ENVIRONMENT PROTECTION GROUP

ENVIRONMENT AUSTRALIA

Treatment Technologies for Destruction

or Management of Arsenic Wastes

May 1998

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ENVIRONMENT PROTECTION GROUP

ENVIRONMENT AUSTRALIA
TREATMENT TECHNOLOGIES FOR ARSENIC WASTE

TABLE OF CONTENTS

GLOSSARY

ANZECC	Australian and New Zealand Environment and Conservation Council.
Chemical fixation	a chemical bonding between a waste material and a stable matrix.
Encapsulation	a process involving the complete coating (eg a sealed container) or enclosure of a waste particle or agglomerate with a binder within a matrix.
Microencapsulation	encapsulation of individual particles.
Macroencapsulation	the encapsulation of an agglomeration of waste particles.
Immobilisation	a broad class of waste treatments that physically or chemically reduce the mobility of hazardous constituents in a waste into their surroundings.
Precipitation	transformation of a material to an insoluble form by means of chemical additives.
Solidification	a process which converts liquids or sludges to stable solids.
Stabilisation	a general and non-specific term describing a chemical transformation to a more stable or less soluble form.

EXECUTIVE SUMMARY

This review has been initiated by Environment Australia to determine the availability of technology in Australia for the treatment of arsenic wastes. It is expected that the review will provide a useful resource for Environment Australia and industry in determining the availability of treatment facilities and the most appropriate strategy for managing such wastes.

In particular, the review is to focus on arsenic-contaminated wastes which may include:

?? organochlorine pesticides;

?? concentrated arsenicals;

?? concentrated arsenical mixtures; and

?? other arsenicals which have been contaminated with pesticides.

The review excludes arsenic contaminated soil, arsenic contaminated cattle dip sites, and arsenic wastes resulting from mining and mineral processing, except insofar as any treatment technologies used to treat these latter wastes are relevant.

Submissions were received from and/or discussions held with the suppliers of the following technologies:

?? Cement Solidification - Oretest
- Chemsal-Hudson
- Cleanaway
- Nationwide

?? Dolocrete

?? GeoMelt

?? Xtaltite

?? BCD Technologies.

?? Eco Logic

A summary of the review is presented in Table 1.

The review reaches the following conclusions:

?? There are no commercial facilities operating in Australia for the extraction or recovery of arsenic from wastes for the purposes of recycling and reuse. Extraction and recovery is unlikely to be commercially available in the future because of the relatively high costs of extraction and recovery, and the absence of a market for the product.

?? There are commercial facilities currently operating in Australia for the treatment of arsenical wastes by stabilisation with cementitious reagents and landfill disposal (eg Chemsal in Victoria, and ....). The process can be applied to concentrated arsenic wastes which do not contain organochlorine pesticides. The process may be applicable to arsenical wastes containing other contaminants such as hexavalent chromium but, in general, testwork will be required to confirm the application of the process to mixed waste types.

?? There are no commercially available facilities in Australia for the treatment of arsenic wastes containing OCPs. While there are commercial treatment facilities available for treatment of wastes containing OCPs, the presence of arsenic causes problems with the treatment process, and the treatment companies currently operating OCP treatment systems (BCD Technologies, ELI Eco Logic, and Haz-Waste Services) have advised that they are not able, nor are they interested in the short term, in treating OCP wastes that contain significant concentrations of arsenic.

?? Of the treatment technologies that are able to treat wastes containing both arsenic and OCPs, the Geosafe vitrification process (GeoMelt) appears to be the process closest to commercial availability.

It can be concluded that there are facilities available in Australia for treating wastes containing arsenic; however, there are no facilities currently available for treating wastes containing both arsenic and OCPs at high concentrations. The treatment systems currently available in Australia for treating OCPs are not able to be applied to OCP wastes that contain arsenic. Of the treatment technologies which may be available in the future, the GeoMelt process can be applied to mixed wastes of diverse physical form, and appears to be the process most likely to be established in Australia in the medium term. Location of a site and obtaining approvals would still have to take place, and to be commercially viable it would appear that the facility would have to win contracts for larger quantities of other wastes.

Table 1
Summary of Available Waste Treatment Technologies and Applicability

Company	Contact Details	Technology	Applicability	Comment
ADI Limited Technology Group Level 2, 77 Parramatta Rd Silverwater NSW 2141	Tai Truong Tech. Mngr Robin Apted Tel: 02 9350 9200 Fax: 02 9350 9140 or 02 9350 9275	Thermal Desorption	Organics. Inorganics would require separate treatment	Currently no service available. Can do OCPs but still working on arsenic contaminated OCPs.
Geosafe Australia P/L P O Box 6105 Halifax St Adelaide SA 5000	Leo Thompson Managing Director Tel: 08 8410 3133 Fax: 08 8410 3122	GeoMelt	Organics, heavy metals, including arsenic, and mixtures of these contaminants.	No existing facility for concentrated arsenicals; technology appears to be suitable but would require large batches. Characterisation of waste stream not required.
ELI Eco Logic Aust P/ L Lot 4 Mason Rd Kwinana WA 6167	Mr Craig McEwan Operations Manager Tel: 09 439 2362 Fax: 09 439 2363	Hydrogenation	Organics. Not suitable for arsenic.	Currently no service available.
Jancassco P/L Trading as Haz-Waste Services PO Box 4012 Dandenong South Vic 3164	Ken Carlisle Tel: 03 9706 7439 Fax: 03 9706 5162	Base Catalysed Dechlorination	Organics. Inorganics would require separate treatment	Currently no service available.
BCD Technologies Pty Ltd PO Box 119 Narangba Qld 4074	Martin Krynen Manager Tel: 07 3203 3400 Fax: 07 3279 3796	PLASCON Plasma Arc and Base Catalysed Dechlorination	Organics. Inorganics would require separate treatment	Currently no service available.
Cleanaway PO Box 450 East Melbourne Vic 3002	Cheryl Batagol Tel: 03 9270 7700 Fax: 03 9662 1456	Cement Solidification	Inorganic arsenic only in existing facility.	Feasible. Existing facility for arsenic.
Oretest Pty Ltd 12 Aitken Way Kewdale WA 6105	Jim Kyle Tel: 08 9353 3326 Fax: 08 9353 1028	Cement Solidification	Inorganic arsenic only.	Feasible existing facility.

Table 1
Summary of Available Waste Treatment Technologies and Applicability

Company	Contact Details	Technology	Applicability	Comment
Greg Eaton & Assoc. P/L Suite 10, 22 Haynes St Kalamunda WA 6076	Greg Eaton Tel: 09 257 2990 Fax: 09 257 2991	Xtaltite - Immobilisation by Chemical Fixation	Inorganic arsenic only.	Developmental, no commercial facility.
Nationwide Industrial Services 30 Potassium St Narangba QLD 4504	Bruce Heath Tel: 07 3204 0822 Fax: 07 3204 0816	Cement Solidification	Inorganic arsenic only.	Commercial facility, not licensed to treat OCPs or OPPs.
Chemsal P/L 83 Dohertys Rd Laverton N VIC 3026 (Chemsal/Hudson Joint Venture) C R Hudson & Assoc P/L 13 Barton Street Surrey Hills VIC 3127	Jason Cran/Steve Weber Tel: 03 9369 4222 Fax: 03 9369 4380 Craig Hudson Tel: 03 9899 4193 Fax: 03 9890 6538	Cement Stabilisation	Inorganic arsenic only.	Feasible. Existing facility for arsenic - Vic EPA licence approval.
Periclase Pty Ltd T/A Dolocrete International PO Box 2173, Burleigh Mail Centre QLD 4220	John Caroll Tel: 07 5593 6399 Fax: 07 5593 6086	Dolocrete Encapsulation	Inorganic arsenic and organics contaminated with arsenic	Technology appears to be suitable
Geo 2	Gottfried Lichti Tel: 03 9337 0715			

1. INTRODUCTION

This review has been initiated by Environment Australia to determine the availability of technology in Australia for the treatment of arsenic wastes. It is expected that the review will provide a useful resource for Environment Australia and industry in determining the availability of treatment facilities and the most appropriate strategy for managing such wastes.

The purpose of the review is to draw together all relevant information on treatment technologies for the destruction or management of arsenic contaminated wastes, particularly those associated with organochlorine pesticides, but including concentrated arsenicals, concentrated arsenical mixtures, and other arsenicals which have been contaminated with pesticides.

During the review, technology and waste treatment providers were contacted to obtain relevant information on the technologies available in Australia. The groups contacted were those known to be active in this field.

Waste treatment technologies are in a state of constant change, and there is continual development occurring which results in new technologies being introduced, and which may also extend the capability of existing technologies. Therefore, this report is not considered to be a comprehensive review of all applicable waste treatment technologies, and the omission of technologies should not be interpreted as indicating that such technologies are not suitable for the treatment of arsenic wastes.

2. ARSENIC WASTES

2.1 Definition of the Wastes

The *National Strategy for the Management of Scheduled Waste* was agreed to by the Australian and New Zealand Environment and Conservation Council (ANZECC). The *National Strategy* aims to establish, through nationally agreed management plans, requirements for the safe management of scheduled wastes. Scheduled wastes are defined by inclusion on ANZECC's Schedule X. Arsenic is not, at present, listed as a scheduled waste. Nevertheless the management and treatment of arsenical wastes is an important issue as they are often mixed with scheduled wastes.

Three management plans have been completed under the *National Strategy*: polychlorinated biphenyls, hexachlorobenzene waste, and organochlorine pesticides (in-principle endorsement).

Arsenic is a common and often problematic waste, which has been used widely as a weedicide and pesticide. It can also be present in waste pesticide mixtures. Because arsenic is not a scheduled waste, a management plan will not be prepared for arsenic-containing wastes under the *National Strategy*.

In particular, the review is to focus on arsenic-contaminated wastes which may include:

- organochlorine pesticides (OCPs);
- concentrated arsenicals;
- concentrated arsenical mixtures; and
- other arsenicals which have been contaminated with pesticides.

The review excludes arsenic contaminated soil, arsenic contaminated cattle dip sites, and arsenic wastes resulting from mining and mineral processing, except insofar as any treatment technologies used to treat these latter wastes are relevant.

2.2 Background

Arsenical wastes are difficult to manage, as it is not possible to "destroy" the material (although it is possible to destroy organic wastes such as pesticides which are mixed with the arsenic). Ultimately, arsenic must be converted to a form which can be safely placed and contained within a landfill or repository. Typically this will involve some form of stabilisation, immobilisation and/or encapsulation.

Because of this, a key question to ask is whether the arsenical waste can be treated (eg stabilised) directly for final disposal, or whether pretreatment is necessary to destroy other wastes (typically OCPs) which are present with the arsenical waste. Arsenic wastes which contain the threshold concentration of OCPs (50 mg/kg OCPs) are defined as scheduled OCP waste. This type of waste is not permitted to be disposed of to landfill, and it would required treatment to destroy the OCPs in accordance with the OCP Waste Management Plan (Draft). Organochlorine arsenical pesticide wastes containing OCPs at 2 mg/kg or less are classified as exempt OCP waste (ie not subject to the OCP Management Plan[1]).

In most cases, the practice in Australia has been to stabilise the waste directly (rather than treating the organic portion of the wastes); however, whether this is satisfactory depends on the form of the other wastes, and the acceptance criteria that are to apply in the landfill or repository to where the stabilised wastes are destined.

Alternatively, arsenic can be recovered from the waste through an extraction process and be reused in the preparation of arsenic based products. As the horticultural/agricultural uses of arsenicals are now restricted and its use in glass making is minor, the major use of arsenic today is in the manufacture of Copper-Chromium-Arsenic timber preservative preparations. Therefore, theoretically arsenic could be recovered and reused in these preparations, provided a quality of greater than 98% arsenic can be produced. In practice, this may be very difficult to achieve given the wastes to be treated are highly variable mixtures. A regular supply in commercially viable quantities would also be required. Purification processes also require good control of occupational exposure to arsenic either as a vapour or a solution, each of which are potentially more harmful than the solid waste. However, if no market exists for the recovered arsenic, an extraction process is of no discernible benefit in the management and treatment of such waste streams.

It should also be recognised that the quantities of concentrated arsenicals are relatively small and, in general, it is necessary for economic reasons to use existing treatment facilities wherever possible. The establishment of advanced treatment systems, other than stabilisation, is unlikely to be economically feasible unless contracts are to be let for the treatment of significant quantities of consolidated arsenical wastes. Such consolidated stores may encourage investment into further research and development, and associated treatment plants.

2.3 Physical and Chemical Characteristics of the Wastes

In practice the wastes are in the form of mixtures, and may include organic and inorganic forms of arsenic, a variety of OCPs and other substances (eg lead, sulphur), and therefore the wastes would require some degree of characterisation (ie nature and concentration of contaminants) prior to treatment with some of the technologies discussed.

[1] ANZECC (1997) *Draft Final Organochlorine Pesticides Waste Management Plan*, Scheduled Wastes Management Group, May 1997.

This review focuses on concentrated arsenicals, and excludes soil or other bulk media contaminated with arsenic wastes. It is expected that most wastes will be in the form of concentrated powders, with liquids forming a smaller proportion of the waste stream.

Part of the liquid waste stream arose from the chemical collection programs. Rinsate from the original waste containers formed part of the waste stockpile during redrumming operations.

Pretreatment may be limited to removing the organic component of a waste, to enable treatment of a concentrated inorganic form of arsenic. Inorganic arsenic may be present as arsenite (As^{III}) or arsenate (As^{V}). Arsenite may need to be oxidised to arsenate prior to stabilisation/solidification to ensure the treated product would meet Toxicity Characteristic Leaching Procedure (TCLP) test criteria.

These forms of arsenic have been used in 'Paris Green' (a copper arsenate) and enamels; for preserving hides; in killing rodents and insects; and in sheep dips and weed killers. Arsenic trioxide was used in cattle dip during the first half of the century and may sometimes be found in association with high levels of DDT.

Arsenic trioxide has a melting point of 275?C, and a boiling point of 465?C, but when slowly heated sublimes. Vapourisation of arsenic becomes apparent at 100?C and is rapid at 450?C. Sublimation occurs at temperatures in excess of 600?C.

2.4 Occupational Health and Safety

The proper handling of waste arsenicals during pretreatment and treatment is essential due to their toxic nature. The identification and proper labelling of waste materials will assist in deploying appropriate procedures for the decanting or transfer of wastes for treatment purposes and may include:

?? ventilation and extraction systems; and

?? the use of personal protective equipment, such as gloves and filter masks.

Material Safety Data Sheets (MSDSs) are available for most chemical products and should be referred to when developing procedures to protect occupational health and safety.

The responsibility for occupational health and safety rests with the treatment plant operator to ensure all wastes and process by-products (if any) are handled in an appropriate manner.

2.5 Technologies considered in this Review

The technologies reviewed have been limited to those for which submissions were received. Discussions with potential technology suppliers indicated that there are other processes which may be suitable for the treatment of arsenical wastes, but the suppliers were not in a position to provide information regarding the process at the time of this review.

Submissions were received from (or discussions were held with) suppliers of the following technologies:

?? Cement Solidification - Oretest
- Chemsal-Hudson
- Cleanaway
- Nationwide

?? Dolocrete

?? GeoMelt

?? Xtaltite

?? BCD Technologies.

?? ELI Eco Logic

?? Geo 2

Although some attempt has been made to verify the information provided by the various proponents it is beyond the scope of this project to verify every claim made with respect to the performance, capacity and availability of the technologies discussed.

2.6 Basis for the Evaluation of the Technologies

The review aims to provide an analysis of the status of the technologies available in Australia for the treatment of arsenic wastes, with the purpose of identifying those technologies that are able, or potentially able to destroy the wastes identified in Section 2.1. The technologies identified have been evaluated with respect to:

?? the waste streams to which the technology may be applied including any components in the waste which place limitations on the application of the technology;

?? the basic chemistry of the treatment technology;

?? the current level of development of the technology, the extent of full scale, commercial operational experience (if any) or the likely time frame for the commencement of commercial operations;

?? the estimated set up and treatment costs for arsenic waste streams;

?? information on the nature of the treated material, the nature of any by-products, disposal options for the treated material, and verification methodology for treated material;

?? information on other process emissions;

?? information on the reliability and safety of the process;

- information on the overall energy or fuel usage of the process;
- information on pre-processing requirements and limitations;
- verification methodology for treated wastes; and
- the ease with which any residuals are able to be disposed.

Not all respondents provided information for all of the areas listed above. It is apparent that many specialised proprietary reagents are used in some technologies and that proponents of the technology do not wish to divulge the nature of these reagents.

3. CEMENT SOLIDIFICATION

3.1 Oretest Pty Ltd

3.1.1 Introduction

Oretest Pty Ltd in Western Australia utilise cement solidification for the treatment of arsenic waste. Cement solidification is a generic technology for the stabilisation and disposal of a range of inorganic wastes, especially those containing toxic metal such as mercury, cadmium, copper, nickel, lead and chromium. It can also be used to stabilise inorganic arsenic in the form of arsenite(As^{III}) or arsenate (As^{V}).

The technology, because of its reliance on cement to provide a physical and chemical barrier to dissolution of the waste components, is not suitable for use with wastes containing organic components.

3.1.2 Technology Description

Free lime in the cement reacts with the arsenite(As^{III}) in the waste to form an insoluble precipitate of calcium arsenite(III). This precipitate is highly insoluble above pH 10-11. The cement contains sufficient free lime to ensure the pH in the cement remains above the pH for dissolution, and hence retains the arsenic as an insoluble precipitate. The cement matrix also acts as a barrier to intrusion of leaching solutions, and extrusion of soluble species. When and if the pH drops, the rate of leaching of the arsenic is very slow, resembling diffusion through a clay barrier.

3.1.3 Proponents

Oretest Pty Ltd in Perth, Western Australia.

3.1.4 Performance

Oretest state that concentrated arsenic wastes are not large waste streams, and can therefore be treated onsite using portable equipment such as a cement mixer truck. The waste-cement-water mixture is poured into drums or bulk bags and allowed to set prior to disposal in a suitable landfill. Quality control (verification) is by TCLP on each batch of waste, with each batch being approximately 1 to 2 tonnes.

3.1.5 Availability in Australia

Oretest has applied this process to large scale waste treatment, of the order of 100 to 150 tonnes per project.

3.1.6 Cost

Costs of cement solidification are generally in the range $800 to $1,000 per tonne plus disposal costs. Disposal costs are generally high due to the fact that the total mass of waste to be disposed is two to three times the total mass of the waste stream.

These costs include equipment hire, commissioning and decommissioning. Energy costs are low.

3.1.7 Safety and Environmental Risks

Oretest state that the treated material is similar to concrete, but with a lower compressive strength. Depending on requirements, the treated material can be set in drums, bulk bags or a tailings dam. There are no process emissions for suitable waste streams. However, the long term stability of the waste is unknown. When intrusion rates of leachants are low, and in low rainfall environments, leaching rates are estimated in geological time frames. The process has had a long history in the US. It is a low technology process using existing equipment, and all reactions occur at ambient temperature. It is therefore safe, reliable and easy to control.

3.1.8 Limitations

The limitations of cement stabilisation technology are:

?? that the original volume of waste is increased (sometimes substantially) by the addition of the immobilisation media;

?? the large mass of waste that is generated which must be disposed to landfill;

?? the process is generally only applicable to inorganic waste streams, or residues from furnace processes; and

?? the long term stability of the waste is unknown.

3.2 Chemsal-Hudson

3.2.1 Introduction

A joint venture was developed by the Chemsal Group of companies and C. R. Hudson and Associates Pty Ltd which utilises a an immobilisation/stabilisation process for the treatment of concentrated arsenic wastes. Arsenic containing sheep dip chemicals, which were prohibited in Victoria in 1987, were the primary target for this work. During the research and development of this process over 50 other techniques and variations were examined, including the use of ferric iron salts to produce ferric arsenate. For the stoichiometric formation of ferric arsenate, large quantities of ferric salt are required giving rise to a 25-30 times bulking factor which is unacceptable according to Chemsal-Hudson. In addition, the Chemsal-Hudson research indicated better TCLP performance with the specialised calcium arsenate approach than the ferric arsenate approach.

3.2.2 Technology Description

The Chemsal-Hudson immobilisation/stabilisation process occurs in two stages. The first stage involves the pretreatment of arsenic based materials in a slurry reactor with the prime aim being to convert all arsenic present to the pentavalent state. This process is tailored to the specific type of material in question and is applicable to solids, liquids and sludges. The second stage converts the arsenic to calcium arsenate by the addition of lime (pH>12) and a blend of cementitious reagents that provide secondary binding of the calcium arsenate into the cementitious matrix ensuring low arsenic TCLP (<5 mg/L arsenic).

3.2.3 Proponents

C R Hudson & Associates in a joint venture with Chemsal Pty Ltd, North Laverton, Victoria.

3.2.4 Performance

Chemsal-Hudson state that wastes containing up to 70% arsenic can be treated, and that their stabilised product readily complies with TCLP leachability requirements of 5 mg/l arsenic for disposal at a suitably licensed landfill.

The plant is capable of processing a wide range of arsenic based chemicals that include, but are not limited to, the following:

- arsenic trioxide-sulphur-rotenone formulations;
- lead arsenate;
- calcium arsenate/arsenite;
- sodium arsenate/arsenite;
- arsenic contaminated soils;
- copper/chrome/arsenate (CCA) sludges;
- arsenic/heavy metal mixtures; and
- arsenic/phenolic/cresylic mixtures.

The materials handling systems are suitable for the processing of powders in sachets and drums, soils, liquids, and sludges.

3.2.5 Availability in Australia

Chemsal-Hudson established their arsenic treatment process in February 1998 under the Victorian EPA Works Approval and Licensing system and is operating on a commercial scale processing a range of concentrated arsenic wastes. It is currently processing Victorian EPA stockpiles of arsenic based agricultural chemicals.

3.2.6 Cost

Plant throughput depends on the materials in question, but can be assumed to be of the order of five to ten tonnes per week. Costs are dependent on the particular waste, but generally will be in the range of $5 to $10 /kg.

3.2.7 Safety and Environmental Risks

The Chemsal-Hudson facility is fully enclosed within a building with all waste handling and processing areas being negatively vented to a dual venturi/packed bed, wet scrubbing system. Detailed attention has been given to the safe depackaging, handling, and processing of arsenic based chemicals.

3.2.8 Limitations

The limitations of cement stabilisation technology are previously stated.

3.3 Chemsal Remediation Pty Ltd

3.3.1 Introduction

Chemsal Remediation Pty Ltd is another joint venture company that combines the infrastructure and expertise of Chemsal with that of Pollution Solutions (Remediation) Pty Ltd of Tasmania. The joint venture is currently pilot testing proprietary technology that has to date demonstrated success in bioremediating an OC/arsenic matrix under benchtop conditions. Under an EPA R&D works approval, Chemsal Remediation is in the process of commissioning two five tonne batch reactors to demonstrate the performance of the technology.

3.3.2 Technology Description

The technology being deployed is bioremediation. Although this technique typically has a number of control and management problems *in situ,* by using a batch process the engineering of optimal conditions (eg nutrient, moisture, pH, oxygen, etc) for the bioremediation of OCPs and other organics can be more readily achieved and maintained.

The company offers a trial of the waste being considered for treatment in a laboratory pilot plant and can usually tell within about two to three weeks whether the waste is suitable for bioremediation by this technique. The exact details of this developmental technology is being kept secret at present.

3.3.3 Proponents

Chemsal Remediation Pty Ltd, joint venture company formed by Chemsal Pty Ltd and Pollution Solutions (Remediation) Pty Ltd.

3.3.4 Performance

It is intended that the product from the pilot plant will be streamed into the arsenic treatment plant for final processing to comply with TCLP leachability acceptance criteria at a licensed landfill. The bioremediation plant is expected to have the capability to treat arsenical compounds contaminated with:

?? organophosphates;

?? polycyclic aromatic hydrocarbons (PAHs);

?? PCBs;

?? aromatic hydrocarbons;

- aliphatic hydrocarbons;
- phenols;
- cresols; and
- halogenated solvents and compounds.

It is intended that the plant would be engineered with the same level of process control and safeguards as the existing arsenic treatment plant.

3.3.5 Availability in Australia

It is anticipated that trials will be complete by August 1998, and it is proposed to commercialise the process by erecting one or two 40 tonne batch reactors (dependent on market demands) during the latter part of 1998.

3.3.6 Cost

Processing costs for bioremediation only, depending on the concentration and complexity of the waste matrix, are expected to range from $5,000 to $10,000 per tonne.

3.3.7 Limitations

The process is not yet commercialised. Following completion of the trials at the end of August this year, further information on the performance and limitations of the process will be available.

Historically, the bioremediation of persistent organochlorine type wastes has not been generally successful. For example, the biodegradation of OCPs such as DDT is known to be difficult. Achieving consistently effective biodegradation of wastes of varying composition and in the presence of arsenic, and potentially other co-contaminants such as copper, lead and chromium, is likely to be very difficult. However, initial results provided by the proponent appear promising.

3.4 Nationwide Industrial Service

3.4.1 Introduction

Nationwide Industrial Services (a division of Nationwide Oil Pty Ltd) specialised in the treatment of difficult to treat waste streams, including arsenicals, using cement fixation technology.

The technology used is capable of handling concentrated arsenicals and arsenical mixtures, particularly sodium arsenite and copper chrome arsenate. Nationwide's existing licence precludes the treatment of organochlorine pesticides (OCPs) or organophosphorus pesticides (OPPs), although such compounds as disodium monomethyl arsonate (DSMA) can be treated.

3.4.2 Technology Description

The basic chemistry of the technology is to form an insoluble arsenic salt (normally a ferrosilicoarsenate or similar species) which is then physically bound within a mixture of flyash and cement. The flyash/cement system acts as both as an entrapment matrix and as a chemical (pH) buffer to prevent re-dissolution of the ferroarsenate.

3.4.3 Proponents

Nationwide Industrial Services, Narangba, QLD, a division of Nationwide Oil Pty Ltd.

3.4.4 Performance

The treated material is a clay-like solid which may be disposed of at a landfill, subject to local or regional regulations. The material must pass appropriate leaching tests prior to disposal. The method appears to be robust, reliable and safe.

3.4.5 Availability in Australia

The technology is fully commercialised and has been used by other treatment facilities for at least 10 years. Nationwide Industrial Services has commercialised the process at their site in Queensland over the last 8 months.

3.4.6 Cost

Not stated. No additional set up costs to those already in place. Energy use is low and there are few, if any, preprocessing requirements. The bulking that results from the use of iron salts and cement can be considerable, and consideration must be given to the cost of landfill disposal of the resultant mixture.

3.4.7 Safety and Environmental Risks

Nationwide state that there are no process emissions

3.4.8 Limitations

Organic components in mixtures may preclude treatment, and OCPs and OPPs are excluded due to licence conditions.

A cheap source of iron is required.

The limitations of cement stabilisation technology are previously stated.

3.5 Cleanaway

3.5.1 Introduction

The waste streams treated by Cleanaway Technical Services (CTS) in Dandenong, Victoria include:

?? CCA treatment (plant residues);

?? copper arsenate residue from phosphate fertiliser manufacture;

?? arsenic pesticides (Coopers Sheepdip) recovery of arsenic.

The principal components of CCA are copper, chromium (hexavalent) and arsenic which are present in percent levels (1 to 10 %). The wastes are generally contaminated with gross solids such as wood, bricks and soils.

Cleanaway Technical Services in Newcastle NSW has been treating arsenic wastes since 1992. This included a variety of arsenic contaminated wastes and materials, with concentrations ranging from parts per million to 50% arsenic. The quantities treated range from small kilogram collections up to 300 tonnes of arsenic sludges and 160 cubic metres of contaminates solid process materials.

The material treated ranged from laboratory chemical and farm chemical collections, to obsolete sheep dip, industrial wastes, contaminated materials from manufacturing plants, and arsenic reclamation industries.

3.5.2 Technology Description

The general chemistry used at Dandenong for treatment of CCA treatment plant residues involves reduction of the hexavalent chromium, followed by neutralisation and fixation with cement.

Arsenic pesticides such as Coopers Sheepdip are treated for extraction and recovery of the arsenic. The general chemistry involves oxidation of the arsenic trioxide, filtration to remove the sulphur component, purification and concentration by a precipitation and extraction process. The end products are:

?? an arsenic acid solution suitable for use in the manufacture of CCA formulations; and

?? a chemically fixed sulphur cake containing some arsenic residues, which requires disposal in a secure landfill.

The only preprocessing required is the decanting of the drums of waste, or bags of Coopers Sheepdip powders.

Coopers Sheepdip requires correct identification of the feed material, and the final arsenic extract must meet the specifications for preparation of CCA formulations.

The treatment process in use at Newcastle varies depending on the material being treated and the concentrations involved. It usually includes the following in a batch process:

?? chemical treatment to convert the arsenic to a suitable form for fixation (eg oxidation to the pentavalent state);

?? chemical fixation;

?? encapsulation or microencapsulation, depending on the nature of the materials being treated;

?? immobilisation; and

?? disposal in a suitable licensed landfill site.

3.5.3 Proponents

Cleanaway Technical Services, Dandenong and Newcastle

3.5.4 Performance

Cleanaway in Dandenong state that the final fixed material has the appearance of friable soil, which is disposed of at a Victorian EPA licensed secure landfill as a prescribed waste. After a number of years of experience, the process has demonstrated to be reliable in reaching the required TCLP limits for the fixed metals. Each batch of cured fixed product is tested prior to disposal to landfill.

The final arsenic extract from Coopers Sheepdip requires analysis to ensure conformance with the specifications for the levels of contaminants that can be tolerated in the preparation of CCA formulations.

Cleanaway in Newcastle provided the following information on the performance of the fixation process during the last two years

Waste Type	% Arsenic in untreated waste	No of batches	TCLP results (As) after fixation (mg/L)	TCLP limit for landfill disposal as solid waste
Arsenic sulfide (Sheep Dip)	38 %	13	0.2 to 1.4	5 mg/L As
Mixed Arsenic Waste from manufacturing plants	0.5 to 15 %	29	<0.1 to 3.5	5 mg/L As
Copper chrome arsenate (CCA) from wood preservative	22 % As 33 % Cr 14 % Cu	5	0.13 to 0.2 As 0.07 to 0.32 Cr 0.06 to 0.15 Cu	5 mg/L As

3.5.5 Availability in Australia

Cleanaway in Dandenong currently implement the cement fixation technology for treatment of CCA treatment plant residues and copper arsenate residue from phosphate manufacture. These waste streams have been processed at this site for several years and are treated on a commercial scale. Approximately 100 tonnes per year are processed.

The technology for the recovery of arsenic from Coopers Sheepdip is not currently available at Cleanaway. It has been demonstrated on a bench scale.

Cleanaway in Newcastle are currently using the processes described above as well as trialing new processes.

3.5.6 Cost

Set up costs include earth moving equipment, fixation mixing bays and curing areas. Treatment costs include chemicals, equipment and labour, and final transport and disposal. Energy requirements are limited to the fuel usage of the earth moving equipment.

The capital cost of treatment of Coopers Sheepdip has been estimated as $250,000 for plant. Assuming there is a market for the end product, an arsenic acid solution, the cost of extraction would be recovered by the sale of the product. Otherwise, the end product would require further treatment, such as cement stabilisation. Energy use is not a significant component of the processing costs, however, analysis of the final product is required.

The only recognised market for arsenic in Australia is the manufacture of CCA formulations for the Treated Pine industry, therefore the viability of extraction and recovery of arsenic is dependent on this market.

3.5.7 Safety and Environmental Risks

Generally no emissions occur during the processing of the waste material. Any drums of dry material are wetted down prior to processing. Testing of the cured fixed product ensures compliance with the receiving landfill’s licence requirements. Testing is conducted by a NATA registered laboratory.

Dust and process emissions associated with the treatment of Coopers Sheepdip would be controlled by suitable collection and scrubbing systems. The reliability of the process is dependent on the consistent nature of the feed stock, and Hazop studies would be used to engineer the risks to a minimum. The chemically fixed sulphur cake would require TCLP analysis to conform with landfill licence agreements.

3.5.8 Limitations

The limitations of cement stabilisation technology are previously stated.

The treatment of arsenic pesticide (Coopers Sheepdip) is limited to when the formulation is in its commercial package. The process is also susceptible to contamination from other metals, particularly iron, and from organic compounds.

The end use of the extracted arsenic is dependent on a market in the Treated Pine industry.

4. DOLOCRETE ENCAPSULAT ION TECHNOLOGY

4.1 Introduction

Periclase Pty Ltd is an R & D company researching materials for the building and construction industry, and encapsulation technology for the safe disposal of toxic waste. The Dolocrete Encapsulation Technology has been developed by Periclase Pty Ltd over four years. The first trial was conducted in January 1996 on arsenic and toxic metal based waste. The technology is applicable to all waste streams with the only limitation being on current allowable practices and landfill limitations.

4.2 Technology Description

Dolocrete may be described as an alternative cementitious material capable of binding together a variety of aggregates, not normally associated with conventional concrete. The main component is "Doloment" which when mixed with a proprietary catalyst additive "Minic" to an aggregate mix, forms a "Dolomitic Cement". The basic technology involves solidification of the matrix with microencapsulation of the waste material. Chemical bonds form within the natural magnesium based matrices. Encapsulation is effected by mixing the waste material with selected readily available chemicals.

The technology differs from conventional cements where additives for concretes are liquid and are added during the mixing process. In Dolocrete technology, a pre-blended powder which include the catalyst (Minic) additive is required to be fully dissolved in the mixing water, prior to adding the mixing water to the agglomerate mix. Use of the powder needs careful supervision to ensure it is fully dissolved prior to use, however the mixing water does not have to be clean and sea water may be used.

A pan-type mixer, having a positive paddle or screw action, is considered to provide the optimum mixing. Drum mixers, using a gravity mixing action, do not function well with the low water Dolocrete mixes, as cohesion of the mixes prevents material falling away from the drum sides during rotation. The resultant dolocrete slurry is then used as an integral part of a settable composition to effectively contain many waste materials in a manner that exceeds the requirements of less than 5 mg/L of the waste elements in the leachate.

The treated material can be given structural integrity, with the strengths required controlled in the treatment process. Tests are normally conducted at 14 days after treatment and again at 28 days, This is generally the longest time needed for solidification and bonding of the process.

Where using cement technology is not always suitable for wastes containing organic material, the Dolocrete Technology encapsulates organic wastes without affecting the integrity of the hardened matrix.

4.3 Proponents

Periclase Pty Ltd trading as Dolocrete International.

4.4 Performance

Trials have been conducted on a variety of waste samples provided by groups including:

- Clough Engineering: waste samples containing an arsenic concentration of 1.405 % in the waste material. After encapsulation and containment using the Dolocrete Encapsulation Technology, leachable fractions results were reported as less than 0.1 mg/L;

- Brisbane City Council: waste metal plating solution containing primarily zinc, copper and nickel with leachate concentrations after treatment of <0.05 mg/L, (zinc and copper) and <0.1 mg/L (nickel);

- From a cattle dip site: soil contaminated with approximately 585 mg/L arsenic, Following treatment results of TCLP analysis were <0.1 mg/L arsenic;

- Department of Primary Industries: 200 L concentrated arsenical pesticide waste. Results of TCLP analysis ranged from 1.5 to 1.9 mg/L arsenic;

- EPA Vic: trialed sodium arsenate waste, sheep dip waste, coal tar and rotenone waste containing 47 % to 72 % arsenic. TCLP analysis results reported 1.6 mg/L arsenic for the liquid sample and 2.3 mg/L for the solid sample.

Wastes able to be treated include organochlorine/arsenical pesticide wastes, and the treated waste is suitable for disposal in conventional landfill sites.

4.5 Availability in Australia

Full scale commercial trials have been successfully completed on arsenic based pesticide wastes and the commencement of commercial operations awaits completion of formal licensing requirements and commissioning of necessary equipment to prepare a supply of the Dolocrete materials in commercial quantities (approximately three months).

4.6 Cost

Costs vary depending on the application:

- mobile units may be employed to treat the arsenical wastes streams *in situ*;

- the waste material will be transported to a licensed treatment facility; or

- the waste may be treated by the generators.

Costing of these processes is “job specific” depending upon the type and concentration of the contaminants to be treated, but ranges from $500 to $8000 per tonne.

Some “low level“ industrial-type wastes (eg CCA waste from timber mills) can be satisfactorily treated and disposed of for approximately $200 to $500 per tonne.

Energy and fuel usage of the process is low. It is merely a mechanical procedure involving blending, mixing and discharge of the materials. At the end of the process, the material is discharged showing a slump of approximately 140 to 160 which may be poured into drums or moulds for curing and subsequent disposal.

4.7 Safety and Environmental Risks

The treated product is a hard concrete-like mass. Dolocrete states that there are no process emissions, and no by-products as a result of the process. All wastes are incorporated in the treated material, including, eg, contaminated overalls and gloves worn for protection. The reliability and safety of the process is governed purely by mixing formulae and good work practice. No inherent problems accompany the treatment material or the process.

Verification of the treated material is by TCLP analysis.

4.8 Limitations

The current allowable disposal options are, by regulation, restricted to landfill. Only those organochlorine arsenical pesticide wastes with less than 50 mg/kg OCPs would be suitable for treatment and disposal to a suitable landfill. Future options (with acceptance of the technology) may include construction projects, eg, as road base material.

5. GEOMELT

5.1 Introduction

The GeoMelt technology is a family of vitrification technologies developed around the *in situ* vitrification (ISV) process. The GeoMelt processes are commercially available mobile, thermal treatment processes that involves the electric melting of contaminated soils, sludges, or other earthen materials, wastes and debris for the purposes of permanently destroying, removing, and / or immobilising hazardous and radioactive contaminants. The GeoMelt-ISV process was developed by Battelle, Pacific Northwest National Laboratory, for the US Department of Energy. The ISV technology has been licensed to Geosafe Corporation and Geosafe has used ISV to successfully treat a number of Superfund sites in the US Geosafe has since developed the ISV process into a wider range of vitrification technologies. The GeoMelt processes are widely applicable to all soil types and all classes of contaminants including organics, heavy metals and radionuclides. The processes are available in Australia through Geosafe Australia Pty. Ltd. The GeoMelt-ISV process is being used at the Maralinga site in South Australia to treat burial pits containing soil and debris contaminated with plutonium and uranium as well as lead, barium, and beryllium.

The GeoMelt process has been successfully used to treat concentrated wastes, including arsenic-bearing waste agricultural chemicals overseas. For this application, the drummed wastes were simply mixed with soil to facilitate the treatment process.

5.2 Technology Description

The GeoMelt process is a batch process that involves forming a pool of molten soil in a treatment zone between an array of four electrodes. The molten soil serves as the heating element of the process wherein electrical energy is converted to heat via joule heating as it passes through the molten soil. Melt temperatures typically range between 1,500 - 2,000°C. Continued application of energy results in the melt pool growing deeper and wider until the desired volume has been treated. When electrical power is shut off, the molten mass solidifies into a vitreous monolith with unequalled physical, chemical, and weathering properties compared to alternative solidification / stabilisation technologies. Individual melts up to 7 m deep and 15 m in diameter are formed during commercial operations. Large volumes of contaminated material requiring more than one batch melt are treated by making a series of adjacent melts resulting in the formation of one massive contiguous monolith. The process is operated on an around the clock basis and can achieve treatment rates of up to 150 tonnes per day.

A stainless steel hood is employed, under a slight vacuum, to collect off-gases from the treatment zone. The off-gas treatment system can be designed to meet site specific requirements.

The GeoMelt processes can be configured in several different ways to treat soils and wastes. The three primary treatment modes are as follows:

?? The GeoMelt-ISV process is the original GeoMelt process. ISV is used to treat contaminated soils and wastes *in situ*, where they are located, without the need for excavation and or other handling. This treatment method is referred to as the GeoMelt- *in situ* mode of treatment.

?? For many projects, contaminated soils, wastes and debris from a variety of on-site locations are collected and staged in a treatment area. This approach allows for more efficient treatment and provides the site owner the opportunity to consolidate many different waste streams. Liquid or concentrated drummed wastes can be mixed with soils and absorbents and treated in the configuration. This treatment configuration is referred to as the GeoMelt-staged *in situ* mode of treatment.

?? A third method of GeoMelt treatment involves the operation of a stationary batch treatment facility. This method involves an on-site treatment facility where wastes are brought to the treatment facility, staged in one or more reusable treatment cells, the wastes treated, the treated product removed from the cells, and the cells reused to treat additional wastes. The facility can be enclosed inside a building if desired. The treated product can be removed in solid form or can be discharged in its molten state. This treatment configuration is referred to as the GeoMelt-stationary batch mode of treatment.

GeoMelt processes result in a 25-50% volume reduction for most soils, and up to a 75% volume reduction for sludges and wastes that de-water and/or decompose during processing.

The volume reduction results in a subsidence volume above the vitreous monolith. In most GeoMelt-ISV or GeoMelt-staged *in situ* applications, the subsidence volume above the melts is filled with clean soil and the monoliths are left in the ground since they are no longer hazardous. Sites treated by the GeoMelt process are normally capable of future use without restriction associated with the vitreous monolith. However, if site requirements dictate that the monoliths be removed, the vitrified monoliths can be fractured and removed with conventional heavy equipment.

5.3 Proponents

Geosafe Australia Pty Ltd offer a range of vitrification technologies, called GeoMelt technologies.

5.4 Performance

The US EPA has evaluated the vitrification of arsenic wastes and considers vitrification to be the best demonstrated available technology for many arsenic compounds. Arsenic concentrations in glass in excess of 20 weight percent have been attained. Geosafe has had good success at retaining the arsenic in the melt during processing and producing a leach resistant glass product. In addition to the treatment of arsenic, Geosafe has had good success at treating other compounds that are typically associated with arsenical wastes some including organochlorines.

Arsenic has been treated successfully by the GeoMelt process. Typically 95 to 99 % of the arsenic is retained in the melt and immobilised in the resulting vitrified product.

Small amounts of arsenic will volatilise from the melt and will be captured by the off-gas treatment system. Arsenic-bearing residues and secondary wastes from the off-gas treatment system are treated in subsequent melts.

The vitreous product generally consists of high concentrations of silica (50-80%) and low levels of alkali oxides (1-5%), which results in an extremely durable and highly leach resistant product. The vitrified products far surpasses TCLP test criteria. The product is typically 10 times stronger than concrete in both tension and compression and is unaffected by freeze/thaw or wet/dry cycles. Long-term durability test results indicate that the vitreous product is typically 5 to 100 times more durable than borosilicate glasses used to immobilise some high level nuclear wastes. Although the vitrified product often consists of crystalline phases intermixed with the vitreous phases, the crystalline phases formed in GeoMelt products are not detrimental to the product's durability. In many cases, the crystallinity results in a localised increase of silica in the vitreous phase, thus increasing the product's durability.

The adequacy of the product is confirmed by conducting TCLP tests on samples of the product. No GeoMelt product has ever failed TCLP leach test performance requirements.

The most significant application of the technology to arsenic wastes involved a project in Japan. Waste agricultural chemicals including hexachlorobenzene (HCB), DDT, parathion, arsenic and lead were mixed with soil and treated with the GeoMelt-ISV process. The pre-treatment concentrations of arsenic were estimated to be 5,280 ppm (0.5%) and concentrations of organic chemicals in the soil exceeded 30% (w/w). The amount of arsenic retained in the melt during processing ranged from 96.75% to 99.91%. The small amounts that volatilised from the melt were removed by the off-gas treatment system.

An advantage of the GeoMelt process is that the waste mixture does not require analysis to determine the components in the mixture prior to treatment. The upfront analytical costs can be a significant part of the total cost of treatment. As the GeoMelt technology is generally independent of the waste characteristics, the problem of the diversity of the wastes resulting from chemical collections is addressed. Arsenic wastes of up to 19,000 ppm (1.9%) have been successfully treated and the associated vitrified product satisfies TCLP test criteria.

5.5 Availability in Australia

The GeoMelt process is represented in Australia and a full-scale GeoMelt-ISV treatment plant has been constructed and operated. The full-scale ISV plant can treat wastes at a rate of up to 150 tonnes per day. A second system is being assembled which will be able to treat between 5 to 50 tonne sized batches.

5.6 Cost

Extrapolating established US costs results in a cost of $500 to $750 per tonne of material treated. The cost will be dependent on the quantity of waste to be treated, and the treatment system establishment cost.

Concentrated liquids and non-soil wastes would be mixed with soil. Treatment costs for liquid and non-soil wastes would depend on the soil mixture ratios.

5.7 Safety and Environmental Risks

The GeoMelt processes are relatively safe and represents a low risk to the environment as demonstrated by successful commercial operations in the US and in Japan. Factors that enhance the safety of the process are:

?? a very high percentage of organic contaminants are destroyed in the ground (typically > 99.9 %);

?? heavy metals and radionuclides are largely retained in the melt so the emissions of these species from the melt to the off-gas treatment system are minimal;

?? the treatment process is relatively slow; the melt grows at a rate of only a few cm per hour resulting in only a small fraction of the waste material being treated at any one time;

?? the off-gas treatment system is robust and has been demonstrated to be effective on a wide range of contaminant types;

?? organic and inorganic debris (eg plastic, wood, paper, steel drums, protective clothing and equipment) are destroyed or incorporated into the melt, therefore, separation and complete characterisation of the waste is not required;

?? for the *in situ* mode of treatment, the process does not require excavation and handling of contaminated soils so the risk to workers, the public, and the environment are minimised;

?? since the process treats wastes on-site, there is no requirement for, or risk from, the off-site transport of wastes;

?? no organic contaminants remain in the vitrified product;

?? the vitrified product is extremely effective at immobilising heavy metals and radionuclides and the product far surpasses TCLP requirements;

?? the process equipment includes back-up safety systems and an alternate power supply in case of equipment or power failure.

5.8 Limitations

GeoMelt requires either soil, sand or some other similar earthen material to serve as the treatment media (melt). Concentrated liquids or other non-soil wastes can be mixed with soil for treatment.

Treatment depths are limited to approximately 7 m from grade level for the *in situ* treatment mode. Other ISV configuration options exist for sites requiring greater treatment depths including restaging the materials.

Soil must have more than 1 % (w/w) combined alkali oxides. Most soils meet this criterion. An additive such as soda ash can be used if needed.

For *in situ* applications, the water recharge rate must be less than 1×10^{-4} cm/s or dewatering or diversion techniques must be used. Fully water-saturated soils and wastes can be treated with the process if the recharge rate is controlled.

Pretreatment is required for applications involving the *in situ* mode of treatment for sites containing high integrity sealed containers, such as drums. Alternatively, unacceptable materials such as sealed drums can be breached and the contents blended with soils when employing the staged *in situ* or stationary batch modes of treatment.

6. BASE-CATALYSED DECHLORINATION

6.1 Introduction

Proponents of the Base-Catalysed Dechlorination (BCD) type of technologies may be able to handle OCP/arsenic type wastes, but may choose not to offer their services for the treatment of these wastes due to the small size of the projects involved. Consolidation of OCP/arsenic wastes into single, large projects may make these and other technologies more viable as the modification or configuration of equipment for larger projects will be more worthwhile. At present, this technology is being used to treat polychlorinated biphenyl (PCB) wastes in a liquid form.

6.2 Technology Description

The Base-Catalysed Dechlorination (or Base-Catalysed Decomposition) (BCD) process was developed to treat halogenated organic compounds, particularly PCBs. The process can involve direct dehalogenation or decomposition of waste materials, although it is essentially a liquids treatment process. More practically the process can be linked with a pretreatment step such as thermal desorption which yields a relatively small quantity of a condensed volatile phase for separate treatment.

The BCD process involves the addition of an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide. The proportions added range from 1 to about 20 percent by weight, the amount required being dependent on the concentration of the halogenated or non-halogenated organic contaminant contained in the medium.

A hydrogen donor compound is employed, such as a paraffin oil solvent, to provide hydrogen for reaction, with the halogenated and non-halogenated contaminants, if these ions are not already present in the contaminated material. In order to activate these compounds to produce hydrogen ions a source of carbon must be added, either in solution or in suspension.

The mixture is heated at a temperature and for a time sufficient to totally dehydrate the medium. After dehydration, the medium is further heated at a temperature between 200?C and 400?C for a time sufficient to effect reductive decomposition of the halogenated and non-halogenated organic contaminant compounds, typically 0.5 to 2 hours. At this temperature the catalyst derived from the carbon source (eg carbohydrate) facilitates hydrogen transfer from donor compound to the organochlorine compound.

Generally, oxygen will not adversely affect the BCD process and therefore air does not need to be excluded. However, when applied to the decontamination of hydrocarbon fluids, either aliphatic or aromatic, air needs to be excluded in order to prevent ignition of the hydrocarbon at the elevated temperature of the BCD reaction. This is achieved by passing nitrogen gas through the reaction vessel. The treatment is usually carried out as a batch process with all steps completed within a single reactor.

OCPs which are contaminated with arsenic could potentially be treated with the BCD process. Trials have been done with ADI using BCD and were successful (Carlisle, 1998). Although no arsenic was involved in these trials, it is believed that it would end up being extracted (via vacuum extraction at 150? C) in an aqueous phase, or in the sludge, which would then require treatment, such as stabilisation.

6.3 Proponents

6.3.1 BCD Technologies

BCD Technologies in Queensland operate the BCD process.

BCD Technologies also operate the plasma arc process, PLASCON. The PLASCON process requires the waste stream to be treated in a liquid or gas phase. OCP wastes contaminated with arsenic may be treated, however pretreatment to produce a liquid or very finely divided material (fine pumpable slurry) may be required and a gas treatment system would be required to collect the inorganics, including arsenic which would then require further treatment. Plasma arc systems can be linked with thermal desorption to treat the organic components of OCP wastes contaminated with arsenic, however the remaining inorganic component would require separate treatment.

The pretreatment requirements for a plasma arc process indicate that PLASCON technology is not as feasible as the BCD process, discussed further in this section.

BCD Technologies are licensed to treat OCPs with 1 ppm arsenic. Using the BCD process, it would be possible to run a trial of material such as OCPs, OPPs, or carbamates contaminated with higher concentrations of arsenic and to verify the concentration of residues in waste water. Approval for a trial would be required from the relevant licensing authority.

The purpose of the trial would be:

?? to determine the efficiency of the process in destroying the OCPs in the waste mixture; and

?? to determine the fate of the arsenic in the waste mixture;

Depending on the form of arsenic in the waste, it may either fume/volatilise and end up in the process air filter network, and therefore not be recoverable, or be separated into the scrubber water.

BCD Technologies' experience is in the treatment of PCBs which are relatively homogeneous wastes streams. The OCP/arsenic waste mixtures are likely to be highly variable as the wastes have already been consolidated. Other inorganic contaminants (such as mercury, tin and copper) may be present in varying quantities in the waste mixture and need consideration in separation and treatment with the arsenic residue. It is also possible that large quantities of scrubber water may be generated, forming a significant waste stream containing inorganics requiring further treatment. (Further treatment of the arsenic would be required if concentrations were in excess of trade waste guidelines)

The OCP treatment process would need to be broad to handle the different organics (in the order of 24 different compounds), and this is achievable. Trials would indicate whether the process can also satisfactorily deal with the various forms of inorganic contaminants in the waste mixtures.

Discussions with BCD Technologies revealed factors which affect the viability of treating OCP/arsenic mixtures. These include:

?? recovering the cost of performing the trial (ie are the quantities of arsenical wastes sufficient to recover the cost of R&D);

?? the cost of treating the OCP/arsenic waste.

It may be necessary to subsidise either the R&D, or the waste treatment, to make the process economically viable (Krynen, 1998).

BCD Technologies would need to established a link with another facility which has the capability to treat (eg immobilise) the inorganic residues.

6.3.2 Haz-Waste Services/Jancassco

Haz-Waste operate the BCD process, and currently has the capability to handle OCPs but would require EPA approval to conduct a trial on a small quantity of the waste mixture containing arsenic. The purpose of the trial would be as stated above (refer BCD Technologies).

In discussion with Haz-Waste Services, factors identified which affect the viability of treating OCP/arsenic mixtures include:

?? recovering the cost of performing the trial (eg having a confirmed order for treatment of quantities of waste, assuming the trials are successful);

?? the cost of treating the OCP/arsenic waste.

Currently, Haz-Waste's capacity to treat waste is utilised by the PCB market.

Trials have been conducted with ADI on OCPs using BCD and they were successful. No arsenic was involved in these trials, but it is believed that the arsenic would separate as an aqueous phase, or as a sludge, which would then require treatment. Haz-Waste do not currently have the capability of treating the resulting arsenic material, and therefore a link needs to be established with a suitably licensed facility for treatment, such as immobilisation, of the arsenic residue.

At present Haz-Waste advise they are not interested in OCPs or arsenic as they have enough PCBs to deal with. However it could be of interest in a few years when the PCB market has disappeared. When that happens they will have to consider other markets in which to apply their technology such as the OCP/arsenic waste management issue.

7. ELI ECO LOGIC

ELI Eco Logic operate the Eco Logic hydrogenation process in Kwinana, WA. Eco Logic is a hydrogenation process based on gas-phase thermo-chemical reaction of hydrogen with organic compounds. At 850? C or higher, hydrogen combines with organic compounds in a reaction known as reduction to form smaller, lighter hydrocarbons, primarily methane. For chlorinated compounds the reduction products include methane and hydrogen chloride. The reaction is enhanced by the presence of water, which acts as a reducing agent and a hydrogen source.

Four waste preparation and feed systems have been proposed to allow the treatment of a variety of waste materials including organic liquid waste streams, contaminated watery wastes, solid wastes such as soil or sediment, and gases, including product gas produced in the process. Product gas may contain products of incomplete destruction and these may be recycled through the system to ensure the product gas meets licensed emission limits.

The mixture of gases and vaporised liquids are passed over electric heating elements situated around a central ceramic-coated steel tube of the reactor. Treated gases pass through a scrubber where water, heat, acid and carbon dioxide are removed. A caustic scrubbing agent is added to neutralise acids.

The process uses hydrogen gas under pressure and care must be taken to operate the system to ensure that explosive air-hydrogen mixtures do not form.

For most of the wastes treated, the product gas generated provides much of the process fuel needs. Chlorinated organics may be converted into fuel, and the chlorine is converted into a salt solution which will require disposal to a sewer (some arsenic may also be expected in the scrubber water). Desorbed solid waste can be disposed of to a landfill if other wastes constituents such as heavy metals are at acceptable levels.

ELI state that they do not treat arsenical wastes (McEwan, 1998). The Eco Logic process is designed for OCP wastes, but is not able to accept OCPs contaminated with arsenic. The Eco Logic process is limited with respect to waste constituents such as arsenic, as the arsenic would volatilise and pass through the process, contaminating the scrubber water. Theoretically, if the arsenic concentrations were low enough initially in the waste, then the concentration in the resultant scrubber water would be low enough for discharge, either to sewer or for irrigation. However, to avoid any potential problems ELI advise that they will not accept OCP wastes that contain arsenic.

8. XTALTITE

8.1 Introduction

Xtaltite? (pronounced crystal-tight) is the trade name for a generic technology for incorporation of toxic waste elements into the crystal lattice structure of synthetic rocks (or polyphase ceramics). The process consolidates, immobilises and permanently isolates a wide range of toxic inorganic waste products. The technology has been developed to meet the demands of mining and industrial operations, such as smelter waste streams, which produce large volumes of toxic inorganic wastes, particularly arsenic trioxide estimated to be 10,000 tons per year.

8.2 Technology Description

Xtaltite Corporation have developed a method of synthetic mineralisation specifically tailored to the stabilisation of heavy metal wastes, which is based on the 'Synroc' principle of synthetic mineral immobilisation of high level radioactive waste. Xtaltite have modified the chemistry of the process to further decrease the solubility of the synthetic mineral analogue.

Characterisation of the waste stream is required, including a good understanding of the variability limits to the waste stream composition. Characterisation is primarily through powder X-ray diffraction in combination with microscopy to ensure the desired mineral assemblage has formed and the waste elements have entered the correct phases. Although the stoichiometry of the chemistry must be precise to be able to produce a durable end product, the general formula is as follows;

Waste + quick lime + simple pre-cursors + oxygen + heat + cement = Xtaltite waste.

Several hours are required to develop the correct pre-cursors for Xtaltite production during firing at the hydrometallurgical stage. This ensures an insoluble Xtaltite product. The simple pre-cursors added to the mixture are proprietary formulations. The addition of alkali or acid, dependent on the waste stream, can act as a catalyst speeding up the hydrometallurgical stage. This may then need to be a batch process.

Major species are oxidised (to a higher valence state) to produce the final waste form phase. The reactions are carried out in two stages, hydrometallurgical and pyrometallurgical, to avoid sublimation of volatile species, particularly arsenolite in arsenic waste streams.

The first stage of hydrometallurgy, where a precipitate is formed, ensures that all the elements are in suitable precursor configurations for a successful second stage. Pyrometallurgy is the second stage in which the precipitate is pressed into pellets and fired in air at temperatures of 1050 to 1200 ?C. This is performed in an oxidising atmosphere to ensure the correct speciation. A binder, either a long-chain polymer or sodium silicate solution, may be added to the slurry enhance the mechanical stability of the unfired pellets.

Xtaltite can be produced in the presence of iron and sulphur, which allows flexibility in pre-processing of any waste containing these elements.

Xtaltite phase assemblages consist mainly of apatite-like minerals having the general formula $A1_4A2_6(BO_4)_6X_2$, where A1 and A2 are larger cations such as Ca^+ and Pb^{2+}, B are smaller cations including As^{5+} and P^{5+}, and X are halogen or hydroxyl ions[2].

The key advantages of the Xtaltite process are:

?? a volume effective, high waste loaded (more than 35 % w/w) ceramic;

?? avoids the formation of secondary waste streams (by volatilisation);

?? stability over geological time scales; and

?? cost effective one-off processing and disposal costs.

8.3 Proponents

Xtaltite Corporation Pty Ltd represented by Greg Eaton & Associates.

8.4 Performance

The process is capable of immobilising arsenic, lead, mercury, thallium, cadmium and antimony. The process incorporates the waste elements into the crystal lattice of a host mineral. The process is different to encapsulation and stabilisation, where the waste is enclosed within a sparingly soluble matrix. Incorporation of the waste in the crystal lattice results in a higher waste loading, and a waste form which is more stable in a variety of environments, even if primary isolation is lost.

The Xtaltite Corporation states that weight loading of over 50% toxic oxides have been achieved, however, waste loadings of 30 to 35 % (w/w) for a particular toxic oxide or combination of oxides, are usually achieved which meet TCLP test international guidelines.

On an industrial scale, key test points and methods are required for Quality Control and Quality Assurance. The ultimate criterion for waste form acceptability is durability as measured by accelerated leach testing.

8.5 Availability in Australia

The Xtaltite process has been demonstrated in the laboratory and in small batch plants. The next step in the development of the technology is either a pilot plant or a pilot followed by a full scale plant. There is no commercial application of the technology in Australia at present.

8.6 Cost

The cost of the waste treatment process is a balance between waste volume, toxicity, repository availability and the requirements of site monitoring (if any). A high waste

[2] Nriagu, 1984, cited in Xtaltite (1988) *A New Process for Disposal of Toxic Elemental Waste*. Xtaltite Corporation Pty Ltd, Western Australia.

loading may result in substantial volume reduction, but may be offset by unacceptable dissolution losses, or the need for monitoring.

Establishment of a plant consuming 5000 tonnes of fume per annum is estimated to cost $5.7 million. The largest component of the cost is the kiln required, estimated as $2.25 million.

Based on a plant which consumes 5000 tonnes of fume per annum, energy inputs are estimated as 3.1 Gjoule ($20) per tonne of fume, producing approximately 1.35 tonnes of Xtaltite.

8.7 Safety and Environmental Risks

Risks associated with the transport and handling of Xtaltite are low as the product is in a pellet or a gravel form of high stability. Leaching tests can verify the stability of the final product, and the waste loading can be modified to achieve low leachability criteria.

8.8 Limitations

It is essential to understand the precise nature of elemental partitioning between the minerals, how such partitioning varies as a function of hydrometallurgical and pyrometallurgical processing, and the response to variations in waste stream composition.

It is essential to ensure incompatible minor phases are avoided, as they may contribute to unacceptably high short term dissolution rates.

There is no commercial application of the technology in Australia. The cost/viability of establishing a facility is dependent on significant quantities of arsenic wastes being locally or regionally available.

9. NEW AND EMERGING TECHNOLOGIES

9.1 Introduction

A review of a recent publication by the USEPA's Superfund Innovative Technology Evaluation (SITE) team indicates that a number of technologies are being developed that may have potential applications to arsenic wastes and OCP wastes containing arsenic.

9.2 Pyrokiln Thermal Encapsulation

Svedala Industries Inc. have developed the Pyrokiln Thermal Encapsulation Process which is designed to improve conventional rotary kiln incineration of hazardous waste. The process introduces inorganic additives (fluxing agents) with the waste to promote incipient slagging or thermal encapsulation reactions near the kiln discharge. The thermal encapsulation is augmented using other additives in either the kiln or in the air pollution control baghouse to stabilise the metals in the fly ash. The process is designed to:

1. immobilise the metals remaining in the kiln ash;

2. produce an easily handled nodular form of ash; and

3. stabilise metals in the fly ash;

while avoiding the problems normally experienced with higher temperature "slagging kiln" operations.

The basis of this process is thermal encapsulation. Thermal encapsulation traps metals in a controlled melting process operating in the temperature range between slagging and nonslagging modes, producing ash nodules that are 60 to 200 mm in diameter.

Wastes containing organic and metallic contaminants are incinerated in a rotary kiln. Metals with high melting points are trapped in the bottom ash from the kiln through the use of fluxing agents that promote agglomeration with controlled nodulisation.

Metals with low melting and vaporising temperatures, such as arsenic, lead, and zinc, are expected to partially volatilise, partitioning between the bottom ash and the fly ash. Metals concentrated in the fly ash may be stabilised, if necessary, by adding reagents to the kiln and to the air pollution controls system to reduce leaching to below TCLP limits.

9.3 Adsorptive Filtration

University of Washington has developed an adsorptive filtration process which removes inorganic contaminants (metals) from aqueous streams. An adsorbent ferrihydrite is applied to the surface of an inert substrate such as sand, which is then placed in one of three vertical columns. The contaminated waste stream is adjusted to a pH of 9 to 10 and passed through the column. The iron-coated sand grains in the column act simultaneously as a filter and adsorbent. When the column's filtration capacity is reached (indicated by partial breakthrough or column blockage), the column is backwashed. When the adsorptive capacity of the column is reached (indicated by breakthrough of soluble metals), the metals are removed and concentrated for subsequent recovery with a pH-induced desorption process.

The technology has the ability to:

1. remove both dissolved and suspended metals from the waste stream;
2. remove a variety of metal complexes;
3. work in the presence of high concentrations of background ions; and
4. remove anionic metals.

The absorptive filtration process removes inorganic contaminants, consisting mainly of metals, from aqueous waste streams with a wide range of contaminants concentrations and pH values.

9.4 Vortec Corporation Oxidation and Vitrification Process

The Vortec Corporation has developed an oxidation and vitrification process for remediating soils, sediments, sludges, and mill tailings contaminated with organics, inorganics, and heavy metals. The process can oxidise and vitrify materials introduced as dry granulated materials or slurries.

The basic elements of the process include:

1. a cyclone melting system;
2. a material handling, storage, and feeding subsystem;
3. a vitrified product separation and reservoir assembly;
4. a waste heat recovery air preheater;
5. and air pollution control subsystem; and
6. a vitrified product handling subsystem.

The cyclone melting system is the primary thermal processing system and consists of two major assemblies: a counter-rotating vortex (CRV) in-flight suspension preheater, and a cyclone melter. First slurried or dry contaminated soil is introduce into the CRV. The CRV

1. uses the auxiliary fuel introduced directly into the CRV;
2. preheats the suspended waste materials along with any glass-forming additives mixed with oil; and
3. oxidises any organic constituents in the soil.

The average temperature of materials leaving the CRV combustion chamber is between 1,200 and 1,500 ?C, depending on the processed soils' melting characteristics.

The preheated solid materials leave the CRV and enter the cyclone melter, where they are dispersed to the chamber walls to form a molten glass product. The vitrified, molten glass product and the exhaust gases discharge from the cyclone melter and are separated.

The exhaust gases then enter an air preheater for waste heat recovery and are subsequently delivered to the air pollution control subsystem for particulate and acid gas removal. The molten glass product is delivered to a water quench assembly for subsequent disposal.

Features of the oxidation and vitrification process include:

- processes solid waste contaminated with both organic and heavy metal contaminants;
- uses various fuels, including gas, oil, coal, and waste;
- handles waste quantities ranging from 5 tons per day to more than 400 tons per day;
- recycles particulate residue collected in the air pollution control subsystem into the cyclone melting system. (These recycled materials are incorporated into the glass product, resulting in zero solid waste discharge); and
- produces a vitrified product that is nontoxic according to USEPA TCLP standards. The product also immobilises heavy metals and has long term stability.

9.5 Coordinate, Chemical Bonding, and Adsorption Process

Western Product Recovery Group Inc. developed the coordinate, chemical bonding, and adsorption (CCBA) process. The process converts heavy metals in soils, sediments, and sludges to nonleaching silicates. The process can also oxidises organic in the waste stream and incorporate the ash into the ceramic pellet matrix. The solid residual consistency varies from a soil and sand density and size distribution to a controlled size distribution ceramic aggregate form. The residue can be placed back in its original location or used as a substitute for conventional aggregate. The process uses clays with specific cation exchange capacity as sites for physical and chemical bonding of heavy metals to the clay.

The process is designed for continuous flow. The input sludge and soil stream are carefully ratioed with specific clays and then mixed in a high intensity mechanical mixer. The mixture is then densified and formed into green or unfired pellets of a desired size. The green pellets are then direct-fired in a rotary kiln for approximately 30 minutes. The pellet temperature slowly rises to 1,100 ?C creating the fired pellet's ceramic nature. Organics on the pellet's surface are oxidised, and organics inside the pellet are pyrolysed as the temperature rises. As the pellets reach 1,100 ?C, the available silica sites in the clay chemically react with the heavy metals in the soil or sludge to form the final metal silicate product.

The process residue is an inert ceramic product, free of organics, with metal silicates providing the molecular bonding structure to preclude leaching. The kiln off-gas is processed in an afterburner and wet scrub system before it is released into the atmosphere. Excess scrubber solution is recycled to the front-end mixing process.

The CCBA process has been demonstrated commercially on metal hydroxide sludges, and can also treat waste water sludges, sediments, and soils contaminated with most mixed organic and heavy metal wastes.

9.6 Geo 2

Geo 2 are working with the NSW Department of Agriculture on a process to remove arsenic and DDT simultaneously from soil at former cattle dip sites in NSW. The technology uses a leaching agent to both destroy the organic components in the contaminated soil and remove arsenic, which ends up in the liquor. It is expected that arsenic would be removed from the liquor as a concentrated precipitate suitable for further treatment prior to disposal.

As such, this process, used at such sites, can be seen as a generator of arsenical wastes, and such sources of waste should be included in any strategy designed to address waste management issues relating arsenical wastes and OCP/arsenical wastes.

10. FUTURE NEEDS FOR RESEARCH AND DEVELOPMENT

Possible areas of further research and development include:

- the toxicity and environmental risk posed by stabilised arsenic-OCP mixtures compared with stabilised arsenic mixtures, and whether the presence of OCPs significantly alters the environmental risk;
- the ability of the available stabilisation methods to adequately stabilise the range of constituents present in the arsenical wastes (such as various forms of arsenic, hexavalent chromium and the OCPs);
- the long term stability of cement and dolomite based stabilisation technologies; and
- the application of pre-treatment technologies for OCPs contaminated with arsenic which will result in a residue which can be treated by commercially available arsenic stabilisation methods.

The question of what constitutes an economic proposition for technology suppliers to become interested, in terms of the quantity of waste to be processed, requires further investigation. There is an economy of scale and many potential treatment technologies will not be economically feasible, or be able to process wastes at a reasonable cost, unless large quantities of waste are available for treatment (or reuse).

In general, the industry considers that the collection and consolidation of waste material by government agencies will encourage the development, refinement and eventual deployment of appropriate technologies.

In particular, consideration should be given to methods of treatment of the relatively large quantities of pesticides which do not contain arsenic, as a pretreatment method for OCP-arsenic mixtures (with subsequent stabilisation of the arsenic residue).

A national collection and consolidation program is desirable to reduce the potential risks to the environment due to *ad hoc* and uncontrolled long term storage and illegal disposal of arsenical wastes. The quantities of waste generated by such a program would send a clear message to the waste management industry that the timely development and implementation of appropriate treatment technologies will have a market in which to be deployed, provided such technologies are environmentally sound and cost-effective.

In addition the cost of collection and storage needs to be compared to the potential cost of the environmental damage that may occur if the management issues relating to arsenical wastes are not properly addressed.

The development of long term management strategies for arsenical wastes could also include some accounting of the problem of arsenical wastes in south east Asia and the Pacific region. The South Pacific Region Environment Program (SPREP) is currently undertaking a comprehensive review of the nature and extent of hazardous wastes and other hazardous materials that exist within nations in the region.

The results of this project should account for the amount of arsenicals that are currently in use and being stored. The amounts of waste within individual nations in the region will probably not be sufficient for commercial waste treaters to invest significantly in arsenic treatment facilities, and Australia may be able to assist by including wastes from these sources into its program. The feasibility of this initiative would require further investigation and consideration of controls under the Basel Convention.

11. CONCLUSIONS

There are a range of technologies available or potentially available to treat arsenical wastes and organochlorine pesticide wastes that contain arsenic compounds and other substances.

The review indicates:

- There are no commercial facilities operating in Australia for the extraction or recovery of arsenic from wastes for the purposes of recycling and reuse. Extraction and recovery is unlikely to be commercially available in the future because of the relatively high costs of extraction and recovery, and the absence of a market for the product.

- There are commercial facilities currently operating in Australia for the treatment of arsenical wastes by stabilisation with cementitious reagents and landfill disposal (eg Chemsal in Victoria, Cleanaway Technical Services (Victoria and NSW) and Nationwide in Queensland). The process can be applied to concentrated arsenic wastes which do not contain organochlorine pesticides. The process may be applicable to arsenical wastes containing other contaminants such as hexavalent chromium but, in general, testwork will be required to confirm the application of the process to mixed waste types.

- The draft organochlorine pesticide management plan does not distinguish between free and stabilised pesticides for the purposes of landfill disposal. While landfilling of stabilised pesticides has been occurring in Queensland, in the longer term the landfill disposal of stabilised arsenic wastes containing OCPs may not be permissible.

- There are no commercially available facilities in Australia for the treatment of arsenic wastes containing OCPs. While there are commercial treatment facilities available for treatment of wastes containing OCPs, the presence of arsenic causes problems with the treatment process, and the treatment companies currently operating OCP treatment systems (BCD Technologies, ELI Eco Logic, and Haz-Waste Services) have advised that they are not able, nor are they interested in the short term, in treating OCP wastes that contain significant concentrations of arsenic.

- Of the treatment technologies that are able to treat wastes containing both arsenic and OCPs, the Geosafe vitrification process (GeoMelt) appears to be the process closest to commercial availability.

- GeoMelt is being applied to radioactive wastes at Maralinga, and is being considered for application to HCB wastes held by Orica in Botany. The application of GeoMelt for treating arsenic wastes containing OCPs would require the location of an appropriate site, obtaining regulatory approval, and construction of the facility. For this process to be commercially viable, it would appear that the facility would have to obtain contracts to treat larger quantities of wastes, such as non-arsenic pesticide wastes, or HCB wastes.

?? Chemsal advise that they are trialing a bioremediation process for the treatment of OCP wastes containing arsenic. It is too early to verify whether a commercial facility based on this technology will eventually be established.

It can be concluded that there are facilities available in Australia for treating wastes containing arsenic; however, there are no facilities currently available for treating wastes containing both arsenic and OCPs at high concentrations. The treatment systems currently available in Australia for treating OCPs are not able to be applied to OCP wastes that contain arsenic. Of the treatment technologies which may be available in the future, the GeoMelt process can be applied to mixed wastes of diverse physical form, and appears to be the process most likely to be established in Australia in the medium term. Location of a site and obtaining approvals would still have to take place, and to be commercially viable it would appear that the facility would have to win contracts for larger quantities of other wastes.

Any long term strategies or programs that are developed for arsenical wastes should include ongoing consultation with the waste management industry and industries that could potentially use recycled arsenic. Any investment by government or industry into storage and/or treatment facilities should also consider the arsenical wastes that may arise from our Asian and Pacific neighbours as part of the longer term strategy for the management of these wastes.

12. REFERENCES

Carlisle, K. (1998) Personal Communication, 23 April 1998. Ken Carlisle is the Managing Director of Jancassco Pty Ltd trading as Haz-Waste Services, Dandenong, Victoria.

McEwan, C. (1998) Personal Communication, 20 April 1998. Mr Craig McEwan is the Operations Manager for ELI Eco Logic in Western Australia.

Krynen, M (1998) Personal Communication, 30 April 1998. Martin Krynen is the Manager of BCD Technologies in Queensland.