

Dolocrete[®]: the economic solution to complex hazardous waste problems

J. Doumbos

Dolomatrix International, Australia

Abstract

The Dolocrete[®] Process is an internationally recognised technology which delivers outstanding performance for the chemical fixation and stabilisation of hazardous wastes. Backed by independent academic assessment and regulatory approval in multiple jurisdictions, Dolocrete[®] is being used on a commercial scale to treat thousands of tonnes of site remediation soils, dredging sediments, mining wastes and industrial process residues.

One significant, signature long term project currently being undertaken by Dolomatrix requires the stabilisation of high level arsenic trioxide (55%) via on-site treatment at a minerals processing facility. Arsenic and other heavy metals represent a key application for the Dolocrete[®] Process, with contaminants being incorporated into a pseudo-mineral matrix formed by the reaction of the proprietary Dolocrete[®] components.

Contaminated soils and sludges containing both organic and inorganic species, and particularly complex wastes containing both, are routinely treated using the Dolocrete[®] Process. As an example, contaminated soil from former gasworks sites typically contains cyanide, benzo-a-pyrene (BaP) and other polyaromatic hydrocarbons (PAHs), and heavy metals such as mercury. The Dolocrete[®] treatment of such soils offers an economic, reliable means of stabilising the full suite of contaminants in a single step.

This paper will detail some of the highly successful applications of the Dolocrete[®] Process, both within Australia and internationally.

Keywords: treatment, stabilisation, hazardous, toxic, waste, remediation, arsenic, contaminated soils.



1 Introduction

Within most jurisdictions, the strict regulatory requirements governing the disposal of industrial and hazardous wastes are being gradually tightened. These regulations demand that materials be made safe prior to disposal.

The Dolocrete[®] Process is recognised as a leading edge fixation and stabilisation treatment process for a wide range of hazardous wastes. It represents a breakthrough in the way hazardous waste is treated.

The technology has been applied to the treatment of a range of inorganic, organic and mixed wastes as either dry materials or sludges. These wastes have come from a number of sources, such as industrial or mining wastes, or soils and sludges resulting from the remediation of contaminated sites.

2 Technology description

2.1 Method

Chemical fixation and solidification (CFS) technologies are a well-established method for the stabilisation of hazardous wastes. To date, an array of CFS technologies have been utilised for the immobilisation of a variety of organic and inorganic compounds.

The Dolocrete[®] Process is classified as a CFS approach. Dolocrete[®] is a magnesium oxide-based cement prepared to a patented process from very high magnesium carbonate content dolomite or magnesite material. This material is crushed, specially calcined, and then specifically formulated to the individual waste stream being treated.

The treatment is focused at immobilising the heavy metals as thermodynamically stable mineral phases and microencapsulating organic contaminants into the mineral structure. The Dolocrete[®] mineralisation process involves a catalytic action with proprietary additives, causing the three dimensional polymerisation of a synthetic mineral matrix designed to mimic naturally occurring structures. The immobilised contaminants are subsequently solidified into a rigid matrix which demonstrates a high degree of compressive strength.

Within the mineral lattice formed, the specific immobilisation of individual contaminants will vary depending on the specific characteristics of each chemical. The mobility of contaminants is not generally controlled by a single retention mechanism in complex systems. Where the ionic charge and size of inorganic compounds are comparable, direct substitution for Mg^{2+} in the matrix will be considered the primary mechanism for immobilisation, while interstitial and interlayer substitution are likely co-mechanisms. Overall, many potential mechanisms exist including precipitation, co-precipitation, absorption, adsorption, lattice substitution and the formation of solid solution. The immobilisation of contaminants in the Dolocrete[®] system should be seen as a continuum of all of these mechanisms with specific mechanisms dominating under specific conditions.



The pH of the Dolocrete[®] system is governed by the dissolution of the mineral matrix and is ultimately limited by the solubility product. Various studies have shown that the pH of the system is limited to pH 9.5-10. This pH range corresponds to the point of zero charge (pzc), which in turn corresponds to the point of minimum solubility for most metal hydroxide precipitates. For example, the pzc for the lead/carbonate/sulfate systems is in the range of pH 8.5-10 depending on the exact nature of the solubility-limiting phase. This pH corresponds exactly to the pH of the Dolocrete[®] system, thus ensuring that lead is at the point of minimum solubility.

2.2 XRD examination

Powder X-ray Diffraction (XRD) studies are used to identify the mineralogical speciation of solid phases. The use of XRD as an analytical tool is generally employed when bulk quantities of a mineral are present (generally >5-10%) as reflections often overlap. With reference to the analysis of typical treated wastes, the XRD patterns may be considered as a near “limit of detection” situation for the contaminant of interest. However, in many cases, specific mineral phases may be identified demonstrating the formation of new mineral phases when contaminated materials are treated with Dolocrete[®]. This confirms lattice substitution as the primary mechanism of stabilisation in many cases.

2.3 Long-term durability

The most widely adopted method of assessing the long-term durability of treated wastes is to subject a sample of waste to the US EPA Multiple Extraction Procedure (MEP). This is considered by regulators to be an important method by which the long-term stability of wastes may be estimated under the dynamic acid environment of a typical landfill. The MEP test has been devised to simulate subjecting the waste to ten successive TCLP events.

Detailed analyses of the pre- and post-treatment results will be provided in a later section of this paper. As may be seen in the accompanying MEP data, the results demonstrate that contaminants are immobilised in the Dolocrete[®] mineral matrix. As such, the only mechanism for leaching is congruent dissolution of the lattice structure during the MEP test. The MEP tests routinely confirm that there is no risk of breakthrough leaching.

3 Commercial projects

Dolomatrix has had extensive current experience with the treatment of hazardous wastes. This has included the full range of waste sources, including contaminated soils, mining wastes, industrial process solids and sludges, and dredging sediments.

Current projects include both on-site and off-site treatment. In such cases, the ability of the Dolocrete[®] Process to utilise contaminated and saline water rather than specifying town water can be a distinct advantage.



For the treated product, options include on-site reuse. Under typical conditions, the treated product is both hydrophobic and physically stable, providing a second layer of protection in addition to the lattice stabilisation outlined above. Small variations in the technology allow the physical characteristics to be optimised for beneficial reuse options, such as the use of treated product as on-site geomechanical fill.

3.1 Arsenic

3.1.1 Case 1: orphan agricultural chemicals

Dolomatrix has treated a number of arsenic materials throughout Australia [2]. Due to the use of arsenic in agricultural pesticides and herbicides, surplus quantities can be stored and forgotten. These hazardous chemicals can collect in farm sheds and other locations as 'orphan' wastes. A number of State Governments have collected these wastes to ensure their safe disposal under the 'ChemCollect' programme, and the Dolocrete[®] technology has been used to treat these wastes under approval from the state regulatory authorities.

Table 1: Orphan As waste data (before and after treatment).

	Before Treatment		After Treatment	Regulatory Requirement (mg/L)
	SCC (mg/kg) 95% UCL	TCLP (mg/L) 95% UCL	TCLP (mg/L) 95% UCL	
Arsenic	400,000	540	2.0	5.0
Lead	13,600	<0.1	<0.1	5.0

Table 2: Orphan As waste MEP data (after treatment).

	EP	MEP1	MEP2	MEP3	MEP4	MEP5	MEP6
As (mg/L)	2.95	2.56	2.27	2.31	2.21	2.09	1.85
					MEP7	MEP8	MEP9
As (mg/L)					1.87	1.75	1.70

Tables 1 and 2 show the effect of the Dolocrete[®] treatment. As can be seen, the mobility of the arsenic was significantly reduced. Further, as shown in the MEP data, the declining trend in the arsenic leachability with repeated acid testing indicates that the mineral matrix formed undergoes congruent dissolution, demonstrating that the arsenic is bound into the mineral matrix. Through lattice and interstitial substitution (noting that more than one mechanism is likely to be involved in the arsenic stabilisation), the arsenic is rendered immobile, such that it is not selectively dissolved from the mineral matrix.

It can be concluded from these results that the treated waste is highly durable and does not pose a risk of breakthrough leaching. In this case, the Unconfined Compressive Strength (UCS) of the treated waste was 7.3 MPa.



3.1.2 Case 2: mining waste

In another example, Dolomatrix has received regulatory approval from the Western Australian Department of Environmental Protection for the treatment of As_2O_3 wastes generated by a Western Australian gold mine. At this facility, gold-bearing arsenopyrite refractory ores are roasted to improve the recovery of gold, in the process volatilising and recovering the contained arsenic as As_2O_3 .

To date, Dolomatrix has successfully treated over 500 tonnes of As_2O_3 on this project. The project will be ongoing over many years.

Dolomatrix is bound by contractual confidentiality on this project and is unable to disclose detailed project information, however average leachate results for treatments to date are shown in Table 3.

Table 3: Mine site As waste data (before and after treatment).

	Before Treatment		After Treatment	Regulatory Requirement (mg/L)
	SCC (mg/kg) 95% UCL	ASLP (mg/L)	ASLP (mg/L) 95% UCL	
Arsenic	416,000	5,500	1.8	5.0

The ASLP refers to the Australian Standard Leach Procedure, which is a variation on the USEPA Method 1311 Toxicity Characteristic Leach Procedure (TCLP). In the ASLP method, demineralised water is used as a leachate instead of acetic acid. This procedure is used as the basis for regulatory assessment in the South Australian and Western Australian jurisdictions.

Table 4: Cyanide waste data (before and after treatment).

	Before Treatment		After Treatment	Regulatory Requirement (mg/L)
	SCC (mg/kg) 95% UCL	TCLP (mg/L)	TCLP (mg/L) 95% UCL	
Cyanide	80,500	Off-scale*	0.9	16.0
TPH (C10-C36)	22,440	-	0.35	Limits based on total conc. only
Total PAH's	3,624	8.08	7.2	
Pb	1,170	4.2	<0.005	5.0
Hg	548	<0.01	<0.001	0.2
Benzo(a)-pyrene	11	<0.002	<0.002	0.16

* Note: CN⁻ TCLP prior to treatment too high to be measured.



3.2 Cyanide and organics

3.2.1 Case 1: industrial waste

Dolomatrix has obtained approval for the treatment and disposal of a complex industrial waste resulting from the precipitation of volatile components from a laden coke oven gas stream. The material contained a mixture of both inorganic and organic contaminants, of which the primary concern was cyanide.

Table 5: Cyanide waste MEP data (after treatment).

	EP	MEP1	MEP2	MEP3	MEP4	MEP5	MEP6
Hg (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
CN (mg/L)	1.80	0.13	0.14	2.75	1.51	1.26	1.40
BaP (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

	MEP7	MEP8	MEP9
Hg (mg/L)	<0.001	<0.001	<0.001
CN (mg/L)	1.19	1.12	1.23
BaP (mg/L)	<0.001	<0.001	<0.001

Measurements of the Unconfined Compressive Strength of this material yielded an average of 5.1 MPa.

3.2.2 Case 2: tar contaminated soil

Dolomatrix has demonstrated the treatment of a petroleum-tar contaminated soil resulting from a spill. This material presented as a sandy soil with large inclusions of viscous tar (typically 100 - 200 mm). This material was pre-treated with small amounts of Dolocrete[®] to yield a loose, friable soil (typically <10mm), which was subsequently homogenised and stabilised using the Dolocrete[®] Process.

Table 6: Petroleum tar waste (before and after treatment).

	Before Treatment		After Treatment	Regulatory Requirement (mg/L)
	SCC (mg/kg) 95% UCL	TCLP (mg/L)	TCLP (mg/L) 95% UCL	
TPH (C10-C36)	3,975	6.77	<0.2	Limit based on total conc. only
Pb	19	0.2	<0.1	5.0
Zn	23	0.9	<0.1	Exempt

3.2.3 Case 3: site remediation waste

Dolomatrix has obtained two approvals in New South Wales for the treatment of soils containing cyanide and polyaromatic hydrocarbons (PAHs), which resulted from the remediation of former gasworks sites.



Throughout Australia and many other areas, gasworks were extensively used throughout the early twentieth century to produce gas from coal, which was used for residential and industrial applications. After decommissioning, these sites were typically found to be highly contaminated with cyanide and organic materials, including localised areas of free tar in the surrounding soil.

Typical results are shown in Table 7. In this case, the data shows the typical 'bulk' soil material, as well as an example of a localised 'high-tar annulus' where higher concentrations of free tar could be found in the soil.

Table 7: Gasworks soil waste data (before and after treatment) [1].

Bulk Hazardous Waste Treatment Results							
	Untreated Material			Results after Treatment			
	BaP Total (mg/kg)	CN Total (mg/kg)	Phenol Total (mg/kg)	BaP TCLP (mg/L)	CN TCLP (mg/L)	Phenol TCLP (mg/L)	UCS (MPa)
95% UCL	39.37	345.06	98.56	0.0048	0.47	1.26	1.60
High-Tar Annulus Hazardous Waste Treatment Results							
	Untreated Material			Results after Treatment			
	BaP Total (mg/kg)	CN Total (mg/kg)	Phenol Total (mg/kg)	BaP TCLP (mg/L)	CN TCLP (mg/L)	Phenol TCLP (mg/L)	UCS (MPa)
95% UCL	108.87	383.77	287.38	0.0026	0.72	4.34	1.93

In this application, the odour absorbing properties associated with Dolocrete[®] were particularly helpful, as was the ability of the Dolocrete[®] to improve the materials handling characteristics of the free phase coal tars in the high annulus materials. The addition of small quantities of Dolocrete[®] on-site allowed the free tars to be converted to a loose, friable soil, making excavation and transport much simpler and more economic.

Table 8: Pesticide soil data (before and after treatment).

	Before Treatment		After Treatment	Regulatory Requirement (mg/L)
	SCC (mg/kg) 95% UCL	TCLP (mg/L)	TCLP (mg/L) 95% UCL	
Chlorpyrifos	4,176	*	0.3	200
Triclopyr	373	*	8.9	2,000
Picloram	66	*	1,320	3,000
Fluroxypyr	178	*	133	2,000
2,4-D	254	*	<1.0	10,000
xylenes	71	*	<3.0	50,000

* No TCLP data available for the untreated pesticide soil.



3.2.4 Pesticides

Dolomatrix has successfully treated pesticide contaminated soils under approval from the relevant EPA. This material resulted from the remediation of a spill site in which a complex mixture of agricultural herbicides and insecticides were lost during a transport accident. Data for this material is shown in Table 8. The UCS for the treated waste averaged 5.2 MPa.

3.3 Other heavy metals

3.3.1 Case 1: zinc

Dolomatrix has demonstrated the treatment of Electric Arc Furnace (EAF) dust waste from the steel industry. Regulatory approval for this application has been sought, and is anticipated to be granted shortly. Data for this material is shown in Table 9. The UCS for the treated waste averaged 9.0 MPa.

Table 9: EAF dust data (before and after treatment).

	Before Treatment		After Treatment	Regulatory Requirement (mg/L)
	SCC (mg/kg) 95% UCL	TCLP (mg/L)	TCLP (mg/L) 95% UCL	
Zinc	373,000	1,230	<0.1	Exempt
Lead	23,000	18	<0.1	5.0
Cadmium	359	10	<0.1	1.0
Chromium (total)	2,800	< 0.1	<0.1	Exempt
Arsenic	34	< 0.1	<0.1	5.0
Nickel	105	< 0.1	<0.1	2.0
Mercury	1.3	< 0.01	<0.01	0.2
Copper	2370	0.6	<0.1	Exempt

Table 10: EAF dust MEP data (after treatment).

	EP	MEP1	MEP2	MEP3	MEP4	MEP5	MEP6
Zn(mg/L)	0.12	0.06	0.06	0.06	0.05	0.05	0.05
Pb (mg/L)	0.44	0.29	0.30	0.36	0.31	0.30	0.26
Cd(mg/L)	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Cu(mg/L)	0.01	0.01	0.01	0.01	0.01	0.01	0.01

	MEP7	MEP8	MEP9
Zn(mg/L)	0.05	0.05	0.05
Pb (mg/L)	0.26	0.24	0.24
Cd(mg/L)	0.01	0.01	0.01
Cu(mg/L)	0.01	0.01	0.01



3.4 Other heavy metals

Dolomatrix has obtained approvals for the treatment and disposal of mercury wastes resulting from an industrial process, as well as contaminated soils containing lead. Additional imminent projects include CCA (copper, chrome, arsenate) wastes from the timber treatment industry, lead-contaminated soils, mixed metal contaminated incinerator wastes

3.5 Summary

Within Australia, Dolomatrix has obtained a total of 12 approvals for the treatment and disposal of a range of wastes. These are listed below:

- mercury waste from an industrial source
- chlorpyrifos contaminated soil
- lead contaminated soil
- PAH, CN and phenol contaminated soil from a Sydney gasworks
- phenol, BaP and PAH contaminated soil from a Newcastle gasworks
- mercury, CN and PAH contaminated process waste
- lead and mixed lead/cadmium contaminated materials
- PAH, BaP and TPH in an industrial waste
- zinc in EAF dust (pending)
- arsenic from a mine roaster
- arsenic in orphan agricultural wastes (3 jurisdictions)

4 Conclusion

The Dolocrete[®] Process offers a highly effective solution to a broad range of hazardous waste problems, spanning a range of industries including mining, manufacturing, and environmental site remediation. Through individual optimisation for specific waste materials, the technology is widely applicable to both inorganic and organic contaminants, and particularly to complex hazardous wastes containing multiple and different contaminant types.

References

- [1] Dolomatrix, The Treatment of Coal Tar Contaminated Soil Using the Dolocrete[®] Technology, Dolomatrix website: www.dolomatrix.com, 2003.
- [2] Dolomatrix, The Treatment of Arsenic Wastes Using the Dolocrete[®] Technology, Dolomatrix website: www.dolomatrix.com, 2003.

