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Journal of Hazardous Materials B76 (2000) 125–138

**Journal of
Hazardous
Materials**

www.elsevier.nl/locate/jhazmat

The management of arsenic wastes: problems and prospects

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Received 30 April 1999; received in revised form 22 February 2000; accepted 24 February 2000

Abstract

Arsenic has found widespread use in agriculture and industry to control a variety of insect and fungicidal pests. Most of these uses have been discontinued, but residues from such activities, together with the ongoing generation of arsenic wastes from the smelting of various ores, have left a legacy of a large number of arsenic-contaminated sites. The treatment and/or removal of arsenic is hindered by the fact that arsenic has a variety of valence states. Arsenic is most effectively removed or stabilized when it is present in the pentavalent arsenate form. For the removal of arsenic from wastewater, coagulation, normally using iron, is the preferred option. The solidification/stabilization of arsenic is not such a clear-cut process. Factors such as the waste's interaction with the additives (e.g. iron or lime), as well as any effect on the cement matrix, all impact on the efficacy of the fixation. Currently, differentiation between available solidification/stabilization processes is speculative, partly due to the large number of differing leaching tests that have been utilized. Differences in the leaching fluid, liquid-to-solid ratio, and agitation time and method all impact significantly on the arsenic leachate concentrations.

This paper reviews options available for dealing with arsenic wastes, both solid and aqueous through an investigation of the methods available for the removal of arsenic from wastewater as well as possible solidification/stabilization options for a variety of waste streams. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic; Toxicity; Solidification/stabilization; Recovery; Removal

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1. Introduction

Management of hazardous wastes, such as arsenic, is of major public concern. Arsenic is an unwanted hazardous waste generated from the processing of a variety of ores including those of copper, gold, nickel, lead and zinc. Arsenic in the past was widely used in many agricultural applications as an active ingredient in many herbicides and insecticides. In addition to the existing problems of arsenic wastes, there will be an increase in the future production of arsenic wastes as industry begins to process more complicated sulphide ores [1,2], such as low-grade gold associated with arsenopyrite and nickel ores with high arsenic contents. There will also be an increase in the global cycling of arsenic due to the progressive industrialization of developing nations.

Arsenic occurs in the environment mainly as the inorganic arsenic oxides, arsenite (+III) and arsenate (+V) and its simpler methylated forms (e.g. $(\text{CH}_3)_3\text{As}$ and $(\text{CH}_3)_2\text{AsOOH}$).

As arsenic is a carcinogen, environmental regulators are adopting a more stringent attitude to arsenic exposure. The World Health Organization revised the guideline for arsenic from 0.050 to 0.010 mg/l in 1993 [3]. Subsequently, the Australian drinking water limits were lowered from 0.050 to 0.007 mg/l [4].

Safe disposal of arsenic wastes poses several problems:

1. Incineration is limited because of the volatilization of arsenic containing compounds.
2. Recovery of arsenic is of little economic interest because of the limited number of uses for the element.

Arsenic cannot be destroyed, it can only be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron.

Arsenic wastes may contain many impurities such as lead, iron and selenium. These elements can often be uneconomic to remove and the arsenic is stockpiled as waste. However, where arsenic of a sufficient purity is produced (purity greater than approximately 95%), the arsenic may be economically recovered for use primarily in the manufacture of the arsenical wood preservative, chromated copper arsenate (CCA), and ammonical copper–zinc arsenate (ACZA). The largest end use for arsenic trioxide is in the production of wood preservatives. Production of chromated copper arsenate (CCA) accounted for more than 90% of the domestic consumption of arsenic trioxide in the United States in 1998 [5]. The demand for arsenic trioxide in the manufacture of wood preservatives has increased noticeably over the last 20 years, increasing from 970 tonnes in 1971 to 9100 tonnes in 1981 and 14,300 tonnes in 1991 [6]. The only other area that has seen an increase in the use of arsenic is the electronics industry. High purity arsenic metal of 99.9999% or higher purity is used in the manufacture of crystalline gallium arsenide, a semiconducting material used in optoelectronic circuitry, high speed computers and other electronic devices. All other areas of arsenic usage, such as in the manufacture of agricultural chemicals, have seen a steady decrease in demand. Global production of arsenic trioxide was estimated to be 43 000 metric tonnes in 1997, with

China (15,000 tonnes) the world's largest producer followed by Belgium (9000 tonnes), the world's second largest producer [5].

In general, there are three options available for dealing with arsenic waste streams:

- Concentration and containment
- Dilution and dispersion
- Encapsulation of the material.

There are two major drawbacks associated with the first option: the cost and safety issues. There is little commercial interest in investing in plants and technology to recover arsenic and its compounds when there is a very limited market for the recovered material (except where the arsenic is of a relative high purity). Additionally, there are safety concerns associated with the storing of arsenic in a concentrated form and possibly dire consequences associated with any accident at the point of storage.

The second option is superficially attractive to the waste disposal and mining industries, as it offers the possibility for combining numerous waste streams together and in a way which dilutes the hazardous contaminants, thus passing any regulatory limits. However, this does not represent any real technical solution to arsenic contamination, but merely a legislative solution. Long-term exposure to low concentrations of arsenic still poses serious health problems, including enhanced risks of skin cancers and various internal carcinomas [7,8].

Therefore, at present, the most attractive option for dealing with arsenic wastes lies in encapsulating the contaminated material, usually through solidification/stabilization techniques and disposing of the treated wastes in secure landfills. The U.S. Environmental Protection Agency (USEPA) also recognizes cementitious solidification as “the best demonstrated available technology” (BDAT) for land disposal of most toxic elements [9]. However, solidification/stabilization is not currently considered BDAT for any arsenic waste or wastewater [10]. The USEPA does not preclude the use of solidification/stabilization for treatment of arsenic, particularly inorganic arsenic wastes. However, given the wide range of chemical characteristics of arsenic wastes, the USEPA recommends that its use be determined on a case by case basis.

2. Treatment and removal of arsenic from waste waters

Techniques for the removal of arsenic from aqueous media fall into several categories: ion exchange; adsorption (activated alumina and activated carbon); ultrafiltration; reverse osmosis; and precipitation or adsorption by metals (predominately ferric chloride) followed by coagulation.

Typically, the removal of arsenic from wastewater is only effective when dealing with relatively low concentrations of arsenic. Most studies concentrate on the removal of arsenic at the low $\mu\text{g}/\text{l}$ level. Harper and Kingham [11], Brewster [12], and Namasiyayam and Senthilkumar [13], however, have investigated the removal by precipitation and/or adsorption of arsenic at higher levels, 31, 56 and 10 mg/l , respectively. In general, the removal of arsenic by precipitation is most effective for small quantities of

highly concentrated arsenic waste. The cost effectiveness of precipitation is diminished when disposing of large quantities of low concentration arsenic wastes.

Adsorption on alumina or carbon is not well suited to handling high concentrations. The possibility of regeneration provides attractive cost effectiveness, although some studies have raised questions concerning the process reliability of adsorption onto alumina. Incomplete regeneration of the media has been observed in several studies [14,15]. When mass balances were done after regeneration, only 70%–80% of the arsenic was recovered. Any subsequent adsorption capacity is decreased as a result of the arsenic, which is irreversibly adsorbed.

In summary, for the removal of arsenic from wastewater.

2.1. Arsenic removals of up to 99% have been demonstrated using a variety of techniques and initial arsenic concentrations

Harper and Kingham [11] used chemical precipitation to treat contaminated water (containing arsenic) from cleanup activities at a former pesticide facility. Initial laboratory treatment studies included precipitation using either alum, Na_2S or FeCl_3 as a coagulant with pH adjustment by hydrated lime. The first sample had an initial arsenic concentration of 9.8 mg/l and coagulant doses were 500 to 1000 mg/l. FeCl_3 with hydrated lime resulted in the greatest arsenic removal, in the range of 98%–99%. In another sample with an arsenic concentration of 31 mg/l, dosages of FeCl_3 ranging from 200 to 1000 mg/l resulted in arsenic removals of 86%–93%. Multiple dosages of coagulants improved the degree of arsenic removal to 98%. The full-scale treatment system, including the addition of hydrated lime and ferric chloride, clarification, filtration and carbon adsorption, achieved arsenic removal rates of 97% to 98%. A total of 650,600 l of wastewater was treated.

Bhattacharyya et al. [16] investigated precipitation of metals with sodium sulfide. Metal sulfide precipitation is possible over a broad pH range because of the high reactivity of sulfides with heavy metal ions and the low solubilities of heavy metal sulfides. At a pH of 8, heavy metals were 98%–99.6% removed with a dosage of 0.6 mole sulfide to mole metal. Arsenic removal was not effective unless sufficient ferric iron was added at a Fe/As mole ratio of 2.

Namasivayam and Senthilkumar [13] investigated the removal of arsenic (V) from aqueous solution using “waste” Fe(III)/Cr(III) hydroxide generated electrolytically in the treatment of Cr(VI) containing wastewaters in a fertilizer industry. The authors were capable of removing 97.8% As(V) of an initial As(V) concentration of 10 mg/l using an adsorbent dose of 400 mg/50 ml.

Haung and Vane [17] investigated arsenic removal (as arsenate) by metal-treated activated carbon in an attempt to improve the adsorption capacity of carbon. The activated carbon was first washed in NaOH or HCl to remove any impurities that might cause interference in the adsorption, and then soaked in various metal solutions, namely, $\text{Ba}(\text{ClO}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$, FeSO_4 , FeCl_2 , $\text{Fe}(\text{ClO}_4)_2$, $\text{Fe}(\text{ClO}_4)_3$ and FeCl_3 prior to adsorption of arsenic. Of these, activated carbon soaked in ferrous perchlorate achieved the highest arsenic removal. An arsenic removal of 99% was achieved on an arsenic solution of concentration 2×10^{-4} M As^{5+} , by using the metal-treated activated carbon.

2.2. Better arsenic removal has been found for arsenic in the +5 state (arsenate) than the +3 state (arsenite)

Cheng et al. [18] investigated coagulation, one of the most common treatment processes for removing arsenic from water, as a possible treatment for removing arsenic from river water. The authors concluded, as have other authors including Scott et al. [19] and Hering et al. [20], that arsenate is more effectively removed than arsenite and that oxidation of arsenite to arsenate is necessary to achieve effective arsenic removal. Hering et al. [21] found that As(V) was much more efficiently removed than As(III) during coagulation with ferric chloride (90% versus 30% removal efficiency, respectively).

Tokunaga et al. [22] investigated the removal of As(V) and As(III) from aqueous solutions using a variety of salts including lanthanum(III), aluminum(III), calcium(II) and iron(III). For As(III) complete removal was not possible, the greatest success was achieved with iron(III) and lanthanum salts. Iron(III) was capable of 40% As(III) removal, while lanthanum(III) was capable of achieving 60% removal. When the same experiments were conducted using As(V), iron(III) was successful in removing 76% As(V) while lanthanum(III) removed in excess of 99% of the As(V). Of the other salts investigated, aluminum and polyaluminium chloride (PAC) were capable of removing 40% As(V). Both aluminum and PAC were not effective in removing As(III) ions. Adjustment of the initial arsenic(V)-to-lanthanum ratio to 1:3 or higher resulted in arsenic removals which were greater than 99%. The studies were conducted using an initial As(V) concentration of 0.25 mM. The optimum pH was 5 to 10. In an earlier work by Tokunaga et al. [23], it was found that the optimum pH was highly dependent upon the form of the lanthanum. The optimum pH range was 3–8, 4–7, and 2–4 for lanthanum hydroxide, lanthanum carbonate and basic lanthanum carbonate, respectively.

2.3. Arsenic removal by coagulation has found to be more effective using iron(III) than alum

Gulledge and O'Connor [24] simulated coagulation, flocculation, sedimentation and filtration for arsenic removal (from a water sample with an initial arsenic concentration of 0.05 mg/l) by alum and ferric sulfate. Ferric sulfate was more effective, leading to 90% to 100% removal of arsenic, at doses of 10 to 50 mg/l over the tested pH range of 5–8. Alum was less effective and only comparable with ferric sulfate at a lower pH (5 or 6), and higher concentration (30–50 mg/l).

Hering et al. [21] investigated arsenic removal by coagulation and found alum was incapable of removing As(III), while ferric chloride was capable of removing approximately 30%. The pH range for As(V) removal with alum was also more restricted than with ferric chloride (6 to 8) versus above 8 for FeCl₃. Edwards [25] also reported that iron(III) is more effective in removing As(III) than alum.

The study by Cheng et al. [18] used both alum and FeCl₃ at three different concentrations, 10, 20 and 30 mg/l, as coagulants. A cationic polymer, added at a concentration of 3 mg/l, was used as a coagulant aid.

The study was applied to both bench and pilot scale trials, with the authors concluding that FeCl₃ is a much more effective coagulant than alum when compared on

an equal weight dosage basis. FeCl_3 coagulation is not pH dependent between 5.5 and 7.0, but increasing coagulant dosage will increase As(V) removal. The pH dependence for alum was much more pronounced than that for the iron.

2.4. Most adsorption onto alumina or carbon takes place within 24 h

Patterson and Passino [26] investigated arsenic removal by adsorption using activated alumina. While no measure of effectiveness was indicated, the authors did provide the optimum conditions for the procedure. Adsorption of arsenic on activated alumina was greatly affected by pH. This phenomenon has also been noted by other authors, including Ghosh and Teoh [27]. Maximum adsorption of arsenate occurs at a pH of 5 or less. Kinetic data for adsorption of arsenate on alumina revealed that the removal was rapid in the first 24 h and then slowed considerably as the reaction approached equilibrium. At pH of 6.5 or less, 95% of the maximum adsorption was attained in less than 24 h. At a surface loading of 67 $\mu\text{mol/g}$, the solution concentration of arsenate decreased from 5 to 0.1 mg/l in a few hours. Ionic strength had no effect on the adsorption, and regardless of temperature, equilibrium adsorption was assumed to be completed in 6 days.

Haug [28] investigated the possibility of using activated carbon as a means of adsorbing arsenic and concluded that, generally, powdered activated carbon had better capacity than granular activated carbon for arsenic removal. Further, lignite-based activated carbon, and high ash content activated carbon, had much better As(V) removal capacities than bituminous-based activated carbons. Diamadopoulos et al. [29] found that the removal of arsenic (V) from water was enhanced up to five times, for the high ash activated carbons. Strong interactions between the arsenate ion and the inorganic part (ash) of the activated carbon were proposed to explain these results. Diamadopoulos et al. [29] investigated the use of fly ash, a high ash carbon, and a by-product of coal-fired power stations, as a means of removing arsenic from solution. The trials were based on arsenic concentrations of 50 mg/l using fly ash added at 1 g/l of arsenic solution.

Experiments were performed at three pH levels. A pH of 4 was the most effective. Most adsorption took place in less than 24 h, and equilibrium was reached within 72 h. Sen and Arnab [30] noted that fly ash adsorbed at a slower rate than activated carbon, but in the end was comparable in capacity. Complete removal of arsenic was possible at pH 4. The greatest arsenic removal was achieved at a pH of 4 (80%), which was up to four times greater than that at the other two pH levels of 7 and 10.

The cost effectiveness of some arsenic treatment options have been ranked by Chen et al. [31]. In general, costs increased in the following order: modified conventional treatment (e.g. coagulation) \ll activated alumina or anion exchange < reverse osmosis. Despite the ranking of Chen et al. [31], the technology that will best remove arsenic depends on the wastewater quality.

Whether anion exchange or activated alumina is the more cost effective method is dependent upon the raw water concentrations of sulfate and arsenic. For example, high influent sulfate is expected to shorten anion exchange runs, thus increasing operating costs. In general, the following trends were observed: in low sulfate water (< 10 mg/l) anion exchange was a more cost effective control strategy for arsenic. In low arsenic water (< 5 $\mu\text{g/l}$), activated alumina was either cost competitive or favored as a least

cost control option, especially when the sulfate concentration exceeded 10 mg/l in the source water, while in very small systems anion exchange treatment remained the favored option for arsenic control through a broader range of initial sulfate concentrations [31]. Possible detriments for anion exchange include using anion exchange beyond the point of sulfate exhaustion. A chromatographic effect allows exhausted exchange resin to release nearly all previously removed arsenic back into treated water at high concentrations [31].

The presence of co-occurring inorganic solutes can have a pronounced effect on the removal of arsenic during coagulation. Co-occurring inorganic solutes, such as sulfates and phosphates, may directly compete for surface binding sites and may also influence the surface charge of the ferric oxide, thus indirectly affecting the adsorption of trace contaminants such as arsenic. While the presence of co-occurring inorganic solutes will more generally cause a decrease in the amount of arsenic removed during coagulation, under certain conditions they can actually increase rather than decrease the removal of trace contaminants by adsorption. At pH 9.0, the removal of As(V) (at an initial concentration of 20 $\mu\text{g/l}$) during coagulation with 4.9 mg/l FeCl_3 was enhanced in the presence of 3.0 mM calcium, probably because the calcium counteracted the slight competitive effect of phosphate [20]. Similar effects were observed for the adsorption of As(V) (at an initial concentration of 35 $\mu\text{g/l}$) onto preformed hydrous ferric oxide [20].

Hering et al. [21] concluded that removal of As(V) by either ferric chloride or alum was relatively insensitive to variations in source water composition below pH 8. At a pH between 8 and 9, the efficiency of As(V) removal by ferric chloride was decreased in the presence of natural organic matter. Removal of As(III) from source waters by ferric chloride was more strongly influenced by source water composition. The presence of sulfate (at pH 4 and 5) and natural organic matter (at pH 4 through 9) adversely affected the efficiency of As(III) removal by ferric chloride.

The preceding paragraphs have provided numerous examples of how arsenic can be successfully removed from waste waters; however, in doing so we are now faced with a new dilemma, that is, how to dispose of the more concentrated arsenic product that we have now created. The most likely and feasible solution to this predicament may be to use one of a number of solidification/stabilization techniques.

3. Solidification /stabilization

Solidification/stabilization (S/S), also known as encapsulation or fixation, is a technology used to transform potentially hazardous liquid or solid wastes into less hazardous or nonhazardous solids before disposal in a landfill, thus preventing the waste from entering the environment. Frequently, fixed wastes must satisfy regulatory requirements on leachability prior to landfill disposal (for example, the U.S. EPA Toxicity Characteristic Leaching Procedure [32], the Federal Extraction Toxicity Test, EPTox [33] and the California Waste Extraction Test (WET) [34] and in Australia, the Australian Bottle Leaching Procedure [35]) and/or must be buried in secure landfill sites. In essence, leaching from the solidified/stabilized form must be below prescribed thresholds and, in addition, leaching into aquifers is controlled/obviated in secure sites.

A number of S/S processes specifically for arsenic have been investigated. These included fixation with:

- Portland cement [36,37]
- Portland cement and iron(II) [38]
- Portland cement and iron(III) [38]
- Portland cement and lime [39]
- Portland cement, iron and lime [40,41]
- Portland cement and fly ash [42,43]
- Portland cement and silicates [42]

In addition to these studies, which have investigated the aforementioned S/S processes, there has also been limited research into the safe disposal of arsenic wastes by incorporation into slags and encapsulation of arsenic wastes using polymers [44–46].

Twidwell and Mehta [44] investigated the stabilization of arsenic in copper smelter flue dust by dissolution in slag matrices. The stabilization process involved converting the arsenic oxide contained in the flue dust to calcium arsenate and arsenite by low temperature air roasting in the presence of lime. The calcium arsenate and arsenite were then dissolved in a molten iron silicate slag matrix. The incorporation of up to 23.5% arsenic into the slags was investigated. All slags passed the U.S. EPA EP Toxicity Test for arsenic extraction. Even the slag with the highest arsenic content (23.5%), which leached 1.8 ppm arsenic, easily passed the EP Toxicity Test limit of 5 ppm arsenic leached.

De Villiers [45] investigated the fixation of arsenic-containing wastes in lead–zinc blast furnace slags using a calcium arsenite containing waste. The waste was mixed with the slag and heated at 1300°C to 1400°C to dissolve the arsenic into the slag. The arsenic-doped slags contained up to 2.3 wt.% arsenic. It was found that arsenic leached out of the slag as the As(III) species and slowly oxidized to As(V) in the leach solutions. Of four arsenic-doped slags, only one passed the Toxicity Characteristic Leaching Procedure regulatory test (having a leachate concentration of less than 5 ppm arsenic).

Carter et al. [46] investigated the potential for encapsulation of waste by combination with two commodity polymers, recycled high density polyethylene (HDPE) and solprene 1204 (a random styrene butadiene copolymer with a 25% styrene content). They concluded that As_2O_3 could not be suitably bound into HDPE, because the processing temperatures generally employed approach the sublimation temperature. This meant the process was both inefficient and hazardous. When As_2O_3 was stabilized with calcium oxide, volatility was decreased, and arsenic loadings of 17 wt.% were possible. The elastomer appeared to have the greater potential, as it proved possible to incorporate As_2O_3 at higher loadings than were possible using HDPE, while calcium arsenite was encapsulated with higher success, with loadings of up to 50 wt.% easily attained. Both of these techniques, i.e. incorporation of arsenic into slags and the encapsulation of arsenic using polymers, require further evaluation to determine their suitability.

Of the solidification/stabilization formulations investigated, the use of cement and fly ash appears to be the least successful. Fixation of metals using Portland cement and fly ash is believed to occur via the combination of producing an impermeable monolith,

which reduces the surface area available for leaching, creating a high pH environment that generally limits the solubility of most metals and limits their leachability, and/or formation of metal complexes with the cement/fly ash matrix [42]. Akhter et al. [43] has raised serious concerns about the benefit of using fly ash. The work of Akhter et al. [43] yielded results which indicated that the leachability of arsenic is much greater from those solidification/stabilization formulations which contained fly ash. The use of fly ash also has associated with it the problem of bulking. Since fixed waste is generally buried in a landfill, it is desirable, for cost and space reasons, to bury the smallest quantity possible. Bulking due to treatment by silicates and metal hydroxides is low, approximately 20% or less, while bulking resulting from treatment with cement/fly ash is high, approximately 100%.

Presently, it appears that the solidification/stabilization of arsenic is most successful when cement, cement and iron, cement and lime, or combinations thereof, are used. Akhter et al. [36] investigated various methods for the immobilization of arsenic, cadmium, chromium and lead in contaminated soil. The soil under investigation had an arsenic concentration of 12,200 ppm. The suitability of various combinations of Portland cement, fly ash, blast furnace slag, lime and silica fume was investigated. The only sample in the study showing reasonable leaching performance was that using Portland cement alone, at a dosage of 1 part soil in 0.44 part cement.

Dutre and Vandecasteele [47] investigated solidification/stabilization of solid waste containing an average of 42% arsenic. Solidification was achieved by adding waste acid (5 M hydrochloric acid containing zinc and iron, each approx. 60 g/l, and lead, approx. 150 mg/l) blast furnace slag, slaked lime, cement and water. This process was carried out over two days. The waste, slags and waste acid were all mixed together and then set aside overnight. The mixture was set aside overnight because it is believed that silicon containing acids (H_2SiO_3) are formed, due to a reaction between the acid and the silicate compounds of the binder materials, and which are responsible for further polymerisation on a long-term basis [47].

The authors also investigated the addition of aluminium and barium salts for lowering the leachability of arsenic from the solidified waste by formation of compounds with low solubility products. However, results indicated that lime, thought to allow the formation of a sparingly soluble calcium arsenic compound, was more effective than either of these.

Subsequent optimization of the initial S/S scheme led to omission from the formulation of the waste acid and blast furnace slag. These two ingredients appeared to have little or no effect on the fixation, despite obviation of the route to silicious acids described earlier. Lime addition was the critical element of the process, and consequent simplification allowed for a one day fixation. The revised S/S recipe was (per 10 g of waste), 10 g of lime and 11 g of cement.

A more recent work by Dutre and Vandecasteele [39] examined the solidification/stabilization of a waste fly ash from the metallurgical industry containing arsenic concentrations ranging from 23% to 47% (wt.%). The optimum solidification/stabilization formulation consisted of 8 g of lime, 6 g of cement and 20 ml of water per 10 g of waste material. The solidification process was capable of reducing the leachate concentration from 5 g/l to approximately 5 mg/l. The extraction test used consisted of

agitating 100 g of the treated material with 1 l of distilled water for 24 h. The reduction in the arsenic concentration was due to the formation of CaHAsO_3 in the leachate, in the presence of Ca(OH)_2 .

Palfy et al. [41] investigated the stabilization of a waste material arising from the carbon dioxide scrubbing in the Vetrocoke technology, where As_2O_3 solution is the activator. The aim of the fixation process was to embed calcium and ferric arsenates/arsenites in a cement matrix. The optimum process utilized a Ca:As ratio of 8 (ratios greater than 8 did not lead to a significant reduction in the residual concentration of arsenic in the solution) and a Fe:As mole ratio of 6. After the fixation process, the leachate concentration was 0.823 mg/l compared to 6430 mg/l for the untreated waste. Leaching tests were conducted in distilled water at 25°C with a solid-to-liquid ratio of 1:10 and a mixing speed of 150 rpm.

Of the successful solidification/stabilization formulations, the use of iron appears to be the most preferred option, partly due to the fact that iron is often a component of process liquors. Hence, the use of iron provides the opportunity to dispose of two waste streams at once. The success of using iron is highly dependent upon the oxidation states of both the iron and arsenic [38]. The use of iron(II) is preferred for arsenic stabilization because it has proven to be more effective over a wider range of mix designs and over the longer term than iron(III). The use of iron(III) is not recommended for arsenate stabilization, because the fresh cement mix adsorbs ferric ions and doesn't allow adequate solidification/stabilization until long cure times elapsed [38]. Taylor and Fuessle [38] suggest that effective conversion of arsenite to arsenate can be accomplished by the addition of hydrogen peroxide at stoichiometric dosages with adequate mixing. Emmett et al. [48] have outlined a process in which dissolved iron(III) in the presence of UV light was used to initiate and sustain the oxidation of arsenic(III) in aqueous acid. The photolysis reactions of iron(III) in water involve the transfer of one electron from the complexed ligand, such as organic, hydroxide or chloride species to the iron(III) centered orbital forming Fe(II) and a free radical. The subsequent reaction of the primary free radical reactions results in oxygens being consumed and the arsenic being oxidized. The presence of elements like Ca, Cd, Zn, Sr, Pb, Cu and Mg have been reported to promote the stability of iron-arsenate precipitates, as the solubility of arsenic can be lowered significantly over a wide pH interval [49–51]. Increasing the iron to arsenic mole ratio also results in a greater success in the solidification/stabilisation of arsenic using iron. Taylor and Fuessle [38] recommended that the iron(II)/arsenic mole ratio be at least six, although slightly lower dosages of iron(II) may be effective if cure times of at least 60 days are used.

While the research to date indicates that the use of iron, lime and cement can be beneficial in the solidification/stabilization of arsenic, it is difficult to differentiate between the results obtained by the numerous researchers and draw any firm conclusions on which S/S processes are the most efficient and effective. This is mainly due to two reasons.

(1) The diverse range of arsenic compounds and oxidation states that can be encountered as arsenic waste.

The complex chemistry of arsenic unfortunately means that a "recipe" which may work with one particular waste may not, and often will not, work with another type of

arsenic waste. The work outlined by Buchler et al. [37] and Johnson et al. [52] are good examples of how the success of the fixation varies drastically with the nature of the waste and simply not just the varying arsenic concentrations.

The work of Buchler et al. [37] illustrates how the successfulness of any S/S process to treat arsenic containing wastes can vary greatly, depending on the particular arsenic compound, and not merely upon the initial arsenic concentration. The TCLP leachate concentrations varied from 510 to 1.7 mg/l. Those S/S processes that contained either sodium arsenate or sodium arsenite were the most successful, with As leachate concentrations of 1.7 and 2.1 mg/l, respectively, while the S/S process which contained arsanilic acid performed least effectively, with arsenic leachate concentrations of 510 mg/l.

The arsenic compounds also have major effects on cement hydration reactions, as shown in solid-state NMR spectra, although there is no direct correlation between the degree of hydration in the matrix and arsenic leachability [37]. The most leachable compound determined by Buchler et al. [37], arsanilic acid, showed the least effect on cement hydration.

Johnson et al. [52] investigated the stabilization of three different arsenic wastes. Waste No. 1, composed mostly of sulfate and chloride salts, contained approximately 2% organic arsenicals. The second material, Waste No. 2, was a yellow, damp (37% moisture) acidic filter cake containing approximately 0.9% arsenic in the form of As_2S_3 , while Waste No. 3 was a fine white powder containing 90% As_2O_3 .

Each waste was subjected to several identical fixation processes (the exact nature of these processes was not revealed). The three wastes were quite different in their response to fixation attempts, with Waste No. 1 by far performing the worst. Even after fixation, Waste No. 1 still leached an average of 78%. Waste No. 3 performed significantly better than Waste No.1, leaching less than 12% arsenic, while Waste No. 2 performed the best, leaching less than 2% arsenic. Unfortunately, given that the exact nature of the fixation processes was not revealed, the information that can be drawn from this work is limited.

(2) The different leaching tests that researchers have utilized to access the leachability of the treated waste.

Due to the differences between the tests, such as the acidity of the leaching fluid, extraction periods, and particle sizes, the results obtained from the various tests can consequently be quite different. A detailed description of the leaching tests is provided elsewhere [53]. Of the common leaching tests used, the TCLP and the EPTox are the most similar. Studies have shown that TCLP concentrations can be up to 3.0 times greater than those for the EPTox Test [53]. The WET test is generally a more aggressive leaching test than the TCLP for several reasons. In the WET, solid wastes are crushed to pass a smaller sieve, and the contact time between leaching solution and waste is greater.

An example illustrating the difficulty of making any comparisons on the successfulness of S/S processes between studies using different leaching tests can be found in the results by Chu et al. [42]. They conducted studies using both the TCLP and WET tests. When using the TCLP test, the treatment using metal hydroxides appeared slightly better than the treatment that utilized either silicates or cement/fly ash. The results were 0.02,

0.03 and 0.09 mg/l arsenic, respectively. However, when the same samples were subjected to the WET tests, there were much larger differences between the results obtained for the numerous S/S processes. When using the WET test, the treatment using silicates yielded significantly better results than those obtained using metal hydroxides or cement/fly ash. The results obtained were: silicates, 3.2 mg/l arsenic; metal hydroxides, 17 mg/l arsenic; and cement/fly ash, 24mg/l arsenic.

4. Conclusion

Many processes produce dusts or sludges containing high concentrations of hazardous materials. For example, arsenic trioxide is a by-product of recovering gold from arsenical gold ores and concentrates. Although the current trend is to minimize wastes and re-use them where possible, there are always some materials produced that cannot be recycled and must be disposed of in an environmentally safe manner. Since the demand for arsenic and its compounds is far less than the amount being produced annually, there is little economic incentive to invest in equipment and technology to recover arsenic. Only where the arsenic produced is of a sufficiently high purity may the arsenic be economically recovered for use in the manufacture of wood preservatives, CCA and ACZA. Not only must the arsenic be recovered, but the recovery process must ensure that there are negligible amounts of contaminants, such as chlorine and iron, which may cause damage to the process equipment or be detrimental to the finished product.

To remove arsenic from waste waters, the most commonly used technologies are adsorption onto activated alumina or carbon, and precipitation or adsorption by metals, predominantly iron(III). The technologies for removal of arsenic from waste waters are most suited to dealing with relatively low concentrations of arsenic, i.e. the low $\mu\text{g/l}$ level. However, the technique of precipitation, generally using iron(III), is suited to higher concentrations, normally at the low mg/l levels. Adsorption on alumina or carbon is an area that seems to be gaining in prominence. However, some recent studies have raised concerns about the possibility of fully regenerating spent alumina [14,15]. While not suited to high concentrations, the attraction to date of using alumina or carbon has been the possibility of regenerating the alumina or carbon without any loss in adsorptive capacity.

The lack of any economic incentive to recover arsenic and the danger associated with the temporary storage of arsenic wastes, be it in drums or any other unsuitable manner that would result in dire consequences in the case of leaks or fire, has led to interest in technologies for long term or “ultimate” disposal of hazardous wastes containing arsenic. Stabilization processes were designed to address the needs of ultimate disposal. Stabilization of hazardous waste involves trapping the waste in a stable solid matrix, thus minimizing the escape of hazardous materials by leaching. This process also involves fixing or immobilizing the toxic elements by physical and or chemical means.

A wide range of processes has been used in an attempt to successfully fix arsenic, and these processes include mixing the arsenic with various combinations of cement, lime, iron, silicates, and fly ash. Unfortunately, the additives listed have not all been

systematically investigated at the same or similar additive to waste ratios, or with similar arsenic compounds. This limits the generality of many of the conclusions that can be drawn from previous research. Unfortunately, due to the complex chemistry of arsenic, the successfulness of any S/S process to attempt to treat arsenic wastes appears to be highly dependent upon the particular arsenic waste and not merely the varying arsenic concentrations, as indicated by the research conducted by Buchler et al. [37] and Johnson et al. [52].

Besides the chemistry of the particular arsenic waste, the greatest hindrance at present in determining just what is the optimum solidification/stabilization process is the large number of differing leaching tests that have been utilized. Aside from the standard leaching tests such as the TCLP [32], many researchers have developed their own leaching methodologies. Thus, it is nearly impossible to draw any reasonable conclusions as to which solidification/stabilization process is the most efficient and effective, since they are based on results obtained from leaching tests utilizing differing solid-to-liquid ratios, differing leaching fluid, agitating methods and contact times.

The encapsulation of arsenic wastes using slags is an avenue that has also been investigated, although not to the same extent as the S/S techniques utilizing cement. The technique offers the benefit of disposing of two wastes with little economic value at once, i.e. the arsenic waste and the slag. However, research to date has yielded results that are far from conclusive. Some studies have had success in the incorporation of up to 23.5% arsenic [44], while others have failed to successfully encapsulate 2.3% [45]. It appears that, like the more common S/S techniques, the process will be highly dependent upon the chemistry of the particular arsenic waste as well as the chemistry of the slag, which is being used to encapsulate the arsenic.

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