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The Disposing Techniques Of Water Treatment Wastes Containing Arsenic — A Review

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Abstract: Solid waste management in developing countries is often unsustainable, relying on uncontrolled disposal in waste dumps. Particular problems arise from the disposal of treatment residues generated by removing arsenic (As) from drinking water because As can be highly mobile and has the potential to leach back to ground and surface waters. This paper reviews the disposal of water treatment wastes containing As, with a particular emphasis on stabilisation/solidification (S/S) technologies which are currently used to treat industrial wastes containing As. These have been assessed for their appropriateness for treating As containing water treatment wastes. Portland cement/lime mixes are expected (at least in part) to be appropriate for wastes from sorptive filters, but may not be appropriate for precipitative sludges, because ferric flocs often used to sorb As can retard cement hydration. Brine resulting from the regeneration of activated alumina filters is likely to accelerate cement hydration. Portland cement can immobilise soluble arsenites and has been successfully used to stabilise As-rich sludges and it may also be suitable for treating sludges generated from precipitative removal units. Oxidation of As(III) to As(V) and the formation of calcium–arsenic compounds are important immobilisation mechanisms for As in cements. Geopolymers are alternative binder systems that are effective for treating wastes rich in alumina and metal hydroxides and may have potential for As wastes generated using activated alumina. The long-term stability of cemented, arsenic-bearing wastes is however uncertain, as like many cements, they are susceptible to carbonation effects which may result in the subsequent re-release of As.
Keywords: Arsenic, Water pollution, Stabilisation/solidification, Portland cement, Leaching.

I. Introduction

Surface water in Bangladesh and India was the source of gastrointestinal diseases that were responsible for very high rates of morbidity and mortality during the 1970s. In response to this, thousands of tube wells were installed as an alternative means of supplying drinking water. The groundwater in these regions often has arsenic (As) levels as high as 500 µg As/l. This is far in excess of the World Health Organisation[1] advised limit of 10 µg As/l. Standard water testing procedures did not initially monitor As levels, and due to the cumulative nature of As on human health, it was several years before acute arsenicosis was diagnosed. By this time several million people had been exposed to As in what has been described as the largest mass poisoning event in history[49]. In response to this, a range of As removal technologies has been developed for both household and municipal uses. In addition to the severe As

problems in Bangladesh and India, it is evident that many other countries (both developed and developing) have detected concentrations of As in drinking water above the 10 µg/l guideline value, confirming the current and global nature of this problem. In response to this, there has been a corresponding intensification of research and development seeking to establish appropriate treatment technologies to remove As from contaminated groundwater sources. Whilst considerable progress has been achieved in terms of water treatment, the disposal of As containing wastes
generated from water treatment processes is a major issue that has received relatively little attention[19]. The primary focus of this paper is to review the issues associated with the disposal of As containing water treatment wastes.

II. Arsenic In Aqueous Solution

Arsenic, like other metalloids close to it in the periodic table, is both redox sensitive and able to formoxyanions, similar to many of the nonmetals. In consequence, the speciation of arsenic is sensitive to both the redox state and pH of the chemical environment. The most stable redox states are −3 (arsine gas, AsH3), −1 (alkyl arsenic), 0 (zero-valent, elemental arsenic), +3 (the arsenites) and +5 (the arsenates), and these latter two states dominate aqueous arsenic solutions. Once dissolved, both As(III) and As(V) species are able to bind with one or more hydrogen ions, forming two deprotonation series, which in turn govern the mobility or fixation of As. The standard electrode potentials (Eo in volts vs SHE) are shown above the solid line separating each redox couple in Fig. 1.

Aqueous species of arsenic in oxidation states III and V are susceptible to sequential deprotonation with increasing pH, the extent of which may be calculated from the dissociation constants for the reactions shown in Table 1.

Table 1 Deprotonation Of Arsenic Species In Solution[11,55]

Deprotonation series of the arsenates AsV)	
As(OH)30 →H++AsO(OH)2	pka′=9.32
AsO(OH)2−1→H++AsO2(OH)−2	pka″=12.10
AsO2(OH)−2→H++AsO3−3	pka‴=13.41
Similarly, for the arsenites (AsIII)	
AsO(OH)30 →H++AsO2(OH) −2	pka′=2.2
AsO2(OH)2−1 → H++AsO3(OH)−2	pka″=6.96
AsO3(OH)−2 → H++AsO4−3	pka‴=11.5

These data allow the abundance of each species to be calculated as a function of solution pH. Fig. 2 (AsV) and Fig. 3 (AsIII) were calculated using the ion-pairing model PHREEQC-I,[40] version 2.13.2 and the Lawrence Livermore database which is releasedwith that code. The solutions chosen to represent an electrolyte buffer of variable pH comprised HCl–NaCl–NaOH mixtures of less than 0.2M total ionic strength. In considering themobility and fixation of arsenicalwastes it is of paramount importance to have a good understanding of the chemical environment. Both the precipitation–dissolution and the sorption–desorption processes which govern arsenic fixation, are strongly influenced by solution chemistry. The reduced trivalent form arsenite (AsIII) dominates under anoxic conditions e.g. in groundwater, whilst the oxidised form arsenate (AsV) is generally dominant in oxygenated or surface waters over the pH range typically encountered in water treatment. Conversion of As(III) to As(V) is thermodynamically favoured in oxygenated water, but the time periods for change in oxidation states are indeterminate and may take several days,weeks or months, depending on the specific conditions[27]. It is important to note that many standard leach tests have not been designed to evaluate the leaching of waste material over realistic periods of time up to typically 24h. This sluggish behaviour is typical of many redox processes and analyses of sampledwaters demonstrate that disequilibrium conditions may persist. Combining Figs. 1–3, allows calculation of a Pourbaix diagram for arsenic in aqueous solution, as shown in Fig. 4.

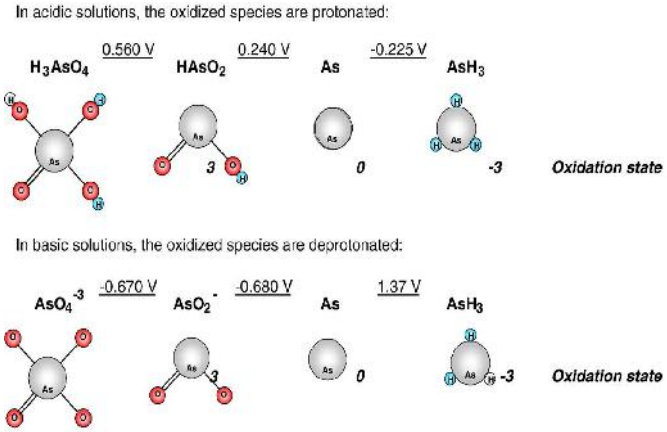

Fig. 1. Schematic speciation of arsenic in oxidation states 5, 3, 0 and −3 in acidic and basic solutions.

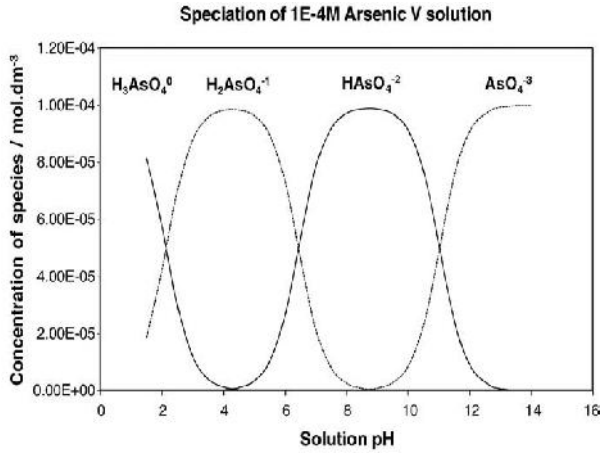

Fig. 2. Aqueous speciation or arsenic V as a function of pH.

Owing to the surface charges developed by ferric and aluminium hydroxides, they are able to remove dissolved As and other metal species from solution by sorption. Ferric precipitates are the most effective at removing arsenates from solution over a wide pH range[26]. Conventional water treatment processes commonly use the addition of iron and aluminium salts, such as ferric chloride [FeCl3] and aluminium sulphate [Al2(SO4)3], in order to separate dissolved and colloidal contaminants, mainly through the precipitation of the Fe or Al hydrolysis products.

Calcium is often used in the form of lime (CaO), hydrated lime (Ca(OH)2) and calcium carbonates, both within water treatment processes as well as some of the technologies discussed within this paper. Whilst investigating the behaviour of arsenic in leachate,[13] observed that arsenates and arsenates chemically bond with hydrated lime to form precipitates:

2H3AsO4 + 3Ca(OH)2 (aq) → Ca3(AsO4)2 (s) + 6H2O
H3AsO3 + Ca(OH)2 (aq) → CaAsO2OH (s) + 2H2O

These Ca–As compounds have been studied extensively in the presence of cements by[22] determined both experimentally and numerically the thermodynamic properties of Ca–As compounds. They demonstrated the utility of thermodynamic modeling in the arsenic–cement–pore solution systems, and showed close agreement between experimentally determined concentrations and their numerical predictions. In the cement pore solutions in the presence of CSH gel and portlandite (Ca(OH)2), they estimate the limiting solubility of CaAsO2OH to be around 7E−4M. Using similar methods, the minimum solubility of calcium arsenate as Ca3(AsO4)2 is approximately twice as soluble, at around 1.2E−3M, as shown in Fig. 5.

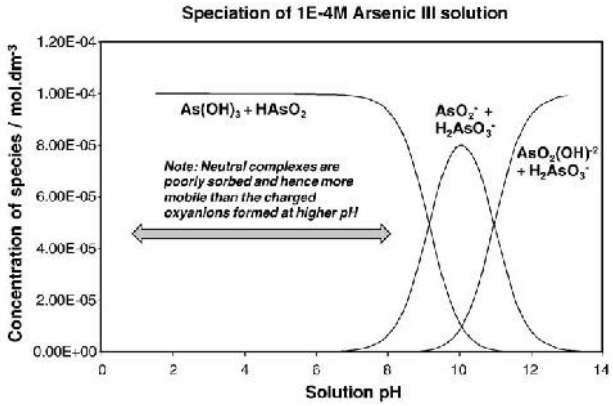

Fig. 3. Aqueous speciation or arsenic III as a function of pH.

Robins (1981)[43] considered the solubility of similar metal arsenates (Mg, Fe, Ca) and presents a comprehensive set of phase diagrams in aqueous systems, and noted their vulnerability to carbonation. Bothe and Brown (1999)[9] studied the stabilisation of arsenic in a range of environments likely to form Ca3(AsO4)2 but did not observe this phase, rather Ca4(OH)2(AsO4)2·4H2O and Ca3(AsO4)2·3 2/3H2O dominating the solid phases. They extended the study to include phosphorus, and found the compound Ca5(AsO4)3OH (arsenate apatite) to be stable and investigated its partial solid solutionwith hydroxyapatite,which proved not to be extensive,with arsenate apatite forming at the expense of Ca5(PO4)3OH.

Arsenate in the form of pure Ca3(AsO4)2 (s) was found to be less soluble than arsenite in the formof CaHAsO3 (s) providing evidence that arsenates are easier to immobilise than arsenates[17]. Itis now accepted that As(V) is more strongly sorbed than As(III) where pH is acidic or near neutral. In oxidizing environmentswith a pHgreater than 4.09, ferric iron hydroxides exist as colloids that will sorb arsenic. Conversely, conditions reducing As(V) to As(III) can be expected to reduce Fe(III) to Fe(II) and so in a reducing environment, any precipitated ferric hydroxide will become soluble, releasing the arsenic previously sorbed[33]. In practice this means that arsenic adsorbed to ferric hydroxides in sediments, will begin to be released as groundwater becomes more reducing. Under these conditions, arsenate is reduced to arsenite and ferric iron to ferrous iron,which is solublewithin the normal pHrange of groundwater. Hering et al. (1997)[26] investigated as removal in the presence of other

contaminants and concluded that although arsenate removal by ferric chloride or alum was not affected by variations in sourcewater composition belowpH 8, the efficiency of ferric chloride at pH 8–9 decreased if organic matterwas present, suggesting that arsenic may not be as strongly sorbed in waste that is rich in organics. Mobilisation of sorbed species by organic colloids is well documented, but is outside the scope of this review[34].

Although predictions of ionic sorption onto charged surfaces are well established[18], data describing arsenic fixation onto metal oxides have been sparse. Appello et al. (2002)[5] made significant advances in closing this knowledge gap in their work on surface complexation of ferrous iron and carbonate on ferrihydrite and mobilisation of As. They employed the double-layer model for surface complexation and derived complexation constants for carbonate and ferrous iron on ferrihydrate, allowing simulations of competitive sorption to be made. The calculations are in good agreement with experimental findings and they concluded that sorption of carbonate, in particular, at common soil and groundwater concentrations reduced the sorption capacity of arsenic on ferrihydrite significantly. This is an important finding as the carbonation of cement-stabilised flocs may be vulnerable not only to denaturing of any arsenic-bearing solids they contain, but to competitive desorption of arsenic by the dissolved carbonate ions.

In conclusion, arsenic may be released from a system by two principal mechanisms, desorption of bound arsenic from solid surfaces and by dissolution of arsenic-bearing phases. Under reducing conditions, solid arsenites, such as arsenopyrite (FeAsS) are free to dissolve, and this is true for many ores of the transition metals in which arsenic is present. The chemistry is further obscured under reducing conditions, as arsenic present in oxidation state (V) is likely to be reduced to As(III) in the anoxic environment. As arsenic (III) is less strongly sorbed than arsenic (V), proportionally more of the element is partitioned into the liquid phase than in oxidizing environments. Smedley and Kinniburgh (2002)[48] described such reducing environments in near-surface waters (river delta sediments in Bangladesh) as a source of arsenic release which ultimately contaminates local groundwater. They went on to show the dramatic desorption of arsenic (V) from ferric oxide surfaces as pH rises above 8.5, especially at very low water/solid ratios. Although high pH environments are rare in nature, restricted mainly to altered, highly saline pore solutions or areas of geothermal activity, the implications for cement-stabilised arsenical wastes are obvious and far-reaching.

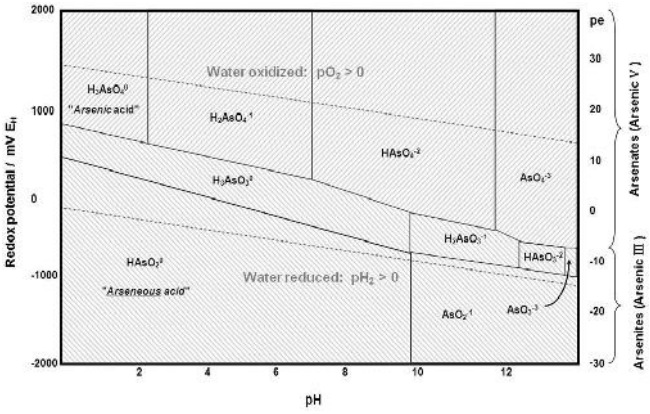

Fig. 4. Pourbaix diagram for arsenic in aqueous solution. [As]=1.0E−4mol dm−3

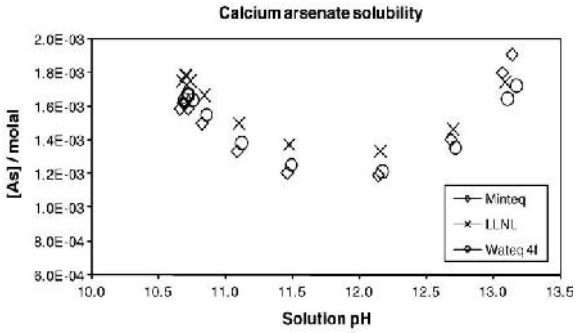

Fig. 5. Predicted solubility of calcium arsenate as a function of solution pH controlled by addition of NaOH and HCl. Three sets of calculations show good agreement between the databases "Minteq", "Wateq-4f" and from the Lawrence Livermore National Laboratory, supplied with PHREEQC-I *[40].*

III. Technologies For Removing Arsenic From Water

The removal technology for As employed at any abstraction point will be determined by the chemical properties of the water (pH, iron content etc) as well as cost and availability. Various technologies have
been developed for household and community /municipal use, but those most commonly used in developing countries may be categorised as co-precipitation/adsorption and sorptive filtration, as shown in Table[27,1,35].

Co-precipitation/adsorption processes for As removal involve the addition of a coagulant, typically ferric chloride or aluminium sulphate. As stated earlier, these coagulants hydrolyse to form

hydroxide precipitates which flocculate into agglomerates that settle ('sweep' flocculation), adsorbing arsenates. The waste generated is a wet sludge with up to 32% water content. Pre-oxidation of arsenite to arsenate is required for all sorptive filtration or coagulation and coprecipitation based technologies[27]as precipitated As(V) is more stable than As(III)[31,46]. Less typically, arsenates can be removed through adsorption and occlusion by precipitates formed during lime softening of water with CaCO3, Mg(OH)2 or Fe(OH)3[23].

Sorptive filtration involves filtering the water through an in-line column containing solid active media which removes arsenates by sorption. Sorptive media include activated alumina (AA), granular activated carbon, granular ferric hydroxide, iron oxide coated sand and iron filings. Essentially arsenate ions (V) sorb to the granules and are held within the media which when spent is either discarded (e.g. iron based media in Chari filters) or regenerated (e.g. AA filters). AA columns are regenerated by washing with dilute alkali such as caustic soda and neutralising using HCl or H2SO4. Alkaline waste sludges result from the regeneration process due to the ratio of alkali to acid used in the washing.

More elegant technologies have been applied to the removal of arsenic from solution but come with the penalty of increased cost. The next most affordable approaches employ electrochemical methods which are dominated by electrocoagulation. Kumar et al. (2004)[29] hypothesized that during electrolysis, electrocoagulation offers the possibility of anodic oxidation and in-situ generation of adsorbents (such as hydrous ferric oxides and hydroxides of aluminium). They worked with iron, aluminium and titanium anodes at modest current densities (0.65 to 1.53mAcm−2) from which metals were stripped by oxidation (to formoxide species on the electrodes) and towards which, the oxyanions of arsenic would be attracted. They compared the treatment of water for As(III) with As(V) removal by this method and with conventional treatment with ferric chloride, concluding that electrocoagulation offers advantages for treatment of As(V) bearing solutions. The practical lower limits they obtained were around 1E−7M (~10 μg/l) and treatment times to reach this effective minimum were tens of minutes. At a larger scale, a recent reviewby [25]described the available technologies for electrocoagulation of arsenic from solution comparing continuous-flow reactors with turbulent flow and air lift reactors, all using sacrificial anodes. They found that solution concentrations less than 2 mg/l (~2E−5m)were readily achievable, but that increasing the current density beyond a maximum value did not improve the process further. They speculate that this is due to passivation of the anode, a view with which we agree.

Considerable interest has been shown in the hydrothermal synthesis of low-solubility arsenic-bearing phases, which offers a route by which this element may be fixed with little risk of remobilisation. Pre-eminent amongst these is the Scorodite process[37.53] in which arsenic is removed from solution by hydrothermal precipitation at temperatures in the range 170–200 °C. The presence of Fe(III) is required for combination with As(V) to form the crystalline, hydrated ferric arsenate known as scorodite (FeAsO4·2H2O). The contained arsenic is effectively immobilised by incorporation into a crystalline, low-solubility compound. Although this has generated interest from the metallurgical and mining industries, it is almost certainly too expensive to be used on the scale necessary to treat waste water treatment residues in Bangladesh and other developing countries.

IV. Characteristics Of Waste Generated By As Removal Technologies

Table 2 summarises the limited information currently available on the physical characteristics of wastes generated by traditional As removal processes, indicating whether the processes are employed at community or household level. All removal technologies generate an arsenic-rich waste product, either as a true precipitate or a sorbent to which the arsenic is bound. Note that chlorine, commonly used within the water treatment process, is a powerful oxidant that in the presence of organic matter will form chlorinated by-products[27].

V. Sustainability Issues For Arsenic Waste Disposal Methods

Sustainable development is concerned with ensuring that design is made with the intention of avoiding unnecessary social, economic or environmental loss that will have consequences for future generations.

In this respect methods of As waste disposal must be effective and reliable or the problem will not be dealt with in the long-term and water supplies may become unsustainable. Disposal of any hazardous waste requires effective management, so wherever As waste is generated there is a need to establish a well-defined protocol for the disposal of the As sludge[38].

Riveros et al. (2001)[42] reviewed current practices in the metallurgical industry, and noted that arsenic disposal procedures currently favoured by industry involve the formation of an insoluble ferric arsenate compound which is allowed to sediment at the bottom of tailings or residue ponds. It has been shown recently that this poorly formed crystalline compound is similar to "arsenical ferrihydrite" which is ferrihydrite containing strongly adsorbed arsenate anions. Despite concerns about the long-term stability on thermodynamic grounds, arsenical ferrihydrite appears to be stable for many years in the proper environment which includes a slightly acidic pH and oxidising conditions. A high Fe/As ratio and the presence of heavy metals appear to increase the stability of arsenical ferrihydrite. High temperature operations, such as those encountered in the autoclave treatment of refractory gold ores, are conducive to the formation of scorodite, FeAsO4·2H2O, and/or a series of ferric arseno-hydroxysulphate compounds depending on the solution composition. Scorodite has several advantages over arsenical ferrihydrite as a disposal compound including a lower iron demand, a higher density and a greater thermodynamic stability. Other approaches to the disposal of As waste are summarised in the following sections.

A. Landfill

Ashraf et al. (2003)[6] reported that in the absence of any clear guideline for the safe disposal of wastes generated from As removal units, such wastes are often disposed of in an uncontrolled manner to the environment. A common method for the disposal of sorptive filter media and regenerative wastes is dumping of the wastes into small sand covered brick-lined pits. The high water content of sludges generated by co-precipitation and adsorption units increases the bulk of waste to be managed, so raw sludges are often air dried before disposal. Pits are typically about 1 m3, are rarely sealed, and are prone to flooding, leading to leaching into the surrounding soil and eventually groundwater.

Sanchez et al. (2000)[45] commented that the characterisation of leaching behaviour of wastes is a crucial step in the environmental assessment for reuse or disposal scenarios. Eriksen-Hamel and Zinia (2003)[19], acting as consultants in Bangladesh, used the toxicity characteristic leaching procedure (TCLP) test to analyse waste media froma number of different types of traditional removal filters in order to determine if sludge disposal methodswere safe and As could not return to contaminate the environment. They detected negligible concentrations of As in the extraction fluid (e.g. b0.001 mg/l) and concluded that none of the samples could be classed as hazardous. Ashraf et al. (2003)[6] conducted TCLP and column leaching tests on waste materials taken from several removal units used in Bangladesh, and found that in general, leaching of As fromthewastes is not significant and that none of the waste samples were hazardous as defined by USEPA.

When considering options for waste disposal it is essential that appropriate leaching tests are applied and results are correctly interpreted. Leist et al. (2003)[31] undertook an evaluation of leaching tests and commented that the tests did not model the conditions that waste would experience when placed in landfill. Badruzzaman (2003)[7] in a study on As leaching reported that the application of the TCLP "may not be suitable for assessment of long-term leaching of As from As-rich waste, because such leaching may be kinetically restricted". Modification of the TCLP to represent a natural leaching environment is therefore required. TCLP analysis is designed to simulate leaching that takes place in a US EPA-recommended sanitary landfill. It is used to determine whether a waste sample is capable of releasing toxic metals or organics in an amount that exceeds EPA regulatory limits when that waste is subjected to the chemical and physical environment typically encountered within a sanitary landfill. This is not the same as open dumping in a country such as Bangladesh.

Furthermore it was observed that sorption of As by ferric hydroxide is reduced in the presence of organic matter at pHN8 [26]. Organic acids are formed by anaerobic reduction of organic species, whilst buffering maintains pH due to dissociation of large volumes of dissolved CO2 showed that redox zonation of landfill forms anaerobic, transition and aerobic zones. Within the anaerobic zone ferric iron (FeIII) is reduced to ferrous iron (FeII) and within this reducing environment at pH 3–8, arsenate is reduced to more mobile arsenite .

B. Mixing with livestock waste

Water treatment wastes containing As are often mixed with cow dung in Bangladesh and India because the micro-organisms present in cow dung reduce soluble arsenic species to gaseous arsine (AsH3) which is released into the atmosphere[38]. The effectiveness of this process has been investigated using stock solutions of arsenic (III) and (V)[4]. Although the solutions used were not representative of the physical or chemical characteristics of As removal wastes, arsine was identified as the form of arsenic released by microbial action. This is commonly regarded as the most toxic form of arsenic[46].

C. Incorporating within construction materials

Incorporation of As sludge into construction materials is common in urban areas of Bangladesh and India. Typical products include cement blocks and cement plinths for latrines. Sanchez et al. (2000) [45] conducted experiments to show how drying and carbonation can influence the release of inorganics from cement based materials during cyclic wetting and storage. Carbonation, occurring during periods of storage, was seen to reduce the release of hydroxide whilst releasing carbonate into solution. This lowering of pH caused respeciation of arsenic. These materials would inevitably be exposed to wear and weathering and when used as plinths in latrines will most certainly be exposed to urine and disinfectants used for cleaning. Existing literature does not include information on dissolution or leaching effects under these exposure conditions.

Sludge has also been mixed with clay for bricks or cement to produce construction blocks for housing. The structural integrity and leaching of As from clay bricks made using As removal waste with high Fe content have been investigated by Rouf and Hossain (2002)[44].It was concluded that the firing temperature is a key factor that determines the quality of the bricks and As leaching characteristics. In addition significant health issues are also related to the amount of As containing dust generated during manufacture and construction.

VI. Stabilisation/Solidification (S/S) Technologies

Stabilisation/solidification (S/S) includes a range of processes that are normally used as a pre-landfill waste treatment technology that aim to make hazardous wastes safe for disposal(Conner, 1990)[12]. . The process involves mixing the waste, either in the form of sludge, liquid or solid, into a cementitious binder system. S/S is most suitable for treating wastes that are predominantly inorganic, as these are considered more compatible with the cementitious binders used. However, a wide range of wastes, including many mixed inorganic/organic materials have been treated using S/S technologies. The aim is to encapsulate and incorporate the waste into the binder system, and produce a monolithic solid with improved structural integrity that exhibits long-term stability and minimal leaching.

S/S technologies inhibit leaching of hazardous components by reducing waste/leachant contact and by forming a stable pH environment in which many heavy metals of environmental concern remain insoluble. A range of other mechanisms are also reported to occur for specific combinations of waste components and binders[56]. The products of S/S treatment tend to be highly variable in composition because the wastes treated will normally vary and the mixing processes causes significant heterogeneity. The cementitious binders used are often a major cost in the process and therefore the minimum amount that enables the S/S waste to pass short-term regulatory test requirements for compressive strength and leaching is normally used. The waste may adversely affect the setting reactions of the binder, and this together with the highly complex chemistry of S/S wastes, makes the prediction of long-term performance and durability difficult.

A. Fundamental studies of As stabilisation/solidification

Halim et al. (2004)[24] reports that As ions are homogeneously dispersed within a calcium silicate hydrate (C–S–H) matrix, the main hydration product of cement. This was thought to be due to adsorption or co-precipitation of As ions with Ca and Si compounds present in the cement.

Mollah et al. (2004)[36] investigated the long-term effects on S/S of As (V) bearing oxyanions in Portland cement, using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) to determine speciation, phase changes and lattice formations over aten year period. It was concluded that As(V) bearing wastes could be immobilised for long periods in a Portland cement matrix. It is important to note however, that this study did not use a waste material but Na2HAsO4·7H2O as the source of As(V). Leist et al. (2003)[31] investigated the effectiveness of stabilizing different As compounds (arsenic trioxide, arsenic pentoxide, sodium arsenite and sodium arsenate) using three solidification binders:

- Portland cement
- Portland cement+iron (II) sulphate
- Portland cement+lime (CaO).

Sequential batch leaching tests were conducted using the Australian Bottle Leaching Procedure[50] using neutral pH extraction fluid and an overall test duration of 18h. Increases in Ca leachate concentrations were associated with decreasing As concentrations. It was concluded that Ca influenced the leaching of cement immobilised As, with formulations containing higher Ca:As mole ratios generally resulting in lower As leaching. The effectiveness of the S/S process depended on the As compound treated. Arsenate was found to have the lowest mobility. This was in agreement with[10], who showed that the effectiveness of As fixation was strongly influenced by the type of As compound present. In a series of experiments several different

As containing compounds were treated with Portland cement under the same conditions and TCLP testing completed on samples cured for 28 days. The results showed that As leaching ranged from 510 mg/l (arsanilic acid) to 1.7 mg/l (arsenate).

Akhter et al. (1997)[3] investigating the long-term effects of "additives" (supplementary cementitious materials, such as slags and ashes) with Type I Portland cement (PC) observed that the TCLP leachability of arsenite and arsenate after 28 days cure compared with 3 years cure showed no appreciable change, for a number of additives. The combination of Portland cement and Class F fly ash however, showed increasing leachability (by TCLP) with time and re-speciation during curing. These results emphasize the importance of long-term testing to identify specific combinations of S/S binders and wastes that may undergo re-speciation and consequent changes in leaching. A detailed analysis of the ratio of As(V) to As(III) ions along with monitoring of the solution pH and redox chemistry would be helpful in assessing the chemical evolution of the pore solution.

B. Stabilisation/solidification of industrial wastes containing As

Early work showed that industrial waste containing As(III) could be successfully treated using S/S technology using lime and cement[14,15]. However, it was later concluded that treating As in its most stable form should be the essence of the stabilisation process[16]. Pre-treatment to oxidise As(III) waste should reduce solubility and toxicity of the As species and solidification can then be continued using an S/S process. This was achieved using 30% solution of H2O2 on fly ash from copper refining sweeps[17]. Oxidation lowered the As concentration in the leachate from 5 mg/l (6.7E−5M) on non-oxidised S/S samples to 0.5 mg/l (6.7E−6M) on oxidised S/S samples, evaluated using the water extraction test DIN 38 414 S4. A significant reduction was observed using semi-dynamic leach tests. It was shown that the decrease in the leachate concentration of As(V) was due to the formation of relatively insoluble Ca3(AsO4)2 in the presence of Ca(OH)2. H2O2 is now used to pre-oxidise waste on an industrial scale, although costly adaptations for heat and emissions control are required.

Portland cement, lime and fly ash were used to treat a waste sludge containing 5.29 mg/g dry weight of As[51]. The main factor reducing the concentration of As in leachate was found to be the addition of lime. This resulted in the formation of insoluble calcium arsenates, and it was concluded that S/S processes using lime and cement could be used to dispose of As-bearing sludges.
This was based on results from the TCLP leaching test which gave average As leachate concentrations of 0.36 mg/l (4.8E−6M).

Leist et al. (2000)[30] found that the complex chemistry of As means that a recipe which may work with a particular waste often will not work with another As containing waste. Palfy et al. (1999)[39] investigated processing As-rich sludge that accumulates during carbon dioxide refining in the Vetrocoke process. The wet sludge had 163,000 mg/l As (2.1 M) and the S/S process used was based on progressive reduction of As solubility via a series of precipitation and solidification agents to produce a solidified Fe–Ca–As precipitate. The final process developed involved:

a) Oxidation using a 30% solution of H2O2
b) Precipitation with powdered lime (8mol CaO:1mol As)
c) Precipitation with ferric sulphate (4mol Fe:6mol As)
d) Solidification using Portland cement.

The fixation mechanism was reported to involve encapsulating Ca and Fe arsenates/arsenites in a cement matrix, reducing the concentration of leached As from 6430 to 0.823 mg/l (8.6E−2M to 1.1E−5M). This method of As stabilisation minimised the effects of carbonation due to the formation of calcite (CaCO3) in the presence of CO2 which sealed pores in the cement matrix and restricting diffusion of CO2 into the interior of the solidified waste. Subsequent to the initial investigation, 2tonnes of As containing industrial waste were successfully treated using this method. Presuming the integrity of the outer, carbonated layer is maintained and that diffusion rates through the matrix remain low, this appears to offer the most cost effective route to isolating arsenic-bearing wastes from the environment.

A cement based system was used to treat fly ash containing 42wt.% As generated from smelting copper ore[14]. In the optimised mix, 10 parts (by weight) of fly ash was mixed with 6 parts of Portland cement and 8 parts of lime (CaO). The concentrations of As leaching reduced from 5000 mg/l (6.7E−2M) for the untreated waste to 5 mg/l (6.7E−5M) after treatment. Leaching of As was associated with arsenite ions (HAsO3 2−), and the reduction in leaching observed was reported to be due to the formation of relatively insoluble CaHAsO3 in a saturated Ca(OH)2 solution.

Akhter et al. (1990)[2] conducted an investigation into the stabilization of soils contaminated with heavy metals and 10,000–12,200 mgl−1 sodium arsenite. Portland cement was found to be the best binder, suggesting that unlike arsenate-bearing wastes, arsenite saturated wastes may be effectively bound using Portland cement without the addition of lime.

C. Stabilisation/solidification of As-bearing waste sludges

Solid wastes containing As have also been treated by S/S using Portland cement, fly ash and polymeric materials such as polymethy lmethacrylate (PMMA) and polystyrene[47], and it was concluded that S/S reduces leaching of As due to the precipitation of calcium arsenite and calcite, which seals pores in the solidified waste. Pozzolanic reaction products also resulted in reduced As leaching when fly ash was present. However, the addition of polymers as cylindrical beads tended to increase As leaching.

The leachability and speciation of As in a water treatment sludge solidified using Portland cement at a cement to sludge ratio of 10:1 have been investigated in specimens cured for up to 2 years[28]. They reported that the As(III) concentration reduced from 51.1% of the total As content in the sludge to 16.3% in the cement-treated sample after 28 days. This was further reduced to 7.4% after curing for 2 years. Consistently lower levels of As were leached after longer curing times, and it was concluded that curing enhanced As(III) oxidation and improved arsenic immobilisation in cementtreated wastes.

Three mechanisms for As fixation were suggested from scanning electron microscopy and X-ray diffraction studies of cement solidified arsenic–iron hydroxide sludge, the waste from As removal by coagulation with ferric chloride[41]. These were sorption onto C–S–H surfaces, replacement of SO4 2− by As in ettringite, and reaction with cement components to form calcium–arsenic compounds. Of these three mechanisms, the formation of calcium– arsenic compounds was considered the most effective immobilization mechanism.

Water is required to initiate cement hydration reactions. The w/c ratio needs to be kept as low as possible if low permeability materials are required. If excess water is used, initially well-mixed slurries may segregate, causing bleed water containing soluble waste components. This is importantwhen dealing with As sludge obtained fromcoagulant and co-precipitative units. Further studies have demonstrated that other components present in wastes may accelerate or retard set, even at low concentrations.

D. Novel stabilisation/solidification systems for As wastes in developing Countries

Geopolymerization involves the chemical reaction of aluminosilicate oxides (Al3+ in IV-fold coordination) with alkali poly-silicates yielding polymeric Si–O–Al bonds. Although metakaolin was originally activated by NaOH and sodium silicate, other natural aluminosilicate minerals and waste materials such as coal fly ash and blast furnace slag have been used to produce geopolymers. Geopolymers have been the subject of extensive research over the last decade due to their improved properties compared to Portland cement including high capacity for hazardous metal immobilisation and high early compressive strength[54]. In the strictest sense, geopolymers are devoid of calcium, comprising a 3-dimensional network of alumina and silica, so perhaps these materials mentioned here should be described as geopolymer like, or simply as blended cements.

Bankowski et al. (2004)[8] demonstrated that inorganic geopolymers can encapsulate As in a similar manner to cement binders. Synthesis of geopolymers is possible using waste materials rich in Al2O3 or SiO2, which are mixed in specific ratios with alkali metal hydroxides and the major component of activated alumina removal units commonly used in Bangladesh and India is Al2O3. It would seem likely that, given the non-metallic character of As, its role as a network former in a geopolymer system would be somewhat limited. Little published information exists to confirm or dispute this, but is seems probable that As would be immobilised by physical occlusion, rather than incorporation into the geopolymer structure.

VII. Discussion

The disposal of As containing wastes generated from water treatment in countries such as Bangladesh and India has used questionable and unsustainable methodswhich have not been properly investigated. Methods such as stabilisation using cow dung are widely practiced without consideration being given to the subsequent toxicity of the by-products and how these should be managed.

Options for disposal are limited. In many cases untreated As contaminated waste is simply dumped or buried, and as a result As has the potential to

leach back into the environment. Although studies have shown that leaching of As from sludge is not always significant, the validity of the leaching tests used is often questionable as they do not simulate true field conditions. Recycling is not a viable option due to limited uses and markets for As. High temperature thermal treatment processes such as incineration volatilise As containing compounds, producing hazardous aerosols or an As containing sludge from cleaning emissions. The only sustainable management option for As containing water treatment sludge is to convert the As into the least mobile or stabilised form and isolate the stabilised material from the environment using a solidification/encapsulation process.

Pre-solidification treatment is concerned with the oxidation of arsenites and is now successfully employed by industry. Pre-oxidation with hydrogen peroxide ensures effective stabilisation with S/S but due to a high heat of reaction, the cost of installing and maintaining control technology in developing countries would need to be weighed against perceived benefits and sustainability. Where abstracted water has been pre-oxidised prior to As removal, most of the sorbed As within the waste will be in the form of arsenates. By maintaining the waste in an oxic environment prior to S/S treatment, re-speciation of As should be limited, removing the need for further oxidation before solidification. Residual effects of chemicals used for pre-oxidation, such as potassium permanganate may influence the S/S reactions. Where wet sludges are generated by coagulant-based removal processes, the sludge may require drying to reduce moisture content. No studies have been reported that indicate the chemical changes likely to occur during drying, and the stability of arsenate ions prior to solidification requires further investigation.

Wastes from water purification always have relatively high water content, making comparison with dry industrial wastes such as fly ash difficult. Palfy et al. (1999)[39] investigated wet As-bearing industrial sludges. The progressive reduction in As solubility requires a series of precipitation and solidification agents to produce a solidified iron–calcium–arsenic precipitate. One of the agents used was ferrous sulphate, which may be present in wastewater sludges resulting from groundwater abstractions. If removal waste is also pre-oxidised the only additional required agents would be lime and cement, both of which are commonly available in developing countries. This process has the added advantage of minimising the effects of carbonation due to restricted diffusion of CO2 into the interior of the material. It cannot be assumed, however, that this formulation will be as successful on removal wastes, as composition can significantly influence the effectiveness of fixation. The addition of ferrous sulphate to other wastes has been found to increase leaching due to its effect on cement[31]. Fixation could be strongly influenced by the valence state of the As compounds present. Further investigation is therefore required to determine the suitability of applying this type of process to As removal wastes.

Studies have shown that arsenate ions are effectively fixed within a calcium silicate hydrate matrix when hydrated with a mix of CaO and Portland cement. Furthermore, the high hydroxyl concentration within
the porous matrix suppresses the solubility of Ca compounds, including calcium arsenates. Leaching occurs largely by diffusion and is most concentrated at the surface of the cement monolith where solid Ca(OH)2 acts as a buffer if alkali As leaching occurs. The formation of a poreblocking surface carbonation layer may further increase the integrity of the stabilised waste form. Portland cement and lime would appear to provide a potential solution, but there is no simple relationship between waste type and the effectiveness of the S/S formulation. For example, arsenite-rich wastes may be more effectively bound using Portland cement without the addition of lime.

For all S/S processes using Portland cement the water/cement ratio needs to as low as possible to ensure that the resulting cement matrix has low permeability. Wet arsenic-bearing wastes from coagulant coprecipitative units may therefore require drying before treatment. Excessive water content may cause bleedwater and increased leaching. Care must be taken to identify any retardants or accelerators in the waste. Typical retardants are acids, inorganic anions and organics. Acids may be present in wastes generated by sorptive filtration, due to regenerative flushing with HCl, whilst organics and phosphates may be present in abstracted waters. It is possible that the flocculent precipitates used to sorb As in coagulant precipitative units (e.g. ferric hydroxides) may also retard set. Conversely, brines associated with activated alumina removal wastes can preferentially accelerate set.

VIII. Conclusions

There has been limited research into sustainable S/S methods that can safely manage and dispose of wastes generated by As removal systems. There is little evidence supporting the effectiveness of current waste management practices employed in

Bangladesh or India. From this review of S/S processes for treating As wastes in developing countries it is concluded that:

a) Portland cement with lime is appropriate for treating waste from sorptive filters but not oxidised precipitative sludges, where the high pH environment promotes desorption. Ferric hydroxides used to sorb As in precipitative units retard cement set and in large quantity may destabilise cements owing to their differential expansion as humidity changes. This can result in a porous matrix with increased leachability. Brine resulting from the regeneration of AA filters may accelerate cement hydration. Optimum moisture content and waste to binder ratios depend on the chemical properties of the waste. There is evidence that Portland cement can immobilise soluble arsenites.

b) Precipitation and solidification has been successfully used to stabilize arsenic-rich sludges and may be suitable for treating sludges generated by precipitative removal units.

c) Geopolymerisation is effective with waste materials rich in alumina and metal hydroxides, making it a potential treatment system for waste generated by AA units. There is potential for geopolymer treatment involving simple operation and low running costs. As would be immobilised by physical occlusion, rather than incorporation into the geopolymer structure and the long-termbehaviour of these materials is not known.

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