Aspects of arsenical materials and their long term stability under environment conditions

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Abstract

A number of potential options exists for the disposal of arsenical wastes namely: arsenical ferrihydrite, calcium arsenates, crystalline ferric arsenates, arsenical cements and arsenical slags. All of the samples can pass the US EPA TCLP test and would be considered suitable for disposal into the environment. However such materials can undergo physical and chemical change and will become progressively more soluble. Therefore testing of a material destined for disposal should also satisfy a test which can assess its long term solubility after exposure to prolonged hydration, dehydration and CO_2 exposure in an attempt to simulate various climatic variations and physical and chemical environments.

Calcium arsenates are susceptible to carbonation (influence of CO_2), have high solubilities and are the least adequate materials for disposal. Arsenical ferrihydrite is produced during the lime neutralisation of arsenical effluents and are highly insoluble while moist, yet when dehydrated their solubility is increased.

The encapsulation of arsenical dusts and other high grade waste into arsenical cements and slags have also been considered. These solidification/stabilisation/dilution procedures reduces the permeability of the solid and reduce the contact with moisture and carbon dioxide. However the matrix materials which encapsulate the arsenic are subject to change. The calcium compounds in the cement can undergo chemical and mechanical breakdown which accelerates its degradation. Whereas glassy arsenical slags may undergo some degree of recrystallisation (devitrification) and allow the more soluble calcium arsenate phases to nucleate and grow from the glassy medium.

Each disposal option has its potential benefits and applications in specific metallurgical operations and may be usefully employed. It is suggested that the solids that are most

suitable for disposal should be composed of crystalline components such as scorodite or a high temperature ferric arsenate phase. These high grade residues would be reasonably stable in the environment and would be expected to have a constant solubility over a prolonged period of time. Hydrothermal precipitation can produce these crystalline materials and has the potential to treat a wide range of arsenical solution concentrations.
Key words - arsenic, arsenate, stability, cements, precipitation, scorodite, ferrihydrite, solubility, EPA, waste, disposal, arsenopyrite.

Introduction

Arsenic will in future present major problems to the metallurgical industries of the world mainly due to its overproduction, and to the tightening of environmental legislation regarding its disposal into the environment. Industry is acutely aware of the problems of heavy metals and are realising that technology and research must be targeted so as to minimise any long term global risks.

Arsenic is currently an unwelcome by-product in the base and precious metal industry and production far exceeds demand, and with the more restrictive arsenic emission levels from off-gases even larger amounts of arsenic will be recovered from pyrometallurgical operations. The environmental restriction on the use of arsenic will also reduce the consumption of arsenic as used in wood preservatives, fungicides, glass, ceramics, non-ferrous alloys and other lesser uses **[5]** and will further lead to the problems of oversupply of arsenic and its eventual disposal.

The mining industry has conventionally exploited the "easy" deposits first and has left the low grade, refractory and metallurgically complex ores which often contain high levels of arsenic. In future environmental regulations will force the metallurgical industries to reduce the levels of heavy elements in flue off-gasses and minimise the waste entering the streams and ground waters. This would be expected to make the exploitation of these ores expensive and will dictate the viability of mining operations by influencing the choice of metallurgical process routes.

The metallurgical treatment route dictates the types of arsenical wastes and effluents that are produced. Smelting and roasting of ores and concentrates usually at temperatures >700˚C volatilises the arsenic and it moves as the As(III) form with the exhaust gases. It is captured in bag houses and electrostatic precipitators as flue dusts (up to 30% arsenic) and recovered as As_2O_3 and/or As_2S_3 and may also contain minor amounts of As_2O_5. Alternatively it can be recovered from the acid plant liquors. Excessive amounts of lime are used to precipitate the arsenic from the sulphuric acid, from which calcium arsenites and arsenates are precipitated together with large amounts of gypsum. These calcium arsenite/arsenate solids are removed and dumped, alternatively the arsenical product can be encapsulated or stored.

Recycling of arsenical dusts (which can contain significant amounts of base metals) to the converter smelter is often practised in an attempt to recover the base metals and

conceivably to incorporate some of the arsenic into the slags. However, the recycling of arsenical dusts which may also contain minor amounts of bismuth, antimony and thallium may be detrimental to the quality of the final metal product. This can also ultimately increase the concentration of arsenic in the anode copper destined for refining **[14, 15]**. In turn this may build up in the refinery electrolyte solutions (up to 20g/L) and have a deleterious effect on the operation and incur significant costs, therefore removal from the smelting-refining cycle is often recommended **[16 - 20]**.

During the hydrometallurgical processing of ores the presence of arsenic in leach liquors and effluents is common and can vary in concentration depending on the ore being treated and the type of leaching techniques being used. At ambient temperatures the effluents which are commonly iron-rich are conventionally neutralised with lime and the arsenic is coprecipitated as arsenical ferrihydrite. Alternatively the solutions could be processed to selectively recover or precipitate the contained arsenic and eventually disposed of as a sludge.

Other suggested options for the disposal of arsenic wastes and effluents include hydrothermal precipitation, and physical encapsulation of the wastes into cements and slags **[10, 11]**. The ideal arsenic compound for disposal must be highly insoluble and have short and long term stability and its formation must be practical and cheap. A totally insoluble arsenical compound is obviously an unobtainable ideal therefore a realistic compromise must be identified so as to confine any soluble arsenic to a metallurgical dump and protect the ground water and surface water flows from any leakage. This paper will review aspects of stabilised arsenical materials and their long term stability in the environment.

Solubility testing of arsenical solids

In the USA the Environmental Protection Agency (EPA) insist that metallurgically derived solids are tested by a toxicity characterisation leach procedure (TCLP) **[12]**. The mining industry which produces most of the arsenical waste products are required to control their arsenic emissions and comply with these restrictions. The test which contacts the solid with a buffered pH liquid is agitated and the filtrate from the test must be below the 5mg/L toxicity threshold. The rational for the test is to control the arsenic released into the environment which could ultimately impact on the ecosystem and domestic water supply.

The concept of stability as applied to arsenical wastes are required to be more clearly defined, short term stability is where the solid in contact with a liquid has a low solubility and passes a prescribed test. Whereas long term stability is where the solid retains its low solubility even after many centuries without being effected by temperature, moisture or carbon dioxide. The short term solubilities of the synthetic and metallurgical samples were assessed by two methods which allowed differences in solubility to be empirically determined. The methods were the US EPA TCLP test and the MARG static bottle test [ref]. The procedures only screen the material with no fundamental intention to define absolute solubility. The long term solubility of the solids must be tested appropriately to local conditions taking into consideration the disposal site characteristics: presence of oxygen, organics and sulphides, in-place permeability and ion diffusivity, pore water characteristics, leaching kinetics and climate for a realistic assessment of their long term behaviour. The MARG static bottle test uses a solid to liquid ratio of 1:500 and test solutions of pHs 3, 5, 7, 9, 11. The pH 3 and 5 samples were adjusted with sulphuric acid, and pHs above 7 adjusted with NaOH.

Under natural conditions arsenic contained within ores as arsenopyrite is only slightly soluble: however, through chemical processing for the recovery of valuable elements the arsenic is often transformed into more soluble compounds (e.g. arsenic oxides) which can lead to the contamination of ground waters. Since water containing high arsenic levels is potentially hazardous knowledge of the nature and solubility of the various arsenate compounds produced from the processing of arsenical waste must be investigated and accurately determined. Synthesising a wide variety of arsenical compounds from numerous simulated hydrometallurgical solution compositions allows the various metallurgical wastes and processing routes to be assessed and the solids predicted as to their long term solubility. For the long term stability of metallurgical dumps arsenic solubility information on metallurgical products coupled with the site-specific geologic and hydrologic data are essential requirements for assessing their impact on the environment. The information will help develop waste management practises and technologies to minimise the dissolution and migration of arsenic.

During initial solubility test trials, when $Ca(OH)_2$ was used in place of NaOH for the adjustment of the pH of the test solutions, major differences in the soluble arsenic levels were observed in the pH 7-11 solutions (see **Figure 1**). The reasons for these differences are thought to be due to the influence of calcium in solution which seems to lower the

apparent solubility of arsenic. Reduced levels of soluble arsenic were also found in solubility tests when gypsum, calcite, lime and calcium nitrate were deliberately added to test the influence of the presence of calcium. Likewise other workers [**ref** }have found that cement gives apparent stabilisation of the arsenic and this too is thought to be due to the influence of high calcium ion concentrations in solution. In the determination of the solubilities of arsenical compounds, the interaction of arsenic with calcium adds complications to the interpretation of the results. For this reason it is preferable to use NaOH to control the pH in solubility tests rather than lime and so avoid these interference effects.

Figure 1. The influence of calcium and sodium hydroxide used for pH adjustment in the MARG static bottle test solutions.

At pH<2.2 scorodite dissolves congruently with the release of iron and arsenic in equimolar proportions. Above this pH dissolution is incongruent with arsenic preferentially entering into solution, whereas the iron is immediately reprecipitated as a ferrihydrite-type compound. For this reason arsenic levels in solution will always be significantly higher than iron **[59].** With increased Fe:As ratio in the solid lower levels of arsenic are released owing to the adsorptive properties of larger amounts of ferrihydrite. If the solid is of a high surface area, ferrihydrite-rich material the arsenic is easily reprecipitated, whereas the crystalline solids are of a low Fe:As ratio (1:1) and a low surface area with only minor reprecipitation and for this reason these compounds will have a higher apparent solubility. Numerous workers **[33, 47 - 49]** have reported that precipitates with an Fe:As ratio of greater than 3:1 are highly insoluble with solubilities as low as 0.05mg/L. Due to ferrihydrites importance as a potential adsorbent for arsenic a significant amount of work has been carried out on this material and its behaviour [refs]. Those compounds with a molar Fe:As greater than 3:1 are highly stable and usually have solubilities less than 1mg/L between pH3 and pH8. Harris and Monette **[32]** found that even after 3 years the solids with Fe:As greater than 3 still showed very low solubilities. The solubilities of arsenical compounds are strongly influenced by the pH of the contacting solution with the higher solubilities occurring at the higher pHs.

Arsenical Slags

Although no quantitative information on the arsenic content of metallurgical slags has

been found in the literature, only minor amounts of arsenic are likely to get incorporated as the oxide has only limited solubility in conventional slags at normal operating conditions **[21]**. However, testwork **[11]** has shown that arsenic (up to 10%) can be preferentially encapsulated as calcium arsenate (iron arsenate form has a lower thermal stability at elevated temperatures) into a slag with low oxygen partial pressure. After quench cooling the calcium arsenate is incorporated as a glassy solid in the slag . The long term stability of this glass is unknown with the possibility that the glass may devitrify with time. If this were to happen the calcium arsenate would recrystallise from the glassy matrix and render the enclosed arsenic to be more soluble. Slow cooling of identical slags produced crystals of calcium arsenate phases which are reasonably soluble as determined from solubility testing **[10]**. Many of the experiments have been carried out on a small scale (20g) ideally future work is required on larger volumes of material to assess its industrial application.

Arsenical Cements

Solidification/stabilisation is process for the disposal of many types of hazardous solids. As applied to arsenical wastes the method would involve mixing sludges and wastes with a cement binder to produce a solid which is structurally sound and relatively impermeable **[99-101]**. The incorporation of up to 70 % solid is possible (As_2O_3, Ca-arsenates or other arsenical compounds), however, for high loading this can detrimentally influence the curing and solidification process. The pore waters in the cement have a high pH and any uncombined arsenic is expected to react with calcium and to be reprecipitated. In the cement ionic transport is decreased as the porosity and permeability are reduced on hardening. From the limited work done [**ref**] it would appear that a significant amount of the arsenic is physical encapsulated on a microscale. No published work has clearly demonstrated the incorporation into the crystalline lattice of the cement phases. Due to the high levels of calcium compounds and lime in the cements they act to increase the calcium content and pH of the test solution during solubility testing and this some how helps passivate the arsenic levels in solution and leads to low arsenic levels in the filtrate well below what should be expected.

While carbonation of calcium bearing compounds in cements can be beneficial by increasing their strength and reducing permeability it may also be detrimental and promote the cements physical and chemical breakdown. Total carbonation and thus

removal of the lime and other calcium compounds in the cements may reduce the ability of the concrete to fix the arsenic. This removal of the buffering capacity in the cements could lead to its migration into the ground waters.

If incorrectly designed the cement may rapidly deteriorate, therefore its formulation must be chosen to suite the arsenical waste so as to take into account the chemistry of the waste constituents and the possible reactions with the cement constituents, water and carbon dioxide. For this reason investigations into the complex chemistry of arsenical cements and other binding materials must continue to be examined. If the cement is placed in a dry, low humidity and carbon dioxide environment and kept at a constant temperature long term stability would be guaranteed

Hydrothermal precipitation

In the processing of arsenic-rich dusts in an attempt to immobilise the arsenic, hydrothermal precipitation as a ferric arsenate is being currently investigated. For arsenic fixation as a ferric arsenate the conversion of As(III) to As(V) in solution is a requisite and is possible by using a number of strong oxidants such as ozone, H_2O_2, chlorine gas, CaOCl or nitric acid **[29, 30, 31]**. In a number of hydrometallurgical processing operations (e.g. pressure oxidation and bacterial oxidation) liquid effluents can contain variable levels of arsenic and may even be present in the As(V) form which could be more beneficial for high temperature processing.

The synthesis work carried out on low pH(<1) solutions suggests that a number of alternatives exist for the production of low solubility arsenate phases. A high temperature ferric arsenate phase designated in this work as the Type-2 compound is formed [refs], this is essentially an anhydrous, sulphate-containing, coarsely crystalline solid which can be produced from iron-rich solutions at temperatures preferably greater than 175˚C. Type-2 materials whether produced at 175, 200, and 225˚C have roughly similar solubilities. Crystalline scorodite which can be easily produced at lower temperatures is also a suitable compound for disposal. The combined structural and solubility results show that, as might be expected, the physical and chemical characteristics of the solids do influence their apparent stabilities. However, it is the structure of the arsenic-containing solid which has an overriding influence on the solubility due to the way that the arsenic is chemically incorporated and bound into the crystalline structure.

The distribution of the phases formed from using iron(III) nitrate and As(V) and lithium sulphate solution compositions at various temperatures is given in **Figures 2**. The distribution of compounds in the different temperatures show that the scorodite forms in a restricted compositional range of solutions. Type-2 compounds form above 175˚C and are tightly constrained. With higher Fe:As ratios arsenical ferrihydrite and hematite are formed. The sulphate in solution has only minimal influence on the type of compounds that form, the Fe:As ratio has a more important influence.

Key to compounds - Type-2 compound (♦), Type-1 compound (●), Hematite (✻), Ferrihydrite (∇), Scorodite (▲)

Figure 2. Distribution of compounds at 150-225˚C relative to the starting composition of the pH<1 solutions

The distribution of the phases formed from using iron(III) sulphate and As(V) solution compositions at various temperatures were also investigated. Above 175˚C the basic iron sulphate and Type-2 form, whereas below this temperature scorodite predominates. The solids are closely controlled by the Fe:As ratio of the starting solution, when >1:1, scorodite or Type-2 will form. The proportion of basic iron sulphate increases with increasing Fe:As ratio (i.e. from 1:1 to 1:0). The basic iron sulphate compound forms in preference to ferrihydrite which forms in sulphate poor solutions at pH<1. Whereas the gelatinous, high surface area, ferrihydrite can adsorb arsenate, the basic iron sulphate compound is crystalline and unlikely either to adsorb or to incorporate any arsenic into its structure.

The EPA TCLP data for the high temperature crystalline compounds are compared with those for Fe:As solids precipitated at ambient temperatures (20˚C) and pH 5 in **Table 1**, the latter solids being analogous to those formed during the neutralisation of arsenical liquors in commercial operations. The high Fe:As ratio (>2.3:1), gelatinous, low temperature solids show lower solubilities than the high temperature crystalline solids precipitated from low pH(<1) solutions. However, low temperature solids precipitated from solutions with Fe:As <2.3:1 show much higher solubilities than the corresponding high temperature precipitates.

	Compound-type	**EPA TCLP filtrate**

	(conditions of synthesis)*	**(As mg/L)**
pH Natural (<1). High	Scorodite (Fe:As 2.3:1, 150˚C)	<0.80
Temperature (>150˚C)	Type-2 (Fe:As 2.3:1, 200˚C)	<0.34
pH 5	Ferrihydrite (Fe:As - 9:1)	0.40
Low Temperature (20˚C)	Ferrihydrite (Fe:As - 2.3:1)	1.20
	Ferrihydrite (Fe:As - 1.5:1)	50.20

* starting solutions of iron(III) sulphate and As(V)

Table 1. Solubilities of high and low temperature precipitates measured by the EPA TCLP method

Long term stability of solid arsenical wastes

Solubility is not necessarily indicative of long term stability, cognisance must be taken of the physical and chemical changes that the compounds can undergo with time. So that while arsenical samples may pass the EPA TCLP test they may become progressively more soluble. During the lime neutralisation of arsenical effluents the arsenic is coprecipitated with ferrihydrite and the arsenic is adsorbed onto the solid. While such solids have a low solubility when moist (high surface area) the rate at which arsenic can be released will change if the ferrihydrite undergoes any changes such as dehydration. If the arsenical ferrihydrite remains moist the solid will retain their surface area and adsorptive properties. Such conditions will prevail if the climatic conditions provide sufficient rainfall to keep the dump wet and avoid the dehydration of the ferrihydrite.

Another treatment route for arsenical effluents is to precipitate the arsenic as a calcium arsenate compound. However, in the long term these compounds can be transformed through carbonation (CO_2) to calcium carbonate and release of the chemically bound arsenic, carbonation will also contribute to the conversion of any excess lime ($Ca(OH)_2$) which can temporarily maintain a high pH (11-12) in a metallurgical dump. If the pH of the ground and pore waters are lowered the calcium arsenate solids become appreciably more soluble. Calcium arsenates and arsenites are currently being precipitated and removed from solutions from acid plants in roaster and smelter operations. However it has been determined from thermodynamic considerations that these are unstable and unsuitable for disposal **[91, 92-96, 51, 97].**

$$Ca(H_2AsO_4)_3 + CO_2 + H_2O \text{ ----> } CaCO_3 + 2H_3AsO_4$$

High concentrations of calcium, and high pHs (>12.5) reduce the concentrations of As(III) and As(V) in solution to below 0.5mg/L this is through the precipitation of $Ca(AsO_2)_2Ca(OH)_2$ and $Ca_3(AsO_4)_2Ca(OH)_2$ compounds. The effect of CO_2 is to reduce the pH of solution by combining with calcium with the conversion of the basic calcium arsenate and arsenate to more soluble intermediate products ($Ca_3(AsO_4)_2$ and $Ca(AsO_2)_2$ respectively). This demonstrates the ineffectiveness of lime in removing arsenic from waste effluents. While CO_2 certainly has an influence on the stability of calcium arsenates with time it is not actually proven whether this could have an influence on iron arsenates.

The possible realistic alternatives for arsenic disposal together with considerations on the

long term stability of the arsenical products are given below in **Table 2**.

Arsenical compound	Long term disposal considerations
Arsenical ferrihydrite (Fe:As >3:1) ambient temperature precipitation	• Dehydration leading to a more unstable compound • Recrystallisation?
Calcium-arsenates + Calcium-arsenites	• High solubility. • Ca-arsenates converted to $CaCO_3$ with release of arsenic (influence of atmospheric CO_2). • High lime levels in the precipitated solids results in high pH's (11-12), with age the lime is converted to $CaCO_3$ - this leads to a reduced pH and an increased solubility of the Calcium arsenate compounds.
Crystalline ferric arsenates (Scorodite or the high temperature crystalline phase - Type-2)	• Low solubility over long periods of time • Little physical or chemical change with time. • Long term stability?
Arsenical slags (up to 10% arsenic)	• Recrystallisation - devitrification • Long term stability unknown - quenched slags show low solubility. • Require highly specific conditions for incorporation into slag low pO_2
Arsenical cements	• If calcium compounds are fully carbonated this may reduce the buffering action and lead to reduced pH and arsenic precipitation. • The arsenic may be chemically bound as calcium arsenate phases which are highly soluble.

Table 2. Long term stability considerations for the various arsenic disposal options

The formation of arsenical ferrihydrites and calcium arsenates and arsenites are attractive options to industry in that they are very cheap and require very simple technology when compared to the arsenical slag, arsenical cements and hydrothermal precipitation routes. However, if one considers the long term stability of the different arsenical products the more expensive processing alternatives should be able to yield products that are significantly more stable.

While the incorporation of arsenical wastes (calcium arsenates) into cement would appear to be the simplest and possibly the cheapest option of the three, the arsenic is mostly physically encapsulated with possibly some incorporated into the cement-type phases. The calcium arsenate compounds are highly soluble and in time the ingress of moisture and CO_2 will promote the breakdown of the arsenical components, this may mechanically breakdown the concrete and release the enclosed arsenic. The slag option **[11, 12]** may well produce an arsenical glass with ultra low solubility but technologically the process has not been demonstrated on a significantly large scale and may not even be practical.

Hydrothermal precipitation is currently within the grasp of modern technology it also has a number of advantages in the removal of arsenic from wastes and effluents including:-

- Process is simple (Autoclave or pipe reactor),
- Low volume of high grade solid residue,
- Good filtration characteristics,
- Low solubility solid produced, and
- Reduced lime consumption

Hydrothermal precipitates have been shown to have low solubility and possibly better long term stability as compared to the other treatment options. The low Fe:As ratio of the solids makes them suitable material for reprocessing and arsenic-recovery if and when arsenic finds a large volume technological use. Having a repository of high grade arsenic waste would also allow future generations to further reprocess and stabilise the

toxic wastes with new technologies and the development of cheap energy resources i.e. fusion energy.

Conclusions

The various disposal options for arsenical waste has been reviewed with emphasis placed on the long term stability of the arsenical materials in the environment. The costs for the production of stabilised waste is obviously of importance to industry but this factor must be balanced against the long term stability of the material. In future if the material becomes unsafe and a hazard to man it will require further reprocessing and incur further costs which may be many times that of the initial stabilisation step. Diluting arsenic wastes into slags, cements and tailings may also need to be reassessed as these become more expensive to reprocess at a later date. Keeping the solid as a high grade crystalline material of low solubility certainly would appear advantageous over time so long as the compounds do not undergo any major mineralogical transformations.

Sustainable rehabilitation after the solids have been disposed of will be inevitable and the mining company who initially exploited the deposit will be responsible. The idea that a mining company can walk away from a deposit after the reserves have been depleted will, be a thing of the past. The dumps will clearly require prolonged passive and active care so as to reduce any mobilisation and dispersal of pollutants. Prevention is better than cure and finding the most convenient compromise for arsenic disposal will be required.

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