Removal of arsenic from drinking water by precipitation and adsorption or cementation: An environmental prospective

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Abstract

The removal of arsenic from process solutions and effluents has been practiced by the mineral process industries for many years. More recently, because of the recognition that arsenic at low concentrations in drinking water causes severe health effects, the technologies that have been used in the mineral industry are being applied to that situation. Removal of arsenic in process solutions can be accomplished for most present day product specifications but the stability of solid and liquid waste materials for long-term disposal or discharge may not meet the regulatory requirements of the future. In the case of drinking water treatment where the requirement is to reduce arsenic to a few parts per billion, the applicable technologies are limited. This paper mentions briefly the aqueous inorganic chemistry of arsenic and the most common methods that have been applied commercially in the mineral industry for arsenic removal, recovery, and disposal. Some techniques, which have been used only in the laboratory, or otherwise suggested as means of eliminating or recovering arsenic from solution, are also outlined. Low cost removal of arsenic from drinking water is likely to be confined to precipitation, adsorption or cementation, but the sludge's created present stability concerns. This paper reviews some of the work done in relation to the mineral industry where there is also application to drinking water. Disposal of stable residues is critical in both situations, and the testing methods for assessing stability need careful consideration.

Keywords: Arsenic, Precipitation, Adsorption or Cementation.

INTRODUCTION

The material, which is mentioned only briefly in this paper, is discussed in greater detail in the publications cited in the paper. Although there are many other excellent relevant references the authors have chosen the papers with which they are most familiar, for convenience and reliability, and these are not necessarily the earliest chronological references. The references also relate mostly to literature on extractive metallurgy and not water treatment since we believe that this work has not been adequately cited by publications in the latter field. The various unit processes that have been considered to deal with arsenic in hydrometallurgical processes include: oxidation-reduction, precipitation and thermal precipitation, co-precipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, membrane separations, precipitate and ion flotation, and biological processing. All of these methods are not considered here, but are detailed in some of the references at the end of this paper [1-4]. Here we will consider only precipitation, adsorption and cementation, which are the processes that are more generally adopted, particularly in relation to drinking water in situations where costs must be given priority. The aqueous solution chemistry of arsenic which relates to hydrometallurgical processes has been extensively covered in the literature, and the use of thermodynamic stability diagrams to describe the chemistry has been widely adopted [5-10]. The important oxidation states of arsenic are -3, 0, +3, and +5, and all have been utilized in some way in hydrometallurgy. The removal of arsenic from solution has relied mostly on precipitation and adsorption processes and it has been considered that arsenic (V) is the oxidation state that leads to the most effective removal by precipitation, since the simple metal arsenates generally have lower solubility than the arsenites. The general assumption that arsenic (V) is always more easily removed

from solution is not correct. Current work has identified mixed oxidation state compounds and also the element and its alloys (formed by either cementation or electrolysis) to be appropriate low solubility materials. Arsenic complexation in solution has had little attention, and it seems that only complexes of arsenic (V) with iron (III) have been studied [6-8]. Oxidation of arsenic (III) in solution to arsenic (V), and reduction of arsenic (V) to arsenic (III) has been investigated [13-15] as part of the overall chemistry relating to hydrometallurgy. Oxidants such as air and oxygen, chlorine and hypochlorite, hydrogen peroxide, permanganate, ozone, and SO_2/O_2 have been investigated, both with and without catalysts. Photochemical oxidation of As (III) to As (V) is a recent innovation [6-8]. The removal of arsenic from gold process solution has been of understandable interest over the years, and has perhaps been investigated more than for other hydrometallurgical processes [11-13]

PRECIPITATION

The insolubility of certain inorganic arsenic (V) compounds is the basis of many hydrometallurgical arsenic removal processes, and the insoluble product is often a disposal material. The most common methods of removing arsenic from aqueous process streams are by precipitation as arsenic (III) sulfide, calcium arsenate, or ferric arsenate, but it has been shown that all of these materials are unstable under certain conditions and therefore not suitable for direct disposal to uncontained tailings as they will produce leach ate containing arsenic [6-8]. The sulfide As_2S_3 has its lowest solubility below pH=4, but that solubility is significantly higher than has been generally accepted [8]. The sulfide is not usually a form that is disposed in residues as it is easily oxidized and increasingly soluble

above pH=4. There have been unsuccessful attempts to use As_2S_3 in landfill in which acidic-anaerobic conditions are maintained, and also in cement cast admixes. Recent work on biological formation of arsenic sulfides may have an application in treating process residues, but containment of waste material remains a problem. There are a number of calcium arsenates that can be precipitated from arsenic (V) solutions, by lime addition to high pH [16-18]. Lime addition in excess can reduce arsenic concentrations in solution to <0.01 mg/L, but those calcium arsenates which are precipitated at pH>8 are not stable with respect to the CO_2 in the atmosphere, which converts them into calcium carbonate, releasing arsenic to solution in balance with appropriate cations [19,20]. Arsenic (V) can also be precipitated from process solutions below about pH=2 with iron (III) to form ferric arsenate, $FeAsO_4.2H_2O$, which is white to very pale green in color. At ambient precipitation temperatures the compound is very small in crystal particle size (<10nm) and is "2-Line" X-ray amorphous, but these particles tend to agglomerate to about 100nm and the material is difficult to de-water by conventional operations. At temperatures above about 90^0C the precipitated compound is crystalline (>100nm) and has a solubility about 2 orders of magnitude lower than the amorphous material (which is the particle size effect). The "amorphous" ferric arsenate exhibits incongruent solubility at about pH=1 (where [As] is about 500 mg/L) and at higher pH will convert very slowly to an arsenic bearing ferriox hydroxide, which initially forms around the surfaces of the ferric arsenate tending to stabilise the material and colouring it yellow to brown. Crystalline ferric arsenate (*scorodite*) has an incongruent solubility point at about pH=2 and is comparatively slow to convert to the arsenic bearing ferrioxy hydroxide at higher pH, and for material of larger crystal particle size, this may take some years. Crystals of $FeAsO_4.2H_2O$ do not grow to appreciable size (greater than about 1 mm) as they have a relatively high positive surface potential right up to the pH of the incongruent point. Ferric arsenate of either form is not thermodynamically stable in the neutral to high pH region (the kinetics of decomposition being related to particle size and solution composition, and being controlled by diffusion through the product). The materials may pass conventional leach tests (such as the TCLP) and are not suited for direct uncontained disposal, but perhaps would satisfy a "slow release criteria" if regulatory authorities would give this option its deserved consideration. Ferric arsenate is also not stable in alkaline cement cast admixes. There are other metal arsenates, such as those of Fe(II), Zn(II), Cu(II) and Pb(II, which are less soluble and more stable in the neutral pH region than the calcium arsenates or ferric arsenate, but these have not been seriously considered as disposal forms. Iron (II) arsenate is of particular interest as a low solubility material and this compound has recently been the basis of a process developed and successfully demonstrated in a variety of applications. Barium (II) arsenate was proposed as being an extremely insoluble arsenate, but this was shown [21-24] to be incorrect. More complex compounds, such as the apatite structured calcium phosphate-arsenate have recently been demonstrated to be of low solubility (including being stable to atmospheric CO_2) and of appropriate stability for disposal consideratio. Ferric arsenite sulfate is also of recent interest and may prove to be useful in stabilising arsenicarsenic(III). One of the most insoluble arsenic compounds is lead (II) chloroarsenate (the mineral form being *mimetite*) which has been studied in detail. Very little attention has been given to mixed oxidation state materials (both Fe(II)-Fe(III) and As(III)-As(V) combination compounds have been tentatively identified, and the authors are currently conducting a

comprehensive study of these systems. The Fe (II)-Fe (III) hydroxy sulfate (known as "green rust") has been shown to incorporate arsenic into the structure at pH<7.

ADSORPTION OF ARSENIC ON FERRIHYDRITE

Over many years there has been much attention directed to the removal of arsenic from hydrometallurgical process solutions and waste waters by precipitation and co-precipitation with iron (III). At relatively high concentrations of iron (III) and arsenic (V) (> about 0.001m) and at low pH, the precipitation results in the formation of ferric arsenate, $FeAsO_4.2H_2O$, as above. At lower concentrations of arsenic (V) and higher iron (III) concentrations the co-precipitation of arsenic with ferrioxi hydroxide (*ferrihydrite*) occurs and this is probably the most effective method of removal of arsenic from aqueous solutions, and leads to a solid phase which can be stable at least for a year or so. The solid co-precipitate has been referred to as "basic ferric arsenate" and in 1985 a controversy commenced as to whether the co-precipitated material was in fact a compound of iron (III) and arsenic (V) or simply an adsorptive binding of arsenic with ferrioxyhydroxide (*ferrihydrite*). There was at that stage sufficient evidence to support the latter contention, but the use of the term "basic ferric arsenate" still exists and formulae such as "$FeAsO_4.xFe(OH)_3$" are used. A number of studies have indicated that various complexes are formed in the adsorption of As (V) on *ferrihydrite*. EXAFS studies on arsenic bearing *ferrihydrite* formed at pH>7, have shown that arsenic (V) is adsorbed to *ferrihydrite* as a strongly bonded inner-sphere complex with either monodentate or bidentate. It has also been reported that monodentate attachment predominates near the optimal pH=4-5 for adsorption. The adsorption of arsenic(III) on *ferrihydrite* has also been investigated but the optimal adsorption in this case occurs at pH 8-9, and although it seems an efficient process there is no evidence that the adsorbed species is in fact arsenic(III). It may be that during the process, oxidation of arsenic(III) will occur with some ease, being balanced by the reduction of Fe(III) to Fe(II) in the *ferrihydrite* structure, as has been shown in preliminary experiments by the authors. It is well known that Fe(II) substitution in *ferrihydrite* does occur. Very little attention has been given to the possibility of modifying the *ferrihydrite* structure to improve its adsorptive capacity for arsenic in solution. It is well known that many cations will incorporate into the *goethite* structure, and therefore possibly into a precursor *ferrihydrite*. The authors have been investigating the coprecipitation of both Al (III) and Mn (III) with Fe (III) to form an aluminic ferrihydrite and a manganic ferrihydrite respectively. Both materials are showing important in this adsorption process. The effective oxidation of As (III) by manganese substituted *goethite* has been studied by XANES spectroscopy, and the implications are obvious in relation to adsorption mechanisms. There is also little work reported on the adsorption of arsenic from solutions initially below say 50 micrograms/kg. This region of concentration is presently of immediate interest in relation to drinking water, where US EPA has introduced a MCL of 5 micrograms/kg (January 2001).

CEMENTATION

It is well known that iron and other metals will replace arsenic from solution to produce arsenic as the element or as an alloy. This method of removing arsenic from solution to levels <2 mg/kg has been demonstrated on ground water at a commercial site at a pilot

scale of 1-5 US gallons per minute. Cementation has also been suggested, and may be appropriate, for the removal of arsenic from drinking water.

TESTING FOR LONG TERM STABILITY

Testing methods for evaluating the stability of hazardous waste residues have been defined by the US EPA in several "Background Document for Toxicity Characteristic Leaching Procedure" publications. The test methods do not adequately assess the long term stability of arsenical residues. Improved test methods must be designed which also include a characterization of physical properties and chemical components (mineralogy) so that more accurate predictions of behavior can be made.

THERMODYNAMIC MODELING

The stability of arsenic species can be characterized by their free energies of formation. Many of the papers referenced below have free energy of formation data for arsenic species, and some contain thermodynamic stability diagrams, which have been invaluable to the authors in gaining a better understanding of these systems. Few of the reputable thermodynamic data bases have sufficient relevant data for modeling aqueous arsenic systems, but the published paper is one of the most comprehensive single sources.

CONCLUSIONS

There have not been any significant and innovative improvements in the methods for removing arsenic from process and effluent solutions, or indeed from drinking water, in the last decade or so. The current needs to remove arsenic from drinking water is now a world problem, apart from the well publicized and critical situation in Bangladesh (Nickson et al., 1998; Nordstrom, 2000),   west Bengal and some district in Chhattisgarh (India) and so must be addressed as a matter of great urgency

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