2.0   Plenary Session

The following extended abstracts are provided for the oral presentations made by invited speakers during Day One of the Workshop, Plenary Session. Speakers were selected by the Steering Committee, and the topics were intended to provide some foundation for subsequent discussions that occurred both formally and informally during the balance of the Workshop. The Plenary Session presentations covered a range of arsenic topics from regulatory to scientific issues. EPA researchers discussed the ORD and OSW perspectives on contamination issues, treatment efforts, treatment standards, and testing issues. Other EPA topics included arsenic sources, research on microbial activity, and the Toxics Release Inventory (TRI). Other researchers discussed arsenic issues for mining, groundwater and drinking water, and arsenic geochemistry, leaching, and treatment options.

Additional oral presentations were made on Day Two during the Breakout Sessions. These presentations were intended to complement the session topics and provide a basis for discussion for each session. The extended abstracts for these oral presentations are presented in Section 3.0, Breakout Sessions.

It should be noted that the abstracts were not part of the formal peer-review process which the remainder of this document underwent, and may represent opinions or personal points of view in some cases. Any references cited in the abstracts are the responsibility of the authors.

Presentation materials (visuals) for the Plenary Session and Breakout Session speakers are not included in this Proceedings document, only abstracts. A few speakers did not prepare abstracts, only presentation materials. However, speaker presentation materials can be viewed online at the EPA Technology Transfer website. The website address for these materials is www.epa.gov/ttbnrmrl/arsenictech.htm. Or, for further information regarding this Technology Transfer product, please contact Doug Grosse via email at: grosse.douglas@epa.gov.

The Current Status of Arsenic Research in the U.S. EPA's Office of Research and Development

Christopher A. Impellitteri and Paul M. Randall
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive, Cincinnati, OH 45268
T: 513-569-7673, F: 513-569-7620
E: Impellitteri.Christopher@epa.gov and Randall.Paul@epa.gov

Notice

Abstract

The mission of EPA's Office of Research and Development (ORD) is "to conduct leading-edge research and foster the sound use of science and technology in fulfilling EPA's mission to protect human health and safeguard the natural environment" (USEPA, 2001). ORD researchers have examined how metabolic processes affect arsenic (As) specia-tion in humans as well as carcinogenic effects of As (USEPA, 1999). An epidemiological study conducted by ORD researchers in Utah, regarding long-term exposure to As in drinking water, has provided essential data to compare with studies concerning non-US populations (Smith et al., 1992; Nickson et al., 1998; Karim, 2000). Other studies have been initiated by ORD scientists and engineers examining As treatment and management in solid wastes and soils. This abstract will briefly discuss the current status of As research within ORD.

Drinking Water Issues

EPA recently decreased the maximum contaminant level (MCL) for As in drinking water from 50 mg/L to 10 mg/L. Two significant issues arise from the lowering of the arsenic MCL in drinking water. The first issue concerns improvement of existing water treatment methods for water treatment plants (WTPs) to cost-effectively meet the new arsenic MCLs. Researchers in ORD's National Risk Management Research Laboratory (NRMRL) address this issue by coordinating studies on chemical and physical removal of As from water. One study found that the removal of natural iron signifi-cantly reduced soluble As (USEPA, 2000a). Another study examined WTPs that employed ion exchange and activated alumina systems. Both systems were found capable of reducing arsenic concentrations from 50 to 70 μg/L to 5 μg/L providing that proper media regeneration (or change-out of exhausted media) was followed (USEPA, 2000b). A third study analyzed the long-term performance of two coagulation/filtration plants and a lime softening plant (USEPA, 2000c). The coagulation/filtration plants consistently achieved low levels of As in treated water (< 5 μg/L). The study suggested that the primary mechanism of As removal was by co-precipitation with metal hydroxides. The lime softening plant did not consistently reduce As levels in treated water to low levels. This study determined that As removal from the water was low because of competition for binding sites by carbonate species and/or pH effects. The second significant issue that would result from reducing the As MCL in drinking water concerns As in WTP residuals. Research funded by NRMRL has provided fundamental data describing As in residuals from water treatment processes (USEPA, 2000d). This research compares As concentrations in residuals from five different water treatment processes and also illus-trates some differences in state policies concerning disposal of As containing residuals.

Closely tied with NRMRL's research on drinking water issues is research that is currently underway in ORD's National Exposure Research Laboratory (NERL). NERL is currently working on methods for preserving As species in drinking water samples and the development of As speciation methodologies for separation of arsenite and arsenate. This work provides data to support water treatment decisions in utilities affected by changes in the As MCL. NERL researchers are also developing analytical methods for As speciation analysis in foods (e.g., seafood) and urine. NERL works in conjunction with the Food and Drug Administration (FDA) on projects that examine methods for speciation of As in daily diets. This work will aid in assessing risk of As exposure associated with diet. On-going NERL research will examine the bioavailability of As species in water, soils, and food constituents (USEPA, 1998).

Health and Toxicological Issues

ORD's National Health and Environmental Effects Research Laboratory (NHEERL) currently conducts research that can be broadly divided into three categories: 1) mechanisms/modes of As as a carcinogen and toxicant; 2) biomarkers and population studies; and 3) modifiers of susceptibility to toxic and carcinogenic effects. Research performed by the NHEERL on the mechanisms and modes of As toxicity has provided critical insight concerning the nature of As toxicity.

For example, NHEERL researchers have shown that methylated trivalent arsenicals appear to be direct-acting genotoxicants, which distinguishes them from other forms of As previously studied (Mass et al., 2001). Research conducted in the area of mechanisms and modes of As toxicity include biomethylation effects, interspecies (rat, mouse, guinea pig, human) comparisons of As carcinogenicity, uptake and fate in living organisms, and protein binding and effects on human cell DNA methylation. Work on biomarkers and population studies include epidemiological studies on human exposure to As, both in the US and abroad, and identification of biomarkers (e.g., heme oxygenase and urinary porphyrins) that could adequately indicate exposure to As species. NHEERL conducts leading-edge research in the area of As susceptibility modifiers. Studies into the characterization and behavior of the enzyme human As methyltransferase will lead to a better understanding of the ability for human populations to develop resistance to As toxicity. Research on modifiers of As behavior in organisms also includes studies on heat shock proteins, selenium and dietary folate deficiencies.

ORD's National Center for Environmental Assessment (NCEA) focuses on human health issues and works in conjunction with NHEERL to advance our understanding of As related exposure and risk assessment. Current NCEA activities include assessment of chronic As exposure from drinking water sources and the effects of As exposure on human reproduction. This long-term study examines data from exposed and control populations in Chile (Hopenhayn-Rich, et al., 2000). The NCEA works closely with the National Cancer Institute and the National Institute of Environmental Health Sciences in the establishment and maintenance of the International Tissue and Tumor Repository on Chronic Arsenosis. This repository holds tissues and fluids from cases of As poisoning and environmental samples (e.g., coal). The repository also safeguards data and literature and develops databases for protocols and methods of specimen handling, storage, transportation and analysis.

Groundwater Issues

NRMRL's Subsurface Protection and Remediation Division (SPRD) leads research pertaining to groundwater issues. Though inextricably linked with solid waste and soil, groundwater will be considered separately here. The SPRD currently conducts research regarding As mobilization in groundwater, oxidation-reduction reactions of As species in groundwater, and remediation of As contaminated groundwater. SPRD researchers perform these studies in both the laboratory and field. For example, work evaluating permeable reactive barriers (PRBs) will examine the efficacy of this remediation technique on As removal (and other contaminants) from groundwater. Pilot-scale PRB studies will be used to identify effective reactant media for successful, long-term uptake of inorganic contaminants, examine metal uptake mechanisms, and evaluate barrier longevity and long-term PRB stability.

Solid Waste/Soil Issues

SPRD also provides essential research in the area of subsurface As fate and transport issues. Research includes attenuation/stabilization of As on solid phases in soil/vadose zone systems, measurement procedures and protocols for sampling of soils for As studies, and geochemical controls on As speciation in soils. In addition to studies in oxic environments, research regarding the fate and transport of As in anoxic systems is underway in the SPRD. Laboratory studies will provide key data for identification of mechanisms and rates of As sorption/precipitation reactions in sulfidic media. This work will provide a better understanding of As behavior in anoxic systems and lead to improved practices for field monitoring in these geochemically complex systems.

The Land Remediation and Pollution Control Division (LRPCD) works in conjunction with the SPRD on As soils/solid waste issues. Researchers in the LRPCD are currently researching As source contamination issues. These studies will focus on As contamination of solids (soils, mine tailings, sediments) from agricultural sources, mine wastes and treated lumber sources. The researchers will examine desorption of As from solids (effects of pH and dissolved organic matter), solution speciation, and As bonding at the molecular level. Research will also be carried out by LRPCD in the application of thermodynamic theories to leaching studies in order to better characterize specific scenarios and provide more focused direction on methods to minimize As mobilization. Other projects include work on As leaching from mineral processing waste (MPW). The researchers will examine several leaching methods on MPW and compare these data with that from the toxicity characteristic leachate procedure (TCLP- EPA Method 1311). These engineers and scientists will also examine the relationships between leachate chemistry data and TCLP data from landfills.

Risk Management

NRMRL's Technology Transfer and Support Division (TTSD) provides a cohesive, cooperative environment where experts in specific fields can meet and formulate Risk Management Evaluations (RMEs). RMEs play a crucial role in providing a balanced approach to policy formulation and regulation based on sound science and engineering research. Findings from ORD's research activities combined with other important aspects such as cost-of-compliance issues and health/economic benefits from risk reduction aid in focusing future research efforts within the ORD.

In addition to the projects mentioned previously, ORD strives to work closely with EPA regional offices. This ensures that certain aspects of research projects focus on site-specific issues. By working closely with regional offices, ORD aids in addressing immediate, site-specific needs while gaining fundamental knowledge for contribution to our understanding of As and its effects on human health and the environment.

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Arsenic Cycling in the Mining Environment

Rob Bowell
SRK Consulting
Summit House, 9 Windsor Place, Cardiff CF10 3RS, Wales, UK
T: +44-2920-235566, F: +44-2920-665413, E: srk003@aol.com

Jeff Parshley
SRK (US) Inc.
5250 Neil Road, Reno, NV
T: 775-828-6800

Occurrence of Arsenic in a Metal Mine

Over 200 As-containing minerals have been identified in nature. Of these 60% are arsenates, 20% sulfides and sulfosalts, 10% are oxides, and the remainder are arsenides, native elements and metal alloys. Arsenic naturally occurs in chalcophile hydrothermal mineral deposits and is more rarely associated with volcanic or magmatic rocks. Rare arsenic phases are also known to occur in fumaroles and geothermal systems. Occasionally arsenic can also occur associated with sedimentary pyrite in sedimentary rocks and in this environment has been considered to be the source for anomalous concentrations of arsenic in drinking water in Wisconsin, Maine and Bangledesh. Within the United States the largest occurrences of arsenic minerals occur associated with the Carlin-type mines of northern Nevada in the form of realgar (AsS), orpiment (As_2S_3) and arsenic-bearing pyrite (up to 5wt%,) and the rare mineral, Galkhaite, a complex sulfosalt with the chemistry ($[Cs,Tl][Hg,Cu,Zn]_6[As,Sb]_4S_{12}$) which also occurs in the belt at the Getchell mine. Within Carlin ores, the arsenic minerals are intimately associated with the ore elements or adjacent host rock.

The most common arsenic mineral, globally, is arsenopyrite. Arsenopyrite is common in many vein gold deposits, such as those of Yellowknife, Canada or Homestake, South Dakota. It also occurs in granite hosted Cu-Sn veins such as those of Cornwall, England.

Arsenic has long been used as an excellent "pathfinder element" because of its low abundance in most rock types and concentration in hydrothermal deposits, as well as its generally low mobility. This coupled with sensitive analytical protocols by conventional methods makes the element extremely useful in mineral exploration. For example, the average concentration of As in hydrothermal ore deposits ranges from 500 ppm up to 10-wt% of an ore or altered host rock. In unmineralized rocks the average concentration is less than 10 ppm, but can be up to 20 ppm in argillaceous sediments.

Release of Arsenic In a Mine Site

Mining does not produce arsenic although it can be liberated when exposed to conditions in which the primary host mineral is unstable and thus oxidises or weathers, for example when placed on a heap or waste rock dump. Alternatively when an As-hosting ore is chemically treated prior to liberation of the ore element such as during smelting, the arsenic mineral may also be liberated from its matrix and in this form become mobile.

The concentration of arsenic liberated from such reactions is dependent on several factors:

· Total concentration available; this in turn is related to geology of the original hydrothermal deposit.
· The Eh-pH regime of the environment in which the arsenic is liberated.
· The chemistry of natural waters in promoting release or attenuation of arsenic.

The total amount of arsenic available is entirely dependent on the proportion of arsenic minerals available in the deposit. So for example, for a volcanogenic massive sulfide, high sulfide-gold deposit, or a Carlin deposit, high concentrations of arsenic would be anticipated.

Control on the release of this arsenic is then dependent on environmental conditions. Typically in very acidic environments, for example those of Iron Mountain in California, arsenic mobility would be high. Equally, in high pH environments high arsenic mobility would be anticipated as the major control would be adsorption onto mineral phases, and this would be predicted to be low at higher pH for arsenic oxyanions. Within ambient systems arsenic can occur as arsenate ($H_nAsO_4^{3-n}$) or arsenite ($H_nAsO_3^{3-n}$) complexes or in the presence of methylating agents as Monomethylarsonic acid (MMAA) or Dimethylarsinic acid (DMAA).

Over the natural pH range of most soils and waters the principal species of As (V) is $H_2AsO_4^{2-}$ and of As (III) is H_3AsO_3, of which the reduced form is the more mobile. For example, the speciation of arsenic in the principal reactions retaining arsenic in soil, sediment and water are in acidic solutions, adsorption by ferric oxyhydroxides and to a lesser extent Al-Mn oxides, clays and organic matter, and in alkaline solutions co-precipitation of As as arsenate and arsenite salts.

However, the rate of change in the oxidation state of arsenic is not rapid, so the predicted proportions of arsenic species based on thermodynamic calculations do not always correspond to actual analytical results.

Due to the strong adsorption effect exerted on As in mildly acidic soils, As uptake by plants tends only to be significant in alkaline soils or where extremely high As levels (>10000 mg/kg As) occur in the substrate.

GROUNDWATER ARSENIC CONCENTRATION FROM GETCHELL ON Eh - pH DIAGRAM
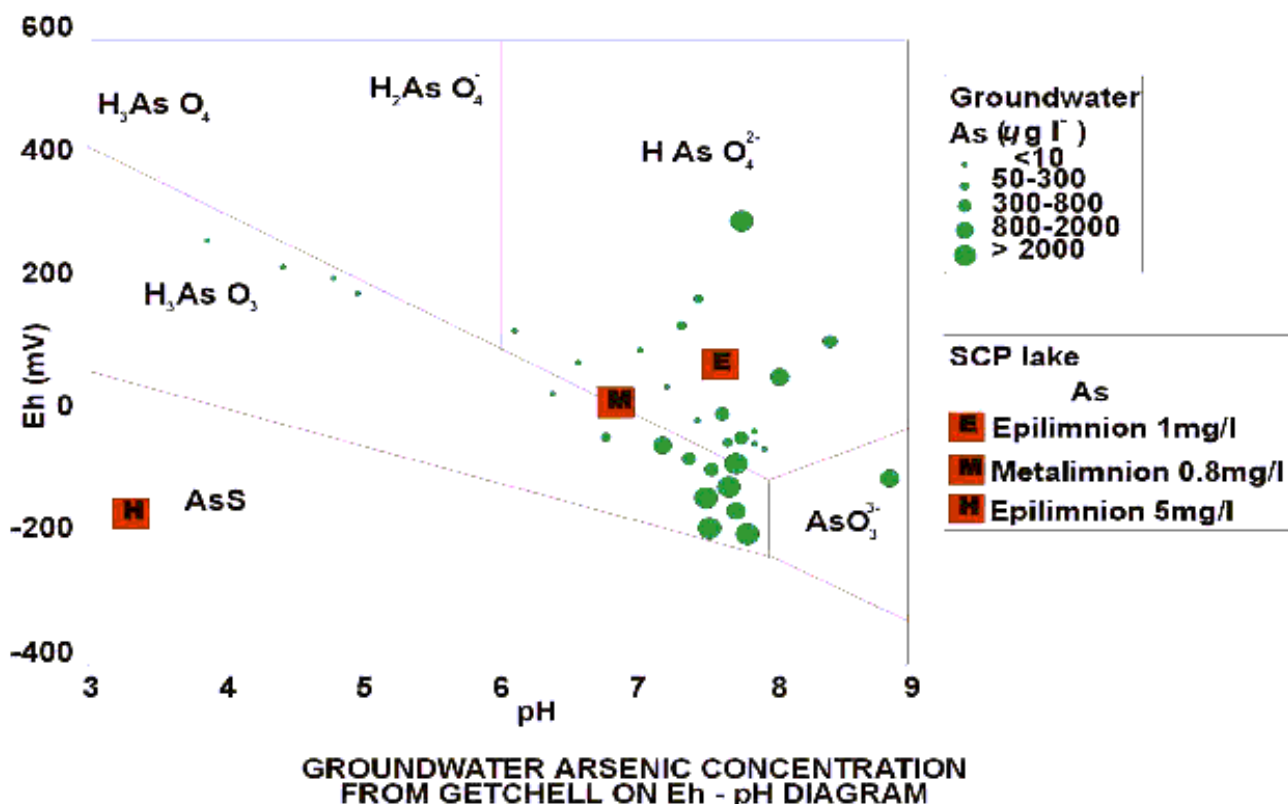
In the Bau area of Sarawak, Malaysia, high As levels in the soil (15-50000 mg/kg As) coupled with an alkaline soil pH (7.5-8.4) has led to high As uptake in bamboo species (up to 4500 mg/kg in roots and 2650 mg/kg in leaves). In the Kelly Basin in northern Nevada, Great Basin Sagebrush shows a similar tolerance and uptake of arsenic that is precipitated out as oxide phases within the vascular part of the plant.

Options for the Control of Arsenic Dispersion

The metals industry is faced with the necessity of disposing of waste material in an *environmentally safe manner*. Over the last two decades significant advances have been made in the design of waste facilities, and in stabilization and treatment of mining effluents.

Arsenic waste disposal generally involves one of four options:

·   Physical stabilization through the use of engineered disposal facilities and institutional controls
·   Chemical stabilization of arsenic containing waste
·   Chemical treatment of effluents to produce saleable products, such as white arsenic oxides by the El Indio or Warox processes or production of an insoluble arsenate such as ferric arsenate
·   Chemical stabilization of the arsenic waste by fixing it within an inert material such as cement, slags or silica material

Currently all options are utilised in the mining industry, and all will be illustrated with examples of use. Future application of such technologies will be discussed in terms of key parameters of cost, environmental stability of products and risks associated with each.

Arsenic in Groundwaters of the United States

Dennis R. Helsel, Ph.D.
Chief, Trace Element Synthesis
U.S. Geological Survey
P.O. Box 25046, MS-415, Denver, CO 80225
T: 303-236-2101 ext. 227, F: 303-236-4912, E: dhelsel@usgs.gov

The U.S. Geological Survey has collected and analyzed arsenic in potable (drinkable) water from 18,850 wells in 595 counties across the U.S. during the past two decades. These wells are used for irrigation, industrial purposes, and research, as well as for public and private water supplies. Arsenic concentrations in samples from these wells have been shown to be similar to those found in source waters for nearby public supplies. Arsenic concentrations in groundwater are generally highest in the West. Parts of the Midwest and Northeast also have arsenic concentrations that exceed 10 μg/L, the World Health Organization's provisional guideline for arsenic in drinking water. Arsenic concentrations appear to be generally lowest in the Southeast. The large number of samples, broad geographic coverage, and consistency of methods produce an accurate and detailed picture of arsenic concentrations across the U.S.

Managing Arsenic Occurrence Information in Drinking Water

Larry Scanlan
Utah Department of Health
46 N Medical Drive, Salt Lake City, UT 84092
T: 801-584-8400, E: lscanlan@doh.state.ut.us

With the advent of the new Drinking Water maximum contaminant level (MCL) for arsenic set at 10 μg/L on January 22, 2001, many states are reviewing their drinking water data for compliance with the new rule. The State of Utah has had a computerized water quality database since 1978. This flat file format was gradually changed to a multiple-table relational database in the mid 1990s. This new database linked an inventory of public water supply sources with global positioning system (GPS) locations, source production, and other data. This data was exported to Microsoft Access in the mid-90s and used to summarize arsenic occurrence in Utah. Detection limits have varied from certified laboratories submitting data since 1978, but an attempt was made to review all available data for each potentially regulated drinking water source under the new rule. Data which obviously did not agree with subsequent analyses results were flagged for exclusion. The remaining data were counted for the number of measurements made, averaged, and a standard deviation of arsenic concentration for each source was computed. This approach allows a confident statement of arsenic concentration where the data allow. Fifty water systems in Utah will need to provide treatment or dilution for eighty sources to meet the new arsenic MCL by 2006. A statewide "compliance" list has been developed to begin working with systems needing treatment. Utah's system, the findings produced from using it thus far, and management of this occurrence information will be presented as a possible model for use by others.

Arsenic Hazardous and Remediation Waste: Sources and Treatment

Linda Fiedler
U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response
Technology Innovation Office
1200 Pennsylvania Avenue, NW (5102G), Washington, DC 20460
T: 703-603-7194; F: 703-603-9135; E: fiedler.linda@epa.gov

Introduction

In 1996 U.S. demand for arsenic was estimated at 22,000 metric tons, making the U.S. the world's largest consumer of arsenic (USEPA, 2001a). Most arsenic is used in wood preservatives, but significant use also occurs in agricultural chemicals, glass production, and metal alloys. These industrial practices, and metals mining and smelting operations, generate arsenic-bearing waste. In addition, past waste disposal practices have resulted in sites containing arsenic-contaminated soil, groundwater, and other media that may pose a risk to human health and the environment. Many additional sites contain naturally-occurring arsenic that may impact drinking water supplies.

Arsenic, especially inorganic forms, is very toxic and a known carcinogen (ATSDR, 1993). The chemical nature of arsenic compounds, in particular their tendency to change valence or chemical form, makes it difficult to assess their fate and mobility in the environment, and to immobilize arsenic effectively for ultimate disposal. Even wastes that have been treated to existing federal standards are found to leach out of landfilled waste (USEPA, 2000d). To support the future study of these and other arsenic-related issues, this paper presents the current state of arsenic waste generation and management. It summarizes the sources and estimated quantities of arsenic industrial and remediation wastes, regulatory treatment standards, and treatment technologies currently used.

Arsenic Industrial Applications

Arsenic metals and compounds have not been produced domestically since 1986. The U.S. imports arsenic primarily from China, Chile, and Mexico at about 30¢ per pound. Of the total 22,000 metric tons of arsenic imported in 1996, almost 20,000 metric tons of arsenic were used in wood preservatives, followed by 1,100 metric tons in agricultural chemicals, 440 metric tons in glass production, and 440 metric tons in metal alloys. The most common wood preservative is chromated copper arsenate (CCA), used at 88% of wood preserving facilities. Agricultural applications of arsenic compounds include feed additives, animal dips, and herbicides. Arsenic metal is consumed in the manufacture of nonferrous alloys, principally lead alloys for use in lead-acid batteries. Small amounts are also found in alloys used in other applications, such as bearings, lead ammunition, and solders. Other uses include electronics and semiconductors, pyrotechnics, and antifouling paints (USEPA, 2001a).

Sources and Quantities of Arsenic Waste

Hazardous Waste

Hazardous waste in the U.S. is regulated under the Resource Conservation and Recovery Act (RCRA). For 29 listed hazardous wastes, EPA has identified arsenic as a hazardous constituent, or has established a land disposal restriction (LDR) standard. Arsenic is also a characteristic waste. A hazardous waste exhibits the toxicity characteristic for arsenic if the arsenic concentration is greater than 5 mg/l when analyzed using the Toxicity Characteristic Leaching Procedure (TCLP). Wastes are listed for arsenic if the arsenic poses a risk; its concentration does not have to exceed 5 mg/l TCLP. Also, there are often higher-concentration constituents present in the waste.

The EPA Biennial Report System (BRS) contains information reported by hazardous waste large quantity generators, and by treatment, storage, and disposal (TSD) facilities. An analysis of BRS data submitted for 1997 was conducted for the 29 hazardous waste codes that can contain arsenic, and for arsenic characteristic waste. For this analysis the conservative assumption was that all of the waste generated in each waste code contained arsenic. In 1997 industry generated a total of 519 million short tons of wastewaters (USEPA, 2000b). Of this total, 55 million tons (11%) can contain arsenic. (One photographic facility accounts for 40 million tons.) The largest generators of arsenic wastewaters are the photographic (74%), plastics (12%), and organic chemicals (9%) industries. Half of this waste is in the form of multi-source leachate, which has over 200 regulated constituents, including arsenic. The analysis includes all of the data submitted, including wastewaters managed in systems that are not RCRA-permitted; these wastes are not included in the national BRS numbers.

In 1997 industry generated 15 million tons of hazardous nonwastewaters. Of this 4 million tons (27%) can contain arsenic. The largest generators are organic chemicals (23% of 4 million tons); steel and iron works (20%); aircraft parts/equipment

(10%); commercial hazardous waste management (13%); national security (i.e., metals, ammunition, explosives) (10%); and copper smelting/refining (7%). The most common forms of these wastes are solvent mixtures (27%), ash and slag (20%), and other waste inorganic solids (12%).

Non-hazardous Waste

The EPA's Toxic Release Inventory (TRI) tracks toxic chemicals manufactured and used at facilities nationally, and amounts of chemicals released and managed on- and off-site. Both hazardous and nonhazardous waste are reported; however, RCRA-exempt (i.e., nonhazardous) waste from the metal mining industry accounts for the vast majority of the arsenic releases reported. The TRI considers arsenic and arsenic compounds to be metals; only the metal portion of the metal compound is considered in TRI calculations, and quantities are reported by mass, not volume.

Arsenic wastes are generated from mining and smelting operations, particularly those involving copper, silver, and gold. Because of the large volume of rock that must be moved as part of the mining operations, even low concentrations of naturally-occurring arsenic that may be present will yield very large TRI reported quantities. Most of the reported metals remain in the waste rock that is returned to the land at mine sites or returned underground as backfill. In 1998 the metal mining industry managed most arsenic waste, over 617 million pounds, or 96% of the total mass of arsenic waste managed (643 million pounds)(USEPA, 2000c). Gold mining accounts for 93% of the arsenic mining waste, followed by copper ores (4%) and silver (3%). Lead, zinc, and iron mining wastes, combined, make up less than 1% of the total.

The other top industries managing arsenic waste are the primary metals industry, 11 million pounds (17% of total arsenic managed); electric utilities, 7 million pounds (1%); and RCRA/solvent recovery, 6 million pounds (1%).

Remediation Waste

Several cleanup programs manage the remediation of contaminated sites that may contain arsenic, including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, also known as Superfund), RCRA corrective action, and the Departments of Energy (DOE) and Defense (DOD). The most detailed data available concern Superfund sites:

1) Almost half (48%) of the1500 Superfund National Priorities List (NPL) sites have arsenic as a contaminant of concern that must be addressed. These data are extrapolated from an analysis of 1177 NPL sites with Records of Decision (RODs) through fiscal year 1998 (USEPA, 2000a). By comparison, lead is of concern at half of NPL sites.

2) For media, 32% of NPL sites have arsenic in groundwater, 32% in soil, and 13% in sediment.

3) Activities at NPL sites with arsenic include wood preserving, municipal and industrial landfills, metal ore mining and smelting, machine shops, battery recycling/disposal, and pesticide/herbicide manufacturing and use.

In addition, about 5% of 137 DOE installations and other DOE cleanup locations, or about 500 sites, contain arsenic. An estimated 20% of RCRA facilities contain arsenic in groundwater, and 13% in soil (USEPA, 1996). Data on DOD sites are not available; however, it is expected that a large number of sites contain arsenic from machine shops, ammunition, and explosives.

Treatment of Arsenic Waste

The chemical nature of arsenic compounds makes them difficult to treat effectively. Arsenic is a semi-metallic element and is labile, readily changing chemical form in the environment (and in waste treatment processes). Arsenic mobility is affected by environmental conditions including acid-base equilibria and overall pH; oxidation-reduction potential and electron activity; the presence of complexing cations and anions (such as sulfides, calcium, and iron); and adsorption/desorption reactions. (USEPA, 2001a)

Arsenic can be readily precipitated from aqueous waste (including As-generated waste and groundwater) if the form of the arsenic and other waste characteristics are considered. Oxidation of arsenic to its less soluble As^{+5} state can increase the effectiveness of precipitation. Ion exchange, carbon adsorption, and membrane filtration are also used. According to the 1997 BRS, 240,000 tons of aqueous hazardous waste can contain arsenic and are managed offsite. The treatment methods used are chemical precipitation (31% of the aqueous waste), other aqueous organic treatment (8%), and incineration of solids or liquids (13%) (USEPA, 2000b).

Of the 1.84 million tons of nonaqueous arsenic hazardous waste managed offsite, 400,000 tons (22%) are treated via stabilization/chemical fixation using cement or pozzolans. Thermal technologies (incineration, energy recovery, or fuel blending) are used for 36% of the wastes, most likely to address the organic fraction of the waste. An additional 11% are subjected to recovery technologies (high temperature metals recovery or secondary smelting), but these data do not indicate whether arsenic is being recovered.

EPA tracks the application of cleanup technologies, primarily at Superfund sites (USEPA, 2001b). Based on this information, stabilization is the most common technology for disposing of nonaqueous remediation waste containing arsenic. At least 45 NPL sites are using stabilization to treat arsenic-contaminated soil, sediments, sludge, and other solids. Cement, lime, and phosphate are the most common stabilization binders used at these sites. Other technologies used at contaminated sites include: soil washing (6 sites), chemical treatment (4), acid extraction with hydrochloric acid (2), in situ soil flushing (2), vitrification (3), and electrical separation (1). Chemical treatment agents used include a combination of ferrous iron/lime/potassium permanganate, oxygenated water with an iron catalyst, and phosphate.

Groundwater contaminated with arsenic usually contains other contaminants, such as chromium or pentachlorophenol, and other wood treating chemicals. Pump-and-treat is typically used to remediate groundwater at these sites. Data are available on nine sites applying pump-and-treat for arsenic-contaminated groundwater. Filtration, carbon adsorption, and chemical precipitation are commonly used to remove both the inorganic and organic groundwater contaminants. A permeable reactive barrier has been installed at two Superfund sites (Monticello Mine Tailings, UT and Tonolli Site, PA) to treat groundwater contaminated with arsenic and metals (USEPA, 2001b; Remediation Technologies Development Forum, 2000).

The RCRA LDRs specify the technologies or treatment levels that must be achieved prior to land disposal of hazardous wastes. The LDR treatment standard for arsenic in wastewater is 1.4 mg/l, based on the performance achievable by chemical precipitation. The standard for nonwastewaters is 5 mg/l as measured by the TCLP, based on slag vitrification of wastes up to almost 25% arsenic. Any technology that is not defined as impermissable dilution under RCRA can be used to achieve these standards. In evaluating arsenic treatment performance, EPA had inconclusive performance data for stabilization of arsenic in three different wastes using nine different binders. EPA found that the effectiveness of any particular stabilization binder appeared to be highly dependent upon the waste type (USEPA, 1990). However, based on the BRS and remediation data, stabilization appears to be the treatment of choice for arsenic in nonaqueous waste, and the technology can meet the 5 mg/l TCLP standard (USEPA, 2001a; USEPA, 2000b; USEPA, 2001b).

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Treatment Options for Arsenic Wastes

Godage B. Wickramanayake, Ph.D., P.E., Senior Program Manager
Battelle
505 King Avenue, Columbus, OH 43201
T: 614-424-4698, F: 614-424-3667, E: wickram@battelle.org

Kim Cizerle, M.S., Manager
ENVIRON International Corporation
202 Carnegie Center, Princeton, NJ 08540
T: 609-243-9858, F: 609-243-0321

Wendy Condit, M.S., Environmental Engineer
Battelle
505 King Avenue, Columbus, OH 43201
T: 614-424-4698, F: 614-424-3667, E: conditw@battelle.org

Since recycling of arsenic-containing materials is technically challenging and cost prohibitive, there is a great demand for the development of effective treatment technologies for the safe disposal of arsenic-contaminated hazardous wastes. The industrial use of arsenic has been curtailed in recent times; however, historic operations have led to significant contamination at some industrial sites where arsenic compounds were previously used to produce pesticides, herbicides, or veterinary pharmaceuticals. Current uses of arsenic are more limited and include the use of chromated copper arsenate for wood-preserving operations and the use of gallium arsenide in the development of semiconductor material for the electronics industry. In addition, mining operations often involve the smelting of ores with high arsenic concentrations.

Currently, arsenic contaminated hazardous wastes are subject to land disposal restrictions under the Resource Conservation and Recovery Act (RCRA) and must be treated to meet toxicity characteristic leaching procedure (TCLP) limits. A RCRA hazardous waste is defined as a waste that produces an extract containing more than 100 times the maximum contaminant level (MCL) in drinking water for that specific chemical. The MCL for arsenic (50 μg/L) was recently subjected to critical review due to concerns about a potential association between long-term exposure to arsenic and serious health problems such as skin and internal cancers and cardiovascular and neurological effects. As a result of these concerns, and after further review of the relevant scientific data by the U.S. Environmental Protection Agency (EPA), a change in the arsenic MCL from 50 to 10 μg/L was promulgated.

Due to these potential changes, there is a need to investigate the impact that a revised rule would have on the treatment and disposal of arsenic-contaminated hazardous wastes under the RCRA program. This presentation assumes that, if EPA changes the TCLP regulatory level, it would also change the required treatment standard (40 CFR 268.40 and 268.48) to a value that is at or below the TCLP regulatory level. It is important to perform an assessment of whether or not the current array of treatment options, both innovative and conventional, will be able to achieve the potentially more stringent treatment requirements.

Due to the existence of alternate treatment standards for soils (40 CFR 268.49), the potential changes to the TCLP limit should not have a major effect on the treatment and disposal of arsenic-contaminated soils. However, the potential changes would alter the treatment cap for soils and the definition of RCRA hazardous waste for arsenic (D004). With these changes, more soils would be considered hazardous than at the current TCLP regulatory level. The existing alternate treatment standards for soil should minimize the impact of any MCL or TCLP revisions. In setting the alternate treatment standards, EPA already reviewed and compiled treatability data to determine cost-effectively achievable treatment goals for arsenic-contaminated soils. Thus, this presentation focuses primarily on arsenic-contaminated wastes, but will briefly review recent innovations in soil treatment technologies.

As an inorganic constituent, arsenic cannot be destroyed, but it can be converted into less soluble or leachable forms to inhibit migration into the environment and subsequent exposure by sensitive receptors. Vitrification was selected by EPA as the Best Demonstrated Achievable Technology (BDAT) for characteristic and listed wastes containing arsenic including D004, K031, K084, K101, K102, P10-12, P36, P38, and U36. Vitrification involves the use of a plasma torch, an electrical current, or other heat source to melt the contaminated material into a glass matrix at extremely high temperatures ranging from 2,900 to 3,650°F. The vitrified material is non-porous, has a high strength, and is much more resistant to leaching than the original feed materials. Although vitrification, as BDAT, would be considered the "conventional" approach to

17

treatment, it is not widely used and has been selected as a treatment option for arsenic-contaminated waste at only one out of twelve Superfund sites identified. The remaining sites with arsenic-impacted soil or other wastes had Record of Decision (ROD) selected remedies that included solidification/stabilization (6), containment/capping (4), and soil washing (1). Vitrification is not used extensively for the following reasons: 1) the cost is prohibitive since the process requires complex, capital-intensive equipment; 2) wastes with elevated moisture content, high metal content, and/or inappropriate physical characteristics may be more expensive or difficult to treat; and 3) significant volatile losses of arsenic can occur unless the waste is properly pre-treated to produce less volatile forms of arsenic.

There are several other treatment options for arsenic-contaminated wastes, including the most commonly applied technology, solidification/stabilization (S/S) with cement, fly ash, sodium silicates, or other binders. S/S relies upon mobility reduction, resulting from a combination of physical entrapment (e.g., encapsulation) and chemical reaction (e.g., precipitation) mechanisms. Cement, silicate, and other S/S binder materials were evaluated by EPA, but not accepted as BDAT for arsenic wastes due to concerns about long-term stability and waste volume increases. However, EPA did not preclude the use of S/S methods for the treatment of arsenic wastes, but instead recommended site-specific treatability studies. Several studies have demonstrated that S/S can be successfully implemented for the treatment of arsenic-contaminated wastes, if pre-treatment methods are employed first to transform arsenic into the appropriate oxidation stage or species and then to decrease the solubility or availability of the arsenic compounds in the solid matrix prior to binding. The following is a list of alternate or innovative treatment technologies that can be applied to treat arsenic-contaminated hazardous wastes:

1. S/S with pretreatment by oxidation using hydrogen peroxide, potassium permanganate, and others
2. S/S with pretreatment by hydrated salt addition including ferric sulfate, ferrous sulfate, ferric chloride, and others
3. S/S with proprietary formulations
4. Slag incorporation
5. Encapsulation with polymer resins

The advantages and limitations of the above technologies will be discussed and their ability to meet potential revisions to the hazardous waste treatment standard will be evaluated in light of available literature and Battelle and ENVIRON's project experience.

Treatability study results for K084 and D004 wastes will be discussed based on a case study from a veterinary pharmaceutical Superfund site. The waste consisted of iron-arsenic sludge and sludge generated from arsenic precipitated with lime. As part of the ROD selected remedy, an estimated 3,800 tons of these arsenic wastes, containing up to 260,000 mg/kg of arsenic, were removed and treated off-site with S/S before disposal at a RCRA Subtitle C landfill. The treatability study tested a total of 88 mixture designs to determine an effective method of treating the vault wastes. Table 1 lists the types of binders and pretreatment additives that were tested.

Table 1. List of Solidification/Stabilization Treatability Study Materials

Binders	Other Pre-Treatment Additives
Type I, II, V Portland Cements	Potassium permanganate (oxidation)
Class F Fly Ash	Hydrogen peroxide (oxidation)
Cement Kiln Dust	Calcium hypochlorite (oxidation)
Lime Kiln Dust	Potassium persulfate (oxidation)
Sodium Silicate	Sodium persulfate (oxidation)
HWT-25, Organophillic Clay With Additives	Calcium chloride (precipitation)
	Ferric chloride (precipitation)
pH Control Additives	Ferric sulfate (precipitation)
Sulfuric acid	Ferrous sulfate (precipitation)
Phosphoric acid	Magnesium oxide (adsorbent)
Buffer solution	Activated carbon (adsorbent)

The final formulation arrived at during the treatability study involved pretreatment with potassium persulfate and ferric sulfate, followed by binding with Type I Portland cement. Initial TCLP levels in the untreated waste were up to 6,900 mg/L for arsenic; post-treatment TCLP results with the final optimized formula ranged from 0.67 to 1.9 mg/L for arsenic. The full-scale system used a similar formulation with the substitution of sodium persulfate for oxidation of arsenic from As(III) to the less soluble and less toxic As(V) form. The final TCLP results from the full-scale system were 1.24 to 3.44 mg/L. The full-scale system experienced several challenges that were not anticipated based on the bench-scale studies including excessive heat production during mixing. The total cost for off-site S/S treatment and disposal of the arsenic-impacted vault wastes was over $900 per ton. The cost for S/S treatment alone was approximately $800 per ton.

Other arsenic-contaminated materials on-site included K101 or distillation tar residues and K102 or activated carbon residues. These materials contained a high enough organic content that incineration was determined to be the appropriate treatment method. The treatment and disposal cost for the 455 tons of K101 and K102 wastes was approximately $2,000 per ton.

These data show the difficulties in treating high-strength arsenic wastes and excessive treatment costs. It will be necessary to understand whether the high treatment costs can be justified by the incremental reduction in potential risk associated with arsenic in treated wastes.

Some Chemical Aspects Relating to Arsenic Remedial Technologies

Robert G. Robins

AquaMin Science Consortium International

25 Adelaide Avenue, Lindfield NSW 2070, Australia

T/F: + 61 2 9416 3928, E: bobrobins@bigpond.com.au

The information that is summarized here originates mostly from publications by well-known and established authors in the field, during their many years of research on this subject. Most of the material is mentioned only briefly, but is found in a publications list, which is available by e-mail from the author. Although there are many other excellent relevant references, the author has chosen the selected papers for their reliability and convenience, but they are not necessarily the earliest chronological references. There are many other statements here which originate from much unpublished work. This extended abstract is an abridged version of the paper (with the references) that is available by e-mail.

Introduction

The removal of arsenic from process solutions and effluents has been practiced by the mineral process industries for many years. Existing hydrometallurgical techniques are adequate for most present day product specifications, but the stability of solid and liquid waste materials for long-term disposal or discharge will not meet the regulatory requirements of the future. The removal and disposal of arsenic from metallurgical process and effluent streams will become a greater problem as minerals with much higher arsenic content are processed in the future, and as regulations become more stringent. Disposal of stable residues will be critical, and the testing methods for assessing stability will need thorough revision.

The various unit processes that have been considered to deal with arsenic in hydrometallurgical processes include: oxidation-reduction, precipitation and thermal precipitation, coprecipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, membrane separations, precipitate and ion flotation, and biological processing. These methods are not considered here, but are detailed in some of the references in the e-mail version of this paper. Here only precipitation, adsorption and cementation are considered, as these are the processes that are presently being more generally adopted and need further investigation.

The aqueous solution chemistry of arsenic and the most common hydrometallurgical methods that have been applied commercially for arsenic removal, recovery, and disposal are only mentioned briefly here, as are some techniques which have been used only in the laboratory, and otherwise suggested as a means of eliminating or recovering arsenic from solution.

The aqueous solution chemistry of arsenic that 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. 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, and also arsenate is more strongly adsorbed on certain substrates, but this is pH dependent. The general assumption that arsenic(V) is more easily removed from solution, even by adsorption, is not correct. Current work has identified other compounds and also the element (formed by either cementation or electrolysis) to be appropriate low solubility materials for effective removal of arsenic from solution. Arsenic complexation in solution has had little attention, and it seems that only complexes of arsenic(V) with iron(III) have been studied to any extent. Oxidation of arsenic(III) in solution to arsenic(V), and reduction of arsenic(V) to arsenic(III) have been investigated 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 arsenic (III) to arsenic(V) is a recent innovation. The removal of arsenic from gold process solutions has been of understandable interest over the years, and has perhaps been investigated more than other hydrometallurgical processes.

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 sites as they will produce leachate containing arsenic.

The sulfide As_2S_3 has its lowest solubility below pH=4, but that solubility is significantly higher than has been generally accepted. The sulfide is not usually the 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 landfills 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. 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.

Arsenic(V) can be precipitated from aqueous solutions below about pH=2 with iron(III) to form ferric arsenate, $FeAsO_4.2H_2O$, which is white to very pale green in colour. 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°C the precipitated compound is crystalline (>100nm) and has a solubility about 2 orders of magnitude lower than the amorphous material (this is a 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 ferrioxyhydroxide, which initially forms around the surfaces of the ferric arsenate tending to stabilize 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 ferrioxyhydroxide, 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 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 rate of decomposition being related to particle size and solution composition, and being controlled by diffusion through both the reactants and the product layer). 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 has 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 to be incorrect. More complex compounds, such as the apatite structured calcium phosphate-arsenate have recently been demonstrated to be of low solubility and of appropriate stability (including being stable to atmospheric CO_2) for disposal considerations. Ferric arsenite sulfate is also of recent interest and may prove to be useful in stabilizing arsenic(III). One of the most insoluble arsenic compounds is lead(II) chloroarsenate, $Pb_5(AsO_4)_3Cl$, (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 author is presently involved in a comprehensive study of these systems). The Fe(II)-Fe(III) hydroxy sulfate, $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4.8H_2O$, (known as "green rust") incorporates arsenic into the structure at pH<7, and is worthy of further study.

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 coprecipitation 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 previously mentioned. At lower concentrations of arsenic(V) and higher iron(III) concentrations (where Fe/As>1), the coprecipitation of arsenic with ferrioxyhydroxide (*ferrihydrite*) which occurs 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 coprecipitate has been referred to as "basic ferric arsenate," and in 1985 a controversy commenced, as to whether the coprecipitated material was in fact a compound of iron(III) and arsenic(V) or simply an adsorptive binding of arsenic with ferrioxyhydroxide (*ferrihydrite*). There was even 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 attachment. 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 at the surface 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 author. It is well known that Fe(II) substitution in ferrihydrite does occur. Currently there is an investigation of the adsorption of As(III)-As(V) mixtures on ferrihydrite. 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 author is aware of current work 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 considerably better capacity for arsenic adsorption. The control of potential is 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 little work reported on the adsorption of arsenic from solutions initially below say 50 μg/kg. This region of concentration is presently of immediate interest in relation to drinking water, where EPA announced a new standard of 10 ppb (10 μg/L) for the maximum level allowed.

Many substrates, other than ferrioxyhydroxide, have been investigated and used commercially for removing arsenic from solution by adsorption. Some of these have shown excellent adsorptive capacity, but there is not the scope here for any details. Of personal interest is "adsorption" on sulfide minerals and titanium oxyhydroxide.

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 μg/L has been demonstrated on groundwater at a commercial site in California at a pilot scale of 1-5 US gallons per minute. Cementation has also been suggested, demonstrated, 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 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 predictions of behavior can be made.

Thermodynamic Modeling

The stability of arsenic species can be characterized by their standard free energies of formation ($\Delta_f G^o$). Many of the papers referenced in the e-mail version of this paper have free energy of formation data for arsenic species that have been invaluable to the author in producing thermodynamic stability diagrams to gain a better understanding of arsenic systems. None of the reputable thermodynamic databases have significant relevant data, but there are a number of publications where reasonable data can be obtained, and it is likely that these data will be evaluated and a compilation produced in the near future.

Conclusions

There have not been any significant and innovative improvements in the methods for removing arsenic from process and effluent solutions, or for stabilizing sludges and residues, in the last decade or so. The current need to remove arsenic from drinking water it seems is now a world problem, and so that too must be addressed.

References

This paper is available with references from bobrobins@bigpond.com.au.

Arsenic Geochemistry: Overview of an Underhanded Element

D. Kirk Nordstrom

U.S. Geological Survey
3215 Marine St., Boulder, CO 80303
T: 303-541-3037, F: 303-447-2505, E: dkn@usgs.gov

Arsenic is 38th in cosmic abundance but only about 52nd in earth and crustal abundance. The formation of the earth apparently discriminated against arsenic. In the ocean, however, it is 26th in abundance, suggesting accumulation in seawater over geologic time. Arsenic is preferentially concentrated in shales relative to other major rock types. Partitioning into shales reflects the strong adsorption tendency of arsenic for clay minerals. During high-temperature processes, arsenic can be expelled from sediments and volcanics and concentrated in the fluid phase, especially at low porosity. This phenomenon may explain high arsenic in hydrothermal fluids and their ore deposits.

The geochemical cycle of arsenic from magmatic-hydrothermal processes through weathering, sedimentation, and diagenesis transforms the element and produces an array of natural sources. Probably the single most abundant mineral source of arsenic is arsenian pyrite. Pyrite is ubiquitous in the earth's crust and arsenic has a strong affinity for the sulfur site in pyrite, substituting up to about 10wt. %. Arsenopyrite contains higher concentrations of arsenic (39-53%) but is a much rarer mineral. Other arsenic-rich minerals include orpiment, realgar, and enargite. Weathering of these minerals in oxidizing environments solubilizes arsenic as As(III) and ultimately as As(V). Arsenate, or As(V), has a strong adsorption affinity for hydrated iron oxides and in oxidized sediments iron oxides can be a source of soluble arsenic if they undergo reductive dissolution during early diagenesis. Geothermal springs are commonly enriched in arsenic, containing 0.1-5 mg/L dissolved arsenic as both As(III) and As(V).

Arsenic concentrations in groundwaters can range from less than a few μg/L to tens or even hundreds of mg/L in locally contaminated environments. Both anthropogenic and natural sources for arsenic in groundwaters occur in many locations worldwide. Natural sources cause or have caused poisoning of populations in India, Bangladesh, Chile, Argentina, Mexico, Taiwan, Mongolia, Japan, and China. Mining activities are responsible for arsenic poisoning in Thailand. Arsenic mass poisoning in Bangladesh is the largest known, affecting nearly 30 million people.

The primary source of industrial and commercial arsenic was arsenic trioxide, produced as a by-product of metal mining and processing. Stockpiles still exist and are releasing soluble arsenic to groundwaters. Several arsenic insecticides, herbicides, desiccants, wood preservatives, animal feed additives, drugs, chemical weapons, and alloys were produced for many years and sites are contaminated from these industries and their applications. Roxarsone, an organic arsenical, is still widely used today to clean parasites out of the stomachs of pigs and poultry.

Arsenic in surface and groundwaters occur dominantly as either arsenite, As(III), or arsenate, As(V). Reduction of arsenic can produce methylated forms of arsenic. Several microorganisms, including species of fungi, algae, and bacteria, catalyze the reduction of arsenic. Oxidation of As(III) is also catalyzed by microbes and it has been demonstrated that soluble As(III) and arsenic sulfide minerals such as arsenopyrite and orpiment can be catalytically oxidized to soluble As(V).

Impact of Microorganisms on Arsenic Geochemistry

Dianne Ahmann
Division of Environmental Science and Engineering, Colorado School of Mines
Golden, CO 80401
T: 303-273-3402, F: 303-273-3413, E: dianne@mines.edu

Introduction

Microbial activities are ubiquitous in the geochemical environment, and they can exert tremendous influences on the biogeochemical cycles of elements by interconverting species that display remarkably different behaviors. Arsenic is one such element, possessing a multi-dimensional biogeochemical cycle with important components contributed both directly, by microbial transformations of arsenic itself, and indirectly, by microbial transformations of elements with biogeochemical cycles that intersect that of arsenic.

Microbial Energy Generation by Catalyzing Redox Reactions

One of the primary tasks of a microorganism is to catalyze chemical reactions that will help it to obtain energy for metabolic growth from its environment, and as a result, many of the biogeochemically significant transformations that microorganisms catalyze are the result of energy-generating endeavors. The greatest energy-generating reactions available to the biosphere are those in which electrons are transferred from one element or compound to another, also known as oxidation-reduction or "redox" reactions (Stumm and Morgan, 1996). Redox reactions necessarily alter the electronic configurations of the compounds involved, and because electronic associations form the basis for much chemical reactivity, redox reactions frequently create dramatic alterations in the behaviors of their substrates (Schlesinger, 1997). In addition, because the microbial incentive to catalyze energy-generating reactions is so great, and because the abiotic rates of redox reactions are frequently so slow, such reactions frequently proceed much more rapidly and to a much greater extent in the presence of microbial catalysis than they would otherwise (Morel et al., 1993).

Aerobic and Anaerobic Respiration

Microorganisms catalyze redox reactions by means of "respiratory" processes, which are those that catalyze the transfer of electrons from one reactant to another. Aerobic respirations couple the oxidation of an electron donor such as organic carbon, H_2, or Fe(II) to the reduction of molecular oxygen, O_2, forming water. These processes necessarily occur in unsaturated soils or well-mixed or oligotrophic surface waters where oxygen is abundant (Brock and Madigan, 1991). In contrast, anaerobic respirations couple the oxidation of an electron donor to the reduction of an alternative electron acceptor such as nitrate, Fe(III), or sulfate, generating N_2, Fe(II), or sulfide, for example (Zehnder and Stumm, 1988). Aerobic and anaerobic respiratory processes form one central class of processes that strongly influences arsenic biogeochemistry, both directly and indirectly.

Respiratory Arsenic Transformations

Within the past seven years, microorganisms have been discovered in a great diversity of anoxic environments that are able to generate energy by coupling the oxidation of H_2 or organic carbon to the reduction of inorganic As(V), arsenate, forming inorganic As(III), arsenite (Ahmann et al., 1994; Cummings et al., 1999; Dowdle et al., 1996; Laverman et al., 1995; Macy et al., 1996; Newman et al., 1997; Newman et al., 1998). Arsenite behaves much differently than arsenate in natural environments; in particular, its sorption onto clay minerals and metal oxides appears to be less rapid and/or less stable, with the result that As(III) is generally much more mobile than As(V) in aqueous systems (Aggett and Kriegman, 1988; Kuhn and Sigg, 1993; Masscheleyn et al., 1991; Mok and Wai, 1994; Onken and Adriano, 1997; Seyler and Martin, 1989; Seyler and Martin, 1990; Spliethoff et al., 1995).

Because arsenate reduction is an energy-generating process for the microorganisms involved, and because arsenite is both more toxic and more mobile than arsenate, this process has the potential to influence greatly the geochemistry of arsenic in anoxic systems, particularly with respect to arsenic mobilization (Ahmann et al., 1997; Cummings et al., 1999). The converse respiratory process, the oxidation of arsenite to arsenate, coupled to the reduction of O_2 to water, has the theoretical potential to generate energy for microbial growth, but has been indicated in only one microorganism to date

(Ilyaletdinov and Abdrashitova, 1981). Nevertheless, a variety of other microorganisms have been shown to oxidize arsenite to arsenate by non-energy-generating mechanisms (Osborne and Ehrlich, 1976; Phillips and Taylor, 1976; Sehlin and Lindstrom, 1992; Wilkie and Hering, 1998).

Respiratory Iron, Manganese, and Sulfur Transformations

Sorption onto iron and manganese oxide solids and precipitation in sulfide solids in anoxic environments appear to be the two primary mechanisms governing arsenic mobility in aqueous, soil, and sedimentary environments (Bodek et al., 1988; Sadiq, 1997). Consequently, microbial activities that affect the abundances of iron or manganese oxides or sulfides have indirect, but potentially very important, influences on arsenic geochemistry. Respiratory iron and manganese reduction are ubiquitous and, in many cases, dominant redox processes in anoxic soils and sediments (Lovley, 1993; Nealson and Saffarini, 1994). Because the reduced forms of iron and manganese are highly soluble, their oxides dissolve readily upon microbial reduction, simultaneously releasing sorbed substances such as arsenic (Commings et al., 1999). When sufficient sulfate is present in an anoxic region, however, microbial sulfate reduction can potentially generate sufficient sulfide to precipitate the arsenic in solids such as amorphous arsenic sulfide, realgar, or orpiment (Moore et al., 1988). The corresponding oxidative processes, microbial oxidation of Fe(II), Mn(II), or S(-II), are known to occur, but are usually restricted to acidic environments (Schlegel, 1993) and have not been shown directly to promote arsenic sorption onto metal oxides nor to promote arsenic sulfide dissolution. While the geochemical significance of the reductive processes for arsenic cycling is well-established, the significance of the oxidative pathways is much less understood.

Arsenic Toxicity

In addition to energy generation, a second important task for microorganisms is to protect themselves from toxic substances. Arsenate, with its structural similarity to phosphate, enters microbial cells readily through phosphate-uptake proteins. Its primary mode of toxicity is then to displace phosphate in the production of adenosine triphosphate (ATP), the primary energy currency of the cell. The resulting molecules hydrolyze spontaneously, causing the cell to deplete its energy stores rapidly (Winship, 1984). Although this mechanism of toxicity is quite effective, many cells are able to induce highly phosphate-specific uptake proteins that improve the exclusion of arsenate (Rosenberg et al., 1977; Torriani, 1990; Willsky and Malamy, 1980). Arsenite, in contrast, is uncharged at neutral pH and appears to gain access to the cytoplasm by less specific mechanisms, possibly including diffusion across the membrane. Once inside, it crosslinks sulfhydryl groups on enzymes, forming stable adducts that permanently disable the enzyme. This mechanism is even more destructive to the cell than that of arsenate (Winship, 1984).

Arsenic Detoxification

To protect themselves against the toxic effects of arsenic, many microorganisms have evolved strategies for detoxification. The best-studied among these is the microbial reduction of arsenate to arsenite by means of the *Ars* system, an enzymatic process in which energy is actually consumed to drive the reduction. The *Ars* system is borne on plasmids that are easily transferred among both Gram-positive and Gram-negative bacteria, and it is induced at arsenic concentrations low enough to be relevant to contaminated environments, with the result that this process is potentially rapid, extensive, and ubiquitous in both oxic and anoxic environments (Ji and Silver, 1995; Silver et al., 1993).

Certain other bacteria and fungi appear to detoxify arsenicals by reducing them to arsine, As(-III), in both inorganic and methylated forms (Cheng and Focht, 1979; Cullen and Reimer, 1989). In addition, some algae have been shown to reduce arsenate to arsenite, presumably for detoxification purposes, but this purpose has not been confirmed (Sanders and Windom, 1980). Finally, certain bacteria and algae, as well as many higher organisms, may incorporate arsenic into organic compounds such as arsenocholine, arsenobetaine, and other arsenosugars (Andreae and Klumpp, 1979; Cullen and Reimer, 1989). Regardless of the utility to the microorganism, however, it is clear that many non-energy-generating microbial transformations of arsenic occur both rapidly and extensively in natural environments, and should be considered potentially important contributors to arsenic geochemistry.

Passive Nucleation

Microbial cell surfaces possess an abundance of surface functional groups that can form complexes with dissolved ions, including arsenic oxyanions, and such complexes have been shown to function as sites of nucleation in the precipitation of certain minerals (Beveridge, 1989). In the case of arsenic, it may be possible that microbial cell surfaces contribute to arsenic geochemical cycling in this passive manner as well, particularly in the instance of nucleating arsenic sulfide precipitation (Newman et al., 1997; Rittle et al. 1995).

Summary

In oxic environments, the dominant microbial influences on arsenic geochemistry appear to be the bacterial and algal oxidations of arsenite to arsenate, diminishing both toxicity and mobility of the arsenic, as well as confirmed detoxification processes, including the *Ars*-mediated reduction of arsenate to arsenite and fungal generation of arsines. In anoxic environments, in contrast, the dominant microbial roles are expected to be the respiratory reductions of arsenate, iron, and manganese, all of which promote arsenic desorption and enhance its mobility, and the respiratory reduction of sulfate, which promotes arsenic immobilization into sulfide solids. While the mechanisms underlying these processes are well understood in many cases, and their geochemical influences are potentially great, the ability to quantify and, more importantly, to predict the rates and extents of these processes in natural environments, remains a tremendous challenge for the future.

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A Framework for Assessing Arsenic Leaching from Soils and Wastes

H. A. van der Sloot
The Netherlands Energy Research Foundation
Westerduinweg 3, P.O. Box 1, Petten, 1755 ZG, The Netherlands
T: (+31) 224-56-4249, F: (+31) 224-56-3163, E: vandersloot@ecn.nl

D. S. Kosson and F. Sanchez
Vanderbilt University, Dept. of Civil and Environmental Engineering
Box 1831, Station B, Nashville, TN 37235
T: 615-322-1064, F: 615-322-3365, E: David.Kosson@vanderbilt.edu,
Florence.Sanchez@vanderbilt.edu

R.N.J. Comans
The Netherlands Energy Research Foundation

Estimating long-term release from wastes and soils by leaching requires a testing and interpretation framework that considers specific management scenarios. However, development of dedicated test methods to simulate the wide variety of environmental scenarios is impractical. An alternative approach, presented here, is to measure a common set of intrinsic leaching parameters and use models that reflect the anticipated environmental scenario to estimate release. Thus, a common set of testing results can be used to compare alternative management scenarios, including site-specific climate and design conditions. Alternatively, a set of default management assumptions can be used to compare the efficacy of different treatment processes. Important intrinsic leaching properties of the soil or waste include: (i) release potential, (ii) solubility and release as a function of pH, (iii) solubility and release as a function of liquid to solid ratio, and (iv) mass transfer rates.

A challenge is simplification of the approach to allow routine implementation. It is proposed to achieve the goal by carrying out testing at two levels: (i) material characterization, and (ii) verification. Initial characterization is carried out to define a class of materials, based on its behavior. Subsequently, simplified testing is carried out to verify that the material being evaluated has not varied significantly from the material class that was subjected to more extensive characterization. Evaluation is further enhanced by development of a multi-party database that facilitates comparison of the leaching behavior for a wide range of materials. This presentation will provide an overview of the leaching framework and comparison of results for arsenic leaching from a variety of wastes and secondary materials. For a soil contaminated with As caused by wood preservation, the geochemical modeling is presented. This illustrates the nature of the solubility controlling phases and the degree to which the model can predict the observed leaching behavior. A second paper presents the testing protocols in more detail (see Sanchez, et al. "Protocols for Estimating Arsenic Leaching from Soils and Solidified Wastes," 3.3 Arsenic Chemistry Session).