Disposal of Heavy Metal bearing Hazardous Waste Using Chemical Fixation and Solidification

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Abstract

The Chemical Fixation and Solidification (CFS) process has been successfully applied to flyash from a glass-manufacturer and to arsenic trioxide wastes from roasting auriferous pyrite concentrates. Both wastetypes have been solidified with or without chemical fixation by addition of various amounts of Portland Cement. Leachability and unconfined compressive strength of the produced solidified waste were used as parameters to assess the efficacy of the CFS process. Leachability data for the solidified wastes was obtained by conducting standard leaching tests such as the Toxicity Characteristic Leaching Procedure (TCLP) and the Dynamic Leach Test (DLT). For the arsenic trioxide waste the leachability data was used to model long term leachability. This paper outlines the results from the application of the CFS process to industrial flyash and of arsenic trioxide waste and discuss the long term leaching models developed to predict leaching from arsenic trioxide waste.

Key words: Heavy metal waste, flyash, arsenic trioxide, waste management, CFS, disposal, TCLP, DLT, Leaching Index, unconfined compressing strength

1 Introduction

Until recently the common Australian practise in Australia for disposal of hazardous liquid and solid heavy metal bearing wastes was landfilling. Today with the realization that this disposal practise poses a hazard to our water resources, regulations for the disposal of hazardous waste have tightened and waste management bodies have been introduced by State Governments to control both the production and the disposal of hazardous waste. However not only have the disposal criteria been tightened, but the heavy metal emission limits to air and water have become increasingly stringent, resulting in an increase in the production of highly concentrated heavy metal residues, now often classified as hazardous. Thus the combination of increasingly stringent disposal and emission criteria demands new sophisticated disposal technologies that can handle the steadily increasing amount of hazardous heavy metal bearing waste in an environmentally sound way. These technologies have to meet the following objectives:

- reduce leachability and toxicity, so that the heavy metals do not cause a danger to public health
- produce a stable solid with a high strength and a low permeability
- be flexible, i.e. can handle a wide variation in residue composition
- be cost-effective

Chemical Fixation and Stabilization (CFS) of hazardous heavy metal bearing wastes is such a technology that achieves the above outlined objectives. CFS is a two step process. In the first step heavy metals are chemically transformed into a less toxic and / or less available precipitate, followed by mixing the precipitate with a binding agent (such as Portland Cement) to produce a stable solid with a very low permeability.

The CFS process has been successfully applied to flyash from a glass-manufacturer at full scale and to arsenic trioxide waste from roasting operations, at laboratory scale.

2 Flyash from Glass-Manufacturer

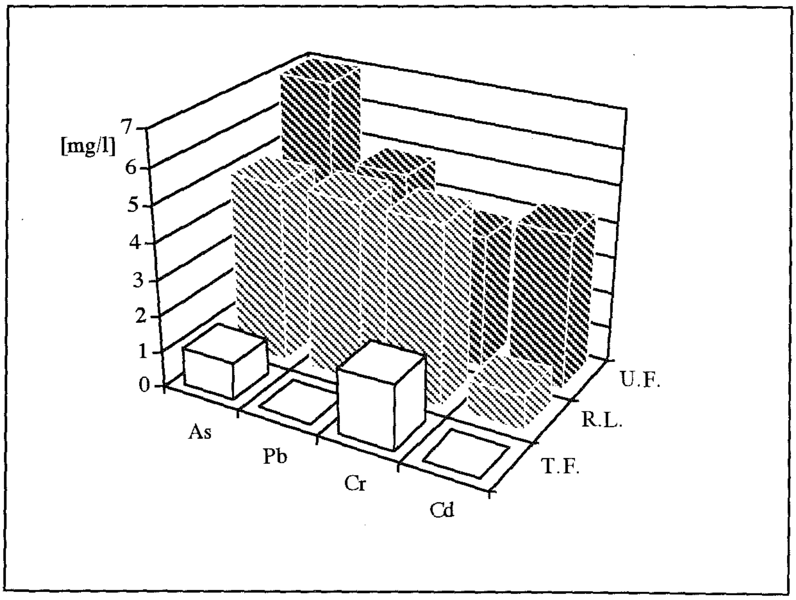
Flyash from smelting furnaces of a large glass-manufacturer containing high concentrations of arsenic, cadmium, chromium and lead (see Table 1) has been safe disposed in an environmental sound manner by means of CFS[1]. Flyash heavy metal concentrations, the TCLP leachability data from both the solidified and the original flyash are listed together with the regulatory levels are shown in Table 1.

Table 1: Flyash Heavy Metal Concentrations, Leachability Data and Regulatory Levels

Contaminant	Arsenic	Cadmium	Chromium	Lead
Flyash [mg/kg]	292	160	827	1377
TCLP Leachability Data [mg/l]				
Flyash	7	4.3	3.7	4.9
CFS-Flyash	< 1.0	< 0.01	1.8	< 0.01
Regulatory level	5	1	5	5

Figure 1 shows the TCLP leaching data of the untreated flyash (U.F.), the treated flyash (T.F.) and the regulatory levels (R.L.).

Figure 1: TCLP Leaching Data of Untreated and Treated Flyash and Regulatory Levels



As can be seen from Figure 1 the untreated flyash exceeds the regulatory levels for both arsenic and cadmium. Applying the CFS process reduced the leachability of all heavy metals well below the regulatory criteria, indicating that the solidified flyash can be disposed of in a regular landfill. The decrease in heavy metal leachability compared to the original waste ranges from 50 to 99.8 %. This was achieved by reducing the chromium in the flyash, present as the highly toxic and soluble chromate ion (CrO_4^{2-}), to chrome (III) with sodium hydrosulfite ($Na_2S_2O_4$). Chrome (III) has a much lower solubility and is less toxic than chrome (VI) compounds. Particularly the significant difference in toxicity between chrome (III) and (VI) has been recognized by the regulatory bodies recently, resulting in the deregulation of chrome (III) levels. The residue from chemical fixation has than been mixed with Portland Cement at a waste to cement ration of 1 to 4 and water[2]. The unconfined compressive strength (UCS) of the solidified cubes ranged from 6.9 to 7.5 MPa, well above the recommended UCS of 3.5 for landfilling. This high strength ensures the long term stability and integrity of the solidified waste. In access of 40 tonnes of flyash has been disposed of in an environmentally acceptable manner via CFS in Western Australia.

3 Arsenic trioxide waste

Two samples of arsenic trioxide waste (labelled A and B) from roasting operations have been provided to the authors to evaluate the application of the CFS process to this specific waste form. The composition of the two samples is summarized in Table 2.

Table 2: Composition of Arsenic Trioxide Samples

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

3.1 Disposal Options for Arsenic Trioxide

Arsenic trioxide has a solubility of 20 g/l (at 25 °C) in water, which increases with increasing temperature and extreme pH. Thus without treatment, arsenic trioxide cannot be safely disposed via landfill. Possible treatment for arsenic trioxide to comply with regulatory criteria are:

a) chemical fixation
b) solidification
c) combination of a) and b).

3.2 Chemical fixation

The currently available data on arsenic fixation have been summarized by Connor[3)]. These data indicate that low leaching levels can be easily obtained from wastes containing only minor amounts of arsenic. However, for high strength arsenic waste the most promising arsenic precipitates are[4,5)]:

- Calcium / Ferric arsenite
- Calcium / Ferric arsenate

The arsenite precipitates have been synthesized by adding calcium hydroxide or ferric sulfate to an arsenic trioxide slurry in water. The arsenates have been prepared by oxidation of arsenic trioxide with hydrogen peroxide prior to the addition of calcium hydroxide or ferric sulfate.

TCLP leaching tests of the calcium-arsenic compounds clearly show that the leachability for the calcium salts correlates inversively with the amount of excess calcium hydroxide, i.e. the more excess calcium hydroxide the lower the leachability. However this finding is not true for the ferric salts. The ferric salts of both arsenite and arsenate release even at relatively low pH-values, only miniscule amount of arsenic. The composition of those compounds with the lowest TCLP leachability, as well as the leaching data, are summarized in Table 3.

Table 3: Composition and Leachability of Arsenic Compounds

Compound	Ca/Fe:As	As [%]	Ca [%]	Fe[%]	pH	TCLP [mg As/l]
Calcium Arsenite	3:1	17.0	31.7	0.8	12.1	4.0
Ferric Arsenite	2:1	5.0	14.3	13.8	7.4	10.0
Calcium Arsenate	3:1	17.0	31.2	0.8	8.2	470
Ferric Arsenate	2:1	5.2	14.6	14.6	6.3	4.0

3.3 Solidification

The arsenic trioxide waste, the calcium arsenate and arsenite and the ferric arsenate were each mixed with various waste to cement to water ratios to produce a solidified product (the cement / waste / water mixture were solidified in 5 x 5 x 5 cm cubes). The leachability of arsenic from the solidified products was examined by using a standard leaching procedure, the Dynamic Leach Test (DLT)[2,6]. The DLT data are used to calculate the apparent diffusion coefficient which is required for the determination of the dimensionless Leachability Index (LX). The composition, physical properties and leaching characteristics of the optimized solidified products are summarized in Table 4.

Table 4: Composition, Physical Properties and Leaching Characteristics

	Relative Amounts of Reagent			Bulk Density	UCS	As	LX Value
Arsenic Form	Waste	Cement	Water	[g/cm³]	[MPa]	[%]	
As_2O_3 (A)[1)]	1.00	1.00	0.89	1.94	10.1	17.8	11.5
As_2O_3 (A)[1)]	1.00	2.00	1.15	1.99	20.3	11.9	12.2
Calcium Arsenate	1.00	2.00	2.03	1.65	11.8	4.4	12.8
Ferric Arsenate	1.00	2.00	1.98	1.62	12.0	3.4	12.7

1) waste sample A was used for the solidification

As can be seen from Table 4 the LX value of all the solidified products exceeds 9, the value recommended by Environment Canada[7)] for landfill disposal. The Leachability Index (LX), a measurement of heavy metal mobility, unlike the TCLP which only considers the heavy metal concentrations in the leachate, appears likely to be adopted worldwide as the disposal criteria for solid waste products.

Furthermore, the high UCS of all products confirms the integrity of the solidified products over long time periods.

3.4 Long term leaching study and modelling

3.4.1 Evaluation of the long term leaching data

Long term leaching tests were undertaken in duplicate with two solidified arsenic trioxide waste specimens[2)]. The cement to waste ratio for both specimens was 1:1 and the sidelength of the solidified cube was 5 cm. The leaching procedure followed that of the DLT, the only difference being that the leachate was only renewed once a week. The leaching period was 294 days and results are illustrated in Figure 2.