	33	33
Metal, Chinese	56	44	40	66	53
Net import reliance[4] as a percent of apparent consumption	100	100	100	100	100

TABLE 9

TABLE 1. CANADA, ARSENIC PRODUCTION AND TRADE, 1989-91

Item No.		1989		1990		1991p	
		(kilograms)	($000)	(kilograms)	($000)	(kilograms)	($000)
PRODUCTION							
	Arsenious trioxide						
	Northwest Territories	x	1 286	x	240	x	247
	Total	x	1 286	x	240	x	247
EXPORTS						(Jan.-Sept.)	
2804.80	Arsenic						
	United States	80 609	277	41 577	884	6 293	342
	Germany[1]	118 871	184	207	76	1	8
	Netherlands	–	–	6 000	54	–	–
	France	8 979	78	4	27	–	–
	Total	208 459	539	47 788	1 042	6 294	350
IMPORTS							
2804.80	Arsenic						
	United States	37 827	149	137 916	341	28 694	92
	People's Republic of China	29 304	49	59 381	255	7 117	20
	Japan	–	–	5 744	20	–	–
	Total	67 132	198	203 041	616	35 811	113
2811.29.10.10	Arsenic pentoxide						
	United States	363 765	269	910 324	691	824 572	739
	United Kingdom	184	. . .	–	–	131	. . .
	Total	363 949	269	910 324	691	824 703	739
2811.29.10.20	Arsenic trioxide						
	France	163 033	150	83 272	74	92 364	95
	United States	13 037	13	2 127	2	2 077	2
	Total	176 070	163	85 399	77	94 441	97

Sources: Energy, Mines and Resources Canada; Statistics Canada.
– Nil; . . . Amount too small to be expressed; p Preliminary; x Confidential.
[1] Where applicable, data for East and West Germany have been combined.
Note: Numbers may not add to totals due to rounding.

TABLE 12: MINERAL PRODUCTION, NORTHWEST TERRITORIES, 1984–1993

MINERAL		1984	1985	1986	1987	1988	1989	1990	1991	1992(R)	1993(P)
Gold	$	191 071 000	177 079 000	205 266 000	223 456 000	205 503 000	177 260 000	223 788 000	222 504 000	180 501 000	192 630 000
	kg	12 713	12 713	12 503	11 740	11 880	12 208	15 557	16 752	13 518	13 016
Silver	$	20 361 000	9 083 000	5 478 000	4 006 000	6 923 000	3 820 000	3 457 000	2 524 000	2 397 000	1 855 000
	kg	59 000	33 000	22 000	13 000	26 000	18 000	19 000	17 000	16 000	11 000
Copper	$	130 000	46 000	1 000	4 000	3 000					
	kg	69 000	23 000	1 000	2 000	1 000					
Lead	$	66 647 000	44 489 000	91 129 000	139 370 000	52 223 000	41 323 000	55 766 000	30 080 000	28 729 000	14 833 000
	kg	90 198 000	77 083 000	133 836 000	131 744 000	51 502 000	39 734 000	46 588 000	35 388 000	39 141 000	28 914 000
Zinc	$	386 813 000	356 415 000	322 064 000	328 781 000	537 756 000	708 009 000	420 550 000	221 464 000	256 878 000	179 760 000
	kg	274 920 000	284 223 000	265 073 000	258 070 000	325 321 000	329 001 000	218 241 000	173 154 000	171 481 000	146 027 000
Cadmium	$	1 034 000	866 000	670 000	501 000	3 172 000	4 405 000	266 000			
	kg	214 000	238 000	175 000	86 000	166 000	269 000	31 000			
Bismuth	$	34 000	60 000								
	kg	3 000	3 000								
Antimony	$				141 000	55 000	43 000	6 000			
	kg				44 000	19 000	18 000	3 000			
Tungsten Trioxide (E)	$	33 584 000	38 918 000	17 363 000							
	kg	3 112 000	3 529 000	2 470 000							
Arsenious Trioxide (E)	$	5 837 000	1 969 000	254 000	666 000	2 366 000	1 286 000	240 000			
	kg	4 684	4 098	406	X	X	X	X			
Sulphur (smelter gas)	$		11 665 000	21 788 000	6 912 000	7 286 000	8 468 000	2 677 000			
	kg		98 000	147 000	59 000	73 000	67 000	17 000			
Sand and Gravel	$	36 323 000	8 981 000	3 281 000	8 132 000	10 966 000	11 813 000	13 856 000	6 739 000	10 673 000	11 585 000
	kg	7 249 000	6 803 000	986 000	2 183 000	2 443 000	2 203 000	3 274 000	1 824 000	2 991 000	2 601 000
Stone	$	4 617 000	434 000	1 011 000	1 486 000	232 000	4 344 000	9 079 000	7 788 000	2 679 000	2 205 000
	kg	729 000	163 000	368 000	472 000	108 000	727 000	1 495 000	1 003 000	884 000	467 000
TOTAL	$	746 451 000	650 005 000	668 305 000	713 455 000	826 485 000	960 771 000	729 685 000	488 099 000	481 858 000	402 868 000

Source: Mining Sector, Natural Resources Canada and Natural Resources and Environment Branch, Indian Affairs and Northern Development.
(P) Preliminary figures (R) Revised figures (E) Estimated (X) Confidential (N/A) Not available

TABLE 11

Natural Resources Canada
Ressources naturelles Canada

Minerals and Metals Sector
Secteur des minéraux et des métaux

CANADA, REPORTED CONSUMPTION OF NONMETALLIC MINERALS

		1991	1992	1993	1994	1995p
Arsenic trioxide	t	125	x	x	x	x
Asbestos	t	3 903	3 855	2 697r	1 191r	1 456
Barite	t	11 629	9 186	13 109	13 732	17 118
Bentonite	t	248 725r	238 867r	230 006r	255 171r	263 294
Calcite	t	149 942	187 641	237 378	275 961	303 247
Ball clay	t	20 814	26 221	38 760	37 769	33 719
China clay	t	407 280	427 621	371 516	393 073	407 663
Fire clay	t	64 187	45 325	34 159	36 526	34 573
Diatomite	t	6 788	6 730	6 259	7 172	6 667
Feldspar	t	1 806	1 476	1 860	1 955	1 492
Fluorspar	t	110 495	93 785	72 624	14 978	16 570
Garnet	t	x	x	x	x	x
Graphite	t	6 248	7 473	7 261	8 147	9 187
Domestic lime, quick and hydrated [1]	t	1 699 912	1 838 853	1 671 848	1 823 282	..
Limestone	t	15 110 276r	14 860 738r	15 362 002r	18 183 575r	18 372 921
Lithium	t	775	563	815	809	764
Magnesia	t	144 869	150 186	149 920	152 802r	144 824
Mica	t	3 555	3 379	3 262	3 040	2 828
Nepheline syenite	t	60 223	63 440	63 134	67 426r	68 704
Phosphate rock	t	1 181 971	1 209 712	1 326 194	1 256 582	1 202 533
Potash (K2O)	t	263 133	259 122	254 237	251 081	210 332
Silica	t	2 227 366	2 405 022	2 337 031	2 334 918r	2 332 209
Sodium sulphate	t	144 287	132 411	134 739	130 845r	121 717
Sulphur	t	879 521	863 950r	844 222	851 187r	905 021
Talc, soapstone, pyrophyllite	t	65 682	72 419	64 348	68 753	98 877
Titanium dioxide	t	43 067	47 201	46 308	52 023r	50 916

Source: Natural Resources Canada.
p Preliminary; r Revised; .. Not available; x Confidential

[1] From producing companies' surveys, not from consumer surveys. Includes merchant market; excludes companies that are completely captive producer/consumers.

Note: Unless otherwise stated, consumption refers to reported consumption of refined metals or nonmetallic minerals by consumers.

Back to Mineral Consumption

TABLE 12

Trade Query Results

Number of rows affected: 7

TYPE	CODE	DESCRIPTION	UOM	YEAR	QTY	VALUE
X	28048000	Arsenic	KGM	1996	37194	54216
X	28048000	Arsenic	KGM	1993	1034	17269
X	28048000	Arsenic	KGM	1992	10514	114413
X	28048000	Arsenic	KGM	1991	6684	376480
X	28048000	Arsenic	KGM	1990	47788	1042136
X	28048000	Arsenic	KGM	1989	208459	539796
X	28048000	Arsenic	KGM	1988	31510	635968

* No values indicates there is no trade during the selected time period.

1A1522 15

Trade Query Results - Résultats d

Number of rows affected: 226

TYPE	CODE	DESCRIPTION	UOM	COUNTRY	US_STATE	PROVINCE	YEAR	MONTH	QTY	VA
M	2804800000	Arsenic	KGM	United States	WI	Quebec	1997	01	1500	
M	2804800000	Arsenic	KGM	United States	WI	Quebec	1994	11	710	
M	2804800000	Arsenic	KGM	United States	WI	Quebec	1994	01	157	
M	2804800000	Arsenic	KGM	United States	WI	Ontario	1996	12	290	
M	2804800000	Arsenic	KGM	United States	WI	Ontario	1995	12	354	
M	2804800000	Arsenic	KGM	United States	WI	Ontario	1994	11	300	
M	2804800000	Arsenic	KGM	United States	WI	Ontario	1992	12	117	
M	2804800000	Arsenic	KGM	United States	WI	Ontario	1992	04	116	
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1992	01	595	2
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1991	06	12326	43
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1991	01	2275	7
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1990	09	4239	14
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1990	07	53	
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1990	05	16531	57
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1990	02	4863	17
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1990	01	136	
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1989	11	60	
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1989	10	5574	19
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1989	09	6846	23
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1989	03	706	2
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1989	02	83	
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1989	01	183	37
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1988	08	241	

M	2804800000	Arsenic	KGM	United States	WA	Columbia	1988	07	9445	24
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1988	05	57	1
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1988	04	1012	3
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1988	03	6614	231
M	2804800000	Arsenic	KGM	United States	WA	British Columbia	1988	02	121	
M	2804800000	Arsenic	KGM	United States	RI	Ontario	1990	06	1259	44
M	2804800000	Arsenic	KGM	United States	PA	Quebec	1997	03	3518	12
M	2804800000	Arsenic	KGM	United States	PA	Quebec	1995	03	207	
M	2804800000	Arsenic	KGM	United States	PA	Ontario	1997	01	1171	40
M	2804800000	Arsenic	KGM	United States	PA	Ontario	1995	12	1075	3
M	2804800000	Arsenic	KGM	United States	PA	Ontario	1995	01	1105	38
M	2804800000	Arsenic	KGM	United States	OR	British Columbia	1995	09	1170	4
M	2804800000	Arsenic	KGM	United States	OR	British Columbia	1995	05	640	2
M	2804800000	Arsenic	KGM	United States	OK	New Brunswick	1995	09	454	1
M	2804800000	Arsenic	KGM	United States	OK	New Brunswick	1993	07	942	3
M	2804800000	Arsenic	KGM	United States	OK	New Brunswick	1992	10	909	31
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	10	16708	20
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	09	1730	20
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	08	896	1
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	07	892	1
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	06	16451	19
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	05	1566	1
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	04	2504	30
M	2804800000	Arsenic	KGM	United States	OH	Ontario	1990	02	1964	2

TYPE	CODE	DESCRIPTION	UOM	COUNTRY	US_STATE	PROVINCE	YEAR	MONTH	QTY	VAL
M	2804800000	Arsenic	KGM	United States	NY	Quebec	1993	09	2721	39
M	2804800000	Arsenic	KGM	United States	NY	Quebec	1993	01	5000	100
M	2804800000	Arsenic	KGM	United States	NY	Quebec	1992	12	4372	153
M	2804800000	Arsenic	KGM	United States	NY	Ontario	1990	08	1059	12
M	2804800000	Arsenic	KGM	United States	NJ	Quebec	1995	10	2268	76
M	2804800000	Arsenic	KGM	United States	NJ	Quebec	1993	06	468	56
M	2804800000	Arsenic	KGM	United States	NJ	Quebec	1988	07	97	3

M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1997	05	90
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1997	02	35
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1996	11	36
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1995	04	33
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1994	07	428
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1994	05	45
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1994	03	43
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1994	01	37
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1993	11	34
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1993	09	1631
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1993	08	119
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1993	05	591
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1993	04	33
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1993	03	72
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1992	12	39
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1992	06	5000
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1992	01	1156
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1991	09	41
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1991	02	711
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1990	10	2425
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1989	02	293
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1989	01	87
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1988	12	92
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1988	11	1704
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1988	06	1378
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1988	04	50
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1988	02	34
M	2804800000	Arsenic	KGM	United States	NJ	Ontario	1988	01	2000
M	2804800000	Arsenic	KGM	United States	NJ	British Columbia	1996	02	4640
M	2804800000	Arsenic	KGM	United States	NH	Ontario	1991	01	40
M	2804800000	Arsenic	KGM	United States	NH	British Columbia	1989	05	685
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1992	08	5200
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1990	12	5000

TYPE	CODE	DESCRIPTION	UOM	COUNTRY	US_STATE	PROVINCE	YEAR	MONTH	QTY	VAL
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1990	04	7111	248
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1990	02	4852	1698
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1989	09	2453	85
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1988	08	4000	95
M	2804800000	Arsenic	KGM	United States	NE	Quebec	1988	04	3350	8
M	2804800000	Arsenic	KGM	United States	NE	Ontario	1996	07	4240	96
M	2804800000	Arsenic	KGM	United States	NE	Ontario	1996	03	962	44
M	2804800000	Arsenic	KGM	United States	NE	Ontario	1994	05	1041	3
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1993	08	574	20
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1992	07	907	20
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1990	12	1600	376
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1990	11	1000	30
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1990	09	1000	281
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1990	03	6690	234
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1990	02	10000	1175
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1989	09	1071	37
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1989	08	2268	77
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1988	06	4002	960
I	2804800000	Arsenic	KGM	United States	NE	Ontario	1988	03	2005	49
I	2804800000	Arsenic	KGM	United States	MN	Ontario	1989	01	146	34
I	2804800000	Arsenic	KGM	United States	MI	Quebec	1992	02	161	5
I	2804800000	Arsenic	KGM	United States	MI	Ontario	1990	06	1291	451
I	2804800000	Arsenic	KGM	United States	MD	Quebec	1992	04	2252	78
I	2804800000	Arsenic	KGM	United States	MD	Quebec	1990	09	5000	145
I	2804800000	Arsenic	KGM	United States	MD	Quebec	1990	06	1833	615
I	2804800000	Arsenic	KGM	United States	MD	Ontario	1989	02	7718	161
I	2804800000	Arsenic	KGM	United States	MD	Alberta	1994	01	34	11
I	2804800000	Arsenic	KGM	United States	MA	Quebec	1996	04	187	6
I	2804800000	Arsenic	KGM	United States	MA	Ontario	1994	08	66	2
I	2804800000	Arsenic	KGM	United States	MA	Ontario	1992	04	460	16
I	2804800000	Arsenic	KGM	United States	MA	Ontario	1992	03	61	2

TYPE	CODE	DESCRIPTION	UOM	COUNTRY	US_STATE	PROVINCE	YEAR	MONTH	QTY	VA
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1991	09	57	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1991	06	753	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1991	03	156	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1991	01	1338	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1990	06	763	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1989	11	158	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1989	05	1157	
M	2804800000	Arsenic	KGM	United States	MA	Ontario	1988	09	713	
M	2804800000	Arsenic	KGM	United States	LA	Saskatchewan	1997	01	20412	1
M	2804800000	Arsenic	KGM	United States	LA	Quebec	1994	09	14443	5
M	2804800000	Arsenic	KGM	United States	LA	Quebec	1990	03	2175	
M	2804800000	Arsenic	KGM	United States	LA	Ontario	1995	05	4610	
M	2804800000	Arsenic	KGM	United States	KY	Quebec	1997	03	107	
M	2804800000	Arsenic	KGM	United States	KY	Ontario	1988	09	60	
M	2804800000	Arsenic	KGM	United States	IL	Ontario	1993	05	1064	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1996	05	298	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1995	05	296	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1994	11	249	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1994	06	465	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1994	03	249	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1993	08	711	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1993	05	233	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1993	03	233	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1992	10	190	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1989	06	103	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1988	12	141	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1988	11	1226	
M	2804800000	Arsenic	KGM	United States	CA	Ontario	1988	08	72	
M	2804800000	Arsenic	KGM	United States	CA	British Columbia	1989	09	2887	1
M	2804800000	Arsenic	KGM	United States	CA	British Columbia	1988	02	3427	1
M	2804800000	Arsenic	KGM	United States	AZ	Quebec	1996	05	607	

M	2804800000	Arsenic	KGM	United States	99	Quebec	1993	11	19019	3
M	2804800000	Arsenic	KGM	United States	99	Quebec	1992	03	3258	114
M	2804800000	Arsenic	KGM	United States	99	Quebec	1991	12	3081	10
M	2804800000	Arsenic	KGM	United States	99	Quebec	1991	11	3041	106
M	2804800000	Arsenic	KGM	United States	99	Ontario	1994	04	68	
M	2804800000	Arsenic	KGM	United States	99	Ontario	1991	09	5000	9
M	2804800000	Arsenic	KGM	United States	99	Ontario	1988	02	2907	68
M	2804800000	Arsenic	KGM	United States	99	British Columbia	1992	05	513	1
M	2804800000	Arsenic	KGM	United States	99	British Columbia	1991	05	5997	209
M	2804800000	Arsenic	KGM	United States		Quebec	1989	02	5350	10
M	2804800000	Arsenic	KGM	United States		British Columbia	1990	07	4461	156
M	2804800000	Arsenic	KGM	United States		British Columbia	1990	06	9064	31
M	2804800000	Arsenic	KGM	United States		British Columbia	1990	03	2800	9
M	2804800000	Arsenic	KGM	United Kingdom		British Columbia	1995	03	175	6
M	2804800000	Arsenic	KGM	Japan		Ontario	1995	12	5881	205
M	2804800000	Arsenic	KGM	Japan		Ontario	1995	11	2532	88
M	2804800000	Arsenic	KGM	Japan		Ontario	1995	03	1998	69
M	2804800000	Arsenic	KGM	Japan		Ontario	1992	12	1573	5
M	2804800000	Arsenic	KGM	Japan		Ontario	1992	04	1491	5
M	2804800000	Arsenic	KGM	Japan		Nova Scotia	1996	06	4804	168
M	2804800000	Arsenic	KGM	Japan		New Brunswick	1997	02	4662	163
M	2804800000	Arsenic	KGM	Japan		British Columbia	1995	03	4129	144
M	2804800000	Arsenic	KGM	Japan		British Columbia	1990	05	4948	173
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1997	05	16824	342
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1997	02	21200	239
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1997	01	21200	239
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	12	21200	229
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	11	2268	76
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	10	21600	240
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	08	44900	558
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	05	17200	244
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	04	21200	265
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	03	15000	370
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1996	01	5004	1453
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1995	06	5830	161

M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1995	05	14966	8
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1995	04	5300	1
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1995	03	2002	
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1994	12	8250	1
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1994	03	7800	1
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1993	09	998	
M	2804800000	Arsenic	KGM	China, P. Rep.		Quebec	1990	10	18000	3

TYPE	CODE	DESCRIPTION	UOM	COUNTRY	US_STATE	PROVINCE	YEAR	MONTH	QTY	VA
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1997	04	2000	
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1997	03	17020	21
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1996	12	2120	
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1996	09	21200	44
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1996	05	2000	4
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1996	04	250	
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1996	02	908	4
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	12	1000	2
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	11	2000	4
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	08	3000	7
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	06	2931	4
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	05	2000	4
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	03	2120	6
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1995	02	6806	15
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1994	12	2007	7
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1994	10	3813	13
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1994	03	2000	3
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1994	01	1000	1
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1993	10	1000	2
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1993	02	656	2
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1992	11	1000	1
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1992	01	4990	9
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1991	12	5300	9
M	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1991	06	2120	4

	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1991	04	1000	2
	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1991	03	1877	656
	2804800000	Arsenic	KGM	China, P. Rep.		Ontario	1991	02	2120	7
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1997	02	1029	17
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1996	12	1000	2
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1996	08	1000	1
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1996	06	530	10
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1995	04	1000	2
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1995	02	100	2
	2804800000	Arsenic	KGM	China, P. Rep.		Manitoba	1994	11	65	
	2804800000	Arsenic	KGM	China, P. Rep.		British Columbia	1990	07	2047	71

No values indicates there is no trade during the selected time period.

APPENDIX C

Economic Data

ARSENIC

By Daniel L. Edelstein

The United States was the world's largest consumer of arsenic in 1996, accounting for about two-thirds of world demand. Domestic apparent demand for arsenic metal and compounds has remained relatively stable over the past 4 years, averaging about 2,000 metric tons of contained arsenic per year. All domestic arsenic requirements were met by imports; arsenic production in the United States was last reported in 1985. On a contained metal basis, arsenic trioxide accounted for 99% of imports in 1996. China, the world's largest producer of both arsenic trioxide and arsenic metal, was the leading source of U.S. imports of both products. Including material shipped through Hong Kong, China accounted for 44% and 84%, respectively, of trioxide and metal imports.

Legislation and Government Programs

Because of the toxicity of arsenic and its compounds, several environmental and workplace regulations proposed or amended during 1996 specify limitations for arsenic releases or exposure levels. In May, the Environmental Protection Agency (EPA) issued rules that raised the minimum level of substance release that requires public notification for 202 substances under the Community Right-to-Know Act of 1986, for its list of extremely hazardous substances (EHS); the list includes four arsenic compounds. However, the reportable quantities for these compounds remained unchanged at the minimum 1 pound per occurrence (U.S. Environmental Protection Agency, 1996b). In July, EPA proposed adding seven groups to the list of industry groups subject to the reporting requirements of the Community Right-to-Know Act, including coal mining, metal mining, and electric utilities. Arsenic compounds were cited as contaminants in coal and oil combustion products at electric powerplants (U.S. Environmental Protection Agency, 1996a).

In July, the Occupational Safety and Health Administration (OSHA), as part of a Presidential directive to remove or revise standards that are out of date, duplicative, or not needed to maintain employee health and safety, proposed revision of medical surveillance requirements for certain workers exposed to inorganic arsenic, including elimination of the semiannual sputum cytology examinations and reduction from semiannual to annual the frequency of required chest x-rays for workers 45 years of age or older or workers having had 10 or more years of exposure to arsenic at levels above the action level. In reevaluating the sputum-cytology provision, OSHA found no studies that addressed the efficacy of this test as a screening tool for lung cancer for employees specifically exposed to inorganic arsenic. Similarly, the efficacy of providing semiannual chest x-rays as a screening tool had not been established (U.S. Department of Labor, 1996).

Consumption

Overall consumption of arsenic remained relatively unchanged in 1996, for the third consecutive year. Estimated demand for arsenic in wood preservatives, which accounted for about 90% of total arsenic demand, was essentially unchanged from that of 1995, despite growth in the domestic housing industry; housing starts and construction spending rose by about 9% and 4%, respectively. Demand for arsenic by wood preservative formulators in 1995 had been boosted by in-process construction and restocking by distributors of pressure-treated lumber following the 1994 surge in housing. Arsenic trioxide was consumed in the production of arsenic acid for formulation of chromated copper arsenate (CCA) wood preservatives by the three principal producers of arsenical wood preservatives: Hickson Corp., Conley, GA; CSI, Harrisburg, NC; and Osmose Corp., Memphis, TN. Osmose also produces arsenic acid for the glass industry as a fining agent to disperse air bubbles.

The demand for arsenic metal for nonferrous alloys especially battery-lead alloys, plummeted for the second consecutive year. Consumers, fearing disruption from Chinese suppliers, may have over-brought in 1994, reducing their need for metal purchases in the 2 subsequent years. Some of the surplus metal inventories may have been exported in 1995, accounting for a rise in metal exports. Also, continued growth in market share for maintenance-free automotive batteries, which require little or no arsenic, may be further lowering demand for arsenic metal. Commercial grade arsenic metal 99% pure, is used in lead- and copper-based alloys as a minor additive (0.01% to 0.5%) to increase strength in the posts and grids of lead-acid storage batteries and to improve corrosion resistance and tensile strength in copper alloys. About 15 tons of high-purity arsenic metal, of 99.9999% or higher purity, was used in the manufacture of crystalline gallium arsenide, a semiconducting material used in optoelectronic circuitry, high-speed computers, and other electronic devices.

Arsenic consumed in agricultural uses continued to decline following the EPA's 1993 cancellation of arsenic acid for use as a cotton desiccant. The remaining agricultural use for arsenic was as an herbicide for control of weeds. ISK Bioscience, Mentor, OH, produced the arsenical herbicide monosodium methanearsonate (MSMA) at a plant in Houston, TX.

Prices

Prices for arsenic trioxide are not published. The average customs value for imported arsenic trioxide in 1996 was 22 cents per pound, down by about 2 cents per pound from that of 1995. The decline was attributed mostly to the lower value of some off-grade material imported from Chile for blending with high-purity material. High-purity trioxide from Mexico averaged 33 cents per pound. Prices for high-grade (minimum 99%) arsenic trioxide generally are quoted at an 8- to 12-cent-per-pound premium to low-grade (minimum 95%) arsenic trioxide. Owing to lowered demand and surplus supplies, prices for arsenic metal declined sharply, the Chinese import price averaging 40 cents per pound, down almost 40% from that of 1995.

World Review

Commercial-grade arsenic trioxide was recovered from the smelting or roasting of nonferrous metal ores or concentrates in at least 18 countries. High-arsenic smelter or roaster dusts and residues that usually are not processed to commercial-grade trioxide are recovered in several other countries as well as at plants in countries producing commercial-grade material. This material is frequently stockpiled and could be available for future processing. Ghana is one such country that has the estimated capacity to produce about 9,000 tons per year of crude trioxide from gold roasting operations. Most countries do not report their arsenic production, and world production values have a high degree of uncertainty. China was the world's largest producer as well as the major source of U.S. imports. Chinese production was estimated to have declined sharply in 1996 owing to the combined impact of environmental constraints, treatment of lower arsenic content ores, and weather-related problems. In France, Societe d'Exploitation Pyrometalurgie Salsigne, formed in November 1992, began commercial production of arsenic trioxide in 1993. The company which purchased the gold smelter and roaster formerly operated by Mines et Products Chimiques de Salsigne, has the capacity to produce significant quantities of refined arsenic trioxide. However, the company faced financial difficulties in 1995 and had filed for bankruptcy. Production had been halted by yearend 1995, and the plant remained idle throughout 1996. A second producer, Metaleurop SA, with capacity to produce about 6,000 tons per year of high purity trioxide, reportedly processed some imported crude trioxide from Ghana.

In Chile, production from the roasting of gold-copper ores at the El Indio Mine increased in 1996, countering the decline in Chinese production. U.S. imports from Chile rose more than 270%, making it the second largest source for domestic imports of arsenic trioxide. Included in both imports and production from Chile in 1996 were an estimated 2,000 tons of stockpiled off-grade material, not previously counted as production, that was imported for blending with high-grade trioxide.

Arsenic metal, which accounts for only 3% of world demand for arsenic, was produced by the reduction of arsenic trioxide. Commercial-grade arsenic metal, 99% pure, accounted for the majority of world arsenic metal production and was produced only in China. High-purity arsenic, 99.9999% pure or greater, for use in the semiconductor industry was produced by about 10 companies. Furukawa Electric Co. Ltd. in Japan and Preussag AG in Germany were believed to be the world's largest producers, with capacities of 30 and 15 metric tons per year, respectively.

Outlook

With the major market for arsenic being the production of arsenical wood preservatives, the demand for arsenic is closely tied to the home construction market, where wooden decks containing arsenical preservatives have become ubiquitous. According to data published by the American Wood Preservative Institute, demand for treated wood rose precipitously in the 5-year period ending in 1988. In 1988, about 450 million cubic feet of wood were treated with waterborne preservatives (98% estimated to be CCA), compared with 300 million cubic feet in 1984. Demand softened in the 1989-91 period before resuming its upward trend. In 1995, the last year for which data are available, the quantity of wood treated with waterborne preservatives, was about 450 million cubic feet, down from about 500 million in 1994. In 1995, waterborne preservatives were used for about 75% of all treated lumber.

The apparent demand for arsenic trioxide in wood preservatives declined slightly in 1996 despite an increase in housing starts. Restocking by wood preservative manufacturers and carry-over from the 13% growth in housing starts in 1994 may have served to boost apparent demand in 1995. Future demand for arsenic is expected to closely follow that for new home construction, although the replacement and renovation markets could increase as a percentage of total market share. The prohibition on use of CCA preservatives in certain applications and the greater acceptance of alternative preservatives could negatively affect future demand.

Despite environmental regulation that has led to global dislocations of production over the past decade, including cessation of production in two historically large producing countries, Sweden and the United States, new suppliers have emerged to fill the voids. Although environmental pressures may continue to cause curtailment of existing capacity, given the abundance of high-arsenic residues from nonferrous metal processing, world supplies of arsenic trioxide are expected to remain adequate to meet projected need. Environmental regulation may, in fact, encourage commercial production from existing stockpiles of noncommercial material.

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Other

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1995 Wood Preserving Industry Production Statistical Report.

TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS 1/

(Metric tons, arsenic content)

	1992	1993	1994	1995	1996
U.S. supply:					
Imports, metal	740	767	1,330	557	252
Imports, compounds	23,300	20,900	20,300	22,100	21,200
Total	24,000	21,600	21,600	22,700	21,400
Distribution of U.S. supply:					
Exports 2/	94	364	79	430	36
Apparent demand	23,900	21,300	21,500	22,300	21,400
Estimated U.S. demand pattern:					
Agricultural chemicals	3,900	3,000	1,200	1,000	950
Glass	900	900	700	700	700
Wood preservatives	17,900	16,200	18,000	19,600	19,200
Nonferrous alloys and electronics	800	800	1,300	600	250
Other	400	400	300	400	300
Total	23,900	21,300	21,500	22,300	21,400

1/ Data are rounded to three significant digits; may not add to totals shown.
2/ Metal only.

TABLE 2
U.S. IMPORTS FOR CONSUMPTION OF ARSENICALS 1/

Class and country	1995		1996	
	Quantity 2/ (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Arsenic trioxide:				
Belgium	786	$420	579	$314
Bolivia	--	--	120	55
Chile	3,210	1,260	8,790	2,930
China	15,900	8,230	11,000	5,650
France	2,820	1,550	2,480	1,360
Hong Kong	1,510	619	1,380	681
Mexico	3,560	2,560	2,980	2,140
Philippines	1,080	430	612	231
United Kingdom	1	2	--	--
Other	195	90	18	20
Total	29,000	15,200	28,000	13,400
Arsenic acid:				
Canada	--	--	(3/)	2
Israel	(3/)	3	1	13
Total	(3/)	3	1	14
Arsenic metal:				
China	491	709	212	185
Germany	37	2,000	10	2,110
Japan	29	1,400	29	1,480
United Kingdom	--	--	(3/)	23
Other	(3/)	3	--	--
Total	557	4,100	252	3,790

1/ Data are rounded to three significant digits; may not add to totals shown.
2/ Data erroneously reported as "thousand metric tons."
3/ Less than 1/2 unit.

Source: Bureau of the Census.

TABLE 3
AVERAGE ARSENIC PRICES

(Cents per pound)

	1995	1996
Trioxide, Mexican	33	33
Metal, Chinese	66	40

Source: Calculated from Bureau of the Census import data

TABLE 4
ARSENIC TRIOXIDE 1/ WORLD PRODUCTION, BY COUNTRY 2/ 3/

(Metric tons)

Country 4/	1992	1993	1994	1995	1996 e/
Belgium e/	2,000	2,000	2,000	2,000	2,000
Bolivia	633	663	341	362 r/	370
Canada e/	250	250	250	250	250
Chile e/	6,016 5/	6,200	6,300	6,400	9,000
China e/	15,000 r/	14,000 r/	18,000 r/	21,000 r/	15,000
France e/	2,000	3,000	6,000	5,000	3,000
Georgia e/	1,500	1,000	500	400	400
Germany e/	300	300	300	250 r/	250
Ghana e/ 6/	500	500	500	500	500
Iran e/	492 5/	500	500	500	500
Japan e/	50	40	40	40	40
Kazakstan e/	2,000	2,000	1,500	1,500	1,500
Mexico	4,293	4,447	4,400 e/	4,500 e/	4,300
Namibia 7/	2,456	2,290	3,047 r/	1,661 r/	1,100
Peru 8/	644 r/	391 r/	286 r/	285 r/ e/	285
Philippines e/	5,000	2,000	2,000	2,000	2,000
Portugal e/	150	150	150	100	100
Russia e/	2,500	2,000	1,500	1,500	1,500
Total	45,800 r/	41,700 r/	47,600 r/	48,200 r/	42,100

e/ Estimated. r/ Revised

1/ Including calculated arsenic trioxide equivalent of output of elemental arsenic and arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production.

2/ World totals and estimated data are rounded to three significant digits; may not add to totals shown.

3/ Table includes data available through Apr. 1, 1997.

4/ Austria, Hungary, the Republic of Korea, South Africa, Spain, the United Kingdom, and former Yugoslavia have produced arsenic and/or arsenic compounds in previous years, but information is inadequate to make reliable estimates of output levels, if any.

5/ Reported figure.

6/ Estimated commercial byproduct of gold ore roasting. Does not include additional byproduct production of noncommercial grade material estimated at 4,000 tons in 1992, and up to 9,000 tons per year in 1993-96.

7/ Output of Tsumeb Corp. Ltd. only.

8/ Output of Empresa Minera del Centro del Peru (Centromin Peru) as reported by the Ministerio de Energia y Minas.

ARSENIC

(Data in metric tons, unless otherwise noted)

Domestic Production and Use: All arsenic metal and compounds consumed in the United States were imported, principally from China. More than 95% of the arsenic consumed was in compound form, principally as arsenic trioxide. Three principal manufacturers of wood preservatives consumed most of the arsenic trioxide for the production of arsenic acid for formulation of chromated copper arsenate (CCA) wood preservatives. Arsenic acid was also consumed by one manufacturer of arsenical herbicides. Metallic arsenic was consumed in the manufacture of nonferrous alloys, principally in lead alloys used in lead-acid batteries. About 15 tons of high-purity arsenic was consumed in the manufacture of semiconductor materials. About 90% of all arsenic was consumed in the production of wood preservatives; the balance was consumed in glass manufacturing, agricultural chemicals, nonferrous alloys, and miscellaneous uses. The value of arsenic metal and compounds consumed was estimated at $20 million.

Salient Statistics—United States:	1992	1993	1994	1995	1996[e]
Imports for consumption:					
Metal	740	767	1,330	557	250
Trioxide[1]	30,700	27,500	26,800	29,000	29,000
Arsenic acid	40	—	5	([2])	1
Exports, metal	94	364	79	430	20
Consumption, apparent, arsenic content	23,900	21,300	21,500	22,300	22,000
Price, cents per pound, average:[3]					
Trioxide, Mexican	29	33	32	33	33
Metal, Chinese	56	44	40	66	53
Net import reliance[4] as a percent of apparent consumption	100	100	100	100	100

Recycling: Process water and contaminated runoff collected at wood treatment plants are reused in pressure treatment. Gallium arsenide scrap from the manufacture of semiconductor devices is reprocessed for gallium and arsenic recovery. Domestically, no arsenic is recovered from arsenical residues and dusts at nonferrous smelters, although some of these materials are processed for recovery of other metals.

Import Sources (1992-95): China, 50%; Chile, 16%; Mexico, 12%; and other, 22%.

Tariff: Item	Number	Most favored nation (MFN) 12/31/96	Non-MFN[5] 12/31/96
Metal	2804.80.0000	Free	13.2¢/kg.
Trioxide	2811.29.1000	Free	Free.
Sulfide	2813.90.1000	Free	Free.
Acid[6]	2811.19.1000	2.3% ad val.	4.9% ad val.

Depletion Allowance: 14% (Domestic), 14% (Foreign).

Government Stockpile: None.

Prepared by **Daniel L. Edelstein, (703) 648-4978 [Fax: (703) 648-7757].**

ARSENIC

Events, Trends, and Issues: Domestic demand for arsenic in the wood preservative industry was relatively unchanged in 1996, despite projected growth in the domestic housing industry. Demand in 1995 had been boosted by in-process construction and restocking by distributors of pressure-treated lumber following the 1994 surge in housing construction. The apparent demand for arsenic metal for nonferrous alloys, especially battery-lead alloys, remained low for the second consecutive year. Consumers, fearing disruptions from Chinese suppliers, may have overbought in 1994, reducing their need for additional material in the subsequent 2 years. Also, continued growth in market share for maintenance-free automotive batteries, which require little or no arsenic, may be further lowering demand for arsenic metal.

Because of the toxicity of arsenic and its compounds, numerous environmental and workplace regulations proposed or amended during 1996 specify limitations for arsenic releases or exposure levels. In May, the Environmental Protection Agency issued revised rules for reportable quantities, under the Community Right-to-Know Act of 1986, for its list of extremely hazardous substances, which includes numerous arsenic compounds. The reportable quantity for arsenic compounds remained at 1 pound. In July, the Occupational Safety and Health Administration, as part of a review process to modify out-of-date regulations, proposed revision of medical surveillance requirements for certain workers exposed to inorganic arsenic, including elimination of the semiannual sputum cytology examinations and reduction, from semiannual to annual, of the frequency of required chest x-rays

World Production, Reserves, and Reserve Base:

	Production (Arsenic trioxide)	
	1995	1996[e]
United States	—	—
Belgium	2,000	2,000
Chile	6,400	6,500
China	13,000	13,000
France	5,000	4,000
Kazakstan	1,500	1,500
Mexico	4,500	4,500
Namibia	2,300	2,300
Philippines	2,000	2,000
Russia	1,500	1,500
Other countries	2,600	3,000
World total	41,000	41,000

Reserves and reserve base[7]
(Arsenic content)

World reserves and reserve base are thought to be about 20 and 30 times, respectively, annual world production.

World Resources: World resources of copper and lead contain about 11 million tons of arsenic. Substantial resources of arsenic occur in copper ores in northern Peru and the Philippines and in copper-gold ores in Chile. In addition, world gold resources, particularly in Canada, contain substantial resources of arsenic.

Substitutes: Substitutes for arsenic compounds exist in most of its major uses, although arsenic compounds may be preferred because of lower cost and superior performance. The wood preservatives pentachlorophenol and creosote may be substituted for CCA when odor and paintability are not problems and where permitted by local regulations. A recently developed alternative, ammoniacal copper quaternary, which avoids using chrome and arsenic, has yet to gain widespread usage. Nonwood alternatives, such as concrete, steel, or plastic lumber, may be substituted in some applications for treated wood. A South American hardwood, ipe, which requires no chemical treatment, has been used in some localities in oceanfront boardwalks

[e] Estimated

[1] Arsenic trioxide (As_2O_3) contains 75.7% arsenic by weight

[2] Less than ½ unit

[3] Calculated from Bureau of the Census import data

[4] Defined as imports - exports + adjustments for Government and industry stock changes

[5] See Appendix B

[6] Tariff is free for Canada, Israel, Caribbean Basin countries, and designated Beneficiary Andean and developing countries

[7] See Appendix C for definitions. The reserve base for the United States was estimated at 80,000 tons

CSI
CHEMICAL SPECIALTIES, INC.

FAX TRANSMISSION

TO:	**Paul Greene**	**FROM:**	**Jill Wilson**
COMPANY:	**Dillon Consulting**	**DATE: 8/13/97**	**PAGE 1 OF 1**
FAX #:	**403-873-3328**	**RE:**	**Arsenic Trioxide**

If you do not receive all pages please contact sender at 704-455-5181, extension 234.

Our plant manager, Steve Novak, has briefed me on the phone conversations he has had with you and Craig Thomas. Per his request the following is our current specification for arsenic trioxide:

As_2O_3	95-99%
Fe	500 – 5000 ppm
Sb	0.5% - 1.0%
Hg	< 300 ppm
Cl	< 100 ppm
H_2O	< 0.5%

If I can be of any further assistance in this matter please give me a call at the number shown above. This appears to be an interesting project you've undertaken.

Cc: S. Novak

CSI PO BOX 610 5910 PHARR MILL ROAD HARRISBURG, NORTH CAROLINA 28075
PHONE 704-455-5181 FAX 704-455-5987

CSI
CHEMICAL SPECIALTIES, INC.

FAX TRANSMISSION

TO: **Paul Greene**
FROM: **Jill Wilson**
COMPANY: **Dillon Consulting**
DATE: 8/14/97 **PAGE 1 OF 1**
FAX #: **403-873-3328**
RE: **General Info CSI**

If you do not receive all pages please contact sender at 704-455-5181, extension 234.

In regards to our company and what we do, we are a subsidiary of Laporte plc out of Bedfordshire, UK. We produce a line of products for use by the wood treatment industry – primarily CCA (combination of copper, chrome and arsenic). We purchase in excess of 10 MM lbs. of arsenic trioxide yearly from several countries around the world.

We have three facilities for production of CCA but the processing of arsenic trioxide into arsenic acid is done at our Harrisburg, NC facility only. We buy the arsenic trioxide in bulk bags of either 1 MT or 1.7 MT capacity.

I realize this isn't a lot of information but hopefully it's what you need at the moment. Please keep me informed as to the progress of your project.

Cc: S. Novak

CSI PO BOX 1330 5910 PHARR MILL ROAD HARRISBURG, NORTH CAROLINA 28075
PHONE 704-455-5181 FAX 704-455-5987

Consommation
et Corporations Canada

Bureau des brevets

Ottawa, Canada
K1A 0C9

Consumer and
Corporate Affairs Canada

Patent Office

(11) (C) **1,314,149**

(21) 554,182

(22) 1987/12/11

(45) 1993/03/09

(52) 53-176

(51) INTL.CL.^{5} C22B-30/04

(19) (CA) **CANADIAN PATENT** (12)

(54) Methods of Recovering Arsenic Values from Waste

(72) Derka, Jaroslav R. , Canada

(73) Same as inventor

(57) 27 Claims

Canada

55417

ABSTRACT

A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process comprising the step of evaporating the arsenic values from the arsenic containing material into a gas stream which gas stream does not react with the arsenic values. A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process utilizing electrical energy for evaporation of arsenic trioxide in an evaporator into a gas stream and after separation of arsenic trioxide and any residue, the clean gas may be recycled to the evaporator thus minimizing possible emissions permitting the process to be carried out in a closed circuit thus substantially eliminating emissions.

FIELD OF INVENTION

This invention relates to methods of recovering arsenic values from arsenic bearing materials.

BACKGROUND OF THE INVENTION

Ores containing arsenic have to be subjected to an arsenic removal step prior to the extraction of other values. A typical example is gold ore - arsinopyrite.

The removal of arsenic is most often accomplished by roasting.

When roasted, Arsenic is oxidized to As_2O_3, and at the roasting temperature leaves the Roaster as a vapour together with the oxidation products of Sulphur, - Sulphur Dioxide and Sulphur Trioxide. The presence of Sulphur oxides with Arsenic complicates the subsequent Gas Cleaning step, resulting in an impure (crude) Arsenic Trioxide dust being trapped in a bag-house, following precipitation from the gas stream by the addition of cold air. The off-gas is usually discharged to the atmosphere with consequent environmental problems.

A major consumer of Arsenic Trioxide (As_2O_3) is the wood preservative industry. Since As_2O_3 from the roasting operation is not of a sufficient purity, a further refining step has to be employed.

Refining is usually accomplished by one of two approaches:

(a) Hot Water Leach, by one of two approaches.
(b) Ammonia Leach

(a) Hot Water Leach:

Approach 1

Hot water is used to dissolve the As_2O_3 from the crude feed material. Undissolved solids are separated from the solution by filtration, and the filtered solution is either cooled or evaporated in a crystallizer to form As_2O_3 crystals.

Approach 2

Due to the positive effect of temperature on solubility of As_2O_3, pressure leaching may be employed with a higher water temperature hence obtaining a higher solubility of As_2O_3. The cost of energy with this approach is improved over Approach 1 but still remains very high.

(b) Ammonia Leach:

The Ammonia Leach process has an advantage over the hot water leach approach in that the solubility of As_2O_3 is higher in ammonia solution. However the only user of this process of which the inventor is presently aware has presently ceased operations due to technical difficulties.

Both approaches additionally have a common problem. Recontamination of the residue is caused by a reaction between dissolved Arsenic and the Iron content of the residue, resulting in a slimy material which is difficult to filter. Since this residue contains in some cases significant amounts of precious metals, this is a serious problem. Further these approaches are generally complicated and have a high operating and capital cost.

U.S. patent 3923478 teaches pyrites-roast gas at 350-400 degrees C composed mainly of SO_2 with As_2O_3, iron oxide dust, SO_3, and other impurities being scrubbed in a closed system with a solvent (preferably aqueous) for As_2O_3. The product is obtained by concentration and crystallization and unwanted deposits formed are removed by dissolution in unsaturated As_2O_3 solution. Using systems in parallel and switching liquid flows makes possible continuous operation, it is alleged, with minimal solid or liquid effluent.

Thus a process and an apparatus is asserted as having been provided for recovering arsenic trioxide from a gas by washing out the oxide from the gas with a liquid having the ability of dissolving arsenic trioxide. The purported invention is characterized that non-desired deposits in the apparatus formed in connection with a saturated solution are removed by

dissolution with an unsaturated solution of arsenic trioxide. See also corresponding Canadian Letters patent 1033538.

U.S. patent 4588564 relates to a process for recovering arsenic trioxide from scrubbing water used to scrub the flue gas of sulfide ore smelting. The crude arsenic trioxide crystals collected from the scrubbing solution which contains plaster as an impurity are purified by treating with hydrochloric acid of a concentration of 50-150 g/l at a temperature not higher than 30°C.

U.S. patent 4605812 purports to teach a process for the removal of arsenic from gases whereby arsines are removed from streams of hydrocarbons or inert gases by contacting the streams with copper (II) chromite catalyst.

U.S. patent 4615731 purports to teach a hydro metallurgical process for treating a feed comprising an aqueous acidic solution containing dissolved therein one or more precious metals selected from the group, platinum group metals and gold and one or more of the nuisance elements bismuth lead, tin, arsenic and antimony, to separate the precious metals from the nuisance elements comprising:

(i) treating the aqueous acidic solution with sulfur dioxide in the presence of selenium and a halide to reduce and precipitate selectively selenium and precious metals, and

(ii) separating the precipitated components from the remaining solution; thereby separating selenium and precious metals from the nuisance elements.

U.S. patent 4489046 purports to teach a method for converting an arsenic-containing waste product to a depositable, substantially arsenic-free form by fuming-off the arsenic content thereof. The method comprises melting the waste product under oxidizing conditions in a furnace to form an oxidic slag melt; causing turbulence of the melt, while maintaining a reducing atmosphere supporting the formation of arsenic (III) oxide at the furnace

temperature driving-off arsenic content of the waste product substantially in the form of gaseous arsenic (III) oxide; separating the formed oxide by condensation and recovering the same and removing from said furnace a substantially arsenic-free depositable slag.

U.S. patent 4244735 purports to teach a process for the hydrometallurgical recovery of metals, such as, lead, silver, gold, antimony, and bismuth from materials such as flue dust in the presence of arsenic, comprising precipitating arsenic as an insoluble ferric-arsenic compound in the first processing step, carrying the insoluble arsenic compound through a chloride leach step, in which it is insoluble, to recover the metals, and disposing of the residue in which the arsenic has been fixed with ferric ions to render it non-polluting, or alternatively, recovering the arsenic by caustic leach and crystallization.

Swiss patent 273779 purports to teach a continuous refining process which it is purported, can be done more intensively and is carried out in equipment which consists of a lined vessel, screw feeder with a rotating disc mounted on it and bearing fixed knives, screening plates. Silite heaters and a discharging screw, moving inside the vessel. The product to be refined is fed on to the rotating disc of the screw feeder having a sealed hopper. The distance between the cover and the disc is relatively small (i.e. 1/5 to 1/8 of the diameter of the disc), as a result of which uniform heating of the reaction zone is obtained and dust-formation of the incoming material is eliminated. The product to be refined is fed on to the disc, which is red-hot (500-600 degrees C), and the Arsenic trioxide is purported to immediately begin to evaporate, which causes the original thickness of the layer of material to diminish. The solid residue, which comprises about 10% of the original material put on the disc, is removed by the fixed knife and the screw being conveyed to the hopper. In this way the disc is cleaned ready for the fresh deposit of material. The vapours of the trioxide go along into a crystallizer of

the usual type. The device operates under minimum vacuum (0.5-1.0 mm of water column).

German reference 131850 purports to teach that Sulphur dioxide gases containing As_2O_3, halides and dust, are cleaned by washing with circulating H_2SO_4 solution of which the concentration is adjusted to such a low value that the halides are being dissolved, separating the H_2SO_4 solution and subjecting this solution to a vacuum evaporation to evaporate the halides and crystalize As_2O_3. The purified H_2SO_4 is recycled.

Once again these approaches are generally complicated and have high operating costs and capital costs.

It is therefore an object of this invention to provide an improved process for the recovery of Arsenic values.

It is a further object of the invention to provide such process at reduced operating and reduced capital costs.

Further and other objects of the invention will be realized by those skilled in the art from the following Summary of the Invention and Detailed Description of Embodiments thereof.

SUMMARY OF THE INVENTION

According to one aspect of the invention, a process is provided for the recovery of Arsenic values from Arsenic containing material which may also contain Sulphur in one embodiment the Arsenic being in the form of As_2O_3, the process comprising the step of evaporating (in a wet or dry state) the Arsenic values from the Arsenic containing material into a gas stream which gas stream does not react with the Arsenic values. The gas stream is then cooled to precipitate the Arsenic. The residue from which the arsenic was evaporated may then be treated for removal of the metal values. The simplicity of the process is reflected in relatively low operating costs and relatively low capital expenditures. Without the presence of Sulphur, the As_2O_3 vapour can be well cleaned of any carry-over solids (prior to precipitation) giving a high purity As_2O_3 product, acceptable to for example the wood preserving industry. Preferably the evaporation of the Arsenic values is as arsenic trioxide (As_2O_3) near its boiling point.

According to another aspect of the invention the evaporation of the arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil or hydrocarbon gas.

(b) Fluid bed heated by combustion of oil or hydrocarbon gas or by electrical energy.

(c) Electrical plasma reactor.

According to another aspect of the invention the arsenic values (for example the arsenic trioxide) are precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water evaporation. Thus the As_2O_3 is deposited on the surface of a cold particle causing it to grow to a form of little balls. The size of the balls of As_2O_3 may be controlled by the amount of precipitation onto the coarse particles. Thus "dusting" during handling of the "balled" material is reduced.

According to another aspect of the invention the process may be carried out utilizing electrical energy for evaporation of arsenic trioxide in an evaporator into a gas stream and after separation of the residue and precipitation of arsenic trioxide, the clean gas stream may be recycled back to the evaporator thus minimizing possible atmospheric emissions.

Thus, according to another aspect of the invention the process may be carried out in a closed circuit thus substantially eliminating emissions giving rise to substantial and significant environmental benefits.

According to another aspect of the invention the process may be carried out utilizing combustion of oil or hydrocarbon gas for evaporation of arsenic trioxide in the evaporator. Due to production of combustion products with this process the gas after cleaning can be vented.

The invention will now be illustrated with reference to the following drawings of embodiments of the invention and the detailed description of the embodiments thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow sheet illustrating a process carried out according to an embodiment of the invention.

Figure 2 is a flow sheet illustrating another process according to another embodiment of the invention.

Figure 3 is a flow sheet illustrating another process according to another embodiment of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

With reference to Figures 1 and 2, two processes are disclosed schematically according to the flow sheets. The difference between the processes relate to the energy source used to generate the heat in the evaporator to evaporate the Arsenic trioxide (As_2O_3).

With reference to Figures 1 and 2, the crude material containing arsenic trioxide 10 is exposed to heat in the evaporator 50. The arsenic trioxide vapour is transported from the evaporator 50 by a stream of other gas e.g. Nitrogen (See Figure 3) and the mixture leaves at a temperature of 250 - 500 degrees C (preferably 350 - 450 degrees C.) 12.

The evaporator 50 could be a:

(a) heated chamber - (for example for fine material which wouldn't stay in a fluid bed)

(b) fluid bed

heated by oil or hydrocarbon gas combustion, (Figure 1), or by electrical energy (Figure 2). The carry-over solids (residue) 24 are removed from the hot gas stream in a solids separator 52, preferably in a double filtration baghouse.

The separated residue 24, usually containing other metallic values is then available for further treatment as the major portion of arsenic was removed. The clean gas 14 containing As_2O_3 vapour, or As_2O_3 vapour and water vapour and other gases, depending on the source of energy used in the evaporator, is then cooled in cooling and As_2O_3 removal section S_4 by injection of water, preferably condensate 20 from the scrubbing circuit to a temperature:

(a) above boiling point of water (110-200 degrees C.) and the precipitated Arsenic trioxide is then removed in the cold baghouse.

b) just above point of Arsenic trioxide precipitation (depending upon concentration of arsenic trioxide in the vapour), generally between 300 degrees C. to 460 degrees C., and the precipitation is accomplished by further cooling in a fluid bed of Arsenic trioxide by spray of water (preferably condensate from scrubbing circuit) 20, to produce a desirable coarse product 26. (See Figure 3). The remaining gas is then scrubbed of Arsenic trioxide in a scrubber - cooler 56 and excess water vapour is condensed. The condensate 20 is recycled for cooling of the hot clean gas 14. The surplus 22 will be disposed of. The scrubbed cooled gas is then:

(a) recycled to the evaporator as Arsenic trioxide vapour carrier via 18 - if electric energy is utilized for heating of the evaporator.

(b) sent to stack. (See 18 of Figure 2).

With reference to Figures 1 and 2, equipment suitable for use

(1) as the evaporator 50 may comprise:

(a) Fluid bed heated by an electrically preheated circulating gas.

(b) Fluid bed heated by inserted electrical heaters.

(c) Fluid bed heated by combustion of oil or hydrocarbon gas.

(d) Evaporation chamber heated by either electricity or by combustion of oil or hydrocarbon gas fine grained crude.

(2) for Solids separation 52 may comprise:

(a) High temperature bag-house, preferably two in series.

(3) For cooling and As_2O_3 removal referred to at 54, the equipment may comprise:

(a) A fluid bed of coarse As_2O_3 particles cooled by spraying with a scrubber solution or water 20. As_2O_3 deposits on the cold particles thus allowing the production of a coarse particle As_2O_3 product. The remaining As_2O_3 dust is removed in a cold bag-house and can be sent to either product storage or back for evaporation.

(b) Injection of scrubber condensate directly to hot gas-adiabatic cooling. The precipitated As_2O_3 is removed from the gas stream in a cold bag-house and sent to product storage.

(c) combination of both - cooling to temperature of As_2O_3 saturation by injection of condensate or water, then precipitation of As_2O_3 as per (a).

(4) As Scrubber and Water Condenser shown at 56:

(a) Scrubbing traces of As_2O_3 from the gas stream is accomplished in a tower or a venturi using the condensate from the following condenser. The amount of condensate to be used for scrubbing is determined by the consumption of Arsenic bearing scrubber solution used for gas cooling.

(b) As a Water condenser:

The water condenser can be a tray or preferably a packed tower which is cooled, depending on scrubber efficiency, by:

- directly injected cooling water - recycled, indirectly cooled condensate

Depending on the temperature of the cooling water, the Gas Cooling-Water Condenser may employ an additional cooling (for example, heat pump) so that a minimum of water vapour is recycled to evaporate.

The operating conditions may be as follows:

(1) Evaporator 50

Temperature 300-600 degrees C., preferably 350-450 degrees C. Pressure in freeboard - approximately minus 1 inch of H_2O.

(2) Hot bag-house

Temperature 300-400 degrees C. Pressure - approximately minus .5 psig.

(3) Precipitator

Temperature 80-150 degrees C. Pressure - approximately minus 1 psig.

(4) Cold bag-house

Temperature 80-150 degrees C., preferably 110-120 degrees C.

(5) As_2O_3 Scrubber

Temperature 65-80 degrees C., preferably 71 degrees C. Pressure - approximately minus 2.1 psig.

(6) Water Condenser

Temperature 5-10 degrees C., preferably lowest possible.

As many changes can be made to the embodiments without departing from the scope of the invention, it is intended that all material contained herein be interpreted as illustrative of the invention and not in a limiting sense.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE AS FOLLOWS:

1. A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process comprising the step of evaporating the arsenic values from the arsenic containing material into a gas stream which gas stream does not react with the arsenic values.

2. The process of Claim 1, wherein the arsenic is in the form of $As_2 0_3$.

3. The process of Claim 1, wherein the gas stream is, after solids separation, cooled to precipitate the arsenic.

4. The process of Claim 2, wherein the gas stream is, after solids separation, cooled to precipitate the arsenic.

5. The process of claim 2, 3, or 4, wherein the evaporation of the arsenic values is as arsenic trioxide ($As_2 0_3$) near its boiling point.

6. The process of Claim 1, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy.

7. The process of Claim 2, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas, or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy; or

(c) Electrical plasma reactor.

8. The process of Claim 3, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas, or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy.

9. The process of Claim 4, wherein the evaporation of the arsenic as arsenic trioxide is performed in:

(a) A chamber heated by a combustion of oil, hydrocarbon gas, or by electrical energy; or

(b) Fluid bed heated by combustion of oil, hydrocarbon gas or by electrical energy.

10. The process of Claim 1 further comprising the step of the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

11. The process of Claim 2, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from

the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

12. The process of Claim 3, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

13. The process of Claim 4, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

14. The process of Claim 6, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

15. The process of Claim 7, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

16. The process of Claim 8, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

17. The process of Claim 9, further comprising the step of wherein the arsenic values (for example the arsenic trioxide) being precipitated from

the clean arsenic trioxide vapour containing gas in a fluidized bed of arsenic trioxide particles cooled by water which allows production of coarse particles.

18. The process of Claim 10, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

19. The process of Claim 11, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

20. The process of Claim 12, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

21. The process of Claim 13, wherein the size of the particles may be controlled by the amount of precipitation of the arsenic onto coarse particles.

22. The process of Claim 14, wherein the size of the particles of As_2O_3 may be controlled by the amount of precipitation of the arsenic onto coarse particles.

23. The process of Claim 15, wherein the size of the particles may be controlled by the amount of precipitation of arsenic onto coarse particles.

24. The process of Claim 16, wherein the size of the particles may be controlled by the amount of precipitation of arsenic onto coarse particles.

25. The process of Claim 17, wherein the size of the particles may be controlled by the amount of precipitation of arsenic onto coarse particles.

26. A process for the recovery of arsenic values from arsenic containing material which may also contain sulphur, the process utilizing electrical energy for evaporation of arsenic trioxide in an evaporator into a gas stream and after separation of arsenic trioxide and any residue, the clean gas may be recycled to the evaporator thus minimizing possible emissions permitting the process to be carried out in a closed circuit thus substantially eliminating emissions.

27. The process of Claim 1, wherein the process utilizes combustion of oil or hydrocarbon gas for evaporation of arsenic trioxide in an evaporator.

*

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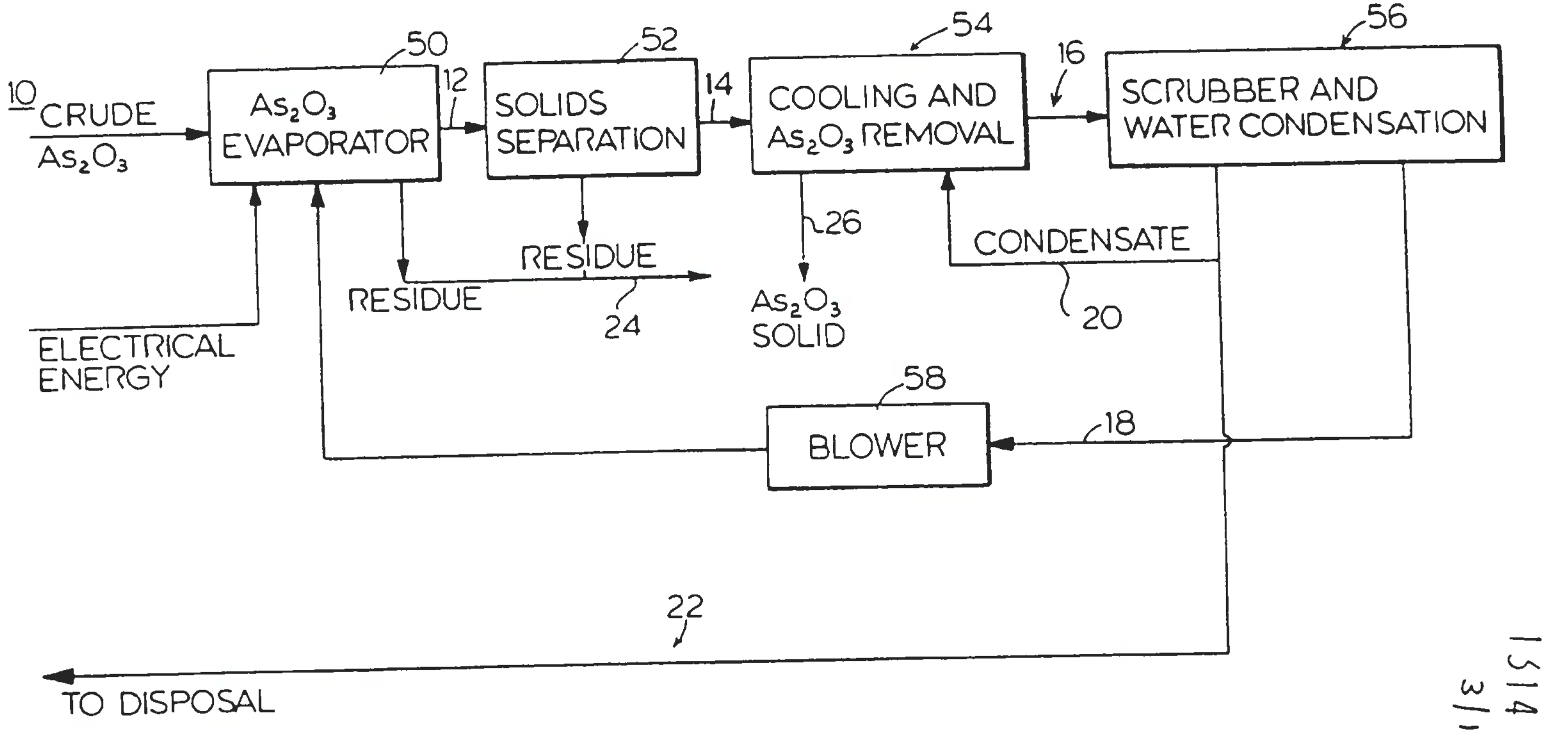
FIG.1.



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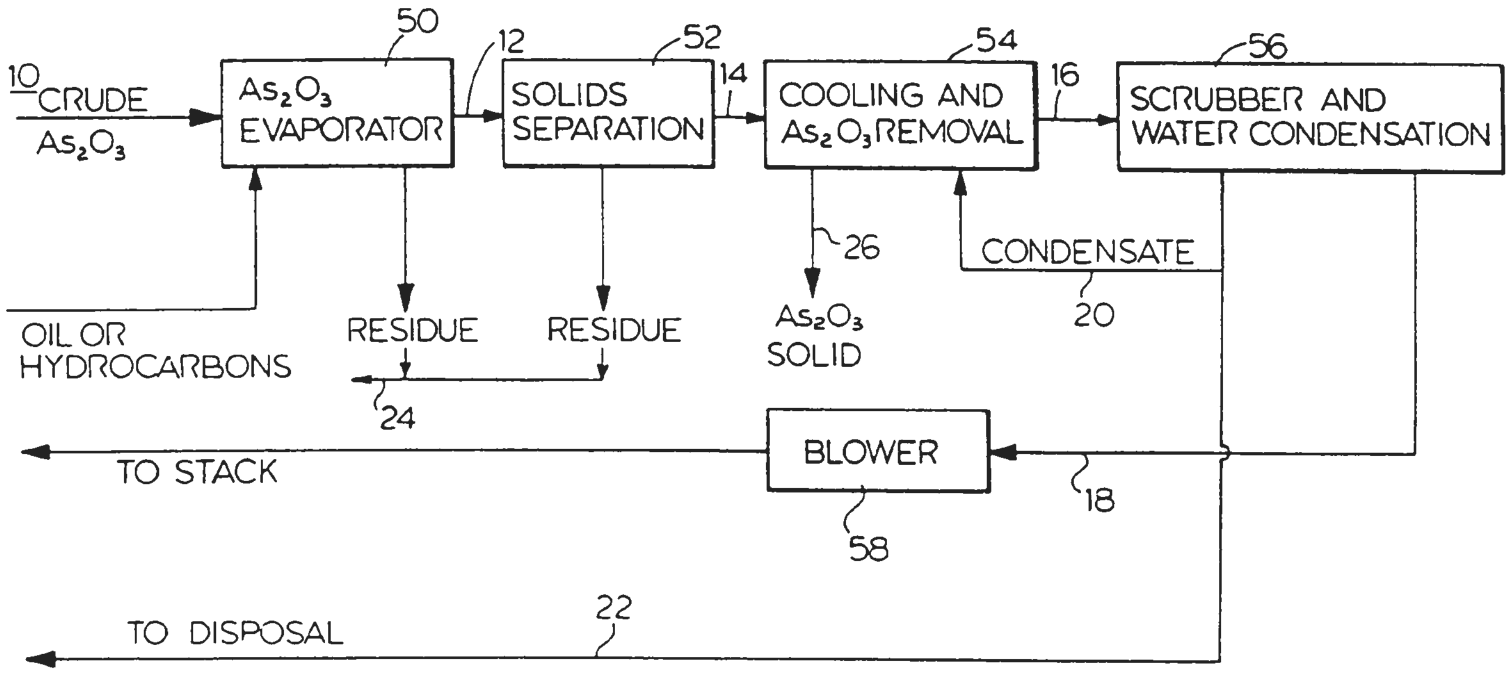

FIG. 2.

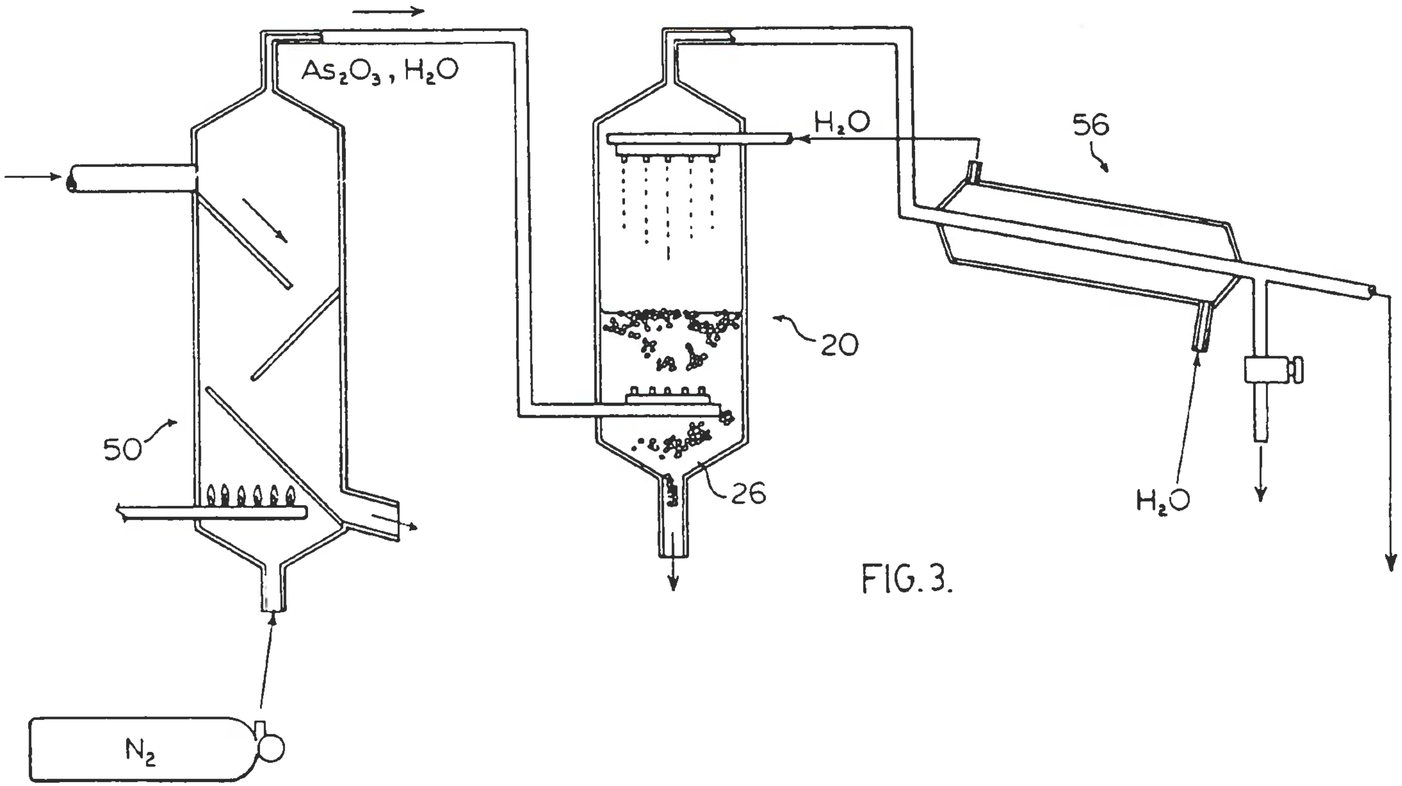

FIG. 3.

APPENDIX E

Gold Recovery Data

dissolution with an unsaturated solution of arsenic trioxide. See also corresponding Canadian Letters patent 1033538.

U.S. patent 4588564 relates to a process for recovering arsenic trioxide from scrubbing water used to scrub the flue gas of sulfide ore smelting. The crude arsenic trioxide crystals collected from the scrubbing solution which contains plaster as an impurity are purified by treating with hydrochloric acid of a concentration of 50-150 g/l at a temperature not higher than 30°C.

U.S. patent 4605812 purports to teach a process for the removal of arsenic from gases whereby arsines are removed from streams of hydrocarbons or inert gases by contacting the streams with copper (II) chromite catalyst.

U.S. patent 4615731 purports to teach a hydro metallurgical process for treating a feed comprising an aqueous acidic solution containing dissolved therein one or more precious metals selected from the group, platinum group metals and gold and one or more of the nuisance elements bismuth lead, tin, arsenic and antimony, to separate the precious metals from the nuisance elements comprising:

(i) treating the aqueous acidic solution with sulfur dioxide in the presence of selenium and a halide to reduce and precipitate selectively selenium and precious metals, and

(ii) separating the precipitated components from the remaining solution; thereby separating selenium and precious metals from the nuisance elements.

U.S. patent 4489046 purports to teach a method for converting an arsenic-containing waste product to a depositable, substantially arsenic-free form by fuming-off the arsenic content thereof. The method comprises melting the waste product under oxidizing conditions in a furnace to form an oxidic slag melt; causing turbulence of the melt, while maintaining a reducing atmosphere supporting the formation of arsenic (III) oxide at the furnace

temperature driving-off arsenic content of the waste product substantially in the form of gaseous arsenic (III) oxide; separating the formed oxide by condensation and recovering the same and removing from said furnace a substantially arsenic-free depositable slag.

U.S. patent 4244735 purports to teach a process for the hydrometallurgical recovery of metals, such as, lead, silver, gold, antimony, and bismuth from materials such as flue dust in the presence of arsenic, comprising precipitating arsenic as an insoluble ferric-arsenic compound in the first processing step, carrying the insoluble arsenic compound through a chloride leach step, in which it is insoluble, to recover the metals, and disposing of the residue in which the arsenic has been fixed with ferric ions to render it non-polluting, or alternatively, recovering the arsenic by caustic leach and crystallization.

Swiss patent 273779 purports to teach a continuous refining process which it is purported, can be done more intensively and is carried out in equipment which consists of a lined vessel, screw feeder with a rotating disc mounted on it and bearing fixed knives, screening plates. Silite heaters and a discharging screw, moving inside the vessel. The product to be refined is fed on to the rotating disc of the screw feeder having a sealed hopper. The distance between the cover and the disc is relatively small (i.e. 1/5 to 1/8 of the diameter of the disc), as a result of which uniform heating of the reaction zone is obtained and dust-formation of the incoming material is eliminated. The product to be refined is fed on to the disc, which is red-hot (500-600 degrees C), and the Arsenic trioxide is purported to immediately begin to evaporate, which causes the original thickness of the layer of material to diminish. The solid residue, which comprises about 10% of the original material put on the disc, is removed by the fixed knife and the screw being conveyed to the hopper. In this way the disc is cleaned ready for the fresh deposit of material. The vapours of the trioxide go along into a crystallizer of

APPENDIX F

Materials Handling & Storage Data

* *
*   TRANSPORT OF DANGEROUS GOODS (TDG)   *
*   *
*   Canadian Centre for Occupational Health and Safety   *
* * * * * * * * * * * * * * * * * Issue: 97-1 (February, 1997) *

RECORD NUMBER: 243
SHIPPING NAME: Arsenic trioxide
NOTE:
Classification 9.2 applies if regulated limit is exceeded.
PRODUCT IDENTIFICATION NUMBER: UN1561
CAS REGISTRY NUMBER: 1327-53-3
CLASSIFICATION: 6.1
9.2
PACKING GROUP: II
REGULATED LIMITS: 230 Kg
SPECIAL PROVISIONS:

109. For the purposes of sections 2.17, 2.23, 3.28 and 3.29 of these Regulations, the consignor shall determine the regulated limit related to this product or substance in accordance with Schedule XIII.

*** LIMITS TO MODE OR METHOD OF TRANSPORT ***

PASSENGER ROAD/RAILWAY VEHICLES: Maximum net quantity per package is 25 kg

*** EMERGENCY RESPONSE GUIDELINE ***

GUIDE 151 NAERG96
SUBSTANCES - TOXIC (NON-COMBUSTIBLE)

POTENTIAL HAZARDS

HEALTH
Highly toxic, may be fatal if inhaled, swallowed or absorbed through skin.
Avoid any skin contact.
Effects of contact or inhalation may be delayed.
Fire may produce irritating, corrosive and/or toxic gases.
Runoff from fire control or dilution water may be corrosive and/or toxic and cause pollution.

FIRE OR EXPLOSION
Non-combustible, substance itself does not burn but may decompose upon heating to produce corrosive and/or toxic fumes.

Containers may explode when heated.
Runoff may pollute waterways.

PUBLIC SAFETY

CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, contact in:

Canada - CANUTEC - 613-996-6666
USA - CHEMTREC(R) - 1-800-424-9300 (USA & Canada) or 703-527-3887
- CHEM-TEL, INC. - 1-800-255-3924 (USA & Canada) or 813-979-0626
- Military Shipments 703-697-0218 (explosives) or 1-800-851-8061
Mexico - SETIQ - 91-800-00-214 or CECOM - 91-800-00-413 (in Mexican Republic)

Isolate spill or leak area immediately for at least 25 to 50 meters (80 to 160 feet) in all directions.
Keep unauthorized personnel away.
Stay upwind.
Keep out of low areas.

PROTECTIVE CLOTHING

Wear positive pressure self-contained breathing apparatus (SCBA).
Wear chemical protective clothing which is specifically recommended by the manufacturer.
Structural firefighters' protective clothing is recommended for fire situations ONLY; it is not effective in spill situations.

EVACUATION

Spill:
Use the Initial Isolation and Protective Action Distances if provided, otherwise increase, in the downwind direction, as necessary, the isolation distance shown under "PUBLIC SAFETY".
Fire:
If tank, rail car or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

EMERGENCY RESPONSE

FIRE

Small Fires:
Dry chemical, CO2 or water spray.
Large Fires:
Water spray, fog or regular foam.
Move containers from fire area if you can do it without risk.
Dike fire control water for later disposal; do not scatter the material.

Do not use straight streams.
Fire involving Tanks or Car/Trailer Loads:
Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
Do not get water inside containers.
Cool containers with flooding quantities of water until well after fire is out.
Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
ALWAYS stay away from the ends of tanks.
For massive fire, use unmanned hose holders or monitor nozzles; if this is impossible, withdraw from area and let fire burn.

SPILL OR LEAK

Do not touch damaged containers or spilled material unless wearing appropriate protective clothing.
Stop leak if you can do it without risk.
Prevent entry into waterways, sewers, basements or confined areas.
Cover with plastic sheet to prevent spreading.
Absorb or cover with dry earth, sand or other non-combustible material and transfer to containers.
DO NOT GET WATER INSIDE CONTAINERS.

FIRST AID

Move victim to fresh air. Call emergency medical care.
Apply artificial respiration if victim is not breathing.
Do not use mouth-to-mouth method if victim ingested or inhaled the substance; induce artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device.
Administer oxygen if breathing is difficult.
Remove and isolate contaminated clothing and shoes.
In case of contact with substance, immediately flush skin or eyes with running water for at least 20 minutes.
For minor skin contact, avoid spreading material on unaffected skin.
Keep victim warm and quiet.
Effects of exposure (inhalation, ingestion or skin contact) to substance may be delayed.
Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves.

*** DISCLAIMER ***

This database is prepared only as a guide and has no legal authority; use the TDG regulations as the final authority. Information in the database reflects regulatory data that was current as of December 1996

The Hazardous **Waste** Superfund Collection is housed in 17 libraries in the EPA Library Network. This publication explains the various document types comprising the Hazardous **Waste** Superfund collection, including sources of documents, contacts, public access, and information pertaining to the availability of documents. This is published annually.

* Hazardous Materials Technical Hotline
Hazardous Materials Technical Center (800) 638-8958
(301) 468-8858
This center provides various services related to hazardous materials, including a clearinghouse technical inquiry line, a newsletter for the U.S. Department of Defense about hazardous materials, maintenance of a collection of publications on hazardous management, and abstracting and publishing of literature related to hazardous materials. The services provided are free only to the U.S. Department of Defense; others must pay a fee to use them.

* Hazardous Material Transportation Accidents
Information Systems Division (DHM-63)
Office of Hazardous Materials Transportation
Research and Special Programs Administration
U.S. Department of Transportation
400 7th Street, SW, Room 8112
Washington, DC 20590 (202) 366-4555
This division collects and analyzes accident data from transporters of hazardous materials by highway, rail, air, and water and from container manufacturers. Information stored in the database includes the hazardous material involved, transporter name and mode, packaging used, cause of accident, and results. Contact the above office for searches. There may be a charge.

* Hazardous Materials Transportation Hotline
U.S. Department of Transportation Department Hotline
400 7th Street, SW, Room 8112
Washington, DC 20590 (202) 366-2301
This U.S. Department of Transportation Hotline provides informational assistance pertaining to federal regulations for transportation of hazardous materials. This includes those regulations contained in CFR-49.

* Hazardous **Waste** Bibliography
and Technology Transfer
Office of Solid **Waste** and Emergency Response
Environmental Protection Agency (EPA)
401 M St., SW
Washington DC 20460 (202) 260-6940
This bibliography, prepared by the Technology Transfer Task Force, lists and abstracts the most important technical materials that should be readily available to all Federal and State hazardous **waste** staffs and their contractors. It assigns each document a level of importance as primary reference documents for Federal and State headquarters, regional, and field staffs. Contact this office to obtain a copy.

* Hazardous **Waste** Hotline
RCRA/Superfund Hotline
Environmental Protection Agency (EPA)

Other Lang |Contacts|Find|Print...|Backtrack|Prev<<|>>Next

Workplace Hazardous Materials Information System - WHMIS

Human Resources Development Canada - HRDC
Status: **Active <<**
Last Verified: 07/10/97
External Links:

SUMMARY

The Workplace Hazardous Materials Information System (WHMIS) is a national system that provides employers, workers and suppliers with information about the hazards of materials produced, sold, imported, or used in the workplace.

ELIGIBILITY CRITERIA

WHMIS applies to all workplaces in Canada.

DESCRIPTION

Federal, provincial and territorial Occupational Safety and Health (OSH) legislation requires employers to provide labels, Material Safety Data sheets (MSDSs), and worker education programs in the workplace.

Employer Responsibilities for Labels

All "controlled products" received from a supplier or produced in the workplace must be properly labelled. A label may be a mark, sign, stamp, sticker, seal, ticket, tag or wrapper which is attached to, imprinted, stencilled or embossed on the controlled product or its container.

Employers must:
- develop and apply workplace labels on all controlled products produced in the workplace or received from the supplier;
- ensure that all workplace labels contain information required by the legislation;
- ensure that workplace labels are not removed, defaced or altered;
- replace all workplace labels which become illegible or which have been removed
- instruct all employees working with controlled products about the content, purpose and significance of labels, including hazard symbols.

A "controlled product" is any product, material or substance which meets any criterion for inclusion in one of the six classes: compressed gases, flammable and combustible material, oxidizing material, poisonous and infectious material, corrosive material, and dangerously reactive material.

For information about controlled products regulations, see document No. 2267 - Controlled Products.

Employer Responsibilities for Material Safety Data Sheets

Material Safety Data Sheets are technical documents which supplement the information provided on labels. MSDSs inform workers about the potential hazards of controlled products; provides control measures to protect workers; and provides emergency procedures.

Employers must:
- develop an MSDS for any controlled product produced in the workplace;
- ensure that all controlled products received from the supplier have up-to-date (less than 3 years old) supplier MSDS when entering the workplace;
- obtain a supplier MSDS or develop an employer MSDS for controlled products received in the workplace;

- make available copies of MSDS to workers and safety and health commitees/representatives;
- educate workers about the content required on the MSDS and the purpose and significance of the MSDS;
- update all MSDS for the workplace every three years; or
- no later than 90 days after updated information is available.

Employer Responsibilities for Worker Education
Employees who work with or near a controlled product, including outside employees, such as contractors or cleaning people must receive training in through a WHMIS worker education program.

Employers must ensure that workers are:
- informed of all hazard information on controlled products received from suppliers;
- advised of any information from a supplier concerning the storage; handling and use in the workplace of the controlled product;
- given all hazard information, including storage, handling and use, about controlled products produced at the workplace;
- able to apply the information they receive for their own safety and health.

To obtain a list of National Sources of Information for WHMIS, see document No. 4529 - WHMIS - Supplement.

Info-FAX #: 1753
Alberta Contact:
Mr. Dan Clarke
Alberta Labour
9th Floor, 10808 - 99 Avenue
Edmonton, Alberta
T5K 0G5
Telephone: (403) 427-2687
Fax: (403) 427-5698

British Columbia Contact:
Mr. Ian Salomon
Human Resources Development Canada - HRDC
P.O. Box 5350
Vancouver, British Columbia
Telephone: (604) 276-3200
Fax: (604) 276-3293

Manitoba Contact:
Mr. Dennis Nikkel
Human Resources Development Canada - HRDC
1000 - 330 St. Mary Avenue
Winnipeg, Manitoba
R3C 3Z5
Telephone: (204) 945-3450
Fax: (204) 945-4556

Ontario Contact:
Dr. Ern Sullivan
Human Resources Development Canada - HRDC
130 Dufferin Avenue, 4th Floor
London, Ontario
N6A 5R2
Telephone: (519) 646-3287
Fax: (519) 672-0268

Québec Contact:
Miss MICHELLE PAQUETTE
Labour Directorate, Québec Region
Human Resources Development Canada - HRDC
Labour Program
715 Peel Street, 3rd Floor
Montréal, Québec
H5B 1C2
Telephone: (514) 283-2214, Sans Frais/Toll Free 1-800-954-2633
Fax: (514) 283-5748

New Brunswick Contact:
Ms. Carmen Comeau Anderson
Human Resources Development Canada - HRDC
1045 Main St. 1st. Floor
P.O Box 1166
Moncton, New Brunswick
E1C 8T9
Telephone: (506) 851-6848.
Fax: (506) 851-6645

Newfoundland Contact:
Mr. Weldon Moores
Human Resources Development Canada - HRDC
P.O. Box 8700
St. John's, Newfoundland
A1B 4J6
Telephone: (709) 729-5548
Fax: (709) 729-6639

Northwest Territories Contact:
Mr. Ray Gagnon
Human Resources Development Canada - HRDC
Box 1320
Yellowknife, Northwest Territories
X1A 2L9

Canada Business Service Centre

Telephone: (403) 873-7489
Fax: (403) 873-0117

Nova Scotia Contact:
Mr. Jim LeBlanc
Human Resources Development Canada - HRDC
5151 Terminal road, Box 697
Halifax, Nova Scotia
B3J 2T8
Telephone: (902) 424-4428
Fax: (902) 424-3239

P.E.I. Contact:
Mr. George Stewart
Human Resources Development Canada - HRDC
31 Gordon Drive
P.O. Box 2000
Charlottetown, Prince Edward Island
C1A 7N8
Telephone: (902) 368-5562
Fax: (902) 368-5526

Saskatchewan Contact:
Ms. R. Coshan
Human Resources Development Canada - HRDC
1870 Albert Street, 6th Floor
Regina, Saskatchewan
S4P 3V7
Telephone: (306) 787-4539
Fax: (306) 787-2208

Yukon Contact:
Mr. Robert McClure
Human Resources Development Canada - HRDC
401 Strickland Street
Whitehorse, Yukon
Y1A 5N8
Telephone: (403) 667-3726
Fax: (403) 668-2079

National Contact:
Ms. Raymonde Lizette, Program Advisor
Occupational Safety and Health Compliance Unit
Human Resources Development Canada - HRDC

Canada Business Service Centre

165 Hôtel de Ville
Place du Portage, Phase II
Hull, Québec
K1A 0J2
Telephone: (819) 953-8090
Fax: (819) 953-0215

Qualified Contact:
The contact information for this document is not available.

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* *
* MSDS *
* *
* Canadian Centre for Occupational Health and Safety *
* * * * * * * * * * * * * * * Issue : 97-2 (May, 1997) *

*** IDENTIFICATION ***

MSDS RECORD NUMBER : 1359893
PRODUCT NAME(S) : ARSENIC TRIOXIDE
Arsenic trioxide; Arsenous oxide, Arsenic (III) oxide
PRODUCT IDENTIFICATION : PRODUCT CODE NUMBER(S): 1990-1
MSDS: 1990-1
CAS No.: 1327-53-3
DATE OF MSDS : 1994-10-03

*** MANUFACTURER INFORMATION ***

MANUFACTURER : Caledon Laboratories Ltd
ADDRESS : 40 Armstrong Avenue
Georgetown Ontario
Canada L7G 4R9
Telephone: 905-877-0101
Fax: 905-877-6666
EMERGENCY TELEPHONE NO. : 613-996-6666 (CANUTEC)

***

Message from Caledon: Caledon Laboratories Ltd believes the information contained herein is reliable and accurate. Caledon makes no warranty with respect thereto and expressly disclaims all liability for reliance thereon. Such information is solely for your consideration, investigation, and verification.

*** MATERIAL SAFETY DATA ***

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MATERIAL SAFETY DATA SHEET ARSENIC TRIOXIDE

===

PRODUCT CODE NUMBER(S): 1990-1

PRODUCT IDENTIFICATION

Chemical Name and Synonyms: Arsenic trioxide; Arsenous oxide, Arsenic (III) oxide
Chemical Family: Metal oxide
Chemical Formula: As2O3
Product Use: For test purposes

HAZARDOUS INGREDIENTS OF MATERIALS

Ingredients	%	CAS No.
Arsenic trioxide	100	1327-53-3

TLV Units
0.1 mg/m3

PHYSICAL DATA

Physical State: Solid
Odour and Appearance: White granular powder
Odour Threshold (ppm): Not available
Vapour Pressure (mm Hg): Not available
Vapour Density (Air=1): Not available
Evaporation Rate: Not applicable
Boiling Point (degrees C): Not available
Freezing Point (degrees C): Not available
pH: Not available
Specific Gravity: 3.738
Coefficient of Water/Oil distribution: Not available

SHIPPING DESCRIPTION

UN: 1561
T.D.G. Class: 6.1, 9.2
Pkg. Group: II

REACTIVITY DATA

Chemical Stability: Stable
Incompatibility with other substances: Heat, acids, oxidizing agents, halogens
Reactivity: May decompose on exposure to moist air or water
Hazardous Decomposition Products: Toxic fumes of arsenic oxides

FIRE AND EXPLOSION DATA

Flammability: Non combustible
Extinguishing Media: Use any means suitable for surrounding fire

Flash Point (Method Used): Not applicable
Autoignition Temperature: Not applicable
Upper Flammable Limit (% by volume): Not applicable
Lower Flammable Limit (% by volume): Not applicable
Hazardous Combustion Products: Not applicable
Sensitivity to Impact: None
Sensitivity to Static discharge: None

TOXICOLOGICAL PROPERTIES AND HEALTH DATA

Toxicological Data:

LD50: (oral, rat) 14,600 microg/kg
LC50: Not available

Effects of Acute Exposure to Product:

Inhaled: Very toxic. May be fatal.
In contact with skin: Very toxic. May be fatal by skin absorption.
In contact with eyes: May cause irritation
Ingested: Very toxic. May be fatal.

Effects of Chronic Exposure to Product:

Carcinogenicity: Human carcinogen. (RTECS No. CG3325000)
Teratogenicity: Suspected teratogen
Reproductive Effects: Harmful effects suspected
Mutagenicity: May alter genetic material.
Synergistic Products: None known

PREVENTIVE MEASURES

Engineering Controls: Local exhaust ventilation required
Respiratory Protection: Approved air-purifying respirator or self-contained breathing apparatus for exposures exceeding TLV. Dust mask for lower concentrations.
Eye Protection: Chemical safety goggles
Skin Protection: Wear impervious gloves, coveralls, apron, boots, etc., as required.
Other Personal Protective Equipment: Safety shower and eye-wash fountain in work area.
Leak and Spill Procedure: Transfer carefully into container and arrange removal by disposal company. Wash site of spillage thoroughly with water and detergent.
Waste Disposal: Follow all federal, provincial and local regulations for disposal.

Handling Procedures and Equipment: Follow routine safe handling procedures. Avoid contact. Avoid generating dust.
Storage Requirements: Store in suitable, labelled containers. Keep containers tightly closed when not in use and when empty. Protect from damage. Store in a cool, dry, well-ventilated area, away from incompatible materials and out of direct sunlight.

FIRST AID MEASURES

Specific Measures:

Eyes: Immediately flush eyes with running water for a minimum of twenty (20) minutes. Hold eyelids open during flushing. If irritation persists, repeat flushing and obtain medical attention immediately.
Skin: Remove contaminated clothing. Wash affected areas with soap and water for a minimum of twenty (20) minutes. If irritation persists, obtain medical advice immediately.
Inhalation: Move victim to fresh air. Give artificial respiration ONLY if breathing has stopped. Give cardiopulmonary resuscitation (CPR) if there is no breathing AND no pulse. Obtain medical advice immediately.

Ingestion: If victim is alert and not convulsing, give several glasses of water and induce vomiting. Have victim lean forward with head down to avoid breathing in of vomitus, rinse mouth and administer more water. Obtain medical attention IMMEDIATELY.

ADDITIONAL INFORMATION AND SOURCES USED

CCINFO disc:
Date Issued: May 6, 1991
Revision 1: October 3, 1994
MSDS: 1990-1
Prepared by: The Caledon Occupational Health &
Safety Committee (905) 877-0101

APPENDIX G

Waste Stabilizaion & Storage Data

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PRODUCTION OF ENVIRONMENTALLY ACCEPTABLE ARSENITES-ARSENATES FROM SOLID ARSENIC TRIOXIDE

M. Stefanakis
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Abstract

Many arsenical sulfide ores or concentrates are being treated lately by roasting, resulting in the production of arsenic trioxide. In view of the environmental limitations imposed on its disposal, a number of process options have been investigated for its transformation into environmentally acceptable forms. In the present paper, the stability of calcium arsenite and arsenate, and of ferrous and ferric arsenate produced from solid As_2O_3 have been investigated. As_2O_3 was dissolved in water and the resulting As was precipitated as calcium arsenite or arsenate with $Ca(OH)_2$. The effect of the Ca/As ratio in solution, precipitation pH, and thermal treatment of the resulting precipitate on its stability is reported. Further, As was precipitated as ferrous or ferric arsenates with lime and Fe^{2+} or Fe^{3+} additions. The effect of the Fe/As ratio in solution, pH and temperature of precipitation, and Fe^{2+}/ Fe^{3+} ratio on the stability of the resulting precipitate is reported.

[redacted]

Introduction

The depletion of pure and high-grade sulfide deposits has led the industry to treat ores and concentrates of lower grade and/or higher impurity contents. This is particularly true for refractory arsenical pyrite gold and arsenical chalcopyrite contentrates. Many of these concentrates are treated by roasting under carefully controlled conditions, whereby most of the contained arsenic is volatilized, and recovered from the roasting gases as impure As_2O_3. Examples of plants treating refractory gold arsenical pyrite concentrates by roasting with simultaneous production of crude As_2O_3 are the Giant Yellowknife [28] and Campbell Red Lake [29] in Canada, the Prince Consort Mine [30] in South Africa, etc. Several other plants, including the El Indio [31] in Chile and the Lepanto in the Philippines, are roasting impure arsenical chalcopyrite concentrates, producing again As_2O_3. On the other hand, application of hydrometallurgical processes (pressure oxidation or biological oxidation) to arsenical gold or uranium sulfidic ores and/or concentrates results in the production of liquids containing As, that have to be purified, usually by a precipitation technique, before being discharged or recycled to the process.

In the past, part of the produced As_2O_3 was placed into the market and the rest was stocked in facilities of varying size and complexity. The enforcement of strict environmental control, coupled with the fact that the limited market of As_2O_3 cannot absorb the ever-increasing quantities produced, has resulted in research towards investigation of methods for fixating the arsenic in insoluble forms, that can be safely disposed of in an environmentally acceptable manner. The same considerations are valid also for the precipitates produced from the purification of arsenic containing liquids.

Arsenic has been fixed for many years as calcium arsenate, which was considered to be insoluble. The investigations have shown that this form is not appropriate anymore, and alternative forms, including ferric arsenate, were considered. Robins [12], based on a thermodynamic analysis of the Fe(III)-As(V)-H_2O system, argued that ferric arsenate is not an acceptable form for arsenic disposal. This has been contradicted by many investigators. Thus, in an elegant experimantal study, Krause and Ettel [18] reported that iron arsenates with arsenic solubility less than 0.05 mg/l could be produced provided the molar Fe/As ratio was kept above 4 in order to precipitate basic ferric arsenates represented by the formula $FeAsO_4 \cdot x\ Fe(OH)_3$. Testwork conducted by METBA in 1986 and 1987 to evaluate the pressure oxidation processes [21,22] for the treatment of Olympias arsenical pyrite concentrate has shown that both the oxidation residue, in which arsenic is fixated as ferric arsenate, as well as the residue resulting from the neutralization of oxidation leach liquor, which is again of the ferric arsenate type, are very insoluble based on the EPA Toxicity Test (20) and that the arsenic solubility is less that 0.05 mg/l. In 1985 Nishimura and Tozawa (17) proposed calcination of calcium arsenite precipitates to enhance arsenic stability. The process may be promising as an alternative to ferric arsenate precipitation.

In the present work, a number of methods for producing environmentally acceptable arsenical compounds from solid As_2O_3 have been investigated. They include calcium arsenites and arsenates, with or without calcination and ferrous-ferric arsenates.

Chukhlasev [1,2] in 1956 gave the solubility products of several metal arsenates, which are reported in Table I. Based on this table, the precipitation of As

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from solutions in the form of $Ca_3(AsO_4)_2$ with lime addition, a process widely applied in the past, was fully justified. In 1976, Laguitton [3] discussed the basic chemistry of the lime addition method for arsenic removal from gold-mine waste waters, without expressing concern for the stability of calcium arsenate; he discussed arsenic removal processes (chemical precipitation, adsorption or flocculation) and he reported that the limiting arsenic concentration by lime addition is 0.46 mg/l based on the solubility product of 3×10^{-6} as measured by Rosehart and Lee [4]; despite that, he reported that somethimes, values of 0.03 mg/l had been obtained, which he attributed to an arsenic flocculation process induced by the precipitation of iron or aluminium hydroxides.

Table I
Solubility products of arsenical compounds[1,2]

	K_{sp}
$Ca_3(AsO_4)_2$	6.8×10^{-19}
$Mg_3(AsO_4)_2$	2.1×10^{-20}
$Zn_3(AsO_4)_2$	1.3×10^{-28}
$Cd_3(AsO_4)_2$	2.2×10^{-33}
$Pb(AsO_4)_2$	4.1×10^{-36}
$AlAsO_4$	1.6×10^{-16}
$FeAsO_4$	5.7×10^{-21}
$Ba_3(As_4)_2$	8.0×10^{-51}

For more effective arsenic removal, addition of phosphoric acid for precipitation of a mixed calcium arsenophosphate has been proposed, whereby removal of arsenic down to 0.03 mg/l had been achieved [3]. Cost comparison data developed by Rosehart and Lee [4] for several arsenic removal methods are given in Table II.

Table II
Cost comparison data for arsenic removal methods (4)

Method	Optimum pH	% Removal	Cost ($ per lb of As removed)*
$FeSO_4$ $7H_2O$	8	94	1.05
$FeCl_3$ $7H_2O$	8-9	90-95	3.18
$Al_2(SO_4)_3$ $18H_2O$	7-8	90-95	1.95
Na_2S	7	80	0.45
CaO	12	95	0.07
NaOH	10	80	0.33

* Price of chemicals as of 1968

In 1978 Tozawa, Umetsu and Nishimura [5] and Nishimura and Tozawa [6] reported a discrepancy from Chukhlasev's solubility data for calcium, magnesium and ferric arsenate which, at high pH values, was higher by two orders of magnitude; this was attributed to the decomposition of the particular arsenate to the hydroxide or carbonate.

In 1981 Robins [7] discussed the solubility of metal arsenates and showed by thermodynamic stability diagrams that calcium arsenate decomposes to calcium carbonate under the effect of atmospheric CO_2. He reported that the minimum solubility of $Ca_3(AsO_4)_2$ is 500 mg/l As at pH of 7.8 and that of $FeAsO_4$ 75 mg/l As at pH of 2.2. Above those pH values both salts decompose to $CaCO_3$ and $Fe(OH)_3$ respectively. Robins and Tozawa [8] in 1982 produced data for other metal arsenates besides calcium, and they reported that the low solubility of several metal arsenates (Pb, Cu, Cd, Ni, Zn) which are present as traces in mineral wastes may explain the reasonable effectiveness of arsenical waste disposal. The merits of using phosphate in the lime system was questioned due again to the decomposition of phosphate to carbonate in alcaline solutions. Indicative structures of two calcium arsenites and five calcium arsenates using XRD and DTA analyses were given by Nishimura, Tozawa and Robins in 1983 [9] and the limitation due to their transformation to carbonates was again stressed. From a number of solubility diagrams for metal arsenites and arsenates it was shown by Robins [10] that arsenites are more soluble than arsenates and barium arsenate was identified as a very insoluble material especially in a sulfate medium. In 1984 Robins [11] reported a minimum solubility of $Fe_3(AsO_4)_2$ of 10 mg/l As at pH = 6-7. An iron (II) - iron (III) - calcium arsenate precipitate produced through ferrous sulfate addition to arsenic (V) solution followed by aeration, resulted in arsenic solubility of 1 mg/l at pH = 7-8. Mixed iron (II) - iron (III) - calcium arsenate precipitates prepared in the lab in such a stoichiometry so as to simulate arsenical minerals reported in literature, do not exhibit higher stability than that of ferric arsenate. Calcium arsenophosphates have a solubility of 1 mg/l As in the pH range of 8.2-9.2 while As_2S_3 shows a very low solubility 0.001 mg/l of As, below pH=4, but above that pH, it becomes soluble due to decomposition of $As_3S_6^{3-}$. In a recent paper, Robins [12], based on a thermodynamic analysis, reported that arsenical compounds previously potentially regarded as a solution to arsenic stabilization were unfit for disposal. Among those, precipitation as $Ba_3(AsO_4)_2$, a method patented by Sherritt [13], and as As_2S_3 or $Mn_3(AsO_4)_2$ were included.

However, as early as 1976, MnO_2 has been used on an industrial scale in the Soviet Union to oxidize As(III) in effluent streams and to precipitate $Mn_3(AsO_4)_2$ which proved very stable with respect to arsenic dissolution [14,15].

Nishimura, Tozawa and Robins in 1985 [16] proved conclusively through XRD analysis, the various stages of decomposition of calcium arsenite and calcium arsenate to calcium carbonate, above pH of 8.3. Below that pH the equilibrium concentration of arsenic is above the current enforced environmental standards. The instability of calcium arsenite and arsenate was overcome by Nishimura and Tozawa [17], who proposed calcination of the precipitates above 700°C at Ca/As ratio of 4.6 and 2.1 respectively. The end result of calcination, which is not accompanied by arsenic evaporation, is the transformation of amorphous arsenical precipitates to crystalline ones exhibiting arsenic solubility only 0.02 mg/l.

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In 1985, Krause and Ettel [18] presented a detailed study on the effect of the Fe/As molar ratio on the stability of the ferric arsenate precipitates. They reported that, by increasing this ratio from 1 (corresponding to the stoichiometric $FeAsO_4$ to 16, the As solubility decreases from 20 to less than 0.05 mg/l respectively. They concluded that although an Fe/As ratio of 4 is required for acceptable stability of the precipitate, a higher ratio is needed to achieve acceptable residual As in the liquid effluent. The precipitates were amorphous, but it was proven by thermal analysis that they consitute definite chemical compounds of the type $FeAsO_4 \cdot x\ Fe(OH)_3$, and that therefore As is chemically bound, and not simply adsorbed on the precipitates. The presence of CO_2 or reactive solids, such as pyrrhotite and pyrite, were not affecting the solubility of As, and aging of the precipitates had only a marginal effect.

In a paper presented by the authors [19] in 1985 it was shown that ferric arsenate precipitates produced from acid leach liquors are well within the environmental guidelines [20] with arsenic solubility lower than 0.1 mg/l.

Testwork conducted by METBA in 1986 and 1987 to evaluate the pressure oxidation processes [21,22] for the treatment of Olympias arsenical pyrite concentrate has shown that both the oxidation residue in which arsenic is fixated as arsenate and the residue resulting from the neutralization of the oxidation leach liquor with lime are very insoluble, as evidenced by the EPA Toxicity Test [20], which showed the arsenic solubility to be less than 0.05 mg/l.

The references reported before are only a small sample of the work that has been published. 716 references are listed in the EPA 600/2-81-049a report [23] prepared by A. Mehta for U.S. Industrial Environmental Research Laboratory, which is regarded as an excellent reference book for arsenic.

Experimental Procedure

A cylindrical glass reactor equipped with a glass stirrer and a thermostatically controled heating mantle was used for all of the dissolution, oxidation, precipitation and solubility tests.

As_2O_3 dissolution

Water or weak aqueous sulfuric acid solutions were used as solvents. The liquid was heated at the required dissolution temperature in the glass reactor, and chemical grade As_2O_3 (Analar) was added. Liquid samples of known volume were withdrawn from time to time, with due care so as not to include undissolved solids, and immediately added in a measured quantity of water heated at the same temperature, in order to avoid As_2O_3 precipitation. Samples from this solution were analyzed for As by Atomic Absorption and double checked with the classical potassium iodate method [24]

As_2O_3 oxidation

Chemical grade As_2O_3 dissolved in water at 85°C was oxidized with H_2O_2 (perydrol), added gradually with a burrette over a period of 1.5 h. As(III) to As(V) oxidation was confirmed by analysing samples for As(III) with the potassium iodate method [24].

FeSO$_4$ Oxidation

Chemical grade FeSO$_4$.7H$_2$O (Analar) was dissolved in water and oxidized with air or oxygen using a Denver flotation cell for effective gas dispersion. Fe(II) and Fe(III) were analyzed by using the K$_2$Cr$_2$O$_7$ method [24].

Calcium Arsenite or Arsenate Precipitation and Calcination

As(III) or As(V) liquors produced from As$_2$O$_3$ dissolution in water, with or without oxidation were neutralized at 80°C with Ca(OH)$_2$ additions, which resulted in the precipitation of calcium arsenite or arsenate. The pH was continuously controlled during precipitation. The precipitate was filtered, washed, and used for solubility testing. In order to study the effect of calcination on their solubility, some of the precipitates were placed in a Ni crucible and heated in an electric furnace at 500-800°C for 4h, under a continuous flow of air. Every 15 min, the contents of the crucible were stirred in order to ensure exposure to the atmosphere.

Ferrous or Ferric Arsenate Precipitation

As(V) and Fe(II)-Fe(III) solutions were prepared separately and mixed in the reactor. Ca(OH)$_2$ was used for neutralization, at 80°C with continuous pH control. The resulting ferrous - ferric arsenate precipitates were filtered, washed, and used for the solubility tests.

Solubility Tests

The stability of the calcium arsenites-arsenates or ferrous-ferric arsenates was evaluated by an As solubility test. Initially, the standard E.P.A. Toxicity Test [20] was adopted. Due to the number of samples to be tested, this procedure was later modified as follows: a 2 g sample of the solid was placed in a 250 ml conical flask with 100 ml of water and the pH was adjusted to the desired value. The flask was shaken continuously at room temperature. Every 24 h, and for a periof of 72 h, the pH was adjusted to the desired value using a 2N-H$_2$SO$_4$ or a 1N-NaOH solution. The 72 h proved adequate for pH stabilization. Arsenic in solution was analyzed by the Gutzeit method and by Atomic Absorption.

Results and Discussion

Dissolution of As$_2$O$_3$

The aqueous solubility of As$_2$O$_3$ as a function of temperature has been reported by LURGI [26] and is presented in Table III. A complex formula, given in ref. [25], has been established by NCR in 1928 to describe the As$_2$O$_3$ solubility. In figure 1, the solubility of As$_2$O$_3$ in aqueous sulfuric acid solutions as a function of temperature is given [27]. The relatively low solubility at 50° Be (62.6% H$_2$SO$_4$ w/w) is the basis for the removal of As$_2$O$_3$ by wet scrubbing of arsenic containing roaster gases.

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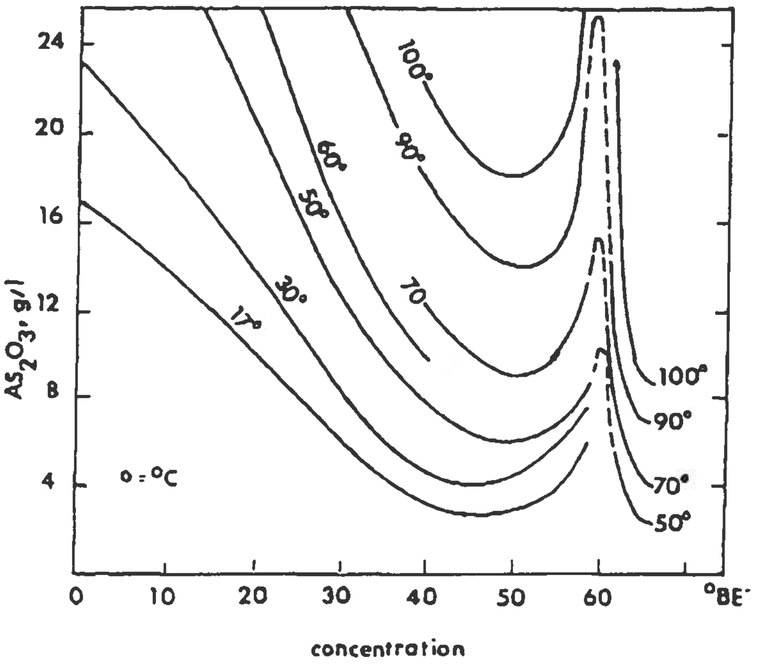

Figure 1 Solubility of As_2O_3 in aqueous sulfuric acid solutions at various temperatures.

[redacted]

Table III
Solubility of As_2O_3 in water as a function of temperature

T, °C	0	15	25	39.8	48.2	62	75	98.
Solubility, g As_2O_3/l	12.1	16.6	20.5	29.3	34.3	44.5	56.2	81.6

In our experiments, As_2O_3 was dissolved in water or weak H_2SO_4 solutions (2 and 5 g/l) at temperatures of 30, 60 and 90° C and for 1 - 6.5 h. The dissolution characteristics of As_2O_3 obtained is presented in table IV. It can be seen that dissolution at high temperatures results in high concentrations of As_2O_3 in solution in relative short time. At high temperatures, the effect of H_2SO_4 addition is slightly negative, as predicted by figure 1, but at low temperature, it is beneficial, in contrast to the general behaviour shown in figure 1. At 90°C, 1h mixing in water is adequate to achieve a dissolution of 84g As_2O_3/l, which appears to be near the theoretical solubility..

Table IV
Dissolution characteristics of As_2O_3

H_2SO_4 conc.	T	Dissolution of As_2O_3, g/l						
		Time, hs						
g/l	°C	1	2	2.5	3	3.5	5	6.5
0	30	0.81			2.34		3.86	4.49
0	60	26.7		43.7		45.4		
0	90	84		83.8		84.9		
2	30	10.7			16.4		18.2	18.2
2	60	44.3			45.1		44.7	44.3
2	90	83			82.9		82.7	83.1
5	30	19.4			21.2		21	20.8
5	60	42.2			45.1		44.7	43.9
5	90	82.9			82.3		82.2	83.6

Following the dissolution of As_2O_3 in water at 90°C the oxidation of As(III) to As(V) was performed at 60°C using H_2O_2 as an oxidant. Almost quantitative oxidation could be achieved (99.5%) in 2h. Both air and oxygen were also tried, but failed to achieve an oxidation of more than 60% in reasonable time. After effecting oxidation to As(V), the solution could be cooled down with no danger of precipitation, as the solubility of As_2O_5 is an order of magnitude higher than that of As_2O_3.

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$FeSO_4$ Production and Oxidation

In order to precipitate large quantities of arsenic from solutions as ferric arsenate, a cheap source of Fe(III) is required. Relatively cheap $Fe_2(SO_4)_3$ can be produced by dissolving scrap iron in sulfuric acid and oxidizing the resulting Fe(II) to Fe(III). A preliminary experimental program was initiated and it was concluded that scrap iron can be leached at 90°C and for a periof of 2 hours with the stoichiometrically required sulphuric acid to produce a solution containing 120 g/l Fe^{2+}. At ambient temperature very slow dissolution was observed. As $FeSO_4$ will be the expected product from a potential cheap sourse of iron, chemically pure $FeSO_4 \cdot 7H_2O$ was used in our experiments. Oxidation of Fe(II) to Fe(III) was ineffective by sparging air or O_2 through the solution, as the maximum oxidation degree obtained was 75% after 11h oxidation at 90°C. The scale of experimentation and its inherent limitations for efficient dispersion might be the cause of this inefficiency. $Fe_2(SO_4)_3$ and $CuSO_4$ additions to catalyze the oxidation did not improve the results. The oxidation was therefore performed by adding the stoichiometric amount of H_2O_2. Quantitative oxidation could be achieved at 90°C within 3h.

Precipitation and stability of calcium arsenites and arsenates

It has been documented in the literature that both calcium arsenites and arsenates are not appropriate forms for arsenic stabilization. Nevertheless it has been reported by Nishimura et al [17] that under certain conditions with respect to Ca/As ratio and the calcination temperature, both precipitates become very insoluble.

In our experimental work arsenite precipitation was effected from a solution containing 53 g/l As(III) which was neutralized with $Ca(OH)_2$ at 80°C over a period of 3 hours. To effect percipitation of arsenates, the same solution was oxidized with perydrol (at 80°C for 1.5 h) prior to precipitation.

The actual Ca/As molar ratio in the solutions was ranging from 1.5 to 7 in the case of arsenite precipitation, and 3 to 14 for arsenate precipitation. Taking into account the stoichiometry of the precipitaiton reactions

$$2\,Ca^{2+} + 2AsO_2^{-} + 2OH^{-} = Ca(AsO_2)_2 \cdot Ca(OH)_2 \quad (1)$$

$$4\,Ca^{2+} + 2AsO_4^{3-} + 2OH^{-} = Ca_3(AsO_4)_2 \cdot Ca(OH)_2 \quad (2)$$

it is obvious that the stoichiometric calcium required for arsenate precipitation is double than that of arsenite. Therefore, the Ca/As molar ratio emploued in all cases was 1.5 to 7 times higher than the stoichiometric requirement.

After each experiment, the filtrate and the precipitate were analyzed for Ca and As, and the stability of the precipitate was tested with an As solubility test at pH =11.5 and 72 h. Further stability tests were performed after calcining the precipitate at 500, 600, 700 and 800°C. The results are presented in Table V.

It can be seen that the arsenates are more stable than the arsenites, even for the same initial Ca/As ratio in the feed solution (it should be noted that, for example, an initial Ca/As ratio of 3 in the feed solution corresponds to 3 or 1.5 times the stoichiometric requirement for the arsenite or the arsenate respectively). Figure 2 shows the solubility of the calcium arsenite - arsenate precipitates versus the excess Ca/As ratio over the stoichiometric requirement.

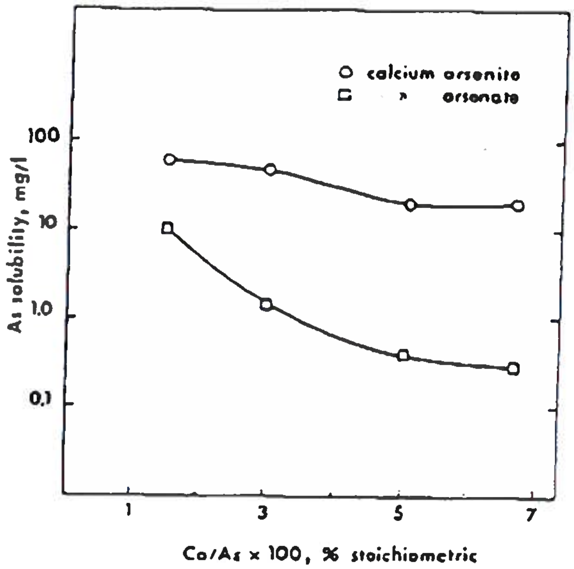

Figure 2 Effect of Ca/As molar ratio expressed as % excess of the stoichiometric requirement of the reactions, on the stability of calcium arsenite and arsenate.

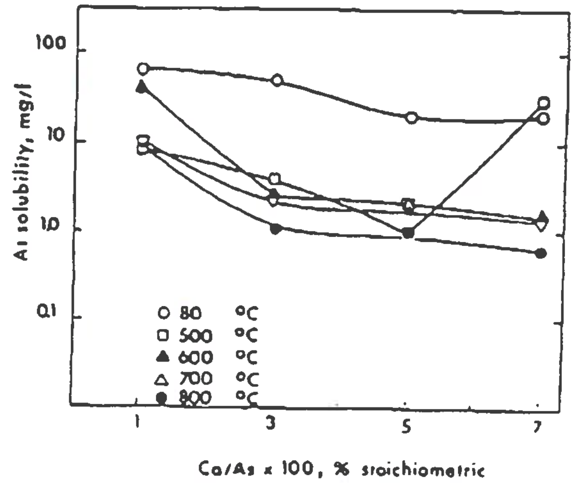

Figure 3 Effect of calcination temperature on the stability of calcium arsenite at various Ca/As molar ratios expressed as % excess of the stoichiometric requirement of the reactions.

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Exp. No	Ca/ (M
1*	7
2*	5
3*	3
4*	1.5
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6**	10
7**	6
8**	3

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Table V
Precipitation and Stability of the Calcium Arsenite and Arsenate Precipitates

Exp. No	Feed Ca/As (M)	Stoic. Ca/As (M)	Filtrate analysis pH	Filtrate analysis Ca g/l	Filtrate analysis As mg/l	Residue analysis Ca %	Residue analysis As %	As SOLUBILITY, mg/l (pH= 11.5, 72 h) CALCINATION NONE	500°C	600°C	700°C	800°C
1*	7	7	11.3	0.59	0	39.6	10	20	30	1.5	1.5	0.6
2*	5	5	11.3	0.66	0	37.1	15.5	20	1.0	2.0	2.0	1.0
3*	3	3	11.3	0.69	0	32.6	23.4	50	4.0	2.5	2.0	1.2
4*	1.5	1.5	11.3	0.58	0	25.3	36.9	60	8.0	40	10	10
5**	14	7	>11.3	0.54	0	41.1	6.3	0.3			2.5	1.5
6**	10	5	>10.9	0.40	0	38.7	8.2	0.4			2.5	0.6
7**	6	3	11.4	0.79	0	35.4	12.1	1.5			2.5	0.5
8**	3	1.5	11.5	0.91	0	33.3	16.6	10			2.5	0.5

* Arsenite Precipitation
** Arsenate Precipitation

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Calcination had a positive effect on the solubility of the arsenites and arsenates. For instance, calcining of the calcium arsenite precipitate with Ca/As = 7 at 800°C decreases the As solubility from 20 to 0.6 mg/l, which is marginally higher than the E.P.A. guideline of 0.5 mg/l. The effect of the Ca/As ratio and calcination temperature on the solubility of As is shown in figure 3. X-Ray Diffraction analysis of the calcium arsenite precipitates showed the presence of calcium arsenite and calcium hydroxide. Calcining resulted in gradual transformation to $Ca_2As_2O_7$, CaO, and $Ca_3(AsO_4)_2$. However, transformation to the arsenate was not complete, even at 800°C. Similarly, the phases detected in the raw arsenate precipitate were $Ca_3(AsO_4)_2{\cdot}4H_2O$ and $Ca_3(AsO_4)_2{\cdot}2H_2O$ which shifted to the anhydrous $Ca_3(AsO_4)_2$ by calcination.

Precipitation and Stability of ferric arsenates

Solutions of As(V), containing 40 g/l As, were prepared by dissolving As_2O_3 in water at 85°C for 3h and oxidizing As(III) to As(V) using H_2O_2. Similarly, solutions containing 26-112 g/l Fe(III) were prepared by dissolving $FeSO_4{\cdot}7H_2O$ in water at room temperature and effecting oxidation to $Fe_2(SO_4)_3$ by H_2SO_4 and H_2O_2. The two solutions were mixed so as to achieve a solution with 20 g/l As and molar ratios of Fe/As in the range 0.83-3.65, and precipitation was effected at 80°C for 3h using $Ca(OH)_2$ as neutralizing agent. The precipitation pH was controlled at approximately 3,5,7 and 9. After effecting the precipitation, the slurry was filtered and the precipitate washed, collected, and tested for As solubility at pH=5. In table VI the original feed solution composition, the filtrate and precipitate analysis, and the As solubility of the precipitate is reported. The effect of the Fe/As ratio on the residual As in the filtrate and on the As solubility of the precipitate is plotted in figure 4.

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Table VI
Precipitation and stability of ferric arsenates

Feed composition			Filtrate analysis				Precipitate analysis				Solubility pH=5
Fe t	Fe 2+	Fe/As	pH	Ca	As	Fe	Ca	As	Fe	SO4 2-	As
g/l	g/l	M		g/l	mg/l	mg/l	%	%	%	%	mg/l
13.2	1.2	0.88	5.2	0.54	105	3.2	27.8	12.4	9.7	36	40
21.1	2	1.41	4.6	0.51	2	0.6	23.2	11.3	12.5	36.8	6
28.1	3.1	1.86	4.6	0.5	1	3.2	21.5	9.7	15	30	0.5
45.0	8.3	2.96	5.1	0.6	0.6	0.4	25.3	6.3	14.8	43.3	0.4
56.3	5.7	3.65	5	0.65	0.6	2.6	25.6	4.0	14.1	42	0.2
45.6	6	2.96	3.2	0.67	0.4	0.3	22.6	6.6	13	40.4	0
43.6	6	2.96	7.5	0.7	5	0	27.9	5.6	11.6	38.9	3.5
45.0	9	2.96	9.1	0.74	4	0	29.6	5.2	11.6	38.6	10.5

It is seen that the solubility of As drops from 40 to 0.4 mg/l with an increase of the Fe/As ratio from 0.88 to 3.65. The precipitation pH also affects significantly the solubility of the precipitate, as shown in figure 5. Increasing the precipitation pH from 3 to 9 results in an increase of the As solubility from 0.01 to 10 mg/l (for precipitates with Fe/As =2.96)

X-ray diffraction analysis of the precipitates failed to show any patterns due to the amorphous character of the Fe/As cakes.

The above results are in accord with those reported by Krause and Ettel [18] and point out to the fact that basic iron arsenates are responsible for the low solubility of arsenic.

Precipitation and Stability of ferrous-ferric arsenates

For this series of experiments, As(V) solutions were prepared as before. Similarly, Fe(II)-Fe(III) solutions were prepared as before, but oxidation of Fe(II) to Fe(III) was controlled so as to effect only the desired partial oxidation. The solutions were mixed, and precipitation was effected by $Ca(OH)_2$ addition at 80°C, and precipitation pH of 5. The initial As concentration in solution was 20 g/l, and the Fe_t/As molar ratio varied between 1.6 and 3.2. The Fe(II)/Fe_t ratio varied between 11 and 100. After completion of the reaction, the precipitate was filtered, analyzed, and subjected to the As solubility test. The filtrate was also analyzed. The experimental results are presented in Table VII.

In figure 6, the effect of the Fe(II)/As molar ratio on the residual As in the filtrate, and of the As solubility of the precipitate is presented. It is seen that, with increasing Fe(II)/AS ratio, the residual As concentration in the filtrate decreases, but the As solubility of the precipitate increases. This can be attribute to the fact that, during the solubility test, the precipitate consumes acid, and for this reason additions of H_2SO_4 have to be made so as to keep the test pH at 5. It is possible that, during the 8-12h period between two successive pH corrections, the pH could have shifted to values where a higher solubility of the precipitate corresponds. By correcting the pH, the excess As dissolved will not reprecipitate.

Finally, in figure 7 the effect of Fe(II)/Fe_t on the As solubility of the precipitate for various values of Fe_t/As is shown. It is seen that, with the exception of the Fe_t/As ratio of 1.6, in all other cases an increase of the Fe(II)/Fe_t ratio

Solubility pH=5 As mg/l
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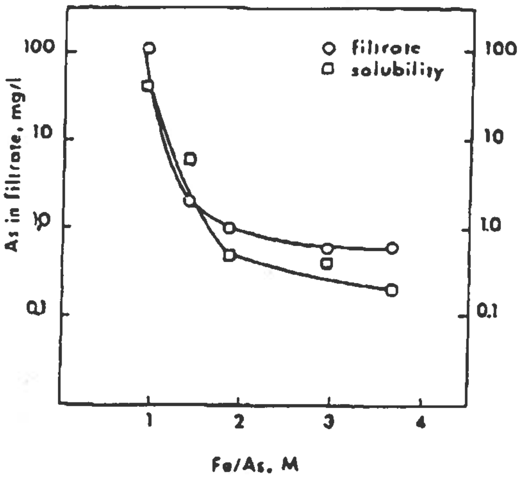

Figure 4 Effect of the Fe/As molar ratio on the residual As in the filtrate and on the As solubility of the ferric arsenate precipitates.

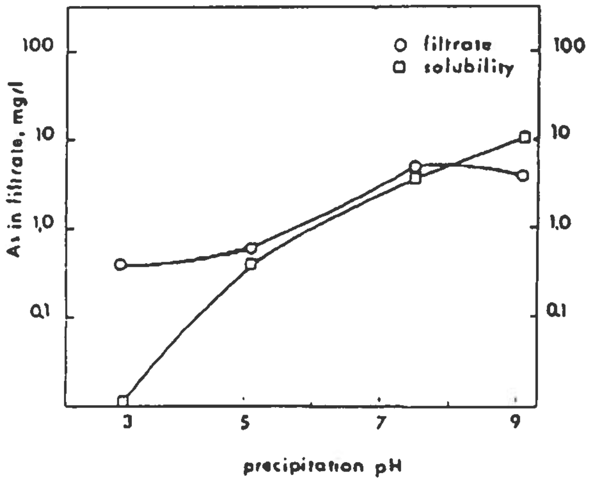

Figure 5 Effect of the precipitation pH on the residual As in the filtrate and on the As solubility of the ferric arsenate precipitates (Fe/As =2.96)

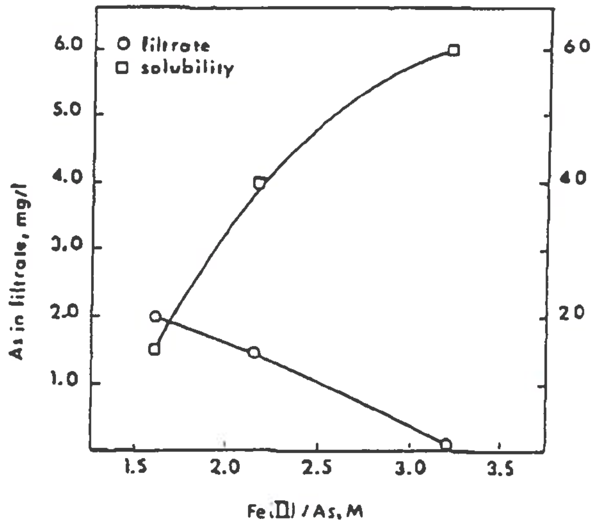

Figure 6 Effect of the Fe(II)/As molar ratio on the residual As in the filtrate and on the As solubility of the ferrous-ferric arsenate precipitates.

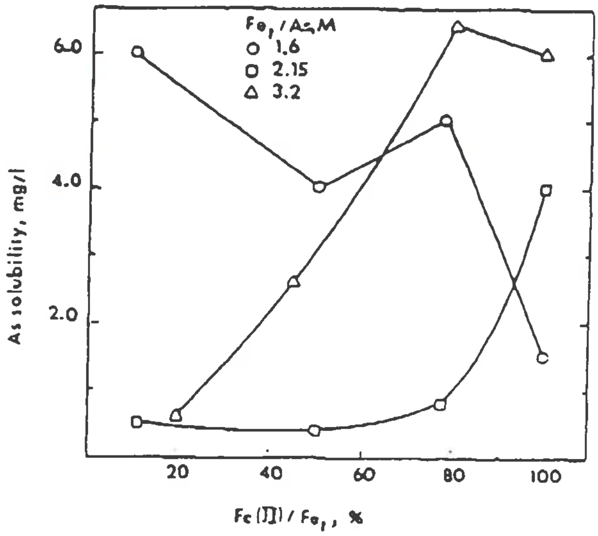

Figure 7 Effect of the Fe_t/As molar ratio and % Fe(II)/Fe_t in solution, on the As solubility of the ferrous-ferric arsenate produced.

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results in an increase of the As solubility. Therefore, mixed ferrous - ferric arsenates are less suitable for arsenic removal and fixation than the ferric arsenates.

Table VII
Precipitation and Stability of ferous-ferric arsenates

	Feed composition			Filtrate analysis			Precip Analysis				Solubility
											pH=5
Exp No	Fe t	Fe t/As	Fe2+/Fe t	Ca	As	Fe	Ca	As	Fe	SO4 2-	As
	g/l	(M)	%	g/l	mg/l	mg/l	%	%	%	%	mg/l
1	23.8	1.6	100	0.54	2	0	19.5	13.4	17.3	31.5	1.5
2	32	2.15	100	0.52	1.5	200	20.5	11.95	22.1	32.5	4.0
3	47.6	3.2	100	0.46	0.1	1500	26.3	6.7	17.7	33	6.0
4	23.8	1.6	77.5	0.48	3	0	27.5	11.7	15.6	33	5.0
5	23.8	1.6	50	0.53	3	0	28.5	11.4	15.3	36	4.0
6	23.8	1.6	9.4	0.51	2	0.6	23.2	11.3	12.5	36.8	6.0
7	32	2.15	77.5	0.53	1	0	22.8	8.9	11.4	34.5	0.8
8	32	2.15	50	0.42	1	0	24	9.3	17.5	36	0.4
9	32	2.15	11	0.50	1	3.2	21.5	9.2	15	38	0.5
10	47.6	3.2	80	0.33	0	7.3	16.4	6	17.5	36	6.5
11	47.6	3.2	45	0.45	0.3	0	23.8	5.7	17.5	42.5	2.6
12	47.6	3.2	20	0.58	0.6	0.3	25.3	6.3	14.8	43.3	0.6

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Conclusions

The issue of arsenic disposal in an environmentally acceptable manner may be successfully tackled taking into account the following:

1. As_2O_3 produced by roasting can be effectively stabilized in the form of ferric arsenate. The process route envisaged is presented in the elementary block diagram shown in figure 8.

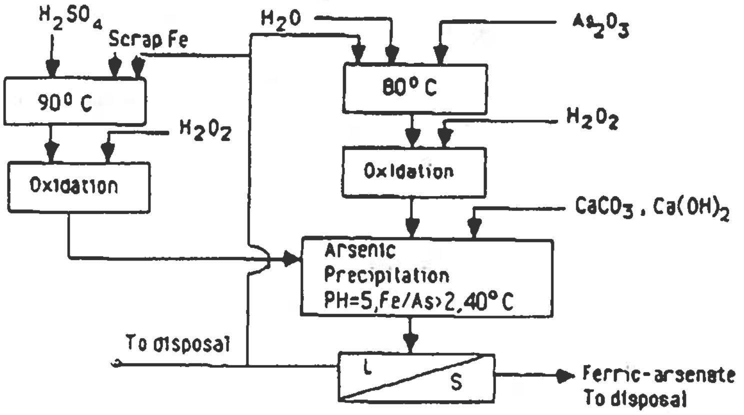

Figure 8 Proposed elementary block-diagram for the fixation of solid As_2O_3 as environmentally acceptable ferric arsenate

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The arsenic solubility of the ferric-arsenate precipitate produced by the route proposed in figure 8, at pH=5 is lower than 0.5 mg/l, and the residual As in the liquid is of the order of 0.6 mg/l. Increase of the precipitation pH and temperature had an adverse effect on the arsenic solubility.

2. Mixed Fe(II)-Fe(III) arsenates are less stable than ferric-arsenates.

3 Calcium arsenates are more insoluble than calcium arsenites for the same Ca/As ratio. To comply with environmental regulations a Ca/As ratio of 7 is required to achieve arsenic solubility of 0.4 mg/l. Calcination at 800°C rendered calcium arsenates acceptable at Ca/As=3.

4. Calcination of calcium arsenites in the temperature range of 500 to 800° C decreased the arsenic solubility, but not to the degree of being acceptable. A higher calcination temperature is probably required as it was indicated by the residual calcium arsenite indentified in the X-ray diffraction spectrum of calcined precipitate.

Acknowledgements

The financial support of the General Secretariat of Research and Technology of Greece (Research Grant No.901) is gratefully acknowledged. Thanks are also due to Mr. D. Ligros for his assistance in the experimental work.

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ZEOLITE-HYDRAULIC CEMENT CONTAINMENT MEDIUM

By

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Gregory L. Turner

ABSTRACT

A zeolite-hydraulic cement containment medium for mining and mineral processing waste material comprising: a hydrated zeolite and a hydraulic cement in a volume ratio of zeolite to cement of from about 1:9 to about 1.1, in which the containment medium is in the form of a monolith and contains less than 50% by volume of the mining or mineral processing waste material.

ZEOLITE-HYDRAULIC CEMENT CONTAINMENT MEDIUM

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention generally relates to a zeolite-hydraulic cement containment medium for hazardous wastes. In particular, the invention relates to a process for preparing a zeolite-portland cement containment medium from a paste prepared by mixing zeolite in amounts from 5-60 weight percent with portland cement in amounts from 95-40 weight percent until a blend is achieved. Thereafter, a chosen amount of small particle size hazardous wastes material is blended with zeolite to form a wastes-zeolite mixture, which is mixed with portland cement. Water is added with mixing to the waste zeolite/portland cement mixture to produce a free flowing paste, and the paste mass is poured into appropriate molds to form a cement monolith after about 7 days.

The zeolite-hydraulic cement containment medium of the invention is not encumbered by the disadvantages attendant to the use of portland cement per se, and is therefore able to contain: (1) high-concentrations and high loading levels of arsenic in the presence of high concentrations of other hazardous elements; (2) high amounts of metal cations which normally make soluble complexes with arsenic in the presence of high arsenic and high metal concentrations; and (3) arsenic in the presence of cations with which it normally makes soluble complexes, and the arsenic is contained in higher concentrations than is usual in portland cement monoliths.

Control of pollution is one of the main concerns in the environment today, and mining, mineral and metallurgical processing wastes in the U.S. accumulate at the rate of thousand of tons per day, and thereby exposes the environment to great risks of pollution. In the field of inorganic hazardous wastes from mining and mineral processing industries, such as the copper mining and processing industry, it has been found that large amounts of oxy-anion wastes (such as arsenic) cannot be disposed of economically. Further, the most common way to solidify and stabilize mining and mineral processing waste solids and waste sludges is cementation using a hydraulic material.

However, cements and other hydraulic material are the most common media for the solidification-stabilization of hazardous waste, and these containment materials after cementation and disposal (by ocean or land) are accompanied by several disadvantageous aspects in that - salts of manganese, tin, zinc, copper, and lead are active in reducing the physical strength of these cements, and anions such as phosphate, iodate, borate, and sulfide retard the setting of these cements, to the extent that, if sufficient quantities of these anions are present, the cement never hardens. In all of these cases, the ions to be contained leach from the cement matrix to some extent.

There are a number of cement-based processes that use various additives in substantial amounts to aid portland cement in the containment of hazardous substances. A general classification of these cement-based processes is a follows: cement/lime, cement/clay, cement/sorbent, and cement/polymer.

pH of the waste containment system to basic values, typically 8-10 in order to form insoluble oxides, insoluble hydroxides, or insoluble calcium salts. Weaknesses of this system are: (1) Some hazardous materials exist as anions which are soluble as calcium salts; and (2) some hazardous cations form hydroxides or complexes at basic pH ranges which are soluble to some extent.

In the cement/clay process, clays are used to adsorb hazardous materials. Weaknesses of this system are: (1) The loading capacities of clays vary with the ion or material being attached (in some cases this loading capacity is quite small); (2) Anions do not adhere well on clays; and (3) The ions or materials are adsorbed or absorbed on clays and not strongly bonded chemically. This means the attached ions or materials may be washed off the clay under the proper conditions. The clay can therefore act as a chromatography bed.

The cement/sorbent system is similar to the cement/clay system, the difference being that the material used to adsorb the hazardous substance is not clay. Sawdust, for example has been used to adsorb oils prior to encapsulation in concrete. The disadvantages of the cement/sorbent systems are essentially the same as the cement/clay system. Additionally, biodegration of the sorbant may occur if the sorbant is organic.

Cement/polymer systems usually consist of the polymer acting as a permeation limiting device by filling cement pores with hydrophobic materials, and by microencapsulation of the waste material. Usually, there is no direct reaction between the waste constituents and the polymer, and the system does not constituents. Biodegration of the polymer may occur. Leaching of exposed hazardous constituents may occur if the cement monolith becomes cracked or broken.

Accordingly, in mining and mineral processing industries, such as the copper mining and processing industry, which produces large amounts of oxy-anion wastes, such as arsenic, there is a need to devise means whereby these oxy-anion wastes can be disposed of economically, as the present way of solidifying and stabilizing mining and mineral processing wastes solids and wastes sludges by cementation is uneconomical.

SUMMARY OF THE INVENTION

One object of the invention is to provide a method for producing a hydraulic containment medium for mining and mineral processing wastes materials that is effective for containment of transition metals, heavy metals, and oxy-anions, such as arsenic.

Another object of the invention is to provide a method for producing a hydraulic containment medium for mineral processing wastes containing arsenic from the refining of copper, lead, cobalt and gold ores.

A yet further object of the invention is to provide a method for producing a hydraulic containment medium for solid wastes or sludges.

In general, the method of the invention utilizes a zeolite-hydraulic cement containment medium for hazardous wastes. The containment medium is prepared by obtaining a zeolite-hydraulic cement paste prepared by mixing from about 5 to 60 weight percent of hydraulic cement until a blend is obtained. The waste is in small particle sizes [Tyler Mesh No. 7 (i.e. 2.80 mm) or higher]. Thereafter, an amount of water sufficient to produce a free flowing paste is added to waste-zeolite/hydraulic cement mixture with mixing, and the paste mass is then poured into an appropriate mold. After a sufficient period of time of from about 24 hours to 7 days, a cement monolith is formed, and can be removed from the mold as a monolith for disposal.

The amount of water added depends upon the characteristics of the waste sample, but may vary between about 20 to about 35% by weight of the combined portland cement plus waste-zeolite mixture. After the paste is poured into the mold, good results are obtained when the temperature is kept at about 25°C - 45°C during a 24 hour to 7 day time period in which the monolith is formed.

DETAILED DESCRIPTION OF THE INVENTION

Portland cement by itself has been used for many years in Japan and elsewhere for solidification of wastes having hazardous constituents before ocean disposal; however, portland cement has several disadvantages when considering cementation for land disposal of hazardous wastes. For example, salts of manganese, tin, zinc, copper and lead are active in reducing the physical strength of portland cement. Further, the anions of phosphate, iodate, borate, and sulfide retard the setting of portland cement, and if sufficient quantities of these anions are present, the cement will never harden. (P. L. Bishop, Leaching

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The zeolite-hydraulic cement containment medium of the invention is an excellent medium for containment of materials having transition metals, heavy metals and oxy-anions, especially oxy-anions of arsenic. Oxy-anions are anions which contain oxygen as one component of the moiety.

The zeolite-hydraulic cement containment medium for wastes containing arsenic from the refining of copper, lead, cobalt and gold ores - as well as solid wastes or sludges is prepared by mixing from about 5 to 60% of zeolite containing waste with about 95 to 40 weight percent of portland cement until an intimate blend is obtained. The hazardous waste is in small particle sizes [Tyler Mesh 7 (i.e. 2.80 mm) or higher]. Thereafter, an amount of water sufficient to produce a free flowing paste is added with mixing to produce paste mass of zeolite-waste/portland cement. The paste is poured into appropriate molds and kept there until a cement monolith is formed.

More particularly, the monolith formation is formed as follows: (1) Arsenic waste is passed through a sieve of Tyler mesh size 100 and intimately combined with the desired amount of zeolite. (2) Dry hydraulic cement is added to the waste-zeolite mixture in small portions and intimately mixed until all the required cement is incorporated. (3) Water is added with constant stirring until a soft paste stage is reached. The amount of water added will depend upon sample characteristics, but can vary between about 20 to 35% of the combined portland cement plus waste-zeolite mixture. (4) The paste is poured into molds which are kept at a constant humidity (88% relative humidity) and temperature (40°C) for 7 days at which time the monoliths are removed from the molds.

However, the usefulness of the invention is not confined to the percent relative humidity, curing time, and temperature, or cementatious material or zeolite class mentioned. Any relative humidity, curing time, and temperature suitable for the cementation process of a hydraulic cement and any zeolite will suffice.

A typical artificial zeolite-hydraulic cement containment medium according to the invention is monoliths of arsenic waste materials. The containment medium consist of a hydrated $Na\cdot(SiAlO_2)$ type zeolite (faujasite) with a cubic structure similar to sodalite, and type 1 portland cement in volume ratios from 1:9 to 1:1 (zeolite to cement). The zeolite contained molar ratios of $Na_2O:Al_2O_3:SiO_2$ with variable amounts of hydrated water present of 1:1:2.8+/- 0.2 respectively. However, the usefulness of the invention is not confined to this group and/or structure of either natural or artificial origin, as other zeolites will perform the same function.

EXAMPLE 1
Containment of Copper Smelter Waste.

Table 1 contains the chemical analysis of a copper smelter waste with typical high metal and high arsenic contents. These high values make containment of copper smelter waste difficult, and usually require large dilution of the waste product. A containment monolith of this material was made using the procedure described above. The monolith contained 30% by volume of the copper smelter waste. The copper smelter waste in the novel zeolite-portland cement containment medium successfully passed EPA's Toxicity Characteristic Leaching Procedure (TCLP) requirements (see Table 2).

Table 1
Copper smelter waste sample analysis

Element	Concentration
Antimony.......mg/kg..	8:87
Arsenic..........pct..	10.7
Barium.........mg/kg..	1400
Cadmium........mg/kg..	1200
Chromium.......mg/kg..	7.7
Copper...........pct..	7.9
Iron...........mg/kg..	97.1
Lead...........mg/kg..	65
Tin............mg/kg..	536

Table 2
Copper smelter waste TCLP analysis, mg/kg

Element	Concentration permitted by EPA	Concentration present
Arsenic	5.0	1.81
Barium	100	<1.00+
Cadmium	1.0	0.03
Chromium	5.0	0.07
Copper*	1.0	0.02
Iron*	.4	<0.05
Lead	5.0	<0.05
Mercury	.2	<0.002
Silver	5.0	<0.01
Tin*	5.0	<0.02

*Drinking water standard.
*Element shown as "<" indicate below detection limit of the analytical method used.

EXAMPLE 2
Containment of Arsenic Acid Production Wastes

Table 3 contains the chemical analysis of an arsenic acid production waste with typical high iron and high arsenic contents. These high values usually make containment of the waste difficult, because arsenic forms a water soluble complex with ferric iron and iron always disproportionates into ferrous and ferric valence states.

Table 3
Crude arsenic acid production waste sample analysis

Element	Concentration
Arsenic..........pct..	32
Barium..........mg/kg..	308
Cadmium........mg/kg..	60
Chromium.......mg/kg..	57
Copper.........mg/kg..	84
Iron..............pct..	2.6
Lead...........mg/kg..	399
Mercury........mg/kg..	79
Silver.........mg/kg..	25
Zinc...........mg/kg..	38

A containment monolith of this arsenic waste material was made using the procedure described above. The monolith contained the waste at a loading of 30% by volume. The crude arsenic acid production waste in the novel zeolite-hydraulic cement containment medium successfully passed EPA's Toxicity Characteristic Leaching Procedure (TCLP) requirements (see Table 4).

Table 4
Crude arsenic acid production waste TCLP analysis, mg/kg

Element	Concentration permitted by EPA	Concentration present
Arsenic	5.0	2.09
Barium	100	<1.00
Cadmium	1.0	<0.02
Chromium	5.0	<0.05
Copper*	1.0	<0.02
Iron*	.4	<0.05
Lead	5.0	<0.05
Mercury	0.2	<0.002
Silver	5.0	<0.01
Tin*	5.0	<0.02

*Drinking water standard.
*Element shown as "<" indicate below detection limit of the analytical method used.

EXAMPLE 3

Containment of Very High Level Artificial Waste

Table 5 contains the chemical analysis of an artificial inorganic hazardous waste. The high ion content for each element present, i.e., 5960 mg/kg of mercury in the waste is not typical for hazardous waste materials. These high values were used as a measure of the potential effectiveness of the invention containment medium for EPA listed inorganic hazardous elements. A containment monolith of this material was made using the procedure described above. The monolith contained 30% by volume of the waste. This sample successfully passed EPA's Toxicity Characteristic Leaching Procedure (TCLP) requirements (see Table 6). Mercury was contained to below detection limits.

Table 5

Artificial inorganic hazardous waste sample analysis, mg/kg

Element	Concentration
Arsenic	6310
Barium	6290
Cadmium	4600
Chromium	5670
Copper	5950
Iron	4930
Lead	5260
Mercury	5940
Silver	6040
Zinc	5530

Table 6

Artificial inorganic hazardous waste sample TCLP analysis, mg/kg

Element	Concentration permitted by EPA	Concentration present
Arsenic	5.0	0.29
Barium	100	.09
Cadmium	1.0	.07
Chromium	5.0	.04
Copper*	1.0	<0.02
Iron*	0.4	.08
Lead	5.0	.51
Mercury	0.2	<0.002
Silver	5.0	.01
Tin*	5.0	.03

*Drinking water standard.
*Element shown as "<" indicate below detection limit of the analytical method used.

Before the advent of the present artificial zeolite-hydraulic cement containment medium, hydraulic cementation has not been very effective with wastes containing oxy-anions, such as arsenate, selenate, etc., or with soluble oxides or hydroxides.

The containment of oxy-anions in the zeolite need not be limited to the direct accessibility of the anion to normal zeolite binding sites. Any form of faujasite zeolite is usable to contain oxy-anions. Further, any zeolite that contains exchangeable mono-valent cations are usable in the context of the invention. Further still, any zeolite that contains divalent or trivalent cations is usable in the context of the invention to bind arsenate or other oxy-anions.

The families of zeolites that are useful in the context of the invention are: faujasite, chabazite, zeolite A, zeolite

Rho, zeolite ZK-5, zeolite X, zeolite Y, wilhendersonite, gmelinite, edingtonite, natrolite, tetranatrolite, paranatrolite, mesolite, seolecite, thomsonite, gonnardite, analcime, wairakite, gismondine amicite, garronite, gobbinsite, zeolite NaP-1, laumonitite, merliontite, paulingite, phillipsite, harmotome, yugawaralite, canerinite, erionite, levynite, zeolite 1, zeolite losed, zeolite omega, sodalite, offretite, mazzite, bikitaite, dachiardite, epistilbite, ferricite, zeolite ZSM-5, mordenite, brewsterite, heulandite, clinoptilolite, stibite, stellerite, barrerite, afghanite, liottite, franzinite, sacrofanite, giuseppettite, svetlozarite, doranite, chiarennite, hsianghualite, lovdarite, wenkite, roggianite, partheite, perlialite, viseite, keoheite, leucite, pollucite, herscheilite, phacolite, leonhardite, wellsite, goosecreekite, cowlesite, zeotypes based on aluminum phosphate, and any zeolites made by modifications of these structures.

The foregoing description of the specific embodiments will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalence of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation.

METLCAP®

What does Metlcap® do?

Metlcap® is a patented chemical cement, for the treatment of hazardous heavy metals, on or in contaminated lands (earth, clay, etc.), waters, and in industrial wastes.

The eight (8) metals designated by the US Environmental Protection Agency (EPA) under the Resource Conservation and Recovery Act (RCRA) are: **arsenic, barium, cadmium,chromium, lead, mercury, selenium and silver.**

Metlcap® combines chemically and physically with the metals to: **stabilize, encapuslate, and solidify** the harmful components in a hardenable chemical cement matrix, that is an insoluble compound.

Other metals, not on the list of hazardous metals, alloys and substances, may also be treated in this manner. (Patent applications are pending in Canada and Mexico.)

This simple method reacts quickly, and renders the hazardous metals **physically immobile, inert and, essentially, harmless**. This economical method is especially useful in remediating hazardous heavy metals:

- On or in contaminated land, soils, sub-soil strata, and waterways;
- In Industrial waste streams, including machining waste, pickle liquor, plating sludge, baghouse dusts, foundry casting sand and media, fly ash, incineration bottom ash, grit-blast waste from removal of coatings, underwater washout and buildup of contaminants in wetlands, navigable waters, bays and harbors; and
- By Small Quantity Generators, performing on-site remediation of generated hazardous waste metals, within 90 days from date of creation of hazardous waste, using **METLCAP®** LAB kits.

Metlcap® remediates toxic, hazardous heavy metals:

(1) On or in contaminated lands and waterways, (2) industrial waste streams from manufacturing, and (3) in laboratory wastes. Metlcap® produces a hardenable cement that can achieve compressive strengths high enough for use as a reusable resource material for roadbed paving base, or other building and construction materials, including low-level radiation shielding.

Metlcap® pretreatment of hazardous wastes containing heavy metals, now required before landfilling, is in compliance with U.S. EPA Land Disposal Restrictions, Subpart D - Treatment Standards, CFR 268.40 .

What are some of the remediation methods utilizing METLCAP®

METLCAP® patented chemical cement, is designed for the treatment of hazardous heavy metals, on or in contaminated lands (earth, clay, etc.), waters, and in industrial wastes.

The eight (8) metals designated by the US Environmental Protection Agency (EPA) under the Resource Conservation and Recovery Act (RCRA) are: **arsenic, barium, cadmium,chromium, lead, mercury, selenium and silver.**

METLCAP® combines chemically and physically with the metals to: **stabilize, encapuslate, and solidify** the harmful components in a hardenable chemical cement matrix, that is an insoluble compound.

What are the remediation methods utilizing METLCAP®?

- Deep Soil Mixing (DSM)
- Shallow Soil Mixing (SSM)
- Jet Soil Mixing (JSM)
- Conventional Soil Mixing (CSM)
- Sludge / Soil Stabilization (SSS)
- High Pressure Injection Grouting (HPIG)
- Slurry Wall Containment Construction (SWCC)
- Mining Lands Reclamation (MLR)
- Combinations of Remediation Methods
- Other Combinations (Currently in Development).

What is Metlcap? | What does it do? | How was it tested? | Applications? | Remediation methods?
Tax incentives | Product availability | Table of results | Homepage

Homepage || What does it do? || How was it tested? || Applications
Remediation methods || Tax incentives || Product availability || Table of results

CENTER FOR BIOREMEDIATION

Weber State University

Issue 001
January 1997

Notes from the Center for Bioremediation Team

A special thanks to Governor Michael Leavitt, Dr. Suzanne Winters, Senator Robert Bennett, Darin Bird and Susan Dixon for their efforts in transferring water and soil remediation capabilities and supporting equipment from the former U.S. Bureau of Mines (USBM) to the Center for Bioremediation.

With closure of the USBM nearly one year ago, the Center was conceived to retain valuable remediation technologies, resources, and expertise within Utah. The Center was formed from collaborative relationships between scientists at the USBM, Weber State University, and the University of Utah. In July, 1996, the Center received State of Utah Center of Excellence status. Program focus is on research, development, and commercialization of improved bioprocesses for metal and mixed metal-organic removal and metal recovery from soils, waters, ores, and mixed metal-inorganic-organic wastes.

Recent transfer of additional remediation equipment, a mobile soil treatment plant and supporting remediation analytical equipment, strengthens the Center's development and marketing base. This will assist the Center in moving former USBM technologies into the private sector.

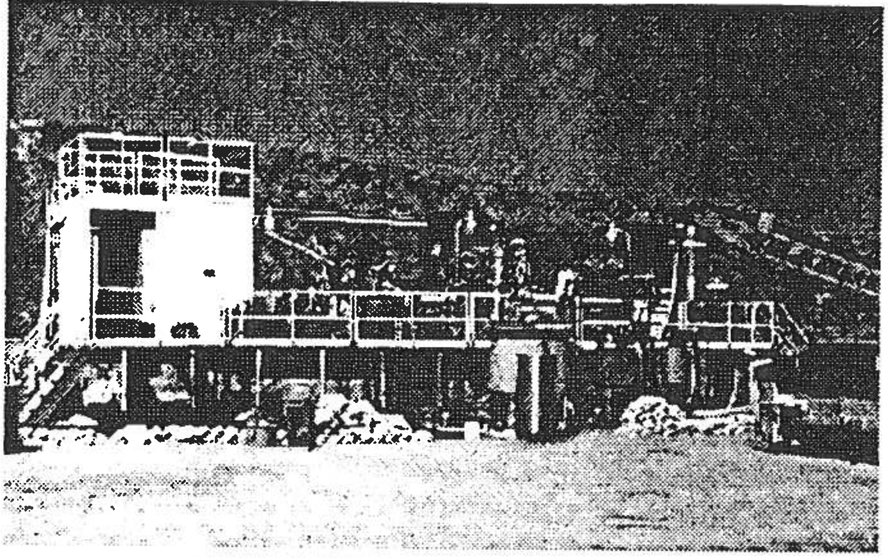
NAS Miramar Lead Removal Demonstration

A mobile soil treatment plant successfully demonstrated on-site remediation of lead-containing firing range soils at Miramar Naval Air Station, near San Diego, CA. The mobile plant consists of adapted minerals-processing and soil-washing equipment and uses a combination of physical, chemical, and biological methods to remove bullets and clean lead from firing range soils.

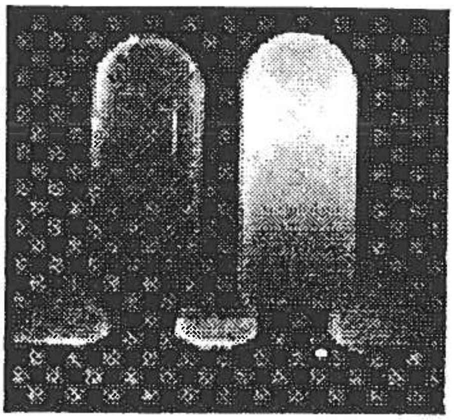
The mobile plant was developed in response to increasingly stringent environmental regulations and observations linking firing range soils to ground and surface water contamination. It was developed and tested in collaboration with Rice University AATDF, U.S. Army Corps of Engineers Waterways Experimental Station (WES), Bureau of Mines, Bureau of Reclamation, and the U.S. Navy. The plant, configured on a 48' trailer to be operational with a 24-48 hour setup, is now co-owned by the Center and WES.

Demonstrated process rates up to 3,000 lb/hr effectively removed bullets and lead from firing range soils. Process and equipment advances will allow remediation of a broader range of soils and contaminants.

Mobile Lead Remediation Plant at NAS Miramar, October, 1996



Immobilized Microbes and Enzymes



A selenium-reducing cell-free preparation in calcium alginate beads produced the red amorphous selenium precipitate on the left. The vial on the right contains a beforetreatment bead sample.

Center research is testing immobilized enzymes (cell-free preparations) derived from field-proven microbes. Two common problems in bioremediation are: (1) microbial sensitivity to contaminants and (2) over-growth/displacement of desired microbes by site bacteria.

Immobilized live microbes and enzyme preparations, have been demonstrated to remove contaminants from environments toxic to unprotected live microbes. Enzyme preparations were produced from cyanide-oxidizing and selenium-reducing microorganisms and immobilized in alginate (seaweed extract) beads.

Cyanide enzyme preparations increased rates of cyanide destruction and functioned at higher cyanide concentrations than do the live cyanide-oxidizing bacteria. Immobilized preparations of live cyanide-oxidizing bacteria tolerated higher cyanide levels than did unprotected bacteria.

Combined enzyme preparations simultaneously removed up to 102 mg/L cyanide and 31.1 mg/L selenium from mining solutions . Simultaneous cyanide and selenium removal, using live microbes, is not possible because cyanide kills or inhibits seleniumreducing bacteria.

Center Custom Microbial Culture Services Assist Industrial Remediation Efforts

The Center for Bioremediation develops custom microbial cultures for remediation of metal and mixed metal/organic contaminated waters and soils. Remediation efficiencies can be greatly improved by development and application of custom site- and contaminant-specific cultures. Our approach uses both indigenous microbes and cultures from the Center microbial repository.

Based on the environmental needs of a client, custom cultures are developed and adapted for application to specific environmental settings. Center custom cultures have been used for on-site remediations and to accelerate closure of gold heap leach operations. One gold operation, which is no longer productive, has 1-2 million gallons of cyanide and heavy-metal contaminated water which must be treated before closure. This project uses two sets of custom cultures, one for cyanide degradation and a second for heavy metal removal. Once cyanide is removed, the second set of microorganisms will be introduced to remove heavy metals from the water and to stabilize metals in the heap.

AQUATRACK - A New Non-invasive Subsurface Pollution Mapping and Monitoring Technology

AQUATRACK, a novel technology that can map and monitor subsurface waters and pollution plumes using surface readings, has been developed by Hydro Geophysics. Hydro Geophysics, a geophysical company working with the Center, has used AQUATRACK to map metal- and organic-contaminated waters, acid mine drainage, and drainage field seeps.

Primary advantages of this technology are:

- Ability to map and monitor subsurface waters and pollution plumes from the surface
- Minimal well drilling
- Insures proper implementation of remediation technologies

The Center and Hydro Geophysics have several cooperative surveys planned for next spring. Hydro Geophysics can be contacted through the Center or at (801) 966-1239 (Dr. Jerry Montgomery).

Winter is the Time of Year for Biotreatability Studies

Due to near or below-freezing temperatures, winter is often not the ideal time to initiate bioremediation projects. However, winter is the ideal time to perform laboratory biotreatability studies for your remediation project. This way, a remediation plan can be in place before spring arrives.

Biotreatability testing includes site-specific soil and water toxicity studies, nutrient optimization, and determines the custom culture for your specific remediation problem and environmental conditions. Toxicity studies determine if there are toxic compounds present that would inhibit microbial growth and interfere with remediation efforts. Nutrient optimization studies optimize microbial nutrient requirements for growth and economics. Most biotreatability studies run about 6-8 weeks and require about one gallon of soil and/or water.

Cooperative Opportunities

The Center is looking for additional industry and government cooperators to participate in research, development, and testing of existing and new bioremediation technologies. Participation in any development phase is welcome.

The Center provides a valuable multi-disciplinary professional resource with capabilities to meet diverse environmental remediation challenges. Partnerships offer additional benefits through potential faculty interaction, opportunities for students and site operators to be trained in research, and testing of interest to the cooperator.

Center Publications - 1996

Montgomery, J.R, siackhams F., Phillips, T.A., and D.J. Adams. **Tracking Mine seeps, In situ Leach Solutions, and Pollution Plumes using Electromagnetics.** Randol Gold Forum Proceedings, squaw Valley, CA, May, 1996.

Heyrend, T., Adams, D.J., and D. Hayes. **Arsenate Reduction to Arsenite by Two Pseudomonas Species Isolated from Mine Drainage waters; Microbial Arsenic Removal using Upflow GAC Columns**. Randol Gold Forum Proceedings, Olympic Valley, CA, May, 1996.

Adams, D.J., Pikett, T.M., and J.R Montgomery. **Biotechnologies for Mebl and Toxic Inorganic Removal from Mining Process and waste Solutions.** Randol Gold Forum Proceedings, Olympic Valley, CA, May, 1996.

Adams, D.J., Fukushi, K, and s. Ghosh. **Developrnent of Enriched Microbial Cultures for Enhanced Metal Removal.** American Chemical society Emerging Technologies in Hazardous waste Management VIil Proceedings, Bimmingham, AL, September, 1996.

Pickett, T.M. and D.J. Adams, **Advances in Biosensor Technology.** American Chemical Society Emerging Technologies in Hazardous Waste Management VIil Proceedings, Birmingham, AL, September, 1996.

Winkler, U., Pickett, T.M., and D. Hudig. **Fractionation of Perforin and Granzymes by Immobilized Metal Amnity Chromatography (IMAC).** Joumal of Immunological Methods, 191, June, 1996.

Montgomery, J.R, Blackham, F., and T.A. Phillips. **Tracking Underground Water Through the Use of Electromagnetics.** American Chemical Society Emerging Technologies in Hazardous Waste Management VIil Proceedings, Birmingham, AL, September, 1996.

Phillips, T.A. and J.R Montgomery. **Development of a Mobile Treatment Unit for the Removal of Lead from Military Rifle Ranges.** American Chemical Society Emerging i Technologies in Hazardous Waste Management VIil Proceedings, Birmingham, AL, September, 1996.

Onguri, K.V., Babu, G.R.V., Adams, D.J., Wolfram, J.H., and K.D. Chapatwalla. **Biotreatment of Mine Water-Containing Cyanides by Using Immobilized Cell Technology.** In Press.

Center Technologies

- Microbial Arsenic Removal
- Microbial/Biopolymer Uranium-Lead Removal
- Microbial/Enzymatic Nitrate Destruction
- Microbial/Enzymatic Cyanide Destruction in Heaps and Process Solutions

- Microbial/Enzymatic Selenium Removal
- Microbial Metal Stabilization
- Surface Tracking of Subsurface Pollutants
- Mobile Soil Remediation Plant
- Accelerated Bioleaching Process
- Site Evaluation and Biotreatibility Studies

Approach | Technologies | Capabilities | Cooperative Opportunities | Newsletter | Publications | Staff | Home

PHYTOREMEDIATION

Phytoremediation: Using plants to remove pollutants from the environment

Soils and waters contaminated with toxic metals pose a major environmental and human health problem which is still in need of an effective and affordable technological solution. The partial success of microbial bioremediation has been limited to degradation of select organic contaminants, and has been ineffective at addressing the challenge of toxic metal contamination, particularly in soils. Current methodologies for remediating toxic metal polluted soils rely mainly on excavation and burial at a hazardous waste site at an average cost of $1,000,000/acre.

In our laboratory at Rutgers University we have developed a cost-effective ^{3}green^2 technology based on the use of specially selected metal accumulating plants to remove toxic metals, including radionuclides, from soils and water. We termed this technology Phytoremediation. Phytoremediation takes advantage of the fact that a living plant can be compared to a solar driven pump, which can extract and concentrate particular elements from the environment. We have exploited this property to develop a method for enhancing the ability of specially selected and/or engineered plants to remove toxic metals from soil and water and to concentrate these metals in harvestable parts. To make phytoremediation possible we have assembled a diverse group of scientists in our laboratory composed of plant biochemists, molecular biologists, soil chemists, agronomists, and environmental engineers. We have also formed close collaborations with other faculty at Rutgers and scientists at other Universities in the US and abroad. This interdisciplinary collaborative approach became the key to our success. Our efforts received a substantial boost after Phytotech Inc., dedicated to commercialization of phytoremediation, was formed in New Jersey in 1993. Productive collaboration with Phytotech's research and business teams greatly accelerated the development of phytoremediation and targeted this development to the most pressing needs of the ^{3}real world^2.

The metals targeted for phytoremediation include lead, cadmium, chromium, arsenic and various radionuclides. The harvested plant tissue, rich in accumulated contaminant, is easily and safely processed by drying, ashing or composting. The volume of toxic waste produced as a result is generally a fraction of that of many current, more invasive remediation technologies and the associated costs are much less. Some metals can be reclaimed from the ash, which further reduces generation of hazardous waste and generates recycling revenues.

Specifically, two subsets of phytoremediation are nearing commercialization. (I) Phytoextraction, in which high biomass metal-accumulating plants and appropriate soil amendments are used to transport and concentrate metals from the soil into above-ground shoots, which are harvested with conventional agricultural methods. (II) Rhizofiltration, in which plant roots grown in water, precipitate and concentrate toxic metals from polluted effluents. Two patents covering phytoremediation technology have been issued to our group, with six more still pending. Our phytoremediation work is covered in peer-reviewed scientific journals and in popular press.

The basic idea that plants can be used for environmental remediation is certainly very old and can not be traced to any particular source. However, a series of fascinating scientific discoveries combined with interdisciplinary research approaches allowed the development of this idea into a promising environmental technology. Laboratory and greenhouse work on phytoremediation started in 1991 as a result of funding received from the US EPA and the State of New Jersey. The effectiveness of phytoremediation in the field for both water and soil was demonstrated for the first time during the summer of 1995.

Successful transfer of phytoremediation from laboratory to the field is a crucial step in the development of this technology. While Phytotech Inc. is making progress in commercialization of phytoremediation our team at Rutgers is directing more of its effort to understanding physiological, biochemical and molecular mechanisms involved in metal uptake accumulation and resistance. We are also developing molecular genetic approaches to improving phytoremediation. In addition, we are starting a program in remediation of organics by plant roots and associated microorganisms.

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APPENDIX H

Materials Management Data

PROECO Corporation
7722 - 9 Street
Edmonton, Alberta, Canada
T6P 1L6
(403) 440-1825 tel
(403) 440-2428 fax

FAX TRANSMISSION

To: *Paul Green*
Company: **Dillon Consulting Limited**
Fax: **403-873-3328**

Total pages: 13
Date: August 18, 1997

Regarding: Disposal Options for Arsenic Trioxide Dust

As per our conversation last week I have put together some information for your review.

There are 3 possible disposal options for this waste material: secure landfill, treatment and incineration. Treatment may be an option depending on the chemical makeup and concentrations of the waste material, but this option would be the most expensive. The secure industrial landfill option would be reliant upon the make-up and concentration of the waste material. This option would be the most cost effective if it meets the criteria. The incineration option would fall in between the other 2 options from a costing standpoint.

Final pricing would be dependent upon the volume of material requiring disposal and the location of the material. Transportation charges may prove to be prohibitive if the site is located in a remote area.

Estimated disposal costs would range from $750/tonne for secure landfill to $1,300/tonne for incineration to $1,600/tonne for treatment.

If you have any questions give me a call at 1-800-661-5792.

Sincerely yours,
PROECO Corporation

Gary Demeriez, B.Sc.
Sales Manager - Western Canada

GD/DILL0001.DOC

Welcome to the Custom Environmental Services Ltd. / Proeco Corporation Home Page

CUSTOM ENVIRONMENTAL SERVICES LTD

PROECO Corporation

PROECO CORPORATION

PCB RECYCLING AND DISPOSAL

PROECO OILFIELD WASTE MANAGEMENT PROGRAM

|CESL| PROECO| OILFIELD PROGRAM| PCB|

YOUR BEST SOLUTION FOR MANAGEMENT OF HAZARDOUS WASTE, HAZARDOUS RECYCLABLES AND PCB's

ENVIRONMENTAL EXPERTISE AND EXPERIENCE WE ARE THE INDUSTRY LEADER

Email us at proeco@planet.eon.net...

CUSTOM ENVIRONMENTAL
SERVICES LTD

Custom Environmental Services Ltd.
7722 - 9th. Street
Edmonton, Alberta, Canada T6P 1L6

Custom Environmental Services Ltd. was established in 1985 to service the needs of industrial, commercial and institutional clients requiring hazardous waste disposal. In 1989 we opened Alberta's first hazardous waste transfer facility.

Custom Environmental Services Ltd. and its affiliate PROECO Corporation are full service hazardous waste and hazardous recyclable management companies.

Custom Environmental's corporate headquarters, treatment, blending, storage, and technology centre is located in Edmonton, Alberta.

Our comprehensive services include:

- Sampling Services
- Packaging Services
- Fuel Blending
- Bulking
- pH Adjustment
- Hazardous Recyclable Processing
- Dry Cleaning Filter Recycling
- PCB Electrical Equipment Recycling
- Aerosal Draining and Recycling
- Heavy Metal - Chemical Stabilization
- Dewatering
- Treatment
- Hazardous Waste Management
- Specialised Cleaning Services
- Biomedical Waste Disposal
- Flourescent Lamp Tube Recycling
- Temporary Storage Facilites
- On-Site Stabilization Services
- Transportation
- Lab-packing
- Household Hazardous Waste Services
- Waste Minimization
- Low Temperature Vacuum Extraction
- Oil Filter Crushing and Recycling
- Drum Washing and Recycling
- Compressed Gas Cyclinder Draining
- Volume Reduction
- Disposal
- Recycling
- Hazardous Recyclables Management
- Delisting of Hazardous Waste
- Packaging Supplies
- Oilfield Waste Management

Custom Environmneta1 Services Ltd. maintains Approvals for the management of waste materials under Alberta Environmental Protection and Enhancement Act; Division 1 Hazardous Waste and Division 2 Hazardous Recyclables as well as the Alberta Energy Utilities Board for Dangerous Oilfield Wastes.

Hazardous Waste Services

Custom Environmental Services Ltd. is fully licensed, insured and bonded to provide handling, transportation, treatment, disposal, recycling and transfer services. Field services are provided by trained technical staff.

Client Site Services

With over 4,500 completed projects Custom Environmental Services has a vast amount of experience in helping our clients solve their waste management problems.

Disposal and Treatment Facilities

Waste materials which can not be declassified at our site are sent to third party facilities for treatment by recycling methods or for final disposal. Custom Environmental uses a network of approved third party licensed end receivers that are capable of handling almost any waste management problem.

Hazardous Waste Transportation Services

Custom Environmental Services Ltd. is a licensed carrier of hazardous waste materials. Vehicles have been specially designed for the transportation of hazardous wastes. Drivers are trained in the requirements under the Transportaiton of Dangerous Goods Act, to insure compliance with regulations.

PCB Waste Management Services

Custom Environmental Services Ltd. opened Canada's first fully licensed private sector PCB waste management facility in 1989.

Field PCB services include: spill sampling, clean-up planning, collection, packaging, transportation, non destructive removal of PCB from cement and associated services; in addition, we have had the opportunity to clean-up after five fires involving PCB electrical equipment.

PCB Electrical Equipment Recycling

In this process the electrical equipment is physically dismantled with non reclaimable materials sent for off-site disposal via high temperature incineration. The reclaimed components (steel, copper, aluminum, ceramics) are tested and sent off site for reuse. Custom Environmental operates one of only 5 such facilities in North America.

Fuel Blending of Organic Wastes

The collection and blending of organic waste streams for use as burner fuel was one of the first recycling programs we developed. Paints, solvents, oils and other hydrocarbon wastes are collected and turned into a fuel source for cement kilns and asphalt plants.

Certification Methods

Custom Environmental Services provides Certificates of Recycling and Disposal for all regulated waste materials. We offer an audit trail tracking program for waste generators who wish to follow their waste from collection through to the end recycling or disposal facility we have chosen.

Contaminated Site Remediation Services

Custom Environmental provides turn key remediation services. Investigation through to site closure are handled by trained technical staff.

Facilities

Corporate Headquarters in Edmonton, Alberta

Administrative, service and sales management functions are provided through the head office location. The Edmonton site is the licensed and approved transfer, processing and storage facility. The site has been in operation since 1989.

Custom Environmental Services Ltd. Permit Numbers

Generator	
Alberta	G-4413
British Columbia	BCG-151198
Transportation Approvals	
Alberta	C-1601
Saskatchewan	C-1601
Manitoba	C-1601
British Columbia	LT-0416
Northwest Territories	NTC-000014
U.S. EPA	WAD90000103
Receiver	
Alberta	R-1062

Operation Of A Hazardous Waste Management Facility

Alberta Approval 95-IND-085
Agreement with the Alberta Special Waste Management Corporation
Public Health Act, Permit to Operate a Waste Management Facility #W 1232

Other Permits

Custom Enviromental Services (Eastern) Inc., Ontario Provisional Certificate of Approval for a Waste Management system No. A 84104

Approved Hazardous Waste and Hazardous Recyclables Classes For Acceptance by Custom Environmental Services Ltd.

Transportation of Dangerous Goods Act Class	Division	Example
Class 1 - Explosives	1.5 Mass Explosion Hazard (but very low risk if initiation)	
Class 2 - Gases	2.1 Flammable Gas 2.2 Non-Flammable; Non-Toxic 2.3 Poison Gas 2.4 Corrosive Gas	Propane Nitrogen Sulphur Dioxide Ammonia, anhydrous liquefied
Class 3 - Flammable and Combustable Liquids	3.1 Extremely Flammable 3.2 Very Flammable 3.3 Moderately Flammable	Gasoline Methanol Styrene monomer, inhibited
Class 4 - Flammable	4.1 Easily Ignited Solids	Safety Matches

Class 4 - Flammable Solids	4.2 Spontaneously Combustible 4.3 Dangerous When Wet	Oily Rags Calcium Carbide
Class 5 - Oxidizers and Organic Peroxides	5.1 Oxidizing Materials 5.2 Organic Peroxides	Ammonium Nitrate Fertilizer Dibenzoyl Peroxide
Class 6 - Poisonous and Infectious Substances	6.1 Toxic by Ingestion, Inhalation, Absorption 6.2 Infectious	Arsenic Infectious Substance
Class 8 - Corrosives	8 Corrosives	Sulphuric acid
Class 9 - Miscellaneous	9.1 Other Dangerous Goods 9.2 Environmentally Dangerous Goods 9.3 Named Hazardous Wastes	PCB White Asbestos, Malathion Waste type 81, spent pickle liquor

Transportation Equipment

Custom Environmental owns and operates a fleet of transportation equipment to support the collection and delivery of hazardous wastes and hazardous recyclables

Service Vans: These enclosed vans are used to transport hazardous waste and hazardous recyclable materials to our Edmonton location. The vans are equipped with a sealed secondary containment steel sump and are equipped with hydraulic lifts for loading cargo at locations without a loading dock.

Tandem Axel Crane Truck: Suitable for the movement of transformers and bulk packaged solids.

Transport drivers have completed training for dangerous goods hauling and emergency response.

Insurance Coverage

Insurance for automobile, environmental and general acidents is included in our client protection package.

Insurance

TYPE OF INSURANCE	LIMITS
General Liability	$5,000,000.00
Auto	$5,000,000 per occurrence
Environmental Impairment Liability	$2,000,000.00 per occurrence $2,000,000.00 aggregate
Worker's Compensation	statutory

For additional information about Custom Environmental Services Ltd. please contact **Brian Winters, President** or **Tim Underwood, Operations Manager.**

By Telephone @ (403) 440-1825 or
Long Distance inside Canada Toll Free @ 1-800-661-5792
In the case of an Emergency, all phones answered 24 hrs.

By Fax @ (403) 440-2428

Email us at proeco@planet.eon.net...

PROECO CORPORATION

PROECO Corporation
7722 - 9th. Street
Edmonton, Alberta, Canada T6P 1L6

PROECO Corporation provides sales and marketing services for Custom Environmental Services Ltd.

In addition services are also provided in the following areas:

Hazardous Materials Services

- Disposal of Hazardous Waste
- Treatment of Hazardous Waste
- Stabilization of Heavy Metal Contaminated Materials
- Recycling of Hazardous Recyclables
- Underground Storage Tank Consulting
- Undergorund Storage Tank Removal
- Underground Storage Tank Sampling
- Environmental or Compliance Audits
- Environmental Remediation Services
- Remediation of Hydrocarbon soils
- Field Services

Environmental Consulting

- Environmental Investigation Services
- Phase I and II Site Assessments
- Environmental Audits for Waste Minimization
- Environmental Audits for Property Transfer
- Sampling Programs
- Oilfield Waste Management Program
- PROECOPAC Waste Management Units
- Dangerous Oilfield Waste Recycling and Disposal

PROECO Corporation is involved in the initial phases of planning for the management of environmental problems.

Site Assessments

From investigation through to site closure PROECO Corporation can assist in development of comprehensive environmental management plans.

Phase I and II Site Assessments

These site assessments require knowledge related to the effects of various chemicals on plant, soil, water and air. PROECO Corporation reviews the historical background of a site and applies in depth review of operations that have taken place on the site to predict if there is potential for environmental concern. When required, samples are taken to verify if the predictions are applicable. Final reports qualify the results including any sampling that was done. These reports can be used to insure that continued development on a site or transfer of ownership do not have liability reflevtive of past operations on the site.

Underground Storage Tank Services

This program is designed to assess the integrity of underground storage tanks. If a tank fails the integrity test Phase II Assessment of the site is performed to ensure that product from the tank has not contaminated the surrounding soil or ground water. A site sensitivity review is completed to determine remediation criteria where contamination is extensive. Site closure is provided when full assessment reveals that there are no environmental problems.

Property Transfer Audits

To ensure that a purchaser or mortgagor is aware of any potential environmental problems associated with a site, property transfer audits are recommended. This buyer be ware review identifies potential and existing environmental problems at a given property. Environmental problems can have a dramatic effect of the value on a property including unexpected remediation and cleanup cost not planned for.

Oilfield Waste Management Program

For additional information about PROECO Corporation please contact:

Brian Winters, President

PCB Waste Services: Gerry Gerke, Sales Manager
Hazardous Waste Disposal, Consulting Services: Gary Demeriez, Sales Manager
Oilfield Waste Services: Larry Loven, Manager

By Telephone @ (403) 440-1825 or
Long Distance inside Canada Toll Free @ 1-800-661-5792
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By Fax @ (403) 440-2428

Email us at proeco@planet.eon.net...

PCB Recycling and Disposal

A Comprehensive Canadian Solution

PROECO CORPORATION

PROECO Corporation

in affiliation with

Custom Environmental Services Ltd.

CUSTOM ENVIRONMENTAL SERVICES LTD

We are proud to announce a complete Canadian recycling and disposal program for PCB waste materials generated in Canada. The services are performed off of your site at our licensed facilities in Edmonton, Alberta. This program is available to all Canadian waste generators.

In 1989 Custom Environmental Services opened the first private Canadian facility for the handling storage and management of PCB wastes. Services were originally only available to Alberta PCB waste generators. When the borders were opened for the importation of PCB wastes into Alberta in November of 1994, Custom Environmental Services began receiving out of Province PCB waste materials for recycling and disposal purposes. We now receive waste PCB materials from across Canada,

Approvals

Custom Environmental Services Ltd. is fully approved to provide the recycling services. Wastes generated from the processing of PCB materials, is sent for final disposal at a fully licensed incineration facility. All these services are maintained and operated under our Alberta Approval 95-IND-085.

Liability

We take ownership and full liability for all waste materials removed from the clients site. Clients are typically responsible for loading the materials onto the transport vehicles, however these services can also be provided by Custom or one of our approved transportation contractors. Certificates of Recycling and Disposal are issued for all PCB waste materials. Wastes received and subsequently generated from our facility are owned by Custom Environmental Services Ltd. Hazardous Waste Manifests list Custom Environmental Services Ltd. as the Generator. Monthly reporting to Environment Canada changes ownership and location of materials which have been registered in the Federal Inventory, so our clients sites are removed from the federal sites listing.

PCB Recycling Programs

All the services we supply are performed off of our clients site at Custom Environmental Services Ltd. fully licensed and approved facility in Edmonton, Alberta. We remove the risk of on site spills and releases. All process residuals are shipped from our facility as waste or product generated by Custom Environmental Services Ltd. The client does not have the risk of being linked to a third party disposal site such as a scrap metal recycler.

Fluorescent Lamp Ballasts

Custom initiated a program for recycling PCB contaminated lamp ballasts in 1992. We received approval from Alberta Environment to offer the program to out of Province generators in 1995.

Our system involves the physical dismantling of the ballast into component parts. The contaminated bitumen and PCB containing capacitor are segregated and shipped for direct disposal via high temperature incineration. The balance of the components are then individually cleaned using proprietary technology, tested to insure that all residual PCB is removed, and then sent for metal recovery.

Our final step provides the cleanest product in the recovery industry. No liquid process is used to increase the volume of waste requiring final treatment and no additional waste materials are generated during the processing steps.

Ballasts can be shipped in drums, or in approved mini bulk containers. We have no minimum quantity requirements and all of the services are provided off of your site in our fully approved Edmonton facility.

PCB Transformers

Custom began recycling transformers contaminated with PCB in 1989. Initially low level <500 PPM were only considered for fill and flush cleaning. In 1995 we refined our process and are now providing recycling services on all PCB contaminated transformer. Transformers sent off of our site are waste materials generated by Custom Environmental Services Ltd. which removes the original generators liability associated with third party sites

In the process, the transformers are solvent washed using a proprietary blend aqueous phase solvent. The process includes separation of the core windings into impervious metal parts and porous items such as wood and paper. The metal components are solvent cleaned, tested and sent for metal recovery. The porous materials are disposed of using high temperature incineration. All waste residues and recovered metal products are shipped from our site as our generated waste materials. The solvent water mixture is separated into two streams with the water component being reused in the process and the solvent component being sent for high temperature incineration.

This same process is used to decontaminate switch gear and other electrical equipment.

A clean metal criteria of <10ug/100cm2 PCB is used for post cleaning testing. Metals passing are sent for recovery and metals witch fail are returned for reprocessing.

Electrical Cable

Electrical cable with PCB saturated internal wrapping is also recycled. The cable jacket is split and the internal cables are stripped of paper wrapping. The porous contaminated non metallic components are shipped off site as process waste to a high temperature incineration facility. The metal components including copper, aluminum and lead are cleaned using the solvent washing process for transformers. The metal components are assessed for PCB residuals and those under the criteria of 50PPM PCB are sent for metal recovery.

Electronic Equipment

Older style electronic equipment with PCB capacitors as components are physically dismantled. The PCB capacitors are sent for disposal and the metal components are recycled. If capacitors have leaked inside of the equipment the balance of the equipment is cleaned using the transformer process.

PCB Contaminated Mineral Oils

Direct ship all volumes of oil to us for recycling by chemical dechlorination. We have no minimum quantity requirements.

Capacitors

We will arrange to have capacitors recycled or disposed of by incineration

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Direct Disposal

Custom Environmental Services Ltd. provides comprehensive programs for recycling and disposal. We can manage all your needs including spill clean-up, fire clean-up, packaging, transportation, volume reduction through the positive step of recycling and final disposal of all the waste materials.

PROECO Corporation provides all marketing and sales programs exclusively for Custom Environmental Services Ltd.

For a cost competitive recycling or disposal quotation please contact:

PROECO Corporation @ 1- 800 - 661- 5792 from anywhere in Canada or fax a request to 403 - 440 - 1825

Head Office: 7722 - 9th. Street, Edmonton, AB T6P 1L6

In Quebec: Call Diane Prieur @ 514 - 683 - 3470 or fax her @ 514 - 683 - 2906

Email us at proeco@planet.eon.net...

, Research Center Library
26 W. St. Clair St.
Cincinnati, OH 45268 (513) 569-7703
The major subjects in this library's collection are bacteriology, biology, biotechnology, chemistry, engineering, hazardous **wastes,** hydrobiology, microbiology, solid **waste** management, toxicology, water pollution, and water quality. Databases maintained here include BRS, CAS On-line, CIS, DIALOG, Dun & Bradstreet, Hazardous **Waste** Database, LEXIS/NEXIS, NLM, Toxline, and Toxnet. General collections include bacteriology, biology, biotechnology, microbiology, physics, solid **waste** management. This library's special collections cover the environment, Canada, legal issues, hazardous **waste,** and solid **waste.**

* Toxic Substances Control Act Hotline
Environmental Protection Agency (EPA)
401 M Street SW
Washington, DC 20460 (202) 554-1404
The Toxic Assistance Office at EPA will answer questions and offer general and technical assistance on the Toxic Substances Control Act. Staff will help you obtain guidance on TSCA regulations including guidance on PCBs and asbestos issues.

* Toxic Substances Non-Confidential Information
Office of Toxic Substances
Non-Confidential Information Center
401 M St., SW (EPA7565)
Northeast Mall, Room B002
Washington, DC 20460 (202) 260-3944
This office's library covers chemical literature in areas of biotechnology, health, chemical industry and process technology, international chemical control, ecology, and pesticides.

* Toxic Substances Rules and Regulations
Office of Toxic Substances
Environmental Protection Agency (EPA)
401 M Street SW
Washington, DC 20460 (202) 260-3587
The Office of Toxic Substances (OTS) Public Information Office houses the official copies of all OTS administrative records supporting regulatory decisions promulgated under the Toxic Substances Control Act (TSCA). The Public Information Office also maintains original materials submitted by industry in compliance with TSCA regulations. The contents of the dockets vary according to the proposed regulation and the particular Section of the Act which is being promulgated. However, generally all dockets contain the following types of supporting documentation: Federal Register notices; various health, environmental, and exposure assessment documents; published references; communications; and test data.

* Transportation of Hazardous Materials
Office of Hazardous Materials Transportation
Research and Special Programs Administration
U.S. Department of Transportation
400 7th Street, SW

management. Contact Kathryn Wagner, the project director, for more information.

* National Response Center Hotline
Coast Guard Hotline (800) 424-8802
(202) 426-2675
This U.S. Department of Transportation National Response Center can be used to report spills of oil and other hazardous materials where required. It can also be used to report incidents in transportation where hazardous materials are responsible for death, serious injury, property damage in excess of $50,000 or continuing danger to life and property.

* New Pesticide Registration
Registration Division
Office of Pesticide Programs
Pesticides and Toxic Substances
Environmental Protection Agency (EPA)
401 M St., SW
Washington DC 20460 (703) 305-5447
The EPA registers (licenses) thousands of pesticide products for use in and around homes. No pesticide may legally be sold in the U.S. unless its label bears an EPA registration number. The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), which governs the registration of pesticides, prohibits the use of any pesticide products in a manner that is inconsistent with product labeling. Contact this office for more information.

* Northeast Industrial **Waste** Clearinghouse
Northeast Industrial **Waste** Exchange (315) 422-6572
The Northeast Industrial **Waste** Exchange provides information on **waste** exchange in the Northeast but with access to other areas. This exchange joins those who generate **waste** with those who desire **waste.**

* Nuclear **Waste** Hydrology
Nuclear **Waste** Program
Water Resources Division
U.S. Geological Survey
National Center, MS 410
Reston, VA 22092 (703) 648-5719
Hydrologic and geologic research and field studies are conducted to develop better understanding of radionuclide transport in ground-water systems. The program also supports Interior's role in the national high-level nuclear **waste** repository program, providing information on the management of low-level nuclear **waste.**

* Ocean Dumping
Office of Marine and Estuarine Protection
Environmental Protection Agency (EPA)
401 M St., SW
Washington DC 20460 (202) 260-1952
This office carries out the duties covered under the Marine Protection, Research and Sanctuaries Act, which is designed to protect the marine environment from the harmful effects of ocean dumping. The Act establishes a permit program to

Ontario Waste Exchange

2395 Speakman Drive
Mississauga, Ontario L5K 1B3
(905) 822-4111 Fax (905) 822-7630

Date: Aug 15/97
Total Pages: 10
Name: John
Company: Dillon Consulting

If you do not receive all of the pages, please call as quickly as possible.

From:

Mary Jane Hanley ext. 358 ☐

~~Alison McNeill~~ ext. 656 ☐

stephen Horniak
~~Margaret Fazio~~ ext. 354 ☐

Message:

John

Here is some information about
the Ontario Waste Exchange
If you have any questions please
call The Ontario Waste Exchange
Thanks: stephen

This list of contacts provided from the OWE database is for the sole use of the recipient to try to bring about a waste transfer. Any other use, distribution/dissemination of this information without permission in writing from the OWE is strictly prohibited.

ORTECH and the Ontario Waste Exchange (OWE) do not recommend or endorse the services of any particular company contained in this database. The information contained herein has been compiled from sources believed to be reliable, however, no warranty or representation, express or implied, is given with respect to the accuracy, completeness or usefulness of the information. In the event any information contained herein has changed, please notify the OWE so that the database can be updated.

It is your responsibility to obtain permits, approvals and other authorization to transport, reuse, recycle, treat or dispose of any materials.

If you succeed in exchanging this waste, please let us know so that we can keep our records up to date, or if you have any difficulties with any of these contacts, please call us so that we might further assist you.

Client Telephone #: ____________________ **Fax #:** ____________________

ORTECH
ISO 9002 Registered

Ministry of
Environment
and Energy
Ontario

EPIC
ENVIRONMENT AND PLASTICS
INSTITUTE OF CANADA

Is the cost of waste treatment and disposal getting you down in the dumps?

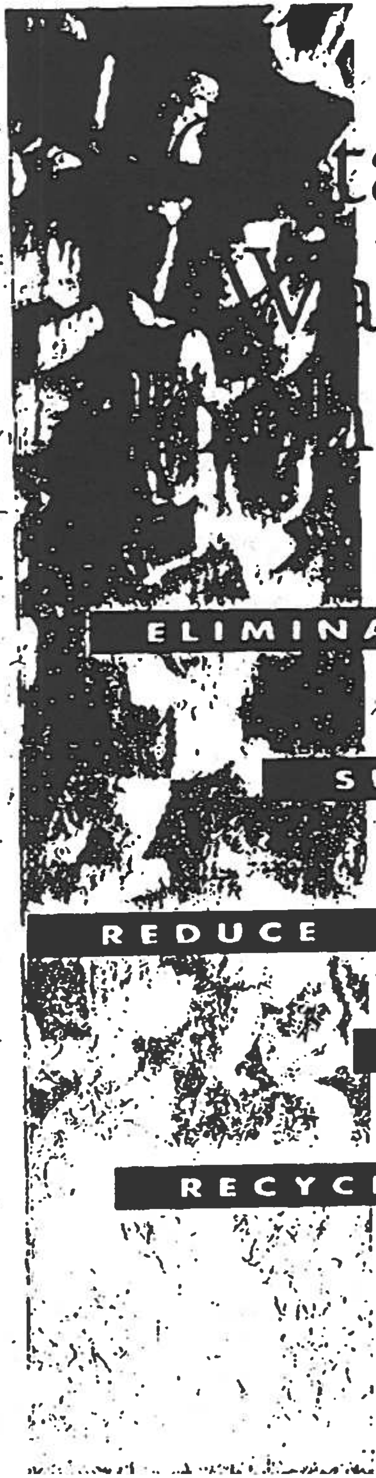
In appreciation of the
Ontario Waste Exchange sponsors:

EPIC ENVIRONMENTAL AND PLASTICS INSTITUTE OF CANADA

ORTECH

The mailing address for both the
Ontario Waste Exchange and the
Canadian Waste Materials Exchange is:

ORTECH Corporation
2395 Speakman Drive
Mississauga, Ontario
Canada L5K 1B3



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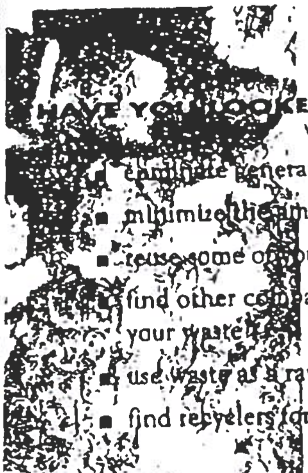


HAVE YOU LOOKED AT WAYS TO:

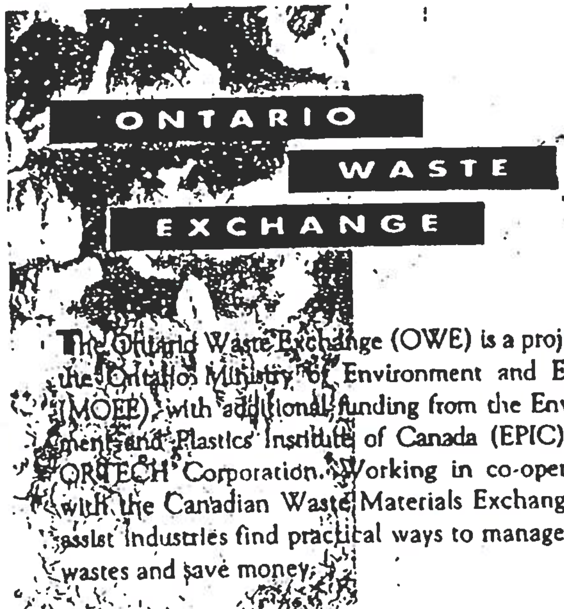
- eliminate generation of your waste?
- minimize the amount of waste you produce?
- reuse some of your wastes?
- find other companies which might reuse your wastes?
- use waste as a raw material substitute?
- find recyclers for your wastes?

WE CAN HELP YOU FIND:

- technologies and guidelines to help minimize waste
- users of waste (waste exchange)
- recyclers of waste
- new business opportunities for waste
- innovative ideas for turning waste into a resource

OWE CAN PROVIDE YOU WITH:

- technical assistance
- reuse and recycling markets directory contacts
- electronic dissemination of 3 R's information
- plant visits, mini research projects, literature searches
- presentations and success stories



ONTARIO WASTE EXCHANGE

The Ontario Waste Exchange (OWE) is a project of the Ontario Ministry of Environment and Energy (MOEE) with additional funding from the Environment and Plastics Institute of Canada (EPIC), and ORTECH Corporation. Working in co-operation with the Canadian Waste Materials Exchange, we assist industries find practical ways to manage their wastes and save money.

We are committed to helping Ontario businesses eliminate or minimize their waste production and find uses and users for those wastes that are produced. We can provide you with the technical advice that will better enable you to deal effectively with these problems. You can get started today! Please call and tell us about your specific problem. We'll try to help you minimize the headaches, costs and liabilities associated with managing the problem.

OWE can also undertake special projects (e.g. solid waste audits) based on their unique information resources. These projects would typically involve more work than normal waste matching activities and are not covered by our current resources. Therefore, they are subject to a nominal fee.

For further information please call the Ontario Waste Exchange at:

ORTECH Corporation
(905) 822-4111 Ext. 656, 354 or 358
Fax: (905) 822-7630 or (905) 823-1446

CANADIAN WASTE EXCHANGE

The Canadian Waste Materials Exchange (CWME) is operated by ORTECH, and has been in existence since 1978. You can find users for your wastes, or waste materials which you can use in your processes, by checking Canadian Waste Exchange Bulletin published bi-monthly by the CWME. The annual subscription cost for the bulletin in 1996 is $70.00 (including GST). Waste Management Service companies can also advertise in the bulletin.

For further information, please call the CWE at:
ORTECH Corporation
(905) 822-4111 Ext. 485 or 266

ACCESSING THE EXCHANGES

CANMEN – Canadian Materials Exchange Network. Anyone with a computer and modem can call the BBS on-line and obtain current materials listings (both available and wanted), view case studies and obtain other 3R's information. For those without a computer and modem, current listings and 3R's information are available by fax.

E-mail: owe@ortech.on.ca

ONTARIO WASTE EXCHANGE (OWE) SPONSORSHIP BENEFITS

The benefits of using the OWE services are numerous and provide both environmental and economical advantages to your company. The benefits of a sponsorship with the OWE are summarized below.

BENEFIT 1. The OWE will offer their technical expertise, prioritize your requests, and disseminate the information to you to help solve your waste management problems.

BENEFIT 2. The OWE will access their databases and provide your company with invaluable information on sources of raw materials (waste generators), markets for waste streams (waste users), waste management equipment suppliers, non toxic substitutes for certain materials, industrial sector specific waste reduction fact sheets or guidelines, and more.

BENEFIT 3. The OWE will utilize their extensive network to source waste materials for your company by cold calling or electronically faxing out thousands of requests to companies and municipalities across Ontario.

BENEFIT 4. The OWE will learn more about your company's waste and will match the waste with potential 3Rs' opportunities (Reduction, Reuse or Recycle). We will use our technical know-how to help you manage your waste. The OWE is fortunate to access the expertise of over 150 scientists at ORTECH.

BENEFIT 5. The OWE will help initiate new 3Rs' projects to enhance your company's profile.

BENEFIT 6. The OWE will provide an annual subscription to the Canadian Waste Materials Exchange Bulletin (CWME). This bulletin lists waste generators and waste users across Canada as well as having an informative section on Waste Management News.

BENEFIT 7. The OWE will share their technical expertise and speak to your company or affiliated association on waste reduction in the workplace.

BENEFIT 8. The OWE will operate your company's internal materials exchange. We will provide the know-how to set up the exchange and provide an effective waste tracking infrastructure within your company. The OWE would secure confidentiality of the materials listed.

BENEFIT 9. The OWE will recognize the sponsorship by placing your company's logo on our letterhead and publications, and acknowledge the support in presentations and other promotional material. Your logo will appear on over 2,000 faxes a month.

BENEFIT 10. The OWE will recognize the sponsorship in an edition of the CWME bulletin (>1,000 distribution), and help market or advertise any services, 3Rs' programmes, etc.

Your sponsorship will be recognized at five support levels, as follows:

Level 1	$25,000+	All benefits
Level 2	$10,000-$25,000	1st 9 benefits
Level 3	$5,000-$10,000	1st 7 benefits
Level 4	$2,000-$5,000	1st 5 benefits
Level 5	$<2,000	1st 4 benefits

The OWE would be happy to discuss further details of a business partnership with you, and please feel free to contact our office for elaboration on any of these benefits.

Ontario Waste Exchange

2395 Speakman Drive
Mississauga, Ontario L5K 1B3
(905) 822-4111 Fax (905) 822-7630

"Due to an overwhelming response that saw Canada's eight waste exchanges divert over 37,000 thousands tonnes of post consumer and post industrial plastics from the solid waste stream, EPIC and the waste exchanges renewed their partnership for another year." The OWE is very excited about year 2 of the OWE/EPIC partnership and we will continue to encourage increased recycling of plastics and market development for the harder to exchange materials. We thank EPIC for the financial, technical and publicity support and yes, EPIC did do more, did listen more and did communicate more. Their product stewardship initiatives and actions, one of which is partnering with waste exchanges across Canada, demonstrated their continued commitment. Their goals are being met by acting on issues and not by just preaching them. Many of our clients commend EPIC highly for their continued support of the OWE services and their support in attaining the goals of product stewardship, resource conservation, industrial ecology and sustainable development.

We also thank the dedicated users of the OWE services for their continued interest and valuable relationship with the programme. And most of all, thanks for all the thank you letters and successful exchanges. These success stories help communicate the success of the OWE/EPIC partnership and encourages other industrial associations to also benefit from such a partnership.

We are presently working with a number of associations that are interested in potentially partnering with the OWE. More and more associations realize that waste exchanges are made up of an "action oriented technical team" that communicates verbally and electronically with the IC&I sector to facilitate the reduction, reuse and recycling of materials. Waste exchanges also follow up with every client to make sure an exchange took place or will take place. If there are any barriers to an exchange, the OWE will try to resolve the problem or discuss the problem at one of OWE's technical committee meetings for further suggestions and actions. Waste exchange technical assistants also answer a variety of technical questions that a client may ask. The OWE is fortunate to operate out of ORTECH Corporation, home of approximately 300 expert scientists and engineers specializing in a vast array of technical capabilities.

The waste exchanges across North America also network electronically with one another through the Material Exchange Listserv (MEL) which was officially launched in April, 1997. The listserv is designed to facilitate cooperation amongst exchange managers and the dissemination of information related to reduction, reuse and recycling of by-products and waste materials. All waste exchanges in North America actively communicate with one another to share valuable information so that we can work more effectively and efficiently in reaching our waste exchange goals. Currently there are 40 materials exchange managers on the list server and this number is growing as we speak. This listserver was also developed from the requests made at the North America's Materials Exchange Managers Workshop so that the unique group of waste exchange managers can keep the dialogue and information flowing electronically. If you would like more information on the waste exchange network, please call Mary Jane Hanley at 905-822-4111 Ext.358.

Stephen Mocniak (x 656) or 354
Mary Jane Hanley (x 358)
Jean Crampton - Bulletin enquiries (x 485)

Ontario Waste Exchange
ORTECH, 2395 Speakman Drive
Mississauga, Ontario L5K 1B3
(905) 822-4111; Fax (905) 822-7630

ORTECH
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Ministry of
Environment
and Energy
Ontario

EPIC
ENVIRONMENT AND PLASTICS INSTITUTE OF CANADA

Ontario Waste Exchange

2395 Speakman Drive
Mississauga, Ontario L5K 1B3
(905) 822-4111 Fax (905) 822-7630

The Ontario Waste Exchange (OWE) is a technical assistance programme designed to help Ontario's industrial, commercial, and institutional waste generators find practical alternatives to disposal. The OWE can help minimize the costs, headaches and liabilities associated with waste management. We assist manufacturers in sourcing raw material substitutes, and help reprocessors find more materials. We try to match the demand side with the supply side.

This programme is co-sponsored by the Environment and Plastics Institute of Canada (EPIC), the Ontario Ministry of Environment and Energy (MOEE), ORTECH Corporation, and frequent OWE users. The OWE accepts commissions as a tax deductible business expense for your company.

funding org'n

We are able to help your company by providing:

- Technical assistance on waste related problems to eliminate, substitute, reduce, reuse, or recycle the waste
- Marketing contacts for potential reuse, or recycling opportunities
- Marketing contacts for potential new sources of raw materials

The OWE has four databases to serve you. Our Generators directory has on average 1,200 active listings which are updated daily. This database can provide invaluable information on sources of raw materials and problem wastes that need an entrepreneurial solution. Approximate volumes can be extrapolated for waste streams available in the Province. Our historical exchange file of over 4,000 records provides actual end uses of materials. There are over 3,000 entries in our Markets directory. These are the companies or individuals who need raw materials generated from waste, reuse packaging or other materials, recycle, haul, and process materials, supply equipment to reduce or process waste streams, or supply non toxic substitutes for hazardous solvents. There are also government contacts for specific wastes, funding sources, and information services. In our Contacts database, we provide the names of the local municipal recyclers, waste exchange connections around the world and over 5,000 other companies and individuals. To assist you in conducting your waste audit, our Wastmin database contains over 1,000 waste reduction tips and industry specific audit models.

In addition to our databases, we are fortunate to have the Business Resource Library at ORTECH and over 150 scientists and researchers to do spot assessments of your waste streams and help to generate new ideas. They have saved companies thousands of dollars over the years by recognizing immediately that an idea has been tried and did not work or by identifying the flaws in a proposed system. The staff is also available to carry out research projects in a myriad of fields ranging from anaerobic digestion to wallboard recycling.

The Ontario Waste Exchange is recognized internationally as one of the most successful waste exchanges in the world. Become part of the solution to reducing waste in Ontario by 50%. Contact the Ontario Waste Exchange at (905) 822-4111, Ext. 656, 354 or 358, or fax us at (905) 822-7630.

ORTECH
ISO 9002 Registered

Ministry of Environment and Energy
Ontario

EPIC
ENVIRONMENT AND PLASTICS INSTITUTE OF CANADA

Waste Minimization and Reuse

Overview, Capabilities and Facilities

Overview

ORTECH provides a full range of technological services to help companies minimize the waste which they produce and to find ways of reusing and recycling residuals which are still produced.

Capabilities

Capabilities include:

- Waste audits conducted at clients' premises to assess opportunities for waste minimization or reuse
- Audits for energy conservation and other environmental emissions
- Development of waste reduction plans which provide opportunities for waste minimization and economic savings
- Operation of both the Ontario and Canadian Waste Exchanges which help companies to find potential users for those wastes which they do generate
- Development of new processes for reclaiming waste materials and new products based on those reclaimed materials

Facilities

Facilities which support these capabilities include:

- In-house information search facility for locating waste minimization reuse and reprocessing opportunities
- Comprehensive laboratory facilities for the development of new products for waste material
- Extensive computer facilities to back up the Ontario and Canadian Waste Material Exchanges
- Unique pilot plant facility, including unit separation process equipment, for the development of viable processes for waste processing and reclamation

For more information about Waste Minimization and Reuse please call ORTECH's
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Ontario Waste Exchange

2395 Speakman Drive
Mississauga, Ontario L5K 1B3
(905) 822-4111 Fax (905) 822-7630

The Ontario Waste Exchange (OWE) is a technical assistance programme designed to help Ontario's industrial, commercial and institutional waste generators find practical alternatives to waste disposal and potentially minimize the costs associated with waste management. This programme is co-sponsored by the Environment and Plastics Industry Council (EPIC), ORTECH Corporation, other associations and frequent OWE users.

We may be able to help your company by providing:

1. Technical assistance on waste related problems to **ELIMINATE, SUBSTITUTE, REDUCE, REUSE** and **RECYCLE** your waste

2. Waste Exchange contacts for potential reuse or raw material substitute opportunities

3. Recycling industry contacts

The OWE can disseminate any of this information quickly to you from our databases.

Also at your service is the Canadian Waste Materials Exchange (CWME) programme which publishes a bi-monthly bulletin listing waste AVAILABLE and wastes WANTED. Your company could list any waste stream in the CWME bulletin at no cost. If you would like to subscribe, please complete the invoice card on the back of the bulletin and return it to us, along with the **1997** subscription fee of **$70.00 including GST.** You will be added to the CWME mailing list for one year.

The Waste Exchange programmes are committed to helping industries minimize their wastes and to find uses and users for the wastes that are produced. We hope that we can be of assistance to your company.

Please feel free to call the OWE at any time, at (905) 822-4111 plus extension, or fax us at (905) 822-7630.

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Press Release

EPIC RENEWS COMMITMENT TO CANADA'S WASTE EXCHANGES

February 28, 1997 (Mississauga, ON) The successful year-long partnership between the Environment and Plastics Industry Council (EPIC, formerly the Environment and Plastics Institute of Canada and now a Council of the Canadian Plastics Industry Association, CPIA) and Canada's eight Waste Exchanges saw over 37,000 tonnes of waste plastics exchanged between interested parties.

EPIC is the first materials association to support these exchanges, and has contributed both technically and financially. In addition to the waste diversion, the program has also generated a lot of interest and public awareness. All of these factors have contributed to the program's overall success and as a result, both parties have agreed to renew their partnership for 1997.

"1996 was very much an experimental year in terms of the new partnership," says Sandra Birkenmayer, Vice President, Environment, Health & Safety, CPIA. "But with all of the positive feedback that we got throughout the year, coupled with the great success that we've achieved to date, the decision to renew our commitment wasn't a very difficult one to make."

"We're very happy to have EPIC working with us again this year," says Dr. Bob Laughlin, Manager of the Canadian Waste Materials Exchange. "The success of the partnership lies in the huge amount of interest that we've generated. It seems almost everyone is interested in turning business waste into a financial plus."

EPIC Renews Commitment...

• For Release 9 a.m. EDT, February 28, 1997

5925 Airport Road, Suite 500, Mississauga, Ontario L4V 1W1
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A Council of the Canadian Plastics Industry Association

Among the 900 new plastic waste streams that were listed on the Waste Exchanges during 1996, many represent ongoing exchanges that will continue throughout 1997 and beyond. Therefore, the 37,000 tonnes of plastic that was diverted throughout the year by the Waste Exchanges represents only a fraction of what may be realized during year two.

The Waste Exchange partnership is just one of many initiatives that EPIC has undertaken for 1997. The exchanges act as material "dating services" by bringing together those parties interested in "selling" waste material with those interested in "purchasing" waste material.

EPIC is committed to the responsible use and recovery of plastics resources and addresses public concerns through the integration of product stewardship and education programs, while delivering positive environmental results.

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For further information, or to obtain an interview, contact Melanie Franner at EPIC. Tel: (905) 678-7405, ext. 223, Fax: (905) 678-0774 or contact Dr. Bob Laughlin at the Canadian Waste Materials Exchange, Tel: (905) 822-4111, ext. 265, Fax: (905) 822-7630.

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CONTAMINANTS AND REMEDIAL OPTIONS AT SELECTED METALS CONTAMINATED

SITES - A TECHNICAL RESOURCE DOCUMENT

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INTRODUCTION

A technical resource document, Contaminants and Remedial Options at Selected Metals-Contaminated Sites, has been produced to assist site remediation managers to select treatment technologies for contaminated soils, sludges, sediments, and waste deposits at sites where inorganic arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), or lead (Pb) are the primary contaminants of concern. These five metals have been addressed because of their toxicity, industrial use, and frequency of occurrence at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites and in Resource Conservation and Recovery Act (RCRA) hazardous wastes. This document should prove useful to all remediation managers, whether their efforts fall under federal, state, or private authority, and whether they are applying standards from RCRA, CERCLA, and/or state programs.

METHODOLOGY

A diligent effort was made (subject to the key limitations noted below), to identify, collect, analyze, and organize information, data, and pertinent references that a remediation manager would find useful for identifying and selecting remedial alternatives for soils, sediments, sludges, and waste deposits in which the principal contaminants are As, Cd, Cr, Hg, or Pb and selected inorganic compounds of these metals. The types of information collected to support preparation of this document include the following.

oBackground information on As, Cd, Cr, Hg, Pb, and associated inorganic compounds regarding mineral origins, processing, uses, common matrices, chemical forms, behavior, transport, fate, and effects.

oExisting remediation performance data, listed below, in rough order of desirability: (a) full-scale remediation of As, Cd, Cr, Hg, and Pb contaminated sites; (b) technology demonstrations on As, Cd, Cr, Hg, or Pb contaminated sites under the EPA Superfund Innovative Technology Evaluation Program; (c) RCRA As, Cd, Cr, Hg, and Pb bearing hazardous wastes for which Best Demonstrated Available Technologies have been established; (d) waste applicability/capacity information for treatment technologies as described in technology guides and the EPA Vendors' Inventory of Superfund Innovative

Treatment Technologies (VISITT) database; (e) feedstock specification information for primary or secondary smelting or recycle/re-use markets; (f) Records of Decision (RODs) and corresponding summaries for As, Cd, Cr, Hg, and Pb contaminated sites; (g) Treatability test data on As, Cd, Cr, Hg, and Pb contaminated matrices where the results are well-documented and in an accessible form (e.g., Alternative Treatment Technology Information Center [ATTIC] and the Risk Reduction Engineering Laboratory treatability database) (h) Superfund National Priority List sites where As, Cd, Cr, Hg, or Pb contaminated media is a primary concern and remedial options are or will be under evaluation.

It is assumed that the remediation manager is familiar with appropriate policy issues (RCRA, CERCLA, and state), site characterization, sampling methods, analytical methods, risk assessment, determination of cleanup levels, and health and safety plans. It is also assumed that the manager or available support staff is familiar with widely available references from which physical and chemical data for the 5 metals of interest and their compounds can be obtained.

Containment and water treatment technologies are primarily addressed by reference, since they are well described and evaluated in recent, available documents, which are referenced in Section 4 of the technical resource document.

To avoid overlap with existing or forthcoming documents, information collection and coverage of four specific types of

H

metals sites [lead battery recycling, wood preserving (As, Cr), pesticides (As, Hg), and mining] was intentionally limited to selected cases where innovative technologies have been chosen or applied.

In the interests of simplicity, brevity, and due to constraints imposed by limited project resources, the reference document does not attempt to systematically address remediation of organometallic compounds, organic-metal mixtures, and multi-metal mixtures. For example, while incineration is noted as a potential pretreatment for an organic-metal-soil mixture, the effects of As, Cd, Cr, Hg, or Pb on the technical and economic feasibility of incineration are not discussed. Another example is that several RCRA Best Demonstrated Available Technologies are cited for multi-metal wastes, but there is no discussion on how, in general, one should select a remedial technology for a multi-metal waste.

RESULTS

An approximately 200-page technical resource document has been produced. Section 4 (Remedial Options) and the appendices cited therein form the heart of the document. This section begins with a brief general discussion of the key applicable or relevant and appropriate regulations that influence cleanup goals. Soil and groundwater action levels and risk goals are tabulated for 24 metal-contaminated sites. TCLP limits for metals in selected metal-bearing RCRA characteristic hazardous wastes are also tabulated.

The bulk of Section 4 addresses the immobilization, and separation/ concentration technologies that are potentially applicable for remediating metal-contaminated solids, with the main emphasis on soils. Each technology is addressed in a similar manner.

- A technology description is provided, followed by a discussion of typical treatment trains, and a discussion of the applicability of the technology to various wastes. Specific reference is made to the 5 metals of interest, when applicable information is available.

- The status (e.g., bench, pilot, full-scale, applications to Superfund remediation) and performance of the technologies are also discussed and, where sufficient examples exist, tabulated.

- Cost factors and costs are also discussed with cost estimates often being drawn from applicable Superfund Innovative Technology Evaluation (SITE) program Applications Analysis Reports.

oFinally, data needs for assessing the applicability of each type of technology are tabulated.

The sub-section on immobilization addresses solidification/ stabilization (cement-based and polymer microencapsulation) and vitrification (in situ and ex situ) technologies. Containment technologies (capping and vertical and horizontal barriers) are noted, but only addressed by reference since: (1) the type of metal contaminant is not crucial to containment system selection, and (2) there is a recent, readily available EPA document (EPA 625/6-91/026) that already addresses the topic at the desired level.

Separation/concentration technologies are subdivided into two categories:

oTechnologies applicable for excavated solids:

-- physical separation technologies [i.e., screening, classification, gravity separation, magnetic separation, and flotation];

-- soil washing technologies [i.e., extraction via water, solvents, or solutions containing surfactants, chelating agents, acids, or bases], and

-- pyrometallurgical separation technologies [i.e., Waelz kiln, flame reactor, molten metal bath, secondary lead smelting via reverberatory and blast furnaces, submerged arc furnace, and mercury roasting and retorting], and

oTechnologies applied in situ (i.e., soil flushing, and electrokinetics).

Water treatment options are very briefly discussed, and a summary table is provided. As with containment options, limited coverage is provided due to the availability of other recent, available EPA documents that address the topic in an adequate manner.

Section 4 on Remedial Options is complemented by a number of key appendices.

oAppendix B summarizes 68 technologies applicable to metals-contaminated media that are undergoing evaluation in the SITE program.

oAppendix C summarizes 67 innovative metals-contaminated technologies from 16 technology categories. This information was excerpted from EPA's Vendor Inventory of Superfund

Innovative Treatment Technologies (VISITT) database version 2.0.

oAppendix D lists and briefly describes 44 selected metals-contaminated National Priority List Sites.

oAppendix E summarizes Best Demonstrated Available Technologies (BDAT) for 60 RCRA hazardous wastes that contain As, Cd, Cr, Hg, and Pb.

oAppendix F supplements the separation/concentration technology portions of Section 4 by providing a review of metal recycling options for metal-contaminated wastes from CERCLA Sites.

Section 2 briefly identifies typical mineral origins, industrial uses, and Superfund matrices of inorganic As, Cd, Cr, Hg, and Pb. Section 3 addresses possible chemical forms for the 5 metals under various conditions. Also described in Section 3 are typical environmental transport, partitioning, and transformation phenomena for the 5 metals in air, soil and sediment, and surface water and ground water. Section 3 also includes a brief overview of the human and environmental toxicity of the five metals and some of their compounds.

CONCLUSIONS

1. The technical resource document consolidates and organizes a substantial body of information pertinent to the remediation of As, Cd, Cr, Hg, and Pb contaminated soils, sediments, and sludges. During the development of remedial investigation and feasibility study (RI/FS) reports, users should be able to considerably reduce time and effort required to identify, describe, and make preliminary assessments of remedial technologies applicable to metals-contaminated sites.

2. The chemistry of these metals, particularly arsenic, mercury, and chromium, is quite complex. Significant differences in solubility, volatility, or toxicity are observed for various species of all five metals. These property differences may have a substantial impact (positive or negative) on the effectiveness, implementability, and cost of remedial alternatives. The technical resource document (Sections 2, 3, and portions of 4) clearly indicates the potential difficulties and thus alerts the RPM to the critical need for early and continuous consideration of the chemistry of these metals by a knowledgable person during site characterization, and remedy evaluation, selection, design, and implementation.

3. In addition to no action and excavation/offsite disposal,

thirteen technologies were identified as be- ing potentially applicable to the remediation of metals-contaminated soils, sediments, and sludges.

oAlthough by no means appropriate for all metal-matrix combinations, the mostly broadly applicable technologies for metals-contaminated soils are capping (not addressed in TRD), vertical barriers (not addressed in TRD), cement-based solidification/ stabilization, screening, gravity separation, and soil washing/acid extraction.

oA second tier of technologies is applicable to a much narrower range of situations due to either effectiveness, implementability, or cost limitations. This second tier of technologies includes horizontal barriers, vitrification, polymer microencapsulation, flotation, pyrometallurgical separation, soil flushing, and electrokinetics.

oThe beneficial role of chemical treatment (e.g., oxidation, reduction, neutralization) is recognized, but not addressed as a separate technology, since it is always closely coupled with another technology (e.g., solidification/ stabilization, vitrification) when treating metal contaminated soils.

oBiotreatment (e.g., extraction of metals from soils using bacteria) was considered for inclusion in the technical resource document, but rejected due to its early stage of development.

oOnly a very limited number of facilities recover the five metals in forms and concentrations likely to be arising from Superfund site remediation. Appendix F lists pertinent facilities, enabling the reader to easily identify and contact recyclers closest to the site to determine interest, acceptance criteria, and costs. Sixteen potential recyclers were identified for lead wastes and 7 for mercury wastes. For 18 other RCRA and specialized metal-bearing wastes containing one or more of the 5 metals of interest, only 18 additional potential recyclers were identified.

4. Inorganic arsenic is difficult to treat successfully. It has multiple valences and can interconvert between species depending on pH and oxidation/reduction potential and species present. Care must be taken during treatment processes to ensure that volatile arsenic compounds are not formed. Arsenic forms anionic compounds in water, and thus does not

form insoluble hydroxides during cement-based stabilization/ solidification. Solidification/stabilization may be applied in instances where arsenic is present in low concentrations. Polymer microencapsulation is an option for arsenic, but no instances of its application were identified. Best Demonstrated Available Technology (BDAT) for arsenic-bearing RCRA hazardous wastes is vitrification, but no Superfund applications of this technology have occurred to date. Potentially viable separation/concentration options include screening, gravity separation, and soil washing/acid/base extraction. These technologies have been selected for remediation of several wood preserving sites. Recycling of recovered arsenic is not very promising -- there is little demand and therefore little or no capacity for recycling arsenic.

5. Inorganic mercury also tends to be difficult to treat. It may be converted by microorganisms under some conditions to volatile organomercury compounds. It is amenable to stabilization/solidification, but only at very low concentrations (e.g., for RCRA hazardous wastes, S/S is a BDAT for Hg < 260 mg/Kg). Mercury does not form insoluble hydroxides, and is not amenable to cement-based S/S at higher concentrations. Polymer microencapsulation is a potential option for mercury immobilization. Physical separation techniques (e.g., screening or gravity separation) and soil washing should be applicable to removal of mercury from soils. These technologies are being evaluated by the Gas Research Institute and U.S. Department of Energy. Given its low solubility in glass and low boiling point, mercury is not a good candidate for vitrification. However, mercury's high vapor pressure, low boiling point, and ready decomposition of its oxides enables it to be separated from soils via thermal desorption and roasting. Only seven facilities appear to be potentially applicable to processing mercury recovered from Superfund remediation.

6. Chromium (III) forms insoluble hydroxides and is amenable to cement-based stabilization/solidification. Chromium (VI) does not form insoluble hydroxides, but it can be subjected to S/S after reduction to Chromium (III). Vitrification may be technically feasible, but cost is likely to pose a problem. Physical separation and soil washing are potentially applicable and have been selected for several wood preserving sites. Soil flushing has been applied at two chromium-contaminated sites. Electrokinetics shows some promise, particularly if success is demonstrated for in situ treatment of clayey soils.

7. Inorganic lead forms insoluble hydroxides, and cement-based solidification/stabilization has been applied full-scale to numerous lead-contaminated soils. Lead is amphoteric, so pH must be carefully controlled during S/S processing to ensure that lead solubility remains at a minimum. Although vitrification and polymer microencapsulation would appear to be technically feasible for lead-contaminated soils, solidification/stabilization would be expected to cost less to implement. Screening, gravity separation, and soil washing/acid extraction have been implemented at two lead-contaminated sites. Whether these separation/concentration technologies can economically attain treatment goals must be determined on a site specific basis. Recycling of lead has been accomplished as part of some lead site remeditions, but the value of the recovered lead typically does not offset processing costs. Soil flushing may be applicable in some circumstances. Electrokinetics may prove to be useful for clayey soils.

8. Inorganic cadmium occurs mostly in the +2 valence state and does not exhibit amphoteric behavior. It is amenable to stabilization/solidification, although pH must be maintained in the alkaline range to ensure that leaching does not occur. Although vitrification and polymer microencapsulation would appear to be technically feasible for cadmium-contaminated soils, solidification/ stabilization would be expected to cost less to implement. Screening, gravity separation, and soil washing/acid leaching are commercially available and would appear to be applicable, but examples of implementation where cadmium was a key contaminant were not found. Facilities that will take cadmium-concentrate from a Superfund remediation are scarce. Soil flushing and electrokinetics may be applicable for special circumstances.

9. While this technical resource document consolidates information from the past in an attempt to accelerate and improve decisions in the future, it is recognized that site-specific factors ultimately drive the selection of the remedial alternative for any particular site. The remedial action objectives should be clearly established and cleanup levels designated. It is of particular importance to develop reasonable estimates of the volume, distribution, and physical and chemical composition of each significant contaminant/co-contaminant/medium combination at the site that will require remediation. It is similarly important to clearly define the parameters (e.g., total metal(s) concentration, leachable metals, filtered/ unfiltered aqueous metal concentrations), test methods (e.g., TCLP, EP Toxicity

Test, other leaching test, total waste analysis), and numerical goals that will be employed to measure treatment effectiveness. A risk assessment should consider transport and fate of contaminants using the best methods available including Eh-pH, equilibrium and/or transport models where applicable.

REFERENCES

Battelle - Columbus Division. Contaminants and Remedial Options at Selected Metals-Contaminated Sites. EPA # Not Assigned Yet, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1995. 200 pp.

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APPENDIX I

Case Studies

8 #2

An Investigation of Disposal Options for Arsenic Trioxide Produced from Roasting Operations

J H KYLE[1] AND D LUNT[2]

INTRODUCTION

Arsenic is classified chemically as a metalloid. That is, it has properties intermediate between those of metals and non-metals. Like non-metals, it combines with many metals to form arsenides (eg arsenopyrite FeAsS, niccolite NiAs, sperrylite $PtAs_2$), but like metals it forms sulphides and oxides (eg realgar AsS, arsenolite As_2O_3). Arsenic is distributed widely in the Earth's crust at an average concentration of 1.5 mg/kg and is present in more than 150 minerals.

The most common commercial source of arsenic is as arsenolite or arsenic trioxide (As_2O_3), a by-product from the extraction of base and precious metals such as copper, lead, zinc and gold. Its major uses are in the production of agricultural pesticides, in wood preservation, and in the glass industry.

Most arsenic compounds are highly toxic, causing dermatitis, acute and chronic poisoning, and possibly cancer. As little as 0.1 grams of arsenic trioxide can be fatal if ingested. It is also highly toxic to plants and animals. Other forms of arsenic, such as arsenic pentoxide (As_2O_5), are also toxic but generally less so.

Production of arsenic trioxide

Arsenic trioxide is a by-product of the roasting of arsenical base metal ores, or auriferous arsenopyritic ores and concentrates.

With the latter, two stage roasting is normally practiced. During the first stage at about 500°C, the arsenopyrite is converted to pyrrhotite and the arsenic is volatilised as arsenic trioxide. It is collected by cooling the off-gases to about 140°C. The second stage, at about 650°C, involves the conversion of the pyrrhotite to hematite and the volatilisation of sulphur as sulphur dioxide.

The arsenic trioxide produced can be of varying purity. It must be either sold on the world market or disposed of in an environmentally acceptable manner. With world production of arsenic trioxide increasing, the sale of this product is becoming increasingly difficult and disposal options for arsenic trioxide need to be investigated.

Disposal options for arsenic trioxide

Arsenic trioxide is reasonably soluble in water. Its solubility increases with temperature, and at both extremes of pH. At low pH, arsenious acid, H_3AsO_3, is formed and at high pH, the anions $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} are progressively formed.

Because of its solubility, arsenic cannot be safely disposed of as arsenic trioxide if it is likely to come in contact with water. As such, it must be either isolated from contact with water and/or converted to a more insoluble form that poses no danger of leaching at unacceptable rates into water catchment areas or groundwater aquifers.

This paper investigates some disposal options available for arsenic trioxide, and their relative efficiencies in minimising the solubility of the arsenic in water.

EXPERIMENTAL PROCEDURES

Arsenic trioxide samples

Arsenic trioxide produced by the roaster at the Western Mining Corporation Windarra Nickel/Gold Project was used in all the testwork. Two separate samples (labelled A and B) were used. They were collected about 12 months apart in 1990 and 1991. The analyses of the samples are reported in Table 1.

TABLE 1

Analyses of arsenic trioxide samples from Windarra nickel/gold project, Laverton WA.

Sample	As_2O_3 (%)	CaO (%)	SO_4 (%)	Fe_2O_3 (%)	SiO_2 (%)
A	47.5	12.6	16.1	1.6	1.5
B	70.0	3.0	11.3	3.0	-

The high calcium content of the waste is due to the addition of limestone to the roast off-gases to neutralise sulphuric acid generated in the process.

Arsenic trioxide dissolution

Water, dilute sulphuric acid, or dilute sodium hydroxide solutions were used as solvents. The solids and solutions were mixed at room temperature, the pH adjusted with dilute H_2SO_4 or dilute NaOH while stirring continuously in a glass reactor. The slurries were allowed to equilibrate for one hour before the solution was sampled for arsenic assays. The process was then repeated at 60° and 90°C. Solution samples taken at elevated temperature were immediately diluted to prevent precipitation of the arsenic trioxide. Comparison of assays for total arsenic by atomic absorption spectroscopy with assays for arsenic(III) by titration with potassium iodate confirmed that virtually all the soluble arsenic was present as arsenic(III).

Arsenic trioxide oxidation

Arsenic trioxide samples were dissolved in water at 90°C. Hydrogen peroxide (50 per cent solution) was then added gradually to the slurry over a period of one hour to a total amount of 1.1 times the stoichiometric requirement according to the equation

$$2\,AsO_3^{2-} + H_2O_2 \dashrightarrow 2\,AsO_4^{3-} + 2\,H^+$$

The reaction was highly exothermic and the solution became very acidic due to the hydrogen ions produced in the oxidation process. The As(III) to As(V) reaction was monitored by analysing the reactant solution for As(III) by titration with potassium iodate.

Arsenic precipitation

Arsenic(III) and arsenic(V) solutions were used to prepare precipitates of arsenite or arsenate salts. Lime slurry was added to

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solutions of arsenite or arsenate ions to neutralise the acidity and to precipitate salts of calcium arsenite and calcium arsenate. The final molar ratio of Ca:As in the salts was between 2:1 and 4:1. The limed slurry was allowed to equilibrate for one hour before filtering and washing the final precipitate.

Ferric arsenite and arsenate precipitates were produced by the addition of ferric sulphate solution to the arsenic(III) and arsenic(V) solutions to produce a final molar ratio of Fe:As of between 2:1 and 4:1. The slurries were then adjusted to pH 5 by the addition of lime slurry to precipitate the iron-arsenic salts.

Solidification of precipitates

The arsenic trioxide waste, or precipitates made therefrom, were mixed with cement and water and, in some cases other additives, to form a hydraulic mixture. The mixture was poured into 50 x 50 x 50 mm cubic moulds, placed in plastic enclosures and left to set for seven days. The set cubes were then removed from the moulds and allowed to age for at least another 21 days before being subjected to a variety of physical and chemical tests.

Physical tests

The bulk density, water content, and unconfined compressive strength (UCS) of the solidified products were measured by standard methods.

Solubility tests

The solubilities of the calcium and ferric arsenite and arsenate precipitates, and the solidified products made therefrom, were evaluated by a standard Multiple Extraction Procedure (MEP) or, in the case of solidified products, a standard Dynamic Leach Test (DLT), as described in Conner (1990). The leachant solution for the MEP was a synthetic groundwater solution, and for the DLT deionised water was used. The leach solutions were analysed for pH, alkalinity, and total arsenic.

RESULTS AND DISCUSSION

Arsenic trioxide solubility

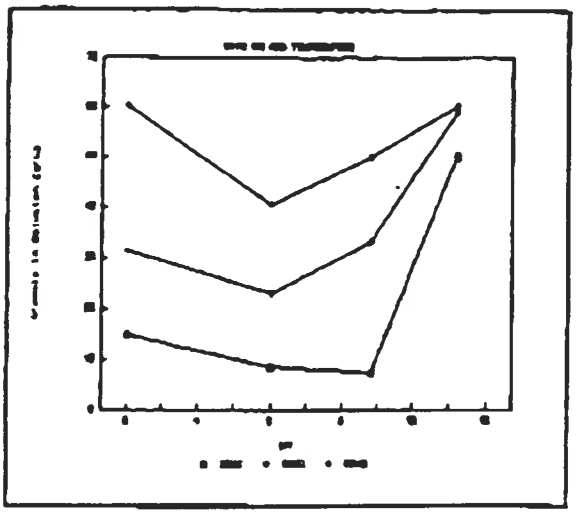

FIG 1 - Solubility of arsenic trioxide waste.

The results of the arsenic trioxide solubility experiments are shown in Figure 1. As expected, because of it's amphoteric nature, the solubility increases at both high and low pH when compared to neutral solutions. The solubility also increased with temperature, although at high pH the temperature dependence on solubility was much less than at lower pH values.

Arsenic precipitates

Calcium arsenite, calcium arsenate, ferric arsenite and ferric arsenate precipitates were prepared according to the details given in Table 2. The precipitates are given the names as above in order to indicate their major constituents rather than their true compositions. The true chemical compounds existing in these

TABLE 2

Experimental conditions used in precipitation of arsenic precipitates.

Ppte. No.	Precipitate Type	Arsenic Waste(B) (g)	Volume Water (L)	Temp (oC)	50% H2O2 (g)	Mass Lime (g)	Other *\# (g)	Mass Ppte. (g)
JK126	Fe Arsenite	300	3.5	90		1330	2250*	2890
JK131	Fe Arsenate	200	2.5	90	110	910	1500*	1921
JK127	Ca Arsenite	300	3.5	90		405		703
JK128	Ca Arsenite	300	3.5	90		615		854
JK129	Ca Arsenite	200	2.5	25		270		525
JK130	Ca Arsenite	200	2.5	25		410		632
JK132	Ca Arsenate	200	2.5	90	110	270		393
JK136	Ca Arsenate	200	2.5	90	110	410		593
JK145	Ca Arsenate	200	2.5	90	110	550		721
JK168	Ca Arsenate	200	2.5	90	140	285	400#	1044

*Ferric Sulphate #Cement

TABLE 3

Solution assays during arsenic precipitation processes.

Ppte. No.	Precipitate Type	Before H2O2		After H2O2		Filtrate
		pH	As(III) (g/L)	pH	As(V) (g/L)	As (mg/L)
JK126	Fe Arsenite	6.7	18.5			
JK131	Fe Arsenate	6.7	16.0	4.5	31.0	1.0
JK127	Ca Arsenite	6.7	17.5			
JK128	Ca Arsenite	6.7	17.5			
JK129	Ca Arsenite	6.7	15.8			
JK130	Ca Arsenite	6.7				
JK132	Ca Arsenate	6.7	16.5	4.8	46.5	11.8
JK136	Ca Arsenate	6.7	16.5	4.8	45.0	<1.0
JK145	Ca Arsenate	1.4	13.1	0.0	41.0	1.0
JK168	Ca Arsenate					<0.5

precipitates is in many cases unknown, or in dispute.

It can be noted from the data of Table 2 that the production of ferric arsenite and arsenate precipitates requires exceedingly large amounts of ferric sulphate and of lime, compared with the production of calcium arsenite and arsenate.

The assays of the arsenic solutions before and after hydrogen peroxide addition, and after precipitation, are given in Table 3. These results indicate that the solubility of arsenic in solution is increased substantially by the oxidation of arsenic(III) to arsenic(V). This is due in part to the acidification of the solution that results from the oxidation reaction, but also to the greater solubility of arsenate(V) compared to arsenite(III).

The arsenic concentrations in the solutions after precipitation are all low, as would be expected for the production of a low solubility precipitate. As expected, the solutions with the lowest arsenic concentrations resulted from the lowest solubility precipitates, as is demonstrated below.

The assays of the precipitates are detailed in Table 4. Based on the molar ratios of the main constituents of each precipitate, the approximate compositions of these precipitates have been calculated. These are summarised in Table 5.

Composition of arsenic precipitates

A number of important observations can be made concerning the composition of the arsenic precipitates. Firstly, the ferric arsenite and arsenate precipitates have only a minor proportion of their iron content associated with the arsenic (less than ten per cent for ferric arsenite and less than 30 per cent for ferric arsenate). Most of the iron is present as ferric hydroxide, or possibly jarosites, which may also account for the high water content of these precipitates.

Secondly, the calcium arsenite and arsenate precipitates are much less bulky than their ferric counterparts, containing a much higher proportion of arsenic and much less water. Some of the excess hydrated lime is probably associated with the arsenic precipitates in the form of double salts, such as $Ca(AsO_2)_2.Ca(OH)_2$ and $Ca_3(AsO_4)_2.Ca(OH)_2$ (Stefanakis and Kontopoulos, 1987).

Thirdly, the high calcium content of the ferric arsenite and arsenate precipitates is initially surprising, considering they were precipitated at pH 5. However, X-ray diffraction studies on these precipitates have indicated the presence of major synthetic calcite as well as gypsum. The calcium arsenate precipitate also contained major $Ca_3(AsO_4)_2.Ca(OH)_2.2H_2O$, whereas the ferric arsenate contained only minor scorodite ($FeAsO_4.2H_2O$) and poorly crystalline $Fe(OH)_3$. This indicates that the ferric arsenate is either amorphous or that the arsenate ions are adsorbed onto a ferric hydroxide precipitate, as has been suggested by Robins (1987).

Solubility of arsenic precipitates

The solubility of the precipitates was tested by using the standard

TABLE 4

Assays on arsenic precipitates.

Ppte. No.	Precipitate Type	Ca:As Ratio	Fe:As Ratio	As (%)	Ca (%)	Fe (%)	SO4 (%)
JK126	Fe Arsenite		2:1	5.0	14.3	13.8	15.7
JK131	Fe Arsenate		2:1	5.2	14.6	14.6	14.7
JK127	Ca Arsenite	2:1		24.5	27.4	1.0	6.8
JK128	Ca Arsenite	3:1		17.0	31.7	0.8	4.8
JK129	Ca Arsenite	2:1		25.0	26.0	1.0	6.5
JK130	Ca Arsenite	3:1		17.0	31.2	0.8	5.1
JK132	Ca Arsenate	2:1		21.5	25.8	0.9	4.4
JK136	Ca Arsenate	3:1		17.6	30.7	0.8	4.9
JK145	Ca Arsenate	4:1		13.7	29.0	0.7	3.4
JK168	Ca Arsenate	2:1	Cement - not analysed				

TABLE 5

Calculated composition of arsenic precipitates (percentage).

Spm. No.	Arsenic Precipitate	Ferric Arsenite	Ferric Arsenate	Calcium Arsenite	Calcium Arsenate	Ferric Hydroxide	Calcium Hydroxide	Calcium Sulphate	Water
JK126	Ferric Arsenite	9.4				24.3	14.5	22.2	30.0
JK131	Ferric Arsenate		13.5			20.3	15.7	20.8	29.3
JK127	Calcium Arsenite (2:1, 90°C)			41.5		1.9	35.1	9.6	11.9
JK128	Calcium Arsenite (3:1, 90°C)			28.8		1.3	48.5	4.9	16.3
JK129	Calcium Arsenite (2:1, 25°C)			42.3		1.9	30.9	9.2	15.7
JK130	Calcium Arsenite (3:1, 25°C)			28.8		1.5	45.4	7.2	17.1
JK133	Calcium Arsenate (2:1)				57.0	1.7	12.4	6.2	22.7
JK136	Calcium Arsenate (3:1)				46.7	1.5	28.9	4.9	18.0
JK143	Calcium Arsenate (4:1)				36.4	1.4	37.4	4.8	20.0

Multiple Extraction Procedure, MEP (Conner, 1990), with a synthetic groundwater solution as the extractant. The synthetic groundwater was prepared to resemble that at the minesite where the stabilised arsenic trioxide was to be stored. An analysis of this synthetic groundwater was as follows:

Cation	Concentration (mg/L)	Anion	Concentration (mg/L)
Na	171	Cl	228
Ca	234	SO_4	8266
Mg	1550	HCO_3	256
TDS	15100	pH	8.6

The results of the MEP leach tests are shown in Figures 2 - 4, which illustrate the cumulative increases in soluble arsenic with time for each of the precipitates (the extractant solution was renewed every 24 hours), together with the accompanying changes in alkalinity and pH. For comparison, the solubility of the raw arsenic waste is also illustrated (Figure 5). The composition of the initial and final residues is listed in Table 6.

The figures indicate the relative rates at which arsenic would be leached from each of the precipitates if they were exposed to groundwater of the composition given above. The results show that the calcium arsenite precipitates leach much more readily than the calcium arsenate precipitates. The concentrations of arsenic in the extractant solutions (40 - 800 mg/L for calcium arsenite and 10-30 mg/L for calcium arsenate at pH 9 - 9.5) are much higher than data published by Stefanakis and Kontopoulos (1987) for pure precipitates at pH 11.3 (20 - 60 and 0.3 - 10 mg/L respectively).

The differences in the data may be due to pH. The presence of excess lime appears to have a large effect on the solubility of these precipitates. Precipitates produced at a molar ratio of Ca:As of 3:1 produced much lower leaching rates than those produced at a ratio of 2:1. This occurs even after the initial excess lime is

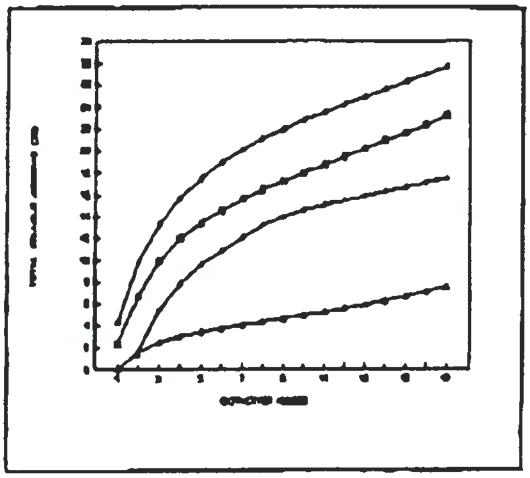

FIG 2 - Multiple extraction leach tests of calcium arsenite precipitates.

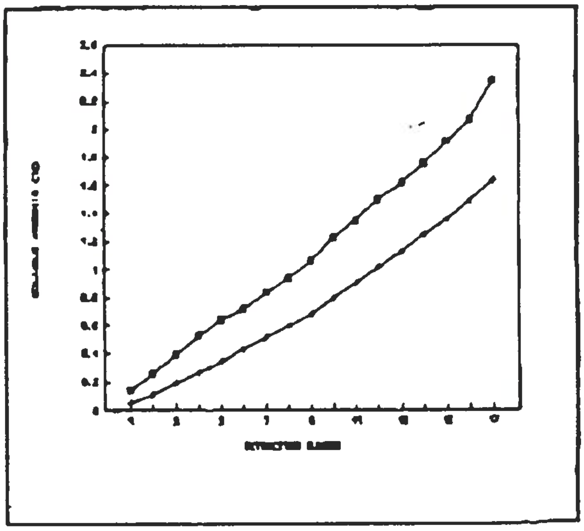

FIG 3 - Multiple extraction leach tests of calcium arsenate precipitates.

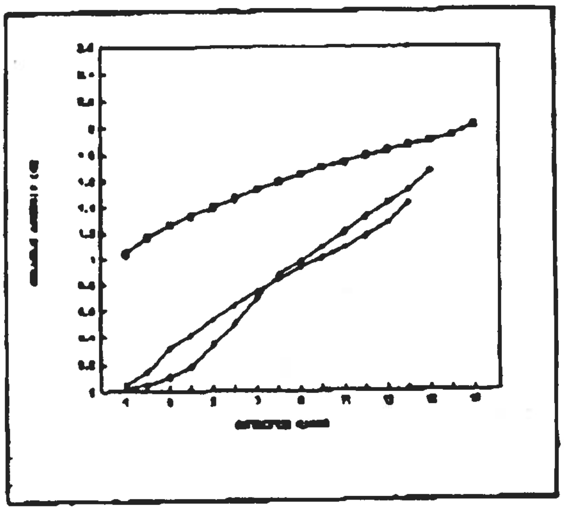

FIG 4 - Multiple extraction leach tests of iron arsenite/arsenate precipitates.

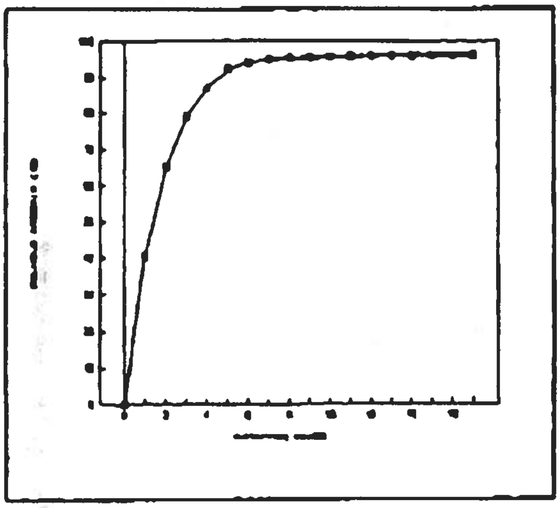

FIG 5 - Multiple extraction leach test of arsenic trioxide waste (B).

leached from the precipitates and the pHs of the extractant solutions are approximately the same. In addition, the high sulphate concentration in the groundwater may also enhance the solubility by removing any soluble calcium as gypsum. The formation of gypsum during the leaching process was confirmed from the analysis of the initial and residual solids, which indicate an incorporation of sulphate into the residue during the leaching process (see Table 6).

The temperature at which the precipitation takes place appears to have little effect on the composition of the calcium arsenite precipitates, but does seem to affect their leaching behaviour. It is difficult to say too much from the present data, however, as the leaching rates of the precipitates produced at ambient temperature were both faster and slower than those produced at 90°C, depending on the lime content.

The solubilities of the ferric arsenite and ferric arsenate precipitates were in general lower than their calcium counterparts (7 - 9 and 2 - 4 mg/L respectively). The ferric arsenate data agree favourably in this case with solubilities reported by Stefanakis and Kontopoulos (1987). However, the lower solubilities of the ferric precipitates must be weighed against the significantly increased quantities of reagents (both ferric sulphate and lime) required for their production. A more cost effective approach may be to minimise the leaching rates of the calcium precipitates by solidification with cement.

TABLE 6

MEP leach tests assays of initial and final residues.

Test No	[illegible]	[illegible]	As (%)	Ca (%)	Fe (%)	SO_3 (%)
JK126	Initial	15.1	5.0	14.3	13.8	34.2
	Final	14.6	5.6	11.0	19.4	31.0
JK127	Initial	13.0	24.5	27.4	1.0	0.8
	Final	17.3	14.1	11.4		21.0
JK128	Initial	15.2	17.0	31.7	0.8	4.9
	Final	23.6	10.7	13.3		27.2
JK129	Initial	15.5	25.0	28.0	1.0	6.5
	Final	13.1	14.8	12.2		13.6
JK130	Initial	16.5	17.3	31.5	0.8	3.1
	Final	19.1	12.3	12.8		20.8
JK131	Initial	15.3	5.2	14.0	14.6	35.3
	Final	13.6	6.1	10.5	17.9	25.4
JK132	Initial	19.8	21.5	25.0	0.9	4.4
	Final	24.2	17.2	11.9		16.3
JK136	Initial	16.4	17.6	30.7	0.8	4.9
	Final	16.6	17.0	17.3		2.8
JK145	Initial	15.0	13.7	29.0	0.7	3.4
	Final	23.7	10.0	10.8		20.1

Solidification of arsenic precipitates

Arsenic trioxide waste and the calcium arsenite, calcium arsenate, and ferric arsenate precipitates were each mixed with cement and water to produce solidified products. Two of the solidified arsenic trioxide products also contained flyash or silica fume as an additive. These additives are known to decrease the porosity of cement, and therefore it was thought, may also decrease the leachability of contaminants from the solidified material. Details of the composition of the solidified products, together with information on their physical properties, are listed in Table 7.

Durable solidified products were produced with all forms of arsenic used except the calcium arsenite, which appeared to interfere with the setting reactions of the cement. These unsolidified products were studied no further. The strength of the solidified products was determined by measuring their unconfined compressive strength (UCS). Normal portland cement mixed with three parts sand and water produces a product with a UCS of about 25 - 30 MPa, whereas a product of less than 1 MPa can be broken with one's fingers.

Leaching characteristics of solidified products

The leaching of arsenic from the solidified products was investigated by subjecting each to a standard Dynamic Leach Test, so called because the driving force for leaching is

TABLE 7

Physical properties of arsenic waste (A) cement solidified products

Arsenic Precipitate	Test No.	Relative Amounts of Reagents				Bulk Density (g/cc)	UCS* (MPa)	Water Content (%)
		Powder	Cement	Water	Additive			
Arsenic Trioxide Waste(A)	FC7	1.00	1.00	0.80		[illegible]	10.1	3.5
	FC9	1.00	2.00	1.15		1.99	20.3	4.1
	FCFA11#	1.00	0.92	0.82	0.08	[illegible]	15.3	10.2
	FCSF11+	1.00	0.94	0.90	0.06	1.92	10.0	11.3
Calcium Arsenate	CAC2	1.00	2.00	2.05		1.65	11.8	27.9
Ferric Arsenate	FBC4	1.00	2.00	1.98		1.42	12.0	22.2
Calcium Arsenate (Cement)	SK160	1.00	0.30	0.86		1.49	1.4	38.7

*UCS = Unconfined Compressive Strength #FA = Flyash as Additive +SF = Silica Fume as Additive

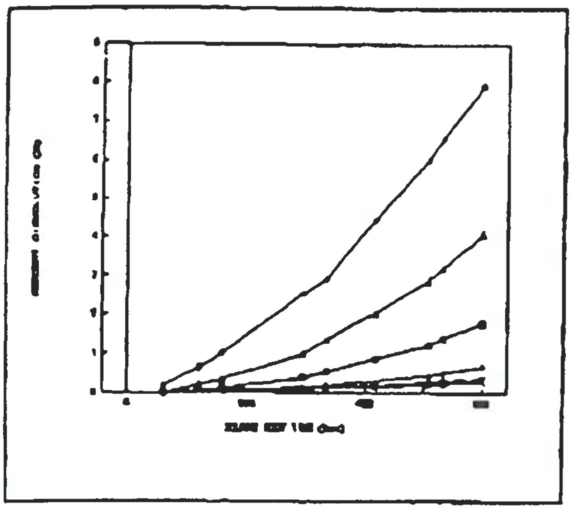

Fig 6 - Dynamic leach tests of arsenic trioxide and precipitates as solidified products.

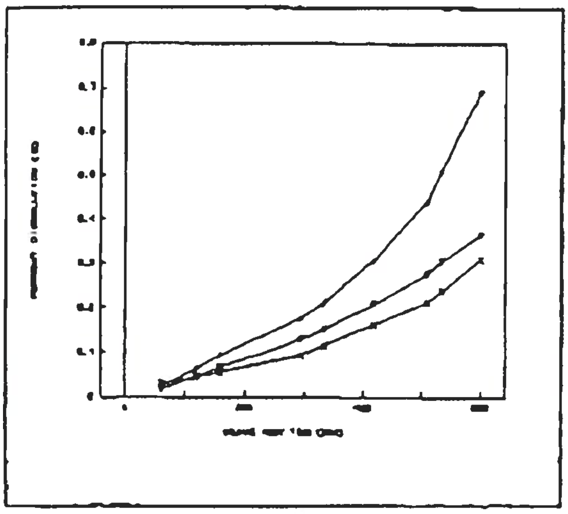

Fig 7 - Dynamic leach tests of calcium arsenate and ferric arsenate

maintained by continually renewing the leachant solution.

The results of these tests are listed in Table 8 and shown graphically in Figures 6 and 7. The graphs are plotted as the percentage of the arsenic in the original sample leached as a function of the square root of time in seconds. For a diffusion controlled reaction, a straight line relationship should be produced. In most cases this is approximately correct over the timespan of the data.

The results indicate that, not unexpectedly, the chemically fixed arsenic, in the form of calcium or ferric arsenate, leaches much more slowly than the unfixed arsenic waste. This is because the arsenic is not only encapsulated in the cement matrix but also stabilised as an insoluble species.

The presence of flyash or silica fume has a negative effect on arsenic fixation producing much higher leaching rates than the straight arsenic-cement mixture. This is probably due to a number of factors. It was noticed during the leaches that the solidified products containing flyash or silica fume produced leachate solutions of lower pH than the other products. In addition, they also had a much higher water content (see Table 7). Both these factors may assist in promoting the dissolution and transport of arsenic from the solid matrix.

It is interesting to compare the three most insoluble solidified forms of arsenic (Figure 7). The calcium arsenate prepared with cement has proven to be more insoluble than that prepared with lime, even though the total quantities of lime and cement used in its production were less. This is thought to be due to chemical fixation of the arsenic rather than physical encapsulation as the physical properties of the solidified product indicate a weaker cement matrix than for the other form of calcium arsenate (see Table 7).

CONCLUSION

A number of disposal options for arsenic trioxide produced as a by-product of roasting operations have been investigated. Theses options were precipitation as arsenite or arsenate salts of calcium of iron(III), chemical fixation of the arsenic trioxide with cement, or a combination of the two processes.

The formation of so-called "ferric arsenate" precipitates produces a very low solubility product but requires large quantities of oxidant, lime and ferric sulphate for its production. Initial cost estimates have indicated this route is not economically

TABLE 8

Summary of dynamic leach test results.

Test No.	Type of Waste	Additive	Relative Amounts of Reagents				As (%)	LX Value
			Water	Cement	Lime	Other		
JK170A	Arsenic Trioxide		1.00	1.00			17.8	11.50
JK171A	Arsenic Trioxide		1.00	2.00			11.9	12.19
JK172A	Arsenic Trioxide	Flyash	1.00	0.92		0.08	17.8	10.06
JK173A	Arsenic Trioxide	Si Fume	1.00	0.94		0.06	17.8	10.33
JK174B	Arsenic Trioxide*		1.00	1.00			29.4	9.60
JK175B	Calcium Arsenate** 2:1		1.00	4.40	1.42		7.5	14.60
JK176A	Calcium Arsenate 1:1		1.00	6.64	2.20		4.4	12.80
JK177A	Ferric Arsenate 1:1	Ferric Sulphate	1.00	7.52	1.02	1.00	3.4	12.67
*Higher arsenic content than others.			**Precipitated with calcium ion first.					

viable unless cheap sources of chemicals are available. Ferric arsenite precipitates, although very insoluble, suffer from the same problems of chemical requirements.

Calcium arsenate is also a low solubility precipitate that requires much less chemicals for its formation than the ferric route. However, the precipitate is known to be thermodynamically unstable in the long term in the presence of atmospheric carbon dioxide or carbonate ions (Robins, 1987).

Calcium arsenite precipitates are too soluble and also suffer from long term instability.

Chemical solidification with cement, either of the arsenic trioxide itself, or after precipitation as calcium arsenate, appears to have prospects as a disposal option, both in terms of the low leachability of arsenic from the matrix, and in terms of preventing contact with atmospheric carbon dioxide or carbonate ions. The long term stability of these solidified products requires further investigation.

ACKNOWLEDGEMENTS

The development work reported in this paper was funded by Minproc Engineers acting on behalf of a major African gold mine, whose cooperation in allowing this work to be published is gratefully acknowledged.

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NERCO CON MINE ARSENIC PLANT - ENVIRONMENTAL MANAGEMENT THROUGH RESOURCE RECOVERY

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Abstract

This paper deals with the Nerco Con Mine arsenic trioxide plant. This operation has demonstrated that a major environmental liability can become an asset through commitment to resource recovery.

The mine was originally owned and operated by Cominco Ltd. From 1940 - 1970, the gold ore was refractory in nature, and was roasted, prior to cyanide leaching and gold precipitation. An arsenic trioxide sludge was produced as a byproduct, and over 70,000 tons were stockpiled.

As a condition of the 1981 water licence, the mine was required to establish environmentally acceptable storage areas. Rather than install a potential long-term liability, an Arsenic Plant was constructed in 1983, to recover the arsenic trioxide as a high grade product using a weak acid leach and crystallization process, tested at Cominco's Technical Research Centre.

When the plant was operating consistently, it was found that the chemistry was unreliable. Leach and crystallization modifiers were felt to be the problem, but were not identified, or removed in the existing process. The plant was shut down in late 1985 and used for tailings water treatment, while further research work continued. This identified the need for several process additions.

Nerco Minerals Inc. purchased the mine in late 1986, and directed a successful remodelling and start-up program in early 1987. The plant is now producing a high purity, crystalline product. Residues from the process contain significant gold and silver values.

General

Nerco Con Mine, Ltd. is located near the City of Yellowknife on the north shore of Great Slave Lake. The mine was operated by Cominco Ltd. until late 1986, at which time it was purchased by Nerco Minerals Inc. It was the Northwest Territories' first gold mine, pouring the first two bricks on September 5, 1938.

In 1941 a roasting plant was added to the cyanidation mill to treat the refractory gold ore. A wet scrubber was operated downstream of the roaster to retrieve the arseniferrous wastes from the roaster off gases. The scrubber effluent was pumped to arsenic storage basins where the slurry was allowed to settle by gravity, forming an arsenic trioxide sludge. The supernatant was decanted and returned to the scrubber for re-use.

Initially one rock basin located on the property was used for storage of the arsenic sludge but later a second basin from the adjacent Negus Mine was used. Accumulation of arsenic sludge continued until November 1970, when the amount of gold-bearing arsenopyrite dropped and roasting was discontinued.

Storage of Arsenic – A Long-Term Problem

The two storage basins contained over 70,000 tons of arsenic sludge and posed a potential environmental hazard. In the summer the surface of the sludge would partially dry out resulting in airborne arsenic trioxide. Surrounding surface water and groundwater were considered threatened by leachate containing soluble arsenic which could possibly escape through the deteriorating dams.

The sludge contains 50% arsenic trioxide as well as 0.70 oz/ton gold and 1.20 oz/ton silver. The material is extremely difficult to handle. It is toxic, very fine, with an average particle size of 85% minus 5 microns, and forms a thixotropic mass containing 35% moisture.

During the late 1970's, the storage ponds became an issue with the N.W.T. Water Board. Conditions were included in the Con Water Licence to submit "detailed proposals for the containment and reclamation of all arsenic oxide storage areas located on the property..."

Cominco Ltd. contracted a consulting engineering firm to undertake a review of alternative methods of dealing with the arsenic sludge. The alternatives considered were divided into three main categories:

- Chemical Fixation Methods – involved the addition of chemicals that will react with the arsenic to form insoluble arsenic compounds.
- Physical Processing Methods – involved the containment of the arsenic sludge within an impermeable system.
- Resource Recovery Methods – involved the processing of the arsenic sludge to recover precious metals and the arsenic trioxide for re-use.

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All of the alternatives were evaluated on the basis of their process feasibility potential for eliminating emissions of arsenic to the environment and economics. Chemical fixation methods and physical processing methods were eliminated due to their high capital and/or operating costs. There were also leaching risks associated with the chemical fixation methods.

Resource recovery was considered technically feasible but the high capital and operating costs meant that a detailed marketing study was required. There were also potential environmental problems associated with the proposed pyrometallurgical process, particularly in the areas of fume and dust control.

Attention was turned toward a new physical containment method which, if successful, would provide a politically and environmentally acceptable alternative. Studies to freeze the sludge in-situ, either naturally or artificially, were initiated. It was concluded that although technically feasible, it would be a costly and difficult method to execute. Long-term monitoring would also be required.

Resource Recovery

A resurgence of market prices for arsenic trioxide in 1980 rekindled interest in the resource recovery alternative.

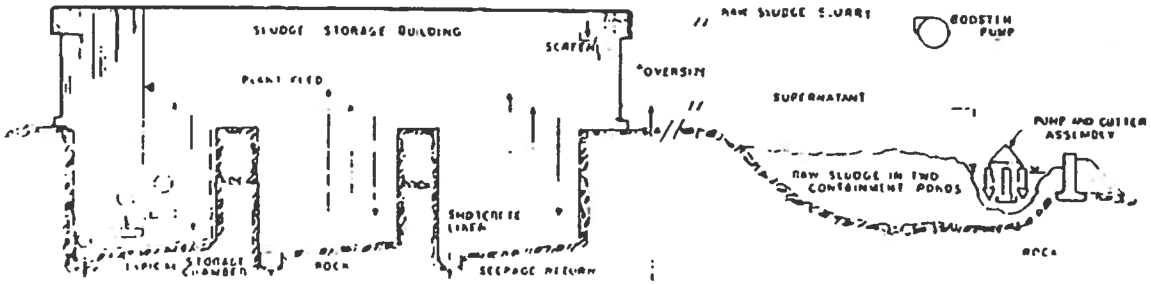
Cominco researchers were aware of the potential of a hot water leach and precipitation process, from work done on other material at their metallurgical complex at Trail, B.C. Although the capital and operating costs of the hot water leach process were higher than a fuming method, the leach process was chosen as being environmentally superior. A laboratory test program was conducted at the Technical Research Centre in Trail during 1980, which established the process design parameters for a full scale plant.

Detailed engineering was then conducted, and Cominco Ltd. received approval from the Water Board in March 1981 to proceed with plans to build the Con Arsenic Trioxide Plant. The plant was built in 1982, and commissioned in early 1983.

Process Design

A system had to be designed that would ensure a constant raw sludge supply, but reclaiming sludge in the winter was out of the question. The system had to be able to reclaim 10,000 tons of raw sludge in the summer and stock it in protected storage for easy winter recovery to feed the plant.

Tanks for stocking the reclaimed sludge were rejected in favour of water-tight chambers excavated below grade in solid rock. Three chambers were blasted out, each 40 feet deep and 60 feet in diameter. These were shotcreted, with drainage sumps cut into the underlying rock so that the chambers could be monitored for seepage. The chambers are covered with a low building, heated to prevent freezing of the material.



SLUDGE STORAGE AND RECOVERY SYSTEM

NERCO CON MINE, LTD.

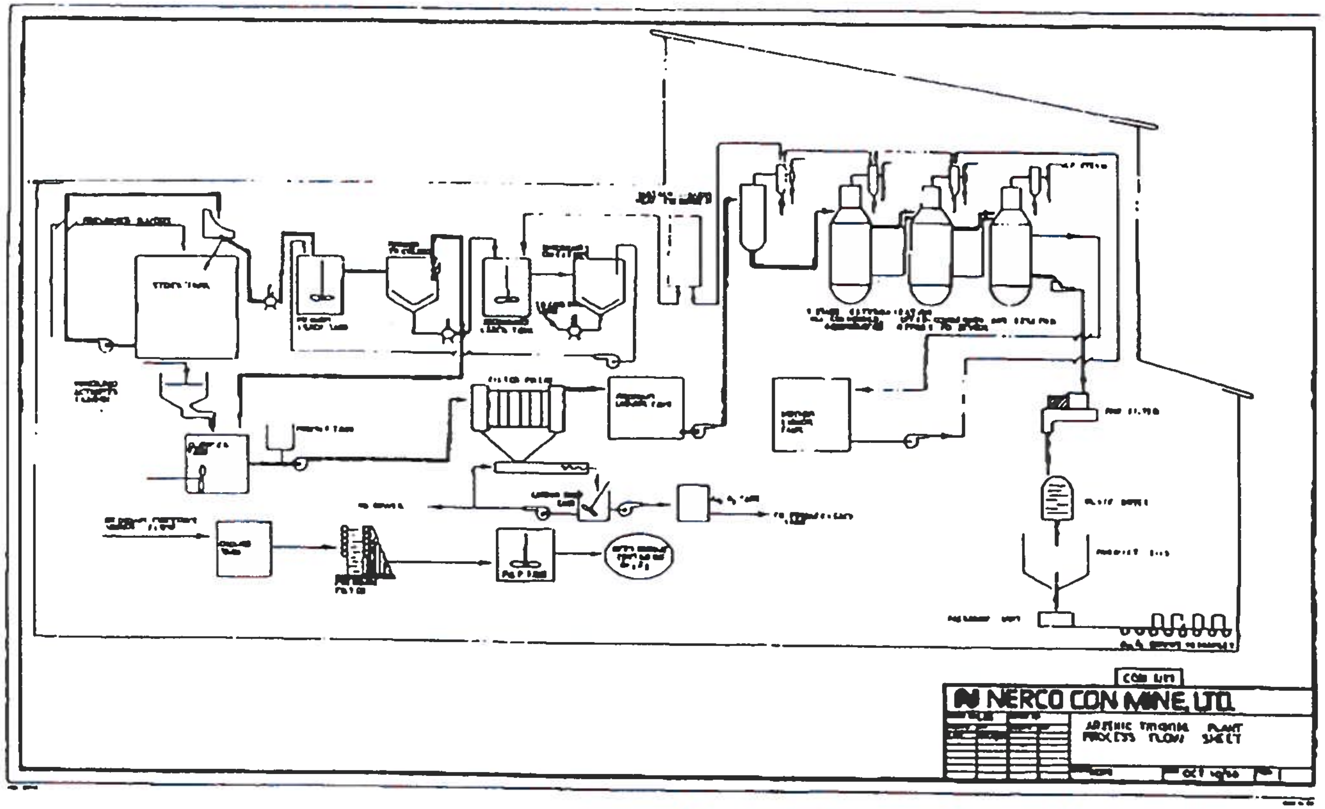
SLUDGE STORAGE AND RECOVERY SYSTEM
PROCESS FLOW SHEET

DRAWING NO CON 2180

Drawn by: L.I
Scale NONE
Date: JUN 15/85
REV 0

SLUDGE STORAGE AND RECOVERY SYSTEM
PROCESS FLOW SHEET
DRAWING NO CON 2188

Drawn By G. L.	Scale NONE	Date JUN '5/65	REV. 0



The extraction process is a two stage countercurrent leach operating at 95°C. The primary stage treats raw arsenic sludge at 20 stpd, extracting over 90% of the available arsenic trioxide, and the secondary stage recovers the remainder. Key process developments are the addition of small amounts of hydrogen peroxide to enhance the leach kinetics, and clarification methods which include thickening followed by powdered activated carbon filtration to remove crystallization modifiers and enhance product purity.

The hot pregnant liquor is subjected to four stages of evaporative cooling and crystallization in growth type units. Over 75% of the process heat released in crystallization is recovered using mother liquor recycle as the cooling medium in surface condensers. In winter, the remaining 25% is used to pre-heat incoming ventilating air. This is believed to be the first commercial application of this technology to produce arsenic trioxide, which is an extremely difficult material to crystallize successfully.

The product from the final stage is dewatered to less than 0.1% moisture and stored in a silo capable of holding four days' production. The arsenic trioxide produced is 99.8% pure and is packaged in extra strength 45 gallon steel drums in 1,000 lb. increments.

The 8 stpd of residue left after the arsenic trioxide is recovered contains 1.2 oz. of gold/ton and 3.5 oz. of silver/ton. This material is currently being stockpiled. Metallurgical evaluation is underway to determine the requirements for precious metals recovery. Final inert residues will be disposed of in the tailings pond, along with 750 stpd of mill tailings.

Problems Associated with Start-up and Operation

As might be expected when starting a plant using untested technology to produce a new product, there were many areas in the plant which required modifications of the process and/or the equipment. The majority of the problems could probably have been avoided by completing a more rigorous metallurgical research and process design program, and by ensuring that adequate hygiene management equipment and procedures were in place, prior to attempting construction and start-up.

From a process standpoint, a major problem was the transport of corrosive, high density slurry in small volumes. In several areas, piping had to be replaced to minimize flow restrictions, increase process flexibility and make allowance to flush out lines. Several pumps had to be replaced to reduce damage to the product, increase or decrease flow rates, reduce maintenance requirements and improve ease of operation.

An area of immediate concern was the dewatering plant. A solid bowl centrifuge was chosen for primary dewatering, however it degraded the final product. A cake was produced which had high moisture content, could not be successfully dried and could not meet product size specifications.

The centrifuge was replaced with an horizontal pan filter which achieved an acceptable discharge moisture content without degrading the product. The dryer discharge was thereby free flowing and dust free.

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Unfortunately, the pan filter and dryer have proven to require excessive operator attention and maintenance. By virtue of the equipment design, neither operation or maintenance can proceed in an environmentally acceptable fashion. This area of operation is currently being evaluated in order to identify and install equipment which will perform the same function, while improving worker health and safety.

Crystallization of arsenic trioxide proved to be difficult from a metallurgical and operational standpoint. Several design problems were found with the crystallizers and their condensers. Three of four units were modified and the fourth was completely replaced. Instrumentation for the crystallizers proved unreliable, resulting in difficult operation. Extensive modification of instrumentation was necessary to allow consistent operation.

As constructed, the plant had very poor ergonomics. Extensive modification was required to allow access to operating areas, equipment, manways, control valves, etc. Plant lighting was very poor, and extensive modification was required.

After two years operation, several mechanical modifications allowed plant availability to exceed 90%. Operator hygiene also improved significantly over this period, proving that the plant could operate consistently and safely. It became obvious, however, that more research work was required, if the plant was to produce consistently.

The presence of crystallization modifiers was suspected to be the cause of inconsistent metallurgical performance. These modifiers were felt to be associated with organic material, which formed part of the feed stock, in varying amounts. This was evidenced by a yellow tint in the crystallization liquor, which varied in intensity as production rates rose and fell. Product colour also varied, between a buff colouration during periods of poor productivity, and near-white when productivity was good.

The plant was shut down in late 1985, and converted to a water treatment plant in order to treat tailings pond water on an emergency basis. During an eight month period, research work continued, in an attempt to identify the crystallization modifiers, and determine the process requirements necessary to ensure their removal.

A laboratory scale mini-plant was constructed in mid-1986. A test program was undertaken which was much more rigorous than the laboratory work used to model the initial design. As a result, the research team was successful in duplicating the inconsistent metallurgical performance experienced in the full scale plant. This allowed evaluation of process modifications which would remove crystallization modifiers and allow consistent production to proceed.

A carbon filtration system was developed which includes mixing of powdered activated carbon with the crystallization liquor, then removing the carbon using a filter press. The resulting solution is water clear, and crystallizes quickly and reliably. Product purity and colour are excellent.

Nerco Minerals Incorporated purchased the Con Mine from Cominco in late 1986. The arsenic plant was modified to incorporate the carbon filtration system, and re-started in early 1987. Productivity and product purity have been excellent, and the plant continues to improve its availability.

Hygiene Control: Training of Operating and Maintenance Personnel

The people working at the Con Mine in 1983 were effective in the operation and maintenance of a 40-year old gold mill. Training these people to work in an environment which included high pressure steam, pumps with mechanical seals, extensive instrumentation, high temperature slurries and a complex hygiene control program proved to be difficult. This difficulty was compounded when key equipment items failed to perform their requirements as designed.

At start-up in 1983, a formal training program was non-existent for any aspect of the operation or its maintenance. As might be expected, several problems were encountered with operator hygiene, plant operating consistency and maintenance procedures.

Training programs now in place include a comprehensive indoctrination, written job procedures for routine and non-routine work, a modular operations training program, respirator training, welding safety and tank entry training and equipment maintenance training for some of the equipment items peculiar to the plant.

The training programs are integral to the hygiene control program, which includes extensive environmental and biological monitoring, a comprehensive plant entry/decontamination procedure, respiratory protection and engineering controls throughout the plant.

Conclusions

The plant modifications, re-commissioning and re-start directed by Nerco Minerals has been very successful. A major component of this success has been the commitment to extensive training of operators and tradespeople in both hygiene control and a specialized area of work.

The plant is now operating at close to 90% availability. The product purity is very high, at +99.8% As_2O_3. Product colour is near white, generally +92% reflectance, and +96% lightness using a chromameter.

The commitment by Cominco Ltd. and Nerco Minerals to pursue resource recovery of a toxic waste has involved a high degree of risk. Over the long term, however, it will ensure that the arsenical wastes are permanently stablized.

In about five years, the two containment ponds will no longer exist. Three products, being arsenic trioxide, gold and silver will have been produced in sufficient quantity to pay off the plant's operating costs. In this way, an environmental liability will have become an economic asset.

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#4

HOW ST. JOE GOLD'S EL INDIO MINE HAS BECOME A MAJOR PRODUCER OF HIGH QUALITY CRUDE ARSENIC TRIOXIDE.

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Abstract

The El Indio high grade gold/silver/copper mine is situated in an arsenic anomalous geological zone, which has necessitated the installation of a de-arsenifying roaster, with the dual objectives of producing arsenic-free calcined flotation concentrates and a readily saleable crude arsenic trioxide. How these objectives have been successfully attained by precise metallurgical and mechanical controls both in the roaster and in the effluent-gas train is described in this paper, with some attention being given to the necessary environmental monitoring.

[redacted]

Introduction

The El Indio mine is located at and above 4000 m. elevation in the Chilean Andes about 180 kilometres east of the city of La Serena, access being by a road which runs up the Elqui Valley, as shown in Figure 1.

In 1975 a St. Joe Minerals Corp. geologist visited the site which was being mined by hand-scale miners, known as "Pirquineros". After accelerated exploration, metallurgical testwork and negociations, a beneficiating plant and concentrate roaster were placed in operation in 1981. A photograph is shown in Figure 2.

Mining of the high grade gold/silver/copper/arsenic ore is performed by open-pit, selective cut-and-fill and long-hole stopping methods. The scale of operations has been to-date about 55,000 t/month of ore treated in the flotation/cyanide plant, with about 60% of the resultant concentrates being roasted to remove arsenic and antimony. After a recent expansion the flotation/cyanide plant is being tuned to treat about 75,000 t/month of ore, and the design and procurement of a second identical roaster is being undertaken.

Since 1983 several improvements to the existing roaster's operating performance have been made, which have resulted in increased throughput, better control over calcine concentrate quality and the off-gas product crude arsenic trioxide (also known as "grey" arsenic trioxide). Present production of crude arsenic trioxide is about 15 t per operating day, and this output will almost double when the planned second roaster is placed in service about the end of 1989.

Geology

Regionally the country rocks are acid volcanic to sub-volcanic, with dominant types being quartz dacite, rhyolites and andesites. Tuffs and agglomerates predominate. There are stocks in the altered zone. These intrusives are generally granodiorites with phaneritic or porphyritic texture and locally diseminated copper mineralization (chalcopyrite) with associated molybdenite.

Adjoining the district to the west is a strongly folded sedimentary series with intercalated gypsum. These sediments appear to form the basement of the volcanic terrain.

Although regional structural control is dominated by north-south faulting paralleling the Andean trend many smaller structures are commonly orientated northeast-southwest. These structures are pre-alteration and provided conduits for alteration solutions and later mineralization.

Locally the El Indio orebodies are a complex vein system in sub-volcanic rocks. Primary mineralization is of two types:

1) Quartz veins - which are important for their high gold values, but also contain significant silver and copper. They are generally brecciated and recemented with silica, and average about 2 m. wide.

2) Massive sulfide veins - typically they are a mixture of pyrite and enargite with accessory quartz and other minerals. With increasing depth, tennantite-tetrahedrite, sphalerite, galena, covellite and digenite begin to appear. Gold where observed, has been in later quartz veins cutting through the sulphides. Veins can be 10 m. wide, and grades 6 to 12% Cu, 8 to 10 g/t Au and 160 g/t Ag.

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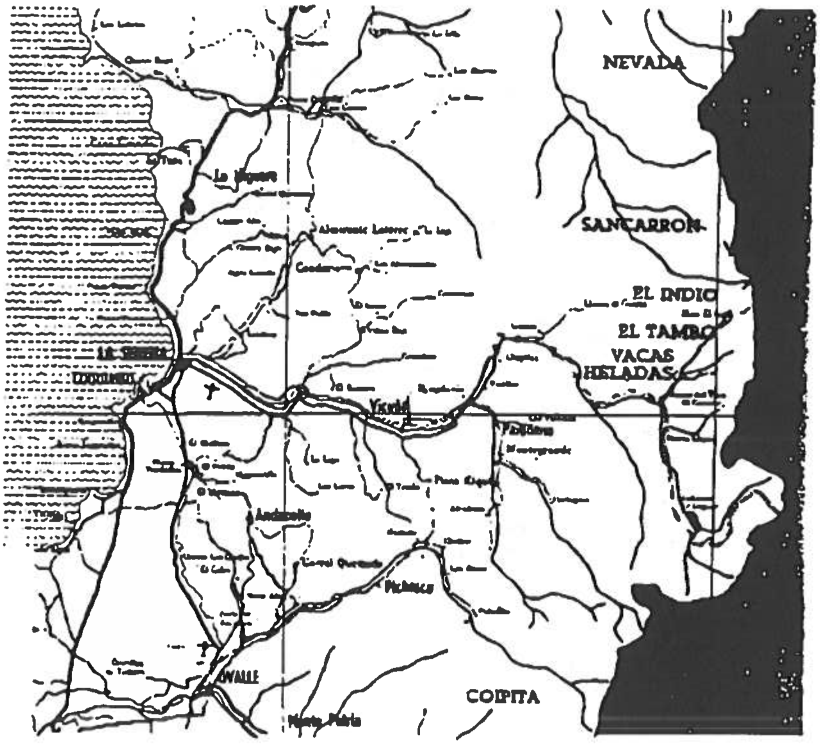

Figure 1 - Map showing El Indio location.

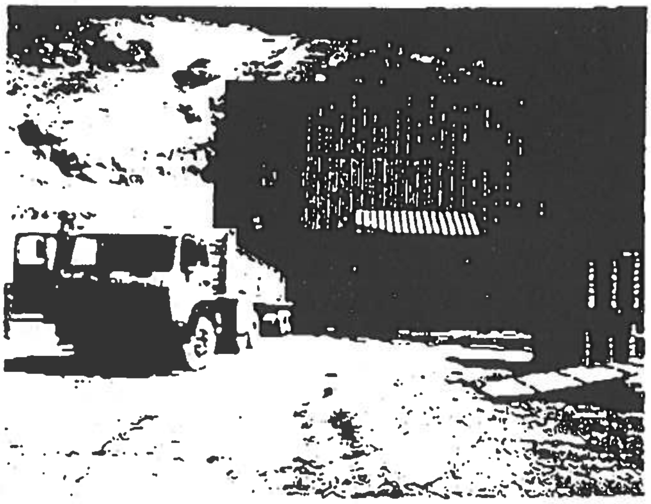

Figure 2 - Photograph El Indio Plant - Arsenic Packaging Facility.

On surface and to 120 m. below surface these veins are leached, characterized by a siliceous gangue and porous boxwork texture derived from leached enargite. Remnant enargite is locally present along with scorodite ($FeAsO_4.2H_2O$), native sulfur and mackayite ($FeTe_2O_5$). Ref. 1.

With respect to arsenic, soil sampling on an area over 100 hectares was conducted. The arsenic content is extremely high, with an average of 370 ppm As. About 3% of the samples gave values over 0.5% As, and in some cases values of over 3% As were obtained. As Figure 3, shows a northeast general trend, relates to the regional structural control of economic mineralization. There also exists a good coincidence between the superficial arsenic anomaly and the underlying geological environment formed by tuffs and tuff breccias, affected by argilic hidrothermal alteration, originated in an environment with strong volcanic activity.

The correlation As-Cu in soil samples for the whole El Indio area shows that only part of the arsenic has its origin in the oxidation process which affected the sulfosalts. Most of the arsenic content in soils at El Indio is a result of the volcanic process itself, which through the circulation of hot solutions with a high content of arsenic and sulphur, impregnated the volcanic rocks already formed and the ones in the formation process, filling their fractures and pores with these elements. Ref. 2.

Mineralogy

The El Indio high grade gold/silver/copper/arsenic ore consists of gold rich quartz veins associated with sulfide mineralization, which are composed almost entirely of copper minerals and pyrite. The following Table I lists the minerals identified to date:

Table I. El Indio Main and Minor Minerals

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1) Main Ore and gangue minerals

Enargite: Cu_3AsS_4
Scorodite: $FeAsO_4.2H_2O$
Gold: Au
Quartz: SiO_2: in low temperature forms, chert, jasper, chalcedony, opal.
Pyrite: FeS_2
Tennantite: $(CuFe)_{12}As_4S_{13}$

2) Minor ore and gangue minerals

Marcasite (FeS_2)
Chalcopyrite ($CuFeS_2$)
Arsenopyrite ($FeAsS$)
Bismuthinite (Bi_2S_3)
Bornite (Cu_5FeS_4)
Colusite ($(Cu_3SnFeVAs)S_4$)
Maltildite ($AgBiS_2$)
Sphalterite (ZnS)
Tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$)
Cinnabar (HgS)
Alunite ($KAl_3(SO_4)_2(OH)_6$)
Huebnerite ($MnWO_4$)
Covellite (CuS)
Galena (PbS)
Leucoxene ($CaTiSiO_5$)
Chalcocite (Cu_2S)
Krennerite ($(AuAg)Te_2$)
Petzite (Ag_3AuTe_2)
Stannite (Cu_2FeSnS_4)
Emlectite ($CuBiS_2$)
Jarosite ($K_2Fe_6(OH)_{12}(SO_4)_4$)
Kaolinite ($Al_2Si_2O_5(OH)_4$)

Part of the feed to the El Indio plant is drawn from a satellite deposit called El Tambo, where the mineralization consists of native gold, minor tellurides of gold and silver and silver sulfides, associated with gangue minerals barite, alunite and jarosite with minor pyrite. No significant arse-

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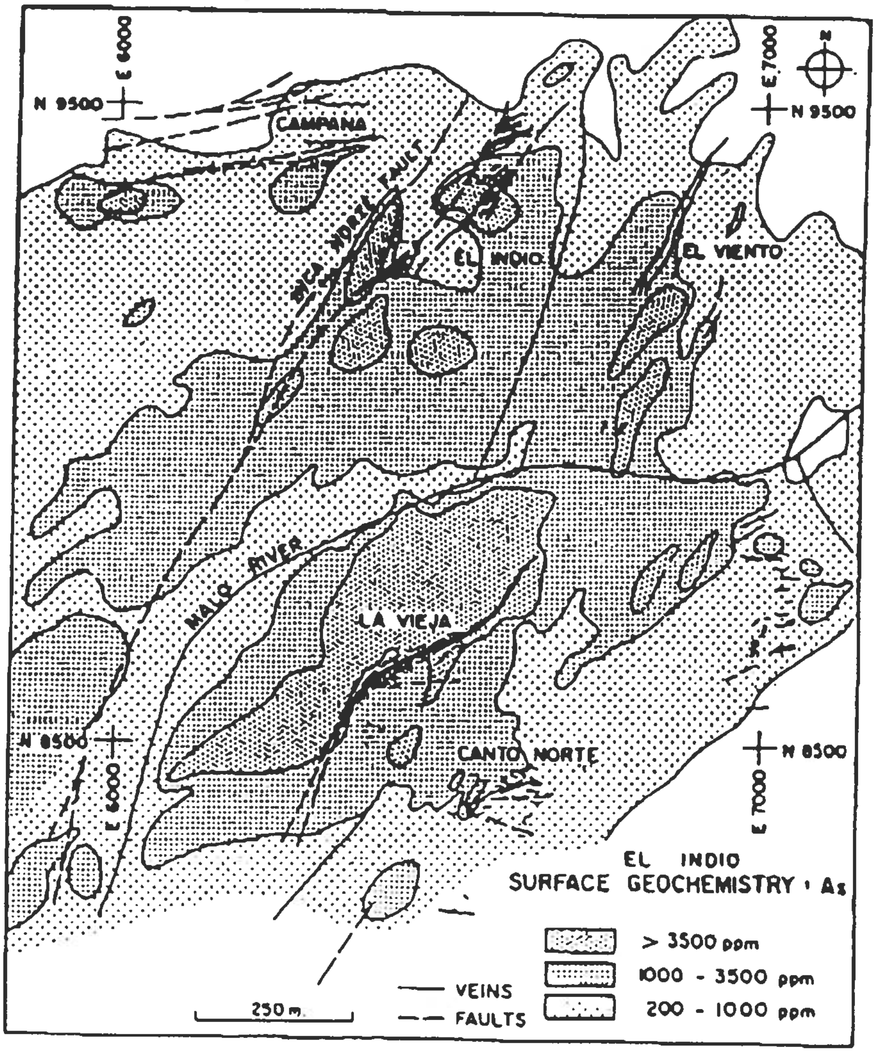

Figure 3 - El Indio Surface Geochemistry showing strong arsenic anomalies.

nic bearing minerals have been encountered to-date in the ore.

In the El Indio area, the mineralogy of arsenic in soils corresponds to a variety of supergenic arsenates and basic sulfates-arsenates. In the superficial areas of the mine, where more detailed mineralogical studies have been made, it is common to find scorodite ($FeAsO_4$) and beaudantite ($PbF_3(AsO_4)(SO_4)(OH)_6$) underground. As essential ore constituents have been recognized enargite (Cu_3AsS_4) and arsenopyrite ($FeAsS$). Ref. 3.

Metallurgy

The El Indio flotation concentrate contains nominally 7 - 10% As, 0.4 - 0.7% Sb and 19 - 24% Cu as well as high levels of Au and Ag, and requires pre-treatment to remove arsenic and antimony to achieve universal salesability.

Pilot plant testing by Nesa of concentrates resulting from original metallurgical tests developed the El Indio multi-hearth inert roast. The general concepts enunciated for the removal of Group V metals from complex sulfide materials were as follows:

I The maximum temperature is that at which these impurities thermally decompose (which may depend upon roaster atmosphere and partial melting points).

II The heating rate has a pronounced effect on the volatilization of these impurities - a low heating rate is required because it promotes surface interaction and porosity, avoiding fusion of eutectic compounds.

III The roast in theory can be carried out in inert, reducing or oxidizing atmospheres. However from a practical standpoint, roasting in oxidizing conditions causes formation of the less volatile pentavalent arsenates and antimonistes, loss of stable sulfide sulfur, excessive formation of oxidized iron compounds, and formation of low melting point eutectics. Because of these objections neutral to reducing conditions are needed to achieve the desired results.

IV Relates to the fact that the volatilization of As, Bi, Sb is enhanced by the presence of free sulfur. Typically, free sulfur is supplied by the decomposition of pyrite (FeS_2).

The above conditions, in the case of El Indio concentrates, are illustrated by the following equations:

For a reducing atmosphere,

$$2\ Cu_3AsS_4 \longrightarrow Cu_2S + 4CuS + As_2S_3(g) \qquad (A)$$

$$2\ FeS_2 \longrightarrow 2\ FeS + S_2(g) \qquad (B)$$

$$8\ FeAsS \longrightarrow 4\ FeAs + 4FeS + As_4S_4(g) \qquad (C)$$

(C) has minimal importance as arsenopyrite is a minor constituent of the El Indio ore.

Recent microscopic and X-ray diffraction examinations of the roaster calcine product have shown it to be actually about 75% $Cu_9Fe_9S_{16}$ and 15% $CuFe_2S_3$ with minor amounts of $CuS_x.CuO_x$ and SiO_2.

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The near oxygen-free atmosphere inside the roaster is protected because any excess oxygen is consumed before it can react with the solids in the beds on each hearth. In fact, part of the heat used in roasting is generated by controlling a flow of air into the upper hearths and thereby taking advantage of these exothermic reactions:

$$S_2(g) + 2\ O_2(g) \longrightarrow 2\ SO_2(g)$$

$$As_4S_4(g) + 7\ O_2(g) \longrightarrow 2\ As_2O_3(g) + 4\ SO_2(g)$$

Ref. 3.

Process Plant

The Process Plant's original capacity was 1250 t/day, and after minor modifications a level 1900 t/day was attained. Subsequent expansion by addition of crushing, milling and flotation equipment will raise capacity to 2400 t/day by the end of 1987.

In Figure 4, are shown the main process unit operations. The run-of-mine ore is blended for constant grade, crushed by jaw-crusher and two stage cone crushing, with the last stage being in closed circuit with classifying screens. The crushed ore is then washed to remove deleterious soluble acidic salts, which cause metallurgical problems in subsequent process stages. The coarse washed mineral is ground and floated in a conventional alkaline ball mill/flotation circuit which produces copper concentrates containing high level of gold, silver and arsenic. The main mineral constituents being enargite and pyrite. The slimes from the washing plant are additionally floated in a separate acid circuit, concentrates being combined with the product from the alkaline circuit.

The high arsenic (and to a lesser extent antimony) containing concentrates are selectively roasted to almost entirely remove the arsenic and antimony. Surplus concentrates above the capacity of the present roaster are sold to smelters which can accept high arsenic/antimony containing concentrates.

The flotation plant tailings are cyanide leached to dissolve additional gold and silver which are adsorbed in a carbon-in-pulp plant. The gold and silver is then eluted from the separated carbon and recovered by electrowinning on steel wool cathodes, which are smelted and sent to refiners.

Roaster Operation

The simplified diagram, Figure 5, shows the multi-hearth roaster, the gas train and the arsenic packing facility. In Table II, are listed the principal equipment.

The roaster is operated continuously, and although the original design rate was 8.5 t/hour, a rate of 10.0 t/hour is now being achieved after making circuit improvements.

The dried flotation concentrate, at 8.5% humidity and about 65% minus 37 microns is fed to the roaster by a front-end loader through a bin, belt, skip hoist and weight-controlling feed belt. The concentrate enters through double sealing flap-gates.

An overload protected rotating centre shaft transfers the calcining concentrate down the roaster by means of attached rabble arms.

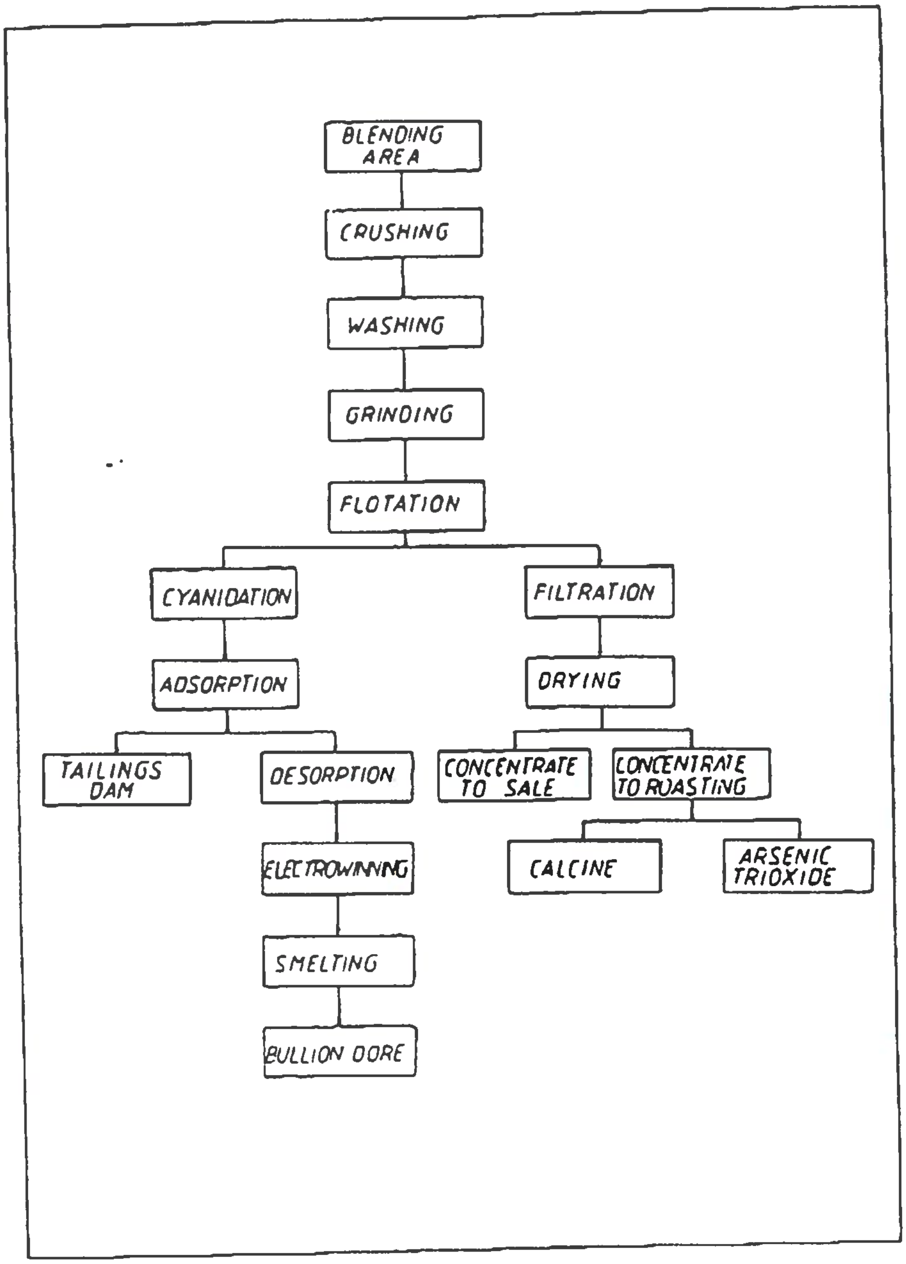
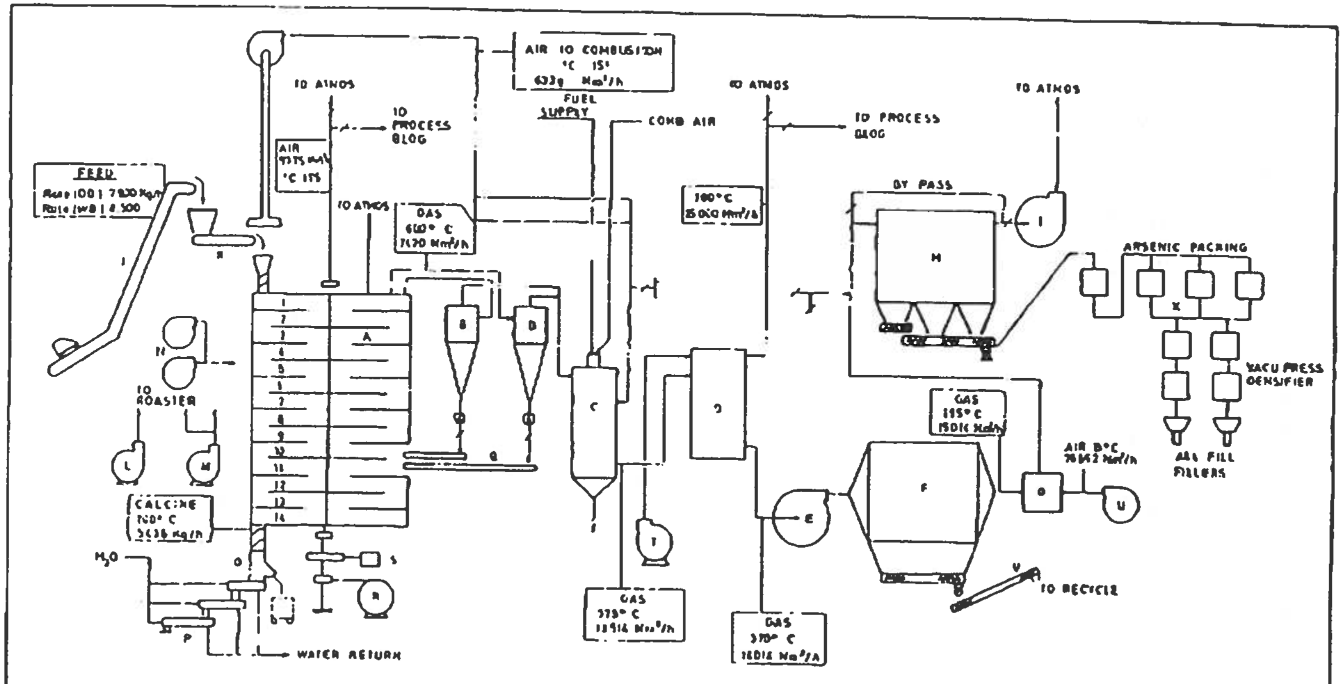


FIGURE No. 4 - FLOWSHEET PROCESS PLANT



A	ROASTER	G	MIXING CHAMBER	M	COMBUSTION AIR FAN	S	DRIVE
B	CYCLONE	H	BAG FILTE	N	OIL PUMPS	T	COOLING AIR FAN
C	POST COMBUSTION CHAMBER	I	EXHAUST GAS FAN	O	ORISTLEY	U	QUENCH AIR FAN
D	HEAT EXCHANGER	J	SKIP HOIST	P	COOLING SCREW CONVEYOR	V	ROTARY DRUM
E	INTERMEDIATE ID FAN	K	WEIGH BELT CONVEYOR	Q	DUST SCREWS	X	STORAGE BINS
F	ELECTROSTATIC PRECIPITATOR	L	PROCESS AIR FAN	R	COOLING AIR FAN		

FIGURE 5 EL INDIO ACTUALIZED PROCESS FLOWSHEET FOR ROASTER AND ARSENIC PACKING FACILITIES

Operating temperatures within the roaster are maintained by 14 North-American diesel burners. Two, diametrically oposite, being situated on each even-numbered hearth. A significant additional source of heat is obtained by injecting air into hearths 1 through 9, to obtain a limited combustion of sulfur gases.

Practice has shown the importance of a correct temperature profile in the roaster, to maintain uninterrupted operations. This is because enargite descomposes to eliminate arsenic trisulfide at about 630 to 640 degrees C. but fuses as close as 690 degrees C. In the upper hearths temperatures are not allowed to rise above 690 degrees C. and only to 720 degrees C. in the lowest hearths.

The product calcine is discharged from the final 14 hearth at 700 degrees C. through sealing flap-gates, and is conducted through two lines of water cooled sealed screws to a conveyor where it is humidified to 8 - 10 % for storage and subsequent truck transport.

In Table III, are shown details of the roaster extraction efficiency.

Table III. El Indio Roaster Extraction of As, Sb and S.

Month	Element	Roaster % Assays Feed	Calcine	Roaster % Extraction
May 1987	As	7.1	0.58	93.5
	Sb	0.48	0.31	48.2
	S	35.9	25.9	42.4
June 1987	As	6.6	0.66	92.1
	Sb	0.49	0.35	43.1
	S	33.8	24.9	41.1
July 1987	As	6.9	0.43	95.2
	Sb	0.52	0.34	48.9
	S	36.1	26.5	42.2
August 1987	As	7.7	0.30	96.1
	Sb	0.65	0.41	35.8
	S	33.5	23.6	40.8
September 87	As	7.5	0.45	95.4
	Sb	0.57	0.40	46.6
	S	32.5	23.5	45.4

The roaster effluent gases containing sulfides of arsenic and antimony, labile sulfur and other volatiles pass through two cyclones in parallel. The cycloned dust returns to hearth 11 of the roaster and the partly cleaned gases pass to a post combustion chamber where enough ambient air is admitted to completely convert all sulfides to oxides. The temperature of oxidation is 750 degrees C. which is maintained by a diesel fuel burner if the exothermic reactions are insufficient. Higher temperatures have been found to cause refractory accretions downstream known as "arsenic glasses". Low temperatures, 500 - 700 degrees C., result in the formation of deleterious SO_3.

The oxidized gas stream is then cooled in a stainless steel tube type heat-exchanger, the cooling-air passing through the tubes. Waste heat is

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TABLE II. MAJOR EQUIPMENT REFERENCE

1.) Roaster Section	
(1) Skip Hoist, 31.1 m., 0.85 m3 Bucket	Beaumont Birch
(1) Surge Hopper, 2.1 m3 (Texas Nuclear Level Detection)	CMEI
(2) Screw Feeders, 1.36 mL × 0.2 m. D.	CMEI
(1) Weight Belt Conveyor, 4.4mL×0.6mL.	Merrick Scale Co.
(2) Double Flap Gate, 0.23m×0.30m.	Plattsburgh Inc.
(1) Nichols Herreshoff 10 Hearth Roaster, Diam. 6.53m, height 25m.	Nichols
(1) Central Shaft Cooling Air Fan, 50 HP	Robinson Ind.
(1) Central Unit Drive	
(14) 189.000Kcal/h Fuel Oil Burners	North American
(1) Combustion Air Turboblower, 40 HP	North American
(1) Process Air Fan, 15 HP	Robinson Ind.
(2) Cyclones, Diam. 0.84m.	Joy Mfg. Co.
(2) Double Flap Gates (Cyclone Discharge)	Plattsburgh Foundry Inc.
(2) Cyclone Dust Return Screw, Diam.0.19m.	Aggregate Equipment Inc.
(1) Double Flap Gate (Calcine Discharge) 0.3m×0.3m.	Plattsburgh Foundry Inc.
(1) Grizzly Assembly Hopper	CMEI
(1) Rotary Drum, 4.9mL×0.7mD	CMEI
(1) Discharge Water Cooled Screw Converyor, 1.3mL×0.3mD.	Christian Eng.
(3) Water Cooled Screw Conveyors in Series, 6.6mL×0.6mD.	Christian Eng.
(1) Belt Conveyor, 29mL.	
(1) Belt Conveyor, 37mL.	
(1) Pug Mill Mixer, 17tph, 3mL×0.7mD.	Renneburg Int.
(1) Second Discharge Line in Reserve	CMEI
2.) Gas Treatment	
(1) Post Combustion Chamber, 12mH×3mD	Nichols Eng.
(1) Post Combustion Process Air Fan, 15HP	Robinson Ind.
(1) Thermal Heat Exchanger, 2.5mL×1.74×7mH, Single Stage, 3 Tubebundles in series.	Thermal Transfer Co.
(1) Heat Exchanger Shot Cleaning System.	Hulter Co.
(1) Heat Exchanger Cooling Air Fan, 45HP	Robinson Ind.
(1) Intermediate I.D. Fan, 125 HP	Robinson Ind.
(1) Electrostatic Precipitator, 9mL×3.8mW×5mH. Collecting surface: 1240m2	Wheelabrator Canada.
(1) Collecting Screw Conveyor 9.6mL×0.3mD	
(1) Gas Mixing Chamber	Hatch Ass.Cons.
(1) Gas Mixer Air Fan, 75HP	Robinson Ind.
(1) Baghouse Collecting System, 3 Modules 3.8mL×3.3mW×5mH. Cloth area 3,281m2 total.	Wheelabrator Canada
(1) Final I.D. Fan System 400HP	Robinson Ind.
(1) Final Stack, 77mH×1.22×1.07mD	
3.) Arsenic Trioxide Packing	
20TPD Design	Olympic Assoc.
(1) Quality Control Bin, 5.7m3	Transco North West Inc.
(1) Storage Bin, 34m3	Transco North
(2) Storage Bins, 22.7 m3	Transco North
(2) Vacu-press	Universal Proc. and Plant Ltd.
(2) Drum Fillers	All-Fill

used as a source of plant heating. A shot-cleaning system is used continuously to clean accretions off the tubes.

At this stage the cooled gases, at 390 degrees C. plus/minus 10, are drawn into a variable speed intermediate blower which maintains a suitable negative pressure in the roaster and blows the gas into a two field jacketed electrostatic precipitator, which removes almost completely all particulate matter. Although the arsenic trioxide is in the vapour phase at this temperature, oxides of antimony and bismuth plus residual entrained concentrate are collected. This electrostatic precipitator, of 1240 m^2 area, requires careful maintenance and cleaning to maintain optimum efficiency, which results finally in the production of high quality crude arsenic trioxide. As an economy measure in the operation of this unit, waste heat from the heat-exchanger will soon be ducted to the jacket of this unit, which was designed to be electrically heated.

The dusts collected by the electrostatic precipitator are cooled and humidified to 9% in a rotary drum, and because of the high content of gold, silver, and copper are mixed with flotation concentrates for re-processing.

The cleaned gas stream leaving the electrostatic precipitator at 300 degrees C. plus/minus 10 is then rapidly cooled to 120 degrees C. in a hatch chamber by direct admixture with cold ambient air, which desublimates the arsenic trioxide. This hatch chamber has a patented design which causes co-axial precipitation. The cold air is drawn into the hatch chamber by a final blower, instead of an auxiliary fan as designed.

The precipitated crude arsenic trioxide is filtered out of the gas stream in a bag house consisting of 1834 teflon tubes contained in 5 modules. The loaded gas enters the bottom of the module and the arsenic trioxide is retained inside the filter tubes. Each module can be discharged by mechanical shaking of its retained arsenic trioxide while the other 4 continue in the filter cycle. This cycle is carefully controlled to limit the pressure loss due to the bag house.

Solid arsenic trioxide falls into bins beneath the bag house and is conducted by screw-feeders and elevators to the packing plant storage bins.

The filtered gas is drawn through a manifold by a final blower and passes up a fibre-glass stack of 1.2 m. diameter by 77 meters high. The final blower has a pressure controller to balance with the intermediate blower.

The arsenic trioxide packing plant has a design capacity of 16 t per 8 hour day, which can be stored in 4 bins. From these bins the arsenic trioxide passes through Vacu-press densifiers before filling 25 gallon and 30 gallon drums by means of All-Fill Feeders.

The 25 gallon drums, each containing 120 kgs plus/,minus 1, are strapped 12 to a pallet, while the 30 gallon drums contain 170 kgs plus/minus 1 and are packed 6 to a pallet. The pallets are trucked to port, and exported in containers.

Analyses of arsenic trioxide produced during recent months are shown in Table IV.

Some process modifications made recently include replacement of acrylic filters by teflon filters in the bag house, which have given far greatest resistance to high temperatures and acidity resulting in longer life and much more reliable operations, the installation of a temperature controlled bag house by-pass, reuse of filters after machine washing with a detergent for nci-

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TABLE IV. EL INDIO ARSENIC TRIOXIDE QUALITY

ELEMENT	MAY 1987		JUNE 1987		JULY 1987		AUG. 1987		SEPT. 1987	
		S		S		S		S		S
As_2O_3 %	97,5	0,71	97,3	0,84	97,0	0,95	97,4	0,32	97,4	0,32
Au gpt	<1,0	0,00	<1,0	0,00	<1,0	0,00	<1,0	0,00	<1,0	0,00
Ag gpt	<2.0	0.00	<2,0	0,00	<2,0	0,00	<2.0	0,00	<2.0	0,00
Cu %	0,06	0,07	0,05	0,03	0,12	0,18	0,05	0,02	0,10	0,04
Fe %	0,10	0,18	0,06	0,03	0,10	0,12	0,04	0,02	0,08	0,04
Te %	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00
Sb %	1,31	0,10	1,21	0,22	1,24	0,19	1,28	0,11	1,26	0,13
Bi %	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00
Se %	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00
Pb %	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00	<0,01	0,00
Zn %	<0,005	0,00	<0,005	0,00	<0,005	0,00	<0,005	0,00	<0,005	0,00
Hg ppm	28	52,5	7	3,6	4,3	48,7	15	7,8	15	5,8
SiO_2 %	0,13	0,07	0,14	0,06	0,24	0,09	0,12	0,03	0,16	0,07
Al_2O_3 %	0,03	0,01	0,03	0,03	0,05	0,05	0,02	0,01	0,03	0,01
H_2O %	0,08	0,07	0,19	0,22	0,20	0,31	0,33	0,34	0,17	0,25
Carbon %	0,12	0,05	0,07	0,03	0,09	0,08	0,04	0,01	0,05	0,02
PRODUCTION MT	269,28		394,56		383,04		309,60		363,96	

S = Standard Deviation

[redacted]

economy, and finally the recirculation of about 30% of the precipitated arsenic back to the hatch chamber to act as a nucleus for precipitation. This latter innovation has increased arsenic trioxide particle size from about 1 micron up about 4 microns, which has considerably improved bag-house efficiency.

Future Development

The newly implemented capacity increase in the flotation/cyanide plant, the added value to concentrates by roasting and a strong demand for arsenic trioxide provided the incentive to begin construction of a second identical roaster. This will result in a total roasting capacity of 130 - 150,000 t of concentrate per year, entering in service late 1989. With this expansion arsenic trioxide production should reach about 30 t per day.

Besides adding the second roaster complete with its own gas train, it is intended to improve the new electrostatic precipitator to three fields and add a third three field unit which can serve as a stand-by for either roaster. The result of these improvements to electrostatic collecting capacity will be to improve arsenic trioxide quality even further.

-With this expansion El Indio will rank as one of the leading producers of high quality crude arsenic trioxide.

At the laboratory level El Indio has investigated the refining of crude arsenic trioxide and the production of various arsenic salts, but for the moment no larger-scale tests are being undertaken.

Human and Environment Controls

The production of trivalent arsenic requires the control of humans and environment by a program designed to monitor biological effects on directly involved workers and sampling of the surrounding areas.

Routine biological monitoring, by the El Indio medical staff includes:

a) Complete medical examination of new employees.

b) Control of arsenic levels in urine of all involved workers, with temporary removal from the roaster area for levels above 210 micrograms per liter As. Frequency is twice per month.

c) Chest X-ray, once per year.

d) Skin and nasal examination. Frequency twice per month.

e) Blood-count analysis. Frequency once per year.

f) Biochemical tests of liver and kidney functions. Frequency once per year.

Environmental controls include:

a) Air samples - taken continuously by a variety of instruments.

b) Water samples taken from drainage streams, once per month.

These tests are applied to both inside the roaster building and the surrounding areas. Ref. 4.

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Marketing

The crude arsenic trioxide marketing policy of St. Joe Minerals Corp./ Compañía Minera El Indio was based upon a consultants report issued in 1981. Ref. 5.

This report showed total demand in 1980 as 41,800 tons arsenic trioxide, which included 18,000 tons of crude (normally defined as less than 99.0% of As_2O_3), with the expectation that by 1990 demand would have risen to 55,500 tons and 28,300 tons respectively. See Table V.

Table V. Aggregate Supply-demand Balance
(metric tons)

Year	Estimated Future: Production	Consumption	Balance
1981	46,400	47,000	- 600
1982	57,400	50,500	+ 6,900
1983	64,200	52,500	+ 11,700
1984	65,200	53,500	+ 11,700
1985	65,200 *	55,500	+ 9,700
1990	65,200 *	55,500	+ 9,700

Source: Consultex * The 1985 high/low scenario range runs from 96,700 tons to a low of 55,200.

Based upon installed roaster capacity it was expected that El Indio crude arsenic trioxide production would be about 5,000 t annually, which proved to be the case once initial start-up problems were overcome.

In view of the very limited market for crude arsenic trioxide a great deal of patience and determination to meet customers quality and packaging needs was required plus the preparedness to stockpile unsold product.

Among the market related problems that had to be overcome were, (1) the product bulk density was increased by a densifier, (2) impurities levels, particulary iron and carbon black had to be reduced by good dust collection in the gas train, and (3) packaging had to meet international regulations for a toxic product.

This marketing effort has required about 3 years, but now sales are in good balance with production, and El Indio feels reasonably confident that it is established as a long term supplier to the arsenic market.

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Acknowledgments

The authors wish to thank the management of holding company St. Joe Gold Corp. (control recently sold by Fluor Corp. to Dallhold Resources) and Compañía Minera El Indio for permission to publish this paper. They also wish to recognize the outstanding contributions of El Indio supervisors P. Pino (Plant Superintendent), J. Foster (Ass. Plant Superintendent), W. Morton (Roaster Foreman) and the strenuous marketing efforts of M. Warner (Sales Manager) and many other able employees too numerous to name individually.

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Solar-energy-powered water electrolysis may move closer to commercialization, following the announcement at Texas A & M University (College Station) of a high-efficiency electrode. According to John Bokris, head of the university's hydrogen research center, the use of inexpensive silicon in the electrode may pave the way for cheap, efficient production of hydrogen from water. Efficiencies of 10-13% (of the fuel value of hydrogen relative to the amount of solar energy intercepted) are possible, he says—at least an order of magnitude higher than previously reported systems (see, for example, *Chem. Eng.*, Oct. 18, p. 23). Further details were not revealed, pending a patent application, and Bokris notes that another two to three years of basic research, and several years of engineering, will be needed before the technology could become commercially available.

Ronan Sioda, a visiting lecturer in electrochemistry at the U. of Georgia (Athens) who is familiar with the Texas A & M work, says that its system is unusual in that the electrodes are not a homogeneous semiconductor material, but rather silicon coated by a thin layer of platinum or other metal. The metal layer, which conducts current to the surrounding solution for electrolysis, is thin enough to let light pass through to the silicon core, where its energy is converted to electricity. This "new angle" in electrode design, he says, "may provide an electrode that offers higher electrical conductivity [than semiconductors alone], while retaining the good photovoltaic properties of silicon, and protecting the silicon from chemical decomposition during operation."

A first-of-its kind facility producing arsenic trioxide from goldmine wastes has been started up by Cominco, Ltd. (Vancouver, B.C.) at its gold mine in Yellowknife, in Canada's Northwest Territories. The plant produces 15 metric tons/d of 99.8% arsenic trioxide from stack scrubbing wastes that the province's Water Board has declared a hazardous pollutant that must be removed. About $13 million (Canadian) was spent on engineering and construction of the facility, says L.R.B. Mullegama, project manager, who adds that the company sought an existing process it might use, "but we couldn't find one, so we developed our own."

In practice, the arseniferous sludge, containing about 20% water, is heated to 95°C and dissolved in a aqueous leach tank. A flocculant is added to thicken the suspended arsenic compounds, and hydrogen peroxide is added to ensure that only arsenic trioxide is formed and not other oxides. After separation, thickening and a second leach, arsenic trioxide crystals are recovered by a four-stage vacuum crystallization process, and dried with a centrifuge and a plate dryer. Mullegama says a critical problem was to provide steady feed during winter. This is expected to be overcome by building a heated, insulated shed over below-grade chambers that store 8,535 m^3 of sludge; heating comes from energy recovery from the crystallization step.

Arsenic trioxide is used in pesticides, desiccants and wood preservatives, and in glass clarification, and the U.S. Bureau of Mines estimates that about 900 short tons of pure arsenic will be manufactured in the U.S. this year. At Yellowknife, subsequent processing of the remaining residue will yield some gold and silver as well.

French researchers have piloted a new wine-stillage-to-methane process; now the hope is that funding can be obtained to build an estimated $700,000 industrial-size plant next year. André Bories, a researcher at the Station d'Oenologie et de Technologie

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